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**EFFECTS OF MONTMORILLONITE CLAY ADDITION ON THE
COMPRESSIVE FRACTURE STRENGTH AND WEAR RESISTANCE OF
GLASS-IONOMER RESTORATIVES**

A thesis submitted to the University of Dublin in fulfillment of the requirements

for

The degree of Doctor of Philosophy by

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May 2010

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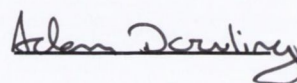
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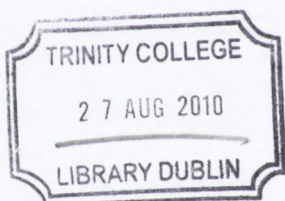
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SUMMARY

The aim of the present investigation was to investigate the influence of montmorillonite (MMT) clay, both as-found (un-modified calcium montmorillonite (Ca-MMT)) and pre-treated to encourage exfoliation (organically-modified MMT clay 12-amino-dodecanoic acid treated-montmorillonite (ADA-MMT)), on the compressive fracture strength, elastic modulus and *in vitro* wear resistance of a variety of commercial GI restorative products. Firstly, the MMT clays were added to the powder and liquid constituents of an anhydrous GI restorative (Chemfil Superior) at concentrations ranging from 0.5 to 2.5 wt.% (in 0.5 wt.% increments). Groups of 30 or more cylindrical specimens (6 mm height, 4 mm diameter) were prepared and the mean compressive fracture strength was determined. The *in vitro* wear resistance was assessed for groups of eight disc-shaped specimens using the OHSU oral wear simulator operating at 20 N abrasion and 90 N attrition forces for 50,000 cycles at a frequency of 1 Hz in the presence of a poppy seed and PMMA bead slurry. The addition of Ca-MMT clay to Chemfil Superior resulted in a steady decrease in the mean compressive fracture strength and *in vitro* wear resistance with increasing Ca-MMT clay concentration. Adding ADA-MMT clay to Chemfil Superior (at concentrations ranging from 0.25 to 1.25 wt.%) resulted in significant increases in the mean compressive fracture strength and *in vitro* wear resistance compared with the control. As a result, ADA-MMT clay was also added (at concentrations of 0.5 and 1.0 wt.%) to the powder and liquid constituents of a variety of conventional GI restoratives consisting of a separate glass containing powder and a polyalkenoic acid liquid solution. In general the addition of ADA-MMT clay to the powder and liquid constituents of the conventional GI restoratives did not increase the mean compressive

fracture strength. The addition of ADA-MMT clay to the GI restoratives increased the powder to liquid mixing ratio and therefore the viscosity of the GI restorative mix which made the GI restoratives more difficult to mix in the time specified by the manufacturers. Therefore the influence of reducing the powder content of hand-mixed GI restoratives (for a constant weight of liquid) on the mean compressive fracture strength, mean elastic modulus and *in vitro* wear resistance was investigated. In addition, encapsulated GI restoratives were also assessed to investigate if encapsulation provides a solution to the operator variability associated with hand-mixing. The mean elastic modulus was also determined from the initial straight portion of the stress-strain plot generated for each cylindrical specimen tested in compression. Reducing the powder content of the hand-mixed GI restoratives in 10% increments (for a constant weight of liquid) resulted in a significant steady deterioration of the mean compressive fracture strength, mean elastic modulus and *in vitro* wear resistance. The mean compressive fracture strength and mean elastic modulus of some encapsulated GI restoratives were influenced by the method of mechanical mixing. Encapsulated GI restoratives provide the clinician with the opportunity to produce GI restoratives consistently with increased compressive fracture strength, elastic modulus and *in vitro* wear resistance without suffering from the operator variability associated with hand-mixed products.

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1 Introduction

The materials which are currently advocated for use as posterior filling materials include dental amalgam and resin-based composites. Dental amalgam restorations necessitate the removal of sound tooth structure prior to placement in the oral environment (Lutz, 1995), are susceptible to corrosion in service (Darvell, 1973), have potential mercury toxicity issues (Lutz, 1995) and are non-tooth coloured which has led the dental profession to investigate alternative posterior filling materials. Resin-based composites are a tooth coloured alternative to dental amalgam, however, resin-based composites are time-consuming and technique-sensitive to place clinically which results in increased patient treatment times and costs (Christensen, 1996). In addition, resin-based composites require a series of preconditioning treatments of the tooth structure to ensure adhesion (Peumans *et al.*, 2005). Alternatively, glass-ionomer (GI) restoratives are tooth-coloured and can be placed clinically in one increment. GI restoratives adhere chemically to sound tooth structure (Akinmade and Nicholson, 1994) which eliminates the need for sound tooth structure removal or the pre-conditioning of the tooth structure to aid retention. Unfortunately, GI restoratives are not advocated for use in load-bearing situations in the oral environment due to inferior mechanical properties compared with dental amalgam and resin-based composites (Mount, 1999).

Montmorillonite (MMT) clay is a tri-layered smectite clay mineral consisting of stacked platelets constructed of an alumina octahedral layer sandwiched between two silica tetrahedral layers. When dispersed individually and homogeneously in a polymeric matrix MMT clay platelets have been shown to improve significantly the

mechanical properties of a variety of polymers including nylon (Okada *et al.*, 1990), poly(methyl methacrylate) (PMMA) (Park and Jana, 2003) and more recently PMMA bone cements (Kwon and Kim, 2007). The aim of the present study was to reinforce the polyalkenoic acid matrix of the GI restoratives with MMT clay and therefore improve the mean compressive fracture strength and *in vitro* wear resistance of the GI restorative.

In addition, the influence of other factors influencing the performance of GI restoratives were assessed, namely, the effect of reducing the powder content (for a constant weight of liquid) of hand-mixed GI restoratives and the influence of the method of mixing of GI restoratives (hand-mixed or mechanically mixed) were investigated.

2 Literature Review

2.1 Restorative Dentistry

The range of dental restorative materials available to a practitioner is extensive and includes resin composite restoratives, amalgams, ceramics, cements or any such material used to restore the function and appearance of lost or damaged tooth structure. The manufacturers' quality claims for these materials arise as a result of a set of standard property tests which are either physical, chemical, biological or mechanical (Craig, 1993a) and reliably give estimates of values that are interpretable. Conventional test methods employed by manufacturers to assess standard material properties (for example compression fracture strength, tensile strength, consistency, working characteristics, resistance to aqueous attack) are performed under specific test conditions designed to identify the safest and most effective materials with potential for clinical longevity (Craig, 1993a). Therefore to achieve good reproducibility of test results for materials under investigation it is imperative that specimen preparation occurs under these ideal standard test conditions.

2.1.1 Standard Property Variability

Some restorative materials, ceramics and cements in particular, are unable to deform plastically under an applied load and consequently these materials are susceptible to brittle fracture. Kingery *et al.* (1976) reported that brittle fracture in ceramics was initiated at defects which were either inherent to the material (such as microcracks and large grains) or introduced during processing (porosity and impurity inclusions). These defects increased in length under the application of an applied stress or load at room temperature so that in a batch of nominally-identical standard ceramic

specimens a distribution of fracture strengths was inevitable since it was impossible to predetermine the size, location and distribution of the most critical defects (Duckworth, 1960; Evans 1982; Ritter, 1994a,b). Therefore the strength of brittle dental materials can never be determined reliably from “average” fracture strengths (McLean and Kedge, 1987).

2.1.1.1 Assessment of Standard Property Variability

International specification standards for dental materials (such as American Dental Association (ADA), British Standard (BS), Fédération Dentaire Internationale (FDI) and International Organisation for Standardisation (ISO)) provide dentists with an impartial and reliable selection process for materials used in clinical practice. Therefore, as long as the materials in question meet the established specifications and are manipulated according to the manufacturers’ instructions the dentist can be assured of the material’s performance when employed in clinical practice (Anusavice, 1996).

Failure in a brittle material occurs as a result of the ‘weakest link’ whereby the most critical defect in the material controls the strength (Davies, 1973; Jayatilaka and Trustrum, 1977). The most critical defect in a brittle material is not necessarily the largest defect but the most favourably orientated defect for crack propagation under an applied stress (Bergman, 1984). Unfortunately, it is impossible to predetermine the distribution of the most critical defects in a body before it is stressed (Davies, 1973; Stanley *et al.*, 1973; Evans 1982; Ritter, 1994a,b). Specification standards attempt to take into account the inherent property variability displayed in brittle materials by introducing a strength limit which a given percentage of the specimens under

investigation must exceed to meet the particular standard. The specification standard for dental acid-base cements (ISO 9917-1 : 2003), manipulated according to the manufacturers' instructions, attempts to take into account the inherent compressive fracture strength variability by ensuring that at least four of the five specimens under investigation exceed a particular strength limit (100 MPa) if the cement is to achieve the particular standard.

2.1.2 Clinical Variability

One of the biggest causes of failure in restorations occurs as a result of manipulation of dental materials (Mitchem, 1982). The techniques employed in manipulating dental restorative materials in clinical practice frequently involve mixing two components, powder and liquid or paste and paste, with the relative proportions being assessed by 'eye' (Fleming *et al.*, 1999a, 2003) or with the aid of crude unreliable operator-dependent measuring systems (Wong and Bryant, 1985; Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a), in an environment (temperature and humidity) and under mixing conditions (time and manipulation technique) which will differ from those employed by the manufacturer to assess the standard material properties. As a result, the final mix composition produced in clinical practice may be subject to considerable variation (Savignac *et al.*, 1965; Monroe and Eames, 1977; Eames *et al.*, 1977; Walton, 1980; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2001) and therefore the physical, chemical, biological and mechanical properties of these materials which are mixed and used in clinical practice are susceptible to an additional clinical variation.

2.1.2.1 Assessment of Clinical Variability

It is often unknown how this additional clinical variability influences the performance of dental materials and as a result an appreciation of the factors affecting these material properties can minimise the problem of failure and increase their scope of application. In the class of restorative dental materials, dental cements and restoratives have comparatively low strengths but are used extensively in restorative procedures for which these cements and restoratives have a decided influence on the success of the restorative procedures (Mitchem, 1982). Unfortunately, the manipulation techniques for dental cements vary greatly (Eames *et al.*, 1977) such that this group of restorative dental materials is probably the most abused with respect to the manipulation techniques employed and powder to liquid mixing ratios used in clinical practice (Savignac *et al.*, 1965; Monroe and Eames, 1977; Walton, 1980; Mitchem, 1982; Billington *et al.*, 1990; Fleming *et al.*, 1999a). Dental restoratives are often placed in load-bearing situations in the oral environment which will invariably exacerbate the influence of clinical variability and therefore can result in poor clinical performance.

2.2 Dental Cements and Restoratives

Dental cements are a versatile class of materials which are used clinically for both the retention of restorations on prepared teeth and the restoration of teeth, which makes them indispensable to the practising dentist (Smith, 1982). These different applications make various and exacting demands on the physical, chemical, biological and mechanical properties of dental cements (Wilson, 1978). For each application a specific cement must be selected and developed since one type of cement is unlikely to perform satisfactorily under all conditions (Wilson, 1975).

Dental cements and restoratives are commonly supplied as separate powder and liquid constituents which are hand-mixed to a paste consistency and set to form a hard brittle mass within six to eight minutes of mixing (Wilson, 1975; Smith, 1982; Wilson and Nicholson, 1993). The relative proportions of the powder and liquid constituents are usually dispensed using the manufacturers' recommended scoop and dropper bottle system prior to hand-mixing. However, the use of scoop and dropper bottle systems can result in powder to liquid mixing ratios that vary considerably from that recommended by the manufacturer (Wong and Bryant, 1985; Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a). The volume of powder dispensed by the operator is dependent on the powder packing density achieved on filling the scoop (Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2003; Mount, 2005) with powder variations of $\pm 10\%$ from that recommended by the manufacturers reported in a laboratory simulation (Mount, 2005). In addition, dropper bottles cannot be relied upon to dispense calibrated volumes of liquid (Eames *et al.*, 1977), as the angle at which the bottle is held and the pressure applied to squeeze a drop will influence the volume of liquid dispensed (Billington *et al.*, 1990;

Fleming *et al.*, 1999a, 2003; Mount, 2005). If the dropper bottle is held on its side rather than being inverted, the volume of the drop of liquid dispensed can vary by including an air bubble in the drop. Alternatively, if the bottle is squeezed too much when dispensing the liquid a squirt rather than a drop may be obtained (Wilson and McLean, 1988a; Mount, 2005). In clinical practice, dental cements and restoratives are routinely mixed to a desired consistency by the technical experience of the operator, namely by 'eye', without the aid of scoop and dropper bottles (Fleming *et al.*, 1999a, 2003). As a result, the powder to liquid mixing ratios employed clinically do not maximise the functional characteristics reported by the manufacturers (Billington *et al.*, 1990; McCabe, 1990; Craig, 1993b; Fleming *et al.*, 1999a). Considerable variation in test results for dental cements and restoratives is obtained when the manufacturers' recommended powder to liquid mixing ratios are not used (Paffenbarger *et al.*, 1933; Savignac *et al.*, 1965; Monroe and Eames, 1977; Eames *et al.*, 1977; Walton, 1980; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2001) and emphasis should be placed on the proportioning, manipulation and properties of the cement or restorative produced as a basis for a practical interpretation of its fundamental physical, chemical, biological and mechanical characteristics (Craig, 1993a).

An alternative to hand mixing dental cements and restoratives was for the manufacturer to proportion the powder and liquid into a sealed capsule for mechanical mixing using an amalgamator (Brauer, 1952; Mount, 1984). Encapsulation of dental cements and restoratives ensures that the manufacturers' powder to liquid mixing ratio is achieved consistently in clinical practice. However, the conventional mechanical mixing process for encapsulated dental cements and restoratives, which vibrates the

capsule back and forth (Capmix; 3M ESPE, Seefeld, Germany) at frequencies ranging from 76 to 82 Hz (Bass and Wing, 1988) was reported to incorporate increased porosity into some dental cements and restoratives (Nomoto and McCabe, 2001; Fleming and Zala, 2003; Nomoto *et al.*, 2004) compared with hand-mixing. As a result, mechanical mixing utilising a combination of rotational and centrifugal action (Rotomix; 3M ESPE, Seefeld, Germany) was introduced to reduce porosity entrapment in the encapsulated cements or restoratives. Studies comparing encapsulated dental cements and restoratives mechanically mixed using the Capmix or Rotomix reported that the Rotomix had a beneficial effect on reducing the porosity of some encapsulated dental cements and restoratives (Nomoto and McCabe, 2001; Fleming and Zala, 2003; Nomoto *et al.*, 2004). However, no significant differences in the mean compressive fracture strength of the encapsulated dental cements and restoratives were evident in the dental literature regardless of the mixing machine employed (Nomoto and McCabe, 2001; Fleming and Zala, 2003; Fleming *et al.*, 2006).

2.2.1 Classification of Dental Cements

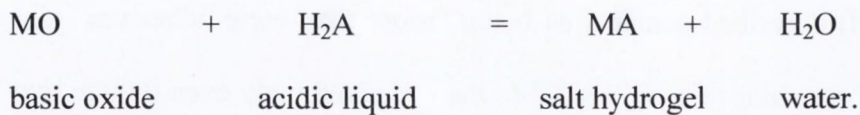
Wygant (1958) described cements as being “more than mere adhesives” since they imparted the behaviour of a rigid solid to the cemented body even though they made up only a small portion of that body. The author classified all cement types into three different categories: dental cements were classed as “reaction cements” as they were produced by mixing two constituents other than water which distinguished them from “hydraulic cements” of which Portland cement, used in buildings, is the most common form, and ‘precipitation cements’ which were essentially single component systems

(primarily gels - alkali silicates being the most common form) which could be thrown out of solution by adjusting the acidity or ion concentration.

Wilson and Nicholson (1993) classified cements into three broad categories namely hydraulic, condensation and acid-base. The essential cement forming feature of a “condensation cement” is the loss of water and condensation of two hydroxyl groups to form a bridging oxygen:



The reaction between the proton-accepting base-like powdered solid and proton-donating acidic liquid is generally accepted to be the mechanism involved in the formation of dental cements which are classed as “acid-base cements”. The product of the reaction is a salt-like hydrogel (a highly absorbent water-insoluble polymer (Hoffmann, 2002)) which binds the unreacted powder particles into a cement mass (Wilson *et al.*, 1979). The general reaction may be simplified as:



For simplicity, the side reactions involving the interactions of the moderating species in both the powder and liquid are ignored since they do not affect the essential features of the overall reaction where both the oxide cation and liquid anion are divalent. The mechanism of the reaction is shown in Figure 2.2.1.

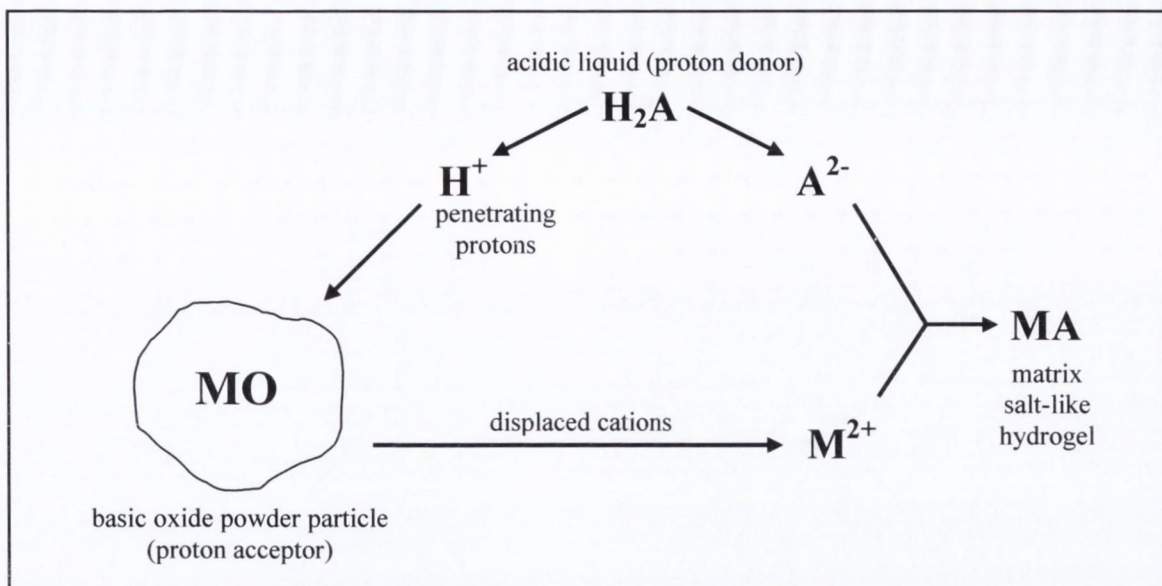


Figure 2.2.1 Schematic representation of the setting reaction in dental cements.

Although dental cements develop their strength rapidly after mixing, strength continues to evolve slowly over a period of several months (Paffenbarger *et al.*, 1938; Crisp *et al.*, 1976; Paddon and Wilson, 1976). Wilson *et al.* (1979) investigated the development of compressive fracture strength, after the initial rapid increase that occurs on mixing, of four different types of dental cement (polycarboxylate, zinc phosphate, silicate, and GI) by determining the total water content of each cement. The condition of the water present was classified as either evaporable (water molecules formed as reaction products) or non-evaporable (tightly bound water molecules which take part in the chemical reaction). The influence of ageing the cement specimens was investigated to assess the extent of hydration of the cements under investigation (the ratio of non-evaporable to evaporable water). It was reported that the initial acid-base reaction was followed by a slower process, namely the hydration of the reaction products, which was thought to be responsible for the slow development of strength in acid-base cements.

Gelation, setting and hardening occur during cement formation as a result of the hydrogen bridges in the acidic liquid phase being progressively replaced by more rigid metal ion bridges (Wilson, 1978). Wygant (1958) reported that during these physical and chemical changes which occur on setting a “continuity of structure” was essential for cement formation. Consequently, crystallisation or any structural changes did not occur during cement formation which would have caused the cement paste to lose coherence (Wilson, 1975, 1978) and the result was an amorphous structure.

The advantage of the cement classification system proposed by Wilson and Nicholson (1993) over that proposed by Wygant (1958) was that it differentiated between phosphate cements formed by a “condensation reaction” (the heat treatment of an acid orthophosphate to form a polyphosphate) from those formed by an “acid-base reaction” i.e. zinc phosphate dental cements (Kingery, 1950a,b). Silicate cements (formed when orthosilicic acid, chemically generated in solution, condenses to form a silicic acid gel) and heat treated acid cements, both “condensation cements” under Wilson and Nicholson’s classification system, were placed into separate categories by Wygant (Wilson and Nicholson, 1993).

2.3 Glass-ionomers (GIs)

2.3.1 Development of GIs

GIs were developed as a result of the pioneering work of Alan Wilson and his co-workers at the Laboratory of the Government Chemist in London. In the 1960s, Wilson and his co-workers set about improving on the performance of dental silicate cement, the strongest cement of the day, however, silicate cements were susceptible to staining and erosion, were non-adhesive to sound tooth structure and adversely reacted with dental tissues (Wilson and Batchelor, 1967a). Although, dental silicate cements had been in use for over 50 years, little was known about their chemistry and structure. Initially, Wilson and Batchelor (1967b, 1968) discovered that aluminium and calcium phosphates formed part of the cement matrix which suggested that an improvement might occur if phosphoric acid was replaced by a less aggressive chelating acid, which could also interact with apatite. As a result, in 1965, a series of acids (namely, pyruvic, tartaric, tannic, fluoroboric, glycerophosphoric and tetraphosphoric) in 35-50% solutions were mixed with the dental silicate cement glass powder (which was based on an alumino-silicate glass) (Wilson, 1996). The cements formed had good handling and working characteristics but all were hydrolytically unstable and susceptible to disintegration (Wilson, 1968). However, when a 25% solution of polyacrylic acid was mixed with the dental silicate glass, the resultant cement demonstrated hydrolytic stability, although, the working time was too short for clinical use (Wilson and Kent, 1971, 1972). To ensure satisfactory setting, it was discovered that a third component was required, in addition to the polyacrylic acid and the alumino-silicate glass (Wilson and Nicholson, 1993). Replacing phosphoric acid with other acids of different strengths and chelating abilities would require the preparation of a series of matching glasses with a range of reactivities (Wilson, 1996).

Wilson and Kent (1972) discovered that the ratio of alumina to silica in the glass frit controlled the reactivity of the glass and as a result the setting characteristics of the cement. Therefore, a series of glasses with alumina to silica ratios ranging from 1.75 to 1 to 2 to 1 (by mass) were prepared and mixed with solutions of 40 and 50% polyacrylic acid. However, the resultant cements were impractical as the working and setting times were again too slow for clinical use (Wilson and Kent, 1972; Wilson, 1996). As a result, further development was required and an extensive series of different glasses were prepared. Unfortunately, the authors reported that cements which had adequate working time, set too slowly, had poor compressive fracture strengths and were susceptible to aqueous attack. Alternatively, cements with sufficient setting time, compressive fracture strength and resistance to aqueous attack had working times which precluded their use clinically (Wilson, 1996).

A breakthrough for Wilson and his co-workers came on the development of their 200th glass, a glass high in fluoride and calcium. The cement formed was reported to have superior working time, compressive fracture strength and resistance to aqueous attack than any of its predecessors, although the translucency and therefore appearance of the cement was insufficient (Wilson and Kent, 1972; Crisp and Wilson, 1974a; Wilson *et al.*, 1976). It was inferred that to attain a cement with a “sharp set”, the addition of a chelating agent was required to control the setting reaction (Wilson *et al.*, 1976). As a result, Wilson *et al.* (1976) investigated a series of additives including citric acid, salicylic acid, acetylacetone, sequestric acid, polyglycol and tartaric acid on the working and setting times. It was reported that tartaric acid was “effective beyond all expectations”, as it had four favourable effects, it lengthened the working time, shortened the setting time, increased the compressive fracture strength and

resistance to acid attack (Wilson *et al.*, 1976; Crisp and Wilson, 1976; Wilson, 1996). In addition, the number of usable glasses that could be employed for cement formation was increased and as a result, the translucency of the cement could be improved. The result was a clinically practical dental material which was given the name “glass-ionomer cement”. However, when the GI was first introduced to the dental market as a replacement for dental silicate cements in anterior applications, it faced stiff competition from the newly-developed resin-based composites (Bowen, 1958). One property unique to GIs was adhesion to sound tooth structure, which when added to the other advantages including fluoride release, stain resistance and biocompatibility provided significant advantages over resin-based composites.

In the 1970s GIs were advocated clinically for the restoration of erosion lesions, as fissure sealants (McLean and Wilson, 1977a,b; Wilson, 1989) and as luting agents (Wilson *et al.*, 1977a). McLean and Wilson (1977a,b) suggested that the most promising area of application for GIs was in the field of preventative dentistry as restoratives. The early GIs had insufficient translucency (Wilson, 1989) and as a result, were not advocated for tooth tissue-like anterior restorations (McLean and Wilson, 1977a,b). The improvements in the translucency of the glass by increasing the silica concentration (Crisp *et al.*, 1979) and reducing the average glass particle size (Wilson, 1989) enabled the use of GIs as tooth-coloured restorations in anterior teeth. However, the compressive fracture strength (Kent *et al.*, 1973), three-point flexure strength (Kent *et al.*, 1973; Prosser *et al.*, 1984) and abrasion wear resistance (Smales and Joyce, 1978) of anterior GI restoratives were insufficient for use in load bearing posterior applications (Wilson, 1989; McLean, 1990). To improve the compressive fracture strength, three-point flexure strength and wear resistance of anterior GI

restoratives and enable use posteriorly whilst maintaining favourable working and setting characteristics, a balance between the powder to liquid mixing ratio used and the form (Guggenberger *et al.*, 1998), concentration (Crisp *et al.*, 1977; Wilson *et al.*, 1977b) and molecular weight (Hill *et al.*, 1989; Wilson *et al.*, 1989) of the polyalkenoic acid constituent was required. An optimum molecular weight and polymeric chain length of the polyalkenoic acid constituent in the GI restorative was chosen (Hill *et al.*, 1989; Wilson *et al.*, 1989) so that the viscosity change of the polyalkenoic acid liquid was kept to a minimum. An increased powder to liquid mixing ratio was achieved by the incorporation of a portion of the polyalkenoic acid constituent (ranging from 7 to 9%) in the glass powder in vacuum-dried form without a significant increase in the initial viscosity of the cement mass (Frankenberger *et al.*, 1997; Guggenberger *et al.*, 1998). Modification of the size, composition and reactivity of the glass constituent of posterior GI restoratives resulted in a faster setting reaction (Nicholson and Croll, 1997; Burke *et al.*, 2007). Additionally, the manufacturers claimed improved initial (1 h) compressive fracture and three-point flexure strengths (Peez and Frank, 2006), resistance to dissolution (Nicholson and Croll, 1997; Burke *et al.*, 2007) and improvements in wear resistance (Frankenberger *et al.*, 1997; Burke *et al.*, 2007) compared with anterior GI restoratives (Burke *et al.*, 2007).

2.3.2 GI Composition

GIs consist of two components, a basic ion-leachable glass (the inorganic phase) and an acidic polyalkenoic constituent (the organic phase) (Kent *et al.*, 1973). The ion-leachable glasses, primarily based on calcium fluoro-alumino-silicates (Kent *et al.*, 1979; Nicholson, 1998), act as a source of ions for the cement-forming reaction (Wilson and Nicholson, 1993; Nicholson, 1998). The polyalkenoic acid generally

consists of homo-polymers of acrylic acid or copolymers with itaconic acid or maleic acid (Crisp and Wilson, 1974c, 1977; Crisp *et al.*, 1980) which are supplied either as a liquid solution or vacuum-dried and mixed with the glass powder (Pearson, 1983; Prosser *et al.* 1984; Wilson and Nicholson, 1993). As a result, GIs are routinely supplied in two forms, either as separate glass powder and polymeric liquid constituents or as a powder containing both the glass and vacuum-dried polyalkenoic acid which is mixed with either water or a dilute aqueous solution of tartaric acid (Pearson, 1983; Prosser *et al.* 1984; Wilson and Nicholson, 1993). The incorporation of vacuum-dried polyalkenoic acid in the powder constituent is preferred by some manufacturers as it avoids the problem of gelation of the polymeric liquid solution which occurs due to intermolecular hydrogen bonding of the polymeric chains (Crisp *et al.*, 1975) and is evident when the transparent liquid solution transforms to an opaque gel. To reduce or eliminate gelation the homo-polymers of acrylic acid were substituted with copolymers of acrylic acid and other polymeric acids such as itaconic acid (Crisp and Wilson, 1977). The organisation of molecules and crystallinity of copolymers is not as regular as homo-polymers and as a result have a reduced tendency to gel in solution (Lovell and Young, 1991).

2.3.2.1 Powder Constituent

The inorganic phase used in commercial GIs is composed of an ion-leachable calcium alumino-silicate glass produced by the fusion of the appropriate mixture of raw ingredients at temperatures ranging from 1200 to 1500 °C (the exact fusion temperature depends on the chemical makeup of the glass mixture) (Wilson and McLean 1988a). The glass melt is shock-cooled by either pouring onto a cool metal plate or quenching in water. The resultant glass is a coarse frit which is ground,

usually by dry milling in a ball mill and sieved to produce the final glass powder (maximum particle size of 45 μm for GI restoratives and 15 μm for GI luting cements (Wilson and Nicholson, 1993)). There are a great number of potential glasses that can be used for GIs, all of which are based on either calcium aluminosilicates ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$) or calcium fluoroaluminosilicates ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2$) (Kent *et al.*, 1979; Wilson and Nicholson, 1993). The addition of fluoride is crucial for GIs as it lowers the fusion temperature of the glass (Wilson and McLean 1988a), decreases the working time (Kent *et al.*, 1979), increases the compressive fracture strength (Kent *et al.*, 1979), enhances the translucency of the final GI (Wilson and McLean 1988a) and has been suggested to inhibit caries formation in the oral environment (Forsten, 1998). However, the ability of a glass to form a useable cement is governed by the ratio of alumina to silica which controls the reactivity of the glass and as a result the setting of the cement (Kent *et al.*, 1979; Wilson, 1996). In general, the rate of setting and hydrolytic stability of the GI increases as the alumina to silica ratio increases. If the alumina to silica ratio rises above 3 to 1 (by mass) the setting time becomes too long (6.5-18 mins), or falls below 2 to 1 (by mass) the GI sets too rapidly (2.5-5 mins) and practical cements cannot be formed (Kent *et al.*, 1979; Wilson and Nicholson, 1993). The optimum alumina to silica ratio lies between 2 to 1 and 3 to 1 (by mass) (Kent *et al.*, 1979; Wilson and Lewis, 1980; Wilson and Nicholson, 1993). Excess alumina confers a negative charge to the glass, increases the basicity and makes the glass more susceptible to attack by the polyalkenoic acid (Hill and Wilson, 1988; Wilson and McLean 1988a; Wilson and Nicholson, 1993). In addition, the compressive fracture strength increases with increasing alumina content, however, the translucency of the GI is decreased (Wilson and McLean 1988a). Commercial glasses are usually more complex and can contain additives such as strontium, zinc, and lanthanum which

confer a degree of radio-opacity to the glasses (Griffin and Hill, 1999) which further increases their applications clinically as they will show up on radiographs.

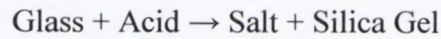
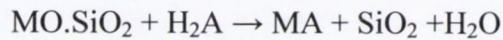
2.3.2.2 Liquid Constituent

The polyalkenoic acids used in GIs generally consists of homo-polymers of acrylic acid or copolymers of acrylic acid with itaconic acid or maleic acid (Crisp and Wilson, 1974a, 1977; Crisp *et al.*, 1980). The acidic solutions are usually prepared by free-radical polymerisation of the polyalkenoic acids in aqueous solution and are concentrated to 40-50% for use (Wilson and Nicholson, 1993). Increasing the concentration of the polyalkenoic acid results in increased compressive fracture strength, however, the working characteristics namely, the working and setting times are generally decreased (Crisp *et al.*, 1977; Wilson *et al.*, 1977b). In addition, increasing the molecular weight of the polyalkenoic acid resulted in an increase in the compressive fracture strength (Crisp *et al.*, 1976; Wilson *et al.*, 1989), double torsion fracture toughness (Hill *et al.*, 1989; Wilson *et al.*, 1989) and *in vitro* wear resistance (Wilson *et al.*, 1989) of the GI restoratives. However, a marked reduction in the working and setting times was observed (Wilson, 1989). Increasing the concentration and molecular weight of the polyalkenoic acid content in GIs increased the rate of the formation of structure which reduced the working and setting times. Furthermore, the viscosity of the polyalkenoic acidic liquid also increased and as a result, it was difficult to incorporate the same volume of powder into the liquid during mixing. To overcome the limitation of reduced working and setting times, anhydrous GI restoratives were developed (Wilson, 1989) where the polyalkenoic acid element was vacuum-dried and contained in the GI powder constituent (Prosser *et al.* 1984; Wilson

and Nicholson, 1993) which enabled the use of higher molecular weight polyalkenoic acids (McLean *et al.*, 1984).

2.3.3 Cement-Forming Reaction

The setting process of GIs occurs by an acid-base reaction (Wilson and Nicholson, 1993) which is initiated when the polyalkenoic acid and the calcium fluoro-alumino-silicate glass powder are mixed (Wilson and Kent, 1971, 1972). The acid-base reaction of GIs occurs between the proton-accepting basic glass powder and the proton-donating polyalkenoic acid and may be simplified as:



The setting process of GIs takes place in several overlapping phases (Mount and Makinson, 1982). The first phase involves the decomposition of the outer surface of the glass and the release of cement forming ions and is known as the dissolution phase. When the polyalkenoic acid and the calcium fluoro-alumino-silicate glass powder come into contact for the first time, an aqueous cement paste is formed. The polyalkenoic acids ionise in the aqueous paste forming hydrated protons, namely, hydrogen ions which attack the periphery of the glass particles (Crisp and Wilson, 1974a; Nicholson, 1998). As a result, calcium, and aluminium ions are liberated from the glass surface (Crisp *et al.*, 1974a; Wasson and Nicholson, 1991). The hydrogen ions released from the polyalkenoic acid diffuse to the glass particles filling the spaces vacated by the liberated ions (Crisp and Wilson, 1974a) resulting in a siliceous hydrogel surface on the glass particles (Crisp *et al.*, 1974) (Figure 2.3.1).

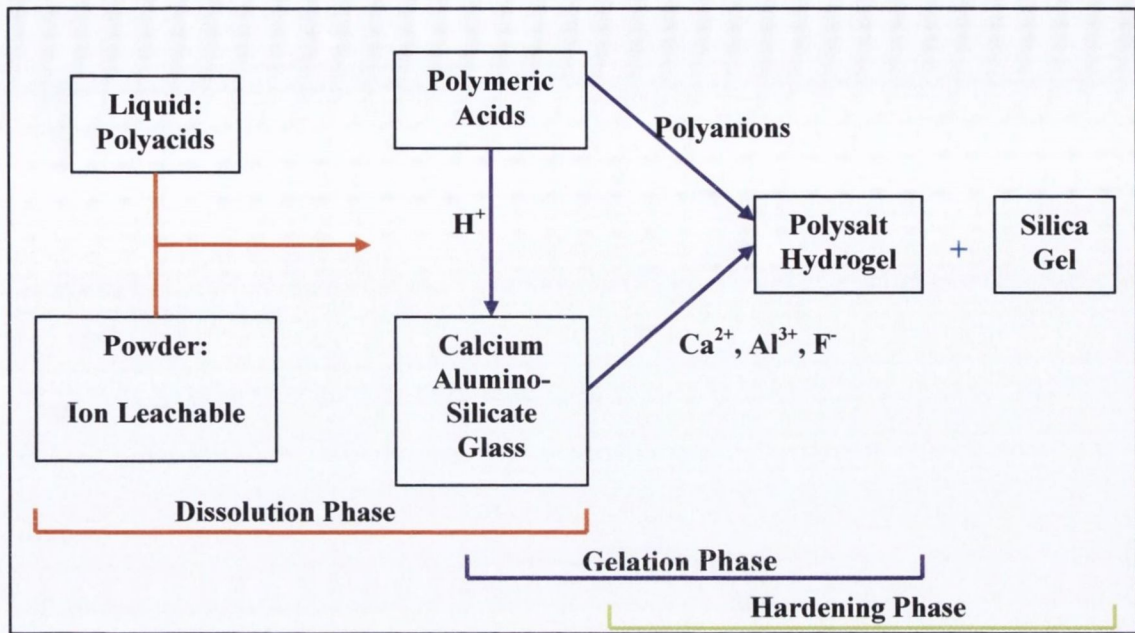


Figure 2.3.1 A diagrammatic representation of setting process of GIs.

The second phase of the setting reaction is known as the gelation phase. As the polyalkenoic acid ionises, the polymeric chains unwind as the negative charge on them increases (Crisp and Wilson, 1974a; Wilson and Nicholson, 1993). In addition, the released calcium and aluminium ions migrate to the aqueous cement paste, where as the pH increases they precipitate out as salts (carboxylates) (Crisp *et al.*, 1974). The carboxylates help to cross-link ionically the polymeric chains causing the cement to harden. Initially, a greater concentration of calcium ions than aluminium ions are released, as hydrolysis of the trivalent aluminium ions is slower than the loosely bound bivalent calcium ions (Nicholson, 1998). Therefore, it takes longer to remove the strongly bonded aluminium from the glass surface. The calcium carboxylates form within the first five to ten minutes of the reaction, while the stronger and more stable aluminium carboxylates form over the first hour and continued for up to 24 h (Crisp and Wilson, 1974b). As a result, the cement has poor initial (up to 30 mins) compressive fracture strength and elastic modulus (Wilson *et al.*, 1979), however, the

properties improve as the aluminium carboxylates form. The calcium and aluminium ions eventually combine to form the salt matrix together (Crisp *et al.*, 1974) (Figure 2.3.1).

The final phase of the setting reaction is known as the hardening phase. The silica-based hydrogel surrounding the glass particles and the calcium and aluminium polycarboxylates hydrate slowly (Wilson *et al.*, 1979) resulting in further improvements in the cements mechanical properties (compressive fracture strength and elastic modulus) which can continue for several months following the onset of the setting reaction (Crisp *et al.*, 1976; Paddon and Wilson, 1976; Wilson *et al.*, 1979). It can take up to 1 h for the aluminium ions to reach significant numbers in the setting GI (Crisp and Wilson, 1974b) and it is the aluminium ions that strongly cross-link the polymeric chains and are responsible for the final hardening of the cement (Crisp *et al.*, 1974).

It is essential that the setting GI is protected from excessive hydration or dehydration, especially during the first two phases of the setting reaction when the GI is most vulnerable (Mount and Makinson, 1982). Early exposure to moisture can upset the setting reaction (Causton, 1981) by causing the loss of aluminium ions (Crisp *et al.*, 1976) which reduces the level of cross-linking in the setting GI and results in reduced compressive fracture strengths and elastic moduli (Wilson *et al.*, 1979). However, the loss of water from the GI during the setting reaction can prevent completion of the cement forming reaction (Wilson and McLean 1988a,b). GIs are susceptible to the effects of exposure to moisture within the first 24 h after the commencement of the setting reaction but especially within the first 20 to 30 mins (Mount and Makinson,

1982). The sensitivity to moisture reduces as the aluminium and calcium ions begin to cross-link with the polymeric chains and become less susceptible to ion leaching (Wilson and McLean 1988a).

2.3.4 GI Structure

Barry *et al.* (1979) analysed the surface of GIs using a scanning electron microscope fitted with an energy dispersive X-ray analyser which enabled the determination of the distribution of calcium, silicon and aluminium on the GI surface. The authors reported that the three elements (calcium, silicon and aluminium) were located on the surface of the glass particles but only calcium and aluminium were found in the polymeric matrix phase of the GI restorative. In addition, it was noted that the glass particles appeared larger when analysed using silicon radiation compared with aluminium radiation which was attributed to the presence of a siliceous layer around the glass particles. As a result, Wilson and Prosser (1984) proposed that the microstructure of set GIs consisted of partially degraded glass particles surrounded by a layer of siliceous gel embedded in a salt-like matrix of polymeric chains cross-linked by calcium and aluminium ions (Figure 2.3.2). According to Brune and Smith (1982) the glass particles adhere to the salt-like polymeric matrix through the siliceous layer surrounding the particles by weak hydrogen bonds. In later studies employing scanning electron microscopy (Swift and Dogan, 1990) and transmission electron microscopy (Hatton and Brook, 1992; Brook and Hatton, 1998) the structure proposed by Wilson and Prosser (1984) was confirmed. The set GI can be regarded as a composite structure where the glass particles act as the filler (Barry *et al.*, 1979) to the salt-like polymeric matrix (Crisp *et al.*, 1976).

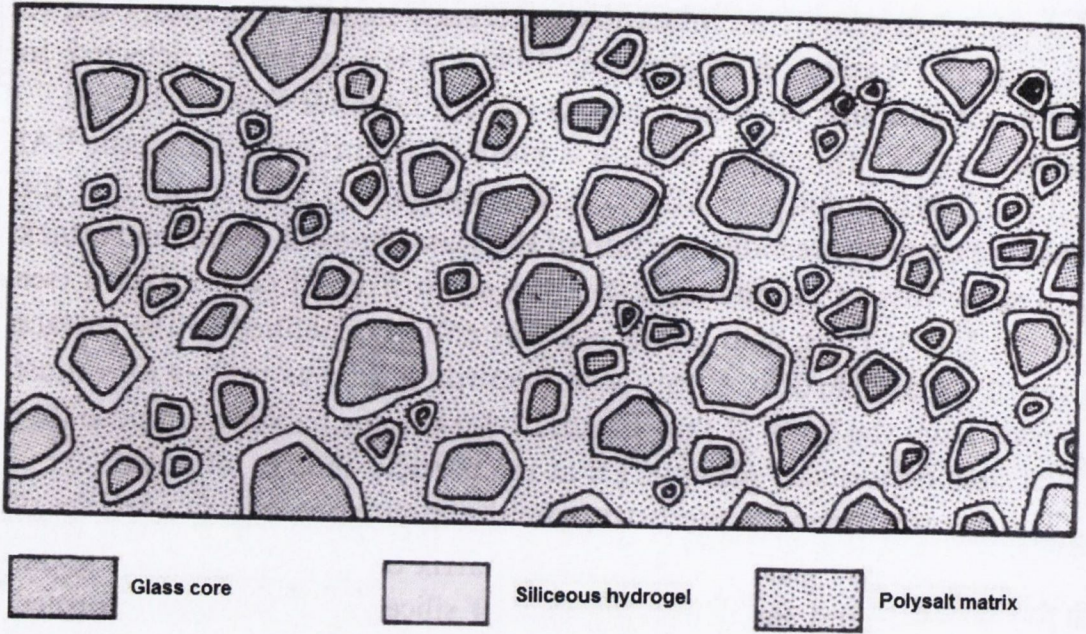


Figure 2.3.2 A diagrammatic representation of the structure of a GI (Wilson and Nicholson, 1993).

2.4 GI - The Ideal Posterior Filling Material?

Cost-effective and predictable dental treatment is central to the achievement of patient satisfaction regardless of whether the treatment is paid privately by the patient or provided by a third party in a similar manner to the General Dental Services (GDS) in England and Wales. Dental researchers and practitioners have conducted systematic reviews of restoration longevity and identified dental amalgam to be the material of choice (Sheldon and Treasure, 1999) due to the durability of the silver-tin alloy composition in the oral environment. Recently an extensive study of an age-stratified sample of GDS patients, clustered by year of birth, was undertaken and included over eighty thousand adult patients (Lucarotti *et al.*, 2005a,b,c; Burke *et al.*, 2005a,b). The data consisted of items gleaned from the payment claims submitted by GDS dentists to the Dental Practice Board (DPB) in Eastbourne, Sussex, England from a representative sample of patients treated in the GDS of England and Wales between 1991 and 2001. The patients accounted for a total of 719,009 claims sent to the DPB within the timeframe (ten years) investigated to determine the dental factors associated with the restoration, including restoration type and size of the cavity.

The results of the extensive study confirmed the view that dental amalgam was the material of choice with single surface amalgam restorations having a survival probability of 58% after ten years (Lucarotti *et al.*, 2005b). Patient demand for a tooth-coloured restorative treatment of cavities in posterior teeth combined with the potential fear of mercury toxicity (Lutz, 1995) has led the dental profession to consider alternative materials to dental amalgam even though the clinical performance of amalgam suggests a median survival time of over eleven years (Lucarotti *et al.*, 2005b). A limitation of the extensive study conducted by Lucarotti *et al.* (2005b) was

that it was not possible to compare the performance of amalgam and tooth-coloured filling materials in load-bearing surfaces of posterior teeth. The GDS Regulations in England and Wales, under whose auspices the data for the study was obtained, preclude the use of either resin-based composites and the GI cements in load-bearing surfaces of posterior teeth (Lucarotti *et al.*, 2005a). Accordingly, the resin-based composites were placed in Class III, IV and V cavities and GIs in Class III and V cavities with associated survival probabilities at ten years of 43 and 38%, respectively (Lucarotti *et al.*, 2005b). The tooth-coloured restoratives were not randomly assigned to different cavities and as a result the relative performance of the tooth coloured materials compared with dental amalgam could not be determined as they had not been applied to clinically similar cases.

When used clinically, dental amalgam relies on mechanical interlocking for adhesion and therefore necessitates the removal of sound tooth structure prior to amalgam placement such that the size of the initial cavity has to be extended (Lutz, 1995). The destruction of sound tooth structure is contraindicated since to date there is no replacement filling material available to dental practitioners with the properties of natural dentition. According to the data of Lucarotti *et al.* (2005b), the re-intervention of amalgam restorations in one in three cases is either extraction or crowning. This appears to confirm the potentially weakening effect of amalgam cavities on sound tooth structure. In addition, Lucarotti *et al.* (2005b) showed that whilst the performance of small class I dental amalgam restorations at ten years had a survival probability of 58%, the figure was reduced to only 43% when larger amalgam restorations such as mesio-occlusal-distal cavities were evaluated after ten years.

At present, methacrylate resin-based composite materials are considered by many dental practitioners to offer a tooth-coloured alternative to dental amalgam in load-bearing surfaces of posterior teeth. The patenting of a novel resin-based composite based on a highly viscous dimethylmethacrylate monomer synthesised from the reaction of bisphenol-A and glycidyl methacrylate (BisGMA) revolutionised resin technology in 1958 (Bowen, 1958). Following the addition of a co-monomer, triethyleneglycol dimethacrylate (TEGDMA) to decrease the viscosity of the mixture and aid incorporation of the filler particles, a resin-based composite for filling cavities in tooth structure was produced (Bowen, 1962). At present there are a number of resin-based composite materials with varying monomeric formulations available to practitioners. However, the free-radical polymerisation of dimethacrylate monomers during light-irradiation of resin-based composite involves bulk contraction (Davidson and Feilzer, 1997). The contraction and as a result polymerisation shrinkage of the resin-based composite material may be manifested as shrinkage stress (Davidson *et al.*, 1984). Cuspal movement on polymerisation may be perceived by the patient as post-operative pain (Christensen, 2000) and possibly lead to bacterial micro-leakage and ultimately marginal staining, pulpal inflammation or necrosis and secondary caries (Lutz *et al.*, 1991). Manufacturers have attempted to address the issues of excessive contraction on setting by removing the diluent TEGDMA from the resin-based composite monomeric formulations. The elimination of the TEGDMA for urethane dimethacrylate (UDMA) and derivatives of BisGMA, such as bisphenol-A ethoxylated dimethacrylate (Bis-EMA) with a similar filler content, resulted in a reduction in the associated shrinkage due to a reduced concentration of carbon-to-carbon double bonds (Asmussen and Peutzfeldt, 1998). However, while cuspal movement on polymerisation was reduced, no reduction in the associated gingival

microleakage at the cervical dentine cavosurface margin was evident (Fleming *et al.*, 2005).

The potential of cationic photo-initiated oxirane-based monomer chemistry and its application to dental resin-based composite materials was investigated by Palin *et al.* (2003, 2005a,b). The cationic ring-opening mechanisms of experimental oxirane-based monomers were proposed to result in improved clinical performance by way of decreased polymerisation shrinkage (Palin *et al.*, 2003) and the associated stresses generated at the tooth-restoration interface (Palin *et al.*, 2005c). The degree of conversion of an experimental oxirane resin-based composite was significantly less compared with methacrylate resin-based composites following 1 h post-irradiation (Palin *et al.*, 2003). Although the potential for a decreased magnitude of shrinkage strain was realised (Palin *et al.*, 2005a), the slow development of strength in the first hour of service was impractical for clinical placement in load bearing situations. Additionally, resin-based composites are time-consuming and technique-sensitive to place clinically compared with dental amalgam, and require a series of preconditioning treatments of the tooth structure to ensure adhesion (Peumans *et al.*, 2005). The development of two-step and one step self-etching systems have not been as successful as the original three-step acid-etch, prime and conditioning steps (Peumans *et al.*, 2005). Burke *et al.* (2005b) reported that the performance of resin-based composites was decreased after 1996 and that resin-based composites as a posterior filling material had a median survival time of under seven years when placed by experienced operators (Lucarotti *et al.*, 2005b). It is suggested that the elimination of the three-step tooth preconditioning treatments and the adoption of two-step and

one-step self-etching systems by dental practitioners may be a possible reason for the poor clinical performance of resin-based composites since 1996.

GIs are a tooth-coloured dental restorative material which chemically adhere to sound tooth structure (Akinmade and Nicholson, 1994) without the need for preconditioning of the tooth structure or the removal of sound tooth structure. Clinically, GIs can be adequately placed and finished by the operator in a single patient visit, and are reported to release fluoride over time which has been claimed to be therapeutic (Forsten, 1998). Unfortunately, conventional GI formulations are not advocated for load-bearing surfaces of posterior teeth in the GDS Regulations in England and Wales. In the investigation by Lucarotti *et al.* (2005b) GIs were generally placed in Class III and Class V cavities with an associated survival probability at ten years of 38%. Despite the poor performance, GIs could be placed in minimal intervention cavities, with no associated loss of sound tooth structure, such that in principle re-intervention of like with like (GI with GI) could allow a tooth to survive indefinitely even if the intervals were short. When placed in the posterior region of the mouth GIs have to resist masticatory forces during function and therefore optimisation of the compressive fracture strength is important. As a result, the minimum compressive strength stated in ISO 9917-1 : 2003 for GI restorative is 100 MPa which is twice that stated for GI luting cements (50 MPa). The question posed here is could an enhanced, stronger GI restorative be developed as a tooth-coloured posterior filling material to replace dental amalgam as a posterior filling material? If so, this material could remove the necessity for the destruction of sound tooth structure associated with dental amalgam and the shrinkage problem and possible biocompatibility concerns regarding unreacted monomer with resin-based composites.

2.5. Attempts at Reinforcement of GIs

To improve the mechanical properties of GIs, a number of researchers have investigated the influence of the addition of fibres (Sced and Wilson, 1980; Oldfield and Ellis, 1991; Kobayashi *et al.*, 2000; Lohbauer *et al.*, 2003), hydroxyapatite (Nicholson *et al.*, 1993; Yap *et al.*, 2002; Moshaverinia *et al.*, 2008), hydroxyapatite-zirconia (Gu *et al.*, 2005), bioactive glass particles (Yli-Urpo *et al.*, 2005) and metallic powders (Sced and Wilson, 1980; Simmons, 1983, 1990; Miller *et al.*, 1984; El Mallakh and Sarkar, 1987; Nakajima *et al.*, 1989) with varying degrees of success.

The addition of a filler to GIs obviously results in a more complex composite structure. The mechanical properties of composite materials arise due to a complex interaction of a number of parameters as the filler and matrix constituents “usually interact in a synergistic way” (Matthews and Rawlings, 1994a). The size, shape, orientation, distribution and quantity of the filler and features of the matrix such as grain size and crystallinity will influence the mechanical properties of the composite material (Schwarz, 1992). However, the most important parameter governing the mechanical properties of composites is the characteristics of the interface between the filler and matrix (Schwarz, 1992; Matthews and Rawlings, 1994a). It is crucial that the interfacial bond strength between the filler and the matrix is sufficient to transfer loads from the matrix to the filler so that the composite is stronger than the unreinforced matrix (Matthews and Rawlings, 1994a).

2.5.1 Fibres

In 1980, Sced and Wilson (1980) examined the influence of the addition of a variety of fillers to a commercial GI (ChemBond; Dentsply Caulk; Milford, DE, USA). The

fillers examined included silica fibres, glass fibres composed of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_3\text{AlF}_6\text{-CaF}_2\text{-AlF}_3\text{-AlPO}_4$ (28.1-16.1-14.9-18.1-13.2-9.6 wt.%, respectively), carbon fibres and alumina fibres. The aspect ratios (the ratio of the particle length to the thickness) of the filler particles were at least 4 to 1 with diameters ranging from 10 to 200 μm and particle lengths of no more than 1000 μm . To incorporate the fibres in the GI system, a portion of the GI powder content was removed so that the handling characteristics of the GI would not be altered. Typically, the authors attempted to incorporate a minimum of 25 vol% of filler into the GI system, however, the exact volume fraction employed differed depending on the type of filler added. The flexural strength was determined in accordance with BS 5199 : 1975 using bar-shaped specimens (25 mm length, 3 mm width, 3 mm thickness). For the GIs reinforced with silica fibres, glass fibres, carbon fibres and alumina fibres the mean flexural strengths were reported as 26, 30, 53 and 44 MPa, respectively compared with the unreinforced GI control (10 MPa). Unfortunately, the number of specimens tested, the testing technique (three- or four-point flexure strength), the standard deviations or the statistical analyses were not reported by the authors. The lack of information provided by the authors in the study makes interpretation of the results difficult.

The measurement of the tensile strength of brittle materials under uni-axial flexure conditions has been determined (Berenbaum and Brodie, 1959) using a bar-shaped specimen subjected to three- or four-point flexural loading and the modulus of rupture was calculated using simple beam theory from the load to failure. The major advantage of the uni-axial flexure test is that a state of pure tension can be established on one side of the specimen (Berenbaum and Brodie, 1959). Modulus of rupture may be equated to the tensile strength of a brittle material because fracture initiates on the

side of the brittle specimen in tension and no plastic yielding occurs (Earnshaw and Smith, 1966). However, the test has serious disadvantages as the stress in the loaded section is not uniform (Williams and Smith, 1971) varying from zero at the neutral axis to a maximum at the outer surfaces which accentuates the effect of surface condition on measured strength (Rudnick *et al.*, 1963) and test results are in excess of the true tensile strength (Wright, 1955; Rudnick *et al.*, 1963; Earnshaw and Smith, 1966). The problems with using bar-shaped specimens for determining the strength of fibre reinforced specimens are exacerbated by the position and orientation of the fibrous reinforcement relative to the state of pure tension established on the bottom surface of the specimen. While marked increases in the mean flexural strength of GIs containing silica, carbon and alumina fibres were reported by Sced and Wilson (1980), no further research on this type of GI reinforcement was conducted by the authors which suggests that the GIs were possibly deficient in other areas. It is likely that the addition of the fillers such as carbon fibres which are black in nature, would darken the colour of the GI and result in a material which is less tooth-like in appearance. Additionally, the replacement of a portion of the GI powder content with a fibrous filler with dimensions of up to 200 μm diameter and 1000 μm length may have made the GI more difficult to mix and place clinically.

In a later study by Oldfield and Ellis (1991), the addition of carbon fibres and alumina fibres to experimental GI systems based on MP4 glass ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O}$ (28.0-35.0-26.0-11.0 wt.%, respectively)) and G338 glass ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2\text{-AlF}_3\text{-AlPO}_4\text{-Na}_3\text{AlF}_6$ (25.2-14.2-12.8-4.5-24.1-19.2 wt.%, respectively)) were investigated. The carbon fibres had a diameter of approximately 8 μm , lengths of 250 and 1000 μm and an elastic modulus of 380-400 GPa. The alumina fibres were approximately 3 μm in

diameter and 500 μm in length with an elastic modulus of 3000 GPa. As a result, the aspect ratio of the carbon fibres ranged from 31 to 125 while the alumina fibres had an aspect ratio of 166. To incorporate the reinforcing fibres into the experimental GI restorative powders it was necessary to reduce the volume of GI powder. The reinforcing fibres were added to the experimental GI restorative powders at concentrations ranging from 0 to 20 vol% in 2.5 vol% increments. The fibres and experimental GI powders were dry-blended with vacuum-dried polyacrylic acid in a mechanical mixer prior to hand-mixing with water to initiate the setting reaction. The flexural strength and modulus were determined for each experimental group by testing cylindrical specimens (4.5 mm diameter, unknown length) using a four-point bending jig attached to a tensile testing machine. The maximum mechanical properties (flexural strength and flexural modulus) were obtained for the experimental glasses MP4 and G338 when 5.0 and 7.5 vol% of carbon fibres were added, respectively which resulted in significantly increased flexural strength and flexural modulus compared with the unreinforced control. The authors attributed the increases in the flexural strength and flexural modulus to the increased work of fracture of the reinforced GIs (Oldfield and Ellis, 1991). A greater energy is required to fracture the GIs containing the carbon fibres as fibre pull-out needs to occur before failure (Matthews and Rawlings, 1994b). Oldfield and Ellis (1991) did not report results for the experimental GIs containing alumina fibres as there was "little, if any, fibre pull-out" due to the brittleness of the alumina fibres. The fact that the alumina fibres broke during testing suggests that some stress-transfer occurred between the GI and the fibres and therefore that the alumina fibres did provide a reinforcing effect, however, this did not result in significant strength increase.

Furthermore, it is confusing how the cylinders were tested using a four-point bending jig as no explanation of the testing set up was reported by the authors. Therefore the flexural strengths and moduli reported by Oldfield and Ellis (1991) are difficult to interpret and given that no further research has been reported in the dental literature regarding the addition of carbon fibres to GIs by the authors, it is postulated that the replacement of a portion of GI powder with black carbon fibres darkened the colour of set GI which may clinically preclude the use of carbon fibre reinforced GIs.

More recently, research in the area of the addition of fibres to GIs has focused on the use of glass fibres (Kobayashi *et al.*, 2000; Lohbauer *et al.*, 2003). Kobayashi *et al.* (2000) investigated the influence of the addition of short glass fibres with varying diameters, lengths and aspect ratios and similar composition to the GI powder constituent (CaO-P₂O₅-SiO₂-Al₂O₃ (32.2-9.3-41.0-17.5 wt.%, respectively)) to a GI (HY BOND GLASIONOMER CX; Shofu Dental Corporation; Fukuine, Japan). The addition of the short glass fibres to the GI powder was facilitated by reducing the powder content by 0, 20, 40, 60, 80 and 100 mass% and the resultant GI powder and short glass fibre mix was hand-mixed with the commercial GI liquid in accordance with the manufacturers' instructions. Disc-shaped specimens (6 mm diameter, 3 mm height) and bar-shaped specimens (25 mm length, 6 mm width, 3 mm thickness) were prepared and the diametral tensile strength and three-point flexure strength, respectively were determined at a loading rate of 0.5 mm/min after 24 h. As the concentration of short glass fibres was increased from 0 to 60 mass% there was a progressive increase in the mean diametral tensile strength (from 11 to 18 MPa) and mean three-point flexure strength (from 8 to 35 MPa). A subsequent deterioration of

diametral and three-point flexure strength was evident when the concentration of short glass fibres was increased above 60 mass%.

The diametral tensile test (Wright, 1955) compresses a disc-shaped specimen diametrically between two knife-edged supports. Ideally, under correct loading conditions tensile stresses are set up along the diametral plane joining the two points of contact normal to that plane. Generally, the compression platens rather than knife edge supports are employed so that intimate point contacts are replaced by an area of contact (Darvell, 1990) which complicates the pattern and propagation of the tensile crack (Kendall, 1978). As a result, the diametral tensile strength determined cannot be regarded as being a true measure of tensile strength (Darvell, 2002) which precludes the diametral tensile test from use in the specification standards. Therefore the diametral tensile strength results reported by Kobayashi *et al.* (2000) in the dental literature provide little useful information for interpreting the reinforcement of GIs. In addition, the position and orientation of the short glass fibres relative to the state of pure tension established on one side of the bar-shaped specimen relative to the loading direction would be expected to markedly influence the three-point flexure strengths reported by Kobayashi *et al.* (2000).

The influence of GIs reinforced with glass fibres composed of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-NaF-AlF}_3\text{-Na}_3\text{AlF}_6$ (33.3-16.7-14.0-3.3-16.5-16.2 wt.%, respectively) was investigated by Lohbauer *et al.* (2003). The glass fibres had a diameter of 26 μm and a length of $580 \pm 160 \mu\text{m}$ which resulted in an aspect ratio ranging from 16 to 28. Initially, to optimise the manufacturing parameters of the glass fibre reinforced GIs, the authors conducted compressive fracture strength tests for a series of fibre reinforced GIs prepared with

varying powder to liquid mixing ratios, glass fibre pre-treatments, glass particle sizes and glass fibre concentrations. The optimum glass fibre reinforcement of the GIs tested in four-point flexure at 24 h using bar-shaped specimens (25 mm length, 2 mm width, 2 mm thickness) at a loading rate of 0.75 mm/min was 16 ± 2 MPa for the GI containing 20 vol% glass fibres compared with 9 ± 2 MPa for the unreinforced control.

The addition of glass fibres to GIs was reported to significantly increase the flexural strength of bar-shaped specimens (Sced and Wilson, 1980; Kobayashi *et al.*, 2000; Lohbauer *et al.*, 2003), however, the diameter, length and composition of the glass fibres and the composition of the GI differed for all the studies investigated. The replacement of a portion of the GI powder with glass fibres provided some reinforcement for the GIs investigated, possibly due to the bridging of fibres across extending cracks and the increased force required to pull-out the glass fibres from the GI matrix (Matthews and Rawlings, 1994b). However, the mechanical testing method employed in many of the studies was difficult to interpret, where the authors employed diametral tensile strength testing, three- and four-point flexure strength testing which makes it difficult to adequately assess if reinforcement of the GI has been achieved in the studies.

2.5.2 Hydroxyapatite

The addition of finely-divided hydroxyapatite to GIs was first proposed by Nicholson *et al.* (1993). In light of the favourable adhesive interaction between hydroxyapatite and GIs, it was thought (Nicholson *et al.*, 1993) that GIs containing hydroxyapatite may exhibit increased biocompatibility and some “interesting mechanical properties”.

Hydroxyapatite powder was added to two experimental glasses (MP4 and G200D (SiO₂-Al₂O₃-Na₃AlF₆-CaF₂-AlF₃-AlPO₄ (29.0-16.6-5.0-34.3-5.3-9.9 wt.%, respectively)) at 2.5, 5, 10, 20, 25, 30, 40 and 50%. The hydroxyapatite GI powders were hand-mixed with a 40% aqueous solution of polyacrylic acid using a powder to liquid mixing ratio of 2 to 1. The mean compressive fracture strengths were determined at 24 h using cylindrical specimens (12 mm height, 6 mm diameter) tested at a loading rate of 1 mm/min in accordance with BS 6039 : 1987. The addition of hydroxyapatite to the GI resulted in a progressive decrease in the mean compressive fracture strength as the percentage of hydroxyapatite was increased.

Yap *et al.* (2002) investigated the addition of hydroxyapatite to an encapsulated GI restorative (Fuji IX; GC Corporation; Tokyo, Japan). The glass component contained in each Fuji IX capsule was substituted with either 4, 12 or 28 vol% of hydroxyapatite and the contents of the capsule were mechanically mixed in accordance with the manufacturer's instructions. The GI restoratives containing hydroxyapatite were prepared for compressive fracture and diametral tensile strength testing using specimens of 8 mm height, 4 mm diameter (n = 5) and 6 mm diameter, 3 mm height (n = 5), respectively. The compressive fracture and diametral tensile strength tests were conducted at a loading rate of 1 mm/min. There was no significant difference in the mean compressive fracture strength and mean diametral tensile strength determined at 24 h for the GI restorative containing 4 vol% hydroxyapatite (142 ± 31 and 12 ± 3 MPa, respectively) compared with the control (150 ± 45 and 12 ± 2 MPa, respectively). Progressively increasing the hydroxyapatite content from 4 to 28 vol% resulted in a progressive deterioration of the mean compressive fracture strength from

142 ± 31 to 133 ± 18 MPa and the mean diametral tensile strength from 12 ± 3 to 8 ± 1 MPa, respectively.

The addition of hydroxyapatite-zirconia powders to an encapsulated GI restorative (Fuji IX) was investigated by Gu *et al.* (2005). The glass constituent of Fuji IX was substituted with 4, 12, 28 and 40 vol% of the hydroxyapatite-zirconia powder. The capsules were activated, the contents were mechanically mixed for 15 s and applied to cylindrical moulds of 8 mm height, 4 mm diameter and 6 mm diameter, 3 mm height for compressive fracture (n = 5) and diametral tensile strength testing (n = 5), respectively at a loading rate of 1 mm/min in accordance with BS 6039 : 1981. For the GI restoratives prepared with 4 and 12 vol% hydroxyapatite-zirconia powders, there were no significant differences in the 24 h mean compressive fracture strength (153 ± 12 and 153 ± 27 MPa, respectively) and 24 h diametral tensile strength (15 ± 3 and 12 ± 2 MPa, respectively) compared with the control (150 ± 45 and 11 ± 2 MPa, respectively). When the concentration of hydroxyapatite-zirconia powder was increased to 28 and 40 vol% there was a deterioration of the 24 h mean compressive fracture strength and 24 h mean diametral tensile strength.

More recently, the effect of hydroxyapatite and fluoroapatite incorporation into a GI restorative (Fuji II; GC Corporation; Tokyo, Japan) was examined by Moshaverinia *et al.* (2008). The hydroxyapatite and fluoroapatite powders were synthesised by an ethanol-based sol-gel method. To prepare the reinforced GI restoratives 5 wt.% of the GI restorative powder was replaced with either hydroxyapatite or fluoroapatite powder. The GI restorative powder containing either hydroxyapatite or fluoroapatite was mixed with a mortar and pestle for 20 mins. The resultant GI restorative powder

was hand-mixed with Fuji II liquid in accordance with the manufacturers' instructions using a powder to liquid mixing ratio of 2.7 to 1. Cylindrical specimens of 6 mm height, 4 mm diameter (n = 6) and 4 mm diameter, 2 mm height (n = 6) were prepared for compressive fracture and diametral tensile strength determination, respectively. In addition, groups of six disc-shaped specimens (10 mm diameter, 1 mm thickness) were prepared for biaxial flexure strength testing. The compressive fracture, diametral tensile and biaxial flexure strength tests were conducted at a loading rate of 0.5 mm/min, 24 h after the commencement of mixing. The authors claimed that the GI restoratives prepared with hydroxyapatite and fluoroapatite powders had increased mean compressive fracture strength (177 ± 16 and 179 ± 17 MPa, respectively), mean diametral tensile strength (16 ± 4 and 17 ± 4 MPa, respectively) and mean biaxial flexure strength (26 ± 6 and 28 ± 7 MPa, respectively) compared with the control (160 ± 21 , 12 ± 3 and 14 ± 5 MPa, respectively). However, no statistical analysis was conducted and, as a result, it is unknown whether the strength increases were significant. The authors suggested that the hydroxyapatite and fluoroapatite additives had an effect on both the setting reaction and the degree of polysalt bridge formation which resulted in the improved mechanical properties of the final set material although no details in terms of the working characteristics were provided.

The suggestion of Nicholson *et al.* (1993) that GIs containing hydroxyapatite would exhibit increased biocompatibility and some "interesting mechanical properties" was not shown in the studies reported in the dental literature (Yap *et al.*, 2002; Gu *et al.*, 2005; Moshaverinia *et al.*, 2008). It was reported that hydroxyapatite hydroxyapatite addition to GIs did not result in significantly improved compressive fracture strength (Nicholson *et al.*, 1993; Yap *et al.*, 2002; Gu *et al.*, 2005; Moshaverinia *et al.*, 2008),

diametral tensile strength (Yap *et al.*, 2002; Gu *et al.*, 2005; Moshaverinia *et al.*, 2008) or biaxial flexure strength (Moshaverinia *et al.*, 2008). Nicholson *et al.* (1993) suggested that hydroxyapatite behaved as an unreactive filler and interfered with the setting reaction which resulted in the decreased mechanical properties. However, hydroxyapatite is the primary mineral constituent in tooth enamel (Zimehl and Hannig, 2001) and has been shown to chemically interact with the polyalkenoic acid constituents of GIs (Yoshida *et al.*, 2001). Therefore, the suggestion of Nicholson *et al.* (1993), that hydroxyapatite acted as an unreactive filler is surprising. It is possible that the particle size and distribution of the hydroxyapatite employed in these studies was not optimised for reinforcement of the GIs and also may not have been homogeneously dispersed in the GI matrix. A heterogeneous dispersion of hydroxyapatite may have led to low strength areas in the structure (Matthews and Rawlings, 1994a) which could have resulted in the significantly decreased compressive fracture strength (Nicholson *et al.*, 1993; Yap *et al.*, 2002; Gu *et al.*, 2005; Moshaverinia *et al.*, 2008), diametral tensile strength (Yap *et al.*, 2002; Gu *et al.*, 2005; Moshaverinia *et al.*, 2008) and biaxial flexure strength (Moshaverinia *et al.*, 2008) reported.

2.5.3 Bioactive Glass Particles

Yli-Urpo *et al.* (2005) replaced 10 wt.% of the glass powder constituent of Fuji II with bioactive glass particles composed of SiO₂-Na₂O-CaO-P₂O₅ (53.0-23.0-20.0-4.0 wt.%, respectively) (mean particle size, 20 µm). The GI restorative powder reinforced with 10 wt.% bioactive glass particles were hand-mixed with the Fuji II liquid using a powder to liquid mixing ratio of 1.7 to 1. Cylindrical specimens (6 mm diameter, 4 mm height) were fabricated and the mean compressive fracture strength was

determined at a loading rate of 1 mm/min. The addition of 10 wt.% bioactive glass particles resulted in a significant reduction in the mean compressive fracture strength determined at 24 h (95 ± 20 MPa) compared with the control group (120 ± 20 MPa). It is likely that the interfacial bond strength between the bioactive glass particles and the GI matrix was insufficient to transfer loads from the matrix to the bioactive glass particles (Matthews and Rawlings, 1994a) which resulted in the decreased mean compressive fracture strength reported compared with the unreinforced control.

2.5.4 Metals

Sced and Wilson (1980) also investigated the addition of a variety of metal filler particles in the form of fibres, acicular or columnar crystals and flakes to the powder constituent of the commercial GI ChemBond. The metal filler particles added to the powder constituent were titanium (99.5% pure), nickel aluminium alloy, aluminium (99.9% pure), chromium and silver-tin alloy which resulted in flexural strengths of 22, 22, 21, 22 and 40 MPa, respectively compared with the unreinforced GI control (10 MPa). The most promising results were achieved with the addition of silver-tin alloy, however, it was reported that the resultant material could not be polished and was not tooth coloured and therefore was not advocated for use clinically (Wilson and Nicholson, 1993).

In 1983, Simmons proposed the addition of spherical silver amalgam alloy powder (Lumi Alloy; GC Corporation; Tokyo, Japan) to Fuji II prior to mixing with a polyacrylic acid solution (Simmons, 1983, 1990). The optimum ratio of GI powder to silver amalgam alloy powder was reported to range from 5 to 1 to 8 to 1 (Miller *et al.*, 1984). When the compressive fracture strength was assessed in accordance with ADA

specification No. 8 (12 mm height, 6 mm diameter cylindrical specimens tested using a loading rate of 0.5 mm/min), a significant increase in the mean compressive fracture strength was reported by the authors (Miller *et al.*, 1984) for the GI restorative containing amalgam alloy powder (197 ± 12 MPa) compared with the control group (151 MPa). Subsequently Fuji II reinforced with silver amalgam alloy powder was marketed as Miracle Mix by GC Corporation (Tokyo, Japan) in 1985.

In a later study by El Mallakh and Sarkar (1987), no significant difference in the 24 h mean compressive fracture strength for 6 mm height, 3 mm diameter cylindrical specimens was reported for Miracle Mix (148 MPa) compared with Fuji II (143 MPa). Similarly, Nakajima *et al.* (1989) reported no significant difference in the 24 h mean compressive fracture strength of Miracle Mix (120 ± 15 MPa) and Fuji II (120 ± 10 MPa) cylindrical specimens (12 mm height, 6 mm diameter tested at a loading rate of 0.5 mm/min). However, when the flexural strength of bar-shaped specimens (25 mm length, 4 mm width, 2 mm thickness) were tested at a loading rate of 0.5 mm/min, there was a significant increase for Miracle Mix (25 ± 3 MPa) compared with Fuji II (18 ± 1 MPa). The authors (Nakajima *et al.*, 1989) suggested that the significant increase in flexural strength indicated that the addition of silver amalgam alloy to the GI changed the mode of fracture. The addition of a ductile filler particle (metal) to the brittle GI may have changed the mode of fracture, however, it is unlikely that the metal fillers are chemically adhered to the GI matrix as the metals used are oxidation-resistant and therefore bonding between the GI and the metal may not be possible (Darvell, 2002). Therefore, the claims of improvements in mean compressive fracture strength (Miller *et al.*, 1984) and mean flexural strength (Nakajima *et al.*, 1989) of Miracle Mix compared with Fuji II are not evident in the dental literature.

An alternative method of combining GIs with metals was proposed by McLean and Gasser (1985), where a metal (typically silver, gold or palladium) was fused with the GI glass constituent. The glass and metal powders were dry-mixed, compressed into pellets using a pelletiser at a pressure of 350 MPa and fused together at 800°C (McLean and Gasser, 1985; McLean, 1990). The resultant metal-glass composite “cermet” was ground to produce a fine powder which was mixed with a 46% solution of acrylic, maleic and tartaric acids to form the cermet cement. The most promising results were achieved using pure silver with an average particle diameter of 3.5 µm. In addition, 5 wt.% titanium dioxide was added to the metal-glass powder to make cermets more tooth-like in appearance, however, cermet cement cannot claim to be tooth-coloured. The authors (McLean and Gasser, 1985; McLean, 1990) claimed that the cermet cement had improved compressive fracture strength and flexural strength compared with the conventional GI. However, the methods employed to assess the compressive fracture strength and flexural strength were not reported. The compressive fracture strength and flexural strength of the cermet cement were reported to be inferior to amalgam and resin-based composites and as a result, cermet cements were not advocated clinically for load bearing situations. Several cermet cements were released to the market by ESPE (Seefeld, Germany), namely, Ketac Silver and Chelon Silver in 1986.

Walls *et al.* (1987) reported a significant increase in the compressive fracture strength of 6 mm height, 4 mm diameter specimens tested at a loading rate of 1mm/min for Ketac Silver (199 ± 33 MPa) compared with its conventional equivalent Ketac Fil (149 ± 32 MPa) (ESPE; Seefeld, Germany). However, the cermet cement exhibited a

significant reduction in three-point flexure strength (29 ± 7 MPa) compared with the conventional GI (45 ± 5 MPa) for bar-shaped specimens (20 mm length, 2.5 mm width, 2.5 mm thickness) tested at a loading rate of 0.5 mm/min. The claimed improvements in some of the compressive fracture strength (McLean and Gasser, 1985; Walls *et al.*, 1987; McLean, 1990) and flexural strength (McLean and Gasser, 1985; McLean, 1990) of cermet cements compared with the original GIs on which they are based suggest that they could be a useful addition to the dentists' armoury. However, given that cermets are not tooth-like in appearance (Darvell, 2002), the range of clinical applications for the material are generally limited to paediatric and domiciliary dental care.

2.5.5 Summary

The assessment of the dental literature in terms of the attempted reinforcement of GIs employing fibres (Sced and Wilson, 1980; Oldfield and Ellis, 1991; Kobayashi *et al.*, 2000; Lohbauer *et al.*, 2003), fillers such as hydroxyapatite (Nicholson *et al.*, 1993; Yap *et al.*, 2002; Moshaverinia *et al.*, 2008), hydroxyapatite-zirconia (Gu *et al.*, 2005), bioactive glass particles (Yli-Urpo *et al.*, 2005) and metallic powders (Sced and Wilson, 1980; Simmons, 1983, 1990; Miller *et al.*, 1984; El Mallakh and Sarkar, 1987; Nakajima *et al.*, 1989) does not provide the reader with optimism. Too often the testing method employed was flawed as in the use of the diametral tensile test or the three- or four-point flexural test and the sample numbers are too small for brittle materials which should be at least 20 for compressive fracture strength testing (McCabe and Carrick, 1986). In addition, details of the testing methods employed in terms of specimen size, rate of loading, specimen preparation, storage conditions and

time of testing are not reported in many of the studies examined which makes it almost impossible to assess adequately the dental literature.

2.6 Montmorillonite Clay Filler

Another filler that could potentially be used to improve the mechanical properties of GIs is montmorillonite (MMT) clay. MMT is a tri-layered smectite clay mineral consisting of stacked platelets constructed of an alumina octahedral layer sandwiched between two silica tetrahedral layers (Alexandre and Dubois, 2000) as illustrated in Figure 2.6.1. Each MMT layer is approximately 1 nm in thickness, however, the lateral dimensions can vary from 200 to 1000 nm, which gives MMT clays an aspect ratio of up to 1000 (Giannelis, 1996; Alexandre and Dubois, 2000). In contrast, the fibrous fillers previously added to GIs had aspect ratios which ranged from 4 (Sced and Wilson, 1980) to 125 (Oldfield and Ellis, 1991). The MMT clay layers form stacks of several thousands (Utracki, 2004) with a regular van der Waals gap between each layer known as the interlayer d-spacing (Giannelis, 1996; Alexandre and Dubois, 2000). The forces between the layers are relatively weak, therefore it is possible to intercalate small molecules between the layers (Alexandre and Dubois, 2000). The hydrated cations of the interlayer can be ion-exchanged with organic cationic surfactants (intercalants) to create an organically-modified clay (Ray and Okamoto, 2003). Organic cations lower the surface energy of the MMT clay surface and can make the clay compatible with the material to which it will be added (Giannelis, 1996). The ion-exchange process results in the intercalation of the MMT platelets. Intercalation is the insertion of a new species in the interlayer spacing between the clay platelets and can be achieved by the insertion of progressively larger molecules into the interlayer spacing which act to push the layers apart (Okamoto, 2003). A second result of intercalation could be the weakening of the MMT interlayer forces resulting in exfoliation (Alexandre and Dubois, 2000). Exfoliation is the complete separation of the platelets and is achieved when the interlayer space becomes too wide

for the van der Waals forces to keep the platelets together (Okamoto, 2003). The specific surface area of exfoliated MMT clays is extensive at 750-800 m²/g (Utracki, 2004) and provides an extensive area for interaction with the parent material. It also means that the parent material can potentially have increased stiffness and strength with less MMT clay content than is required with conventional fillers (Giannelis, 1996).

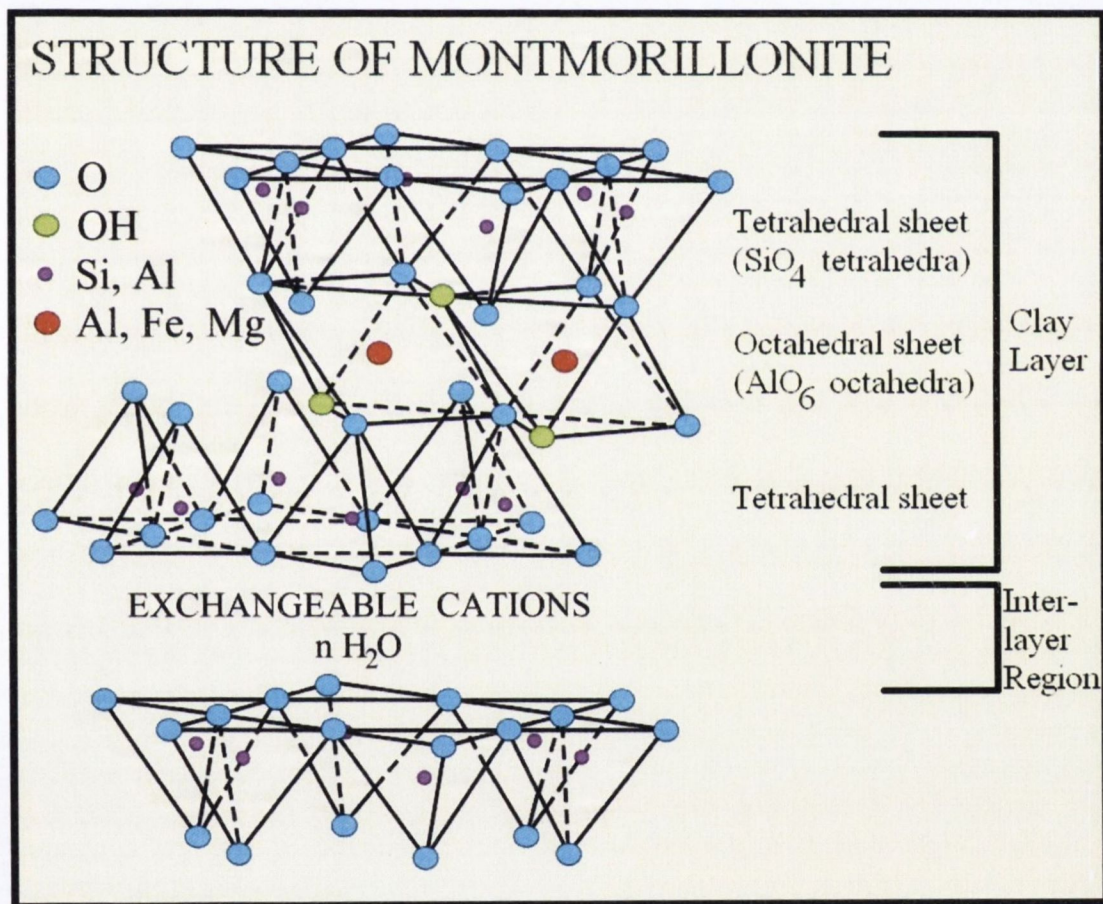


Figure 2.6.1 Graphical representation of an MMT clay platelet adapted from <http://pubs.usgs.gov>.

The addition of MMT clay at low filler loadings (< 5 wt.%) has been reported to significantly improve the tensile strength and tensile modulus of polymers such as

nylon (Okada *et al.*, 1990) and PMMA (Park and Jana, 2003) and more recently the compressive fracture strength of PMMA bone cements (Kwon and Kim, 2007). Okada *et al.* (1990) polymerised ϵ -caprolactam into the interlayer spacing of MMT clay to produce a nylon 6-clay hybrid with 4.2 wt.% of MMT clay which had significantly increased tensile strength (107 MPa) and tensile modulus (2.1 GPa) compared with pure nylon 6 (69 MPa and 1.1 GPa, respectively) when tested in accordance with the relevant ASTM standard. In a later study, Park and Jana (2003) added an organically-modified MMT clay (Cloisite 30B; Southern Clay Products, Gonzales, TX, USA) at 2 wt.% to PMMA-epoxy blends (80-20%) and reported significantly increased tensile strength (37 MPa) and tensile modulus (1.1 GPa) compared with the non-reinforced control group (27 MPa and 0.8 GPa, respectively) when tested in accordance with ASTM D-638. The significant increases in the tensile strength and tensile modulus reported by Okada *et al.* (1990) and Park and Jana (2003) were attributed to the increased interlayer spacing of the MMT clay which resulted in an enormous surface area for ionic bonding between the organic polymer and inorganic silicate sheet (Okada *et al.*, 1990) and a homogeneous dispersion of MMT clay in the polymer matrix (Park and Jana, 2003). There are a multitude of other similar studies reported in the literature where the addition of MMT clays to polymeric systems result in significant improvements in the tensile and compressive fracture strength compared with the unreinforced controls.

Kwon and Kim (2007) attempted to add both an un-modified MMT clay and an organically-modified MMT clay (Cloisite Na⁺ and Cloisite 25A, respectively; Southern Clay Products, Gonzales, TX, USA) to a more complex system, namely a PMMA bone cement. The authors added the MMT clays at concentrations ranging

from 0.5 to 2.0 wt.% to both the powder and liquid constituents of the bone cement prior to mixing. The compressive fracture strength was assessed in accordance with ASTM F451-86 (12 mm height, 6 mm diameter cylindrical specimens tested using a loading rate of 20 mm/min). The organically-modified MMT clay dispersed more homogeneously in the bone cement than the un-modified MMT clay. However, there were no significant differences in the mean compressive fracture strength between the groups containing the organically-modified and un-modified MMT clays. The authors showed that a greater reinforcing effect was achieved when both of the MMT clays were added to the liquid constituent of the bone cement compared with adding to the powder constituent. It was suggested that the addition of the MMT clays to the liquid element of the bone cement allowed for a greater interaction between the clay and the polymeric constituent of the bone cement which possibly resulted in the increased compressive fracture strength.

In the present study, the addition of the un-modified MMT clay calcium-montmorillonite (Ca-MMT) clay and the organically-modified MMT clay 12-amino-dodecanoic acid-treated montmorillonite (ADA-MMT) clay was investigated. The constituents of the polyalkenoic acid constituent of GI restoratives differ considerably between commercial GI restoratives. ADA-MMT clay was chosen as it has been employed extensively in the literature to reinforce a variety of polymers including poly(ethylene terephthalate) (Hao *et al.*, 2006), poly(etherimide) (Chen *et al.*, 2006) and poly(propylene) (Zhang *et al.*, 2008). It was therefore thought that the use of an organically-modified MMT clay with a wide range of potential applications (ADA-MMT clay) could potentially reinforce the polyalkenoic acid matrix of a number of GI restorative products. Ca-MMT was also examined so that the influence of adding an

un-modified MMT clay and an organically-modified MMT clay to a GI restorative could be compared.

2.7 **Aim and Objective**

Given that many reports in the literature have indicated increases in strength and stiffness with the inclusion of MMT clay to polymeric matrices, and the evident inadequacy in both properties (as well as wear resistance) associated with GI restoratives in clinical service, the question arises whether MMT clay addition to GI restoratives could provide any benefit, whether as particles or dispersed platelets, in respect of those properties. Accordingly, it is proposed to investigate the influence of MMT clay, both as-found (un-modified Ca-MMT clay) and pre-treated to encourage exfoliation (organically-modified ADA-MMT clay), on the compressive fracture strength, elastic modulus and *in vitro* wear resistance of a variety of commercial GI restorative products. In addition, the role of various manipulative factors (powder to liquid mixing ratio, method of mixing) require clarification as there may be interactions that detract from the expected behaviour.

3 General Materials and Methods

The materials and methods which apply to most of the experiments conducted in this thesis are described in this section, however, procedures which are specific to particular experiments will be described in the relevant subsections.

3.1 Materials Studied

Six hand-mixed glass-ionomer (GI) restoratives were studied, three were indicated for anterior use while three were indicated for posterior use. In addition, five encapsulated GI restoratives were studied, two indicated for anterior use and three indicated for posterior use.

3.1.1 Hand-Mixed GI Restoratives

The details for the hand-mixed anterior and posterior GI restoratives investigated are listed in Table 3.1.1.

GI Restorative	Manufacturer Details	Shade	Batch
Ketac Fil Plus (A)	3M ESPE; Seefeld, Germany	A2	266794
Fuji II (A)	GC Europe; Leuven, Belgium	22	0611091
Chemfil Superior (A)	Dentsply DeTrey; Konstanz, Germany	L(2)	0608001031
Ketac Molar Easymix (P)	3M ESPE; Seefeld, Germany	A3	255865
Fuji IX (P)	GC Europe; Leuven, Belgium	A3	0412031
ChemFlex (P)	Dentsply DeTrey; Konstanz, Germany	A3	0501001320

Table 3.1.1 The manufacturers details, shade and batch number for the hand-mixed anterior and posterior GI restoratives. A: anterior GI restorative, P: posterior GI restorative.

The GI restoratives Ketac Fil Plus and Fuji II were supplied as two constituents, a powder and a liquid, however, the compositions were not reported by the manufacturers.

Chemfil Superior was supplied in anhydrous form, where the polyacrylic acid constituent was vacuum-dried and contained in the powder constituent (Pearson, 1983). The liquid constituent used could be either distilled or deionised water. The manufacturer claimed that 1 g of powder was composed of 0.84 g of an aluminium-sodium-calcium fluoro-phosphoro-silicate glass in a ratio of 18 : 9 : 8 : 16 : 3 : 46 and 0.15 g of polyacrylic acid with a molecular weight ranging from 30,000 to 45,000.

Ketac Molar Easymix was presented as a radiopaque aluminium-calcium lanthanum-fluoro-silicate glass powder and a solution of polycarboxylic acid (a co-polymer of acrylic and maleic acid). The glass powder particle size distribution, reported by the manufacturers, ranged from < 1 to 9.6 μm with a mean particle size of 2.8 μm , however, the proportions of the glass elements were not disclosed. It was claimed that 60% of the polycarboxylic acid was contained in the powder constituent. The liquid constituent was reported to consist of an aqueous solution of polycarboxylic acid and tartaric acid, however, the molecular weight and concentration of the acids in solution were not reported.

Fuji IX was supplied as a separate powder and liquid, but the compositions were not disclosed by the manufacturer.

ChemFlex was supplied as a powder composed of a strontium-alumino-fluoro-silicate glass, polyacrylic acid, tartaric acid and pigments and a liquid solution of polyacrylic acid. However, the relative proportions of the glass, the acids and the pigments in the powder along with the molecular weight and concentration of the polyacrylic acid in solution were not disclosed.

3.1.2 Encapsulated GI Restoratives

The encapsulated anterior and posterior GI restoratives investigated are shown in Table 3.1.2.

GI Restorative	Manufacturer Details	Shade	Batch
Ketac Fil Plus Aplicap (A)	3M ESPE; Seefeld, Germany	A2	277249
Fuji II Capsule (A)	GC Europe; Leuven, Belgium	22	0610201
Ketac Molar Aplicap (P)	3M ESPE; Seefeld, Germany	A3	276540
Fuji IX Fast Capsule (P)	GC Europe; Leuven, Belgium	A3	0610204
ChemFlex in Caps (P)	Dentsply DeTrey; Konstanz, Germany	A3	0512001557

Table 3.1.2 The manufacturers details, shade and batch number for the encapsulated anterior and posterior GI restoratives. A: anterior GI restorative, P: posterior GI restorative.

The composition and relative proportions of the powder and liquid constituents contained in each Ketac Fil Plus Aplicap capsule were not stated by the manufacturers, however, it was claimed that a minimum of 0.11 mL of the GI restorative was dispensable from each capsule when mechanically mixed.

Each Fuji II Capsule was reported to contain 0.3 g of powder and 0.11 g (0.09 mL) of liquid, however, the composition of the powder and liquid were not stated. It was

reported that at least 0.12 mL of Fuji II Capsule was dispensable from each capsule following mechanical mixing.

The powder in the Ketac Molar Aplicap capsule consisted of a 95% aluminium-calcium lanthanum-fluoro-silicate glass and 5% spray-dried polycarboxylic acid and the liquid was a polycarboxylic and tartaric acid liquid solution. The glass particle size distribution was reported to be the same as Ketac Molar Easymix, however, the proportions of the glass components were not stated. It was claimed that 75% of the polycarboxylic and tartaric acid content was contained in the liquid, but the molecular weight and composition of the acids were not disclosed. The proportions of powder and liquid contained in each capsule were not available from the manufacturer, however, it was claimed that a minimum of 0.1 mL of Ketac Molar Aplicap was dispensable from each capsule following mechanical mixing.

Fuji IX Fast Capsule was stated to contain 0.4 g of powder and 0.11 g (0.09 mL) of liquid, however, the composition of the powder and liquid were not reported. The dispensable quantity from each Fuji IX Fast Capsule was claimed to be at least 0.14 mL when mechanically mixed.

ChemFlex in Caps was reported to contain 0.355 g of powder consisting of a strontium-alumino-fluoro-silicate glass, polyacrylic and tartaric acids and pigments. The liquid solution contained 0.102 g of polyacrylic acid. However, the manufacturer did not state the proportions of glass, acids and pigments in the powder or the molecular weight and concentration of the polyacrylic acid in solution. It was reported

that 0.68 ± 0.02 g of ChemFlex in Caps was dispensable from each capsule after mechanical mixing.

3.1.3 MMT Clay

Two montmorillonite (MMT) clay minerals were used: an un-modified MMT clay, Ca-MMT supplied by Süd Chemie (Munich, Germany) and an organically-modified MMT clay, ADA-MMT supplied by Nanocor Inc. (Arlington Heights, IL, USA). The ADA-MMT clay was synthesised by an ion-exchange reaction between sodium-montmorillonite clay (Na-MMT) (with a cation exchange capacity of 110/100 milliequivalents/g) and 12-amino-dodecanoic acid.

3.2 GI Restorative Preparation

3.2.1 Hand-Mixed GI Restoratives

The hand-mixed GI restorative control groups were prepared using the manufacturers' recommended powder to liquid mixing ratios shown in Table 3.2.1. To provide a sufficient quantity of material, 0.9 g of the GI restorative powder was used. A glass slab was placed on a balance with a resolution of 0.001 g (Sartorius Expert; Sartorius AG, Goettingen, Germany). The appropriate quantity of GI restorative liquid corresponding to 0.9 g of GI restorative powder (as shown in Table 3.2.1) was dispensed onto one end of the glass slab using an adjustable 200 μ L pipette (Gilson, Middleton, WI, USA) and the glass slab was removed from the balance. The quantity of GI restorative liquid was covered with an upturned weight boat to prevent evaporation. The powder was measured into a weigh-boat using the balance and dispensed onto the opposing end of the glass slab. The powder was separated into two parts, the first part was mixed with all the GI restorative liquid for the time specified

by the manufacturer (Table 3.2.1) using a stainless steel spatula. The remaining powder was added to the mix and spatulated for a further time period so that the powder and liquid constituents were mixed for the total time specified by the manufacturer as shown in Table 3.2.1.

Hand-mixed GI restorative	Powder to liquid mixing ratio (g/g)	Liquid content (g) (for 0.9 g powder)	Mixing time (s)		
			1 st Part	2 nd Part	Total
Ketac Fil Plus	3.2/1.0	0.281	30	30	60
Fuji II	2.7/1.0	0.333	10	20	30
Chemfil Superior	7.4/1.0	0.122	5	15	20
Ketac Molar Easymix	4.5/1.0	0.2	15	15	30
Fuji IX	3.6/1.0	0.25	10	20	30
ChemFlex	3.8/1.0	0.237	5	15	20

Table 3.2.1 The powder to liquid mixing ratio, appropriate quantity of GI restorative liquid (for 0.9 g powder) and recommended mixing times for the hand-mixed GI restoratives.

3.2.2 Encapsulated GI Restoratives

The membrane which separates the powder and liquid constituents in an encapsulated GI restorative must be ruptured prior to mechanical mixing to allow for the interaction of the powder and liquid constituents. However, the procedure recommended by the manufacturer to rupture the membrane and activate the capsules differed for the encapsulated GI restorative products investigated. The 3M ESPE products Ketac Fil Plus Aplicap and Ketac Molar Aplicap were placed in the Aplicap Activator (3M ESPE, Seefeld, Germany) and activated by pressing the lever for 2 s. The encapsulated GI restoratives supplied by GC (Fuji II Capsule and Fuji IX Fast Capsule) were tapped on the laboratory bench to loosen the powder and the plunger

on the end of the capsule was pressed using the GC Capsule Applier (GC Europe: Leuven, Belgium) to activate the capsules. To activate ChemFlex in Caps the capsule was placed in the Aplicap Applier (3M ESPE, Seefeld, Germany) and the plunger was pressed for 2 s. The activated capsule was placed into either a Capmix or Rotomix mechanical mixing machine and vibratory mixed (Capmix) or rotationally mixed followed by immediate centrifuging (Rotomix) for the times specified by the manufacturer (Table 3.2.2). Immediately following mechanical mixing the 3M ESPE and Dentsply DeTrey products were placed in the Aplicap Applier while the GC products were placed in the GC Capsule Applier to facilitate the extrusion of the GI restorative mix.

Encapsulated GI restorative	Powder to liquid mixing ratio (g/g)	Mixing time (s)	
		Capmix	Rotomix
Ketac Fil Plus Aplicap (A)	3.2/1.0	10	8 + 3
Fuji II Capsule (A)	2.7/1.0	10	8 + 3
Ketac Molar Aplicap (P)	3.4/1.0	15	10 + 3
Fuji IX Fast Capsule (P)	3.6/1.0	10	8 + 3
ChemFlex in Caps (P)	3.5/1.0	10	8 + 3

Table 3.2.2 The powder to liquid mixing ratios and recommended mechanical mixing times for the encapsulated GI restoratives.

3.3 Mechanical Testing Protocol

3.3.1 Compression Testing

3.3.1.1 Specimen Preparation

Cylindrical GI restorative specimens (6.0 ± 0.1 mm height and 4.0 ± 0.1 mm diameter) were prepared in accordance with ISO 9917-1 : 2003 using a polytetrafluoroethylene (PTFE) split-mould. The PTFE split-mould, capable of holding twelve specimens was placed on a PTFE base which was covered with an acetate strip to prevent the GI restorative from adhering to the base of the mould. The two halves of the split-mould were aligned using a 4 mm diameter holding pin which was located in the first hole of the mould. To allow equal pressure to be applied along the length of the split-mould two nylon sliding wedges were fitted to one side of the mould (Figure 3.3.1).

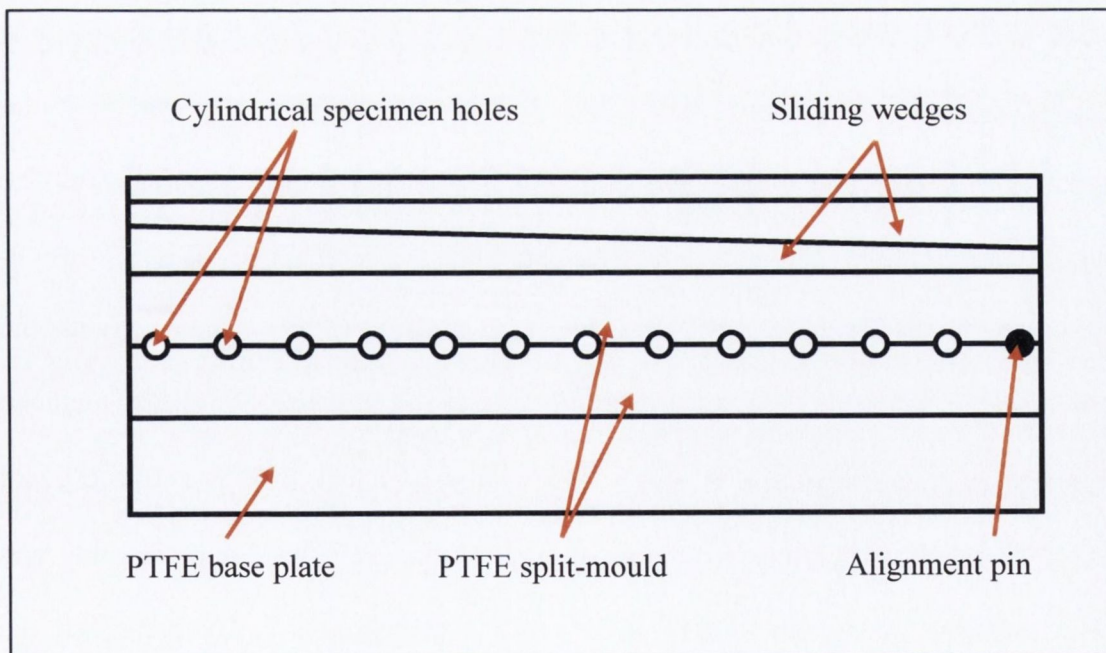


Figure 3.3.1 The PTFE split-mould assembly used to manufacture the cylindrical GI restorative specimens.

Prior to the commencement of mixing, the time of day was recorded to the nearest hour. The hand-mixed GI restorative mix was applied to the split-mould using a stainless steel spatula within 60 s of the completion of mixing. To minimise the incorporation of air bubbles into the specimens, the largest convenient portion of the mix was conveyed to one side of an individual hole in the split-mould and allowed to flow into the mould. The encapsulated GI restoratives were applied to the split-mould within 10 s of the completion of mechanical mixing. To eliminate the incorporation of air bubbles, the GI restorative was initially extruded so that the mix was visible in the capsule nozzle prior to application into the split-mould. In addition, the capsule nozzle was positioned to one side of an individual hole of the split-mould and the mix extruded slowly to reduce the likelihood of introducing air bubbles to the cylindrical specimens.

Each hole in the split-mould was filled sequentially from the alignment pin towards the opposite end of the mould. The filled split-mould assembly was covered with an acetate strip and isolated from the surrounding atmosphere using a glass slab. The mould assembly was clamped and equal pressure was applied to all specimens to ensure parallelism of the cylindrical specimen ends for uniform contact with the compressive platens of the testing apparatus (Lloyd and Mitchell, 1984). The clamped assembly was transferred to a water-bath maintained at 37 ± 1 °C within 60 s of applying the GI restorative mix into the split-mould. The split-mould assembly was removed from the water bath 1 h after the commencement of mixing and the cylindrical GI restorative specimens were numbered in sequence starting from the specimen nearest the alignment pin to the opposite end of the mould. The specimens were then removed from the mould. The flash produced on clamping was removed

through hand-lapping on P600 silicon carbide (SiC) abrasive paper (Buehler, Lake Bluff, IL, USA) using water as a lubricant. Specimens that contained visible defects such as chipped edges, non-parallel ends or pores were discarded. The specimens without any visually-apparent defects were stored in glass containers filled with 50 mL of distilled water maintained at 37 ± 1 °C in an incubator (Climate Cabinet; Firlabo, Meyzieu, France) for a further 23 h prior to compression testing. The specimen preparation procedure was repeated so that a minimum of 30 cylindrical GI restorative specimens were manufactured for each group under investigation.

3.3.1.2 Compression Testing Procedure

Twenty-four hours after the commencement of mixing the mean diameter of each cylindrical GI restorative specimen was determined from three measurements taken using a digital micrometer reading to 10 µm (Mitutoyo, Kawasaki, Japan). The specimens were tested 'wet' to mimic the oral environment by placing a piece of wet filter paper on the flat ends of each cylindrical specimen in accordance with ISO 9917-1 : 2003. The specimens were placed upright in a universal testing machine, (Instron Model 5565, High Wycombe, England), a compressive load was applied to the long axis of the cylindrical specimen, at a cross-head speed of 1 mm/min and the maximum load at failure was recorded.

The compressive fracture strength P (MPa) was determined for each individual cylindrical GI restorative specimen by dividing the fracture force by the original cross-sectional area

$$P = \frac{4F_f}{\pi d^2}$$

Equation 3.1

where F_f was the load at fracture (N) and d was the mean of the original diameter of the specimen (mm). The elastic modulus (GPa) was determined by calculating the slope of the initial linear portion of the stress-strain plot generated for each individual cylindrical GI restorative specimen tested in compression prior to fracture as shown in Figure 3.3.2.

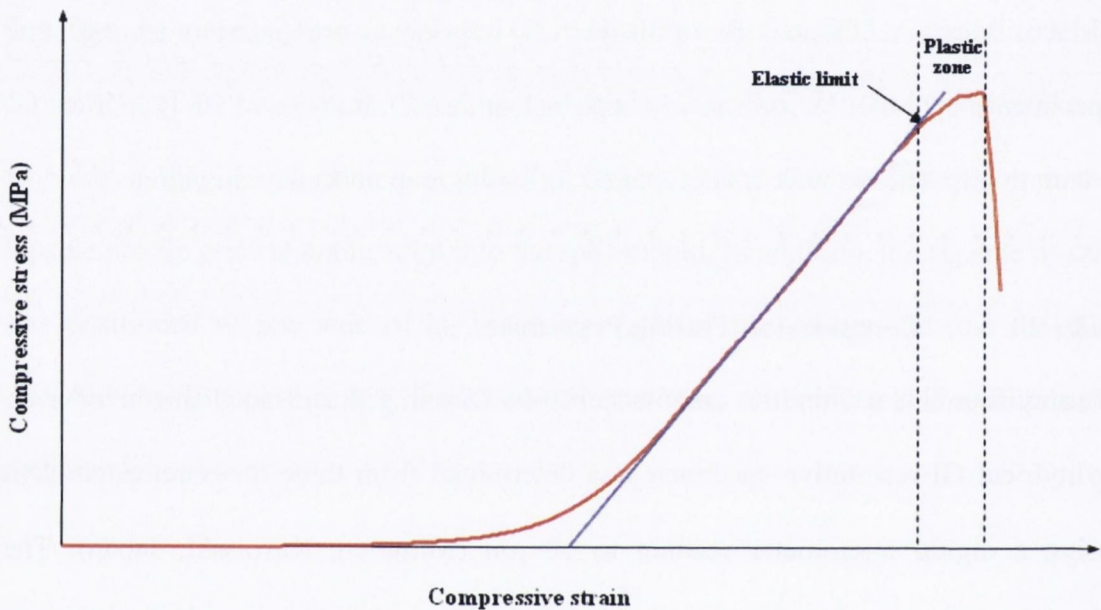


Figure 3.3.2 A diagrammatic representation of the rate of change of compressive strain as a function of compressive stress (MPa) for a typical cylindrical GI restorative under a compressive load.

3.3.2 *In vitro* Wear Resistance

3.3.2.1 Specimen Preparation

Disc-shaped specimens (15.0 ± 0.1 mm diameter and 1.5 ± 0.1 mm thickness) for *in vitro* wear resistance testing were prepared using a Perspex mould. The mould was positioned on a Perspex base plate which was covered with an acetate strip to prevent the disc-shaped specimens from adhering to the base plate.

The hand-mixed GI restorative mix was applied to the Perspex mould within 60 s of the completion of hand-mixing using a stainless steel spatula. The mix was placed directly into the centre of the mould, a second acetate strip was placed on top and a glass slab was applied to spread the GI restorative evenly in the disc-shaped mould. It was necessary to mechanically mix two capsules of each encapsulated GI restorative to fabricate a disc-shaped specimen for wear testing. Immediately after mixing the first capsule (as outlined in Section 3.2.2), the second capsule was activated and mechanically mixed. The GI restorative mix from the first capsule was extruded slowly directly into the centre of the mould using the appropriate capsule applicator before the mix from the second capsule was added. The GI restorative mix was covered with an acetate strip and a glass slab was placed on top to spread the mix evenly in the mould. To ensure that flat disc-shaped specimens were produced, the filled mould was secured between the base plate and the glass slab using a G-clamp. The mould assembly was immersed in a water-bath maintained at 37 ± 1 °C within 60 s of completion of mixing.

The disc-shaped specimens were removed from the mould 1 h after the commencement of mixing. Specimens which contained visible defects such as chipped edges or pores were discarded. The specimens which did not contain visually-apparent defects were stored in glass containers filled with 50 mL of distilled water maintained at 37 ± 1 °C in an incubator for a further 22 h.

The disc-shaped GI restorative specimens were removed from the distilled water 23 h after the commencement of mixing and mounted in a two part cold-setting acrylic resin (Varidur; Buehler, Lake Bluff, IL, USA) to produce cylinders (25.0 ± 0.1 mm

diameter and 10.0 ± 0.1 mm height) compatible with the chambers of the wear testing apparatus. Prior to mixing the acrylic resin, the disc-shaped GI restorative specimens were positioned in the centre of individual cylindrical mounting cups (Metset Cups; Buehler, Lake Bluff, IL, USA). The acrylic resin was mixed using 24 g of powder and 12 mL of liquid for 30 s using a stainless steel spatula in accordance with the manufacturers' instructions and carefully poured on top of the GI specimens. To ensure that the specimens were positioned centrally and flat on the bottom of the mounting cups the specimens were manoeuvred using the spatula prior to the acrylic resin setting. The mounted specimens were removed from the mounting cups 45 min after the commencement of mixing the acrylic resin and ground on a Alpha and Beta Grinder-Polisher (Buehler, Lake Bluff, IL, USA) with P600 SiC abrasive paper at a force of 10 N per specimen for 30 s using water as a lubricant. The specimen grinding procedure was repeated using P1200 SiC abrasive paper to provide a reproducible surface roughness conducive to wear testing (Condon and Ferracane, 1996).

3.3.2.2 *In vitro* Wear Resistance Testing Procedure

The *in vitro* wear resistance testing of the disc-shaped GI restorative specimens was conducted 24 h after the commencement of mixing using the Oregon Health Science University (OHSU) four chamber oral wear simulator (Condon and Ferracane, 1996). The wear regime of the OHSU oral wear simulator forced a steatite antagonist into contact with the specimens in the presence of a food-like slurry (De Gee *et al.*, 1986) and imparted a 20 N sliding abrasion force along a 7 mm linear path (Condon and Ferracane, 1996, 1997a,b). At the end of the 7 mm linear sliding path a direct static 90 N attrition force was applied (Condon and Ferracane, 1996, 1997a,b). The steatite

antagonist was raised at the end of each wear cycle and returned to the start of the 7 mm path and the wear regime repeated for the appropriate number of cycles.

The antagonist used in the OHSU oral wear simulator consists of a steatite sphere of 10.0 ± 0.1 mm diameter (Union Process Inc., Akron, OH, USA) fixed to a nylon screw (Radionics Ltd., Dublin, Ireland) using a light-cured resin-based composite (Grandio; Voco GmbH, Cuxhaven, Germany). To prepare an antagonist a steatite sphere was pressed into resin-based composite which was placed on the headed end of a nylon screw. The antagonists were light-irradiated for 40 s using a halogen light-curing unit (Optilux 501; Kerr, Orange, CA, USA) with an output intensity of 650 ± 18 mW/cm². The steatite antagonists were inserted in the OHSU oral wear simulator and the height adjusted using a custom made jig so that the head of the antagonist was positioned 1 mm above the disc-shaped specimens.

The embedded disc-shaped specimens were secured into each individual wear chamber and attached to the OHSU oral wear simulator. To simulate three-body wear a food-like slurry which consisted of 1 g of poppy seeds (Holland and Barrett, Burton-upon-Trent, England), 0.5 g of poly(methyl methacrylate) beads with a mean particle size of 50-100 μ m (Special Tray; Dentsply DeTrey, Konstanz, Germany) and 5 mL of distilled water (De Gee *et al.*, 1986) was placed into each wear chamber prior to the commencement of testing. The poppy seeds required for one test (4 g) were ground using 100 strokes in a mortar and pestle. Each disc-shaped GI restorative specimen was subjected to 50,000 wear cycles at a frequency of 1 Hz which was taken to be equivalent of six months wear in the oral environment (Condon and Ferracane, 1996). The specimen preparation and testing procedure was repeated so that the *in vitro* wear

resistance of eight disc-shaped specimens was conducted for each GI restorative group under investigation.

3.3.2.3 Wear Facet Analysis

The OHSU oral wear simulator produced a tear-drop wear facet on the surface of each disc-shaped specimen (Figure 3.3.3). The wear facets were scanned using a non-contact optical profilometer (Talysurf CLI 2000; Taylor-Hobson Precision, Leicester, England) which employed a 3 mm range chromatic length aberration gauge with a resolution of 0.1 μm (z-axis) when scanning at a speed of 2 mm/s. A series of horizontal traces (perpendicular to the sliding direction of the OHSU wear simulator) were conducted across the wear facet at 4 μm intervals (y-axis) with longitudinal measurements (parallel to the sliding direction of the OHSU wear simulator) were recorded at 4 μm intervals (x-axis). A detailed three-dimensional representation of the wear facet was generated using the TalyMap analysis software package (Taylor-Hobson Precision, Leicester, England) as shown in Figure 3.3.3. The mean total volumetric wear (mm^3) and mean maximum wear depth (mm) for each individual wear facet for all the GI restorative groups investigated were quantified using the non-worn areas surrounding the wear facet as the reference plane.

The accuracy and precision of the total volumetric wear and maximum wear depth measurements were assessed prior to the analysis of the GI restorative wear facets using a standard representative wear facet with a total volume of 7.405 mm^3 and a maximum wear depth of 0.701 mm. The representative wear facet was scanned and analysed ten times using the profilometric protocol outlined. The accuracy was calculated as the mean error from the true value, whilst the precision was quantified as

the standard deviation of the errors measured (DeLong, 2006). The accuracy and the precision for the total volumetric wear were 0.0099 and 0.0063 mm³, respectively. For the maximum wear depth the accuracy and precision were 0.94 and 0.89 μm, respectively.

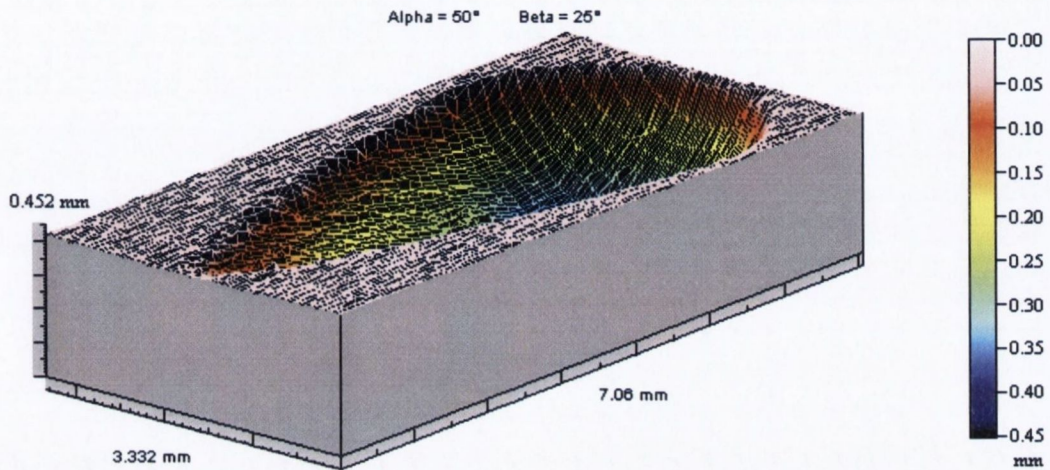


Figure 3.3.3 A three-dimensional representation of the tear-drop wear facet produced on the surface of each disc-shaped GI restorative specimen.

3.3.3 Working Characteristics

The working characteristics, namely the working and setting times of the GI restorative groups were determined using an oscillating rheometer (Bovis *et al.*, 1971). At the commencement of mixing the GI restorative, a timer was started and a mark was made on the chart recorder. The GI restorative was mixed for the time specified by the manufacturers as outlined in Section 3.1.2 and transferred to the lower platen of the oscillating rheometer. The upper plate was lowered into position and secured so that the thickness of the material between the plates was 1 mm. An oscillating trace was recorded on the chart recorder moving at a speed of 10 mm/min which decreased in width as the GI restorative set. The working time was recorded at

23 ± 1 °C as the time when the width of the rheometer trace was reduced to 95% of its original width (Wilson, 1966). The setting time was recorded at 37 ± 1 °C as the time when the rheometer trace was reduced to a straight line (Wilson, 1966). Three measurements were performed for both the working and the setting times for each restorative group investigated.

3.3.4 Data Handling

Each specimen group under investigation was tested for normality using the Shapiro-Wilk test with an alpha of 0.05 used as the critical value. To determine if the time of day at which the cylindrical specimens were fabricated had an influence on the compressive fracture strength and elastic modulus data, all of the data for each section was pooled together, a plot of the mean value versus time of day was prepared and regression analyses were conducted. In addition, the influence of cylindrical specimen mould position on the compressive fracture strength and elastic modulus data was examined by pooling all the data from each section together, plotting the mean value against mould position and performing regression analyses. The influence of the time of day and specimen mould position on the compressive fracture strength and elastic modulus data for the control groups are shown in this section, the data for the remaining sections are given in Appendices. In all regression analyses, the coefficient of variation of the data was checked for uniformity, to ensure that transformation of the data was not necessary. The coefficient of variation data for all experiments conducted are available in Appendices.

3.4 Results

The results of the normality tests for the compressive fracture strength, elastic modulus and *in vitro* wear resistance data for the hand-mixed GI restorative control groups are shown in Tables 3.4.1 and 3.4.2. Normality tests were not performed for the working characteristics data as the sample size ($n = 3$) was too small to detect non-normally distributed data. In none of the specimen groups under investigation was there a significant departure from normality detected, beyond sampling variation.

Hand-mixed GI restorative	Shapiro-Wilk Significance	
	CFS	EM
Ketac Fil Plus	0.783	0.061
Fuji II	0.249	0.553
Chemfil Superior	0.792	0.310
Ketac Molar Easymix	0.615	0.405
Fuji IX	0.655	0.398
ChemFlex	0.244	0.934

Table 3.4.1 Shapiro-Wilk normality test results: hand-mixed GI restorative control groups. CFS: compressive fracture strength, EM: elastic modulus.

Hand-mixed GI restorative	Shapiro-Wilk Significance	
	Volume	Depth
Ketac Fil Plus	0.619	0.342
Fuji II	0.491	0.234
Chemfil Superior	0.900	0.227
Ketac Molar Easymix	0.689	0.225
Fuji IX	0.145	0.929
ChemFlex	0.575	0.546

Table 3.4.2 Shapiro-Wilk normality test results: hand-mixed GI restorative control groups. Volume: total volumetric wear, Depth: maximum wear depth.

The plots of compressive fracture strength and elastic modulus data versus the time of day of specimen fabrication are shown in Figures 3.41 and 3.42, respectively. The linear regression analysis (Tables 3.4.3 and 3.4.5) showed that the time of day did not significantly influence the compressive fracture strength ($p = 0.621$) or elastic modulus ($p = 0.553$). However, a significant effect of time of day on the compressive fracture strength ($p = 0.021$) and elastic modulus ($p = 0.033$) data was shown when a quadratic regression analysis was conducted (Tables 3.4.4 and 3.4.6).

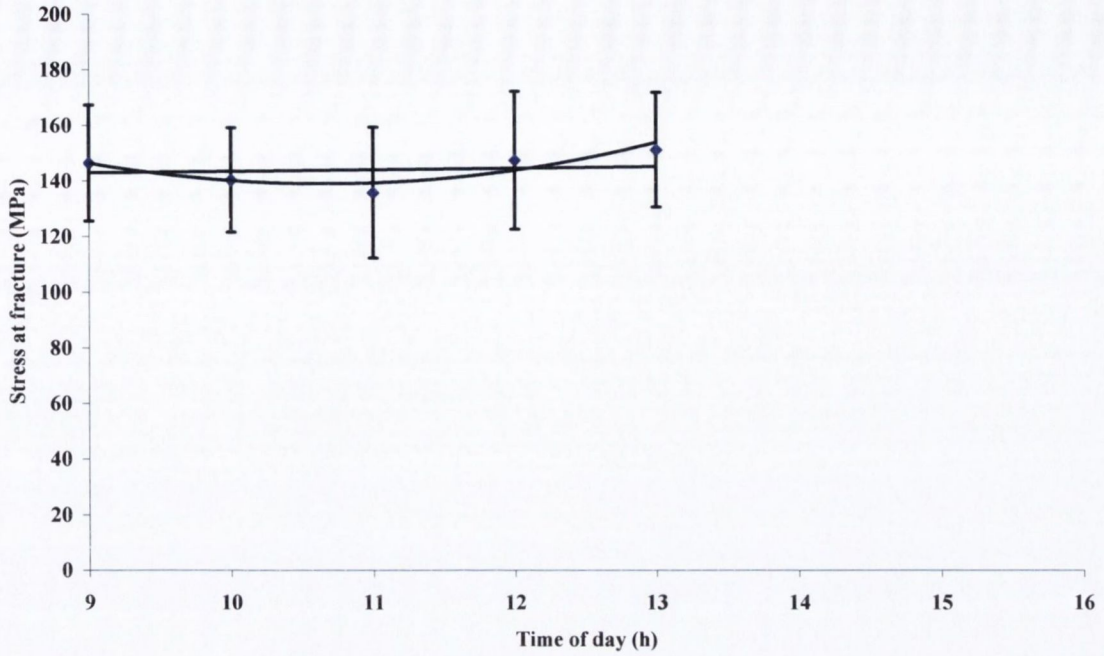


Figure 3.4.1 Variation of compressive fracture strength with time of day: hand-mixed GI restorative control groups, data for all materials pooled.

Fitted lines:

$$y = 0.58x + 137.64 \quad r^2 = 0.001 \quad p = 0.621 \quad df = 200$$

$$y = 2.72x^2 - 57.96x + 447.66 \quad r^2 = 0.038 \quad p = 0.021 \quad df = 199$$

Dependent variable.. Strength Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .03499
R Square .00122
Adjusted R Square -.00377
Standard Error 21.94371

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	118.063	118.06332
Residuals	200	96305.316	481.52658

F = .24519 Signif F = .6210

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
TimeOfDa	.575477	1.162199	.034992	.495	.6210
(Constant)	142.284523	3.290244		43.244	.0000

Table 3.4.3 Regression analysis: Compressive fracture strength versus time of day.

Dependent variable.. Strength Method.. QUADRATI

Listwise Deletion of Missing Data

Multiple R .19481
 R Square .03795
 Adjusted R Square .02828
 Standard Error 21.59054

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	2	3659.279	1829.6395
Residuals	199	92764.100	466.1513

F = 3.92499 Signif F = .0213

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
TimeOfDa	-14.441306	5.567044	-.878102	-2.594	.0102
TimeOf_1	2.715437	.985206	.932988	2.756	.0064
(Constant)	158.062660	6.576530		24.034	.0000

Abbreviated Name	Extended Name
TimeOf_1	TimeOfDay**2
TimeOfDa	TimeOfDay

Table 3.4.4 Quadratic regression analysis: Compressive fracture strength versus time of day.

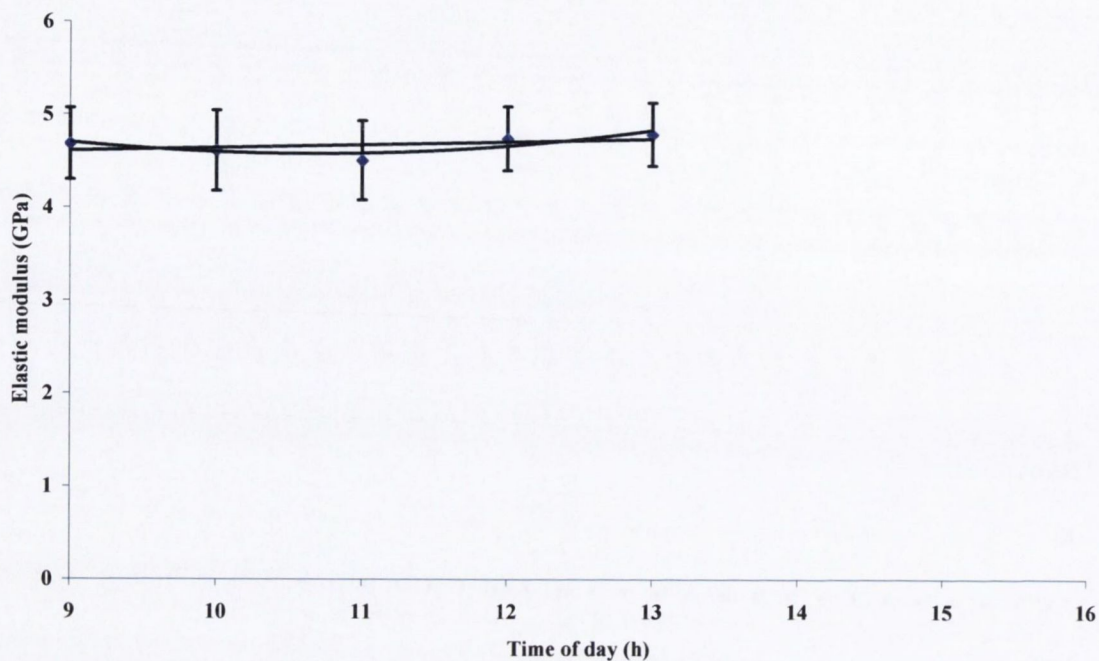


Figure 3.4.2 Variation of elastic modulus with time of day: hand-mixed GI restorative control groups, data for all materials pooled.

Fitted lines:

$$y = 0.03x + 4.30 \quad r^2 = 0.002 \quad p = 0.553 \quad df = 200$$

$$y = 0.05x^2 - 0.98x + 9.78 \quad r^2 = 0.034 \quad p = 0.033 \quad df = 199$$

Dependent variable.. Modulus Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .04201
R Square .00177
Adjusted R Square -.00323
Standard Error .39945

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	.056424	.05642419
Residuals	200	31.911933	.15955967

F = .35362 Signif F = .5527

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
TimeOfDa	.012581	.021156	.042012	.595	.5527
(Constant)	4.628123	.059893		77.273	.0000

Table 3.4.5 Regression analysis: Elastic modulus versus time of day.

Dependent variable.. Modulus Method.. QUADRATI

Listwise Deletion of Missing Data

Multiple R .18375
 R Square .03376
 Adjusted R Square .02405
 Standard Error .39398

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	2	1.079350	.53967508
Residuals	199	30.889007	.15522114

F = 3.47681 Signif F = .0328

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
TimeOfDa	-.242644	.101587	-.810288	-2.389	.0179
TimeOf_1	.046151	.017978	.870869	2.567	.0110
(Constant)	4.896287	.120008		40.800	.0000

Abbreviated Name	Extended Name
TimeOf_1	TimeOfDay**2
TimeOfDa	TimeOfDay

Table 3.4.6 Quadratic regression analysis: Elastic modulus versus time of day.

The plots of compressive fracture strength (Figure 3.4.3) and elastic modulus (Figure 3.4.4) versus mould position are shown. Mould position had a significant effect on the compressive fracture strength data for all the hand-mixed GI restorative groups as shown by the linear ($p = 0.023$) and quadratic ($p = 0.015$) regression analyses (Tables 3.4.7 and 3.4.8, respectively). The linear ($p = 0.282$) and quadratic ($p = 0.561$) regression analyses showed no significant influence of mould position on the elastic modulus data (Tables 3.4.9 and 3.4.10, respectively).

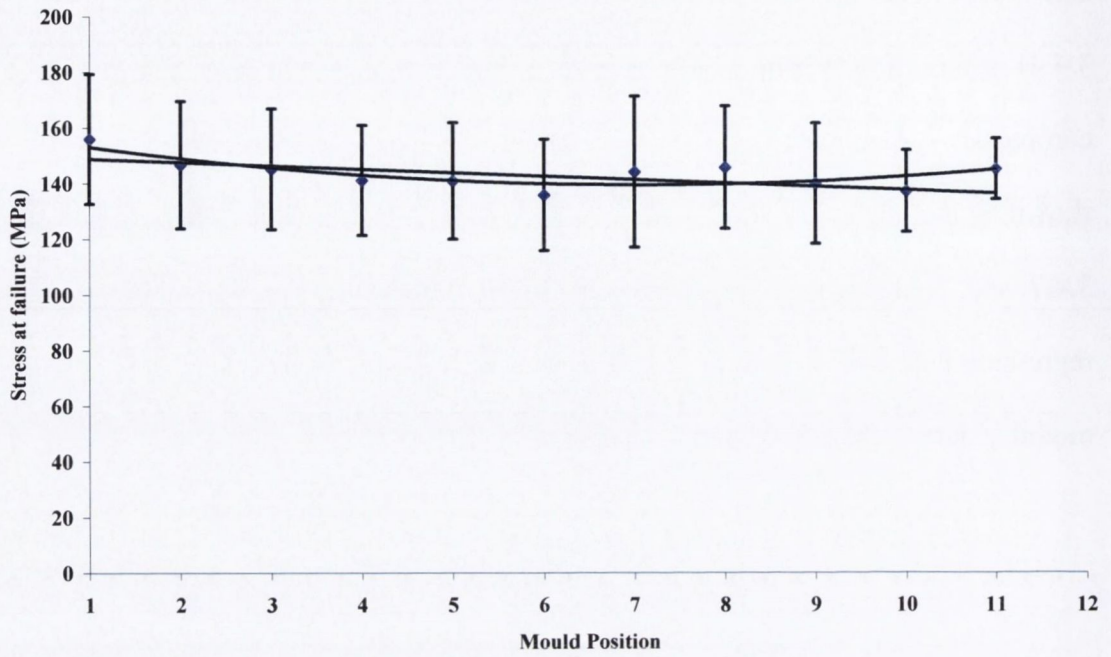


Figure 3.4.3 Variation of compressive fracture strength with mould position: hand-mixed GI restorative control groups, data for all materials pooled.

Fitted lines:

$$y = -1.25x + 150.04 \quad r^2 = 0.026 \quad p = 0.023 \quad df = 200$$

$$y = 0.37x^2 - 5.21x + 157.82 \quad r^2 = 0.042 \quad p = 0.015 \quad df = 199$$

Dependent variable.. Strength

Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .16033
R Square .02570
Adjusted R Square .02083
Standard Error 21.67313

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	2478.483	2478.4829
Residuals	200	93944.896	469.7245

F = 5.27646 Signif F = .0227

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MouldPos	-1.252224	.545143	-.160325	-2.297	.0227
(Constant)	150.040128	3.144503		47.715	.0000

Table 3.4.7 Regression analysis: Compressive fracture strength versus mould position.

Dependent variable.. Strength Method.. QUADRATI

Listwise Deletion of Missing Data

Multiple R .20416
 R Square .04168
 Adjusted R Square .03205
 Standard Error 21.54862

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	2	4019.155	2009.5774
Residuals	199	92404.224	464.3428

F = 4.32779 Signif F = .0145

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MouldPos	-5.209438	2.239063	-.666977	-2.327	.0210
MouldP_1	.366150	.201012	.522182	1.822	.0700
(Constant)	157.819879	5.293023		29.817	.0000

Abbreviated Name	Extended Name
MouldP_1	MouldPosition**2
MouldPos	MouldPosition

Table 3.4.8 Quadratic regression analysis: Compressive fracture strength versus mould position.

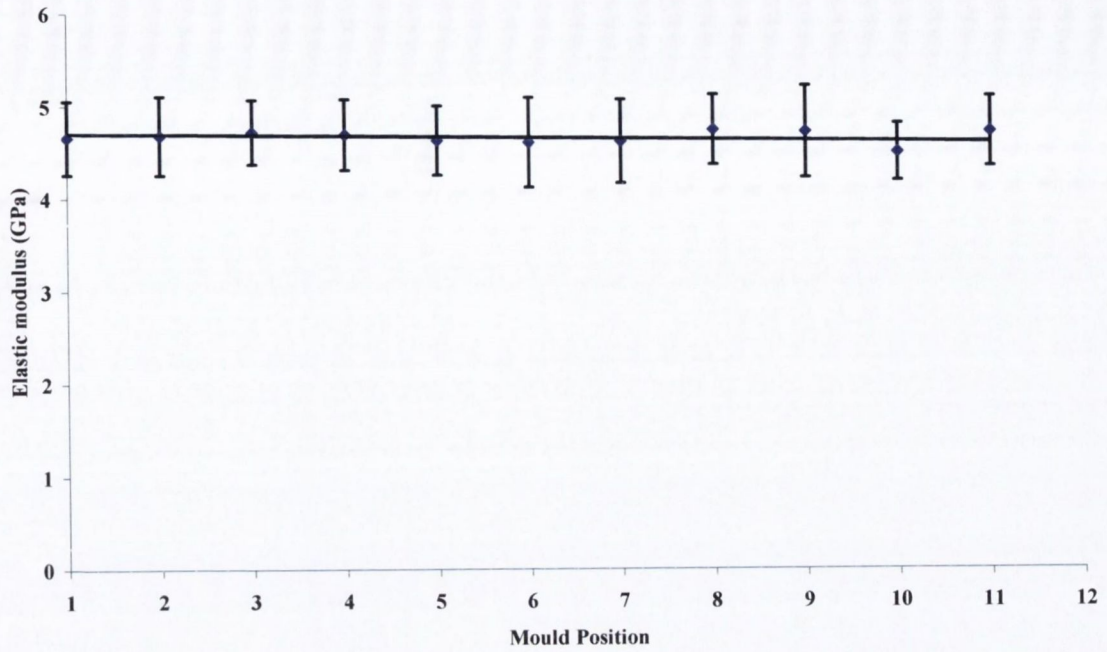


Figure 3.4.4 Variation of elastic modulus with mould position: hand-mixed GI restorative control groups, data for all materials pooled.

Fitted lines:

$$y = -0.01x + 4.71 \quad r^2 = 0.006 \quad p = 0.282 \quad df = 200$$

$$y = -0.0003x^2 - 0.01x + 4.71 \quad r^2 = 0.006 \quad p = 0.561 \quad df = 199$$

Dependent variable.. Modulus Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .07600
R Square .00578
Adjusted R Square .00080
Standard Error .39865

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	.184635	.18463547
Residuals	200	31.783722	.15891861

F = 1.16182 Signif F = .2824

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MouldPos	-.010808	.010027	-.075997	-1.078	.2824
(Constant)	4.714096	.057839		81.504	.0000

Table 3.4.9 Regression analysis: Elastic modulus versus mould position.

4 Experimental

4.1 Addition of Ca-MMT to Chemfil Superior

The purpose of this experiment was to examine the effect, in terms of compressive fracture strength, *in vitro* wear resistance and working characteristics, of adding an un-modified clay mineral (Ca-MMT) to either the powder or liquid constituents of an anhydrous GI restorative (Chemfil Superior) at 0.5, 1.0, 1.5, 2.0, 2.5, 5.0 and 10.0 wt.%.

4.1.1 Materials and Methods

To prepare the Chemfil Superior powders containing Ca-MMT clay, 0.9 g of GI restorative powder and the appropriate weight of Ca-MMT clay powder (Table 4.1.1) were measured into separate weigh-boats. The GI restorative and Ca-MMT clay powders were dispensed onto a glass slab and mixed together using a stainless steel spatula for 20 s. The glass slab was placed on the balance and 0.122 mL of distilled water (Table 3.1.1) was dispensed onto the opposite end of the glass slab. The GI restorative powder containing Ca-MMT clay was hand-mixed with the distilled water using with the procedure outlined in Section 3.2.1.

The Chemfil Superior liquids containing Ca-MMT clay were prepared by placing the appropriate mass of Ca-MMT (Table 4.1.1) onto one end of a glass slab and dispensing 0.122 mL of distilled water using the adjustable 200 μ L pipette. The Ca-MMT clay and distilled water were spatulated for 20 s using the spatula. The distilled water and Ca-MMT clay solution was hand-mixed with 0.9 g of Chemfil Superior powder using the procedure outlined previously (Section 3.2.1).

Ca-MMT concentration (wt.%)	Ca-MMT added (g)
0.25	0.002
0.5	0.005
0.75	0.007
1.0	0.009
1.25	0.011
1.5	0.014
2.0	0.019
2.5	0.023
5.0	0.046
10.0	0.092

Table 4.1.1 MMT quantities added to powder and liquid constituent of Chemfil Superior.

The compressive fracture strength, *in vitro* wear resistance and working characteristics were determined for each group following the procedures described in Sections 3.3.1, 3.3.2 and 3.3.3, respectively.

4.1.2 Results

The results of the compressive fracture strength test for the Chemfil Superior groups prepared with Ca-MMT clay additions to the powder and liquid constituents (Figure 4.1.1) are illustrated and the corresponding statistical analysis is given in Tables 4.1.2 and 4.1.3, respectively. There was a steady decline in the mean compressive fracture strength with increasing Ca-MMT concentration (Figure 4.1.1). The slope of the regression line was significant when Ca-MMT clay was added to the powder ($p < 0.001$) and liquid ($p < 0.001$) constituents of Chemfil Superior.

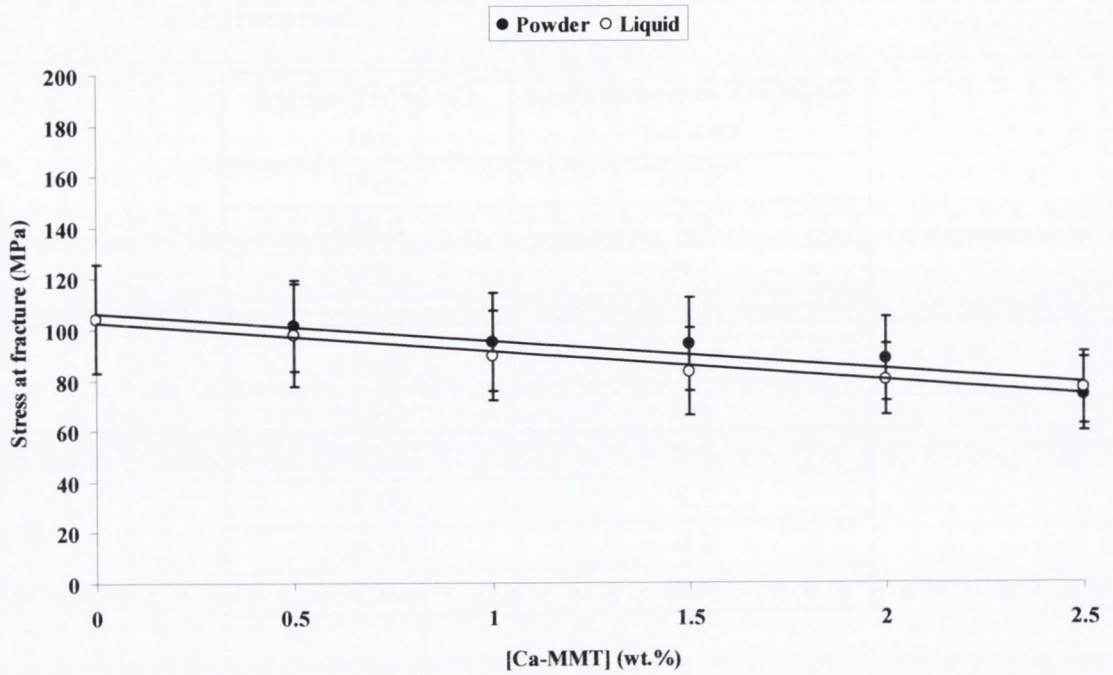


Figure 4.1.1 Variation of mean compressive fracture strength with Ca-MMT concentration for Chemfil Superior:

Fitted lines:

Powder: $y = -3.25x + 110.53$ $r^2 = 0.194$ $p < 0.001$ $df = 202$

Liquid: $y = -3.48x + 107.73$ $r^2 = 0.239$ $p < 0.001$ $df = 194$

Dependent variable.. Strength Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .44056
R Square .19409
Adjusted R Square .19010
Standard Error 18.66213

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	16942.879	16942.879
Residuals	202	70351.574	348.275

F = 48.64797 Signif F = .0000

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-3.245501	.465317	-.440555	-6.975	.0000
(Constant)	110.534974	2.893828		38.197	.0000

Table 4.1.2 Regression analysis: Compressive fracture strength for Ca-MMT in the Chemfil Superior powder constituent.

Dependent variable.. Strength Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .48966
R Square .23977
Adjusted R Square .23585
Standard Error 17.51434

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	18768.861	18768.861
Residuals	194	59509.876	306.752

F = 61.18580 Signif F = .0000

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-3.480919	.445009	-.489663	-7.822	.0000
(Constant)	107.726441	2.746716		39.220	.0000

Table 4.1.3 Regression analysis: Compressive fracture strength for Ca-MMT in the Chemfil Superior liquid constituent.

The influence of Ca-MMT addition to the Chemfil Superior powder constituent on the *in vitro* wear resistance (total volumetric wear and maximum wear depth) is illustrated in Figure 4.1.2. The statistical analysis of the total volumetric wear and maximum wear depth data is given in Tables 4.1.4 and 4.1.5, respectively. There were significant slopes for both the total volumetric wear ($p < 0.001$) and maximum wear depth ($p < 0.001$) as the concentration of Ca-MMT in the powder constituent was increased.

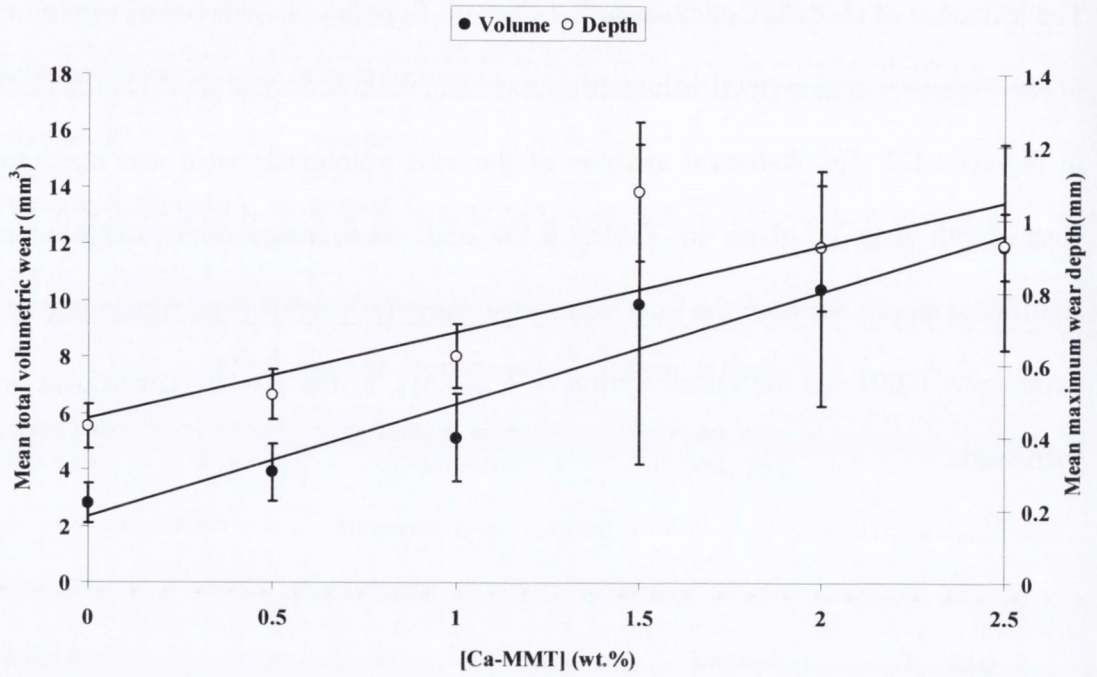


Figure 4.1.2 Variation of mean total volumetric wear and mean maximum wear depth with Ca-MMT concentration for Chemfil Superior:

Fitted lines:

Volume: $y = 1.211x + 0.681$ $r^2 = 0.528$ $p < 0.001$ $df = 46$

Depth: $y = 0.076x + 0.331$ $r^2 = 0.659$ $p < 0.001$ $df = 46$

Dependent variable.. Volume

Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .72646
 R Square .52774
 Adjusted R Square .51747
 Standard Error 3.29171

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	556.97769	556.97769
Residuals	46	498.42581	10.83534

F = 51.40379 Signif F = .0000

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	1.210674	.168861	.726457	7.170	.0000
(Constant)	.681461	1.043210		.653	.5169

Table 4.1.4 Regression analysis: Total volumetric wear for Ca-MMT in the Chemfil

Superior powder constituent.

The plots of working time and setting time versus Ca-MMT concentration are shown in Figures 4.1.3 and 4.1.4, respectively. The statistical analysis of the working characteristics data is given in Tables 4.1.6 to 4.1.9. The addition of Ca-MMT clay to the Chemfil Superior powder or liquid constituent did not have a significant effect on the working time ($p = 0.877$ and 0.055 , respectively) or the setting time ($p = 0.056$ and 0.065 , respectively).

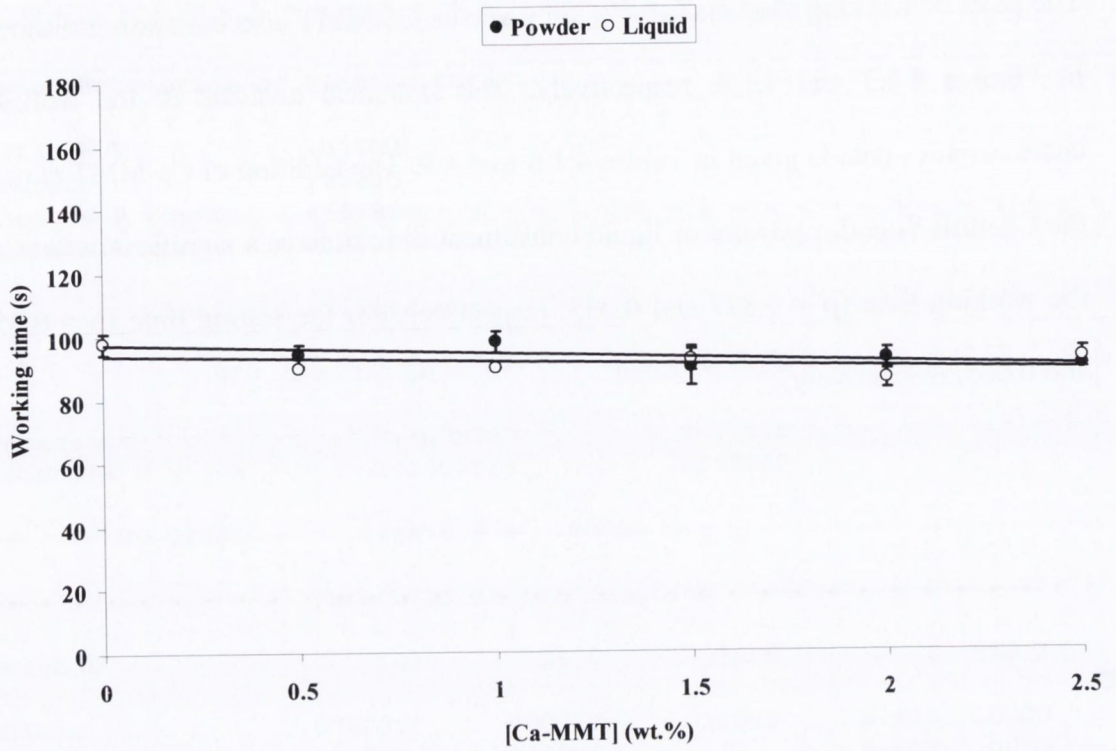


Figure 4.1.3 Variation of mean working time with Ca-MMT concentration for Chemfil Superior:

Fitted lines:

Powder: $y = -0.063x + 94.014$ $r^2 = 0.002$ $p = 0.877$ $df = 16$

Liquid: $y = -0.758x + 95.502$ $r^2 = 0.250$ $p = 0.055$ $df = 16$

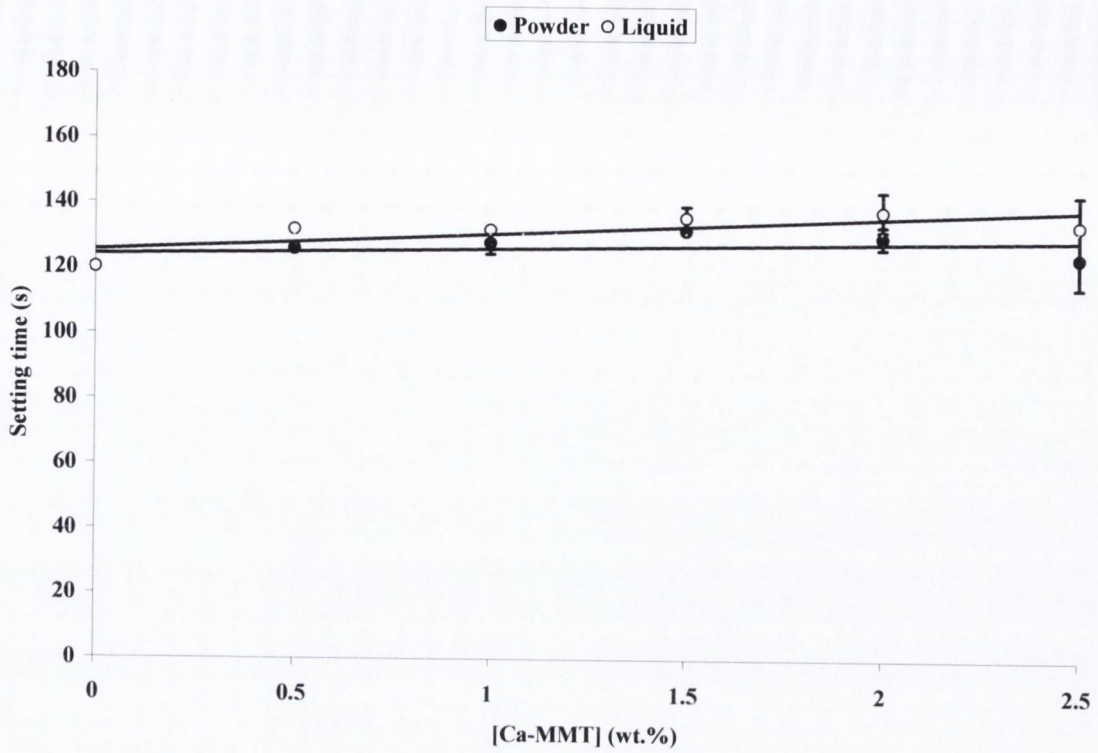


Figure 4.1.4 Variation of mean setting time with Ca-MMT concentration for Chemfil Superior:

Fitted lines:

Powder: $y = 0.926x + 121.572$ $r^2 = 0.247$ $p = 0.056$ $df = 16$

Liquid: $y = 1.095x + 125.979$ $r^2 = 0.198$ $p = 0.065$ $df = 16$

Dependent variable.. WorkingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .03920
R Square .00154
Adjusted R Square -.06087
Standard Error 4.80515

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	.56842	.568421
Residuals	16	369.43158	23.089474

F = .02462 Signif F = .8773

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-.063158	.402531	-.039195	-.157	.8773
(Constant)	94.014035	2.486805		37.805	.0000

Table 4.1.6 Regression analysis: Working time for Ca-MMT in the Chemfil Superior powder constituent.

Dependent variable.. WorkingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .49955
R Square .24955
Adjusted R Square .20265
Standard Error 3.92227

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	81.85263	81.852632
Residuals	16	246.14737	15.384211

F = 5.32056 Signif F = .0548

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-.757895	.328572	-.499551	-2.307	.0548
(Constant)	95.501754	2.029889		47.048	.0000

Table 4.1.7 Regression analysis: Working time for Ca-MMT in the Chemfil Superior liquid constituent.

Dependent variable.. SettingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .49651
R Square .24652
Adjusted R Square .19943
Standard Error 4.83300

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	122.27368	122.27368
Residuals	16	373.72632	23.35789

F = 5.23479 Signif F = .0561

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	.926316	.404864	.496507	2.288	.0561
(Constant)	121.571930	2.501218		48.605	.0000

Table 4.1.8 Regression analysis: Setting time for Ca-MMT in the Chemfil Superior powder constituent.

Dependent variable.. SettingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .44459
R Square .19766
Adjusted R Square .14751
Standard Error 6.58227

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	170.77895	170.77895
Residuals	16	693.22105	43.32632

F = 3.94169 Signif F = .0645

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	1.094737	.551402	.444591	1.985	.0645
(Constant)	125.978947	3.406517		36.982	.0000

Table 4.1.9 Regression analysis: Setting time for Ca-MMT in the Chemfil Superior liquid constituent.

A comparison of the mean compressive fracture strength, mean working time and mean setting time for the Chemfil Superior groups prepared with Ca-MMT clay added to either the powder or liquid constituent was conducted using a two-sample independent Student's t-test. The results are shown in Table 4.1.10 and the statistical analysis is given in Tables 4.1.11 to 4.1.13, respectively. The addition of Ca-MMT clay to the powder constituent of Chemfil Superior resulted in a significant increase in the mean compressive fracture strength ($p = 0.021$) compared with adding Ca-MMT clay to the liquid constituent. Adding Ca-MMT clay to either the powder or liquid constituent of Chemfil Superior did not have a significant influence on the mean working time ($p = 0.059$), however, the mean setting time was significantly increased when Ca-MMT clay was added to the powder constituent ($p = 0.001$).

	Student's t-test significance
Compressive fracture strength	0.021
Working time	0.059
Setting time	0.001

Table 4.1.10 Two-sample independent Student's t-test results for the mean compressive fracture strength, mean working time and mean setting time for Chemfil Superior containing Ca-MMT clay added to either the powder or liquid constituent.

	PorL	N	Mean	Std. Deviation	Std. Error Mean
Strength	Powder	171	90.242887	19.8695089	1.5194593
	Liquid	163	85.409438	18.2165209	1.4268280

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
Strength	Equal variances assumed	2.794	.096	2.314	332	.021	4.9334487	2.0887122	.7246697	8.9422276
	Equal variances not assumed			2.319	331.503	.021	4.9334487	2.0843692	.7331905	8.9337068

Table 4.1.11 Two-sample independent Student's t-test: Compressive fracture strength for Ca-MMT in the Chemfil Superior powder or liquid constituent.

	PorL	N	Mean	Std. Deviation	Std. Error Mean
WorkTime	Powder	15	92.800000	4.4593401	1.1513967
	Liquid	15	90.000000	3.2071349	.8280787

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
WorkTime	Equal variances assumed	5.944	.021	1.974	28	.058	2.8000000	1.4182484	-1.051502	5.7051502
	Equal variances not assumed			1.974	25.426	.059	2.8000000	1.4182484	-1.184584	5.7184584

Table 4.1.12 Two-sample independent Student's t-test: Working time for Ca-MMT in the Chemfil Superior powder or liquid constituent.

	PorL	N	Mean	Std. Deviation	Std. Error Mean
WorkTime	Powder	15	128.0000	4.8989795	1.2649111
	Liquid	15	134.4000	4.9684720	1.2828540

Independent Samples Test

		Levene's Test for Equality of Variances		t-test for Equality of Means						
		F	Sig.	t	df	Sig. (2-tailed)	Mean Difference	Std. Error Difference	95% Confidence Interval of the Difference	
									Lower	Upper
WorkTime	Equal variances assumed	.064	.802	-3.552	28	.001	-6.4000000	1.8015866	-10.0904	-2.70962
	Equal variances not assumed			-3.552	27.994	.001	-6.4000000	1.8015866	-10.0904	-2.70958

Table 4.1.13 Two-sample independent Student's t-test: Setting time for Ca-MMT in the Chemfil Superior powder or liquid constituent.

4.1.3 Preliminary Remarks

Although Ca-MMT clay additions of up to 2.5 wt.% to the powder and liquid constituents of Chemfil Superior did not significantly influence the working and setting time, additions in excess of 2.5 wt.%, namely 5.0 and 10.0 wt.%, resulted in GI restoratives which were impossible to mix at the manufacturers' recommended powder to liquid mixing ratio and as a result, no data is presented. The addition of the un-modified Ca-MMT clay to the powder and liquid constituents of Chemfil Superior resulted in a reduction in the compressive fracture strength and *in vitro* wear resistance. As a result, a further investigation, examining the influence of adding an organically-modified MMT clay (pre-treated to encourage exfoliation) to Chemfil Superior was conducted.

4.2 Addition of ADA-MMT to Chemfil Superior

The object of this section of the experiment was to investigate the effect of adding an organically-modified clay mineral (ADA-MMT) to either the powder or liquid constituent of the anhydrous GI restorative Chemfil Superior at 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0 and 2.5 wt.% on the compressive fracture strength, *in vitro* wear resistance and working characteristics.

4.2.1 Materials and Methods

The Chemfil Superior groups containing ADA-MMT clay added to the powder and liquid were prepared in line with the procedures outlined in Section 4.1.1 for Ca-MMT clay. The compressive fracture strength, *in vitro* wear resistance and working characteristics were determined following the procedures outlined in Sections 3.3.1, 3.3.2 and 3.3.3, respectively.

4.2.2 Results

The plots of compressive fracture strength for Chemfil Superior prepared with ADA-MMT clay added to the powder and liquid constituents are shown in Figures 4.2.1 and 4.2.2, respectively. The mean compressive fracture strength reached a maximum at 0.5 wt.% ADA-MMT clay addition to both the powder and liquid constituent of Chemfil Superior and there was an steady decline with increasing ADA-MMT clay concentration (Figures 4.2.1 and 4.2.2). The different mean compressive fracture strength behaviour for ADA-MMT clay addition compared with the steady decline observed for Ca-MMT clay addition merited further consideration in the following sections. Significance values are quoted rather than providing the individual regression analyses, although all statistical analyses are available in Appendices. The

slopes of the regression lines plotted from the control (0.0 wt.%) to 0.5 wt.% ADA-MMT clay were not significant when ADA-MMT clay was added to the powder ($p = 0.269$) and liquid ($p = 0.237$) constituent of Chemfil Superior. However, there were significant slopes when the concentration of ADA-MMT clay added to the powder and liquid constituents was increased from 0.5 to 2.5 wt.% ($p < 0.001$ and $p < 0.001$, respectively).

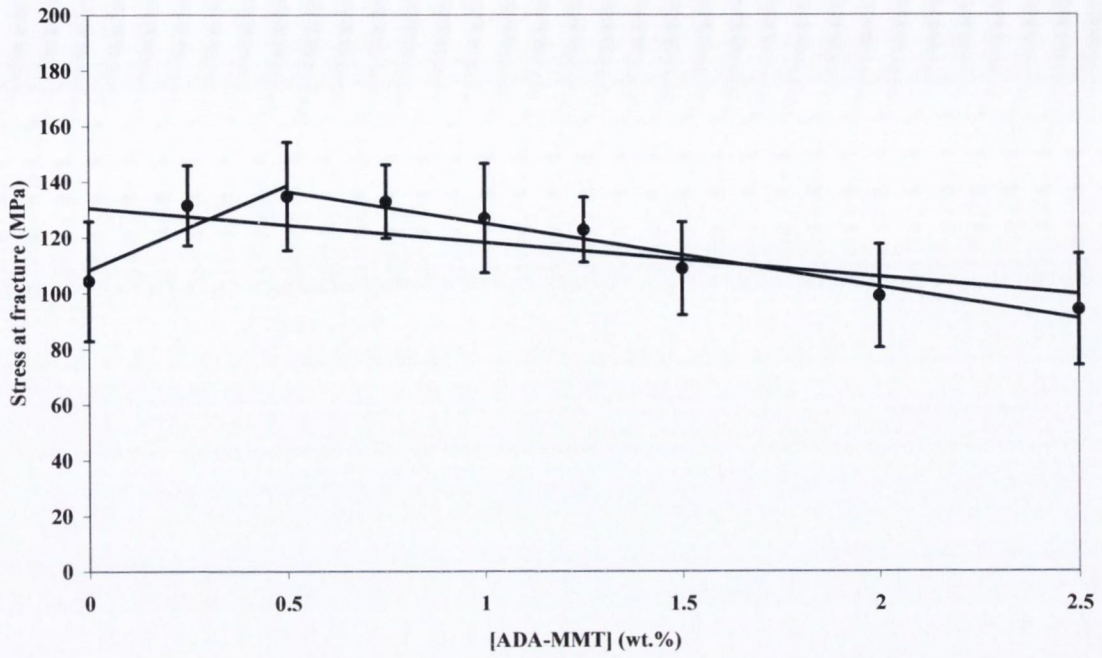


Figure 4.2.1 Variation of mean compressive fracture strength with ADA-MMT concentration in Chemfil Superior powder constituent:

Fitted lines:

0.0 to 2.5 wt.%, $y = -3.35x + 133.53$ $r^2 = 0.138$ $p < 0.001$ $df = 291$

0.0 to 0.5 wt.%, $y = 60.76x + 108.32$ $r^2 = 0.581$ $p = 0.269$ $df = 96$

0.5 to 2.5 wt.%, $y = -18.32x + 145.83$ $r^2 = 0.648$ $p < 0.001$ $df = 195$

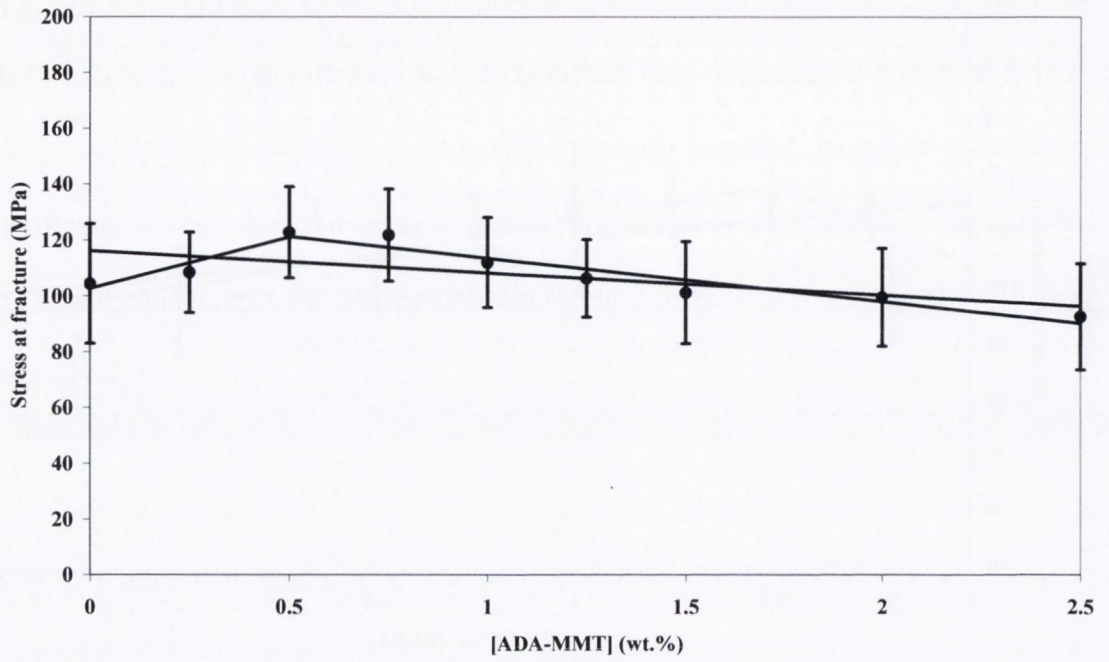


Figure 4.2.2 Variation of mean compressive fracture strength with ADA-MMT concentration in Chemfil Superior liquid constituent:

Fitted lines:

0.0 to 2.5 wt.%: $y = -2.22x + 118.78$ $r^2 = 0.089$ $p < 0.001$ $df = 293$

0.0 to 0.5 wt.% $y = 36.60x + 102.68$ $r^2 = 0.497$ $p = 0.237$ $df = 97$

0.5 to 2.5 wt.% $y = -14.49x + 129.03$ $r^2 = 0.618$ $p < 0.001$ $df = 196$

A one-way analysis of variance (ANOVA) of the mean compressive fracture strengths for the groups containing 0.25 to 2.5 wt.% ADA-MMT clay added to both the powder and liquid constituent of Chemfil Superior and the Chemfil Superior control group is given in Table 4.2.1.

Between-Subjects Factors

	Value Label	N	
MMTConc	1.00	0.00	33
	2.00	0.25 P	30
	3.00	0.5 P	34
	4.00	0.75 P	30
	5.00	1.0 P	35
	6.00	1.25 P	30
	7.00	1.5 P	35
	8.00	2.0 P	35
	9.00	2.5 P	31
	10.00	0.25 L	30
	11.00	0.5 L	35
	12.00	0.75 L	30
	13.00	1.0 L	34
	14.00	1.25 L	30
	15.00	1.5 L	33
	16.00	2.0 L	35
	17.00	2.5 L	35

Tests of Between-Subjects Effects

Dependent Variable: Strength

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	102475.076 ^a	16	6404.692	21.333	.000
Intercept	7031816.186	1	7031816.186	23421.331	.000
MMTConc	102475.076	16	6404.692	21.333	.000
Error	161524.428	538	300.231		
Total	7293201.362	555			
Corrected Total	263999.504	554			

a. R Squared = .388 (Adjusted R Squared = .370)

Table 4.2.1 One-way analysis of variance of compressive fracture strength data: Chemfil Superior groups containing ADA-MMT clay addition.

The results of a Tukey's post-hoc test comparing the mean compressive fracture strengths of the Chemfil Superior groups containing ADA-MMT clay additions and the control group are shown in Table 4.2.2. The groups containing 0.25, 0.5, 0.75, 1.0 and 1.25 wt.% ADA-MMT clay added to the powder constituent and 0.5 and 0.75 wt.% ADA-MMT clay added to the liquid constituent had significantly increased mean compressive fracture strengths compared with the Chemfil superior control.

ADA-MMT clay concentration (wt.%)	P value
0.25 (P)	<0.001
0.5 (P)	<0.001
0.75 (P)	<0.001
1.0 (P)	<0.001
1.25 (P)	0.004
1.5 (P)	1.000
2.0 (P)	0.556
2.5 (P)	0.993
0.25 (L)	1.000
0.5 (L)	0.002
0.75 (L)	0.009
1.0 (L)	0.933
1.25 (L)	1.000
1.5 (L)	1.000
2.0 (L)	0.999
2.5 (L)	0.404

Table 4.2.2 Tukey's post-hoc test results for Chemfil Superior control with selected groups containing ADA-MMT clay. P: added to powder, L: added to liquid.

The results of the *in vitro* wear resistance tests for Chemfil Superior with ADA-MMT clay added to the powder constituent are shown in Figure 4.2.3. Statistical analyses of the total volumetric wear and maximum wear depth data are given in Tables 4.2.4 and 4.2.5, respectively. The slopes of the regression lines were not significant for the total volumetric wear data ($p = 0.052$) and maximum wear depth data ($p = 0.052$) as the concentration of ADA-MMT clay was increased.

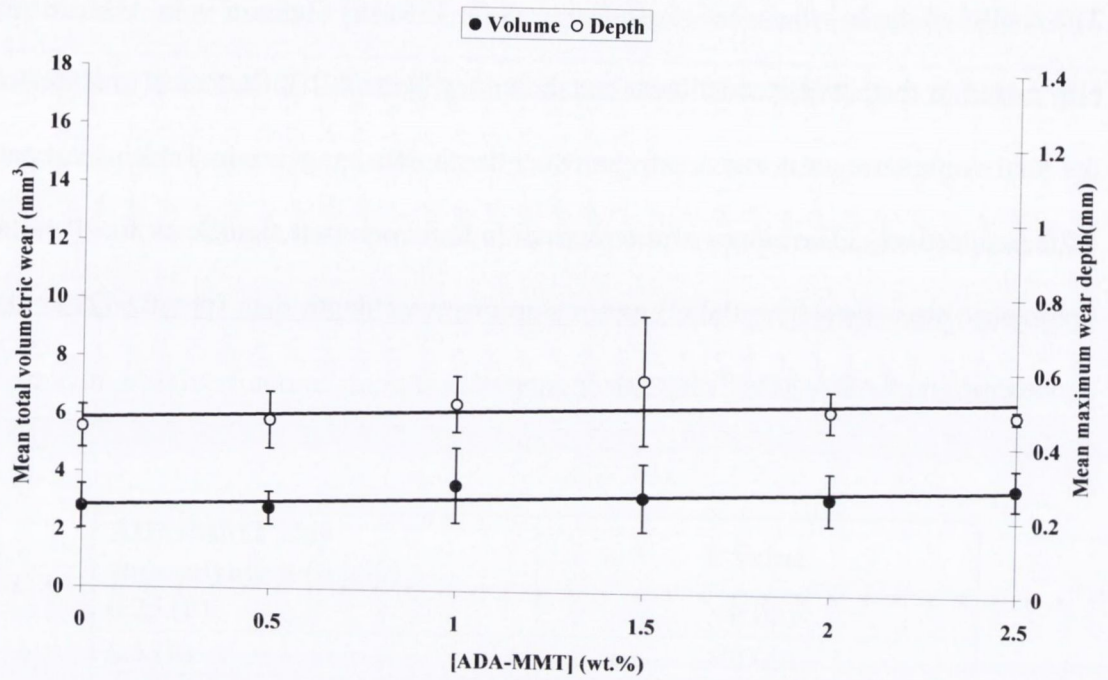


Figure 4.2.3 Variation of mean total volumetric wear and mean maximum wear depth with ADA-MMT concentration for Chemfil Superior:

Fitted lines:

Volume: $y = 0.988x + 2.715$ $r^2 = 0.087$ $p = 0.052$ $df = 46$

Depth: $y = 0.009x + 0.436$ $r^2 = 0.080$ $p = 0.052$ $df = 46$

Dependent variable.. Volume

Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .29519
 R Square .08714
 Adjusted R Square .06729
 Standard Error .91945

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	3.712114	3.7121141
Residuals	46	38.887704	.8453849

F = 4.39103 Signif F = .0517

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	.098837	.047167	.295193	2.095	.0517
(Constant)	2.714981	.291392		9.317	.0000

Table 4.2.4 Regression analysis: Total volumetric wear for ADA-MMT in the Chemfil Superior powder constituent.

Plots of the working time and setting time versus ADA-MMT concentration for Chemfil Superior with ADA-MMT clay added to the powder and constituents are illustrated in Figures 4.2.4 and 4.2.5, respectively. The statistical analysis of the working characteristics data shown in Tables 4.2.6 to 4.2.9 illustrate that ADA-MMT clay addition to the Chemfil Superior powder or liquid constituents did not have a significant influence on the working time ($p = 0.116$ and 0.409 , respectively) or the setting time ($p = 0.174$ and 0.060 , respectively).

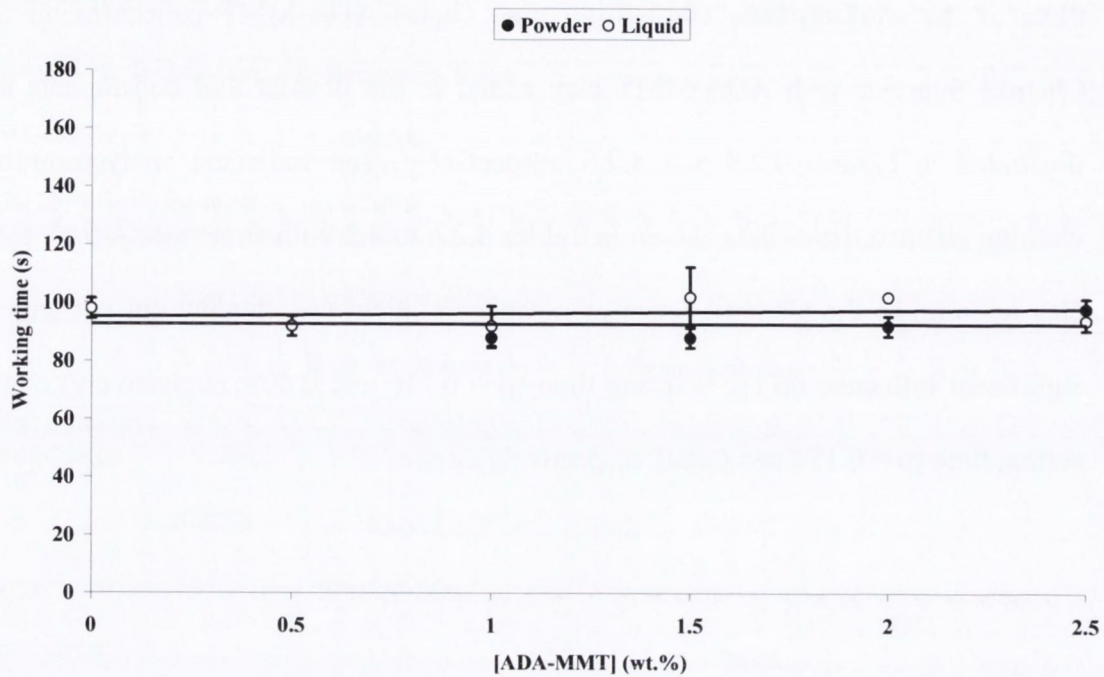


Figure 4.2.4 Variation of mean working time with ADA-MMT concentration for Chemfil Superior:

Fitted lines:

Powder: $y = -1.221x + 99.382$ $r^2 = 0.474$ $p = 0.116$ $df = 16$

Liquid: $y = -0.463x + 99.214$ $r^2 = 0.430$ $p = 0.409$ $df = 16$

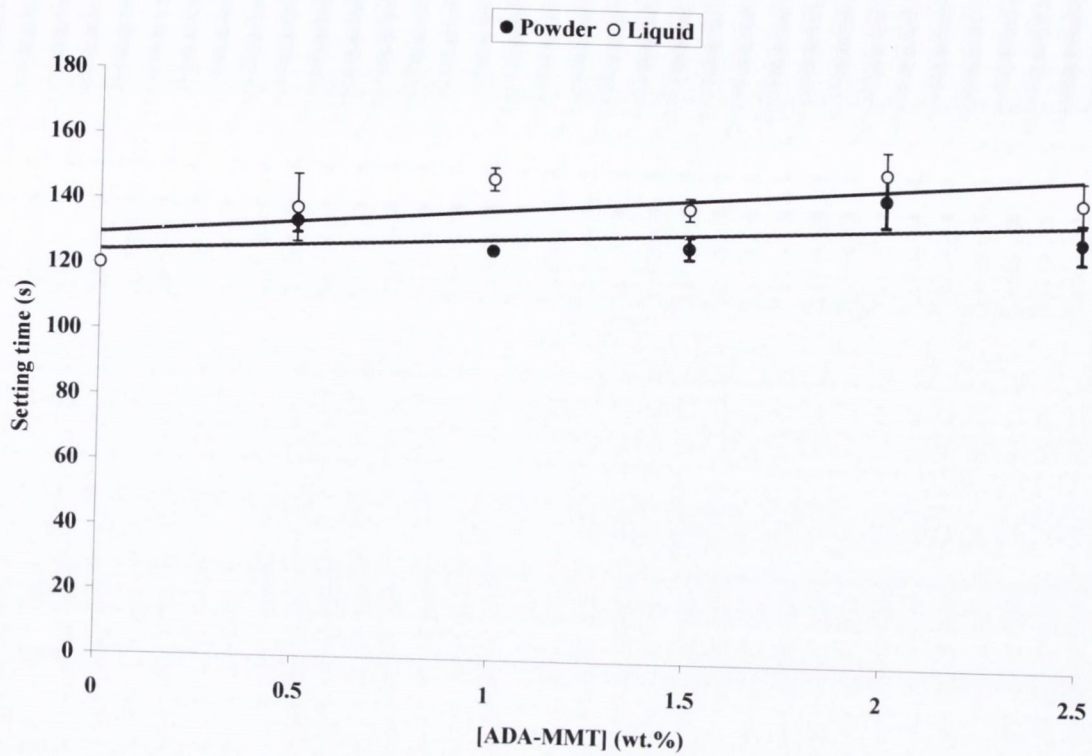


Figure 4.2.4 Variation of mean setting time with ADA-MMT concentration for Chemfil Superior:

Fitted lines:

Powder: $y = 0.793x + 125.082$ $r^2 = 0.112$ $p = 0.174$ $df = 16$

Liquid: $y = 1.832x + 130.259$ $r^2 = 0.204$ $p = 0.060$ $df = 16$

Dependent variable.. WorkingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .68866
R Square .47425
Adjusted R Square .44139
Standard Error 3.83680

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	212.46316	212.46316
Residuals	16	235.53684	14.72105

F = 14.43261 Signif F = .1161

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-1.221053	.321412	-.688657	-3.799	.1161
(Constant)	99.382456	1.985656		50.050	.0000

Table 4.2.6 Regression analysis: Working time for ADA-MMT in the Chemfil Superior powder constituent.

Dependent variable.. WorkingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .20720
R Square .04293
Adjusted R Square -.01688
Standard Error 6.52606

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	30.56842	30.568421
Residuals	16	681.43158	42.589474

F = .71775 Signif F = .4094

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	-.463158	.546693	-.207203	-.847	.4094
(Constant)	99.214035	3.377426		29.376	.0000

Table 4.2.7 Regression analysis: Working time for ADA-MMT in the Chemfil Superior liquid constituent.

Dependent variable.. SettingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .33500
R Square .11223
Adjusted R Square .05674
Standard Error 6.65600

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	89.60702	89.607018
Residuals	16	708.83743	44.302339

F = 2.02262 Signif F = .1742

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	.792982	.557578	.335003	1.422	.1742
(Constant)	125.083041	3.444673		36.312	.0000

Table 4.2.8 Regression analysis: Setting time for ADA-MMT in the Chemfil Superior powder constituent.

Dependent variable.. SettingTime Method.. LINEAR

Listwise Deletion of Missing Data

Multiple R .45218
R Square .20447
Adjusted R Square .15475
Standard Error 10.78181

Analysis of Variance:

	DF	Sum of Squares	Mean Square
Regression	1	478.0421	478.04211
Residuals	16	1859.9579	116.24737

F = 4.11228 Signif F = .0596

----- Variables in the Equation -----

Variable	B	SE B	Beta	T	Sig T
MMTConc	1.831579	.903200	.452179	2.028	.0596
(Constant)	130.259649	5.579898		23.344	.0000

Table 4.2.9 Regression analysis: Setting time for ADA-MMT in the Chemfil Superior liquid constituent.

The mean compressive fracture strength, mean working time and mean setting time for the Chemfil Superior groups containing ADA-MMT clay added to either the powder or liquid constituent were compared using the two-sample independent Student's t-test and the data is given in Table 4.2.10. The individual two-sample independent Student's t-tests are available in Appendices. Adding ADA-MMT clay to the powder constituent of Chemfil Superior resulted in a significant increase in the mean compressive fracture strength ($p < 0.001$) compared with adding the clay to the liquid constituent of Chemfil Superior. The mean working time ($p = 0.038$) and setting time ($p < 0.001$) were significantly increased when ADA-MMT clay was added to liquid constituent of Chemfil Superior compared with adding the clay to the powder constituent.

	Student's t-test significance
Compressive fracture strength	<0.001
Working time	0.038
Setting time	<0.001

Table 4.2.10 Two-sample independent Student's t-test comparisons of the mean compressive fracture strength, mean working time and mean setting time for Chemfil Superior containing ADA-MMT clay added to either the powder or liquid constituent.

4.2.3 Preliminary Remarks

The addition of ADA-MMT clay to Chemfil Superior up to 1.0 wt.% resulted in significantly increased mean compressive fracture strengths without influencing the *in vitro* wear resistance or the working characteristics compared with the control group. As a result, a further investigation examining the influence of ADA-MMT clay addition to conventionally supplied GI restoratives consisting of a separate powder and a polyalkenoic acid liquid solution was conducted.

4.3 Addition of ADA-MMT to Conventional GI Restoratives

The object of this experiment was to investigate the influence of adding ADA-MMT to the powder or liquid constituents of several conventionally supplied GI restoratives at concentrations of 0.5 and 1.0 wt.% on the compressive fracture strength.

4.3.1 Materials and Methods

The conventional GI restorative groups containing ADA-MMT clay added to the powder constituent were prepared following the procedure outlined in Section 4.2.1. To prepare the GI restorative liquids containing ADA-MMT clay a glass vial was incrementally filled with 2.5 mL of GI restorative liquid using the adjustable 200 μ L pipette and the appropriate quantity of ADA-MMT clay (Table 4.3.1) was added. The weight of ADA-MMT clay added was calculated based on the quantity of GI restorative powder corresponding to 2.5 mL of GI restorative liquid and is given in Table 4.3.1.

ADA-MMT clay concentration (wt.%)	ADA-MMT clay added to 2.5 g GI restorative liquid (g)				
	Kf	F _{II}	Km	F _{IX}	Cx
0.5	0.040	0.034	0.056	0.045	0.048
1.0	0.090	0.068	0.113	0.090	0.095

Table 4.3.1 ADA-MMT quantities added to liquid constituent of the conventional GI restoratives. Kf: Ketac Fil Plus, F_{II}: Fuji II, Km: Ketac Molar Easymix, F_{IX}: Fuji IX, Cx: ChemFlex.

The glass vial was placed onto the centre of a stirring hotplate, a magnetic stirrer bar inserted and the GI restorative liquid solution containing ADA-MMT clay was

mechanically stirred for 3 h at 80 ± 5 °C at a speed of 300 rpm. Following mechanical stirring the GI restorative-ADA-MMT liquids were stored in the glass vials at room temperature (23 ± 1 °C) for 24 h prior to use. To maintain the manufacturers' recommended powder to liquid mixing ratio when hand-mixing the GI restorative groups with ADA-MMT clay added to the liquid, the weight of liquid was increased by 0.005 g for the 0.5 wt.% groups and 0.009 g for the 1.0 wt.% groups. The GI restorative groups containing ADA-MMT clay added to the GI restorative liquid were hand-mixed with the GI restorative powder as reported in Section 4.2.1. The mean compressive fracture strength was determined for each group using the procedure outlined in Section 3.3.1.

4.3.2 Results

Plots of the mean compressive fracture strength versus ADA-MMT clay concentration (added to the powder and liquid constituent) for Ketac Fil Plus, Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex are shown in Figures 4.3.1 to 4.3.5, respectively. The slopes of the regression lines plotted on Figures 4.3.1 to 4.3.5, the corresponding statistical significances and degrees of freedom (df) are given in Table 4.3.2. Individual regression analyses for the mean compressive fracture strength data versus ADA-MMT clay concentration are available in Appendices. There was a significant slope increase ($p = 0.034$) as the concentration of ADA-MMT clay added to the Ketac Fil Plus powder constituent was increased. Increasing the concentration of ADA-MMT clay to the powder and liquid constituents of Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex resulted in a significant decrease in the mean compressive fracture strength (Table 4.3.2).

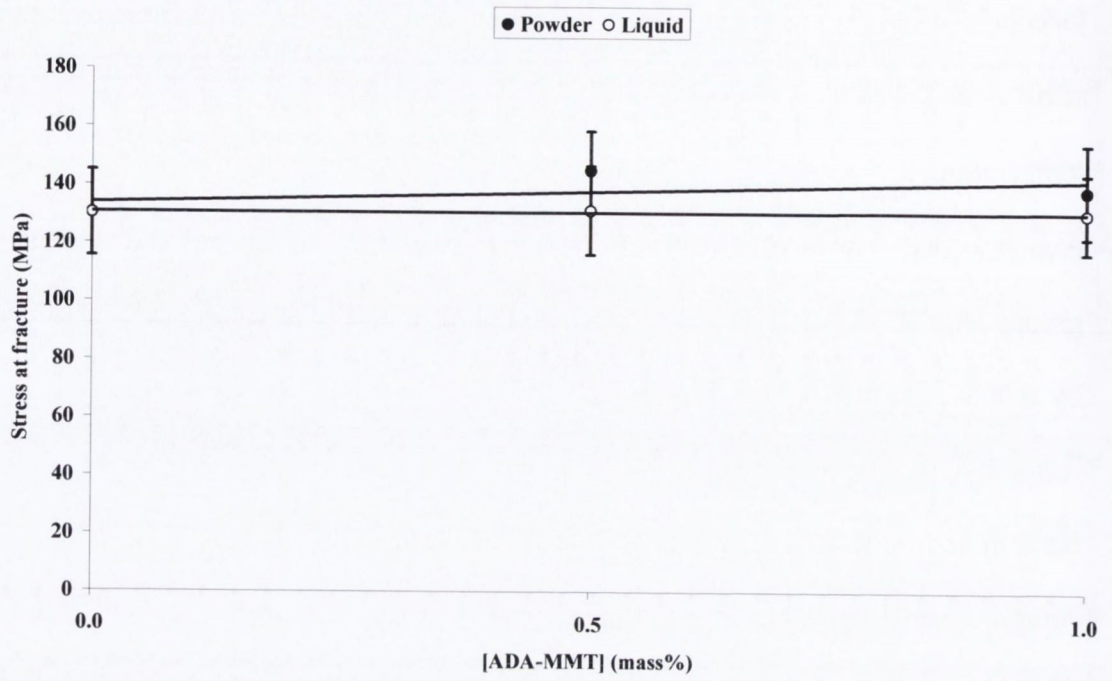


Figure 4.3.1 Variation of mean compressive fracture strength with ADA-MMT concentration: Ketac Fil Plus.

Fitted lines:

Powder: $y = 4.20x + 129.30$ $r^2 = 0.048$ $p = 0.034$ $df = 93$

Liquid: $y = 0.12x + 130.44$ $r^2 < 0.001$ $p = 0.949$ $df = 93$

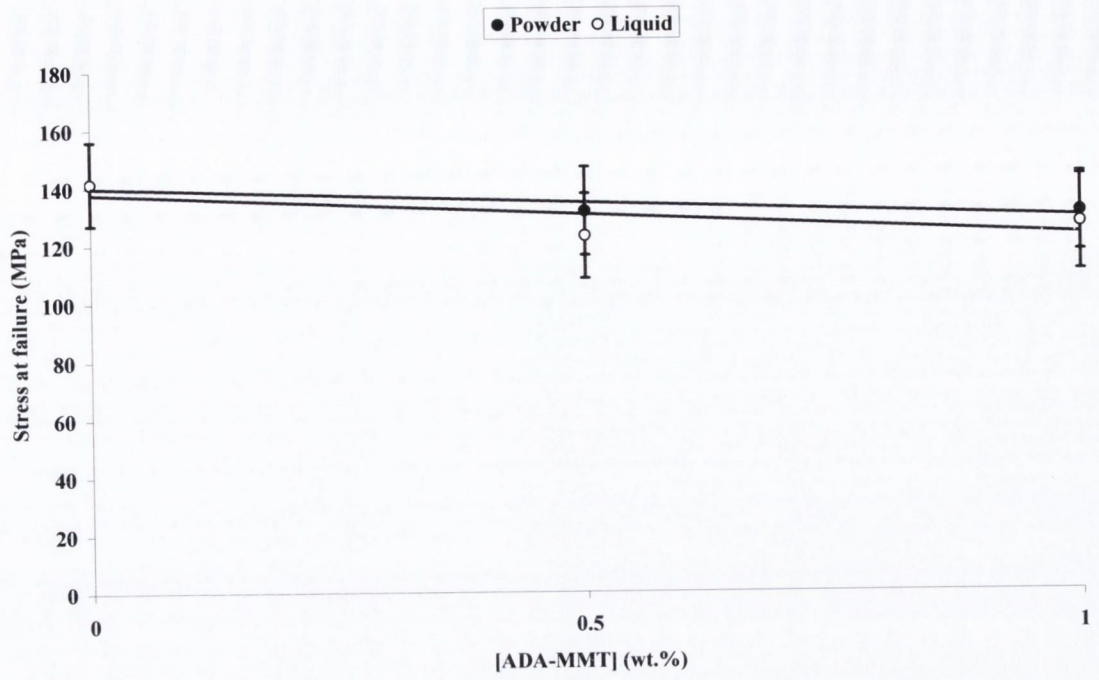


Figure 4.3.2 Variation of mean compressive fracture strength with ADA-MMT concentration: Fuji II.

Fitted lines:

Powder: $y = -11.45x + 148.49$ $r^2 = 0.263$ $p < 0.001$ $df = 92$

Liquid: $y = -7.71x + 145.78$ $r^2 = 0.140$ $p < 0.001$ $df = 92$

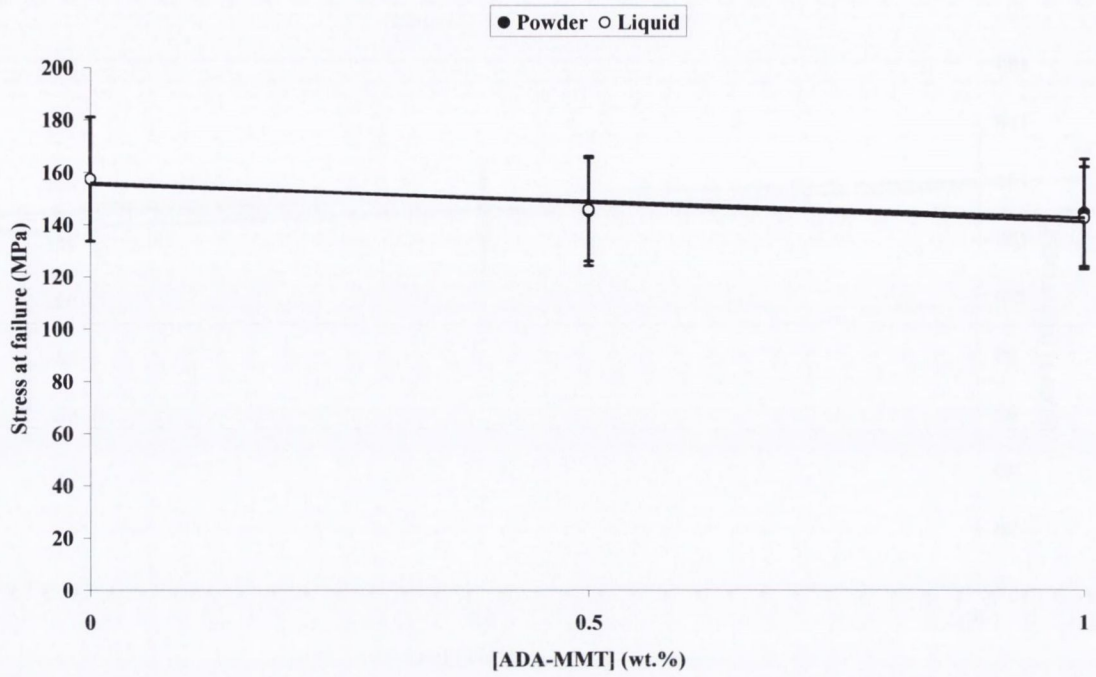


Figure 4.3.2 Variation of mean compressive fracture strength with ADA-MMT concentration: Ketac Molar Easymix.

Fitted lines:

Powder: $y = -6.60x + 162.29$ $r^2 = 0.059$ $p = 0.017$ $df = 94$

Liquid: $y = -7.57x + 163.70$ $r^2 = 0.081$ $p = 0.005$ $df = 94$

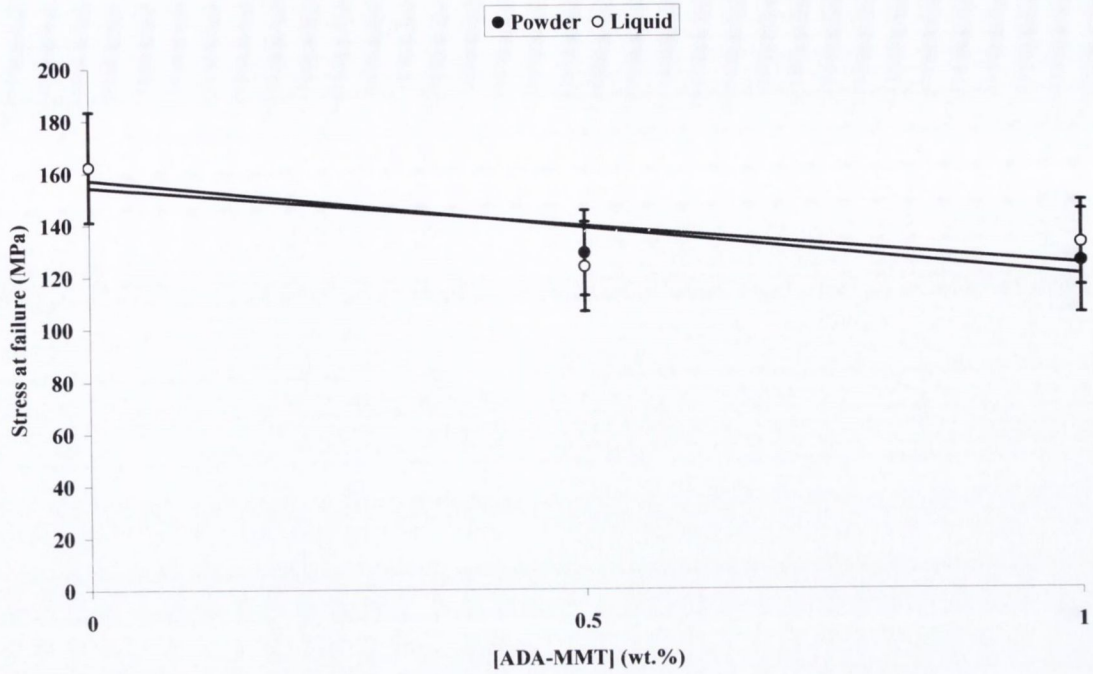


Figure 4.3.2 Variation of mean compressive fracture strength with ADA-MMT concentration: Fuji IX.

Fitted lines:

Powder: $y = -18.69x + 176.29$ $r^2 = 0.366$ $p < 0.001$ $df = 91$

Liquid: $y = -15.42x + 170.30$ $r^2 = 0.264$ $p < 0.001$ $df = 91$

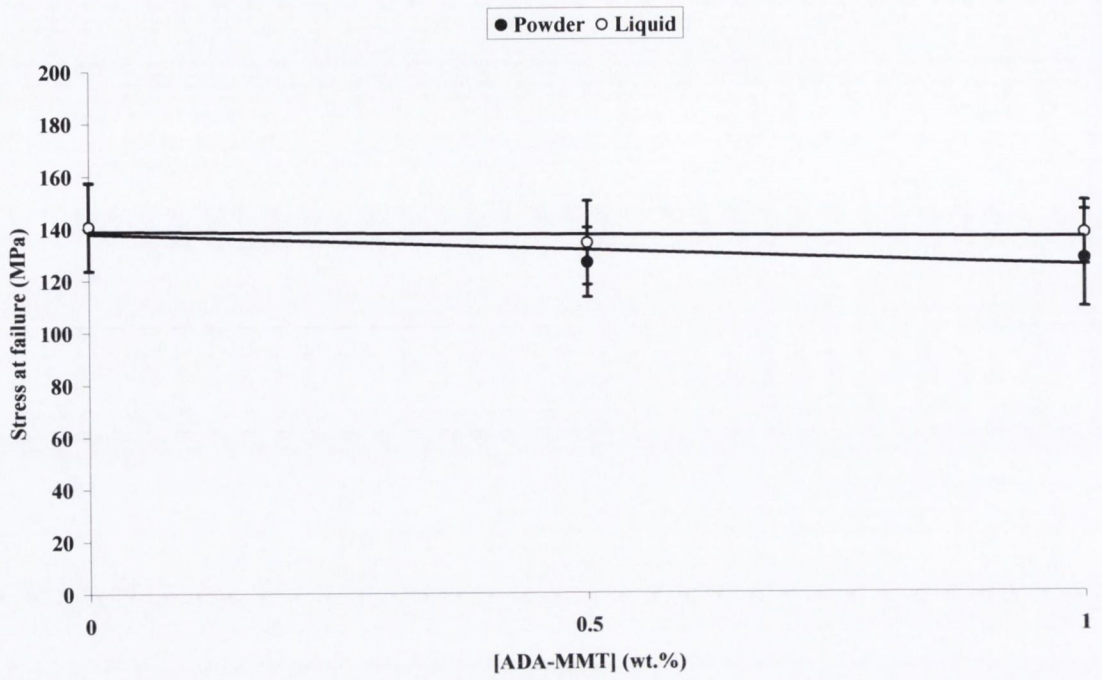


Figure 4.3.2 Variation of mean compressive fracture strength with ADA-MMT concentration: ChemFlex.

Fitted lines:

Powder: $y = -6.49x + 144.42$ $r^2 = 0.096$ $p = 0.002$ $df = 93$

Liquid: $y = -1.90x + 140.72$ $r^2 = 0.011$ $p = 0.033$ $df = 93$

Material		Slope	r²	p value	df
Ketac Fil Plus	P	4.20	0.048	0.034	93
	L	0.12	< 0.001	0.949	93
Fuji II	P	-11.45	0.263	< 0.001	92
	L	-7.71	0.140	< 0.001	92
Ketac Molar Easymix	P	-6.60	0.059	0.017	94
	L	-7.57	0.081	0.005	94
Fuji IX	P	-18.69	0.366	< 0.001	91
	L	-15.42	0.264	< 0.001	91
ChemFlex	P	-6.49	0.096	0.002	93
	L	-1.90	0.011	0.033	93

Table 4.3.2 Comparison of regression line slopes, r² values, p values and degrees of freedom (df) of the compressive fracture strength data for ADA-MMT clay addition to the powder and liquid constituents of Ketac Fil Plus, Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex. P: added to the powder, L: added to the liquid.

A three-way ANOVA (GI restorative material x method of ADA-MMT clay addition x ADA-MMT concentration) of the compressive fracture strength data identified no significant interaction between GI restorative material, method of ADA-MMT clay addition (either to the powder or liquid constituent) and ADA-MMT clay concentration ($p = 0.540$) (Table 4.3.3). There was no significant interaction between GI restorative material and ADA-MMT clay concentration ($p = 0.466$) and method of ADA-MMT clay addition and ADA-MMT clay concentration ($p = 0.183$). As a result, a two-way ANOVA (GI restorative material x method of ADA-MMT clay addition) of the compressive fracture strength data was conducted which showed a significant interaction between GI restorative material and method of ADA-MMT clay addition ($p < 0.001$) and is shown in Table 4.3.4.

Between-Subjects Factors

		Value Label	N
Material	1.00	Ketac Fil Plus	154
	2.00	Fuji II	153
	3.00	Ketac Molar Easymix	155
	4.00	Fuji IX	152
	5.00	ChemFlex	154
Added	1.00	Powder	300
	2.00	Liquid	300
	3.00	Control	168
Concentration	1.00	0.0wt%	168
	2.00	0.5wt. %	300
	3.00	1.0wt. %	300

Tests of Between-Subjects Effects

Dependent Variable: Strength

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	95625.286 ^a	24	3984.387	13.630	.000
Intercept	13801535.4	1	13801535.40	47212.076	.000
Material	35281.994	4	8820.498	30.173	.000
Added	101.426	1	101.426	.347	.556
Concentration	4.428	1	4.428	.015	.902
Material * Added	6747.254	4	1686.813	5.770	.000
Material * Concentration	1047.094	4	261.773	.895	.466
Added * Concentration	518.253	1	518.253	1.773	.183
Material * Added * Concentration	909.561	4	227.390	.778	.540
Error	217201.649	743	292.331		
Total	14350922.0	768			
Corrected Total	312826.935	767			

a. R Squared = .306 (Adjusted R Squared = .283)

Table 4.3.3 Three-way analysis of variance of GI restorative material x method of ADA-MMT clay addition x ADA-MMT clay concentration for the compressive fracture strength data.

Between-Subjects Factors

		Value Label	N
Material	1.00	Ketac Fil Plus	154
	2.00	Fuji II	153
	3.00	Ketac Molar Easymix	155
	4.00	Fuji IX	152
	5.00	ChemFlex	154
Added	1.00	Control	168
	2.00	Powder	300
	3.00	Liquid	300

Tests of Between-Subjects Effects

Dependent Variable: Strength

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	87348.793 ^a	14	6239.200	20.836	.000
Intercept	13350086.4	1	13350086.39	44583.546	.000
Material	34211.598	4	8552.900	28.563	.000
Added	26389.019	2	13194.509	44.064	.000
Material * Added	24334.147	8	3041.768	10.158	.000
Error	225478.142	753	299.440		
Total	14350922.0	768			
Corrected Total	312826.935	767			

a. R Squared = .279 (Adjusted R Squared = .266)

Table 4.3.4 Two-way analysis of variance of GI restorative material x method of ADA-MMT clay addition for the compressive fracture strength data.

The influence of adding ADA-MMT clay to the powder or the liquid constituent of individual GI restorative materials was examined for the mean compressive fracture strength data using the two-sample independent Student's t-test and the results are given in Table 4.3.5. There were significant increases in the mean compressive fracture strength for Ketac Fil Plus when ADA-MMT clay was added to the powder constituent ($p < 0.001$) and for Fuji II and ChemFlex when ADA-MMT clay was added to the liquid constituent ($p = 0.018$ and $p = 0.004$, respectively). However, there was no significant difference in the mean compressive fracture strength for Ketac Molar Easymix ($p = 0.843$) and Fuji IX ($p = 0.823$) with ADA-MMT clay addition to the powder or liquid constituent (Table 4.3.5).

GI restorative	Student's t-test significance
Ketac Fil Plus	<0.001
Fuji II	0.018
Ketac Molar Easymix	0.843
Fuji IX	0.823
ChemFlex	0.004

Table 4.3.5 Two-sample independent Student's t-test results for the mean compressive fracture strengths of the individual GI restorative materials prepared with ADA-MMT clay addition to either the powder or the liquid constituent.

The mean compressive fracture strength data for the individual GI restorative products containing ADA-MMT clay and their respective controls were analysed using a one-way ANOVA and a Tukey's post-hoc test. The results of the Tukey's post-hoc tests are shown in Table 4.3.6 and the individual one-way ANOVAs are available in Appendices. The addition of ADA-MMT clay to the powder constituent of Ketac Fil Plus at 0.5 resulted in a significant increase in the mean compressive fracture strength compared with the control group ($p = 0.001$). The mean compressive fracture strength of the remaining groups containing ADA-MMT clay additions were either not significantly different or significantly decreased (Table 4.3.6).

Material	ADA-MMT added to powder		ADA-MMT added to liquid	
	0.5 wt. %	1.0 wt. %	0.5 wt. %	1.0 wt. %
Ketac Fil Plus	0.001	0.195	0.998	1.000
Fuji II	< 0.001	< 0.001	< 0.001	0.001
Ketac Molar Easymix	0.139	0.104	0.173	0.039
Fuji IX	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex	0.006	0.012	0.514	0.885

Table 4.3.6 Tukey's post-hoc test results of the mean compressive fracture strengths for individual GI restorative materials containing ADA-MMT clay added compared with their control.

4.3.3 Preliminary Remarks

The addition of ADA-MMT clay to the powder and liquid constituents of GI restoratives (at concentrations of up to 1.0 wt.%) resulted in significant increases in the mean compressive fracture strength for some of the GI restoratives investigated (Chemfil Superior and Ketac Fil Plus). However, the GI restoratives containing ADA-MMT clay additions were more difficult to mix at the manufacturers' recommended powder to liquid mixing ratio. As a result, the possibility of reducing the powder content of the GI restoratives from that recommended by the manufacturers was investigated to identify the lowest powder content that could potentially be used for ADA-MMT reinforcement without a significant reduction in the mechanical properties (compressive fracture strength, elastic modulus and *in vitro* wear resistance).

4.4 Influence of Reducing GI restorative Powder Content

The object of this experiment was to investigate the influence of reducing the powder content of hand-mixed GI restoratives, for a constant weight of liquid, on the compressive fracture strength, elastic modulus and *in vitro* wear resistance.

4.4.1 Materials and Methods

The GI restorative control groups were prepared using the procedure outlined in Section 3.2.1. To prepare the GI restorative groups with powder contents reduced from that recommended (100%), the weight of liquid used remained constant for each GI restorative investigated. The constant weight of liquid employed for Ketac Fil Plus, Fuji II, Chemfil Superior, Ketac Molar Easymix, Fuji IX and ChemFlex was 0.281, 0.333, 0.122, 0.2, 0.25 and 0.237, respectively as shown in Table 3.2.1. The specimen groups containing powder contents reduced from 100% to 90, 80, 70, 60 and 50% of that recommended were prepared by reducing the mass of each GI restorative powder used from 0.9 g to 0.81, 0.72, 0.63, 0.54 and 0.45 g, respectively. The compressive fracture strength, elastic modulus and the *in vitro* wear resistance were determined as outlined in Sections 3.3.1 and 3.3.2, respectively.

4.4.2 Results

The plots of mean compressive fracture strength versus powder content for Ketac Fil Plus, Fuji II, Chemfil Superior, Ketac Molar Easymix, Fuji IX and ChemFlex are illustrated in Figures 4.4.1 to 4.4.6, respectively.

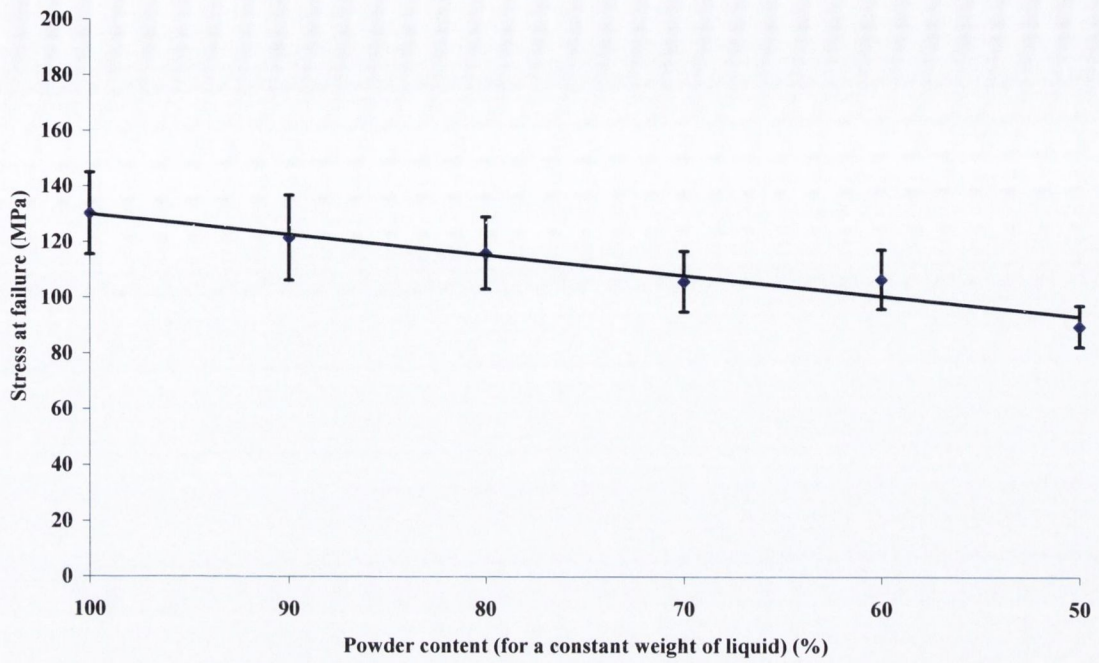


Figure 4.4.1 Variation of mean compressive fracture strength with decreasing powder content: Ketac Fil Plus.

Fitted line: $y = -7.27x + 137.30$ $r^2 = 0.496$ $p < 0.001$ $df = 203$

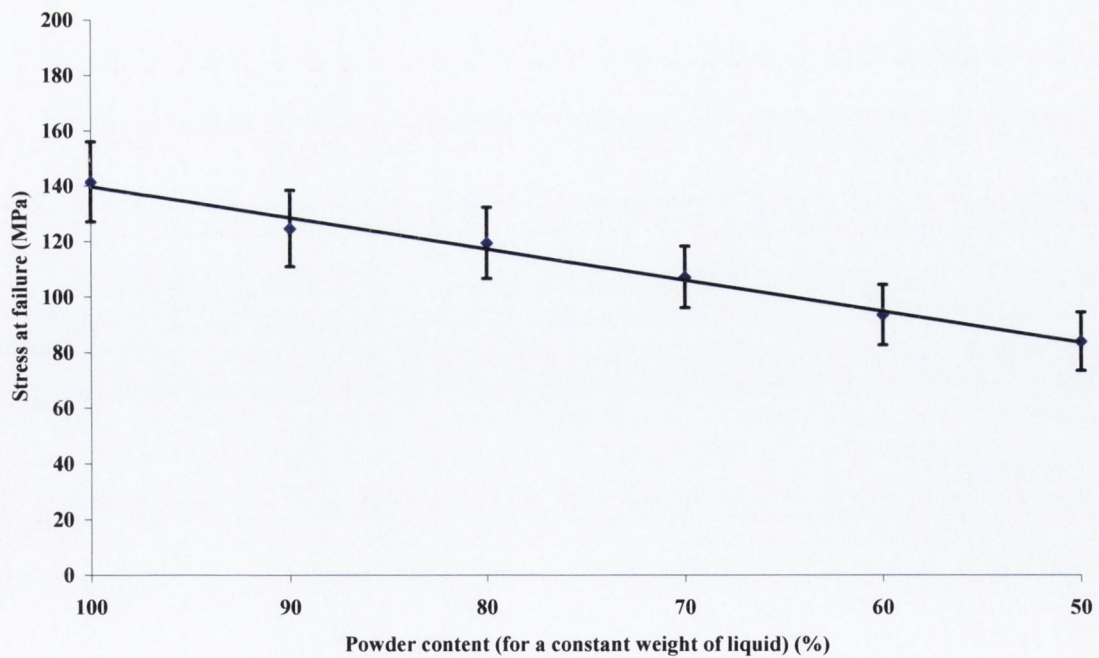


Figure 4.4.2 Variation of mean compressive fracture strength with decreasing powder content: Fuji II.

Fitted line: $y = -11.50x + 151.76$ $r^2 = 0.689$ $p < 0.001$ $df = 193$

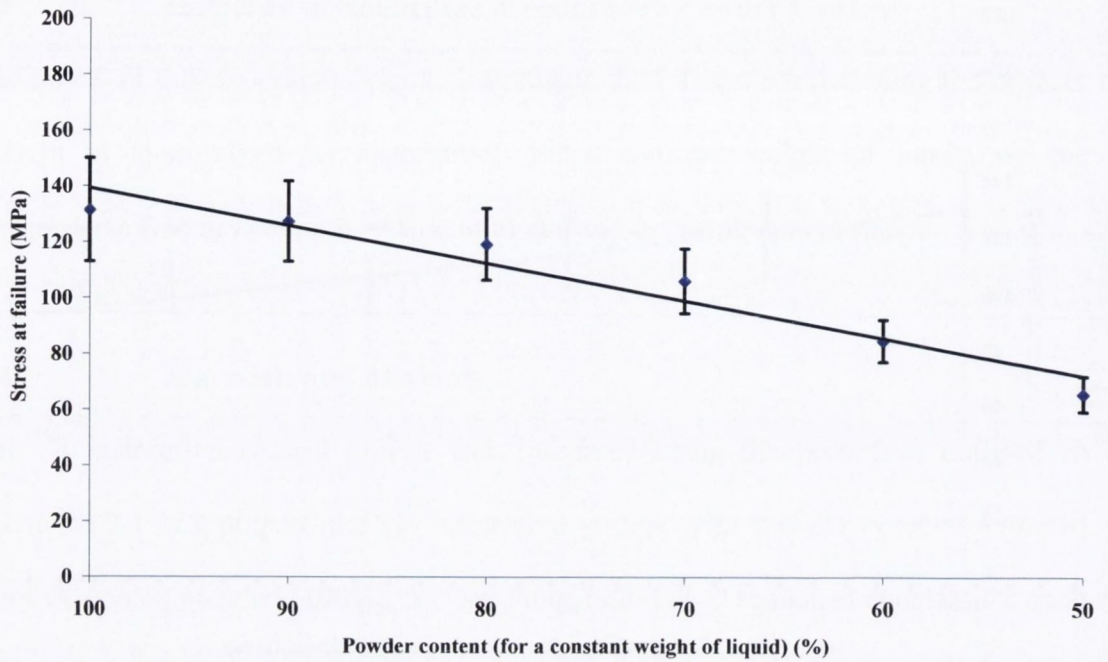


Figure 4.4.3 Variation of mean compressive fracture strength with decreasing powder content: Chemfil Superior.

Fitted line: $y = -13.22x + 152.27$ $r^2 = 0.729$ $p < 0.001$ $df = 198$

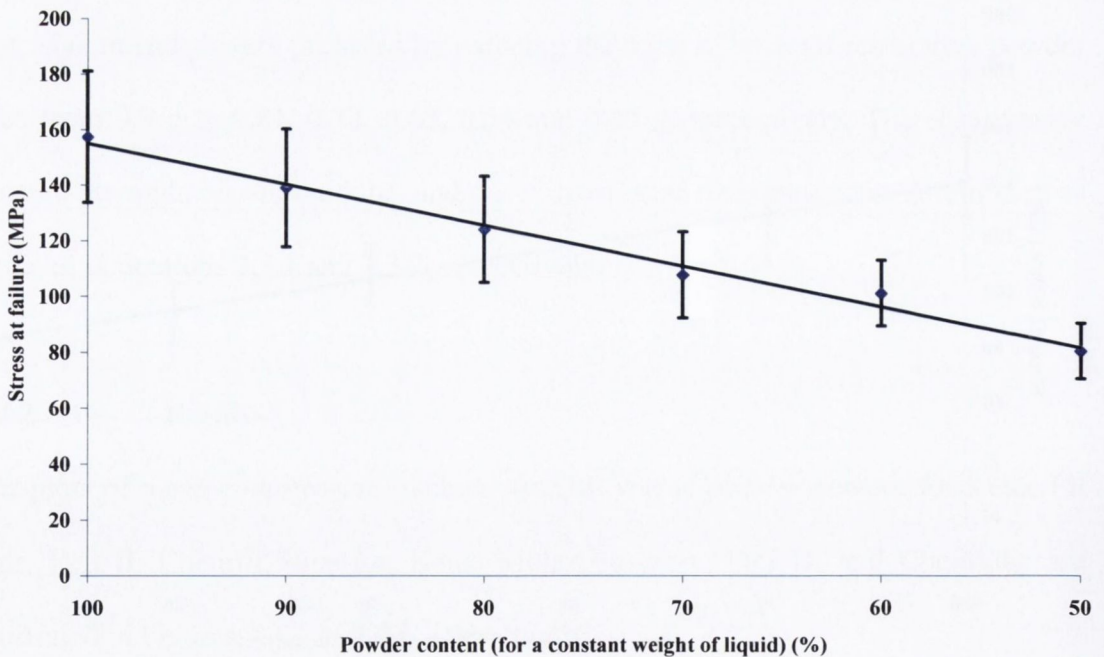


Figure 4.4.4 Variation of mean compressive fracture strength with decreasing powder content: Ketac Molar Easymix.

Fitted line: $y = -14.62x + 169.76$ $r^2 = 0.666$ $p < 0.001$ $df = 202$

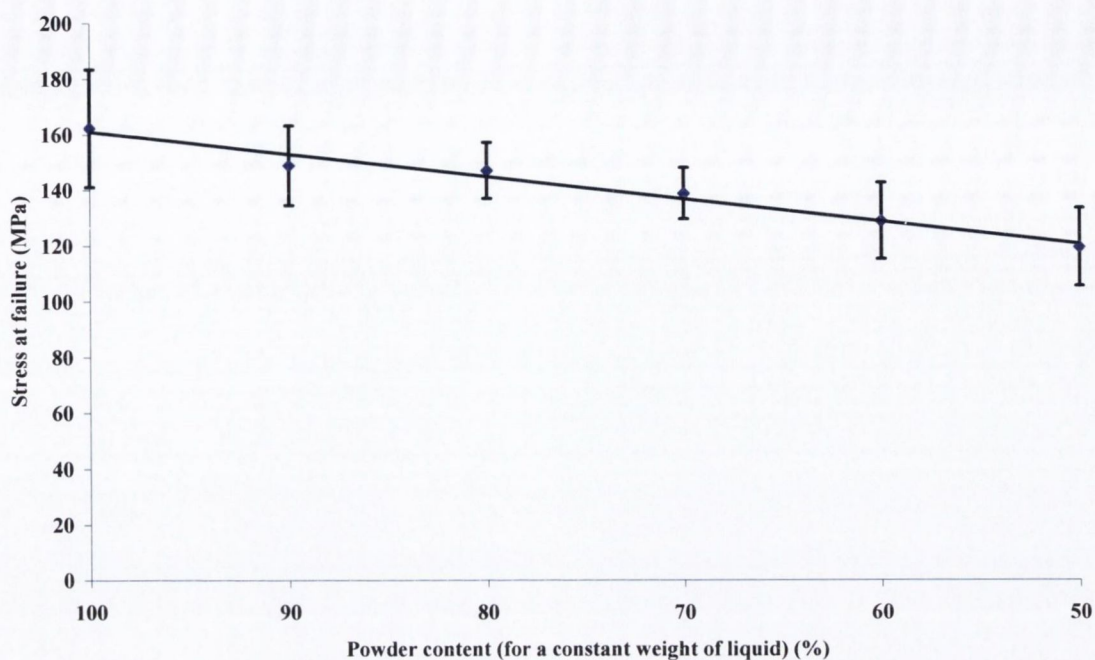


Figure 4.4.5 Variation of mean compressive fracture strength with decreasing powder content: Fuji IX.

Fitted line: $y = -8.04x + 169.01$ $r^2 = 0.478$ $p < 0.001$ $df = 199$

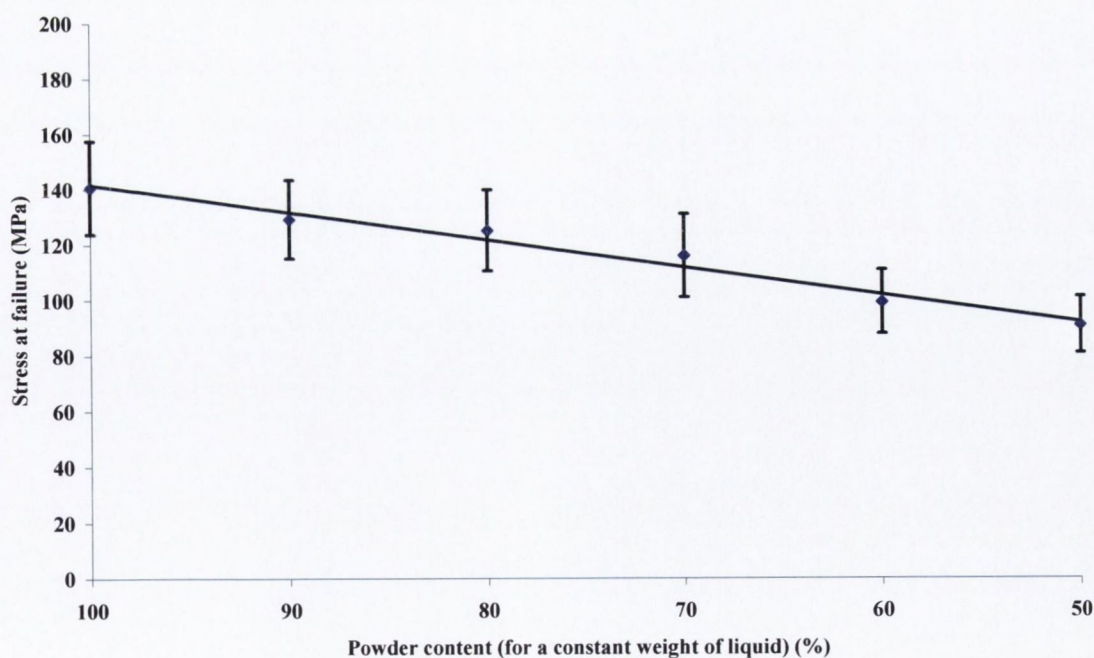


Figure 4.4.6 Variation of mean compressive fracture strength with decreasing powder content: ChemFlex.

Fitted line: $y = -9.79x + 151.35$ $r^2 = 0.597$ $p < 0.001$ $df = 203$

The regression line slopes, r^2 values, p values and degrees of freedom for the compressive fracture strength data are summarised in Table 4.4.1 with the individual regression analyses given in Appendices. Reducing the powder content from that recommended by the manufacturer (for a constant weight of liquid) had a significant influence on the compressive fracture strength data for all the GI restoratives investigated (Table 4.4.1).

Material	Slope	r^2	p value	df
Ketac Fil Plus	-7.27	0.496	< 0.001	203
Fuji II	-11.05	0.689	< 0.001	193
Chemfil Superior	-13.22	0.729	< 0.001	198
Ketac Molar Easymix	-14.62	0.666	< 0.001	202
Fuji IX	-8.04	0.478	< 0.001	199
ChemFlex	-9.79	0.597	< 0.001	203

Table 4.4.1 Comparison of regression line slopes, r^2 values, p values and degrees of freedom for the compressive fracture strength data for the GI restoratives prepared with reduced powder content.

The mean compressive fracture strength data for the individual GI restorative products prepared with powder contents reduced from that recommended by the manufacturers were analysed using a one-way ANOVA and a Tukey's post-hoc test. The results of the Tukey's post-hoc tests are shown in Table 4.4.2 with the individual one-way ANOVAs given in Appendices. A 10% reduction in powder content resulted in a significant decrease in the mean compressive fracture strength for Ketac Fil Plus, Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex compared with the respective control group, while a 20% reduction in powder content resulted in a significant decrease for Chemfil Superior (Table 4.4.2).

Material	P value				
	90	80	70	60	50
Ketac Fil Plus	0.050	< 0.001	< 0.001	< 0.001	< 0.001
Fuji II	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Chemfil Superior	0.773	0.001	< 0.001	< 0.001	< 0.001
Ketac Molar Easymix	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX	0.002	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex	0.016	< 0.001	< 0.001	< 0.001	< 0.001

Table 4.4.2 Tukey's post-hoc test results for the mean compressive fracture strength of the GI restorative control groups compared with groups prepared with reduced powder contents.

The plots of the mean elastic modulus versus powder content for Ketac Fil Plus, Fuji II, Chemfil Superior, Ketac Molar Easymix, Fuji IX and ChemFlex are shown in Figures 4.4.7 to 4.4.12, respectively.

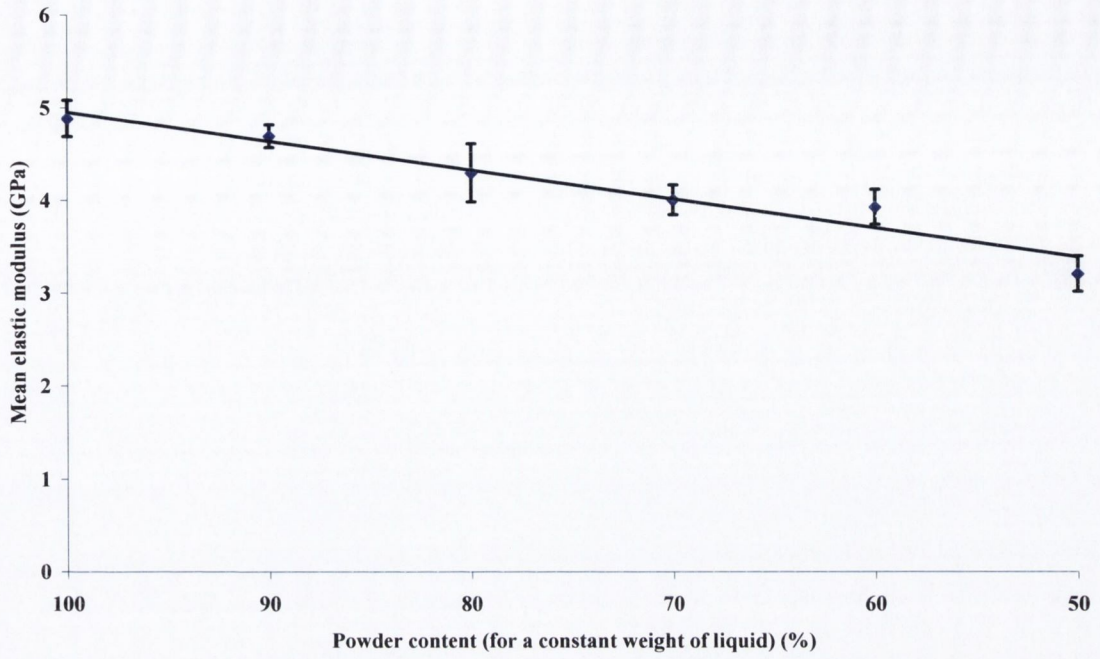


Figure 4.4.7 Variation of mean elastic modulus with decreasing powder content: Ketac Fil Plus.

Fitted line: $y = -0.311x + 5.262$ $r^2 = 0.833$ $p < 0.001$ $df = 203$

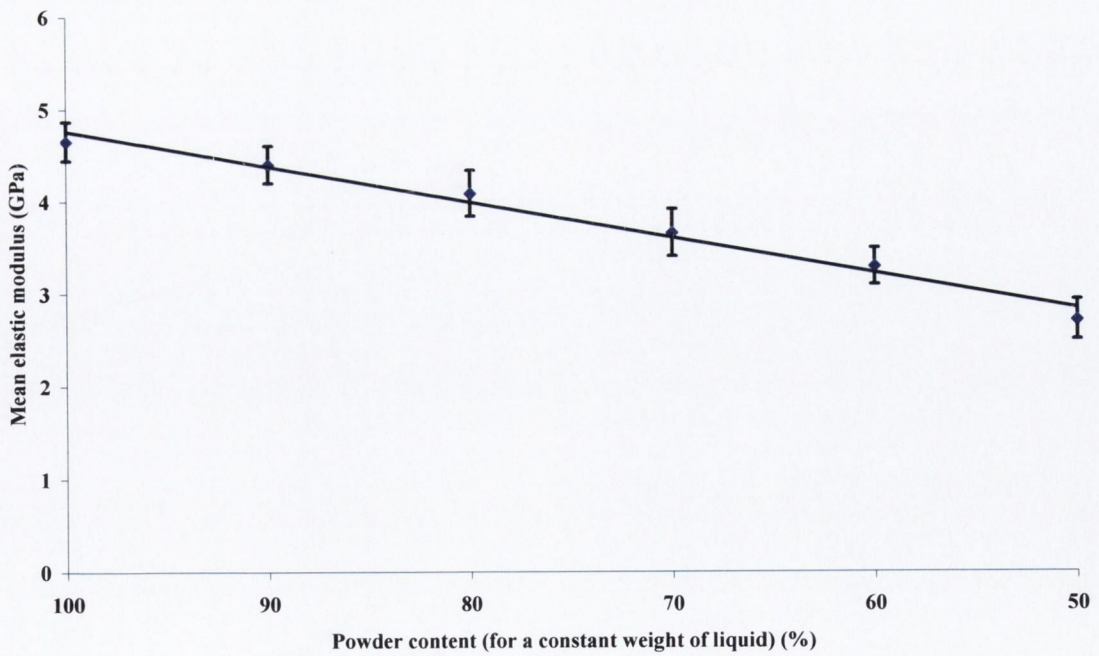


Figure 4.4.8 Variation of mean elastic modulus with decreasing powder content: Fuji II.

Fitted line: $y = -0.374x + 5.136$ $r^2 = 0.862$ $p < 0.001$ $df = 193$

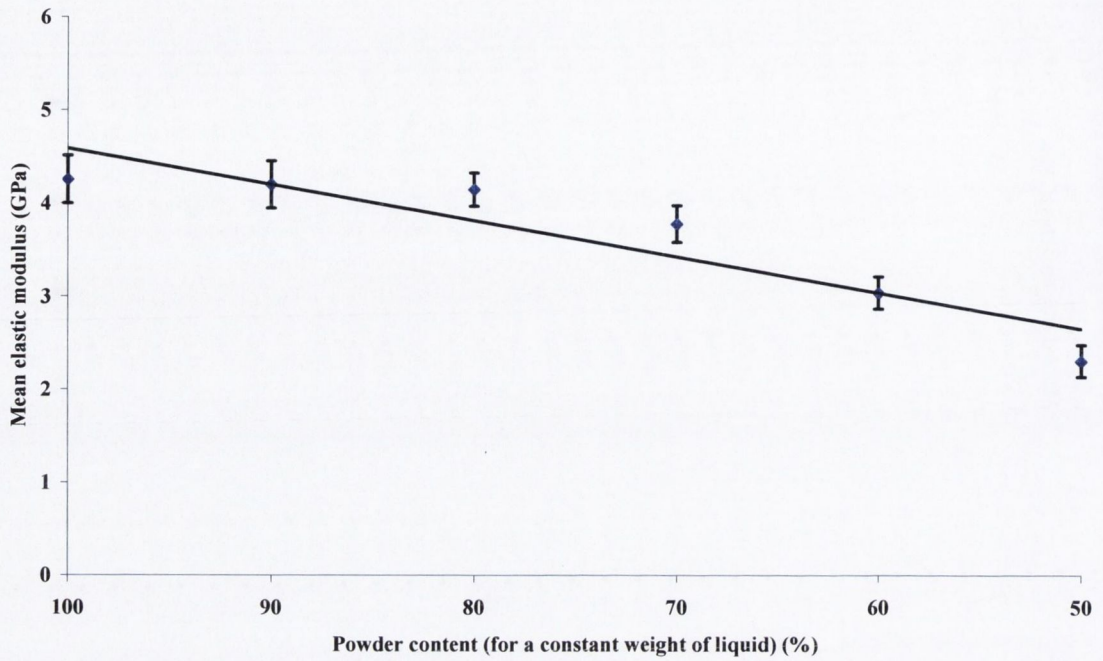


Figure 4.4.9 Variation of mean elastic modulus with decreasing powder content: Chemfil Superior.

Fitted line: $y = -0.384x + 4.968$ $r^2 = 0.781$ $p < 0.001$ $df = 198$

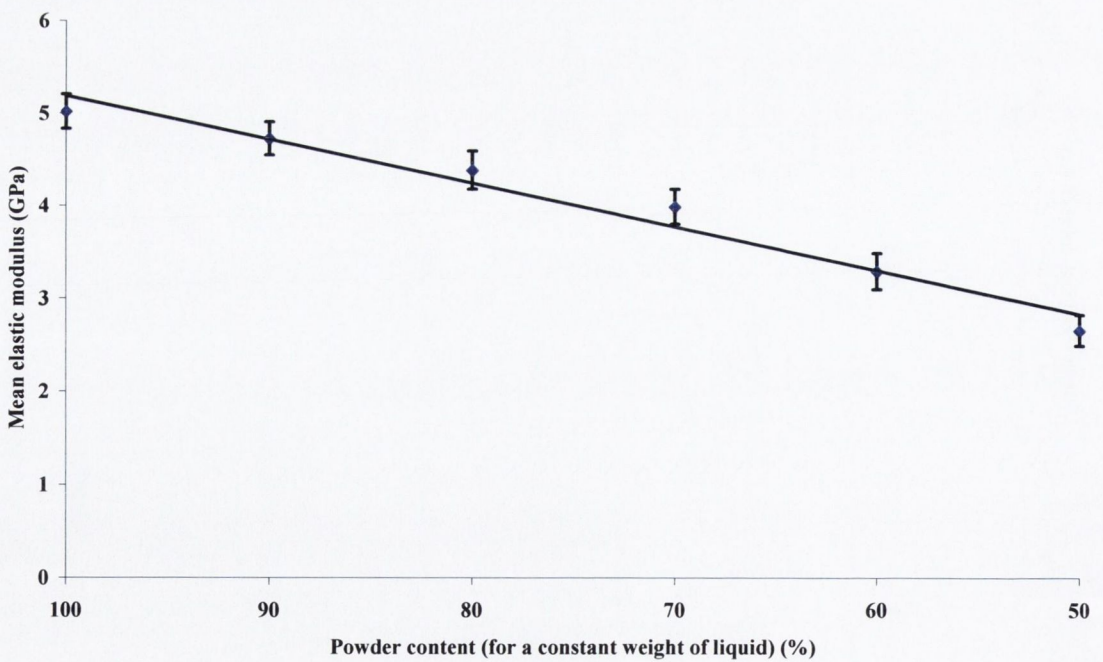


Figure 4.4.10 Variation of mean elastic modulus with decreasing powder content: Ketac Molar Easymix.

Fitted line: $y = -0.469x + 5.654$ $r^2 = 0.922$ $p < 0.001$ $df = 202$

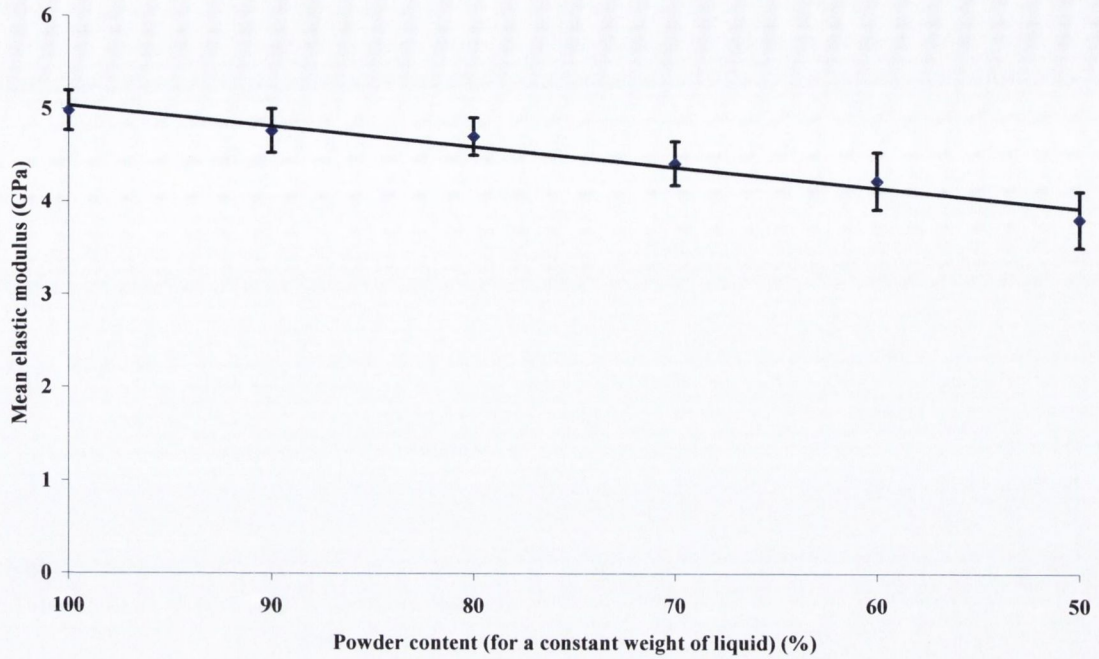


Figure 4.4.11 Variation of mean elastic modulus with decreasing powder content: Fuji IX.

Fitted line: $y = -0.220x + 5.263$ $r^2 = 0.668$ $p < 0.001$ $df = 199$

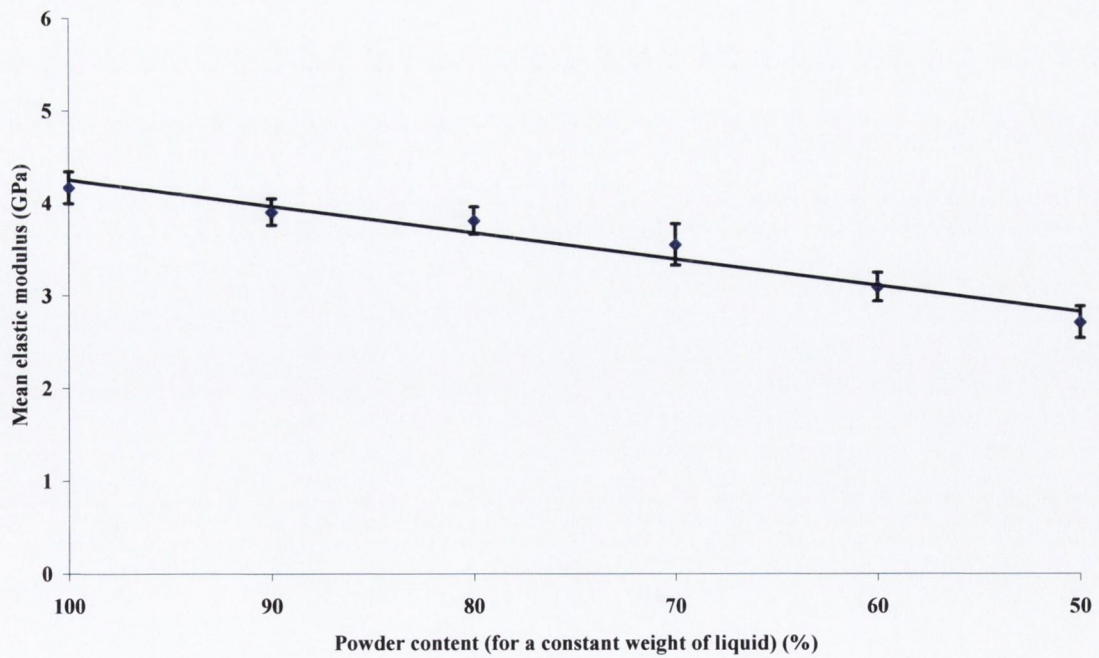


Figure 4.4.12 Variation of mean elastic modulus with decreasing powder content: ChemFlex.

Fitted line: $y = -0.282x + 4.536$ $r^2 = 0.854$ $p < 0.001$ $df = 203$

The results of the regression analyses for the elastic modulus data versus powder content are given in Table 4.4.3 and the individual regression analyses are available in Appendices. Reducing the powder content had a significant influence on the elastic modulus data for all the GI restoratives investigated.

Material	Slope	r²	p value	df
Ketac Fil Plus	-0.311	0.833	< 0.001	203
Fuji II	-0.374	0.862	< 0.001	193
Chemfil Superior	-0.384	0.781	< 0.001	198
Ketac Molar Easymix	-0.469	0.922	< 0.001	202
Fuji IX	-0.220	0.668	< 0.001	199
ChemFlex	-0.282	0.854	< 0.001	203

Table 4.4.3 Comparison of regression line slopes, r² values, p values and degrees of freedom for the elastic modulus data for the GI restoratives prepared with reduced powder content.

The mean elastic modulus for the GI restorative control groups were compared with the groups prepared with powder contents reduced from that recommended by the manufacturers using a one-way ANOVA and a Tukey's post-hoc test and the results are given in Table 4.4.4. Individual one-way ANOVAs are available in Appendices Reducing the powder content of Ketac Fil Plus, Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex by 10% resulted in a significant decrease in the mean elastic modulus compared with the control groups. There was a significant decrease in the mean elastic modulus for Chemfil Superior when the powder content was decreased by 20% (Table 4.4.4).

Material	P value				
	90	80	70	60	50
Ketac Fil Plus	0.003	< 0.001	< 0.001	< 0.001	< 0.001
Fuji II	0.006	< 0.001	< 0.001	< 0.001	< 0.001
Chemfil Superior	0.897	0.276	< 0.001	< 0.001	< 0.001
Ketac Molar Easymix	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX	0.005	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Table 4.4.4 Tukey's post-hoc test results for the mean elastic modulus of the GI restorative control groups compared with groups prepared with reduced powder contents.

The results of the *in vitro* wear resistance tests for the GI restoratives prepared with reduced powder contents are illustrated in Figures 4.4.13 to 4.4.18.

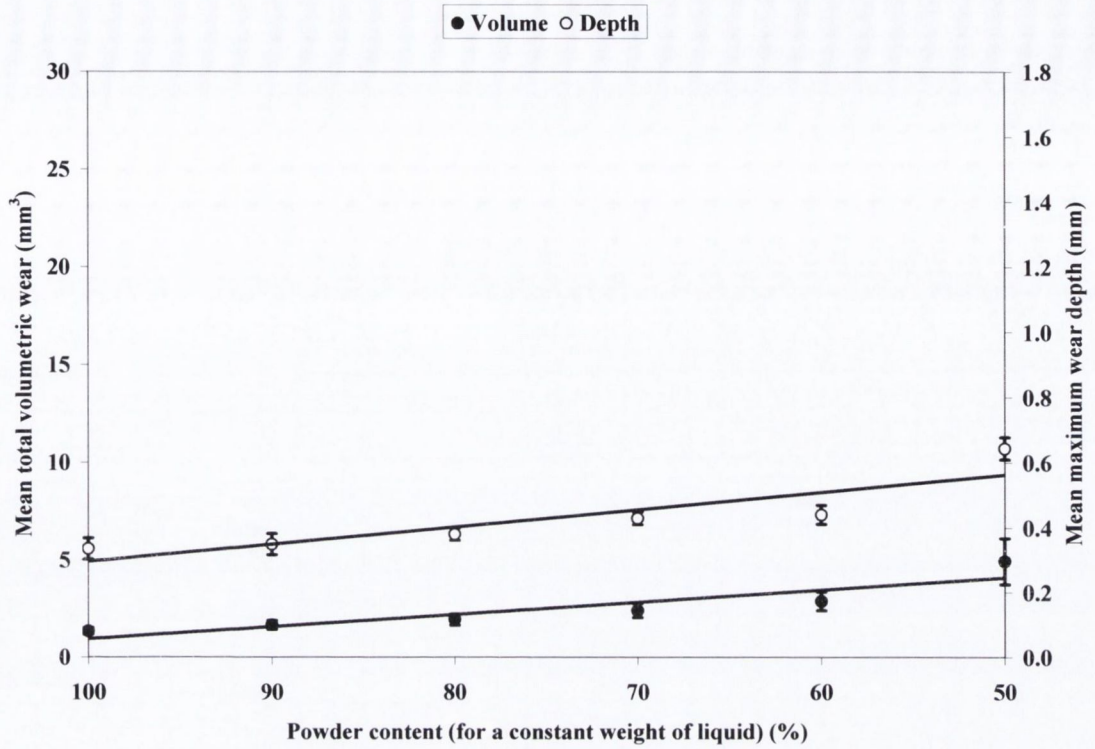


Figure 4.4.13 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: Ketac Fil Plus.

Fitted lines:

Volume: $y = 0.633x + 0.321$ $r^2 = 0.689$ $p < 0.001$ $df = 46$

Depth: $y = 0.053x + 0.242$ $r^2 = 0.731$ $p < 0.001$ $df = 46$

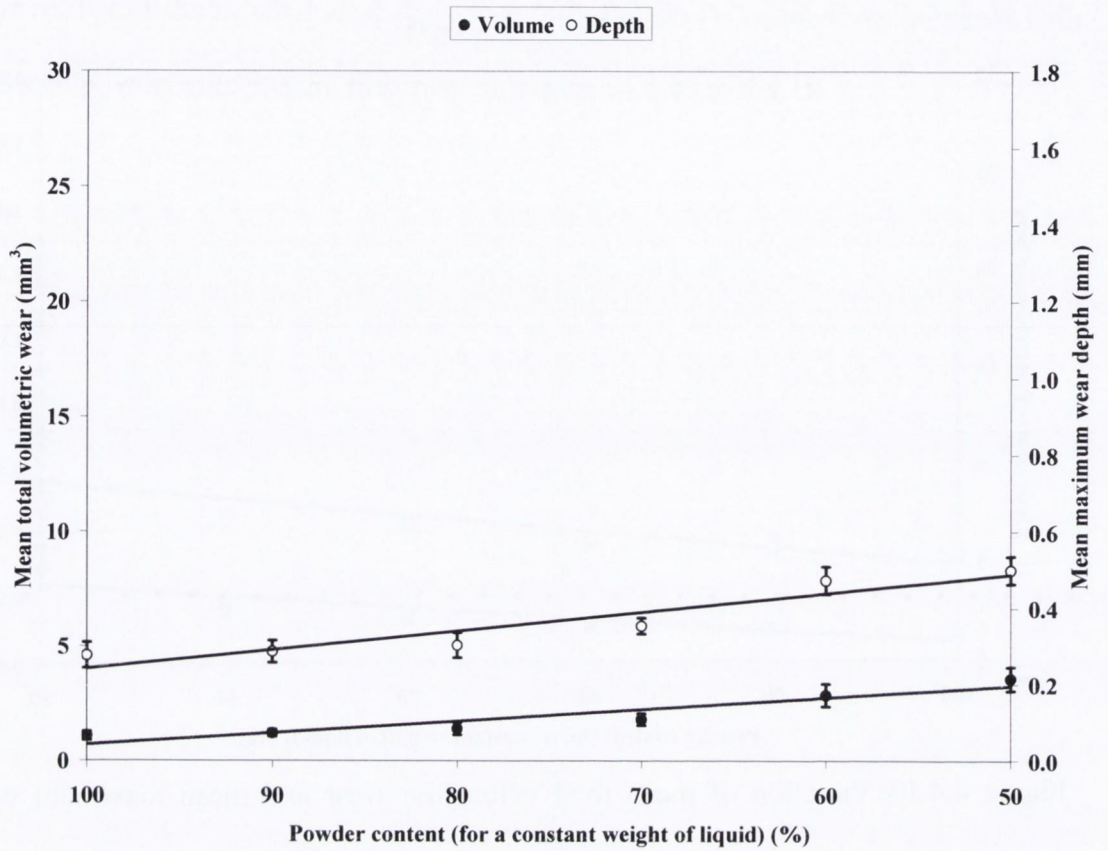


Figure 4.4.14 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: Fuji II.

Fitted lines:

Volume:	$y = 0.513x + 0.199$	$r^2 = 0.796$	$p < 0.001$	$df = 46$
Depth:	$y = 0.049x + 0.192$	$r^2 = 0.803$	$p < 0.001$	$df = 46$

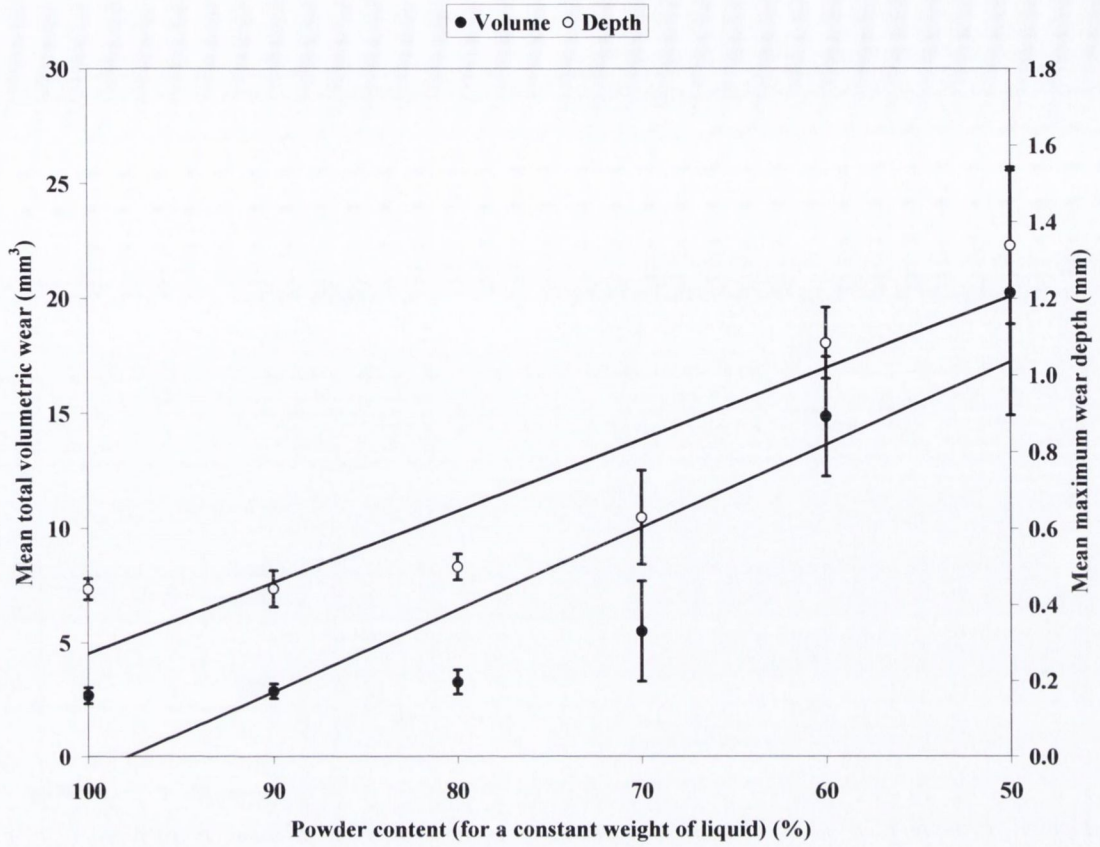


Figure 4.4.15 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: Chemfil Superior.

Fitted lines:

Volume: $y = 3.601x + 0.321$ $r^2 = 0.719$ $p < 0.001$ $df = 46$

Depth: $y = 0.187x + 0.085$ $r^2 = 0.777$ $p < 0.001$ $df = 46$

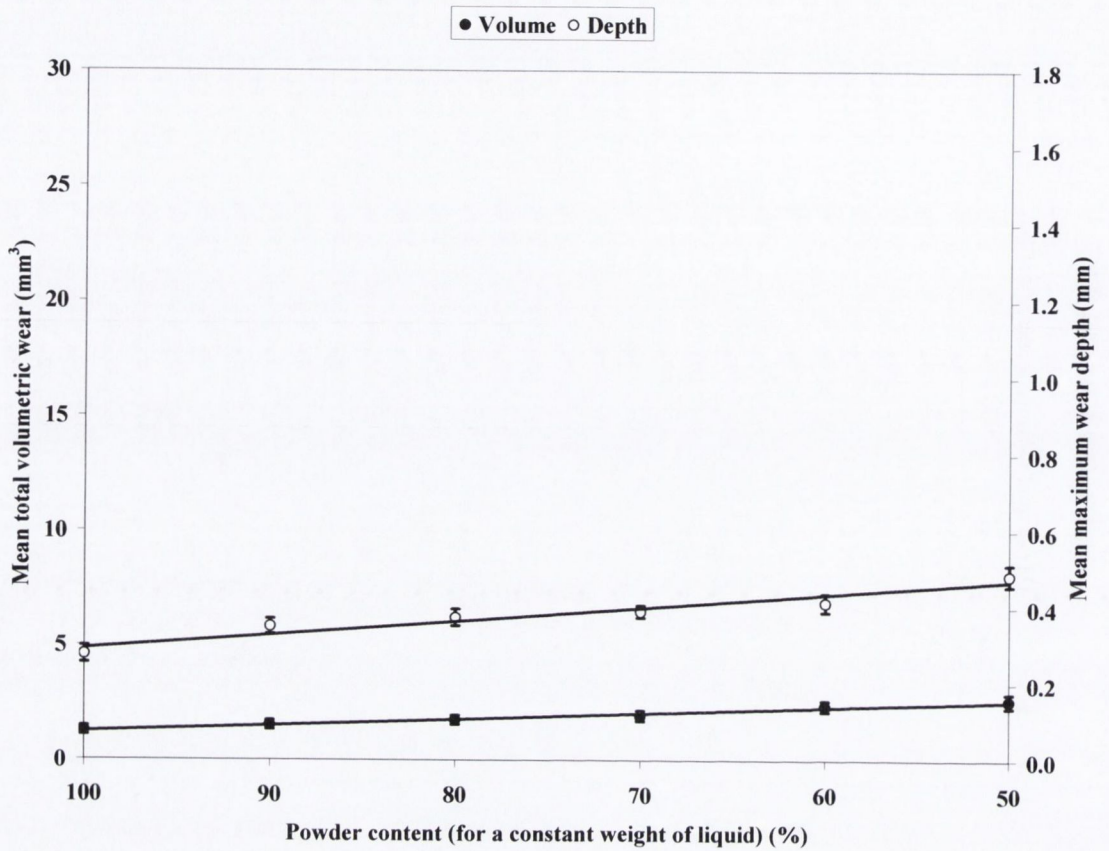


Figure 4.4.16 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: Ketac Molar Easymix.

Fitted lines:

Volume: $y = 0.490x + 0.546$ $r^2 = 0.308$ $p < 0.001$ $df = 46$

Depth: $y = 0.036x + 0.256$ $r^2 = 0.831$ $p < 0.001$ $df = 46$

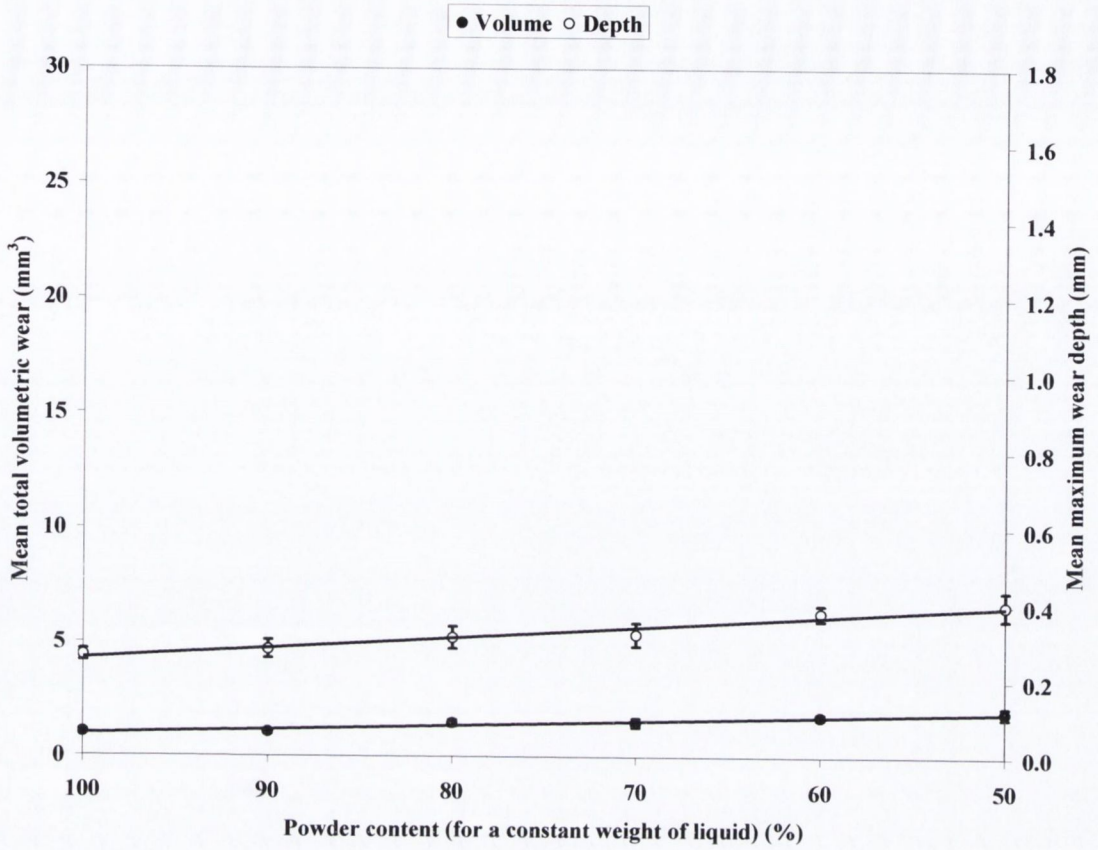


Figure 4.4.17 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: Fuji IX.

Fitted lines:

Volume: $y = 0.195x + 0.799$ $r^2 = 0.801$ $p < 0.001$ $df = 46$

Depth: $y = 0.028x + 0.231$ $r^2 = 0.753$ $p < 0.001$ $df = 46$

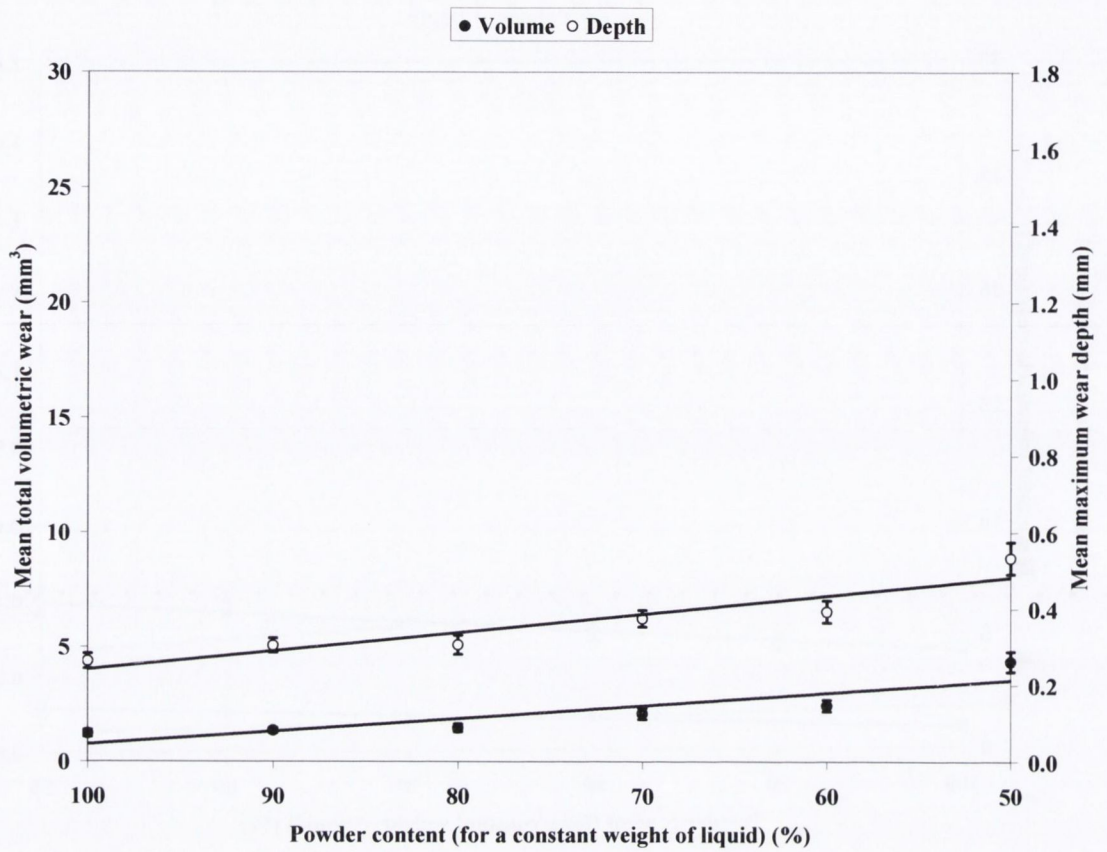


Figure 4.4.18 Variation of mean total volumetric wear and mean maximum wear depth with decreasing powder content: ChemFlex.

Fitted lines:

Volume: $y = 0.589x + 0.204$ $r^2 = 0.750$ $p < 0.001$ $df = 46$

Depth: $y = 0.048x + 0.194$ $r^2 = 0.803$ $p < 0.001$ $df = 46$

The results of the regression analyses for the total volumetric wear and maximum wear depth data are shown in Tables 4.4.5 and 4.4.6, respectively with the individual regression analyses shown in Appendices. The slopes of the regression lines were significant for the total volumetric wear data and maximum wear depth data for all the GI restoratives as the powder content was reduced.

Material	Slope	r²	p value	df
Ketac Fil Plus	0.633	0.689	< 0.001	46
Fuji II	0.513	0.796	< 0.001	46
Chemfil Superior	3.601	0.719	< 0.001	46
Ketac Molar Easymix	0.490	0.777	< 0.001	46
Fuji IX	0.195	0.801	< 0.001	46
ChemFlex	0.559	0.750	< 0.001	46

Table 4.4.5 Comparison of regression line slopes, r² values, p values and degrees of freedom for the total volumetric wear data for the GI restoratives prepared with reduced powder content.

Material	Slope	r²	p value	df
Ketac Fil Plus	0.053	0.731	< 0.001	46
Fuji II	0.049	0.803	< 0.001	46
Chemfil Superior	0.187	0.777	< 0.001	46
Ketac Molar Easymix	0.036	0.831	< 0.001	46
Fuji IX	0.028	0.753	< 0.001	46
ChemFlex	0.048	0.803	< 0.001	46

Table 4.4.6 Comparison of regression line slopes, r² values, p values and degrees of freedom for the maximum wear depth data for the GI restoratives prepared with reduced powder content.

Comparisons of the mean total volumetric wear and mean maximum wear depth data of the GI restorative control groups with the groups prepared with reduced powder contents were made using a one-way ANOVA and a Tukey's post-hoc test with the Tukey's post-hoc test results shown in Tables 4.4.7 and 4.4.8, respectively. There was a significant increase in the mean total volumetric wear compared with the control groups for Ketac Molar Easymix and Fuji IX when the powder content was reduced by 20%, for Ketac Fil Plus, Fuji II and ChemFlex when the powder content was reduced by 30% and for Chemfil Superior when the powder content was reduced by 40% (Table 4.4.7). Reducing the powder content of Ketac Molar Easymix by 10%, Ketac Fil Plus, Fuji IX and ChemFlex by 20% and Fuji II and Chemfil Superior by 30% resulted in a significant decrease in the mean maximum wear depth compared with the control groups as shown in Table 4.4.8.

Material	P value				
	90	80	70	60	50
Ketac Fil Plus	0.865	0.317	0.007	< 0.001	< 0.001
Fuji II	0.979	0.438	0.002	< 0.001	< 0.001
Chemfil Superior	1.000	0.997	0.271	< 0.001	< 0.001
Ketac Molar Easymix	0.249	0.002	< 0.001	< 0.001	< 0.001
Fuji IX	0.997	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex	0.903	0.429	< 0.001	< 0.001	< 0.001

Table 4.4.7 Tukey's post-hoc test results for the mean total volumetric wear of the GI restorative control groups compared with groups prepared with reduced powder contents.

Material	P value				
	90	80	70	60	50
Ketac Fil Plus	0.933	0.038	< 0.001	< 0.001	< 0.001
Fuji II	0.990	0.544	< 0.001	< 0.001	< 0.001
Chemfil Superior	1.000	0.891	0.014	< 0.001	< 0.001
Ketac Molar Easymix	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX	0.805	0.011	< 0.001	< 0.001	< 0.001
ChemFlex	0.058	0.034	< 0.001	< 0.001	< 0.001

Table 4.4.8 Tukey's post-hoc test results for the mean maximum wear depth of the GI restorative control groups compared with groups prepared with reduced powder contents.

4.4.3 Preliminary Remarks

Reducing the powder content of the hand-mixed GI restoratives from that recommended by the manufacturers resulted in a steady decrease in the mean compressive fracture strength and mean elastic modulus with a concomitant steady increase in the mean total volumetric wear and mean maximum wear depth.

4.5 Influence of the Method of Mixing

The purpose of this experiment was to investigate the influence that the method of mixing (either mechanical mixing using a Capmix or Rotomix or hand-mixing) has on the compressive fracture strength, elastic modulus and *in vitro* wear resistance of GI restoratives.

4.5.1 Materials and Methods

The encapsulated GI restoratives investigated (Table 3.2.2) were mechanically mixed using either a Capmix or Rotomix following the procedure outlined in Section 3.2.2. The compressive fracture strength, elastic modulus and *in vitro* wear resistance of the encapsulated GI restoratives were determined using the procedures outlined previously in Sections 3.3.1 and 3.3.2, respectively.

4.5.2 Results

The results of the mechanical tests for the encapsulated GI restoratives are summarised in Table 4.5.1. A comparison of the mean compressive fracture strength, mean elastic modulus, mean total volumetric wear and mean maximum wear depth for the encapsulated GI restoratives mechanically mixed using either the Capmix or Rotomix using the two-sample independent Student's t-test is given in Table 4.5.2. Mechanical mixing of Fuji IX Fast Capsule and ChemFlex in Caps using the Rotomix resulted in significantly increased mean compressive fracture strength ($p = 0.034$ and 0.011 , respectively) and mean elastic modulus ($p < 0.001$ and < 0.001 , respectively) compared with mechanical mixing in the Capmix (Table 4.5.2). However, there were no significant differences in the mean compressive fracture strength and mean elastic modulus for Ketac Fil Plus Aplicap, Fuji II Capsule and Ketac Molar Aplicap

following mechanical mixing in either the Capmix or Rotomix. There were no significant differences in the mean total volumetric wear and mean maximum wear depth for all the encapsulated GI restoratives (Table 4.5.2).

		CFS (MPa)	EM (GPa)	Volume (mm³)	Depth (mm)
Ketac Fil Plus Aplicap	C	124 (16)	4.446 (0.425)	1.130 (0.148)	0.344 (0.033)
	R	125 (16)	4.572 (0.368)	1.102 (0.142)	0.329 (0.023)
Fuji II Capsule	C	127 (14)	4.226 (0.245)	1.077 (0.165)	0.279 (0.022)
	R	130 (16)	4.264 (0.212)	1.045 (0.129)	0.281 (0.029)
Ketac Molar Aplicap	C	150 (17)	4.964 (0.186)	1.058 (0.121)	0.280 (0.017)
	R	150 (21)	5.029 (0.222)	1.006 (0.106)	0.280 (0.013)
Fuji IX Fast Capsule	C	136 (17)	4.751 (0.190)	0.920 (0.087)	0.263 (0.015)
	R	144 (13)	4.961 (0.124)	0.904 (0.074)	0.257 (0.012)
ChemFlex in Caps	C	131 (16)	3.989 (0.181)	1.051 (0.142)	0.280 (0.026)
	R	140 (11)	4.287 (0.118)	1.031 (0.134)	0.277 (0.022)

Table 4.5.1 A summary of mechanical property data of the encapsulated GI restoratives mechanically mixed in either the Capmix (C) or Rotomix (R). CFS: Mean compressive fracture strength, EM: Mean elastic modulus, Volume: Mean total volumetric wear, Depth: Mean maximum wear depth.

	CFS	EM	Volume	Depth
Ketac Fil Plus Aplicap	0.778	0.216	0.700	0.295
Fuji II Capsule	0.453	0.314	0.537	0.841
Ketac Molar Aplicap	0.902	0.238	0.375	0.948
Fuji IX Fast Capsule	0.034	< 0.001	0.687	0.382
ChemFlex in Caps	0.011	< 0.001	0.775	0.848

Table 4.5.2 Two-sample independent Student's t-test results for the mean compressive fracture strength, mean elastic modulus, mean total volumetric wear and mean maximum wear depth for the encapsulated GI restoratives mechanically mixed using either the Capmix or Rotomix.

Statistical analyses (Tukey's post-hoc test) are shown for the mean compressive fracture strength (Table 4.5.3), mean elastic modulus (Table 4.5.4), mean total volumetric wear (Table 4.5.5) and mean maximum wear depth (Table 4.5.6) for the encapsulated GI restoratives compared with their hand-mixed equivalents prepared with powder contents reduced (in 10% increments) from 100 to 50% of that recommended by the manufacturers. Individual one-way ANOVAs are available in Appendices. Reducing the powder content of Ketac Fil Plus to 80%, Fuji II to 80%, Ketac Molar Easymix to 80%, Fuji IX to 60% and ChemFlex to 80% resulted in a significant decrease in the mean compressive fracture strength compared with their encapsulated equivalents (Table 4.5.3). The mean elastic modulus of the encapsulated GI restoratives Ketac Fil Plus Aplicap and Fuji II Capsule were significantly increased compared with their hand-mixed equivalents (Table 4.5.4). Reducing the powder content of Ketac Molar Easymix to 90%, Fuji IX to 80% and ChemFlex to 90% resulted in a significant decrease in the mean elastic modulus compared with the encapsulated equivalents as shown in Table 4.5.4.

Material	P value					
	100	90	80	70	60	50
Ketac Fil Plus Aplicap	0.427	0.934	0.040	< 0.001	< 0.001	< 0.001
Fuji II Capsule	< 0.001	0.945	0.040	< 0.001	< 0.001	< 0.001
Ketac Molar Aplicap	0.456	0.067	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX Fast Capsule	< 0.001	0.054	0.228	1.000	0.009	< 0.001
ChemFlex in Caps	0.633	0.427	0.032	< 0.001	< 0.001	< 0.001

Table 4.5.3 Tukey's post-hoc test results for the mean compressive fracture strength data of the encapsulated GI restoratives compared with their hand-mixed equivalents.

Material	P value					
	100	90	80	70	60	50
Ketac Fil Plus Aplicap	< 0.001	0.025	0.004	< 0.001	< 0.001	< 0.001
Fuji II Capsule	< 0.001	0.005	0.021	< 0.001	< 0.001	< 0.001
Ketac Molar Aplicap	0.998	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX Fast Capsule	0.183	0.633	0.086	< 0.001	< 0.001	< 0.001
ChemFlex in Caps	0.982	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

Table 4.5.4 Tukey's post-hoc test results for the mean elastic modulus data of the encapsulated GI restoratives compared with their hand-mixed equivalents.

The mean total volumetric wear was significantly increased for Ketac Fil Plus and Fuji II compared with their encapsulated equivalents (Table 4.5.5). When the powder content of Ketac Molar Easymix was reduced to 90%, Fuji IX to 80% and ChemFlex to 70% of that recommended by the manufacturers a significant increase in the mean total volumetric wear compared with the encapsulated equivalents. Reducing the powder content of Ketac Molar Easymix and ChemFlex to 90%, Fuji IX to 80% and Ketac Fil Plus and Fuji II to 70% of that recommended resulted in a significant increase in the mean maximum wear depth compared with their encapsulated equivalents (Table 4.5.6).

Material	P value					
	100	90	80	70	60	50
Ketac Fil Plus Aplicap	0.001	0.007	< 0.001	< 0.001	< 0.001	< 0.001
Fuji II Capsule	0.004	0.003	< 0.001	< 0.001	< 0.001	< 0.001
Ketac Molar Aplicap	0.990	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX Fast Capsule	0.996	0.287	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex in Caps	0.890	0.290	0.210	< 0.001	< 0.001	< 0.001

Table 4.5.5 Tukey's post-hoc test results for the mean total volumetric wear data of the encapsulated GI restoratives compared with their hand-mixed equivalents.

Material	P value					
	100	90	80	70	60	50
Ketac Fil Plus Aplicap	1.000	0.993	0.318	< 0.001	< 0.001	< 0.001
Fuji II Capsule	0.626	0.497	0.262	< 0.001	< 0.001	< 0.001
Ketac Molar Aplicap	0.134	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Fuji IX Fast Capsule	0.368	0.115	< 0.001	< 0.001	< 0.001	< 0.001
ChemFlex in Caps	0.474	0.030	0.001	< 0.001	< 0.001	< 0.001

Table 4.5.6 Tukey's post-hoc test results of the mean maximum wear depth data of the encapsulated GI restoratives compared with their hand-mixed equivalents.

4.5.3 Preliminary Remarks

The compressive fracture strength and elastic modulus of some of the encapsulated products investigated were influenced by the method of mechanical mixing, however, the *in vitro* wear resistance was not. In general, encapsulated GI restoratives provide significantly increased compressive fracture strength and elastic modulus and significantly decreased total volumetric wear and maximum wear depth compared with their hand-mixed equivalents when powder contents of < 70% are employed, however, the extent of the increase is product dependant.

5 Discussion

5.1 Statistical Approach

The compressive fracture strength, elastic modulus, total volumetric wear and maximum wear depth data groups were tested for normality using the Shapiro-Wilk test. The data were normally distributed with the exception of three of the 92 compressive fracture strength data groups, three of the 56 total volumetric wear data groups and one of the 56 maximum wear depth data groups. Therefore a significant departure from normality was not detected in any of the specimen groups, beyond sampling variation and the non-normally distributed data are likely due to randomness. As a result, no transformation of the data groups was required and the group means could be analysed using regression analysis.

The linear regression analyses of the compressive fracture strength and elastic modulus data versus the time of day of specimen fabrication for the control groups showed no effect of the time of day. A significant effect was evident when a quadratic regression analysis was conducted which showed a decrease in the compressive fracture strength and elastic modulus values achieved at eleven o'clock. However, given that the variation in the compressive fracture strength and elastic modulus data throughout the day was less than 10%, it was likely due to randomness. The compressive fracture strength and elastic modulus data pooled from the other sections behaved similarly with regard to time of day, where the variability was less than 10%. As a result the variation of the compressive fracture strength and elastic modulus data over the course of the day was considered unlikely to affect subsequent analysis.

Some of the pooled compressive fracture strength and the elastic modulus data from the different sections in this thesis were significantly influenced by the cylindrical specimen mould position. However, given that the variability within the data sets was always less than 10%, it is likely that the significant effects were due to the randomness in the data. Also, the entire mould was not always used as some groups under investigation produced more or less GI restorative required to fill twelve holes. The result was that some mould positions had less data points than others, particularly mould positions eleven and twelve, which may have skewed the data and resulted in the significant effects shown. Therefore, it was unlikely that the specimen mould position would affect the compressive fracture strength and elastic modulus data and as a result was not accounted for when analysing the data in the present investigation.

5.2 Equipment and Testing Methodologies Employed

5.2.1 Compressive Fracture Strength and Elastic Modulus

The performance of the anterior and posterior GI restoratives investigated was assessed using the compressive fracture strength testing methodology outlined in ISO 9917-1 : 2003. The term “compressive fracture strength” may be misleading as fracture occurs as a result of a combination of tensile and shear forces, therefore, the test provides information on the “bearing capacity” of the GI restoratives investigated (Darvell, 1990). In 1976, Yettram *et al.* (1976) showed using two-dimensional finite element stress analysis that compressive stresses were evident in a second premolar tooth model when subjected to a masticatory load. As a result, White and Yu (1993) suggested that the compressive fracture strength was a critical indicator for clinical success, as a high compressive fracture strength was necessary to tolerate the masticatory forces routinely encountered in the posterior region of the mouth.

Furthermore, the compressive fracture strength is the only strength test specified in ISO 9917-1 : 2003 and is seen as the “gold standard” by GI restorative manufacturers who choose to report it over three-point and bi-axial flexure strengths. Brittle materials such as GI restoratives are stronger in compression than in tension (Ashby and Jones, 1998) and as a result, compressive fracture strength testing provides a larger value than three-point or bi-axial flexure strength testing. The larger value produced in compressive fracture strength testing may provide an explanation for the predominant use of compressive fracture strength by GI restorative manufacturers.

In 1990, an investigation of test-house variability (McCabe *et al.*, 1990) using the compressive fracture strength testing method outlined in ISO DP 9917 (Harmonization of Test Methods for Dental Cements) reported differences in the compressive fracture strength of three groups of ten GI cement (Ketac Fil) specimens (6 mm height and 4 mm diameter), prepared at each of three different test centres. The protocol of the study by McCabe *et al.* (1990) involved the investigation of three groups of ten specimens, however, the pass fail criteria employed was markedly different from that specified in ISO DP 9917. The compressive fracture strength test outlined in ISO DP 9917 required that five cylindrical specimens were prepared and tested. If four of these specimens resulted in a compressive fracture strength ≥ 130 MPa the material passed the test. However, if only three of the specimens tested resulted in a compressive fracture strength ≥ 130 MPa, a further ten specimens had to be prepared and tested. Out of the fifteen specimens at least eight needed to result in compressive fracture strengths ≥ 130 MPa for the material to pass the test.

In one of the test centres in the study by McCabe *et al.* (1990), the first batch of ten specimens produced a mean compressive fracture strength and standard deviation of 114 ± 19 MPa, with nine of the specimens resulting in compressive fracture strengths of < 130 MPa. The second batch of ten specimens resulted in a mean compressive fracture strength of 112 MPa and a standard deviation of 15 MPa with nine specimens producing compressive fracture strengths < 130 MPa. For the third batch of specimens, the mean compressive fracture strength and standard deviation was 117 ± 15 MPa, however, nine of specimens had compressive fracture strengths < 130 MPa. The mean compressive fracture strength and associated standard deviation for the 30 specimens from the first test centre was 114 ± 16 MPa. Following the ISO DP 9917 criteria stringently, where the specimens from the first test centre were divided into six batches of five specimens, a clear fail was still evident.

For the second test centre investigated, the first batch of ten specimens resulted in a mean compressive fracture strength and standard deviation of 140 ± 27 MPa, however, three specimens had compressive fracture strengths < 130 MPa. The second batch of specimens produced a mean compressive fracture strength of 136 MPa and a standard deviation of 15 MPa with three specimens producing a compressive fracture strength < 130 MPa. The mean compressive fracture strength and standard deviation of the third batch of specimens was reported as 134 ± 16 MPa with a total of five of the ten specimens resulting in compressive fracture strengths < 130 MPa. The 30 specimens from the second test centre produced a mean compressive fracture strength and standard deviation of 137 ± 19 MPa. When the 30 specimens were divided into six batches of five specimens, two of the batches passed while four failed, indicating that the results from the second test centre were inconclusive and a borderline

between pass and fail using the ISO DP 9917 criteria was evident (McCabe *et al.*, 1990).

The third test centre examined, produced a mean compressive fracture strength and standard deviation for the first batch of ten specimens of 170 ± 28 MPa with all specimens having a compressive fracture strength > 130 MPa. The second batch of specimens resulted in a mean compressive fracture strength and standard deviation of 152 ± 23 MPa and one specimen had a compressive fracture strength < 130 MPa. For the third batch of ten specimens, the mean compressive fracture strength and standard deviation was 160 ± 33 MPa and one specimen had a compressive fracture strength < 130 MPa. The mean compressive fracture strength and standard deviation for the 30 specimens from the third test centre was 161 ± 28 MPa. Splitting the 30 specimens into six groups of five specimens and stringently following the criteria identified a clear pass for the third test centre.

The study by McCabe *et al.* (1990) identified that inter-operator variability was considerable, however, the results also showed that individual operator variability was evident as emphasised by the differences in mean compressive fracture strength between batches for individual operators. The inconclusive results achieved by the second test centre where only two out of the six batches passed shows that using the criteria outlined in ISO DP 9917 may therefore provide inaccurate results. The authors concluded that the compressive fracture strength testing methodology was inappropriate for inclusion in ISO DP 9917 due to the variation in test results achieved. As a result, the authors suggested an alternative means of evaluating dental cements should be identified. However, nearly 20 years later compressive fracture

strength is still the only strength test specified in ISO 9917-1 : 2003, the most recent specification for dental acid-base cements. The minimum compressive fracture strength for the criteria was reduced from 130 to 100 MPa for ISO 9917-1 : 2003, which may be due to an inability of operators to consistently achieve compressive fracture strengths of 130 MPa.

An examination of the dental literature regarding the hand-mixed GI restoratives investigated reinforces the perceived wisdom of McCabe *et al.* (1990) that little correlation exists for the 24 h mean compressive fracture strengths reported by independent researchers in different test centres. The mean compressive fracture strengths and standard deviations reported in the dental literature for these six GI restoratives under investigation here are shown in Table 5.2.1.

Material	Study	Mean compressive fracture strength (MPa)
Ketac Fil Plus	Fleming and Zala, 2003	62 ± 15
	Pereira <i>et al.</i> , 2002	146 ± 12
	Present study	130 ± 15
Fuji II	Yli-Urpo <i>et al.</i> , 2005	120 ± 20
	Higgs <i>et al.</i> , 2001a	153 ± 9
	Wu <i>et al.</i> , 2003	191 ± 19
	Xie <i>et al.</i> , 2000	202 ± 10
	Present study	142 ± 15
Chemfil Superior	Fleming <i>et al.</i> , 2003	102 ± 23
	Musa <i>et al.</i> , 1996	143 ± 18
	McKenzie <i>et al.</i> , 2003	177 ± 15
	Present study	132 ± 19
Ketac Molar*	Camilleri <i>et al.</i> , 2008	48 ± 16
	Pereira <i>et al.</i> , 2002	149 ± 15
	Deb <i>et al.</i> , 2003	178 ± 21
	Nomoto and McCabe, 2001	219 ± 24
	Xie <i>et al.</i> , 2000	301 ± 10
	Present study	157 ± 24
Fuji IX	Fleming and Zala, 2003	68 ± 16
	Mazzaoui <i>et al.</i> , 2003	138 ± 21
	Bresciani <i>et al.</i> , 2004	148 ± 18
	Deb <i>et al.</i> , 2003	148 ± 26
	Pereira <i>et al.</i> , 2002	152 ± 14
	Xu and Burgess, 2003	168 ± 14
	Higgs <i>et al.</i> , 2001a	211 ± 28
	Present study	163 ± 21
ChemFlex	Fleming and Zala, 2003	69 ± 17
	McKenzie <i>et al.</i> , 2003	198 ± 20
	Present study	141 ± 17

Table 5.2.1 Comparison of the mean compressive fracture strengths (\pm standard deviation) reported in the dental literature for the six GI restoratives investigated here. *No mean compressive fracture strength data was available in the dental literature for Ketac Molar Easymix; the values reported are for its predecessor Ketac Molar with the exception of the present study.

It is clear from the information available in the dental literature that variations in the mean compressive fracture strength exist amongst different test centres. However, in these studies cylindrical specimen dimensions of 6 mm height and 3 mm diameter (Deb *et al.*, 2003), 6 mm height and 4 mm diameter (Musa *et al.*, 1996; Higgs *et al.*, 2001a; Nomoto and McCabe, 2001; Fleming *et al.*, 2003, Fleming and Zala, 2003; Mazzaoui *et al.*, 2003; McKenzie *et al.*, 2003; Yli-Urpo *et al.*, 2005), 8 mm height and 4 mm diameter (Xie *et al.*, 2000; Wu *et al.*, 2003), 9 mm height and 4 mm diameter (Xu and Burgess, 2003) and 12 mm height and 6 mm diameter (Pereira *et al.*, 2002; Bresciani *et al.*, 2004; Camilleri *et al.*, 2008) were employed. It must be remembered that although compressive fracture strength testing is specified in ISO 9917-1 : 2003 for GI restoratives, compressive fracture strength is not an intrinsic material property (Kelly, 1995; Darvell, 1990; Ashby and Jones, 1998). The height and diameter of the cylindrical specimen influences the load to failure and therefore the mean compressive fracture strength recorded (Darvell, 1990, 2002). In theory, the larger the specimen volume the greater the likelihood of introducing a crack initiating defect and therefore one would expect a lower mean compressive fracture strength (Ritter, 1995; Ashby and Jones, 1998). However, when the dental literature for Fuji II was assessed, mean compressive fracture strengths and associated standard deviations of 191 ± 19 MPa (Wu *et al.*, 2003) and 202 ± 10 MPa (Xie *et al.*, 2000) were reported when specimen dimensions of 8 mm height and 4 mm diameter were used compared with 120 ± 20 MPa (Yli-Urpo *et al.*, 2005) and 153 ± 9 MPa (Higgs *et al.*, 2001a) when the specimen dimensions were 6 mm height and 4 mm diameter, thereby not following the prediction of Ritter (1995) and Ashby and Jones (1998) and re-emphasising the difficulties associated with the compressive fracture strength testing methodology.

Variations in the mean compressive fracture strengths were shown when compressive loading rates of 0.5 mm/min (McKenzie *et al.*, 2003), 0.75 mm/min (Nomoto and McCabe, 2001) and 1.0 mm/min (Musa *et al.*, 1996; Xie *et al.*, 2000; Higgs *et al.*, 2001a; Pereira *et al.*, 2002; Deb *et al.*, 2003; Fleming *et al.*, 2003, Fleming and Zala, 2003; Mazzaoui *et al.*, 2003; Wu *et al.*, 2003; Xu and Burgess, 2003; Bresciani *et al.*, 2004; Yli-Urpo *et al.*, 2005; Camilleri *et al.*, 2008) were used. Brittle materials such as GI restoratives are sensitive to the rate of compressive loading, demonstrating an increased compressive fracture strength with increased testing speed (Kingery *et al.*, 1976; Higgs *et al.*, 2001a) as there is less time for slow crack growth to occur (Li and White, 1999). Again, this phenomenon was not emphasised in the dental literature as the mean compressive fracture strength and associated standard deviation of Chemfil Superior was reported as 177 ± 15 MPa when the loading rate was 0.5 mm/min (McKenzie *et al.*, 2003) and 102 ± 23 MPa when the loading rate was 1.0 mm/min (Fleming *et al.*, 2003).

The surface finish of the mould can influence the test results also, as a highly polished mould would be expected to produce specimens with a better surface finish than a tarnished mould (McCabe *et al.*, 1990). A poor specimen surface finish would be expected to result in an increased surface roughness and as a result an increased number of defects (which may not be visible to the naked eye) on the specimen surface which could lead to stress concentrations when the specimen is stressed under loading (Mitsuhashi *et al.*, 2003) and an underestimation of the 'true' mean compressive fracture strength.

It is also essential that uniform contact exists between the cylindrical specimen ends and the platens of the testing apparatus, therefore, the specimen ends must be flat and parallel to prevent localised stress concentrations manifested as a more complicated stress distribution in the test cylinder during compressive testing and possibly premature failure (Lloyd and Mitchell, 1984). In an attempt to accommodate non-parallel specimen ends, padding has been used, where a layer of material is placed between the test cylinder and the platens of the testing apparatus. However, the mechanical properties of the padding material also affects the compressive fracture strength determined (Darvell, 1990).

The combination of the variation in specimen dimensions (Ritter, 1995; Ashby and Jones, 1998), rate of compressive loading (Kingery *et al.*, 1976; Li and White, 1999; Higgs *et al.*, 2001a), surface finish of the split-mould (McCabe *et al.*, 1990), unparallel specimen ends (Lloyd and Mitchell, 1984) and the use of a padding material (Darvell, 1990) can all contribute to the variation in the compressive fracture strengths shown in the dental literature for the same materials tested in different test centres.

As reported previously, the quantity of powder and liquid of hand-mixed GI restoratives dispensed using a scoop and dropper bottle system can vary markedly from that recommended by the manufacturers (Wong and Bryant, 1985; Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a). The volume of powder dispensed can vary due to the powder packing density achieved on filling the scoop (Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2003). Dropper bottles cannot be relied upon to dispense calibrated volumes of liquid (Eames

et al., 1977), as the angle and pressure at which the bottle is held will influence the volume of liquid dispensed (Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2003; Mount, 2005). In the present investigation, the powder and liquid constituents of the hand-mixed GI restoratives were weighed using a balance with a resolution of 0.001 g prior to manipulation. The method of dispensing the powder and liquid constituents was not stated in a considerable number of the studies highlighted (Musa *et al.*, 1996; Pereira *et al.*, 2002; Wu *et al.*, 2003; McKenzie *et al.*, 2003; Bresciani *et al.*, 2004; Camilleri *et al.*, 2008) which may further explain the variations in the mean compressive fracture strength reported in the dental literature for the GI restoratives investigated here.

Furthermore, operator skill may explain the variations in the mean compressive fracture strengths reported in the dental literature (Wasson and Nicholson, 1994). In one test centre with the same testing protocol (specimen dimensions (6 mm height and 4 mm diameter), rate of compressive loading (1.0 mm/min), PTFE split-mould (surface finish), parallelism of specimen ends and the use of a padding material) being used by three different operators valuable insights are provided with considerable variations in the mean compressive fracture strengths reported. Mean compressive fracture strengths and standard deviations of 62 ± 15 MPa (Fleming and Zala, 2003) and 132 ± 19 MPa (present study) were reported for Ketac Fil Plus while 102 ± 23 MPa (Fleming *et al.*, 2003) and 130 ± 15 MPa (present study) were reported for Chemfil Superior. In addition, mean compressive fracture strengths and standard deviations of 68 ± 16 MPa (Fleming and Zala, 2003) and 163 ± 21 MPa (present study) were reported for Fuji IX and 69 ± 17 MPa (Fleming and Zala, 2003) and 141 ± 17 MPa (present study) for ChemFlex. It is suggested that the technique used to mix

the GI restoratives could have influenced the mean compressive fracture strengths. It is imperative that the powder and liquid constituents are mixed thoroughly for the time specified by the manufacturer, to produce a homogeneous consistency and ensure a uniform dispersion of glass particles in the set GI restorative structure. A non-uniform dispersion of glass particles in the GI restorative may increase the number of defects in the set structure which can act as crack initiating sites when the specimen is stressed under loading, thereby possibly resulting in variations in the mean compressive fracture strengths reported (Fleming *et al.*, 2001, 2003).

However, when an encapsulated GI restorative (Ketac Fil Plus Aplicap) was tested in the same test centre by three operators using the same testing protocol as outlined previously (6 mm height and 4 mm diameter specimens prepared in a PTFE split-mould with the insurance of parallel specimen ends and tested at 1.0 mm/min using a padding material) following mechanical mixing in the Rotomix, the mean compressive fracture strengths and associated standard deviations reported were 68 ± 15 MPa (Fleming and Zala, 2003), 125 ± 16 MPa (present study) and 160 ± 21 MPa (Fleming *et al.*, 2006). The encapsulated product eliminated variation due to inaccurate dispensing of the constituents prior to mixing, and mixing variability introduced by the operator since the mixing regime was standardised by mechanical mixing using the same machine (Rotomix) in accordance with the manufacturers' instructions. Given the large variation in the mean compressive fracture strengths reported (from 68-160 MPa), it is suggested that an operator effect on filling the split-mould was probably as important a factor influencing the compressive fracture strength as any other for the GI restorative investigated.

Cylindrical specimens of brittle materials subjected to compressive axial loading do not fail directly by compressive stresses. Shear stresses at the contact points with the loading platens are resolved into cones generated at either end which drive into the specimen resulting in tensile forces acting outward from the central axis of the cylinder and, as a result, the exact failure mechanisms operating are difficult to interpret (Darvell, 2002). Cylindrical GI restorative specimens experience plastic deformation prior to fracture (Wilson and Lewis, 1980) (represented by a decrease in the ratio of stress to strain above the elastic limit as shown in Figure 3.3.2) which add further difficulty to identifying the exact failure mechanisms operative during compressive loading. When calculating the compressive fracture strength the maximum load at failure lies above the elastic limit, however, there is no strain component in the compressive fracture strength equation (Equation 3.1) to accommodate the change in the relationship between stress and strain. It is suggested that calculating the elastic modulus (from the ratio of stress to strain in the elastic range of a GI restorative) would offer a further insight into how the material performs as the elastic modulus is an intrinsic material property independent of the specimen dimensions which can be linked directly to the bonding between atoms (Li and White, 1999; Askeland and Phulé, 2005).

There are a limited number of studies in the dental literature which have determined the elastic modulus of GI restoratives using the stress/strain profile obtained from the compressive fracture strength test. Mitra and Kedrowski (1994) reported mean elastic moduli and standard deviations of 8.00 ± 0.60 GPa for Ketac Fil and 7.10 ± 0.20 GPa for Fuji II. The mean elastic moduli and standard deviation reported by Higgs *et al.* (2001a) for Fuji II and Fuji IX were 10.18 ± 2.06 and 14.34 ± 2.65 GPa, respectively.

Yli-Urpo *et al.* (2005) reported a mean elastic modulus and standard deviation of 0.80 ± 0.10 GPa for Fuji II. The mean elastic moduli and standard deviations for Ketac Fil Plus, Fuji II and Fuji IX reported in this study were 4.88 ± 0.20 , 4.65 ± 0.21 and 4.99 ± 0.22 GPa, respectively. The variously reported mean elastic moduli in the dental literature are difficult to interpret.

The study of Mitra and Kedrowski (1994) used specimen dimensions of 8 mm height and 4 mm diameter, Higgs *et al.* (2001a), Yli-Urpo *et al.* (2005) and this study used specimens of 6 mm height and 4 mm diameter while all the studies were conducted at a compressive loading rate of 1.0 mm/min. One would not expect the elastic modulus results to be influenced by the specimen dimensions since elastic modulus is an intrinsic material property, however, the variations of 0.80 ± 0.10 to 10.18 ± 2.06 GPa for Fuji II suggest other possibilities need to be explored.

Reasons for the variously reported mean elastic moduli could be due to the moulds used to fabricate the specimens and the insurance of parallel specimen ends. Mitra and Kedrowski (1994) used glass tubes, Higgs *et al.* (2001a) provided no information on the mould type employed, Yli-Urpo *et al.* (2005) used a stainless steel mould while a PTFE split-mould was employed in this study. None of the authors (Mitra and Kedrowski, 1994; Higgs *et al.*, 2001a; Yli-Urpo *et al.*, 2005) stated if they had insured parallel specimen ends (Lloyd and Mitchell, 1984). Therefore, the surface finish of the GI restorative specimens would be expected to have varied between studies and uniform contact between the cylindrical specimen ends and the platens of the testing apparatus may not have occurred. As a result, it is possible that the cylindrical specimens experienced localised stress concentrations in the cylinder during

compressive loading resulting in a more complicated stress distribution (Lloyd and Mitchell, 1984) which may have contributed to the variations in the mean elastic modulus reported in the dental literature. In this study, immediately after applying the GI restoratives to the mould, the mould assembly was clamped so that equal pressure was applied to all specimens to ensure parallelism of the cylindrical specimen ends. Furthermore, padding in the form of wet filter paper was used in the present study but was not reported in the three studies examined (Mitra and Kedrowski, 1994; Higgs *et al.*, 2001a; Yli-Urpo *et al.*, 2005) and may have had an influence on the elastic modulus values reported. The method of dispensing and mixing the powder and liquid constituents of the GI restoratives investigated in the three studies (Mitra and Kedrowski, 1994; Higgs *et al.*, 2001a; Yli-Urpo *et al.*, 2005) was reported to conform to the manufacturers' instructions. However, as reported previously, it is imperative that the powder and liquid constituents are mixed thoroughly, for the time specified by the manufacturer, to ensure homogeneity and therefore a uniform dispersion of glass particles in the set GI restorative structure. Prentice *et al.* (2005) reported that a more homogeneously mixed GI restorative would have an increased elastic modulus as it would contain less undissolved polymer which is more susceptible to moisture, erosion and fracture. In addition, the method of filling the mould with the GI restorative was not provided by the authors of the three studies (Mitra and Kedrowski, 1994; Higgs *et al.*, 2001a; Yli-Urpo *et al.*, 2005) and the introduction of pores into the cylindrical specimens would also be expected to reduce the likelihood of achieving consistent results between different test centres.

The reasons provided for the variation in the mean elastic modulus data relating to the testing methodology (mould type, parallelism of the cylindrical specimens and the use

of a padding material) or mixing and filling the mould should not in theory result in the increases from 0.80 ± 0.10 GPa (Yli-Urpo *et al.*, 2005) to 4.65 ± 0.21 GPa (present study), 7.10 ± 0.20 GPa (Mitra and Kedrowski, 1994) and 10.18 ± 2.06 GPa (Higgs *et al.*, 2001a) for Fuji II tested in four different test centres. Mitra and Kedrowski (1994) are not independent researchers and although the results were published in a peer reviewed journal, the likelihood of negative results or samples being included may be low. No evidence is provided by Mitra and Kedrowski to suggest why the elastic modulus values were so high and doubts always exist when interpreting in-house data from manufacturers which may explain the increased mean elastic modulus compared with this study. Careful examination of the methodology employed by Higgs *et al.* (2001a) may account for the mean elastic modulus increase compared with this study. The Fuji II specimens were coated with FujiCoat (GC Corporation, Tokyo, Japan) after fabrication to prevent desiccation. Coating materials have the effect of preventing desiccation, dehydration and moisture loss from the surface of GIs (Earl *et al.*, 1989; Miyazacki *et al.*, 1996) and protect against cracking (Higgs *et al.*, 2001b). Previously it was reported that coating Fuji II specimens with FujiCoat significantly increased the flexural modulus determined using the three-point flexure strength testing method from 13.6 ± 1.2 to 16.2 ± 1.8 GPa (Miyazacki *et al.*, 1996). The study by Yli-Urpo *et al.* (2005) produced the most difficult result to interpret, however, following a personal communication with the author (Yli-Urpo, 2006), Yli-Urpo accepted that her calculations were incorrect and the values reported did not accurately reflect the true mean elastic modulus of Fuji II. Unfortunately, the data was not available to Yli-Urpo to re-calculate the elastic modulus and as a result the value reported, although recorded in the dental literature appears to be meaningless.

5.2.2 *In vitro* Wear Resistance Testing

Wear is the inevitable result of the interaction of opposing surfaces (Mair, 1992) and the fundamental wear mechanisms operating in the oral environment include two-body abrasion, three-body abrasion, attrition, adhesion, fatigue and erosion, however, these mechanisms rarely act in isolation (Mair *et al.*, 1996). The assessment of the *in vivo* wear of dental restoratives has previously been conducted through either direct observation of the restoration at regular patient visits (Cvar and Ryge, 1971) or by the indirect analysis of tooth replicas of the restoration (Leinfelder *et al.*, 1983, 1986). In the United States Public Health Service (USPHS) technique reported by Cvar and Ryge (1971), two or more independent clinical observers directly evaluated the wear of amalgam or resin-based composite restorations at regular patient visits and rated the wear in accordance with a written criterion (Ryge and Snyder, 1973; Ryge, 1980). Restorations with contours that were “continuous with the existing anatomical form” were classified as Alpha (clinically ideal). If the contours of the restoration were “discontinuous with the existing anatomical form but the dentine or base was not exposed” it was classified as Bravo (clinically acceptable). A rating of Charlie (clinically unacceptable) was given if a sufficient quantity of the restoration was lost “to expose the dentine or base or affect occlusion”. A further rating of Delta (clinically unacceptable) was given if the “restoration was missing” or the wear was “excessive and synonymous with ongoing damage to the tooth or the surrounding tissue” (Ryge and Snyder, 1973). One of the drawbacks of the USPHS technique was that clinical observers were subjective in their assessment of the *in vivo* wear of restorations. Therefore, clinical observers often disagreed over ratings such that restorations were rated as Bravo at one visit and Alpha at a later patient visit (Taylor

et al., 1989) when wear would have been expected to increase in the time between patient visits. In addition, it was also difficult to achieve the continuity of clinical observers for subsequent patient visits, notwithstanding patient attendance and compliance issues in conjunction with the high costs associated with the direct observation USPHS technique (DeLong, 2006).

The indirect analysis of tooth replicas technique reported by Leinfelder *et al.* (1983, 1986) quantitatively determined the wear of amalgam or resin-based composite restorations by comparing stone cast replicas of teeth containing restorations to six standard casts which corresponded to specific wear depths, ranging from 0 to 500 μm in 100 μm intervals. The evaluator had to decide whether the stone cast replica of the restoration matched one of the standard casts or fell between two casts and then had to assign an appropriate wear depth value to the restoration (Leinfelder *et al.*, 1986). As a result, the wear value was extremely subjective to the operator and the standard casts were insufficiently sensitive to detect increases in the wear depth value. Furthermore, the Leinfelder indirect observation technique required negative and positive impressions of the restored teeth to be taken using impression and stone materials, respectively. The impression and stone materials are known to be susceptible to dimensional changes on setting (Price *et al.*, 1991), thereby impeding the dimensional accuracy and precision of the replicas. As a result, confidence amongst practitioners in the direct observation of *in vivo* restorative wear data from the Leinfelder indirect observation technique remained low (Taylor *et al.*, 1989).

In view of the problems with the direct USPHS and indirect Leinfelder techniques to assess the *in vivo* wear of dental restoratives, an attempt to mimic the masticatory

processes encountered in the oral environment has led to the development of a variety of devices to simulate the wear of restorative materials *in vitro*. The purpose of these *in vitro* wear simulators was to assess the wear resistance of restorative materials prior to placement in the oral environment, to provide an initial screening of potential restorative materials which would obviate expensive and time-consuming clinical trials on substandard restorative materials. The *in vitro* wear assessment of restorative materials has been conducted using a number of machines which simulate a variety of different wear mechanisms including the Materials Testing and Simulation artificial oral environment (DeLong and Douglas, 1983), the Academisch Centrum for Tandheelkunde Amsterdam (ACTA) (De Gee *et al.*, 1986) and University of Alabama (Leinfelder *et al.*, 1989) wear machines and the OHSU oral wear simulator (Condon and Ferracane, 1996). However, there is no internationally recognised standard for the *in vitro* wear assessment of dental restoratives and it is suggested that the lack of an internationally recognised standard is due to the difficulties involved in simulating the complexity of wear behaviour mechanisms operative in the oral environment. As a result, there is no single *in vitro* wear machine currently available that can simulate all clinical wear mechanisms operative in the oral environment and instead the machines outlined simulate one, two or in some cases three of the individual wear mechanisms outlined by Mair *et al.* (1996). Therefore, there is considerable difficulty in correlating both *in vivo* and *in vitro* wear studies on dental restoratives not to mention the difficulties in interpreting wear data between different *in vitro* wear machines and even similar *in vitro* wear machines in different test centres (Heintze, 2006).

The forces encountered in the oral environment during mastication can vary considerably depending on the hardness, toughness and viscoelasticity of the food

substance that is being chewed (Schindler *et al.*, 1998; Heintze, 2006). Schindler *et al.* (1998) measured the forces encountered in the posterior region of the mouth during mastication using a three-link fixed partial denture containing two strain gauges which enabled the determination of both the horizontal (sliding abrasion) and vertical (direct attrition) forces. A horizontal sliding force of approximately 7 N was reported when the subjects involved in the study chewed boiled potatoes while horizontal sliding forces of approximately 18 and 42 N were reported when raw carrots and wine gums, respectively, were chewed (Schindler *et al.*, 1998). Schindler *et al.* (1998) also reported that the direct vertical forces used to chew boiled potatoes, raw carrots and wine gums were approximately 20, 50 and 120 N, respectively. As a result, in this wear resistance investigation, an abrasion force of 20 N and an attrition force of 90 N were used to represent forces routinely encountered in the posterior region of the mouth during mastication. Steatite was chosen as the antagonist material as it has wear characteristics similar to that of human enamel in the oral environment when opposing dental restorative materials (Wassell *et al.*, 1994, Condon and Ferracane, 1997a, 2002). In addition, steatite spheres can be mass produced with consistent mechanical properties whilst the mechanical properties of human enamel can vary from donor to donor. The food-like slurry used here (1 g of poppy seeds, 0.5 g of PMMA beads and 5 ml of distilled water) was identified by De Gee *et al.* (1986) to produce a similar ranking of *in vitro* wear rates for a variety of dental restorative materials in the ACTA wear machine that were comparable with the *in vivo* clinical wear studies of Lutz *et al.* (1984) and Lambrechts *et al.* (1985).

The OHSU oral wear simulator subjects specimens to three wear mechanisms, namely, abrasion, three-body abrasion and attrition (Condon and Ferracane, 1996,

1997a,b). Abrasion wear which is caused by the sliding action of one surface over another (Mair *et al.*, 1996; Mortensen, 2007) results in material loss from the specimen as the hard asperities of the steatite antagonist ploughs through the exposed asperities of the specimen structure as it travels along the sliding path (Mair, 1992). Three-body abrasion wear also occurred during the wear regime employed where the presence of the food like slurry and wear debris between the two opposing surfaces further exacerbated the abrasion of the specimen. Three-body wear occurs clinically during mastication when the food bolus is pressed into and dragged across the occlusal surfaces of teeth resulting in fine scratches (Sulong and Aziz, 1990). It has been suggested that the abrasive medium 'hollows out' the softer phases of heterogeneous surfaces resulting in the harder reinforcing phase protruding from the surface (Mair, 1992; Yap *et al.*, 2001). When the steatite antagonist is forced into the specimen to simulate attrition wear, (the direct static contact between opposing surfaces (Mair *et al.*, 1996; Mortensen, 2007)), subsurface microcracks form which may propagate under cyclic loading (Mair *et al.*, 1996) and result in the removal of material from the surface (Kunzelmann *et al.*, 2003). The loss of material due to the attrition force is synergistic to sliding abrasion wear. The attrition force acts upon an area of the specimen where the material has been worn previously by the sliding abrasive force. The higher force imparted upon the specimen by the attrition regime therefore acts upon a pre-stressed area of the material which assists the further removal of material. In the present investigation, the low abrasion (20 N) and high attrition (90 N) forces were manifested on the surface of the GI restorative specimens as a tear-drop shaped wear facet as illustrated in Figure 3.3.3.

The tear-drop wear facet produced on the surface of the specimen by the OHSU was traditionally analysed by taking ten profilometric traces across the facet (Condon and Ferracane, 1996, 1997a,b). From these ten traces, traces four, five and six taken in the middle of the facet were considered by Condon and Ferracane (1996, 1997a,b) to be representative of abrasion wear. Traces eight and nine, taken at the deepest part of the facet were considered to be representative of attrition wear (Condon and Ferracane 1996, 1997a,b). In this study, a series of profilometric traces were taken across the wear facet at 4 μm intervals resulting in up to 1000 traces in total, depending on the size of the wear facet. It was also possible to divide up the wear facet into regions using the TalySurf software. Since Condon and Ferracane (1996, 1997a,b) used traces four, five and six to measure abrasion wear, the region encompassing 40 to 60% of the wear facet was sectioned and analysed independently in the current study (Figure 5.1.1a). Similarly, the region encompassing 80 to 90% of the wear trace was sectioned and analysed independently (Figure 5.1.1b).. It was suggested by Condon and Ferracane (1996, 1997a,b) that the region encompassing 40 to 60% of the wear trace contained the most uniform section of the wear facet for resin-based composite materials and was therefore representative of sliding abrasion wear. Condon and Ferracane (1996, 1997a,b) also suggested that the region encompassing 80 to 90% of the wear trace where the antagonist was stationary and applying a direct static force, was representative of attrition wear.

When the three-dimensional representation of the wear facets for the GI restorative control groups were analysed the wear depths measured varied by as much as 0.22 and 0.19 mm over the abrasion and attrition regions, respectively suggesting that the abrasion and attrition regions were not uniform (Figure 5.1.1a-b) as was expected for

resin-based composites. It should be noted that the *in vitro* wear resistance of resin-based composite materials is markedly higher than that of GI restoratives (Hickel *et al.*, 1998), so it is possible that while the abrasion and attrition regions were not uniform for GI restoratives, they may well be uniform for resin-based composites. In view of this fact, the mean total volumetric wear and mean maximum wear depth of each entire wear facet were calculated for the purpose of the present investigation into GI restoratives.

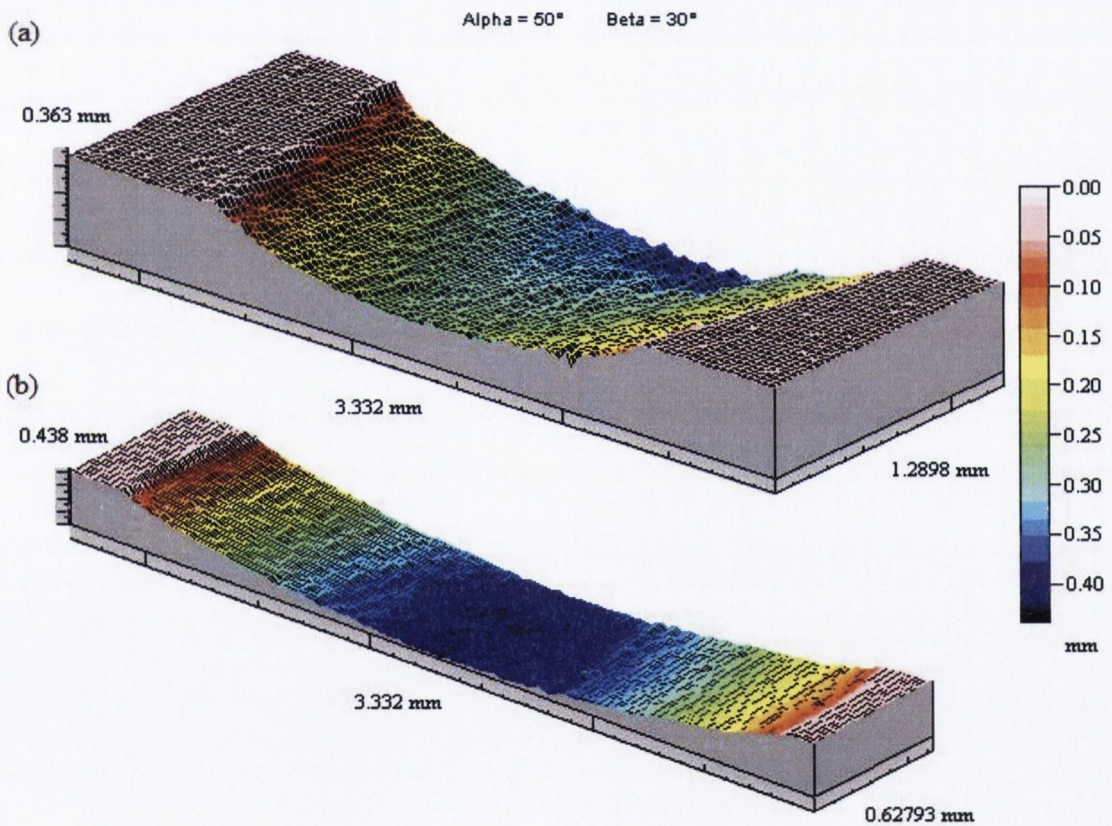


Figure 5.1.1 A three-dimensional representation of (a) the abrasion region and (b) the attrition region of the wear facet sectioned from the wear facet trace from Figure 3.3.3.

In a recent review questioning the “need for *in vitro* wear simulating devices” Ferracane concluded that to standardise wear testing methodologies and data reporting

an appropriate wear quantity namely, area, depth or volume was critical (Ferracane, 2006). DeLong (2006) suggested that the ideal wear quantity for data reporting should be clinically relevant and easily measured both *in vivo* and *in vitro* using similar or comparable methods. The assessment of the *in vivo* wear of tooth structures and dental restorative materials in terms of area and depth were recently described by DeLong (2006) as being “indirect wear measures” since both the wear area and wear depth were dependent upon occlusal factors and vary with time. The wear of tooth structures and dental restorative materials *in vivo* is a dynamic process, since the contact points and orientation of opposing dentition continually changes with time and the progression of wear (Zhou and Zheng, 2008). Therefore, wear is likely to “cease in one location and move to a second location”, however, if the change in orientation of opposing dentition is small, the locations where wear occurs may overlap and as a result, the assessment of area and depth as appropriate wear quantities are “difficult, if not impossible” to combine (DeLong, 2006).

To date, the assessment of the *in vivo* or *in vitro* wear resistance of dental restoratives such as dental amalgam and resin-based composite restorations has been evaluated in terms of the wear depth of material removed rather than the wear area. As reported previously, the wear depth assessment of dental amalgam and resin-based composite restorations has been assessed *in vivo* using the indirect Leinfelder technique (Leinfelder *et al.*, 1983, 1986), however, the wear depth value was extremely subjective to the operator and the technique was insufficiently sensitive to detect increases in the wear depth value. In addition, DeLong (2006) reported that depth was “not a good parameter for comparing wear” as wear depth was dependant on the location and direction from which the depth was measured. The *in vitro* wear

investigations of dental amalgams and resin-based composites have evaluated wear in terms of the mean wear depth of material removed following *in vitro* wear simulation (De Gee *et al.*, 1986; Leinfelder *et al.*, 1989; Condon and Ferracane, 1996). However, the reproducibility of mean wear depth results from different test centres (Condon and Ferracane, 2002; Sorensen and Pham, 2002; Seghi *et al.*, 2002) was limited, as differences of 33–56% were reported, when the OHSU was employed to test three conventional resin-based composite materials (Heliomolar (Ivoclar Vivadent, Schaan, Liechtenstein), Herculite (Kerr, Orange, CA, USA) and Z100 (3M ESPE, Seefeld, Germany)) using a 20 N abrasion force (in the presence of a food like slurry) (Heintze, 2006). The mean wear depth measurements observed for the attrition regime when the OHSU was employed using the same methodology varied from 31–78% when attrition loads varying from 70–90 N were used (Condon and Ferracane, 2002; Sorensen and Pham, 2002; Seghi *et al.*, 2002). It is therefore appears that there are marked difficulties with using mean wear depth measurements to report the *in vitro* wear resistance of dental restorative materials.

Recently, DeLong (2006) recommended the use of volumetric wear as the parameter of choice for data reporting when measuring the *in vivo* and *in vitro* wear of dental restorative materials suggesting that volumetric wear had clinical significance as it was independent of occlusal factors. Also, the volume of material removed due to the interaction of opposing dentition at one or more locations or even overlapping locations can be combined (DeLong, 2006). The determination of the volume of material removed due to the interaction of opposing surfaces was first suggested by Archard in 1953 (Archard, 1953). Archard's wear equation calculated wear as the volume (V) (mm^3) per unit sliding distance (L) (mm) which was dependant upon a

dimensionless wear coefficient (k), the applied load (P) (N) and the radii of the contacting asperities (a) (mm)

$$Wear = \frac{V}{L} = \frac{kP}{3a} \quad \text{Equation 5.1.}$$

Therefore, based on Archard's wear equation (1953), the volume of material removed due to the interaction of opposing surfaces is dependant on the force applied times the distance travelled which is a measure of the work done and implies that the wear volume is a material property (DeLong, 2006). However, the determination of volumetric wear *in vivo* and *in vitro* requires sophisticated three-dimensional scanning equipment, which has not been widely used as the cost of scanning equipment and specialised software has been high (DeLong, 2006).

5.2.3 Working Characteristics

Plant *et al.* (1972) used the oscillating rheometer to investigate the setting characteristics of lining and cementing materials, however, the method was developed initially by Bovis *et al.* (1971) to assess the setting characteristics of self-cured composite filling materials. The oscillating rheometer had the advantages of being quick and simple to use, along with the ability to produce consistent test results for the working characteristics in the present study. However, the reliability of the test procedure is the subject of considerable controversy in the dental literature (Bovis *et al.*, 1971; Plant *et al.*, 1972; Jacobson and von Fraunhofer, 1974; Jacobson, 1976; Vermilyea *et al.*, 1977; Cook and Brockhurst, 1979). The sensitivity of the oscillating rheometer was determined by the tension of the springs in resisting the movement of the oscillating platen (Jacobsen and von Fraunhofer, 1974). Weaker springs are more sensitive to differences during the initial setting of GI restoratives when the viscosity of the mix is low. As the setting process of the GI restorative continues the mix

becomes more viscous and weak springs become less sensitive to differences in the working characteristics (Bovis *et al.*, 1971). Stronger springs produce more discernible results during the final stages of setting but are less sensitive to differences during the initial setting process (Bovis *et al.*, 1971). Although the rheometer indicated the resistance to shear forces in the setting material, small changes on setting may not be revealed until a certain viscosity (resistance to shearing force) was reached by the material under investigation (Jacobson and von Fraunhofer, 1974; Jacobson, 1976). Vermilyea *et al.* (1977) found that the viscosity of a zinc phosphate dental cement (the powder to liquid mixing ratio was not stated by the authors) decreased by 11% when a rotating-t-bar spindle, whose continuous mixing motion stirred the cement, was used compared with a cylindrical bar which did not interfere with the setting cement. The authors suggested that the continued mixing motion of the rotating-t-bar spindle may have inhibited matrix formation and resulted in lower viscosities with prolonged working and setting times compared with those obtained by the cylindrical bar.

It is likely that the working times estimated from the rheometer traces in the current study provide an overestimation of the 'real' working time as a result of the continued mixing motion of the lower plate of the oscillating rheometer inhibiting matrix formation (Cook and Brockhurst, 1979). Therefore, the oscillating rheometer did not provide an exact measurement for the working and setting times of the GI restoratives investigated. It is therefore suggested that the combination of the sensitivity range determined by the spring tension selected to restrict the motion of the lower oscillating plate and the continued mixing motion of the lower plate may have masked differences in the working characteristics for the GI restoratives investigated.

Therefore, the working characteristics were assessed only for the first part of this study, namely, the investigation of MMT clay addition to Chemfil Superior. The oscillating rheometer only provided a guide to the setting characteristics of Chemfil Superior with MMT clay addition and a more fundamental and theoretically-founded method of monitoring the rate of set needs to be developed for dental restoratives in the future.

5.3 MMT Clay Addition Effects

X-ray diffraction (XRD) is a well established method for characterising MMT clays which enables determination of the interlayer d-spacings of the clays and provides an indication of the level of intercalation or exfoliation of the clay layers (Alexandre and Dubois, 2000; Ray and Okamoto, 2003; Okamoto, 2003; Utracki, 2004). An intercalated MMT clay is manifested on an XRD pattern as a shifting of the first peak encountered to a lower 2θ angle, whereas the complete elimination of this peak is indicative of an exfoliated system (Alexandre and Dubois, 2000; Ray and Okamoto, 2003; Okamoto, 2003; Utracki, 2004). In the present study, XRD showed that the interlayer d-spacing of the un-modified Ca-MMT clay was 1.04 nm while the interlayer d-spacing of the organically-modified ADA-MMT clay was 1.74 nm as shown in Figure 5.2.1.

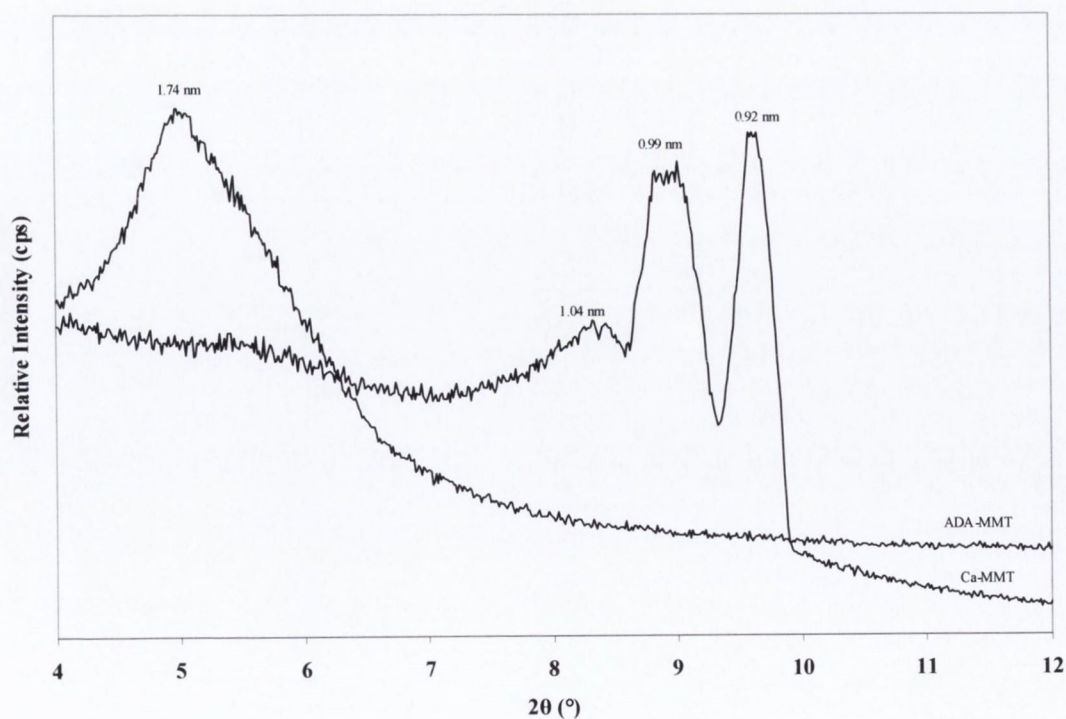


Figure 5.2.1 XRD patterns of Ca-MMT and ADA-MMT clay.

The increase in the interlayer d-spacing for ADA-MMT clay compared with Ca-MMT clay (0.7 nm) provides an increased opportunity for the polymeric chains of the GI restorative to diffuse into the ADA-MMT clay layers during manipulation of the GI restorative. Diffusion of polymeric chains between the MMT clay layers is likely to further intercalate or exfoliate the MMT clay platelets (Alexandre and Dubois, 2000) which will result in a more homogeneous dispersion of MMT clay platelets (LeBaron *et al.*, 1999) in the set GI restorative. A more homogeneous dispersion of MMT clay platelets in polymers has been reported to increase the stiffness and the strength of the polymer (Giannelis, 1996; LeBaron *et al.*, 1999).

5.3.1 Ca-MMT Clay Addition to Chemfil Superior

5.3.1.1 Compressive Fracture Strength

The addition of Ca-MMT clay to the powder and liquid constituent of Chemfil Superior did not provide a reinforcing effect and resulted in a significant steady decline in the mean compressive fracture strength with increasing Ca-MMT clay concentration from 0.5 to 2.5 wt.% (Tables 4.1.2 and 4.1.3, respectively). Unmodified MMT clays such as Ca-MMT have been reported to have an average particle size of 8 μm consisting of approximately 3000 stacked clay platelets (Utracki, 2004). It is supposed that the addition of Ca-MMT clay to the powder constituent of the GI restorative and the spatulation of the two powders for 20 s may have been insufficient to break up the clay particles into smaller particles or individual platelets. As a result, the 8 μm Ca-MMT clay particles present in the set GI restorative structure are likely to act as stress concentrations and defects where cracks can initiate (Uhl *et al.*, 2004). Also, cracks are likely to pass through the clay particles more easily than the GI restorative matrix, splitting the clay layers apart resulting in failure at lower loads.

The number of Ca-MMT clay particles in the GI restorative structure increased with increasing clay concentration which would be expected to introduce further defects in the GI restorative structure which possibly resulted in the steady deterioration of the mean compressive fracture strength reported. However, the distribution of Ca-MMT clay particles in the GI restorative structure could not be verified using scanning electron microscopy. The use of a more sensitive technique such as transmission electron microscopy may have identified the distribution and arrangements of the Ca-MMT clay particles. However, it has been reported that transmission electron microscopy cannot discriminate between single clay platelets and stacks of platelets (Ploehn and Liu, 2006) and therefore the technique may be limited.

Hydrophilic un-modified sodium-montmorillonite (Na-MMT) clays have been reported to swell in water (Grimshaw, 1980) resulting in an expansion of the interlayer d-spacing from 0.96 to approximately 1.25 nm due to the diffusion of a water monolayer (approximately 0.28 nm thickness) into the interlayer spacing (Utracki, 2004). However, the un-modified Ca-MMT clay employed in the current study was not hydrophilic compared with a Na-MMT clay (Banin and Lahav, 1968, Utracki, 2004) and therefore it is unlikely that swelling and the concomitant increase in the interlayer d-spacing would have occurred for Ca-MMT clay in water (Banin and Lahav, 1968). Therefore, it is unlikely that the polymeric chains of the GI restorative were able to diffuse into the un-modified Ca-MMT clay layers when immersed initially in water upon mixing. As a result, the intercalation or exfoliation of the clay in the GI restorative matrix would not be expected to occur in the presence of water. This may explain the poor performance of Chemfil Superior with Ca-MMT clay addition to liquid constituent compared with the powder constituent. While it is

postulated that the addition of Ca-MMT clay to water prior to mixing did not result in the swelling of the clay and an increased interlayer d-spacing, it was not possible to analyse moist MMT clay samples using the XRD machine employed in the current study and as a result, the interlayer d-spacing of Ca-MMT clay in the presence of water could not be confirmed.

The addition of Ca-MMT clay to the GI restorative powder constituent of Chemfil Superior resulted in a significant increase in the mean compressive fracture strength compared with adding the clay to the liquid constituent (Table 4.1.10). It is postulated that the Ca-MMT clay absorbed more of the available water when added to the GI restorative liquid constituent (water) than when added to the powder constituent. If less water was available for interaction with the powder constituent of the GI restorative during mixing it is likely that the powder to liquid mixing ratio would be increased above that recommended by the manufacturers. Increasing the powder to liquid mixing ratio above that recommended by the manufacturers decreases the amount of GI restorative matrix available in the set GI restorative to bind the glass particles effectively which results in reduced mean compressive fracture strengths (Prosser *et al.*, 1986).

5.3.1.2 *In vitro* Wear Resistance

The *in vitro* wear resistance was only assessed for the Chemfil Superior groups containing MMT clay additions to the GI restorative powder constituent based on the significantly increased mean compressive fracture strength data for the Chemfil Superior groups containing MMT clay added to powder constituent compared with the liquid constituent. There was a significant steady increase in the mean total

volumetric wear and mean maximum wear depth for the Chemfil Superior groups containing Ca-MMT clay additions as the concentration of Ca-MMT clay was increased from 0.0 to 2.5 wt.% (Tables 4.1.4 and 4.1.5, respectively). Previously, Dasari *et al.* (2005) reported that the wear resistance of nylon 6 containing unmodified Na-MMT clay was decreased compared with unmodified nylon 6. The authors stated that the repeated loading of the pin-on-disc wear apparatus resulted in debonding of the clay layers in the Na-MMT clay particles which resulted in voids in the set polymer structure. The expansion of these voids and the weakening of the interface between the Na-MMT clay particle and the nylon 6 matrix under the cyclic loading of the wear regime resulted in a decrease in the wear resistance compared with unmodified nylon 6 (Dasari *et al.*, 2005). In the present investigation, it is likely that debonding of the Ca-MMT clay layers in the 8 μm diameter clay particles occurred during the repeated cyclic loading of the OHSU wear regime and as a result the Ca-MMT clay particles were readily removed from the GI restorative structure as the wear regime progressed. Increasing the concentration of Ca-MMT clay added to Chemfil Superior increased the number of Ca-MMT clay particles present in the set GI restorative structure which resulted in the steady increase in the mean total volumetric wear and the mean maximum wear depth.

5.3.1.3 Working Characteristics

The addition of Ca-MMT clay to Chemfil Superior increased the powder to liquid mixing ratio and therefore made the GI restorative more difficult to mix in the time specified by the manufacturer which would be expected to result in a reduction of the mean working time. In addition, it is likely that the Ca-MMT clay competed with the Chemfil Superior powder for the available water on mixing which would also be

expected to influence the working time. The extent of the competition between the Ca-MMT clay and the GI restorative powder is as yet unknown and further experiment and analysis is required to fully understand the interaction. However, the addition of Ca-MMT clay to the Chemfil Superior powder or liquid constituent did not have a significant influence on the working time (Tables 4.1.6 and 4.1.7, respectively) as Ca-MMT clay concentration was increased.

The mean setting time for the Chemfil Superior groups prepared with Ca-MMT clay added to the powder or liquid constituent was not significantly influenced by increasing Ca-MMT clay concentration (Tables 4.1.8 and 4.1.9, respectively). Again, it was expected that the increase in the powder to liquid mixing ratio with the addition of Ca-MMT clay would influence the setting time. However, as reported previously, it is likely that the spring tension sensitivity selected (Bovis *et al.*, 1971) and the continued mixing motion of the lower plate of the oscillating rheometer (Cook and Brockhurst, 1979) may have masked any differences in the working and setting times of the GI restoratives investigated.

The mean setting time for the groups containing Ca-MMT clay added to the liquid constituent of Chemfil Superior was significantly increased compared with the groups containing Ca-MMT clay added to the powder constituent, however, there was no significant difference in the mean working time (Table 4.1.10). Previously, it was postulated by the author that Ca-MMT clay may have absorbed more water when added to the liquid constituent (water) than when added to the powder constituent of the GI restorative. If the absorbed water retained by the Ca-MMT clay was gradually released as the setting reaction continued, it is possible that the mean setting time

would be increased. However, further experiment and analysis are required to fully test this hypothesis.

5.3.2 ADA-MMT Clay Addition to Chemfil Superior

5.3.2.1 Compressive Fracture Strength

The addition of ADA-MMT clay to the powder constituent of Chemfil Superior had a reinforcing effect as indicated by the significant increases in the mean compressive fracture strength reported for the groups prepared with 0.25, 0.5, 0.75, 1.0 and 1.25 wt.% ADA-MMT clay compared with the control group (0.0 wt.%) (Table 4.2.2). The pre-treatment process of the ADA-MMT clay resulted in smaller particles (of approximately 2 μm (Utracki, 2004)) and an increase in interlayer d-spacing of 0.7 nm compared with the un-modified Ca-MMT clay. The reduced particle size of the ADA-MMT clay in conjunction with the larger interlayer d-spacing, demonstrated through XRD compared with the Ca-MMT clay, resulted in a larger surface area available for reaction with the GI restorative matrix which would be expected to confer a greater reinforcing effect (Giannelis, 1996; LeBaron *et al.*, 1999). In addition, the increased interlayer d-spacing may have allowed for the movement of the polymeric chains of the GI restorative between the layered ADA-MMT clay platelets and potentially the intercalation or exfoliation of the clay in the GI restorative matrix, however, this could not be verified using XRD. The mean compressive fracture strength reached a maximum when the ADA-MMT clay concentration added to the GI restorative powder was 0.5 wt.% and there was a significant decrease as the concentration was increased to 2.5 wt.% (Figure 4.2.1). As the concentration of ADA-MMT clay was increased, the likelihood of an inhomogeneous distribution of clay platelets was also increased (Wang *et al.*, 2005) which may have limited any further strengthening effect

and resulted in the steady deterioration of the mean compressive fracture strength reported when the concentration of ADA-MMT clay was increased above 0.5 wt.%.

There was also a reinforcing effect when the ADA-MMT clay was added to the liquid constituent at concentrations of 0.5 and 0.75 wt.% (Table 4.2.2). The addition of the more hydrophilic ADA-MMT clay to the water prior to mixing was expected to swell the clay (Grimshaw, 1980), increase the interlayer d-spacing (Utracki, 2004), increase the potential for polymer chain diffusion between the layered ADA-MMT clay platelets and therefore result in a greater reinforcing effect compared with adding the clay to the powder constituent. However, the two-sample independent Student's t-test showed a significant increase in the mean compressive fracture strength when ADA-MMT clay was added to the powder constituent compared with adding to the liquid constituent of the GI restorative (Table 4.2.10). It is suggested that exposing the ADA-MMT clay to the water prior to mixing may not have swollen the clay further in 20 s and therefore not increased the interlayer d-spacing as the swelling process for MMT clays is diffusion controlled and can take from minutes to days for equilibrium to be achieved (Utracki, 2004). Furthermore, the addition of ADA-MMT clay to the anhydrous powder of Chemfil Superior may have created a greater opportunity for interaction between the ADA-MMT clay and the polymeric constituent of the GI restorative as the vacuum-dried polymer was reconstituted on mixing with water. It is possible that the ADA-MMT clay was dispersed more homogeneously in the polymeric constituent of the GI restorative when dry-mixed with the powder constituent prior to mixing compared with adding to the liquid constituent.

The coefficient of variation which is defined as the measure of the relative dispersion of data points in a data series (Siegel and Morgan, 2008). A low value of coefficient of variation is indicative of a narrower distribution of the compressive fracture strength data while a high value is indicative of a wider distribution of compressive fracture strength data. The coefficient of variation of the compressive fracture strength data is influenced by the defects and porosity in the cylindrical GI restorative specimens. A specimen group containing specimens with more defects and porosity is likely to have a wider distribution of compressive fracture strength data and therefore a higher coefficient of variation value. However, no method was employed in the current investigation to assess the internal porosity in the cylindrical GI restorative specimens. There were no significant trends in the coefficient of variation of the compressive fracture strength data shown as the concentration of Ca-MMT clay and ADA-MMT clay (available in Appendices) added to the GI restorative powder and liquid constituents was increased. Therefore, the addition of Ca-MMT clay or ADA-MMT clay to the GI restorative at concentrations of up to 2.5 wt.% did not increase the defects and porosity in the specimens.

5.3.2.2 *In vitro* Wear Resistance

The addition of ADA-MMT clay to the Chemfil Superior powder, which had a reinforcing effect on the mean compressive fracture strength data, did not have a significant influence on the *in vitro* wear resistance, namely, the mean total volumetric wear (Table 4.2.4) and the mean maximum wear depth (Table 4.2.5). There were no significant trends in the mean total volumetric wear and the mean maximum wear depth as the concentration of ADA-MMT clay was increased from 0.0 to 2.5 wt.%. The study by Dasari *et al.* (2005) reported that the wear resistance of nylon 6

containing an organically-modified MMT clay was increased compared with nylon 6 containing the un-modified MMT clay. However, the authors reported that while debonding of the clay layers in some of the organically-modified MMT clay particles occurred during the wear regime, the wear resistance of nylon containing organically-modified MMT clay was improved compared with nylon containing un-modified MMT clay. In the present investigation, the mean total volumetric wear and maximum wear depth were reduced for the GI restorative containing ADA-MMT clay compared with the GI restorative containing Ca-MMT clay. The smaller particles of ADA-MMT clay (2 μm) compared with Ca-MMT clay (8 μm) are less likely to suffer from debonding of the clay layers and therefore were not readily removed from the set GI restorative structure by the OHSU wear regime.

5.3.2.3 Working Characteristics

The addition of ADA-MMT clay to the GI restorative powder and liquid constituents did not have a significant effect on the mean working time (Tables 4.2.6 and 4.2.7, respectively) or the mean setting time (Tables 4.2.8 and 4.2.9, respectively) as ADA-MMT clay concentration was increased. Again, it was expected that the increased powder to liquid mixing ratio and the competition between the ADA-MMT clay and the Chemfil Superior powder for the available water on mixing would influence the mean working time and mean setting time. This further emphasises that the oscillating rheometer does not provide an exact measurement of the working and setting times for GI restoratives and that a more fundamental and theoretically-founded method of monitoring the rate of set needs to be considered and developed in the dental literature.

There was a significant increase in the mean working and setting time for the Chemfil Superior groups prepared with ADA-MMT clay added to the GI restorative liquid compared with the groups containing ADA-MMT clay additions to the powder constituent ($p = 0.038$ and < 0.001 , respectively) (Table 4.1.10). Again, it is postulated that the ADA-MMT clay absorbed more water when added to the GI restorative liquid constituent than when added to the powder constituent and slowly released the water as the setting reaction of the GI restorative progressed which increased the mean setting time.

5.3.3 ADA-MMT Clay Addition to Conventional GI restoratives

There was a significant increase in the mean compressive fracture strength for the Ketac Fil Plus group prepared with 0.5 wt.% ADA-MMT clay added to the powder compared with the Ketac Fil Plus control group (Table 4.3.6). However, the mean compressive fracture strengths for Ketac Molar Easymix, Fuji II, Fuji IX and ChemFlex containing 0.5 and 1.0 wt.% ADA-MMT clay added to the powder constituent were significantly decreased compared with the corresponding control groups. Previously, it was suggested that the addition of ADA-MMT clay to the powder constituent of the anhydrous GI restorative Chemfil Superior allowed for an interaction between the clay and the polymeric constituent of the GI restorative when the vacuum-dried polymer was reconstituted on mixing with water which may have resulted in a reinforcing effect. The polymeric constituent of conventional GI restoratives is supplied as a liquid solution, however, a portion of the polymeric constituent can be contained in the GI restorative powder in vacuum-dried form (Guggenberger *et al.*, 1998). Unfortunately, the proportion of the polymeric constituent contained in the powder element of Ketac Fil Plus, Fuji II, Fuji IX and

ChemFlex was not reported by the manufacturers. However, the manufacturers of Ketac Molar Easymix claimed that 60% of the polymeric constituent of the GI restorative was contained in the powder in vacuum-dried form. Therefore, it was expected that Ketac Molar Easymix containing ADA-MMT clay added to the powder constituent would have increased mean compressive fracture strengths compared with the control, however, this did not occur. This finding suggests that there are other factors which influenced the interaction between the ADA-MMT clay and the polymeric constituent of the GI restoratives such as the composition of the powder and liquid constituents. The exact composition of the powder and liquid constituents of the GI restoratives was not stated by many of the manufacturers, therefore it is difficult to determine which powder and liquid compositions offer the best opportunity for GI reinforcement with ADA-MMT clay. Further experiment using experimental GI restoratives with known powder and liquid compositions could determine the optimum compositions required to provide an ADA-MMT clay reinforced GI restorative.

The addition of the 0.5 and 1.0 wt.% ADA-MMT clay to the liquid constituents of the conventional GI restoratives prior to hand-mixing did not result in significant increases in the mean compressive fracture strengths compared with the control groups (Table 4.3.6). It was expected that the mechanical stirring of the ADA-MMT clay and the GI restorative liquids would result in intercalated or exfoliated clay platelets in the GI restorative liquid when the liquid was mixed with the GI restorative powder and therefore result in increased mean compressive fracture strength. It is possible that the viscosity of the commercial GI restorative liquids were too high to allow the diffusion of the polymeric chains into the ADA-MMT clay layers. The

studies by Tran *et al.* (2005, 2006) used low viscosity 5% aqueous solutions of polyacrylic acid, whilst the polymeric acids in commercial GI restorative liquids are usually supplied with concentrations of 40 to 50% (Wilson and Nicholson, 1993). The molecular weight of the polymeric acids in the commercial GI restorative liquids may also have influenced the diffusion of the polymeric chains into the ADA-MMT clay layers as low molecular weight polymers are more likely to penetrate into the interlayer d-spacings of MMT clays than higher molecular weight polymers (Hwang and Dixon, 2000).

The two-way ANOVA (GI restorative material x method of ADA-MMT clay addition x ADA-MMT concentration) of the compressive fracture strength data showed that there was a significant interaction between the GI restorative material and method of ADA-MMT clay addition (either to the powder or liquid constituent of the GI restorative) (Table 4.3.4). When the mean compressive fracture strengths for the individual GI restoratives containing ADA-MMT clay added to the powder or liquid constituent were compared using a two-sample independent Student's t-test, significant increases were shown for Ketac Fil Plus with ADA-MMT clay added to the powder constituent and for Fuji II and ChemFlex with ADA-MMT clay added to the liquid constituent (Table 4.3.5). Therefore, the addition of ADA-MMT clay to the powder or liquid constituent of different GI restoratives does not have the same influence on the mean compressive fracture strength for all GI restorative materials. The overall effect is likely to be influenced by the composition of the powder and liquid constituents, the proportion of vacuum-dried polymer in the powder constituent, the viscosity, molecular weight and type of polymeric acid and the powder to liquid mixing ratio of the GI restorative.

The present investigation has shown that the addition of up to 1.25 wt.% ADA-MMT clay to the powder and liquid constituents of GI restoratives significantly increased the mean compressive fracture strength for some of the GI restoratives investigated (Chemfil Superior and Ketac Fil Plus). However, there were difficulties encountered when incorporating ADA-MMT clay into the viscous polymeric liquids of the conventional GI restoratives. In addition, the GI restoratives containing ADA-MMT clay were more difficult to mix at the manufacturers' recommended powder to liquid mixing ratio. It is also likely that the intercalation or exfoliation of the ADA-MMT clay in the polymeric constituent of the GI restorative would further increase the viscosity of the GI restorative mix. Therefore the effect of reducing the powder content of the GI restoratives from that recommended by the manufacturers was investigated to identify the lowest powder content that could potentially be used for MMT reinforcement without a significant reduction in the mechanical properties (compressive fracture strength, elastic modulus and *in vitro* wear resistance).

5.4 Influence of Reducing GI restorative Powder Content

5.4.1 Manufacturers Recommended Powder to Liquid Mixing Ratio

The mean compressive fracture strengths for the control groups of the three posterior hand-mixed GI restoratives (Ketac Molar Easymix, Fuji IX and ChemFlex) were significantly increased compared with their anterior equivalents Ketac Fil Plus ($p < 0.001$), Fuji II ($p < 0.001$) and Chemfil Superior ($p = 0.015$), respectively when assessed using a two-sample independent Student's t-test. Similarly, the mean elastic moduli for Ketac Molar Easymix and Fuji IX were significantly increased compared with their anterior equivalents Ketac Fil Plus ($p = 0.002$) and Fuji II ($p < 0.001$), respectively. However, there was no significant difference in the mean elastic modulus for ChemFlex compared with Chemfil Superior ($p = 0.093$). The primary difference between the anterior and posterior GI restoratives from 3M ESPE (Ketac Molar Easymix and Ketac Fil Plus, respectively) and GC Europe (Fuji IX and Fuji II, respectively) is an increased powder to liquid mixing ratio for the posterior GI restoratives. As shown in Table 3.2.1, the powder to liquid mixing ratios of Ketac Molar Easymix (4.5 to 1) and Fuji IX (3.6 to 1) were increased compared with Ketac Fil Plus (3.2 to 1) and Fuji II (2.7 to 1), respectively. Increasing the powder content for a constant weight of liquid increases the initial viscosity of the GI restorative mix. However, if a portion of the polyalkenoic acid constituent is incorporated into the GI restorative powder constituent in vacuum-dried form, increased powder to liquid mixing ratios can be achieved without increasing the initial viscosity of the GI restorative mix (Frankenberger *et al.*, 1997; Guggenberger *et al.*, 1998). In addition, the molecular weight and polymeric chain length of the polyalkenoic acid constituent in posterior GI restoratives can be optimised (Hill *et al.*, 1989; Wilson *et al.*, 1989) so that the viscosity of the polyalkenoic acid liquid is not increased. Furthermore,

modification of the size, composition and reactivity of the glass constituent of posterior GI restoratives can result in a faster setting reaction (Nicholson and Croll, 1997; Burke *et al.*, 2007) so that the GI restoratives can achieve sufficient mechanical properties within 1 h of mixing (Peez and Frank, 2006 Burke *et al.*, 2007). The exact compositional differences between the anterior and posterior GI restoratives from the same manufacturer were not disclosed by the manufacturers. However, it is likely that some if not all of the modifications mentioned have been employed which may explain why Ketac Molar Easymix and Fuji IX had significantly increased mean compressive fracture strength and mean elastic modulus compared with Ketac Fil Plus and Fuji II.

The anterior GI restorative supplied by Dentsply Chemfil Superior has an increased powder to liquid mixing ratio (7.4 to 1) compared with its posterior equivalent ChemFlex (3.8 to 1). However, Chemfil Superior was supplied in anhydrous form, where the polyacrylic acid constituent of the GI restorative was vacuum-dried and contained in the powder constituent (Pearson, 1983; Prosser *et al.*, 1984). In addition to the different presentational forms of Chemfil Superior and ChemFlex, the composition of the glass constituent was also different which may explain why the posterior GI restorative did not exhibit significantly improved mean elastic modulus compared with the anterior GI restorative.

5.4.2 Implications of Operator Variability on Mixing

5.4.2.1 Compressive Fracture Strength and Elastic Modulus

The results of the present investigation show that reducing the powder content of the hand-mixed GI restoratives in 10% increments (for a constant weight of liquid) results

in a significant steady decline in the mean compressive fracture strength (Table 4.4.1). These findings are in agreement with the study of Fleming *et al.* (2003), who reported a progressive decrease in the mean compressive fracture strength for the hand-mixed GI restorative Chemfil Superior when the powder content was reduced from that recommended by the manufacturer (100%) to 90, 80 and 50% (for a constant volume of liquid). When the results of the study of Fleming *et al.* (2003) were further analysed by the author of the current investigation using a regression analysis, a significant decrease in the mean compressive fracture strength with decreasing powder content was evident ($p = 0.001$). Similarly, in a later study by Fleming *et al.* (2006) the mean compressive fracture strength of an encapsulated GI restorative (Ketac Fil Plus Aplicap) was shown to progressively decrease as the powder content was reduced (for a constant volume of liquid) from 100 to 90, 85 and 80% of that recommended regardless of the method of mechanical mixing (Capmix or Rotomix). Analysing the mean compressive fracture strength results reported by Fleming *et al.* (2006) using regression analyses also showed significant decreases in the mean compressive fracture strength with reducing powder content for Ketac Fil Plus Aplicap mechanically mixed using the Capmix ($p = 0.048$) and Rotomix ($p = 0.036$). The compressive fracture strength of GI restoratives can be attributed to the reinforcing glass particles present in the set GI restorative structure which resist compressive forces on loading rather than the matrix phase (Brune and Smith, 1982; Xie *et al.*, 2000; Fleming *et al.*, 2003). Reducing the powder content of the hand-mixed GI restoratives reduced the volume of reinforcing glass particles in the set GI restorative structure. Therefore, the ratio of glass particles to polymeric matrix was also decreased with reducing powder content which reduced the ability of the GI restoratives to resist crack growth when stressed under compressive loading (Fleming

et al., 2003). As a result of the reduced crack stopping potential of the GI restoratives, prepared with progressively reduced powder contents, there was a significant steady decrease in the mean compressive fracture strength.

The one-way ANOVA and Tukey's post-hoc test results for the mean compressive fracture strengths (Table 4.4.2) and mean elastic moduli (Table 4.4.4) showed significant decreases for the conventional GI restoratives (Ketac Fil Plus, Fuji II, Ketac Molar Easymix, Fuji IX and ChemFlex) when the powder content was reduced by 10%. A 20% reduction in powder content resulted in a significant mean compressive fracture strength decrease for Chemfil Superior. A sharp decline in the mean compressive fracture strength (Figure 4.4.3) and elastic moduli (Figure 4.4.9) was evident for Chemfil Superior when the powder content was reduced below 80% (for a constant weight of liquid). The study by Fleming *et al.* (2003), which also examined the influence of reducing the powder content of Chemfil Superior did not report a sharp decline in the mean compressive fracture strength when the powder content was reduced below 80%. However, Fleming *et al.* (2003) did not investigate groups with 70 and 60% of the powder content as was done in the current study. As a result, a sharp decline in mean compressive fracture strength when the powder content was reduced below 80% was not reported previously by the Fleming *et al.* (2003). Chemfil Superior was supplied in anhydrous form where the polyalkenoic acid element was vacuum-dried and contained in the powder constituent (Pearson, 1983; Prosser *et al.*, 1984). The anhydrous Chemfil Superior powder was mixed with distilled water to initiate the acid-base reaction (Prosser *et al.*, 1984; Wilson and Nicholson, 1993) rather than mixing with a polyalkenoic acidic liquid. As a result, reducing the powder content also reduced the proportion of the polyalkenoic acid

constituent which provides an explanation for the differing compressive fracture strength behaviour of Chemfil Superior compared with the conventionally supplied GI restoratives. The conventional GI restoratives were prepared with a constant weight of polyalkenoic acid liquid whereas Chemfil Superior was prepared with a progressively reduced polyalkenoic acid constituent. Therefore the ratio of reinforcing glass particles to polymeric matrix remained constant, for a constant weight of the liquid element (water), resulting in the differing compressive fracture strength and elastic modulus behaviour evident in the current study.

The compressive fracture strength of brittle dental materials such as GI restoratives is dependant on the distribution of defects in the specimens when tested (Davies, 1973; Jayatilaka and Trustrum, 1977). Specimens containing visible surface defects were discarded in the current study prior to testing, however, it was not possible to visually detect internal defects. The variation in size, shape, orientation and severity of the defects in a batch of specimens invariably results in a range of compressive fracture strengths which can be as much as $\pm 25\%$ from the mean (Jayatilaka and Trustrum, 1977; Glandus and Boch, 1984; Bergman, 1984). To assess the internal porosity in GIs, researchers have employed a range of techniques including image analysis of 40 μm film thicknesses (Mitchell and Douglas, 1997), scanning electron microscopy (Nomoto and McCabe, 2001), X-ray microfocus computerised tomography (Nomoto *et al.*, 2004), stereological methods (Fleming *et al.*, 2003; Fleming and Zala, 2003; Fleming *et al.*, 2006) and mercury intrusion porosimetry (Milutinovic-Nikolic *et al.*, 2007). The technique reported by Mitchell and Douglas (1997) used image analysis software (Optimas, version 5.2; Optimas Corporation, WA, USA) to detect large ($> 0.01 \text{ mm}^2$) and small ($> 0.01 \text{ mm}^2$) pores in a GI luting cement with a film thickness

of 40 μm . To enable detection of large pores by the computer program, a line had to be manually drawn around each pore using the computer software. To detect the small pores, the area boundaries surrounding the pores had to be manually set which meant that porosity determination was influenced by the operator. Furthermore, the porosity population determined was more likely representative of the porosity encountered clinically for GI luting cements rather than for GI restoratives (Mitchell and Douglas, 1997) given the 40 μm film thickness investigated. Nomoto and McCabe (2001) used scanning electron microscopy images of the fractured surfaces of cylindrical specimens tested in compression to highlight pore inclusions which may have resulted in failure. However, the fractured surface represented a two-dimensional cross-section of the specimen and is therefore not representative of the cylindrical specimen “as a whole”. Additionally, it is questionable that fractured cylindrical specimens are a viable option for porosity analysis as the majority of the specimen has disintegrated following compression testing. Nomoto *et al.* (2004) also assessed the internal porosity in cylindrical GI restorative specimens using X-ray microfocus computerised tomography where 201 X-ray images of a cylindrical specimen (6 mm height and 4 mm diameter) were taken horizontally along the length of the specimen and reconstructed using computer software (TRI/3D-Bon; Ratoc System Engineering Co., Tokyo, Japan) to form a three-dimensional image of the cylindrical specimen. The size, number and total volume ratio of pores in the cylindrical specimens were determined from the three-dimensional image using the computer software, however, pores of less than 26 μm diameter could not be detected and two connected pores were counted as one giving a spurious result (Nomoto *et al.*, 2004). As a result, X-ray microfocus computerised tomography does not appear to be sensitive enough in terms

of resolution to accurately assess the internal porosity in cylindrical GI restorative specimens, a fact possibly emphasised by the lack of literature on the subject area.

The internal porosity in GI restorative specimens has also been assessed using stereological methods (Fleming *et al.*, 2003; Fleming and Zala, 2003; Fleming *et al.*, 2006) according to the theory outlined by Weibel (1979a,b) where cylindrical specimens were serially sectioned transversally at 0.4 mm increments and the pores in each section were automatically isolated using image analysis software (Optimas, version 4.0; Bioscan Inc., WA, USA). It is likely that the two-dimensional cross sections through the cylindrical specimens do not determine the diameter of a pore at its largest point. Pores may be sectioned at their lowest detectable diameter and are therefore not representative of the true pore diameter. As a result the stereological technique provided a “lower bound” approximation of the true pore size distribution in the cylindrical specimens (Fleming *et al.*, 1999b, 2003). Recently, Milutinovic-Nikolic *et al.* (2007) reported a method to quantify the pore distribution in cylindrical GI cement specimens using high pressure mercury intrusion porosimetry. Mercury is forced into the pores of the specimen at pressures ranging from 0.1 to 200 MPa, where the greater pressures are required to force the mercury into the smallest pores. However, the use of mercury intrusion porosimetry to determine the distribution of pores in GIs does not seem plausible as one of the requirements of the test is that the specimen is desiccated and tested dry (Abell *et al.*, 1999). Desiccation of GI specimens is likely to cause crazing and cracking (Wang and Darvell, 2009), which will also absorb some of the mercury and skew the porosity measurement.

None of the techniques reported in the dental literature can accurately quantify the distribution of pores in GI restorative specimens. As a result, no method was employed in the current investigation to assess the internal porosity in the cylindrical GI restorative specimens. The coefficient of variation provides an indication of the grouping of the compressive fracture strength data in a group of specimens where a lower value is indicative of a closer distribution of the compressive fracture strength data and a higher value is indicative of a wide distribution of compressive fracture strength data. It is postulated by the author that the coefficient of variation of the compressive fracture strength data would be expected to be influenced by the defects and porosity in the cylindrical GI restorative specimens. In a previous study (Fleming *et al.*, 2003), where the powder content of Chemfil Superior was reduced from 100 to 90, 80 and 50% of that recommended (for a constant volume of liquid), a marked decrease in the maximum pore diameter (assessed by stereological methods) from 158 to 117, 86 and 51 μm , respectively was reported. However, when the coefficient of variation of the compressive fracture strength data reported by Fleming *et al.* (2003) for Chemfil Superior was determined (by the author of the current study), no significant trend was evident with decreasing powder content ($p = 0.108$). In a later study (Fleming *et al.*, 2006), when the powder content of the encapsulated GI restorative Ketac Fil Plus Aplicap was reduced from 100 to 90, 85 and 80% of that recommended, the maximum pore diameter was shown to markedly decrease from 112 to 89, 50 and 43 μm , respectively when mixed in the Capmix and from 99 to 72, 45 and 44 μm , respectively when mixed in the Rotomix. The coefficient of variation of the compressive fracture strength data for Ketac Fil Plus Aplicap reported by Fleming *et al.* (2006) significantly decreased as the powder content was reduced when mechanically mixed in the Capmix ($p = 0.013$) and the Rotomix ($p = 0.012$). In the

current study, a significant decrease in the coefficient of variation of the compressive fracture strength data with reducing powder content was shown for Ketac Fil Plus, Chemfil Superior and Ketac Molar Easymix, however, no significant trend was evident for the other GI restoratives investigated (Fuji II, Fuji IX and ChemFlex) (Available in Appendices). The variation in the coefficient of variation of the compressive fracture strength data was less than 10% for all materials and was therefore considered unlikely to affect subsequent analyses. There is not sufficient evidence to confirm that the coefficient of variation of the compressive fracture strength data is influenced by the defects and porosity in the cylindrical GI restorative specimens. However, the stereological method employed by Fleming *et al.* (2003, 2006) to assess the porosity in the cylindrical specimens, where only three cylindrical specimens were analysed per group, may not be entirely representative of the internal porosity in a specimen group of 20 or 30 specimens. Therefore, there are difficulties correlating the porosity determined in cylindrical GI restorative specimens using stereological methods and the coefficient of variation of the compressive fracture strength data.

The GI restoratives prepared using the manufacturers' recommended powder to liquid mixing ratio were the most viscous of all the groups investigated and were therefore more difficult to mix in the recommended time to ensure a homogeneous consistency and a uniform dispersion of glass particles in the set GI restorative structure. Insufficient mixing of the GI restorative may result in an increased number of defects in the set structure which can act as crack initiating sites when the specimen is stressed under loading (Fleming *et al.*, 2001, 2003). In addition, the more viscous GI restoratives prepared at the manufacturers' recommended powder to liquid mixing

ratio were more difficult to apply to the split-mould within 60 s of the completion of mixing and therefore were more prone to the incorporation of air bubbles in the cylindrical GI restorative specimens (Fleming *et al.*, 2003). It is suggested that the combination of defects introduced into the GI restorative during mixing and the air bubbles introduced into the cylindrical specimens during application to the split-mould resulted in the coefficient of variation of the compressive fracture strength data values reported for the control groups. As the powder content was reduced from that recommended, the GI restoratives became easier to mix and flowed more readily into the split-mould. Therefore, it is likely that less defects and air bubbles were introduced to the specimens as the powder content was reduced (Fleming *et al.*, 2003) which possibly resulted in the significantly decreased coefficient of variation of the compressive fracture strength data reported for Ketac Fil Plus, Chemfil Superior and Ketac Molar Easymix.

It cannot be assumed that GI restoratives from different manufacturers will show exactly the same pattern of variability and that different products will be more or less sensitive to operator variability on mixing. The patterns of variability will predominantly be influenced by the type (Kent *et al.*, 1979; Nicholson, 1998), volume and particle size distribution of the glass particles (Crisp *et al.*, 1976), the type (Crisp *et al.*, 1980), concentration (Crisp *et al.*, 1977; Wilson *et al.*, 1977b) and molecular weight (Hill *et al.*, 1989; Wilson *et al.*, 1989) of the polyalkenoic acid element and the amount of polyalkenoic acid contained in dried form in the glass powder (Prosser *et al.* 1984; Guggenberger *et al.*, 1998) or in solution in the liquid (Wilson and Nicholson, 1993).

5.4.2.2 *In vitro* Wear Resistance

A progressive significant increase in the mean total volumetric wear and mean maximum wear depth for the hand-mixed GI restoratives was shown with reducing powder content (Tables 4.4.5 and 4.4.6, respectively). Behr *et al.* (2008) recently assessed the *in vitro* wear resistance of a GI luting cement (Ketac Cem; 3M ESPE, Seefeld, Germany) using the ACTA wear machine when the powder content was reduced from that recommended by the manufacturer (100%) to 86 and 63% for a constant weight of liquid. The wear regime employed a stainless steel antagonist which applied a force of 15 N for 200,000 cycles and the wear track produced was assessed using profilometry. The specimens prepared with 63% of the recommended powder content failed during wear testing and therefore could not be analysed. The authors reported a near double increase in the mean wear depth of the wear track produced on the surface of the specimen by the ACTA wear machine for the group prepared with 86% of the recommended powder content ($102 \pm 9 \mu\text{m}$) compared with the control group ($54 \pm 12 \mu\text{m}$). There was not such a marked increase in the mean total volumetric wear or the maximum wear depth reported in the current study when the powder content of the GI restoratives was reduced from 100 to 90 or 80% of that recommended by the manufacturer. However, the powder to liquid mixing ratio and viscosity of GI luting cements are markedly lower than that used for GI restoratives and therefore GI luting cements would be expected to be less resistant to wear. The wear resistance of GI restoratives can be attributed to the reinforcing glass particles (Xie *et al.*, 2000), which resist crack growth when a load is applied (Brune and Smith, 1982; Fleming *et al.*, 2001, 2003) and protect the polymeric matrix from wear (Bayne *et al.*, 1992). The cyclical nature of the OHSU wear regime would be expected to continually loosen and dislodge the reinforcing glass particles from the GI restorative

surface and expose the underlying GI restorative matrix to the wear regime (Pelka *et al.*, 1996; Kunzelmann *et al.*, 2003). Therefore, when the volume of the reinforcing glass particles in the GI restoratives was reduced there was less resistance to the wear regime of the OHSU which resulted in the progressive increases in the mean total volumetric wear and mean maximum wear depth observed.

There was a significant increase in the coefficient of variation of the total volumetric wear data for one of the GI restoratives investigated (Ketac Fil Plus) with reducing powder content, however, there was no significant difference for the other materials tested (available in Appendices). The coefficient of variation of the maximum wear depth data for Fuji II was significantly increased as powder content was reduced but there was no significant difference evident for the other materials. There does not appear to be a trend in the coefficient of variation data for the mean total volumetric wear and the mean maximum wear depth data and as a result it is difficult to interpret the data reported in the current study. Traditionally, the *in vitro* wear resistance data reported in the dental literature has large standard deviations (Heintze, 2006) when compared with other mechanical property data such as mean compressive fracture and flexure strengths and mean elastic moduli. Similar findings were shown in the current investigation which may have masked any trend in the coefficient of variation of total volumetric wear data and the maximum wear depth data.

5.4.2.3 Clinical Implications

ISO 9917-1 states that four out of every five cylindrical GI restorative specimens prepared and tested achieve a minimum compressive fracture strength of 100 MPa regardless of whether the restoratives are indicated for anterior or posterior use.

Clearly when manipulated at the manufacturers' recommended powder to liquid mixing ratio and tested using the protocol employed in the current study each of the three anterior and three posterior GI restoratives fulfil the ISO specification of 100 MPa easily even allowing for the criteria specified in ISO 9917-1. However, it is clear from the operator variability of a GI restorative (Billington *et al.*, 1990) and a zinc phosphate luting cement (Fleming *et al.*, 1999) that the manufacturers' recommended powder to liquid mixing ratios are not commonly employed clinically and that inferior restoratives and cements are routinely used in clinical practice. Hand-mixed GI restoratives are susceptible to operator variability due to the inaccurate dispensing of the powder and liquid constituents using the manufacturers' recommended scoop (Wilson and McLean, 1988a; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2003; Mount, 2005) and dropper bottle (Eames *et al.*, 1977; Billington *et al.*, 1990; Fleming *et al.*, 1999a, 2003; Mount, 2005). It is suggested that powder to liquid mixing ratio variations are further exacerbated in the clinical environment when scoop and dropper bottle systems are not used and the powder and liquid constituents are mixed by 'eye' to the desired consistency of the operator (Fleming *et al.*, 1999a, 2003).

A clinical simulation assessing the powder to liquid mixing ratios routinely employed clinically for a GI restorative (ChemFil II, Dentsply, Reichenaustrasse, West Germany) by 22 dental surgery assistants showed that the mean powder content utilised was 74% of that recommended by the manufacturer for a constant volume of liquid (Billington *et al.*, 1990). It was also reported that individual dental surgery assistants regularly achieved consistent mixes, however, inter-operator variability was considerable (Billington *et al.*, 1990). None of the dental surgery assistants assessed achieved the manufacturers' recommended powder to liquid mixing ratio with powder

contents as low as 37% (for a constant volume of liquid) routinely being employed (Billington *et al.*, 1990). A preliminary investigation by the author showed that the preparation of GI restoratives with 37% of the manufacturers' recommended powder content (for a constant weight of liquid) resulted in GI restoratives which had not set after 1 h incubation in the water-bath at 37 ± 1 °C and therefore could not be included in the current investigation which followed the specimen manufacturing procedure outlined in ISO 9917-1 : 2003. When the powder content of the GI restoratives was reduced from 100 to 50% of that recommended by the manufacturers (for a constant weight of liquid) the mean compressive fracture strength decreased by 32% for Ketac Fil Plus, 40% for Fuji II, 45% for Ketac Molar Easymix, 26% for Fuji IX and 35% for ChemFlex. If the compressive fracture strength data for the GI restorative groups prepared with 50% of the recommended powder content for a constant weight of liquid is assessed using the criteria specified in ISO 9917-1 a clear fail is evident for five of the materials tested while one material passes (Fuji IX). Therefore, the compressive fracture strength test specified in ISO 9917-1 is limited in scope as it cannot predict the performance of the restorative or luting material in clinical practice (Fleming *et al.*, 2001). This emphasises the view of Wilson (1975) that the compressive fracture strength provided an assessment of the "quality of the cement" rather than a "predictive value" of "direct clinical significance" and that cements with compressive fracture strengths significantly lower than the 100 MPa value recommended were "unsatisfactory and deficient in other respects". Therefore, while the compressive fracture strength of 100 MPa is arbitrarily chosen in ISO 9917-1 it does not have any "real" clinical significance, since reduced powder contents are routinely employed in clinical practice as a result of operator variability, but the use of GIs with reduced powder contents may be problematic when employed clinically.

The mechanical properties of GIs are susceptible to the effects of exposure to moisture during setting (Causton, 1981; Mount and Makinson, 1982). Exposure to moisture can cause the loss of aluminium ions from the cement forming reaction (Crisp *et al.*, 1976) which reduces the level of cross-linking in the setting GI and reduces the mechanical properties (Wilson *et al.*, 1979). The employment of a powder to liquid mixing ratio below that specified by the manufacturers will increase the working and setting times and therefore increase the time available for moisture contamination of the GI in the oral environment during placement and finishing. In the oral environment, dissolution (Earl and Ibbetson, 1986) and erosion (Knibbs and Walls, 1989) of the constituents of GIs are also reported to occur (Forss, 1993). When powder to liquid mixing ratios below that recommended by the manufacturers are employed, the volume of reinforcing glass particles is reduced and therefore more of the GI matrix is exposed to the erosive and dissolution potential of the oral environment which would be expected to result in reduced clinical performance. Additionally, GIs have been reported to have a pH of approximately 2.0 within the first minute of mixing when prepared using the manufacturers' recommended powder to liquid mixing ratio (Smith and Ruse, 1986; Wasson and Nicholson, 1993). As the setting reaction proceeds the pH gradually increases towards neutrality and 24 h after the commencement of mixing reaches a value of approximately 6.0 (Smith and Ruse, 1986; Wasson and Nicholson, 1993). Reducing the powder content for a constant weight of liquid for GIs increases the proportion of the unreacted acidic liquid and therefore increases the acidity of the setting cement. In addition, the time that the GI remains at low pH is lengthened which may compromise the tooth structure and as a result the restoration.

Lucarotti *et al.* (2005b), reported on the outcome of direct restorations placed in the GDS of England and Wales between 1991 and 2001 in terms of restoration type and re-intervention. A total of 503,965 tooth restoration occasions were analysed for over 80,000 adult patients using a modified Kaplan-Meier analysis. In the GDS, GIs may not be placed in load bearing situations and were therefore predominantly placed in Class IV and Class III cavities. The one, five and ten year survival rates for the 63,549 GI tooth restoration occasions were 84, 53 and 38%, respectively. The GI restorations performed markedly worse than single surface amalgam restorations (93, 72 and 58%, respectively) and just worse than resin-based composite restorations (87, 58 and 43%, respectively). While the figures reported for GI and resin-based composite restorations are poor at best, they probably accurately reflect the true performance of tooth coloured restorations in the 'real' world of dentistry. The performance of the GI restorations became much clearer when the authors of the study further examined the data in terms of time of placement (Burke *et al.*, 2005b). GI restorations were reported to perform "less well as the study progresses" from 1991 to 2001. In view of the considerable development of GI restoratives throughout the 1990s, the "less well" performance "as the study progresses" is difficult to explain. The authors (Burke *et al.*, 2005b) tentatively suggested that the decline in performance was due to either an "operator effect" or simply because dentists did not switch to new improved materials when they became available. The operator effect suggested by Burke *et al.* (2005b) was related to the dentists becoming "more familiar with the handling and clinical use of the material" with time and as a result stretching the limitations of the material in terms of attempting "to place larger and larger restorations in that material". The

comment regarding the slow uptake of new improved materials by dentists when they became available was conjecture by the authors (Burke *et al.*, 2005b).

It is suggested by the author of the present study that the operator effect suggested by Burke *et al.* (2005b) could more likely have been the result of powder to liquid mixing ratios below that recommended by the manufacturers being routinely used clinically in line with the observations for GI restoratives in the study by Billington *et al.* (1990). The laboratory implications of employing reduced powder contents (for a constant weight of liquid) for GI restoratives has been shown in the current study to be detrimental in terms of the mechanical properties (compressive fracture strength, elastic modulus and *in vitro* wear resistance). In addition, for clinically placed GI restoratives, the increased likelihood for moisture contamination (Causton, 1981; Mount and Makinson, 1982), erosion (Knibbs and Walls, 1989), dissolution (Earl and Ibbetson, 1986) and the increased time the GI restorative remains at low pH levels at the tooth restorative interface (Smith and Ruse, 1986; Wasson and Nicholson, 1993) with reduced powder contents could manifest itself as the poor clinical performance shown by Burke *et al.* (2005b). In the present investigation Chemfil Superior was shown to be more sensitive to operator variability than the other GI restorative materials investigated demonstrating an exacerbated deterioration of the compressive fracture strength, elastic modulus and *in vitro* wear resistance when prepared with reduced powder contents below 80% due to the anhydrous formulation. Chemfil Superior was the GI restorative market leader in the UK throughout the timeframe of the study by Burke *et al.* (2005b) from 1991 to 2001 (Caple, 2006), which would agree with the suggestion of Burke *et al.* (2005b) that newer materials were slowly adopted in clinical practice. Therefore, the author of the present study suggests that

the poor performance of GI restorations placed in the GDS of England and Wales between 1991 and 2001 (Lucarotti *et al.*, 2005b; Burke *et al.*, 2005b) could be due in part to operator variability in GI restoratives placed clinically, however, the performance could have been further compromised if anhydrous GI formulations were used by the operators.

5.5 Influence of Method of Mixing

5.5.1 Compressive Fracture Strength and Elastic Modulus

There were significant increases in the mean compressive fracture strength for Fuji IX Fast Capsule and ChemFlex in Caps when mixed in the Rotomix compared with the Capmix. These results are not in agreement with the study of Fleming and Zala (2003) who reported no significant differences in the mean compressive fracture strengths for Fuji IX Fast Capsule and ChemFlex in Caps mixed using the Capmix or Rotomix. Fleming and Zala (2003) determined the pore distribution in the cylindrical GI restorative specimens using stereological methods. It was shown that mechanically mixing the Fuji IX Fast Capsule in the Rotomix reduced the maximum pore diameter in the cylindrical specimens from 140 to 43 μm and reduced the number of pores present ($> 26 \mu\text{m}$) from 9.4 ± 7.2 to 1.3 ± 1.8 compared with mixing using the Capmix. However, when the coefficient of variation of the compressive fracture strength data for the Fuji IX Fast Capsule specimen groups reported by Fleming and Zala (2003) were determined by the author of the current study, no difference in the coefficient of variation of the compressive fracture strength data was shown for the groups mechanically mixed using the Rotomix (0.12) compared with the Capmix (0.12). Given that the coefficient of variation of the compressive fracture strength data represents the distribution of the compressive fracture strengths reported, it was expected that the groups containing markedly reduced internal porosity would have a narrower distribution of compressive fracture strengths and therefore a lower coefficient of variation. However, the coefficient of variation of the compressive fracture strength data reported by Fleming and Zala (2003) for Fuji IX Fast Capsule mechanically mixed in the Capmix and Rotomix was the same which suggests that the internal porosity in the cylindrical specimens was similar. The pore distribution data

reported by Fleming and Zala (2003) for the ChemFlex in Caps specimen groups mechanically mixed using the Capmix and Rotomix showed that while the largest pore diameter of the ChemFlex in Caps specimens was essentially unchanged (increased from 49 to 62 μm), the number of pores ($> 26 \mu\text{m}$) was moderately decreased from 8.0 ± 2.7 to 5.7 ± 3.3 when the Rotomix was employed compared with the Capmix. The coefficient of variation of the compressive fracture strength data reported by Fleming and Zala (2003) for ChemFlex in Caps showed a marked decrease for the specimens mechanically mixed in the Rotomix (0.12) compared with the Capmix (0.16). These findings make interpretation of the results in the current study difficult, as it is not possible to directly link the marked differences in the coefficient of variation of the compressive fracture strength data for Fuji IX Fast Capsule and ChemFlex in Caps when mixed in the Rotomix compared with the Capmix with differences in the pore distribution. It appears that the stereological method employed by the authors (Fleming and Zala, 2003), where three cylindrical specimens were analysed for each group, may not be entirely representative of the internal porosity in a specimen group of 30 specimens and provided at best a “lower bound” approximation of the true pore size distribution in the cylindrical specimens (Fleming *et al.*, 1999b, 2003). The stereological method is a destructive test and the cylindrical specimen cannot be tested in compression afterwards so no correlation between the internal porosity and the compressive fracture strength of a single cylindrical specimen can be made. Unfortunately, no other technique has proved successful in quantifying the porosity distribution in GI restorative specimens so it remains difficult to show potential differences in the internal porosity and link them to significant increases in the mean compressive fracture strength.

The mean compressive fracture strength data for Ketac Fil Plus Aplicap and Ketac Molar Aplicap reported in the current study are in agreement with the dental literature where no significant differences in the mean compressive fracture strengths were reported for the GI restoratives mechanically mixed in the Capmix or Rotomix (Nomoto and McCabe, 2001; Fleming and Zala, 2003; Fleming *et al.*, 2006). The pore distribution in cylindrical specimens of Ketac Fil Plus Aplicap were also analysed by Fleming and Zala (2003) and Fleming *et al.* (2006) using stereological methods. Fleming and Zala (2003) reported no difference in the largest pore diameter (118 and 122 μm , respectively) and a moderate increase in the number of pores ($> 26 \mu\text{m}$) from 6.3 ± 7.9 to 8.3 ± 3.8 for the Ketac Fil Plus Aplicap specimens mechanically mixed in the Rotomix compared with the Capmix. However, determining the coefficient of variation of the compressive fracture strength data reported by Fleming and Zala (2003) showed a decrease for the Ketac Fil Plus Aplicap specimens mechanically mixed in the Rotomix (0.21) compared with the Capmix (0.24) when the porosity distribution data reported would suggest the opposite. Similarly, when Ketac Fil Plus Aplicap was examined in a later study by Fleming *et al.* (2006), no difference in the largest pore diameter (111 and 99 μm , respectively) was reported, while an increase in the number of pores ($> 26 \mu\text{m}$) from 5.0 ± 5.7 to 13.0 ± 7.4 was shown following mechanical mixing in the Rotomix compared with the Capmix. However, the coefficient of variation of the compressive fracture strength data reported by Fleming *et al.* (2006) was increased for Ketac Fil Plus Aplicap mechanically mixed in the Rotomix (0.13) compared with the Capmix (0.10). These findings reemphasise that it was not possible to correlate the coefficient of variation of the compressive fracture strength data with the pore distribution determined using stereological methods.

The study by Nomoto *et al.* (2004) reported that mechanically mixing Ketac Molar Aplicap in the Rotomix resulted in a reduction in the volume percentage of pores (from 0.22 ± 0.23 to 0.06 ± 0.12), the total number of pores (from 53 ± 16 to 28 ± 12) and maximum diameter of pores (from 440 ± 220 to 250 ± 160 μm) compared with the Capmix when the cylindrical specimens were assessed using X-ray microfocus computerised tomography. The porosity data reported by Nomoto *et al.* (2004) correlates with the coefficient of variation of the compressive fracture strength data determined from the study of Nomoto and McCabe (2001) which shows a reduction for Ketac Molar Aplicap mechanically mixed in the Rotomix (0.05) compared with the Capmix (0.10). However, there were three years between the studies and there is no indication from the studies that the specimens were mixed and placed by the same operator. Also, there is no data reported by the authors (Nomoto *et al.*, 2004) which directly correlates the internal porosity in a single GI restorative specimen to its specific compressive fracture strength. The porosity data reported by Nomoto *et al.* (2004) is excessive and it is unlikely that Ketac Molar Aplicap specimens mechanically mixed using the Capmix and Rotomix with average maximum pores of 440 ± 220 and 250 ± 160 μm , respectively could produce mean compressive fracture strengths of 222 ± 23 and 238 ± 13 MPa, respectively. In addition, The sensitivity of the X-ray microfocus computerised tomography technique reported by Nomoto *et al.* (2004) in terms of resolution may not be accurate enough to assess the internal porosity in cylindrical GI restorative specimens as pores of less than 26 μm are not detected and two connected pores are counted as one (Nomoto *et al.*, 2004). This may suggest a reason why there is a the lack of literature relating to the use of X-ray microfocus computerised tomography in the dental literature. The porosity data reported in the dental literature for Fuji IX Fast Capsule, ChemFlex in Caps, Ketac Fil

Plus Aplicap and Ketac Molar Aplicap (Fleming and Zala, 2003; Nomoto *et al.*, 2004; Fleming *et al.*, 2006) does not indicate that the Rotomix is more beneficial at reducing the porosity for GI restoratives than the Capmix as is suggested by the manufacturer of the machines. However, there is currently no technique reported in the dental literature which can accurately determine the internal porosity in cylindrical specimens.

The mean elastic modulus was significantly increased for Fuji IX Fast Capsule and ChemFlex in Caps when mixed in the Rotomix compared with the Capmix. In a recent study, Prentice *et al.* (2005) reported that increasing the mixing time of an experimental encapsulated GI restorative in 2 s increments to 12 s progressively increased the mean elastic modulus due to the increased homogeneity of the viscous mix. It is suggested that the increased mixing time of the Rotomix (11 s) in comparison with the Capmix (10 s) for Fuji IX Fast Capsule and ChemFlex in Caps may have accelerated the setting reaction of the GI restoratives and therefore increased the mean elastic modulus determined at 24 h (Prentice *et al.*, 2005). Prentice *et al.* (2005) reported that a more homogeneously mixed GI restorative would have an increased elastic modulus as it would contain less undissolved polymer in the restorative which is more susceptible to moisture, erosion and fracture. It is possible that increasing the mechanical mixing time increased the energy input to the capsule which reduced the amount of undissolved polymer present in the restorative (Prentice *et al.*, 2005) and therefore increased the homogeneity of the GI restorative mix. A more homogeneously mixed GI restorative would be expected to contain an increased number of chemical bonds between the reinforcing glass particles and the polymeric matrix which may result in an increased mean elastic modulus (Prentice *et al.*, 2005).

However, the increased mixing time of the Capmix (15 s) compared with the Rotomix (13 s) for Ketac Molar Aplicap did not result in increased mean elastic modulus. The study by Prentice *et al.* (2005) also reported no significant increase in the mean elastic modulus of the experimental encapsulated GI restorative when the mechanical mixing time was increased from 12 to 14 s. It was suggested by the authors (Prentice *et al.*, 2005) that the initial gelation phase of the setting reaction of the GI restorative had occurred after 12 s and that continued mixing may have broken the gelation matrix which prevented an increase in the mean elastic modulus.

It cannot be assumed that mechanical mixing in the Rotomix compared with the Capmix will result in the exact pattern of variability in the compressive fracture strength and elastic modulus data for all the encapsulated GI restoratives investigated. The overall effects may be influenced by the powder to liquid mixing ratio (Nomoto and McCabe, 2001; Fleming *et al.*, 2006), the initial viscosity of the cement mix (Nomoto and McCabe, 2001; Fleming *et al.*, 2006), the capsule design (Fleming and Zala, 2003) and the flow which is influenced by the exit diameter of the nozzle (Fleming *et al.*, 1999b, 2002).

5.5.2 *In vitro* Wear Resistance

There were no significant differences found in the mean total volumetric wear and mean maximum wear depth for the encapsulated anterior and posterior GI restoratives investigated in the current study when mechanically mixed in the Capmix or Rotomix. Previously, the assessment of the *in vitro* wear resistance of Ketac Fil Aplicap, Ketac Molar Aplicap and Fuji IX following mechanical mixing in either the Capmix or Rotomix was conducted by Lohbauer *et al.* (1999) using the ACTA wear machine.

Lohbauer *et al.* (1999) reported that although the encapsulated GI restoratives mixed in the Rotomix were more homogeneous and contained less porosity than the restoratives mixed in the Capmix when observed using scanning electron microscopy, there was no significant difference in the mean wear depths measured. However, the porosity level when measured using scanning electron microscopy is ambiguous as a two-dimensional cross-section of a specimen is not a true representation of the pore distribution throughout the specimen as a whole. In addition, the study by Lohbauer *et al.* (1999) was an abstract and no extensive follow on study regarding the *in vitro* wear resistance of encapsulated GI restoratives mechanically mixed using either the Capmix or Rotomix was conducted by the authors. Therefore, little or no information on the wear testing regimen and wear facet analysis utilised in the study (Lohbauer *et al.*, 1999) was provided by the authors and as a result, there is difficulty in fully interpreting the results presented.

5.5.3 Clinical Implications

In 1990, it was reported that powder contents as low as 37% (Billington *et al.*, 1990) of that recommended by the manufacturer (for a constant volume of liquid) were routinely used clinically for a hand-mixed GI restorative. Although GI restoratives have undergone significant developments since the study by Billington *et al.* (1990) and newer materials are claimed by manufacturers to be easier to mix than their predecessors (Peez and Frank, 2006), the same methods of dispensing the powder and liquid constituents, namely scoop and dropper bottles are still employed. In addition, the author suggests that the mixing of the powder and liquid constituents by 'eye' to the desired consistency of the operator (Fleming *et al.*, 1999a, 2003) may result in the employment of markedly reduced powder contents (below 50%) in clinical practice.

In the current study, significant increases in the mean compressive fracture strength, mean elastic modulus, mean total volumetric wear and mean maximum wear depth for all the encapsulated GI restoratives were evident when compared with their hand-mixed equivalents with the powder content reduced to 60, 70, 70 and 70%, respectively. Encapsulation of GI restoratives eliminates the operator variability associated with hand-mixing (Fleming *et al.*, 1999b; Nomoto and McCabe, 2001) and provides consistent mixes prepared to the manufacturers' recommended powder to liquid mixing ratio where the mixing technique and times are standardised. Therefore, it is suggested that employing encapsulated GI restoratives will provide the operator with restoratives with increased compressive fracture strength, elastic modulus and *in vitro* wear resistance when compared conventional hand-mixed GI restoratives which was susceptible to operator variability. As a result, the author advocates the use of encapsulated GI restoratives clinically, provided the operators are fully aware of the recommended activation procedure, mixing time and extrusion technique for the GI restorative being employed.

Since many of the studies in the dental literature fail to follow the instructions of ISO 9917-1 stringently, there is little correlation of the 24 h mean compressive fracture strength reported for the same GI restoratives prepared at different test centres.

The assessment of *in vitro* wear resistance in terms of wear depth is inappropriate as it depends on the location and direction from which the depth is measured. Volumetric wear is a more appropriate wear parameter as the volume of material removed at one or more locations can be combined.

Despite the optimism arising from other reported studies, the use of un-modified Ca-MMT clay has no appreciable benefit for the compressive fracture strength and *in vitro* wear resistance of GI restorative materials.

There was a benefit to the compressive fracture strength and *in vitro* wear resistance of the GI restorative materials with the addition of ADA-MMT clay at low concentrations (≤ 1.0 wt.%), however, the benefits were specific to individual GI restoratives.

The effects of operator variability in terms of preparing hand-mixed GI restoratives with reduced powder contents are striking, as significant decreases in the compressive fracture strength, elastic modulus and *in vitro* wear resistance are evident when powder contents of less than 80% of the recommended are employed.

Mechanically mixing encapsulated GI restoratives provides a solution to the operator variability associated with hand-mixed GI restoratives regardless of the method used to mechanically mix the encapsulated GI restoratives.

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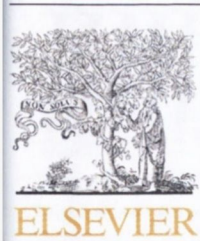
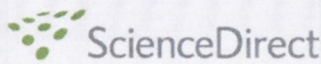
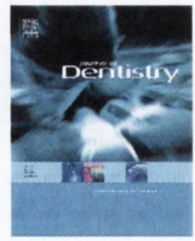
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The influence of montmorillonite clay reinforcement on the performance of a glass ionomer restorative

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ABSTRACT

Objectives: A pristine calcium montmorillonite (Ca-MMT) and an organically modified 12-amino-dodecanoic acid treated montmorillonite (ADA-MMT) clay were evaluated to determine the reinforcement effect on the performance of a glass ionomer (GI) restorative ChemFil[®] Superior (Dentsply DeTrey, Kanstanz, Germany) to assess the potential as a posterior filling material.

Methods: Mean compressive fracture strengths and standard deviations were determined for groups of 30 cylindrical specimens with 0.5–2.5 wt.% Ca-MMT and ADA-MMT additions to either the powder or the liquid elements of the GI. Working characteristics were assessed using an oscillating rheometer, the interlayer *d*-spacings (d_{001}) of each MMT clay was determined using X-ray diffraction (XRD) and the set cement structure was determined by scanning electron microscopy (SEM).

Results: The addition of up to 1.0 wt.% ADA-MMT resulted in a significant increase in the mean compressive fracture strength of the GI utilising the one-way ANOVA and Tukey test comparisons at $P < 0.05$. When Ca-MMT clay was added to the GI a significant reduction in mean strength was recorded ($P < 0.05$). MMT clay addition to the powder and liquid element of the GI in excess of 1.0 wt.% resulted in no significant differences in working characteristics although increases in setting times were evident for MMT addition up to 1.0 wt.%. XRD patterns identified the d_{001} peaks for Ca- and ADA-MMT at 2θ angles of 8.44° and 5.07° and d_{001} spacings of 1.04 and 1.74 nm, respectively.

Conclusions: The increased interlayer *d*-spacings recorded for ADA-MMT clay demonstrates that the clay had expanded layers which may have provided an increased opportunity for the polyacrylic acid chains of the GI restorative to diffuse into the MMT galleries. It is postulated that the increased interlayer *d*-spacings for the ADA-MMT clay had a positive reinforcing effect on the GI compared with the Ca-MMT clay where no increased performance was identified. The study has highlighted the potential for increasing the performance of GI restoratives when using an organically modified clay as a reinforcement which could increase the potential of GIs as posterior filling materials.

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1. Introduction

Glass ionomers (GIs) have been used in various dental applications including luting cements, cavity liners and bases

since their development by Wilson and Kent.¹ The reported advantages that GI cements possess over traditional dental cements, such as silicates and zinc phosphates, are the ability to chemically adhere to sound tooth structure without any

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pre-treatment and the ability to release fluoride over time.² GI cements are easier to manipulate than many dental materials and can be conventionally mixed by hand spatulation or alternatively by mechanical trituration. A further application of GIs is as restorative materials where the powder to liquid mixing ratio is increased to facilitate increased loads, but unfortunately they are too weak to withstand the masticatory loads encountered in the posterior region of the mouth due to their poor mechanical properties.³ As a result GI restoratives are therefore only advocated for class V lesions and cavities and class III cavities in posterior teeth.⁴ To improve the mechanical properties of GI cements, resin-modified GI cements (RMGICs) were developed and displayed significantly increased compressive fracture strength and fracture toughness for single-edge-notch (SEN) bar-shaped specimens.⁵ However, RMGICs have limited working times due to their sensitivity to ambient light,⁶ a tendency to absorb water⁷ and require pre-treatments like etching, conditioning and priming in order to achieve good chemical bonding to tooth structure⁸ which limits their appeal clinically.

Various fillers have been applied to conventional GI restoratives to improve their mechanical properties and enable posterior use clinically, including alumino-silicate fibres,⁹ bioactive glass particles,¹⁰ zirconia¹¹ and hydroxyapatite¹² with varying degrees of success. Kobayashi et al.⁹ added short alumino-silicate fibres to a conventional GIC and reported a linear increase in diametral tensile strength with the incorporation of up to 60 mass% fibre content. Yli-Urpo et al.¹⁰ added bioactive glass particles to the powder of a conventional GI cement at 10 and 30 wt.% but compromised the compressive fracture strength, Young's modulus and Vickers hardness. The addition of yttria stabilised zirconia powders to GI cements was investigated by Gu et al.¹¹ and a significant reduction in the mean compressive fracture strengths was reported when compared with conventional GI cements. Hydroxyapatite was used to replace 8 wt.% of glass powder in Fuji IX GP by Lucas et al.¹² and significantly increased the SEN fracture toughness of bar-shaped specimens loaded in transverse bending following 24 h water immersion.¹³

Montmorillonite (MMT) clay additions have been shown to significantly improve the mechanical properties of polymers such as Nylon^{14,15} and acrylic.¹⁶ MMT is a tri-layered smectite clay consisting of stacked platelets constructed of an alumina octahedral layer sandwiched between two silica tetrahedral layers.¹⁷ MMT clays may be treated by ion-exchanging organic cationic surfactants (intercalants), such as 12-amino-dodecanoic acid to create an organically modified clay (or organo-clay).¹⁸ The ion-exchange process acts to intercalate and/or exfoliate the MMT platelets and make the clay compatible with the parent material. Intercalation is the widening of the interlayer spacing between the clay platelets and can be achieved by the insertion of progressively larger molecules into the interlayer spacing which act to push the layers apart.¹⁹ Exfoliation is the complete separation of the platelets and is achieved when the interlayer space becomes too wide for the weak van der Waals forces to keep the platelets together.¹⁹ X-ray diffraction (XRD) has been used repeatedly¹⁷⁻¹⁹ to determine the level of intercalation or exfoliation within MMT clay reinforced materials. An intercalated clay is

manifested on an XRD pattern by a shifting of the d_{001} peak to a lower 2θ angle whereas the complete elimination of this peak is indicative of an exfoliated system.¹⁷⁻¹⁹ Individual clay platelets have aspect ratios (the ratio of the surface dimensions to the thickness) in the range of 10-1000. The extensive surface area chemically interacts with the parent material to which they are added, providing increased stiffness and strength.¹⁸ The dispersion of the clay platelets within the parent material is of great importance as a uniform dispersion will result in less agglomeration and improve the reinforcing effect of the clay platelets. Scanning electron microscopy (SEM) has also been employed previously to enable an investigation of the MMT clay dispersion within epoxy-clay nanocomposites.²⁰

The two MMT clays used in the current study included a pristine clay, calcium montmorillonite (Ca-MMT) (Süd Chemie, Munich, Germany), and an organically modified clay, 12-amino-dodecanoic acid treated montmorillonite (ADA-MMT) (Nanacor Inc., IL, USA). The ADA-MMT was synthesised by an ion exchange reaction between Na^+ -montmorillonite (with a cation exchange capacity of 110/100 mequiv./g) and 12-amino-dodecanoic acid. To develop a detailed understanding of MMT clay addition to GI restoratives the two clays were added firstly to the powder and secondly to the liquid elements of the GI restorative under investigation at 0.5, 1.0, 1.5, 2.0 and 2.5 wt.% prior to mixing. Preliminary investigations by the authors²¹ highlighted that MMT clay additions in excess of 2.5 wt.%, namely 5.0 and 10.0 wt.%, resulted in restorations that were difficult to mix to a reproducible consistency and as a result the authors have precluded these clay additions from the study. In addition, the incorporation of MMT clay additions in excess of 2.5 wt.%, namely 5.0 and 10.0 wt.%, resulted in a less aesthetic (darker) appearance for the restoratives which further precluded the use of these sample groups.

The current study focussed on the compressive fracture strength of pristine Ca-MMT clay and organically modified ADA-MMT clay reinforced GI restoratives to provide an indication of their potential for posterior use clinically as compressive fracture strength is crucial for posterior restoratives due to the masticatory forces encountered in service.²² In addition, GI restoratives are known to have superior working characteristics compared with resin-based composites and as a result the working and setting times of the pristine Ca-MMT clay and the organically modified ADA-MMT clay reinforced GI restoratives were compared with the conventional GI restorative investigated to ensure MMT reinforcement had no adverse influence on the working characteristics.

The hypothesis proposed in the current study was that MMT reinforcement would improve the compressive fracture strength and influence the working characteristics of the GI restorative investigated. The aim of the study was to investigate the potential for increasing the performance of GI restoratives when using a MMT clay as a reinforcement which could increase the potential of GIs as posterior filling materials. Quantification of the degree of exfoliation was determined by XRD analysis and scanning electron microscopy was employed to illustrate the clays dispersion within the GI restorative matrix.

2. Materials and methods

2.1. Glass ionomer restorative manipulation

The posterior GI restorative used in the current study was ChemFil[®] Superior (Dentsply DeTrey, Kanstanz, Germany). Cylindrical GI restorative specimens (6.0 ± 0.1 mm height and 4.0 ± 0.1 mm diameter) were prepared by a single operator for compressive fracture strength testing by hand mixing 0.925 g of powder with 125 μ l of distilled water to a powder/liquid mixing ratio of 7.4/1.0 g/ml. The restorative was mixed according to the manufacturers' instructions for 40 s whereby the powder was measured onto a glass slab and separated into two equal parts; the liquid was then dispensed onto the glass slab using a pipette (Gilson, Middleton, WI, USA). Half the powder was mixed with the liquid for 20 s, the remainder added and mixed for a further 20 s using a non-corrodible stainless steel spatula. The restorative specimens were created using a PTFE split-mould capable of holding eight specimens which was pre-coated with a PTFE dry film lubricant (Fisher Scientific, Loughborough, UK) to enable the removal of the set restorative specimens. An aluminium jig was covered with an acetate strip and the split-mould assembly was aligned with a wedge and locating pin to ensure equal pressure was applied along the wedge to the entire mould assembly (Fig. 1). The mould was filled within 60 s of the completion of mixing, whereby the restorative was allowed to flow into the mould to minimise the incorporation of air bubbles. The filled mould was covered with a second acetate strip, isolated from the atmosphere with a glass slab, clamped to apply equal pressure along the mould assembly and transferred to a water-bath maintained at 37 ± 1 °C. After 1 h the specimens were removed from the water-bath, inspected and specimens that contained visual defects were discarded. The flat ends of the specimens were ground on P800 silicon carbide (SiC) paper (Beuhler, Lake Bluff, IL, USA) using water as a lubricant to provide two flat parallel ends for uniform contact with the testing machines compressive plates. A series of 30 restorative control specimens (group A) were stored in glass containers filled with distilled water in an incubator maintained at 37 ± 1 °C for a further 23 h prior to testing.

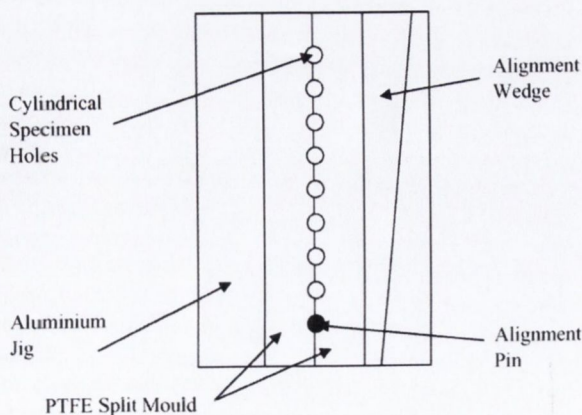


Fig. 1 – The PTFE split-mould assembly used for the manufacture of the nominally identical standard cylindrical restorative specimens.

2.2. Montmorillonite clay manipulation

0.5 wt.% (group B), 1.0 wt.% (group C), 1.5 wt.% (group D), 2.0 wt.% (group E) and 2.5 wt.% (group F) of the pristine Ca-MMT clay (corresponding to 0.005, 0.009, 0.014, 0.019 and 0.023 g, respectively) were weighed on a balance accurate to 0.0001 g (TS4000, Ohaus, Pine Brook, NJ, USA) and added to the 0.925 g of control restorative powder. The powders were mixed together using a spatula for 20 s and the Ca-MMT containing restorative powder was mixed with 125 μ l of distilled water in accordance with the manufacturers' instructions for Chem-Fil[®] Superior so that a minimum of 30 nominally identical cylindrical specimens were created for each specimen group. The organically modified ADA-MMT reinforced GI restorative powder specimens were created using a similar procedure whereby the powders were spatulated together for 20 s prior to manipulation in accordance with the manufacturers' instructions to produce 30 nominally identical cylindrical specimens for each group containing 0.5 wt.% (group G), 1.0 wt.% (group H), 1.5 wt.% (group I), 2.0 wt.% (group J) and 2.5 wt.% (group K) of ADA-MMT clay.

To create the liquid controls the individual weights of Ca-MMT clay corresponding to 0.5 wt.% (group L), 1.0 wt.% (group M), 1.5 wt.% (group N), 2.0 wt.% (group O) and 2.5 wt.% (group P) were measured onto one end of a glass slab and spatulated for 20 s with 125 μ l of distilled water until the clay was dispersed into the liquid. 0.925 g of GI restorative powder was mixed with the clay-liquid mixture in accordance with the manufacturers' instructions so that a minimum of 30 nominally identical cylindrical specimens were created for each specimen group (groups L–P, respectively). The ADA-MMT clay was also added to the liquid of the GI restorative at 0.5 wt.% (group Q), 1.0 wt.% (group R), 1.5 wt.% (group S), 2.0 wt.% (group T) and 2.5 wt.% (group U). The ADA-MMT clay was dispersed into 125 μ l of distilled water and spatulated for 20 s prior to mixing with 0.925 g of GI restorative powder in accordance with the manufacturers' instructions. The resultant nominally identical cylindrical standard specimens were produced using the PTFE split-mould to ensure that 30 specimens were produced for each group (groups Q–U, respectively).

2.3. Compressive fracture strength

The diameter of the specimens was measured at three points with a digital micrometer accurate to 10 μ m (Mitutoyo, Kawasaki, Japan) and the average specimen diameter was recorded. The specimens were tested 'wet' by placing a piece of wet filter paper on the flat ends and a compressive load was applied to the long axis of the specimen at a cross-head speed of 1 mm/min and the maximum load to failure recorded. The procedure was repeated so that 30 nominally identical cylindrical specimens were fractured for each sample group. The compressive fracture strength P (MPa) was calculated for each individual specimen using the following equation:

$$P = \frac{4F}{\pi D^2} \quad (1)$$

where F is the load at fracture in Newton's (N) and D is the average diameter of the specimen in millimetres (mm).

2.4. Statistical analysis

Multiple comparisons of the specimen group means were made using a one-way analysis of variance (ANOVA) and a Tukey's multiple range test was employed at a significance level of $P < 0.05$. However, the strength distributions of quasi-brittle materials like ceramics are more properly described by Weibull statistics rather than mean strength values determined based on a Gauss strength distribution. Consequently, the compressive fracture strength data was ranked in ascending order and a Weibull analysis²³ was performed on the resultant data. The basic form of the Weibull distribution is shown in the following equation:

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (2)$$

where σ_0 and m are the constants. m is known as the Weibull modulus characterising the 'brittleness' of a material. A higher value of m indicates a close grouping of the flexure stress data²⁴ and σ_0 is the normalising constant or the characteristic stress (MPa) which is calculated at 63.21% failure probability. The confidence limits for the groups were calculated and differences were considered to be significant when the confidence intervals did not overlap.²⁵

2.5. Working characteristics

An oscillating rheometer²⁶ was used to determine the working characteristics, namely the working and setting times for the GI restoratives (groups A-P) under investigation. The working time is defined as the period of time from the commencement of spatulation until the cement no longer exhibits sufficient plasticity to render it workable and the setting time is the period of time from the commencement of spatulation until the cement formed takes on a brittle nature.²⁷ Three measurements were taken for both the working and the setting times for each specimen group investigated. The oscillating rheometer operates under the principle that the lower plate of the apparatus oscillates continuously and as the cement sets the viscosity increases, thereby impeding the oscillatory motion until eventually the material sets. The oscillatory motion of the lower plate transfers to a chart recorder moving continuously at 10 mm/min which records the rheometer trace. At the commencement of mixing a timer was started and the cement was mixed for 40 s (in accordance with the manufacturers' instructions) before being transferred to the lower plate of the apparatus. The upper plate was lowered at exactly 60 s and the thickness of the material between the plates was 1 mm. The working time was recorded at 23 ± 1 °C as the time when the width of the rheometer trace was reduced to 95% the original width and the setting time was recorded at 37 ± 1 °C as the time when the rheometer trace was reduced to a straight line.²⁷

2.6. X-ray diffraction

X-ray diffractograms of the two clays, the pristine Ca-MMT and the organically modified ADA-MMT were produced to determine the interlayer basal spacings from the position of the d_{001} peak in the XRD pattern using Bragg's law.²⁸ XRD

analysis was conducted using a D5005 Diffractometer (Bruker AXS, Karlsruhe, Germany) using Cu K α radiation with a wavelength of $\lambda = 0.15418$ nm. The diffraction data was recorded between 2θ angles of 4° and 25° at a step size of 0.014° and a count time of 1 s/step.

2.7. Scanning electron microscopy

A scanning electron microscope (Hitachi S-3500N, Hitachi High Technologies UK, Berkshire, UK) was used under low vacuum conditions, in back-scattered electron mode at an operating voltage of 20 kV, to characterise the morphology of the reinforced and conventional GI restoratives. Two cylindrical specimens similar to those prepared for the compressive fracture strength study, for groups A-P, were mounted horizontally into a two part cold-setting acrylic resin (Varidur, Beuhler, Lake Bluff, IL, USA). The specimens were ground on a Beta grinder-polisher machine (Beuhler, Lake Bluff, IL, USA) through a series of SiC abrasive papers (P320, P600, P1200 and P2400) at a force of 10 N with an exchange of SiC abrasive paper every 30 s for each grade employed using water as a lubricant.

3. Results

3.1. GI restorative cement

The mean compressive fracture strength for the GI restorative control (Group A) was 105 MPa with a standard deviation of 22 MPa and the range of compressive fracture strengths varied from 71 to 153 MPa. The Weibull constants (m and σ_0) were 5.25 (0.96) and 111 MPa with associated 95% confidence intervals of 4.8-5.7.

3.2. Reinforced GI restorative

3.2.1. Ca-MMT

When the compressive fracture strength data for the GI restoratives reinforced with Ca-MMT added to the powder (groups B-F) were analysed no significant differences between the mean compressive fracture strengths were identified for groups B-D when compared with the control (group A). Interestingly, there was a significant reduction in the mean compressive fracture strengths of groups E and F (2.0 and 2.5 wt.%, respectively) when the one-way ANOVA and Tukey's test comparisons were analysed at the 95% significance level compared with the control (Table 1). The characteristic stress (σ_0) was also identified to decrease with increasing Ca-MMT wt.% additive. Increasing the Ca-MMT wt.% additive to 0.5 wt.% (group B) resulted in a more reliable strength distribution than when 1.0, 1.5 and 2.0 wt.% additive was incorporated (groups C-E, respectively). Whilst increasing the Ca-MMT wt.% additive concentration to 2.5 wt.% (group F) resulted in the most reliable strength distribution with the confidence intervals failing to overlap with groups A-E the reduced mean compressive fracture strength negated the improved reliability (Table 1).

The specimens created by adding the Ca-MMT powder to the liquid element of the GI restorative (groups L-P) also resulted in no significant difference in mean compressive fracture strengths for group L (0.5 wt.%) when compared with

Table 1 – Physical property data for a series of 30 cylindrical specimens of the GI restorative ChemFil[®] Superior prepared with varying percentage weights of Ca-MMT (standard deviations are shown in brackets)

Property	Group					
	A	B	C	D	E	F
Calcium-montmorillonite (powder)						
Clay concentration (wt.%)	0.0	0.5	1.0	1.5	2.0	2.5
Compressive fracture strength range (MPa)	71-153	62-128	53-132	57-130	51-116	55-103
Mean compressive fracture strength (MPa)	105 (22)	100 (19)	94 (19)	92 (20)	86 (19)	77 (13)
Weibull modulus (m)	5.25 (0.96)	5.71 (1.04)	4.91 (0.89)	4.99 (0.91)	4.92 (0.89)	6.71 (1.23)
R ² -value	0.954	0.987	0.983	0.978	0.986	0.949
Confidence intervals (95%)	4.8-5.7	5.5-6.0	4.7-5.2	4.7-5.3	4.7-5.2	6.1-7.3
Characteristic stress (MPa) (σ_0)	111	106	105	100	95	82
	A	L	M	N	O	P
Calcium-montmorillonite (liquid)						
Clay concentration (wt.%)	0.0	0.5	1.0	1.5	2.0	2.5
Compressive fracture strength range (MPa)	71-153	65-133	63-135	59-126	62-107	65-103
Mean fracture compressive strength (MPa)	105 (22)	100 (19)	91 (14)	87 (17)	83 (11)	80 (10)
Weibull modulus (m)	5.25 (0.96)	5.51 (1.01)	6.22 (1.14)	5.80 (1.06)	8.28 (1.51)	8.33 (1.53)
R ² -value	0.954	0.976	0.968	0.962	0.976	0.904
Confidence intervals (95%)	4.8-5.7	5.2-5.8	5.8-6.7	5.4-6.3	7.8-8.8	7.3-9.4
Characteristic stress (MPa) (σ_0)	111	106	96	93	85	82

the control (group A). Interestingly groups M-P (1.0, 1.5, 2.0 and 2.5 wt.%, respectively) resulted in a significant decrease in the mean compressive fracture strengths when the one-way ANOVA and Tukey's test comparisons were analysed at the 95% significance level compared with the GI control. The characteristic stress (σ_0) was also identified to decrease with increasing Ca-MMT wt.% added to the liquid (Table 1). Increasing the Ca-MMT wt.% additive to 0.5 wt.% (group L) resulted in a similar strength distribution to the control. However, when the wt.% Ca-MMT incorporated into the liquid was increased above 0.5 wt.% (groups M-P, respectively) the

reliability of the strength distributions were generally increased compared with the control (group A) with the confidence intervals failing to overlap although again the reduction in mean compressive fracture strength negated the improved reliability (Table 1).

3.2.2. ADA-MMT

The specimens created by adding ADA-MMT clay to the powder of the GI restorative (groups G-K) displayed a significant increase in the mean compressive fracture strength data for groups G and H (0.5 and 1.0 wt.%) when the one-way

Table 2 – Physical property data for a series of 30 cylindrical specimens of the GI restorative ChemFil[®] Superior prepared with varying percentage weights of ADA-MMT (standard deviations are shown in brackets)

Property	Group					
	A	G	H	I	J	K
12-amino-dodecanoicacid-montmorillonite (powder)						
Clay concentration (wt.%)	0.0	0.5	1.0	1.5	2.0	2.5
Compressive fracture strength range (MPa)	71-153	97-165	89-164	86-137	71-130	68-127
Mean fracture compressive strength (MPa)	105 (22)	133 (20)	128 (22)	110 (15)	98 (18)	97 (17)
Weibull modulus (m)	5.25 (0.96)	5.41 (0.99)	4.95 (0.90)	6.25 (1.14)	4.68 (0.85)	4.55 (0.83)
R ² -value	0.954	0.978	0.977	0.989	0.965	0.993
Confidence intervals (95%)	4.8-5.7	5.1-5.7	4.7-5.2	6.0-6.5	4.3-5.2	4.4-4.7
Characteristic stress (MPa) (σ_0)	111	141	139	114	103	104
	A	Q	R	S	T	U
12-amino-dodecanoicacid-montmorillonite (liquid)						
Clay concentration (wt.%)	0.0	0.5	1.0	1.5	2.0	2.5
Compressive fracture strength range (MPa)	71-153	87-150	85-141	69-134	64-127	63-126
Mean compressive fracture strength (MPa)	105 (22)	123 (19)	113 (17)	97 (20)	98 (16)	97 (19)
Weibull modulus (m)	5.25 (0.96)	5.16 (0.94)	6.75 (1.23)	4.67 (0.853)	6.71 (1.23)	4.92 (0.90)
R ² -value	0.954	0.979	0.979	0.959	0.989	0.972
Confidence intervals (95%)	4.8-5.7	4.9-5.4	6.4-7.1	4.3-5.0	6.4-7.0	4.6-5.2
Characteristic stress (MPa) (σ_0)	111	133	117	99	103	109

ANOVA and Tukey's test comparisons were analysed at the 95% significance level compared with group A (Table 2). The mean compressive fracture strengths for groups I-K (1.5, 2.0 and 2.5 wt.%, respectively) highlighted no significant increase when compared with the mean compressive fracture strength for group A. The characteristic stress (σ_0) was identified to increase with increasing ADA-MMT additive up to 1.5 wt.% (groups G-I, respectively) and decreased for ADA-MMT additive above 1.5 wt.% (groups J and K). Increasing the ADA-MMT wt.% additive to 1.0 wt.% (groups G and H) resulted in similar strength distributions to the control (group A) with the confidence intervals overlapping. Increasing the ADA-MMT wt.% additive concentration to 1.5 wt.% (group I) resulted in the most reliable strength distribution with the confidence intervals failing to overlap with groups A, G-H and J-K (Table 2).

The addition of ADA-MMT clay to the liquid element of the GI restorative (groups Q-U) resulted in a significant increase for group Q (0.5 wt.%) when the one-way ANOVA and Tukey's test comparisons were analysed at the 95% significance level compared to the GI control. The mean compressive fracture strengths for groups R-U (1.0, 1.5, 2.0 and 2.5 wt.%, respectively) showed no significant increase or decrease when compared to the control group (group A). The characteristic stress (σ_0) was identified to increase with increasing ADA-MMT additive up to 1.0 wt.% (groups Q-R, respectively) and decreased for ADA-MMT added to the liquid above 1.0 wt.% (groups S-U). Increasing the ADA-MMT wt.% additive to 0.5 wt.% (group Q) resulted in similar strength distributions to the control (group A) with the confidence intervals overlapping. Further increasing the ADA-MMT wt.% additive concentration to 1.0 wt.% (group R) and 2.0 wt.% (group T) resulted in the most reliable strength distribution with the confidence intervals failing to overlap with groups A, Q, S and U although the mean compressive fracture strengths were reduced.

3.3. Working characteristics

In general the working times recorded for the GI restorative reinforced with both the Ca-MMT and the ADA-MMT clays were not significantly different from that of the conventional GI restorative (Table 3). The setting times for specimen groups B-F and G-K created by adding the MMT clays to the powders did not differ significantly from the control ($P < 0.05$). However, there is a significant increase in setting times for specimen groups L-P and Q-U created by adding the clays to the liquid. Interestingly the increase in setting times recorded for the Ca-MMT and ADA-MMT clays added to the liquid element of the GI restorative decreased as wt.% increased with the longest setting times recorded at 0.5 wt.% for both clays.

3.4. X-ray diffraction

The two-dimensional XRD patterns determined for the Ca-MMT and ADA-MMT clays are presented in Fig. 2. The XRD patterns identified a difference in the initial characteristic smectite d_{001} peaks for the Ca-MMT and ADA-MMT clays which were located at 2θ angles of 8.44° and 5.07° , respectively. The d_{001} spacings, calculated using Bragg's law²⁸ for Ca-MMT and ADA-MMT were 1.04 and 1.74 nm, respectively.

Table 3 - The mean working characteristics for the series of ChemFil[®] Superior GI restoratives prepared with varying amounts of clay added to both the powder and liquid elements of the GI restorative (figures in brackets represent standard deviations ($n = 3$)).

Concentration (wt.%)	Group	Working time (s)	Setting time (s)
Calcium-montmorillonite			
0.0	A	98 (3.46)	120 (0)
Powder			
0.5	B	88 (3.46)	124 (9.16)
1.0	C	92 (3.46)	130 (3.46)
1.5	D	90 (6.00)	132 (0)
2.0	E	98 (3.46)	128 (3.46)
2.5	F	94 (3.46)	126 (0)
Liquid			
0.5	L	92 (3.46)	152 (9.16)
1.0	M	86 (3.46)	142 (6.93)
1.5	N	92 (3.46)	136 (3.46)
2.0	O	90 (0)	132 (0)
2.5	P	90 (0)	132 (0)
12-amino-dodecanoicacid-montmorillonite			
0.0	A	98 (3.46)	120 (0)
Powder			
0.5	G	98 (3.46)	132 (6.00)
1.0	H	92 (3.46)	144 (8.08)
1.5	I	88 (3.46)	128 (3.46)
2.0	J	88 (3.46)	126 (0)
2.5	K	92 (3.46)	134 (3.46)
Liquid			
0.5	Q	94 (3.46)	160 (6.93)
1.0	R	102 (0)	148 (3.46)
1.5	S	102 (10.39)	140 (3.46)
2.0	T	92 (6.93)	148 (3.46)
2.5	U	92 (3.46)	138 (10.39)

3.5. Scanning electron microscopy (SEM)

The scanning electron micrographs in Fig. 3 illustrate the composite structure of the GI restorative containing the high strength dispersion phase (the aluminosilicate glass powder) and a lower strength salt-gel¹⁻³ polymer matrix (polyacid). In

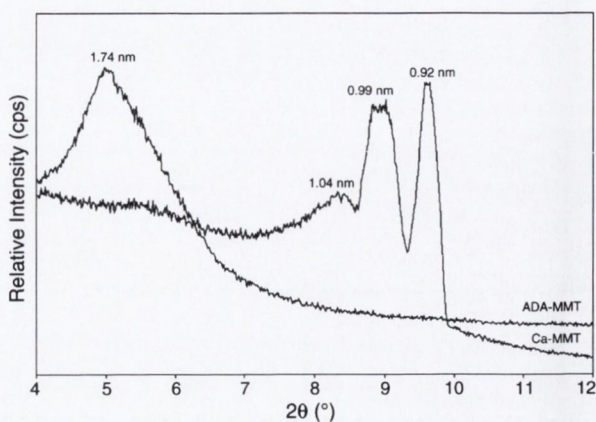


Fig. 2 - X-ray diffraction patterns of Ca-MMT and ADA-MMT clay powders prior to addition to the GI restorative.

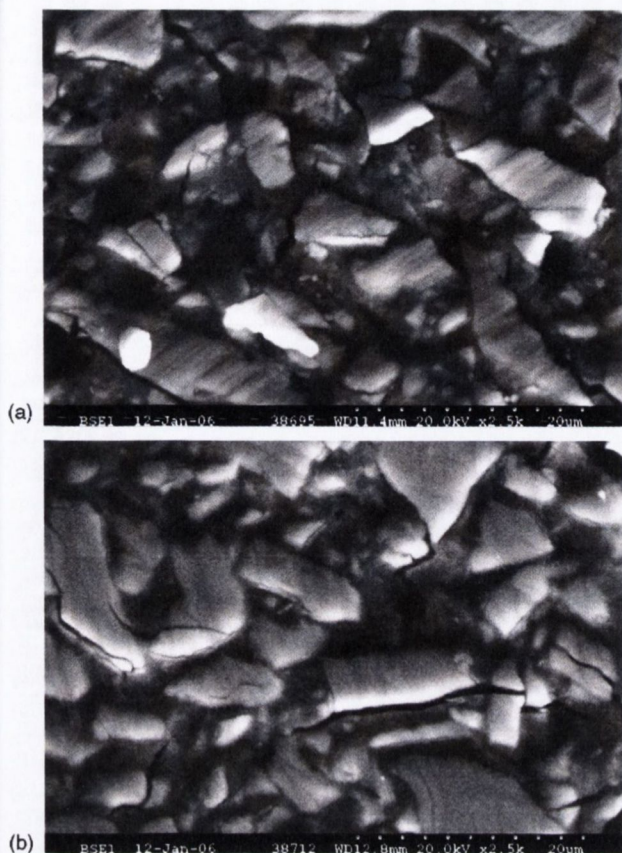


Fig. 3 – Scanning electron micrographs of 0.5 wt.% additions of (a) Ca-MMT and (b) ADA-MMT to the GI restorative where crack propagation appears to be hindered less by the ADA-MMT clay powder matrix.

Fig. 3a it is proposed that the dehydration cracks in the GI restorative material travel more easily through the matrix phase of the Ca-MMT reinforced restorative compared with the ADA-MMT reinforced GI restorative (Fig. 3b).

4. Discussion

4.1. Compressive fracture strength

The average particle size of Ca-MMT and ADA-MMT clays are $8\ \mu\text{m}$ (equating to an agglomeration of approximately 3000 stacked clay platelets) and $2\ \mu\text{m}$ (equating to approximately 800 stacked clay platelets), respectively.²⁹ According to Fischer,³⁰ an increased concentration of a smaller reinforcing element results in a large internal surface area and an increased tendency for agglomeration rather than homogeneous dispersion in a polymeric matrix such as polyacrylic acid. In the current study, at higher clay concentrations (namely increased MMT additions in excess of 1.5 wt.%) the clays agglomerated into disorganised structures of stacked clay platelets, which decreases the overall surface area available for reaction thereby minimising any potential reinforcing effect. In addition, clay agglomerations and the associated poor packing efficiency of

the stacked clay platelets within the set GI restorative structure would be expected to act like voids. Void formation would be expected to weaken the restorative by introducing a further defect distribution thereby disrupting the conventional structure of the high strength dispersion phase (glass particles) set in a weak salt-gel matrix of crosslinked polyacrylic chains. It is likely that there may be localised areas within the set GI restorative where the stacked clay platelets act as the reinforcing phase rather than the reinforcing glass particles as expected in conventional GI restoratives. It is suggested that the increased concentrations of Ca-MMT clay added to the GI restorative powder in groups D–F (1.5–2.5 wt.% additions) and added to the GI restorative liquid in groups M–P (1.0–2.5 wt.% additions) would have been responsible for the significant decreases in the mean compressive fracture strength when compared with the non-reinforced control (group A) manifested by increased agglomeration and therefore increased void formation. It is possible that the poor packing efficiency of the stacked clay platelet agglomerates resulted in localised porous areas (Fig. 3) which would be expected to act as crack initiation sites thereby resulting in the significant reduction in the compressive fracture strength data as highlighted in Table 1. It is suggested that the non-significant reduction in the mean compressive fracture strengths recorded when lower concentrations of Ca-MMT clay (additions of 0.5–1.0 wt.%, respectively) were added to the GI restorative powder (groups B and C, respectively) and to the GI restorative liquid (group L) would have resulted from the inability of the clay to form large agglomerates within the GI restorative structure. The likelihood is that during the manipulation of reinforced GI restoratives at higher Ca-MMT clay concentrations, the clay platelets would form larger agglomerates rather than interact with the GI restorative structure. Therefore, the study has highlighted that there is no potential for increasing the performance of GI restoratives as posterior filling materials when using a pristine Ca-MMT clay as a reinforcement.

The combination of the reduced particle size of the ADA-MMT clay, compared with the Ca-MMT clay, in conjunction with the larger d_{001} spacing demonstrated through XRD, created a larger surface area available for reaction with the GI restorative. The significant increase in mean compressive fracture strengths recorded when ADA-MMT clay was added to the GI restorative powder (groups G and H, respectively) and to the GI restorative liquid (group Q) demonstrated that ADA-MMT clay had a positive reinforcing effect on the GI restorative at low concentrations when compared with the GI restorative containing no ADA-MMT reinforcement (group A) as highlighted in Table 2. It is likely that at higher ADA-MMT clay concentrations (groups I–K and R–U) where no significant difference in the mean compressive fracture strengths were evident compared with the control (group A) that the clay may have agglomerated. It is suggested that this finding supported the observation of Fischer³⁰ that smaller reinforcing elements contain less imperfections and have a greater reinforcing effect on the mechanical properties of the material system to which they have been added. It is likely that one of the major reasons that there was a positive effect on the mean compressive fracture strength of GI restoratives reinforced with ADA-MMT clay was due to the pre-treatment process of the clay which resulted in particles with a reduced tendency to

agglomerate and an increase in interlayer *d*-spacing (d_{001}). Furthermore, the increased d_{001} may allow for the movement of polyacid chains between the layered montmorillonite platelets and possibly the formation of hydrogen bonds between the carboxylic acid groups of polyacid and the amine groups of the ADA-MMT reinforced GI. Therefore, it is suggested that the study has highlighted the possible potential for increasing the performance of GI restoratives as posterior filling materials when using an organically modified 12-amino-dodecanoic acid treated ADA-MMT clay as a reinforcement.

A recent study by Tran et al.³¹ suggested that polyacrylic acid, which is the polymeric constituent of GI restoratives could expand pristine MMT clay layers from 1.3 to 1.6 nm through mixing at room temperature for 24 h. In the current study the MMT clays were spatulated with the GI powder or GI liquid for 20 s and the suggestion is that the polyacrylic acid of the GI restorative may not have intercalated the MMT clay layers further in this short period of time. Also, it was noted that the vigorous mechanical mixing of a clay and polyacrylic acid solution over 24 h would be expected to break up the pristine MMT clay agglomerates and increase the potential to disperse the clay homogeneously within the matrix of polyacrylic acid as observed by Tran et al.³¹

4.2. Working characteristics

The sensitivity of the oscillating rheometer is determined by the spring tension that reduces motion of the lower platen so that if the chosen springs were weak the initial changes during setting were emphasised and if the chosen springs were too strong the final stages of setting would be more discernible.³²⁻³⁴ In the current study a spring tensions was chosen in accordance with the recommendations of the designers²⁶ to minimise the inaccuracy of the apparatus resulting from spring tension. GI restoratives are formed through an acid-base reaction between a polyacrylic acid and a basic ion-leachable glass powder in aqueous solution, whereby following the commencement of mixing the polyacrylic acid attacks the glass particles releasing metal ions which act to ionically crosslink the polymeric chains resulting in the hardening of the restorative. The set GI restorative structure may be interpreted as a composite material where glass particles surrounded by a silica gel are set in a matrix of crosslinked polyacrylic chains. The influence of the addition of MMT clays to the chemical reaction and set GI restorative structure is as yet not fully understood. It is proposed that the Ca-MMT clay when added to the GI restorative powder would compete for the available liquid manifested as a reduction (although not significant) in the associated working time. The GI liquid absorbed by the Ca-MMT clay initially during manipulation would have been bound within the clay layers and may have been gradually released as the setting reaction proceeded. The continual release of GI liquid as the setting process continued would have resulted in the extension of the setting times of the GI restoratives created with Ca-MMT clay added to the GI restorative powder. It is suggested that when Ca-MMT clay was added to the GI restorative liquid prior to mixing the clay component absorbed more GI restorative liquid (compared with when added to the GI restorative powder) which was manifested by a decrease in the working times recorded

between the two reinforced GI restorative preparation methods as highlighted in Table 3. By initially reducing the GI restorative liquid volume available a decrease in the working times would be expected and the gradual release of GI restorative liquid from the clay layers as the setting process continued may have resulted in the extension of the setting times. At lower concentrations of Ca-MMT clay (0.5–1.0 wt.%) the likelihood for agglomeration is reduced which would create a greater available surface area for GI liquid absorption. The increased surface area would be able to hold more GI restorative liquid and therefore release more as the reaction progressed, resulting in the higher setting times at the lower Ca-MMT concentrations. Incidentally as concentration of Ca-MMT clay increased the setting time decreased which was attributed to the presence of agglomerates with poor packing efficiencies which absorbed less GI restorative liquid and offer more free GI liquid to the reaction.

The minor decreases recorded in working times when ADA-MMT was added to the GI restorative powder compared with the control (group A) could have been the result of competition between the clay powder and the GI restorative powder for the GI restorative liquid. It is suggested that the slow release of bound GI liquid from the ADA-MMT clay during the setting reaction was responsible for extending the setting times of the GI restoratives created by addition of ADA-MMT clay to the GI restorative powder. The non-significant differences recorded in the working times when ADA-MMT clay was added to the GI restorative liquid are again probably the result of competition between the clay and powder for the free GI liquid. It was observed during manipulation of the GI liquid controls that Ca-MMT clay dispersed more easily in the GI restorative liquid than ADA-MMT clay, the reduced hydrophilicity of the ADA-MMT would suggest that setting times would decrease in comparison to the Ca-MMT liquid controls but there was an increase indicated in the working characteristic data highlighted in Table 3. It is therefore suggested that the increase in setting time would be due to the reduced particle size of ADA-MMT and the larger number of smaller agglomerates which would absorb more GI restorative liquid and release it slowly as the reaction progresses. However, the study highlighted no potential for reducing the performance of GI restoratives as posterior filling materials when using the ADA-MMT clay as a reinforcement due to the working characteristics.

4.3. X-ray diffraction

XRD is a well established method for characterising clays and organically modified clays enabling the determination of the interlayer *d*-spacings (d_{001}) of the clays which provide an indication of the level of intercalation or exfoliation of the clay layers. The XRD patterns of the pristine Ca-MMT and the organically modified ADA-MMT clay are shown in Fig. 2 where an expansion of 0.7 nm is evident in the d_{001} spacing for ADA-MMT when compared to Ca-MMT. The increase in the interlayer *d*-spacings (d_{001}) recorded for ADA-MMT clay demonstrates that the ADA-MMT clay has expanded layers which may provide an increased opportunity for the polyacrylic acid chains of the GI restorative to diffuse into the MMT galleries during manipulation.³⁵ In reality GI restoratives could be likened to a composite material containing reinforcing

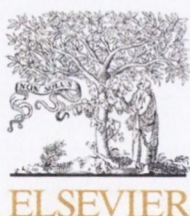
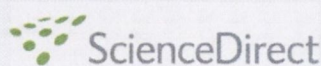
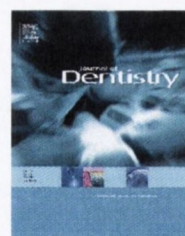
glass particles in a weak salt-like gel matrix. The ADA-MMT reinforced salt-like gel matrix would be the weak element and it is suggested that reinforcement with intercalated or exfoliated clay platelets would increase the mechanical properties of the matrix which in turn would increase the compressive fracture strength of the composite material by reinforcement of the weakest phase.

5. Conclusions

When the pristine clay (Ca-MMT) was added to the GI restorative no significant reinforcement or increased performance was identified highlighting that there was no potential for increasing the performance of GIs as posterior filling materials when using a pristine Ca-MMT clay as a reinforcement. However, ADA-MMT addition to the powder and liquid elements of the GI up to 1.0 wt.% had a positive reinforcing effect on the GI although the setting time was increased. The increase in ($d_{0.1}$) recorded for ADA-MMT clay demonstrates that the clay has expanded layers which may have provided an increased opportunity for the polyacrylic acid chains of the GI restorative to diffuse into the MMT galleries during manipulation resulting in the improved strength and increased setting times. Therefore, it is suggested that the study has identified the potential for increasing the performance of GI restoratives as posterior filling materials when using organically modified 12-amino-dodecanoic acid treated MMT clay as the reinforcement.

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The impact of montmorillonite clay addition on the *in vitro* wear resistance of a glass-ionomer restorative

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ABSTRACT

Objectives: The *in vitro* wear resistance of a glass-ionomer (GI) restorative ChemFil[®] Superior (Dentsply DeTrey, Kanstanz, Germany) reinforced with either a pristine calcium montmorillonite (Ca-MMT) or an organically modified 12-amino-dodecanoic acid treated montmorillonite (ADA-MMT) clay was evaluated to investigate the potential of MMT reinforced GI restoratives as posterior filling materials.

Methods: The wear resistance of a GI restorative reinforced with 0.5–2.5 wt.% Ca-MMT and ADA-MMT was assessed for groups of four disc-shaped specimens using the OHSU oral wear simulator operating at 20 N abrasion and 90 N attrition forces for 50,000 cycles at a frequency of 1 Hz in the presence of a poppy seed and PMMA micro-sphere slurry. The wear facet of each specimen was quantified by measuring the mean wear depth and mean volumetric wear in the abrasion (40–60% of wear facet) and attrition (80–90%) regions in conjunction with the mean total wear depth and mean total volumetric wear.

Results: The addition of Ca-MMT clay resulted in a significant increase in the mean total volumetric wear and mean total wear depth of the GI restorative as the concentration of clay was increased utilising the one-way ANOVA and Tukey's test comparisons at a 95% significance level. When ADA-MMT clay was added to the GI no significant differences in mean total volumetric wear and mean total wear depth were evident ($P < 0.05$).

Conclusions: The addition of Ca-MMT clay to the GI restorative resulted in a significant decrease in the *in vitro* wear resistance. ADA-MMT clay additions to the powder element of the GI restorative did not significantly enhance the *in vitro* wear resistance.

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1. Introduction

Dental amalgam restorations necessitate the removal of sound tooth structure prior to placement in the oral environment,¹ are susceptible to corrosion in service,² have potential mercury toxicity issues³ and are non-tooth coloured which has led the dental profession to investigate alternative potential posterior restorative materials.⁴ Resin-based composites (RBCs) are advantageous compared with dental amalgam in that they are tooth coloured, but RBCs are time consuming to place resulting in increased patient treatment

times.⁵ In addition, RBCs are technique sensitive to place clinically with an associated increased treatment cost to the patient.⁵ Glass-ionomer (GI) restoratives can be easily manipulated, placed in one increment and offer chemical adherence to natural dentition,⁶ thereby eliminating the need for sound tooth structure removal necessitated for dental amalgam restorations. GI cements were reported by Wilson and Kent⁷ and have undergone significant changes in formulation to improve the working characteristics and the mechanical properties.⁸ GIs are a versatile dental material advocated clinically as luting cements, cavity bases and liners⁹

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and more recently as restorative materials where the powder to liquid mixing ratio was increased to counter the masticatory loads routinely encountered in the posterior region of the mouth.

Wear is a tribological process resulting in the loss of material due to the interaction of opposing surfaces.¹⁰ In the oral environment the opposing wear of dental surfaces results from a variety of mechanical interactions including abrasion, attrition, adhesion, fatigue and erosion or a combination of these interactions.¹⁰ The assessment of the wear of restorations *in vivo* can be conducted through either direct observation of the restoration at regular patient visits¹¹ or by the indirect analysis of tooth replicas of the restorations.¹² In the United States Public Health Service (USPHS) technique reported by Cvar and Ryge,¹¹ two or more independent clinical observers directly evaluated the wear of restorations after regular time intervals and rated them as either clinically ideal (Alpha), clinically acceptable (Bravo) or clinically unacceptable (Charlie).¹³ One of the drawbacks of the USPHS technique was that clinical observers were subjective in their assessment and often disagreed over ratings such that restorations were rated as Bravo at one visit and Alpha at a later revisit¹⁴ when wear would be expected to increase with time. In addition, it was difficult to achieve the continuity of clinical observers for subsequent patient visits, notwithstanding patient attendance, expense and compliance issues. The technique reported by Leinfelder et al.¹² quantitatively assessed restorative wear indirectly by comparing stone cast replicas of teeth containing restorations to six standard casts corresponding to specific wear depths. The Leinfelder technique required positive and negative impressions of the restored teeth to be taken, however, both dental impression and stone materials are susceptible to dimensional instability on setting, thereby impeding the dimensional precision of the replicas and as a result the confidence in the *in vivo* restorative wear data. The imprecision of both the direct (USPHS) and indirect (Leinfelder) *in vivo* methods routinely employed to assess the wear resistance of impression materials drove the dental profession to investigate the potential of computerised three-dimensional (3D) mapping techniques such as the Michigan computer graphic technique¹⁵ and 3D profilometry¹⁶ to evaluate *in vivo* wear of dental structures.

The *in vitro* wear evaluation of dental restoratives has been assessed using a variety of machines including the Materials Testing and Simulation (MTS) artificial oral environment,¹⁷ the Academisch Centrum for Tandheelkunde Amsterdam (ACTA) wear machine,¹⁸ the University of Alabama wear machine¹⁹ and the Oregon Health Science University (OHSU) oral wear simulator²⁰ all of which simulate a variety of different wear mechanisms. The purpose of an *in vitro* wear simulation is to assess the wear resistance of dental materials prior to placement in the mouth to provide an initial screening to potential restorative materials which would avert the need for expensive and time consuming clinical trials on substandard materials. However, there is no internationally recognised standard for the *in vitro* wear assessment of dental restoratives possibly due to the difficulties involved in simulating the complexity of wear behaviour in the oral environment. As a result, currently there is no single *in vitro* wear machine that can simulate clinical wear in the oral environment as the

machines outlined previously simulate one or two of the individual wear mechanisms outlined by Mair et al.¹⁰ and consequently there is difficulty in correlating *in vitro* and *in vivo* wear studies.

The *in vitro* wear research investigating the potential of GI restoratives as posterior filling materials is limited, however, a number of studies have evaluated the wear of GI restoratives using the ACTA wear machine.²¹⁻²⁵ Pelka et al.²¹ examined four conventional GI restoratives which displayed 4.6 times more wear than a dental amalgam restorative against a stainless steel antagonist wheel loaded at 15 N for 50,000 cycles at a frequency of 1 Hz in the presence of a rice and millet seed slurry. de Gee et al.²² investigated the wear resistance of conventional GIs, resin modified GIs (RMGIs) and metal reinforced GIs (MRGIs) at time intervals of 8 h, 1, 2, 16 and 52 weeks after the commencement of mixing using a similar test protocol to Pelka et al.²¹ for 200,000 cycles. The authors reported that the wear resistance of RMGIs was significantly reduced when compared with the conventional GIs and MRGIs at all time intervals.²² In contrast to the significant early improvement in wear resistance of MRGIs reported by de Gee et al.,²² Kunzelmann et al.²³ reported that a similar MRGI exhibited significantly less wear resistance than conventional GIs when tested in the ACTA wear machine 24 h after manipulation using the same procedure outlined previously by de Gee et al.²² In 1998, de Gee et al.²⁴ used a similar test protocol with a reduced load of 10 N to test the early (8 h) and long-term (1 and 16 weeks) wear resistance of conventional GIs and RMGIs and reported that conventional GIs exhibited less wear than RMGIs at each time interval. The authors^{22,24} suggested that the significant decrease in wear resistance associated with RMGIs in comparison with conventional GIs was due to the inferior coherence of the filler particles within the matrix. The wear resistance of 'fast-set' GIs and their conventional counterparts was evaluated by van Duinen et al.²⁵ using the procedure outlined by de Gee et al.²² (15 N load, for 200,000 cycles at 1 Hz in rice and millet seed slurry) in the ACTA wear machine at 1, 4, 7, 30, 90 and 365 days after the commencement of mixing. The study indicated that the faster setting GIs did not develop improved wear resistance quicker than conventional GIs. Interestingly, the wear resistance of the conventional GI restoratives incubated for up to 1 year storage at $37 \pm 1^\circ\text{C}$ progressively increased with storage time.^{21,24,25}

In a recent study the addition of 0.5 and 1.0 wt.% organically modified 12-amino-dodecanoic acid montmorillonite (ADA-MMT) to a GI restorative was reported to significantly improve the mean compressive fracture strength²⁶ compared with the unreinforced GI restorative. The addition of a pristine calcium montmorillonite (Ca-MMT) to the GI restorative was reported to progressively decrease the mean compressive fracture strengths as the concentration of Ca-MMT was increased. The aim of the current study was to assess the influence of ADA-MMT and Ca-MMT reinforcement on the *in vitro* wear resistance of a GI restorative using the OHSU oral wear simulator²⁰ to investigate the potential of MMT reinforced GI restoratives as posterior filling materials. In line with the observations of the previous study²⁶ the hypothesis proposed was that the reinforcement with ADA-MMT would significantly enhance, whilst the addition of

Ca-MMT would significantly deteriorate, the wear resistance of the GI restorative investigated.

2. Materials and methods

2.1. Glass-ionomer restorative manipulation

Disc-shaped ChemFil[®] Superior (Dentsply DeTrey, Kanstanz, Germany) GI restorative specimens (15.0 ± 0.1 mm diameter and 1.7 ± 0.1 mm height) were prepared by a single operator by hand mixing 0.833 g of GI restorative powder with 112.5 μ l of GI liquid for 40 s according to the manufacturers' recommended powder to liquid mixing ratio (7.4 g to 1.0 ml). The powder was weighed on a balance accurate to 0.001 g (Sartorius Expert, Sartorius AG, Goettingen, Germany), placed onto a glass slab and separated into two equal parts. The liquid was dispensed onto the glass slab using a micro-pipette (Gilson, Middleton, WI, USA) and mixed with one half of the GI powder for 20 s using a non-corrodible stainless steel spatula. The remaining powder was added and mixed for a further 20 s in accordance with the manufacturers instructions.²⁷ The disc-shaped specimens were manufactured using a Perspex mould which was pre-coated with a PTFE dry film lubricant (Fisher Scientific, Loughborough, UK) to enable the removal of the set specimens. The mould was placed on a Perspex base plate covered with an acetate strip and the GI restorative plastic mass was placed in the centre of the mould. A second acetate strip and Perspex plate were placed on top and pressurised using a 1 kg weight to spread the restorative within the mould and minimise pore incorporation. The mould assembly was fixed using a G-clamp to ensure equal pressure was applied to the specimens and transferred to a water-bath maintained at 37 ± 1 °C. After 1 h the specimens were removed from the mould, the flash removed by grinding on P600 silicon carbide (SiC) abrasive paper and specimens containing visual defects were discarded. Four control specimens (group A) were produced and stored in glass containers filled with 50 ml of distilled water in an incubator maintained at 37 ± 1 °C for a further 23 h prior to testing and analysis.

2.2. Montmorillonite clay manipulation

Two montmorillonite (MMT) clays which were previously employed by the author,²⁶ a pristine clay, Ca-MMT (Süd Chemie, Munich, Germany) (average particle size 8 μ m),²⁸ and an organically modified clay, ADA-MMT (Nanacor Inc., IL, USA) (average particle size 2 μ m)²⁸ were used to attempt to improve the wear resistance of the GI restorative. The Ca-MMT and GI powder mixture was then manipulated with the liquid in accordance with the manufacturers' recommended procedure outlined above. The ADA-MMT clay was reported by the manufacturers to be synthesised by an ion exchange reaction between 12-amino-dodecanoic acid and Na⁺-montmorillonite with a cation exchange capacity of 110/100 milliequivalents/g.

A series of Ca-MMT clay reinforced GI restorative specimens were manufactured by adding 0.5 wt.% (group B), 1.0 wt.% (group C), 1.5 wt.% (group D), 2.0 wt.% (group E) and 2.5 wt.% (group F) of the Ca-MMT (corresponding to 0.004, 0.008, 0.013, 0.016 and 0.021 g, respectively) to the powder

element of the GI restorative prior to manipulation. The manufacturers recommended powder to liquid mixing ratio was maintained at 7.4 g to 1.0 ml for all specimen groups with the proportion of Ca-MMT added to each group calculated as a wt.% of the powder element of the restorative. The Ca-MMT powder and the GI restorative powder were spatulated together for 20 s on a glass slab in accordance with the procedure outlined previously by the authors.²⁶ Four nominally identical disc-shaped specimens were manufactured for each specimen group (groups B-F). The specimens were placed in a water bath maintained at 37 ± 1 °C for 1 h following manipulation and stored in 50 ml of distilled water maintained at 37 ± 1 °C in an incubator for a further 23 h prior to testing in accordance with the procedure outlined previously. Additionally, a series of ADA-MMT clay reinforced restorative specimens were manufactured by adding the ADA-MMT to the powder element of the restorative and spatulating for 20 s prior to manipulation to a powder to liquid mixing ratio of 7.4 g to 1.0 ml. Four nominally identical disc-shaped specimens were produced for each group containing 0.5 wt.% (group G), 1.0 wt.% (group H), 1.5 wt.% (group I), 2.0 wt.% (group J) and 2.5 wt.% (group K) of ADA-MMT clay reinforcement in accordance with the GI restorative manipulation procedure outlined previously.

2.3. Wear testing

The disc-shaped specimens were removed from the incubator 24 h after manipulation and embedded into acrylic rings (20.0 ± 0.1 mm inner diameter and 10.0 ± 0.1 mm height) using a two part cold-setting acrylic resin (Varidur, Beuhler, Lake Bluff, IL, USA). The acrylic resin was mixed according to manufacturers' instructions, with a powder to liquid mixing ratio of 1.0 g to 1.0 ml. A preliminary study highlighted the need to scour the inner surface of each acrylic ring with an acrylic trimming bur operating in a slow speed hand-piece to aid mechanical adhesion of the acrylic resin. The embedded specimens were ground on a Beta grinder-polisher machine (Beuhler, Lake Bluff, IL, USA) with P1200 SiC abrasive paper at a force of 10 N per specimen for 30 s using water as a lubricant to provide a reproducible surface roughness conducive to wear testing.²⁰

The wear test was conducted using the OHSU four chamber oral wear simulator employing ceramic antagonists to simultaneously produce abrasion wear (the sliding action of one surface over another)¹⁰ and attrition wear (the direct contact of surfaces where the load level is higher than abrasion). The basic experimental approach is well established in the dental literature and is therefore not described in detail.^{20,29,30} Each embedded specimen was placed into an individual wear chamber and tightened in place before a food like slurry, consisting of 1.0 g of poppy seeds (Holland & Barrett, Burton-upon-Trent, England) 0.5 g of PMMA microspheres with an average size range of 50-100 μ m diameter (G. Kisker GbR, Steinfurt, Germany) and 5 ml of double distilled water, was placed into each chamber prior to the commencement of testing.¹⁸ The slurry was shown by de Gee et al.¹⁸ to produce wear rates comparable with those identified clinically. In addition, the miscibility of the poppy seeds was improved by grinding using 100 strokes in a ceramic mortar

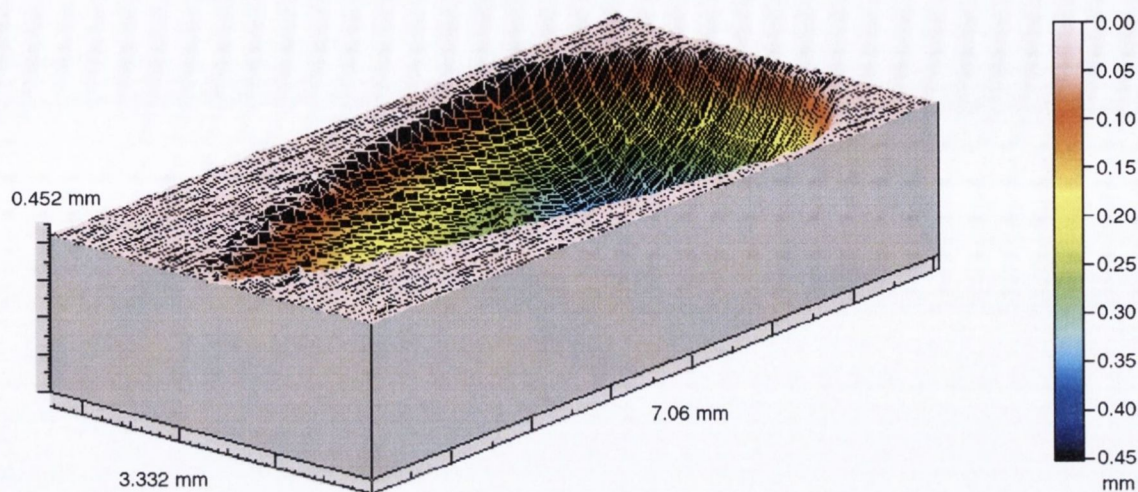


Fig. 1 – A three-dimensional representation of the total wear facet for the 7 mm sliding path produced from the wear regime employed using the OHSU oral wear simulator.

and pestle. The ceramic antagonists were 10.0 ± 0.1 mm diameter steatite balls affixed to the top of nylon screws using a light cured composite (Filtek[®] Supreme, 3 M ESPE, St. Paul, MN, USA). The wear regime imposed upon each specimen consisted of a 20 N sliding force travelling along a 7 mm path to simulate abrasion wear and a 90 N force applied directly to each specimen at the end of the 7 mm path to simulate attrition wear.^{20,29,30} At the end of each cycle the antagonist was raised and returned to the start of the 7 mm path and the wear regime repeated. Each specimen was subjected to 50,000 wear cycles conducted at a frequency of 1 Hz which was the equivalent of 6 months wear in the oral environment.²⁰ The wear regime produced a tear drop shaped wear facet on each specimen which was analysed using an optical profilometer (Talysurf CLI 2000, Taylor-Hobson Precision, Leicester, England) consisting of a non-contact 3 mm range chromatic length aberration gauge with a resolution of 100 nm scanning at a speed of 2 mm/s. A 3D profile of the wear facet was generated by performing longitudinal traces along

the wear facet at 4 μ m intervals and a detailed representation of the wear facet was produced using the TalyMap analysis software package (Taylor-Hobson Precision, Leicester, England) (Fig. 1). Abrasion wear was assumed to have occurred in the region encompassing 40–60% of the wear trace from the start of the 7 mm wear path, as reported by the investigators who developed the OHSU oral wear simulator^{20,29,30} since the region was reported to contain the most uniform section of the wear pattern and therefore the best representation of sliding abrasion wear (Fig. 2). Similarly, the region of the wear trace encompassing 80–90% of the wear trace, where the antagonist was stationary and applying a direct force was attributed to attrition wear^{20,29,30} (Fig. 3). The abrasion and attrition regions of each wear facet were sectioned from each 3D trace and analysed individually. More recent studies by the original investigators^{31,32} calculated both the mean total volumetric wear (mm^3) and the mean total wear depth (mm) rather than the previously reported mean wear depths (mm) in the abrasion and attrition regions.

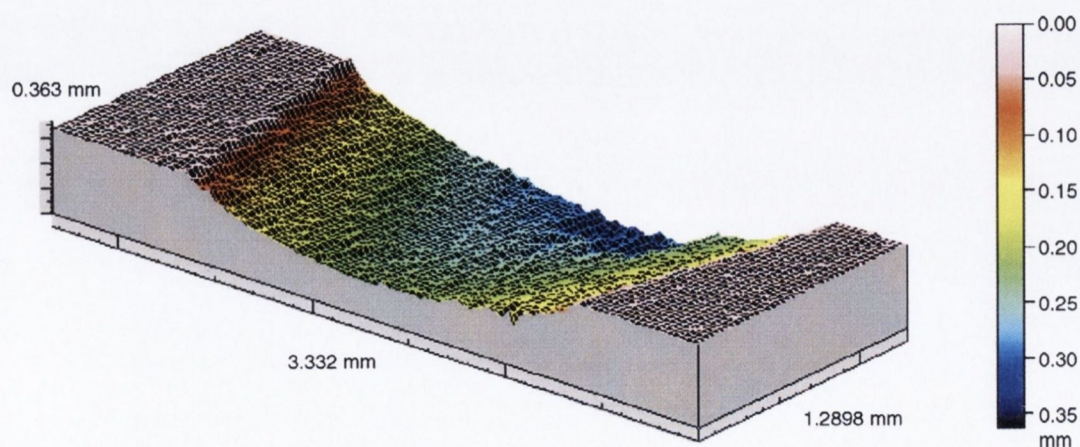


Fig. 2 – A three-dimensional representation of the abrasion region of the wear facet sectioned from 40 to 60% of the wear facet.

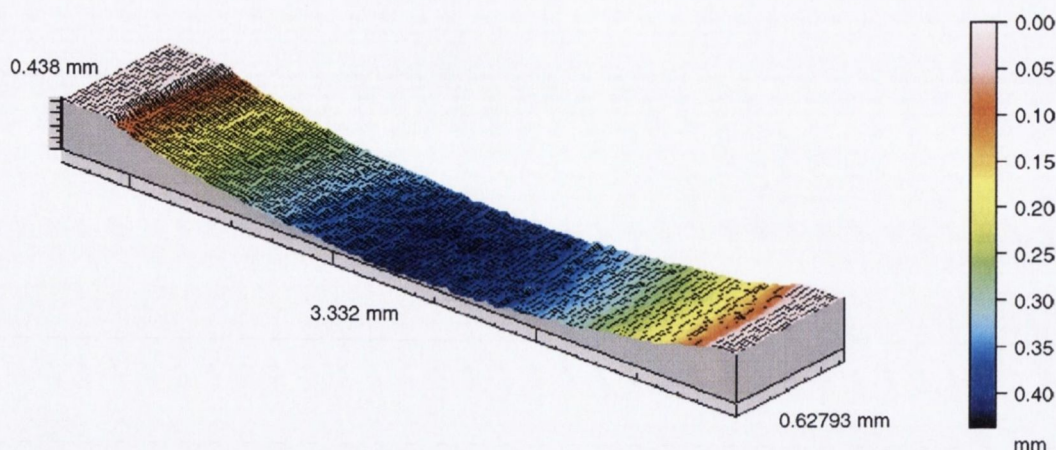


Fig. 3 – A three-dimensional representation of the attrition region of the wear facet sectioned from 80 to 90% of the wear facet.

To develop a detailed understanding of the material loss due to wear of the MMT reinforced GI restoratives investigated in the current study the mean wear depth and mean volumetric wear due to abrasion and attrition were calculated. In addition, the mean total volumetric wear and mean total wear depth were also calculated to determine the overall wear rate during the simulated masticatory wear regime. The mean wear depth and mean volumetric wear were quantified utilising the non-worn areas around the wear facet as a reference. Multiple comparisons of group means were made using a one-way analysis of variance (ANOVA) and a Tukey's multiple range test was employed at a significance level of $P < 0.05$.

3. Results

3.1. GI restorative

The mean wear depth and mean volumetric wear in the abrasion region for the GI restorative control (group A) were

0.32 (0.05) mm and $0.79 (0.21) \text{ mm}^3$, respectively, where the values in brackets represent the standard deviation for the four specimens. In the attrition region, the mean wear depth and mean volumetric wear were 0.35 (0.05) mm and $0.42 (0.12) \text{ mm}^3$, respectively. Interestingly, the mean total volumetric wear was $2.81 (0.76) \text{ mm}^3$ and the mean total wear depth was 0.43 (0.06) mm for the GI restorative (Table 1).

3.2. Ca-MMT reinforced restorative

When the mean wear depth in the abrasion region for the GI restoratives reinforced with 0.5–2.5 wt.% Ca-MMT (groups B–F, respectively) were analysed significant increases were identified for all groups when compared with the control (group A) using the one-way ANOVA and Tukey's test comparisons at the 95% significance level. Reinforcement with 0.5 wt.% Ca-MMT (group B) resulted in no significant difference in mean wear depth in the attrition region when compared with the control (group A). However, significant increases in the mean wear depth in the attrition region were identified when the Ca-MMT concentration was increased above 1.0 wt.% (groups C–F)

Table 1 – *In vitro* wear resistance data for the GI restorative ChemFil[®] Superior reinforced with varying concentrations of Ca-MMT (standard deviation in parentheses)

	Groups					
	A 0.0 ^a	B 0.5 ^a	C 1.0 ^a	D 1.5 ^a	E 2.0 ^a	F 2.5 ^a
Abrasion regime						
Mean volumetric wear (mm^3)	0.79 (0.21)	1.25 (0.32)	1.53 (0.36)	2.99 (1.66)	3.18 (1.24)	3.66 (0.85)
Mean wear depth (mm)	0.32 (0.05)	0.43 (0.06)	0.49 (0.05)	0.70 (0.23)	0.74 (0.18)	0.81 (0.12)
Attrition regime						
Mean volumetric wear (mm^3)	0.42 (0.12)	0.51 (0.12)	0.66 (0.21)	1.18 (0.60)	1.17 (0.35)	1.28 (0.36)
Mean wear depth (mm)	0.35 (0.05)	0.37 (0.04)	0.42 (0.07)	0.64 (0.17)	0.62 (0.11)	0.66 (0.11)
Total wear facet						
Mean total volumetric wear (mm^3)	2.81 (0.76)	3.91 (1.00)	5.13 (1.55)	9.88 (5.65)	10.42 (4.16)	11.90 (3.63)
Mean total wear depth (mm)	0.43 (0.06)	0.52 (0.07)	0.62 (0.09)	1.08 (0.19)	0.92 (0.17)	0.93 (0.09)

^a Concentration (wt.%).

in comparison with the GI control (Table 1). The mean wear depth caused by abrasion and attrition wear progressively increased as the wt.% of Ca-MMT clay added to the GI restorative was increased. In addition, when the mean volumetric wear in the abrasion region for the Ca-MMT reinforced GI restoratives (groups B-F) were compared with the control (group A) a significant increase in mean volumetric wear in the abrasion region (40-60%) for all groups tested was identified ($P < 0.05$). The addition of 0.5 Ca-MMT (group B) to the GI restorative produced statistically similar mean volumetric wear in the attrition region (80-90%) when compared with group A, however, when 1.0-2.5 wt.% (groups C-F) Ca-MMT was added to the GI restorative a significant increase in mean volumetric wear in the attrition region was identified when the one-way ANOVA and Tukey's test comparisons were analysed ($P < 0.05$). The mean total volumetric wear for the Ca-MMT reinforced restoratives (groups B-F) were significantly increased compared with the control (Table 1). Also, the mean total volumetric wear increased as the wt.% of Ca-MMT reinforcement added to the GI restorative was increased. Interestingly, the mean total wear depth recorded for each wt.% of Ca-MMT additive were also significantly increased in comparison to the control when the one-way ANOVA and Tukey's test comparisons were analysed at the 95% significance level (Table 1).

3.3. ADA-MMT reinforced restorative

The addition of ADA-MMT to the GI restorative (groups G-K) had no significant influence on the mean wear depth in the abrasion and attrition regions when the one-way ANOVA and Tukey's test comparisons were analysed at a significance level of $P < 0.05$ (Table 2). No significant differences were recorded in the mean volumetric wear in the abrasion and attrition regions for the groups reinforced with ADA-MMT (groups G-K) when compared with the GI control (group A). There were also no significant differences in the mean total volumetric wear or the mean total wear depth for the GI restoratives reinforced with ADA-MMT when compared with the conventional GI restorative using the one-way ANOVA and Tukey's test comparisons at the 95% significance level (Table 2).

4. Discussion

The wear regime imposed by the OHSU oral wear simulator resulted in material loss from the GI restorative due to the steatite antagonist which represents an enamel substitute²⁰ ploughing through the exposed asperities of the GI restorative structure along the 7 mm sliding abrasion path. The ploughing action results in the loosening and dislodgment of the reinforcing glass particles from the GI polymeric matrix. In addition, three-body abrasion wear also occurred during the wear regime, where the presence of the food like slurry and wear debris between the two opposing surfaces further abraded the GI restorative. Three-body wear occurs clinically during mastication when the food bolus is pressed into and dragged across the occlusal surfaces of teeth resulting in fine scratches.³³ The loss of material due to the attrition force encountered at the end of the 7 mm path is synergistic to sliding abrasion wear. The attrition force acts upon an area of the GI restorative specimen where the material has been worn previously by the sliding abrasive force. The higher force imparted upon the specimen by the attrition regime therefore acted upon a pre-stressed area of the material which assisted the further removal of material. The low abrasion and high attrition forces were manifested on the GI restorative specimen surfaces as a tear drop shaped wear facet (Fig. 1).

In the current study, the mean volumetric wear in conjunction with the mean wear depth due to abrasion and attrition and the mean total volumetric wear in conjunction with the mean total wear depth were calculated to develop a detailed appreciation of the wear performance of MMT reinforced GI restoratives. The abrasion and attrition regions of each wear facet were analysed in accordance with the research conducted by the developers of the oral wear machine.^{20,29-32} The abrasion region was chosen as 40-60% of the wear facet (Fig. 2), where the developers of the OHSU wear machine²⁰ suggested the wear due to sliding abrasion was uniform. However, when the 3D profilometry results were analysed the wear depth varied by as much as 0.22 mm between specimens over this region in the non-reinforced control group (group A). A similar discrepancy in wear depth

Table 2 - *In vitro* wear resistance data for the GI restorative ChemFil[®] Superior reinforced with varying concentrations of ADA-MMT (standard deviation in parentheses)

	Groups					
	A 0.0 ^a	G 0.5 ^a	H 1.0 ^a	I 1.5 ^a	J 2.0 ^a	K 2.5 ^a
Abrasion regime						
Mean volumetric wear (mm ³)	0.79 (0.21)	0.89 (0.23)	1.08 (0.39)	1.06 (0.40)	0.98 (0.24)	0.93 (0.32)
Mean wear depth (mm)	0.32 (0.05)	0.34 (0.05)	0.40 (0.09)	0.39 (0.09)	0.39 (0.05)	0.39 (0.05)
Attrition regime						
Mean volumetric wear (mm ³)	0.42 (0.12)	0.35 (0.10)	0.43 (0.13)	0.42 (0.21)	0.38 (0.09)	0.48 (0.14)
Mean wear depth (mm)	0.35 (0.05)	0.30 (0.04)	0.35 (0.05)	0.35 (0.11)	0.34 (0.04)	0.38 (0.02)
Total wear facet						
Mean total volumetric wear (mm ³)	2.81 (0.76)	2.79 (0.56)	3.65 (1.29)	3.29 (1.17)	3.31 (0.90)	3.70 (0.70)
Mean total wear depth (mm)	0.43 (0.06)	0.45 (0.08)	0.50 (0.08)	0.57 (0.17)	0.49 (0.06)	0.48 (0.02)

^a Concentration (wt.%).

measurements was highlighted in the attrition region (80–90% of wear facet) (Fig. 3), where the wear depth varied by as much as 0.19 mm between specimens in the control group (group A). As a result the determination of the mean total volumetric wear of the wear facet was proposed as a more accurate parameter for evaluating material loss due to wear as suggested in a recent study by DeLong.³⁴

The calculation of material removed due to the interaction of contacting surfaces was suggested by Archard in 1953 to be more accurately described in terms of volume loss.³⁵ Archard's wear equation calculated wear as the volume V (mm³) per unit sliding distance L (mm) which was dependant upon the dimensionless wear coefficient k , the applied load P (N) and the radii of the contacting asperities a (mm) as shown in Eq. (1)

$$\text{Wear} = \frac{V}{L} = \frac{kP}{3a} \quad (1)$$

DeLong et al.³⁶ evaluated the *in vitro* wear of dental amalgam in the MTS artificial mouth by measuring the volume of material removed and suggested that wear volume was a measure of the work done to remove material, implying that the wear volume was a material property independent of occlusal factors.³⁴

In a recent review questioning the "need for *in vitro* wear simulating devices" Ferracane concluded that to standardise wear testing methodologies and data reporting an appropriate wear quantity, namely depth, area or volume was critical.³⁷ To date *in vitro* wear investigations of RBCs and dental amalgams have evaluated the wear in terms of the mean wear depth of material removed following *in vitro* wear simulation.¹⁸⁻²⁰ Interestingly, a comparison of the mean wear depth measurements using the same methodology (OHSU) and abrasion parameters (20 N in the presence of a food like slurry) identified differences of 33–56% for three conventional RBC materials.³⁸ Increased differences were observed for the

attrition regime using the same methodology, namely 31–78%, although the attrition load varied from 70 to 90 N in the studies highlighted³⁹⁻⁴¹ suggesting difficulties with using mean wear depth measurements for data reporting. In addition, the area of the wear region was described recently by DeLong as being an "indirect measure of wear", the author further qualified the statement by suggesting that the wear area was dependent upon occlusal factors³⁴ as demonstrated by the variation in tooth wear *in situ* in young adults over a 2 year period.⁴² As a result, the authors of the current study whilst reporting mean wear depth measurements have focused on the wear volume as the appropriate wear quantity.

The results of the current study demonstrated that the mean total volumetric wear of Ca-MMT reinforced GI restoratives increased as the concentration of Ca-MMT was increased (Table 1), which agrees with the observation of the previous study²⁶ that the addition of the pristine Ca-MMT to GI restoratives significantly decreases the mechanical properties of the GI restorative possibly due to the increased tendency for Ca-MMT platelets to agglomerate at higher concentrations.⁴³ Indeed when the mean compressive fracture strengths achieved by the authors previously were plotted against the mean total volumetric wear a linear relationship was obtained with an associated correlation coefficient (R value) of 0.93 with increasing Ca-MMT addition from 0.5 to 2.5 wt.% (Fig. 4). Increased agglomeration of Ca-MMT platelets created porous low strength regions²⁶ within the set GI structure reinforced with Ca-MMT agglomerates which were readily removed by the ploughing action of the antagonist and were manifested as an increase in the mean total volumetric wear in comparison with the GI restorative control. The repeated cyclic loading of the simulated wear regime may have accentuated the defects thereby increasing the potential for crack growth and therefore increasing the total volumetric wear of the set GI restorative.

The addition of ADA-MMT up to 2.5 wt.% did not have a significant effect on the wear resistance of the GI restorative

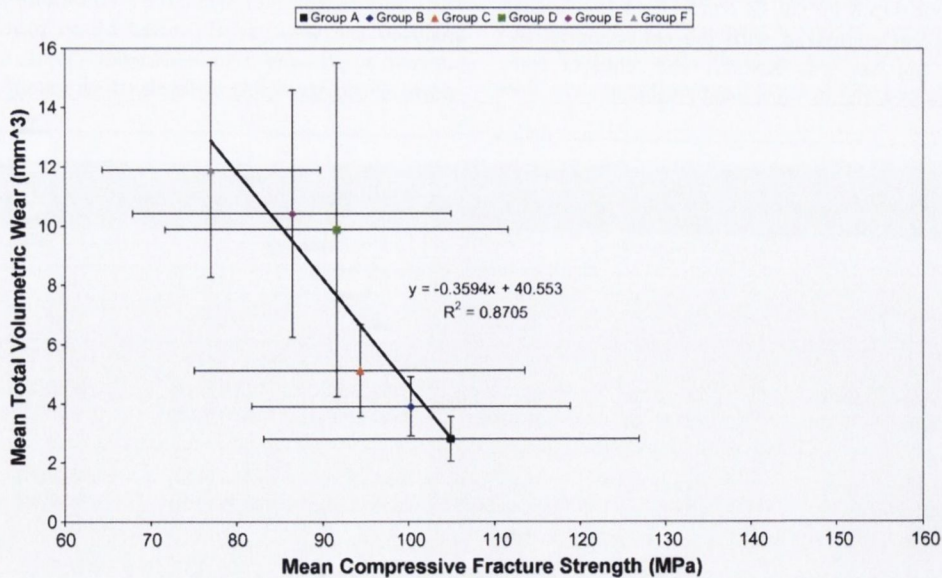


Fig. 4 – A plot of the mean total volumetric wear (mm³) against the mean compressive fracture strength (MPa)³¹ for the GI restorative ChemFil® Superior prepared with varying Ca-MMT wt.% additions (standard deviations indicated by error bars).

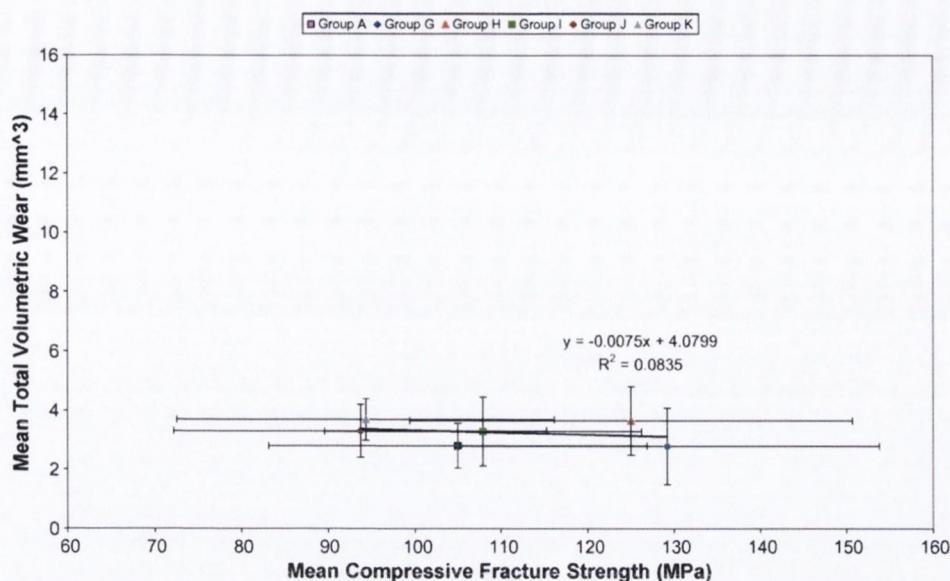


Fig. 5 – A plot of the mean total volumetric wear (mm^3) against the mean compressive fracture strength (MPa)³¹ for the GI restorative ChemFil[®] Superior prepared with varying ADA-MMT wt.% additions (standard deviations indicated by error bars).

(Table 2) manifested by the non-significant differences recorded for the mean total volumetric wear of the ADA-MMT reinforced GI restoratives (groups G–K) in comparison with the control (group A). The reinforcement of the polymeric matrix of the GI restorative with up to 1.0 wt.% of ADA-MMT, which significantly improved the mean compressive fracture strength of the GI restorative,²⁶ did not impact upon the mean total volumetric wear. Previously it has been suggested⁴³ that smaller reinforcing elements with larger surface areas have a greater reinforcing effect on material systems to which they are added. In the current study reduced mean total volumetric wear measurements were recorded for the GI restorative reinforced with ADA-MMT (average particle size $2\ \mu\text{m}$) compared with the GI restorative reinforced with Ca-MMT (average particle size $8\ \mu\text{m}$).²⁸ The smaller particle size and increased d_{001} spacing of the ADA-MMT, highlighted through X-ray diffraction previously²⁶ allowed for a more homogenous dispersion of ADA-MMT particles within the GI restorative structure and the greater potential for polymer chain ingrowth between the MMT layers which would increase the number of entanglements within the system.²⁶ The consistency of the mean total volumetric wear measurements was further highlighted by the lack of correlation (R value = 0.289) with the mean compressive fracture strength data recorded previously²⁶ for the ADA-MMT reinforced GI restoratives (Fig. 5).

The wear of MMT reinforced materials has been investigated previously by Dasari et al.⁴⁴ who added a pristine and an organically modified MMT to nylon 6. The wear resistance of the pristine clay/nylon 6 composite was significantly lower than that of the conventional nylon 6. The authors related the reduction in wear resistance to the presence of large aggregations or agglomerations of clay particles within the polymeric structure which were easier to delaminate and

debond from the polymer thereby decreasing the wear resistance of the material. The reduction in the wear resistance discovered by Dasari et al. is in agreement with the results from the current study where the mean total volumetric wear of the Ca-MMT reinforced GI restoratives was progressively reduced in comparison with the conventional GI restorative as the concentration of pristine Ca-MMT increased. Dasari et al.⁴⁴ reported that the organically modified clay/nylon 6 composite had higher wear resistance in comparison to the pristine clay/nylon 6 composite. The authors attributed the increase in wear resistance to the homogeneity of the clay platelet dispersion within the material matrix and the interfacial adhesion between the clay platelets and the polymeric matrix. However, the wear resistance of both the pristine and organically modified MMT reinforced nylon 6 composites were reduced compared with the nylon 6 control.

5. Conclusions

The current study has highlighted the potential for ADA-MMT (which has been shown previously by the authors²⁶ to significantly improve the mean compressive strength of GI restoratives) to be employed to reinforce GI restoratives without impacting on the wear behaviour. The study has also shown that optical profilometry can be a valuable tool in assessing 3D wear facets and measuring total volumetric wear.

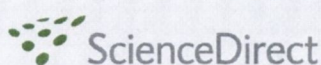
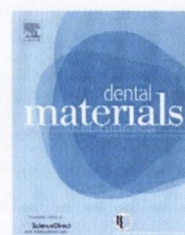
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Is encapsulation of posterior glass-ionomer restoratives the solution to clinically induced variability introduced on mixing?

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ABSTRACT

Objectives. Three GI restorative systems were evaluated to determine if encapsulated GI restoratives performed more favorably than the hand-mixed equivalents prepared with powder contents progressively decreased from that recommended by manufacturers in 10% increments for a constant weight of liquid which are routinely employed in clinical practice. **Methods.** Mean compressive fracture strengths, associated Weibull moduli and mean elastic moduli were determined for series of 30 nominally identical cylindrical specimens for three hand-mixed GI restoratives prepared with 100–50% of the recommended powder content for a constant weight of liquid and the equivalent encapsulated GI restoratives mechanically mixed in the Capmix™ or Rotomix™ machines.

Results. Decreasing the powder content of the three hand-mixed GI restoratives for a constant weight of liquid from that recommended by the manufacturers resulted in a progressive deterioration of the mean compressive fracture strengths and the mean elastic modulus. The elastic modulus was more sensitive than the compressive fracture strength to highlighting the impact of mixing ratio variations in the GI restoratives. There were no significant differences between mean compressive fracture strengths of mechanically mixed encapsulated GI restoratives, however, variations in mean elastic modulus were dependent upon the mixing time employed.

Conclusions. The employment of an intrinsic material property was more sensitive than a non-intrinsic material property to highlight the impact of mixing ratio variations in hand-mixed restoratives and the effect that the method of mechanical mixing has on encapsulated GI restoratives. Encapsulated GI restoratives are a potential solution to the operator induced variability associated with hand-mixed GI restoratives.

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1. Introduction

Glass-ionomers (GIs) were introduced to the dental profession as luting cements in 1971 by Wilson and Kent [1] and the range of uses has expanded today to include cavity bases and liners [2] and restoratives for anterior and posterior teeth [3].

GIs are commonly supplied as powder and liquid constituents, which are dispensed using a scoop and dropper bottle system prior to hand-mixing by the operator. Scoop and dropper bottle systems can result in powder to liquid mixing ratios that vary considerably from that recommended by the manufacturer [4,5]. The volume of powder dispensed by the operator is

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dependent on the powder packing density achieved on filling the scoop [4-7] with powder variations of $\pm 10.0\%$ from that recommended by the manufacturers reported under laboratory conditions for GIs [8]. In addition, the volume of liquid dispensed from a dropper bottle is dependent upon the angle at which the bottle is held and the pressure applied to squeeze a drop [4-7]. In clinical practice, dental cements are routinely mixed to a desired consistency by the technical experience of the operator, namely by eye, without the aid of scoop and dropper bottles. Billington et al. [4] and Fleming et al. [5] reported that individual operators regularly achieved consistent mixes when manipulating GI and zinc phosphate luting cements, respectively, however, inter-operator variability was considerable. Powder contents as low as 37% [4] and 34% [5] of that recommended by the manufacturer was reported for 22 [4] and 40 [5] operators when GI and zinc phosphate luting cements were manipulated in a clinical simulation, respectively.

Encapsulated luting cements eliminate operator induced variability [9,10] by standardizing the relative proportions of powder and liquid in a sealed capsule. Conventional mechanical mixing machines (Capmix™; 3M ESPE, Seefeld, Germany) vibrate at speeds of 4560-4940 cycles per minute [11] equivalent to vibratory frequencies of 76-82 Hz, respectively. However, the vibratory action incorporates porosity into the cement mix [10,12]. Mechanical mixing utilizing a combination of rotational and centrifugal action (Rotomix™; 3M ESPE, Seefeld, Germany) was introduced to reduce porosity entrapment of encapsulated cements. Studies comparing encapsulated GIs mechanically mixed using a Capmix™ or Rotomix™ machine reported that the Rotomix™ had a beneficial effect on reducing the porosity of some encapsulated GIs [3,9,13]. However, no significant differences in the mean compressive fracture strength of encapsulated GIs were evident in the dental literature regardless of the mixing machine employed [3,9,12,13].

The mechanical properties required for the ideal posterior restorative material include compressive fracture strength and elastic modulus due to the stresses developed in the back of the mouth during mastication [14]. Therefore, to maximize the functional characteristics of hand-mixed GI restoratives for use posteriorly it is essential that the optimum powder to liquid mixing ratio recommended by the manufacturer is utilized in clinical practice. The manipulation of GI restoratives to powder to liquid mixing ratios lower than those advocated by the manufacturer was reported to significantly reduce the mean compressive fracture strength [3,6] when the dental literature was assessed. Burke et al. [15] reported the performance of GI restoratives placed in non-load bearing Class V

lesions and Class III cavities, in the General Dental Services in England and Wales, progressively decreased over a 10 year period from 1991 to 2001. The progressive decline in GI performance was suggested to be an operator effect [15] most likely the result of powder to liquid mixing ratio variations encountered clinically.

The aim of the current study was to investigate the influence of powder to liquid mixing ratio variations routinely encountered clinically on the mean compressive fracture strength and mean elastic modulus of three commercially available hand-mixed posterior GI restoratives and their encapsulated equivalents (Table 1) following mechanical mixing in a Capmix™ or Rotomix™ machine. The first stated hypothesis was that reducing the powder content of hand-mixed posterior GI restoratives below that advocated by the manufacturer for a constant weight of liquid would significantly decrease the mean compressive fracture strength and mean elastic modulus. The second hypothesis was that there would be no significant difference in the mean compressive fracture strength and mean elastic modulus of encapsulated GI restoratives mechanically mixed in a Capmix™ or Rotomix™ machine. The third hypothesis was that the mean compressive fracture strength and mean elastic modulus of the encapsulated GI restoratives would be increased compared with their hand-mixed equivalents prepared with powder contents reduced from that recommended by the manufacturers for a constant weight of liquid.

2. Materials and methods

2.1. GI restorative manipulation

The hand-mixed posterior GI restoratives tested were Ketac™ Molar Easymix (Km; Lot No. 255865, shade A3), Fuji IX (Fix; Lot No. 0609081, shade A3) and ChemFlex™ (Cx; Lot No. 0611000325, shade A3). The control groups were prepared consisting of GI restorative specimens (Km100, Fix100 and Cx100) manipulated to the manufacturers' recommended powder to liquid mixing ratio (Table 1). The appropriate GI liquid weight was dispensed onto a glass slab which was placed on a balance accurate to 0.001 g (Sartorius Expert, Sartorius AG, Goettingen, Germany) using a 200 μ l pipette (Gilson, Middleton, WI, USA). The GI powder was measured into a weigh-boat using the balance, placed on the glass slab and separated into two equal parts. Half the powder was mixed with the liquid for 20 s, using a non-corrodible stainless steel spatula, the remaining powder was added and mixed for a further 20 s in accordance with manufacturers' instructions. To mimic the distribution

Table 1 - The manufacturers' details for the GI restoratives under investigation and the recommended powder to liquid mixing ratios

Product Name	Type	Manufacturer	Powder to liquid ratio (g/g)
Ketac™ Molar Easymix (Km)	Hand-mixed	3M ESPE, Seefeld, Germany	4.5/1.0
Fuji IX (Fix)	Hand-mixed	GC Europe, Leuven, Belgium	3.6/1.0
ChemFlex™ (Cx)	Hand-mixed	Dentsply DeTrey, Kanstanz, Germany	3.8/1.0
Ketac™ Molar Aplicap™	Encapsulated	3M ESPE, Seefeld, Germany	3.4/1.0
Fuji IX Fast Capsule	Encapsulated	GC Europe, Leuven, Belgium	3.6/1.0
ChemFlex™ in Caps	Encapsulated	Dentsply DeTrey, Kanstanz, Germany	3.5/1.0

of powder to liquid mixing ratios routinely achieved clinically, specimen groups were manipulated with 90% (Km90, F_{IX}90 and Cx90), 80% (Km80, F_{IX}80 and Cx80), 70% (Km70, F_{IX}70 and Cx70), 60% (Km60, F_{IX}60 and Cx60) and 50% (Km50, F_{IX}50 and Cx50) of the manufacturers' recommended powder content for a constant weight of liquid for each posterior restorative.

2.2. Encapsulated GI restorative manipulation

The encapsulated posterior GI restoratives tested were Ketac™ Molar Aplicap™ (Lot No. 222004, shade A3), Fuji IX Fast Capsule (Lot No. 0610204, shade A3) and ChemFlex™ in Caps (Lot No. 0512001557, shade A3) (Table 1). The capsules were tapped for 5 s to aerate the powder, activated for 2 s to rupture the membrane separating the constituents and placed into the holder of the Capmix™ or Rotomix™ mechanical mixing machine. The Ketac™ Molar Aplicap™ capsules were vibratory mixed for 15 s or 10 s with 3 s of centrifuging and the Fuji IX Fast Capsule and ChemFlex in Caps capsules were mixed for 10 s or 8 s with 3 s of centrifuging in the Capmix™ or Rotomix™ machine, respectively in accordance with manufacturers' instructions. The capsules were placed in an applicator to extrude the plastic mass.

2.3. Compressive fracture strength

Cylindrical specimens (6.0 ± 0.1 mm height and 4.0 ± 0.1 mm diameter) were prepared by a single operator for compressive fracture strength testing by applying the GI restorative plastic mass to a polytetrafluoroethylene (PTFE) split-mould capable of holding eight specimens [16]. The base of the split-mould was covered with an acetate strip, the split-mould aligned with nylon wedges and a locating pin to ensure equal pressure was applied along the mould. The hand-mixed plastic mass was applied to the split-mould using a stainless steel spatula and allowed to flow into the mould to minimize the incorporation of air bubbles. To facilitate the application of the encapsulated plastic mass and minimize the incorporation of air bubbles, the nozzle of the capsule was positioned to one side of the unfilled mould and the plastic mass extruded slowly to provide laminar flow. The filled mould was covered with a second acetate strip and isolated with a glass slab. To provide parallel cylindrical specimen ends for uniform contact with the compressive plates of the testing apparatus [17] the mould was clamped and equal pressure was applied to all specimens. The mould assembly was transferred to a water-bath maintained at 37 ± 1 °C. The specimens were removed from the mould after 1 h and those that contained visual defects were discarded. The flash was removed through hand-lapping on P600 silicon carbide (SiC) paper (Beuhler, Lake Bluff, Illinois, USA) using water as a lubricant. The specimens were stored in glass containers filled with 50 ml of distilled water maintained at 37 ± 1 °C for a further 23 h prior to testing. The procedure was repeated so that 30 nominally identical cylindrical specimens were manufactured for each hand-mixed powder to liquid mixing ratio and encapsulated mixing regime investigated.

The diameter of each cylindrical specimen was measured at three points with a digital micrometer accurate to 10 μm (Mitutoyo, Kawasaki, Japan) and the average diameter

recorded. The compressive fracture strength was determined using a tensile testing apparatus (Instron Model 5565, High Wycombe, England) which applied a compressive load to the long axis of the specimen at a cross-head speed of 1 mm/min. The specimens were tested 'wet' to mimic the oral environment by placing a piece of wet filter paper on the flat ends of each specimen. The load to failure was recorded for 30 specimens from each hand-mixed powder to liquid mixing ratio and encapsulated mixing regime investigated. The compressive fracture strength P (MPa) was calculated using Eq. (1)

$$P = \frac{4F_f}{\pi d^2} \quad (1)$$

where F_f is load at fracture (N) and d the mean diameter of the specimen (mm). In addition, individual stress/strain plots were derived for each specimen tested in compression and the elastic modulus (the ratio of stress to strain below the fracture limit) was determined by calculating the slope of the initial straight section of the stress/strain plot prior to fracture. The procedure was repeated and the elastic modulus for the 30 specimens from each hand-mixed powder to liquid mixing ratio and encapsulated mixing regime investigated were determined.

2.4. Statistical analysis

Multiple comparisons of the compressive fracture strength and elastic modulus group means were made using a one-way analysis of variance (ANOVA) and a Tukey's multiple range test employed at a significance of $P < 0.05$. Compressive fracture strength distributions of quasi brittle materials are more properly described by Weibull statistics rather than mean strength values determined based on a Gaussian strength distribution [18]. The compressive fracture strength data was ranked in ascending order and a Weibull analysis [19] was performed. The basic form of the Weibull distribution is shown in Eq. (2)

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (2)$$

where m and σ_0 are constants. m is known as the Weibull modulus characterizing the 'brittleness' of a material [20] with a higher value of m indicative of a closer grouping of the fracture strength data. σ_0 is the normalizing constant or the characteristic stress (MPa) which is calculated at a 63.21% failure probability. The 95% confidence limits of the Weibull modulus for the groups were calculated and differences were considered to be significant when the confidence intervals did not overlap [21].

3. Results

3.1. Hand-mixed powder to liquid mixing ratio variations

The mean compressive fracture strengths and associated standard deviations (in parenthesis) of the three GI restorative control groups (Km100, F_{IX}100 and Cx100) were 149 (24), 163 (21) and 141 (17) MPa, respectively. Decreasing the powder

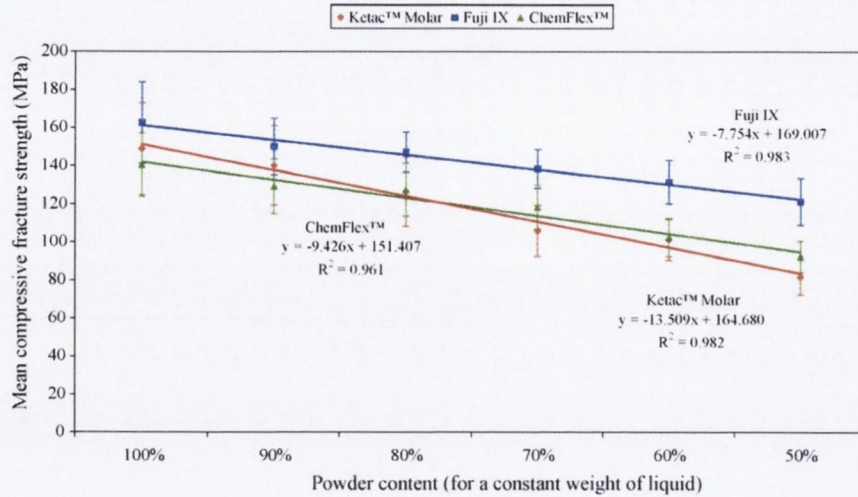


Fig. 1 – A plot of the mean compressive fracture strength versus the percentage of powder content (for a constant weight of liquid) for the GI restoratives Ketac™ Molar Easymix, Fuji IX and ChemFlex™ highlighting the progressive deterioration of the mean compressive fracture strength with powder content (error bars indicate standard deviations).

content from that recommended by the manufacturers for a constant weight of liquid resulted in a progressive deterioration of the mean compressive fracture strengths and as a result the 63.21% failure probability (σ_0) for the three GI restoratives (Fig. 1). There were significant decreases in the mean compressive fracture strength for each hand-mixed GI restorative prepared with progressively reduced powder contents for a constant weight of liquid when the one-way ANOVA and Tukey’s test comparisons at $P < 0.05$ were analyzed. However, a statistically significant progressive deterioration of the mean compressive fracture strengths did not occur between consecutive groups. In general, the Weibull modulus of the GI restoratives was not significantly increased as the powder

content was progressively reduced by 10% from that recommended by the manufacturers for a constant weight of liquid as the 95% confidence intervals overlapped between successive consecutive groups. However, progressively reducing the powder content by 10% significantly increased the Weibull modulus in three of the 18 groups investigated, namely, from Km70 to Km60, F_{IX}100 to F_{IX}90 and F_{IX}90 to F_{IX}80 (Fig. 2).

The mean elastic modulus and associated standard deviations (in parenthesis) of the hand-mixed control groups were 5.0 (0.2), 5.0 (0.3) and 4.2 (0.2) GPa for Ketac™ Molar Easymix, Fuji IX and ChemFlex™, respectively. Reducing the powder content of the three GI restoratives from that recommended by the manufacturers for a constant weight of liquid resulted

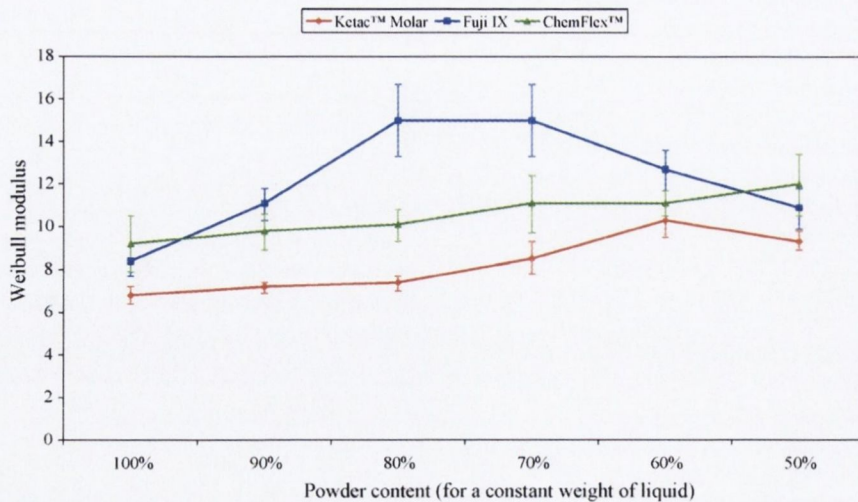


Fig. 2 – A plot of Weibull modulus versus the percentage of powder content (for a constant weight of liquid) for the GI restoratives Ketac™ Molar Easymix, Fuji IX and ChemFlex™ indicating the non significant differences in Weibull modulus between consecutive hand-mixed GI restorative groups prepared with progressively reduced powder content (by 10%) for a constant weight of liquid with the exception of Km70 to Km60, F_{IX}100 to F_{IX}90 and F_{IX}90 to F_{IX}80 (error bars indicate 95% confidence intervals).

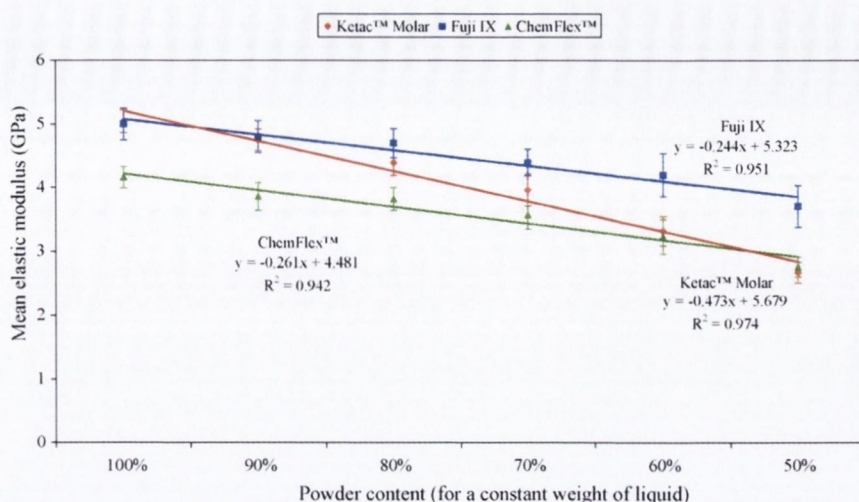


Fig. 3 – A plot of the mean elastic modulus versus the percentage of powder content (for a constant weight of liquid) for the GI restoratives Ketac™ Molar Easymix, Fuji IX and ChemFlex™ highlighting the progressive deterioration of the elastic modulus with powder content (error bars indicate standard deviations).

in a deterioration of the mean elastic modulus (Fig. 3). There was a progressive significant deterioration in the mean elastic modulus between consecutive Ketac™ Molar Easymix groups prepared with progressively reduced (by 10%) powder contents from that recommended by the manufacturers for a constant weight of liquid when the one-way ANOVA and Tukey's test comparisons were analyzed at $P < 0.05$. A progressive significant deterioration ($P < 0.05$) in mean elastic modulus was also identified for the hand-mixed Fuji IX and ChemFlex™ groups prepared with progressively reduced powder content for a constant weight of liquid with the exception of F_{IX90} to F_{IX80} , F_{IX70} to F_{IX60} and $Cx90$ to $Cx80$.

3.2. Encapsulated GI restoratives

There were no significant differences in the mean compressive fracture strength for GI restoratives mixed in the Capmix™ or Rotomix™ mechanical mixing machine when the one-way ANOVA and Tukey's test comparisons at $P < 0.05$ were analyzed (Table 2a–c). Mechanical mixing resulted in no significant difference in m for Ketac™ Molar Aplicap™ and Fuji IX Fast Capsule. However, a significant increase in m was identified for the ChemFlex™ in Caps group mechanically mixed in the Rotomix™ machine compared with the Capmix™ machine as the 95% confidence intervals did not overlap.

The mean elastic modulus of Fuji IX Fast Capsule and ChemFlex™ in Caps were identified to be significantly increased following mechanical mixing in the Rotomix™ machine compared with the Capmix™ machine when the one-way ANOVA and Tukey's test comparisons were analyzed at $P < 0.05$. No significant differences in the mean elastic modulus were evident for Ketac™ Molar Aplicap™ mechanically mixed in either the Capmix™ or Rotomix™ machines (Table 2a–c).

3.3. Encapsulated versus hand-mixed GI restoratives

The mean compressive fracture strength and σ_0 of the hand-mixed Fuji IX prepared at the manufacturers recommended mixing ratio was significantly increased compared with the mechanically mixed Fuji IX Fast Capsule groups mechanically mixed in the Capmix™ and Rotomix™ machines, when the one-way ANOVA and Tukey's test comparisons were analyzed at $P < 0.05$ (Table 2b). There was no significant difference in m for the hand-mixed Fuji IX and encapsulated Fuji IX Fast Capsule groups mechanically mixed in the Capmix™ and Rotomix™ machines.

There were no significant differences in the mean compressive fracture strength and σ_0 for the Ketac™ Molar Easymix and ChemFlex™ groups hand-mixed at the manufacturers recommended mixing ratio compared with the Ketac™ Molar Aplicap™ and ChemFlex™ in Caps groups mechanically mixed in the Capmix™ and Rotomix™ machines, respectively (Table 2a and c). However, the m for the hand-mixed Ketac™ Molar Easymix group was significantly reduced in comparison with the mechanically mixed Ketac™ Molar Aplicap™ groups. Mechanical mixing of ChemFlex™ in Caps in the Rotomix™ machine resulted in a significant increase in m compared with mechanical mixing in the Capmix™ machine and hand-mixing the ChemFlex™ at the manufacturers' recommended powder to liquid mixing ratio.

The mean elastic modulus for the Fuji IX and ChemFlex™ groups hand-mixed with the manufacturers' recommended powder content for a constant weight of liquid and the Fuji IX Fast Capsule and ChemFlex™ in Caps groups mechanically mixed in the Rotomix™ machine were significantly increased compared with the Fuji IX Fast Capsule and ChemFlex™ in Caps groups mechanically mixed in the Capmix™ machine ($P < 0.05$) (Table 2b and c). There was no significant difference in the mean elastic modulus for the hand-mixed Ketac™ Molar Easymix group compared with the Ketac™ Molar Aplicap™

Table 2 – Physical property data for the series of 30 nominally identical cylindrical specimens of the hand-mixed GI restoratives (a) Ketac™ Molar Easymix, (b) Fuji IX and (c) ChemFlex™ prepared at the manufacturers' recommended powder to liquid mixing ratio and the encapsulated GI restoratives (a) Ketac™ Molar Aplicap™, (b) Fuji IX Fast Capsule and (c) ChemFlex™ in Caps mechanically mixed with either the Capmix™ or Rotomix™ machine (standard deviations are shown in parenthesis)

Group	Ketac™ Molar Easymix		Ketac™ Molar Aplicap™	
	Hand-mixed	Capmix™	Rotomix™	
(a)				
Compressive fracture strength range (MPa)	103–201	124–180	124–189	
Mean compressive fracture strength (MPa)	149 (24) ^a	152 (15) ^a	151 (19) ^a	
Weibull modulus (<i>m</i>)	6.8 (1.2)	10.8 (2.0)	8.8 (1.6)	
Confidence intervals (95%)	6.4–7.2	9.7–11.6	7.7–9.9	
Characteristic stress (MPa) (σ_0)	155	157	156	
Elastic modulus range (GPa)	4.6–5.3	4.7–5.3	4.6–5.4	
Mean elastic modulus (GPa)	5.0 (0.2) ^b	5.0 (0.2) ^b	5.0 (0.2) ^b	
Group	Fuji IX		Fuji IX Fast Capsule	
	Hand-mixed	Capmix™	Rotomix™	
(b)				
Compressive fracture strength range (MPa)	121–218	108–165	115–184	
Mean compressive fracture strength (MPa)	163 (21) ^a	137 (16) ^b	144 (16) ^b	
Weibull modulus (<i>m</i>)	8.4 (1.5)	9.5 (1.7)	10.5 (1.9)	
Confidence intervals (95%)	7.7–9.1	8.8–10.2	8.2–11.4	
Characteristic stress (MPa) (σ_0)	168	140	144	
Elastic modulus range (GPa)	4.3–5.5	4.2–5.1	4.1–5.2	
Mean elastic modulus (GPa)	5.0 (0.3) ^c	4.7 (0.2) ^d	4.9 (0.2) ^c	
Group	ChemFlex™		ChemFlex™ in Caps	
	Hand-mixed	Capmix™	Rotomix™	
(c)				
Compressive fracture strength range (MPa)	117–178	104–164	116–169	
Mean compressive fracture strength (MPa)	141 (17) ^a	134 (16) ^a	140 (11) ^a	
Weibull modulus (<i>m</i>)	9.2 (1.7)	9.1 (1.7)	13.4 (2.4)	
Confidence intervals (95%)	7.9–10.5	8.2–10.1	12.0–14.8	
Characteristic stress (MPa) (σ_0)	141	136	142	
Elastic modulus range (GPa)	3.8–4.5	3.6–4.3	4.0–4.6	
Mean elastic modulus (GPa)	4.2 (0.2) ^b	4.0 (0.2) ^c	4.3 (0.1) ^b	

Individual GI restorative group means connected by same letter are not significantly different (Tukey's test comparisons) ($P < 0.05$).

groups mechanically mixed in the Capmix™ and Rotomix™ (Table 2a).

4. Discussion

4.1. Hand-mixed powder to liquid mixing ratio variations

The current study highlighted that the mean compressive fracture strength of the three hand-mixed GI restoratives investigated progressively decreased as powder content was reduced for a constant weight of liquid (Fig. 1). In line with previous findings, reducing the volume of reinforcing glass particles in the mixed cement for a constant weight of liquid reduced the crack stopping ability of the GI restorative [6,22,23] resulting in the reduced mean compressive fracture strengths recorded with reduced powder contents. Interestingly, the one-way ANOVA and Tukey's test comparisons at $P < 0.05$ of the mean compressive fracture strengths for the

three GI restoratives highlighted no significant differences between the means of successive groups with powder contents progressively decreased by 10% from that recommended by manufacturers for a constant weight of liquid.

The mean compressive fracture strength is important for posterior GI restoratives due to the high masticatory forces encountered in the back of the mouth during service [14]. However, little correlation exists in the dental literature for the 24 h mean compressive fracture strengths of hand-mixed GI restoratives reported by independent researchers. The mean compressive fracture strength of cylindrical specimens of a hand-mixed GI restorative (Fuji IX) tested at a cross-head speed of 1 mm/min were reported as 148 (26) MPa (6.0 mm height, 3.0 mm diameter) [24], 68 (16) MPa [13], 138 (21) MPa [25] and 163 (21) MPa in the current study (6.0 mm height, 4.0 mm diameter), 168 (14) MPa (9.0 mm height, 4.0 mm diameter) [26] and 148 (18) MPa (12.0 mm height, 6.0 mm diameter) [27], respectively. Strength is not an intrinsic material property [28,29] as the diameter and height of the cylindrical specimen influence the load to failure and therefore the mean

compressive fracture strength [29,30]. In theory, the larger the specimen volume the greater the likelihood of introducing a crack initiating defect and therefore one would expect a lower mean compressive fracture strength [31,32]. However, it is clear from the information available in the dental literature [13,24–27] that variations in the mean compressive fracture strength exist among test centers when specimens of different dimensions (68–168 MPa [13,24–27]) and even similar dimensions (68–163 MPa [13,25]) were employed.

The GI restorative powder and liquid constituents may be inaccurately dispensed prior to mixing by employing the manufacturers' scoop and dropper bottles as outlined previously [7,8]. The powder and liquid constituents should be mixed thoroughly, for the time specified by the manufacturer, to ensure that there are no unreacted powder particles present in the GI restorative plastic mass which can act as crack initiating defects when the specimen is stressed under loading thereby possibly resulting in reduced mean compressive fracture strengths [6]. It is essential that uniform contact exists between the cylindrical specimen ends and the platens of the testing apparatus, therefore the specimen ends must be flat, parallel and free of asperities which lead to localized stress concentrations and premature failure [14]. A wet testing environment would be expected to reduce the load at failure compared with a dry environment due to the influence of environmental assisted crack growth [33]. It is suggested that the combination of inaccurate dispensation prior to mixing, erratic mixing, unparallel specimen ends and variations in the testing environment can all impact upon the compressive fracture strength data and in many of the studies highlighted [13,24–27] one or more (if not all) of these variables are not specified which results in the variations reported in the dental literature.

The authors of the current study suggest also an operator effect on filling the mould could be the most important factor influencing the compressive fracture strength data. Operators from the same test center who received the same training, used the same testing protocol to assess the mean compressive fracture strength of an encapsulated GI restorative (Ketac™ Fil Plus Aplicap™; 3M ESPE, Seefeld, Germany) when mechanically mixed in the Rotomix™ machine and tested in accordance with ISO 9917-1 [34] reported mean compressive fracture strengths of 68 (15) MPa [13], 160 (21) MPa [3] and 129 (19) MPa [35]. The variations in the mean compressive fracture strength were further emphasized when the reliability of the strength data was assessed using the Weibull moduli (m) and associated 95% confidence intervals (in parenthesis) with values of 4.7 (4.4–5.0) [13], 8.5 (8.0–9.0) [3] and 7.5 (6.9–8.1) [35] indicating significant differences between operators. The encapsulated product eliminated inaccurate dispensation prior to mixing and the mixing regime was standardized by mechanical mixing in accordance with the manufacturers' instructions. Specimen preparation to ensure parallel ends, the testing environment and the split-mould were all consistent due to the same testing protocol being employed with the only variable being filling the mould with the material. Interestingly, following an analysis of the pore distribution by stereological methods [36,37] the maximum pore diameter in the cylindrical specimens increased from 99.1 μm [3] to 121.9 μm [13] with the number of large pores

($\geq 26 \mu\text{m}$) increasing from 5.0 (5.7) [3] to 8.3 (3.8) [13] resulting in the significant mean compressive fracture strength decrease from 160 MPa [3] to 68 MPa [13]. Therefore, the porosity, due to the presence of crack initiating defects, introduced to the cylindrical specimen upon filling the split-mould clearly impacts significantly on the mean compressive fracture strengths achieved between operators.

Cylindrical specimens of brittle materials subjected to a compressive axial load do not fail directly by compressive stresses. Shear stresses at the contact points with the loading platens are resolved into cones generated at either end which drive into the specimen resulting in tensile forces acting outward from the central axis of the cylinder and as a result the exact failure mechanisms operative are difficult to interpret [30]. A further complication to identifying the exact failure mechanisms operative during compressive testing is that the cylindrical GI restorative specimens experience plastic deformation prior to fracture (represented by a decrease in the ratio of stress to strain above the elastic limit). However, when calculating the compressive fracture strength the maximum load at failure lies above the elastic limit and there is no strain component in the compressive fracture strength equation to accommodate the change in the relationship between stress and strain (Eq. (1)). It is suggested that calculating the elastic modulus (from the ratio of stress to strain in the elastic range of a GI restorative) would offer a further insight into how the material performs as the elastic modulus is an intrinsic material property independent of the specimen dimensions. Additionally, the elastic modulus can be linked directly to the bonding between atoms [38] and therefore is not sensitive to microstructure or crack initiating defects in the same way as compressive fracture strength [28].

The mean elastic moduli for the Ketac™ Molar Easymix groups manipulated by reducing the powder content (by 10%) from that recommended by the manufacturer (for a constant weight of liquid) showed a progressive significant deterioration. The authors suggest that employing an intrinsic material property (mean elastic modulus) is more sensitive than a non-intrinsic material property (mean compressive fracture strength) to highlighting the impact of mixing variations in hand-mixed restoratives. In addition, the mean elastic modulus was identified to be progressively reduced for the hand-mixed ChemFlex™ groups (with the exception of Cx90 to Cx80) and was more sensitive than the non-significant differences reported in the mean compressive fracture strengths in groups Cx100 to Cx80 and Cx80 to Cx70. Fuji IX was identified to be the least sensitive restorative investigated to powder variations for a constant weight of liquid. The mean elastic modulus of Fuji IX resulted in non-significant differences in groups F_{IX}90 to F_{IX}80 and F_{IX}70 to F_{IX}60 while non-significant differences in mean compressive fracture strengths were reported in F_{IX}100 to F_{IX}80, F_{IX}80 to F_{IX}70 and F_{IX}70 to F_{IX}60. These results further emphasize that employing an intrinsic material property (mean elastic modulus) is more sensitive than employing a non-intrinsic material property (mean compressive fracture strength) to highlight the impact of mixing variations in hand-mixed restoratives. The first stated hypothesis in the current study was that employing powder to liquid mixing ratio variations routinely encountered clinically would progressively deteriorate the mean compressive

fracture strength and mean elastic modulus of the hand-mixed restoratives employed and the hypothesis was accepted.

4.2. Encapsulated GI restoratives

The 24 h mean compressive fracture strengths reported for the three encapsulated GI restoratives investigated in the current study are in agreement with previous studies [3,9,13] which indicated that there was no significant differences between individual GI restoratives when mechanically mixed in the Capmix™ or Rotomix™ machine, respectively ($P < 0.05$). However, the reliability of the compressive fracture strength data indicated that the m of ChemFlex™ in Caps was increased following mechanical mixing in the Rotomix™ machine. The finding is not in agreement with the study of Fleming and Zala [13] who found the 95% confidence limits of the m overlapped compared with the current study where the 95% confidence limits of the mechanically mixed Capmix™ or Rotomix™ specimens did not overlap. The Fuji IX Fast Capsule and Ketac™ Molar Aplicap™ restoratives did not result in increased m when mechanically mixed using a Capmix™ or Rotomix™ mixing machine in the current study. These results are not in agreement with the studies of Fleming and Zala [13] and Nomoto and McCabe [9] who reported an increased reliability for Fuji IX Fast Capsule and Ketac™ Molar Aplicap™ when mechanically mixed in the Rotomix™ ($m = 8.8$ and 20.1 , respectively) compared with a Capmix™ machine ($m = 5.3$ and 10.8 , respectively). Fleming and Zala [13] used stereological methods [36,37] to identify that the maximum pore diameter for the Fuji IX Fast Capsule following mechanical mixing was reduced using the Rotomix™ (in comparison with the Capmix™) to 42.9 compared with 140.2 μm with an associated increase in the number of pores between 4 and 42 μm when the Capmix™ machine was employed. In addition, Nomoto et al. [12] reported the mechanical mixing regime of the Rotomix™ (in comparison with the Capmix™) machine to significantly reduce the total pore volume ratio from 0.22 (0.23) to 0.06 (0.12), the total number of pores from 53 (16) to 28 (12) and the maximum diameter of the pores from 0.44 (0.22) to 0.25 (0.16) mm for Ketac™ Molar Aplicap™. As a result, the porosity namely crack initiating defects, introduced to the cylindrical specimen upon filling the split-mould following mechanical mixing clearly impacts significantly on the reliability of the compressive fracture strength data achieved between operators. The reliability of the compressive fracture strength data in the dental literature has been proposed to be markedly influenced by the mixing method [3,6,9,12,13], mixing time [39], initial viscosity of the cement mix [3], the powder to liquid mixing ratio [6] and the capsule design and exit diameter of the nozzle [10]. In addition, it is suggested in the current study that the method of filling the split-mould by the operator may also have a profound effect on the reliability of the compressive fracture strength data for reasons other than those specified previously [3,6,9,10,12,13,39].

The mean elastic modulus for Fuji IX Fast Capsule and ChemFlex™ in Caps mechanically mixed in the Rotomix™ machine were significantly increased in comparison with the Capmix™ machine. In a recent study, Prentice et al. [39] reported that increasing the mixing time of an experimental

encapsulated GI restorative in 2 s increments to 12 s progressively increased the mean elastic modulus. It is proposed that the increased mixing time of the Rotomix™ machine (11 s) in comparison with the Capmix™ machine (10 s) for Fuji IX Fast Capsule and ChemFlex™ in Caps may have accelerated the setting reaction of the GI restoratives and therefore increased the mean elastic modulus determined at 24 h [39]. Furthermore, it is likely that the non-significant differences reported in the mean elastic modulus for the Ketac™ Molar Aplicap™ groups mechanically mixed in the Capmix™ or Rotomix™ machine was the result of the reduced mixing time of the Rotomix™ machine (13 s) in comparison with the Capmix™ machine (15 s). It is possible that increasing the mixing time increased the energy input to the capsule [39] and therefore increased the homogeneity of the GI restorative mix as the amount of unreacted powder particles present within the restorative was reduced. A more homogeneously mixed GI restorative would contain an increased number of chemical bonds between the reinforcing glass particles and the polymeric matrix which would result in increased mean elastic modulus [39]. The results would appear to further emphasize that the employment of an intrinsic material property is more sensitive than a non-intrinsic material property to highlight the effects that the method of mechanical mixing has on encapsulated GI restoratives. The second hypothesis was that the encapsulated GI restoratives following mechanical mixing in a Capmix™ or Rotomix™ machine would perform equally favorably in terms of mean compressive fracture strength and mean elastic modulus despite the mixing regime employed. The hypothesis was partially accepted as the mean elastic modulus varied depending on the mixing times employed.

4.3. Encapsulated versus hand-mixed GI restoratives

The mean compressive fracture strength of cylindrical specimens (6.0 mm height, 4.0 mm diameter) of a hand-mixed Fuji IX GI restorative tested at a cross-head speed of 1 mm/min were reported as 68 (16) MPa [13], 138 (21) MPa [25] and 163 (21) MPa in the current study. The mean compressive fracture strength of cylindrical specimens (6.0 mm height, 4.0 mm diameter) of the hand-mixed ChemFlex™ GI restorative tested at a cross-head speed of 1 mm/min was reported as 69 (17) MPa compared with the value of 141 (17) MPa in the current study. There was a significant reduction in the mean compressive fracture strength for the encapsulated Fuji IX Fast Capsule groups compared with hand-mixed Fuji IX group prepared at the manufacturers' recommended mixing ratio. The powder to liquid ratio employed for Fuji IX and Fuji IX Fast Capsule were similar suggesting that hand-mixing was beneficial in terms of the mean compressive fracture strength. It is suggested that the longer mixing time for the hand-mixed Fuji IX (40 s) resulted in a more homogeneously mixed material compared with the encapsulated Fuji IX Fast Capsule. However, the mean compressive fracture strengths of Ketac™ Molar Aplicap™ and ChemFlex™ in Caps were not significantly different when compared with Ketac™ Molar Easy mix and ChemFlex™, respectively. The encapsulated materials had a reduced powder content (for a constant volume of liquid) compared with the hand-mixed materials which would have been expected to reduce the viscosity of the cement mix

and increase the homogeneity of the encapsulated mix due to the reduction in the powder content. In general, reducing the powder content would be expected to reduce the mechanical properties [3,6] but as suggested previously by Nomoto and McCabe [9] the relationship between mixing and mechanical property development is not a simple one. It cannot be assumed that mechanically mixing different GI restoratives will reproduce the exact patterns of variability demonstrated in the current study. However, given the variability in the range of GI powder to liquid mixing ratios routinely employed clinically [4,5], the authors suggest that employing encapsulated materials will provide the operator with restoratives with increased compressive fracture strength and elastic modulus compared with when the powder and liquid constituents are mixed by eye or with the aid of unreliable scoop and dropper bottle systems. Therefore the third hypothesis that encapsulated GI restoratives mixed in a Capmix™ or Rotomix™ machine would perform more favorably in terms of mean compressive fracture strength and mean elastic modulus to their hand-mixed equivalents manipulated at the mixing ratios routinely used clinically was accepted.

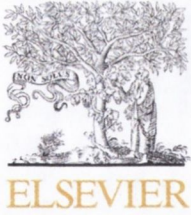
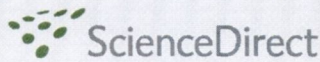
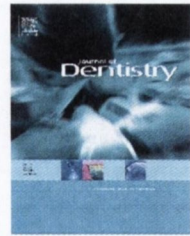
5. Conclusions

The use of an intrinsic material property (elastic modulus) offers a further tool to the dental materials scientist in looking at compressive fracture strength data rather than solely relying upon the mean compressive fracture strength that is not an intrinsic material property. Encapsulated GI restoratives appear to afford the clinician the opportunity to produce consistent mean compressive fracture strengths and mean elastic modulus values without suffering from operator induced variability routinely associated with hand-mixed products. The mechanical mixing regime utilizing either vibrational action or a combination of vibratory and centrifugal action did not influence the mean compressive fracture strengths of the encapsulated materials investigated, however, variations in the mean elastic modulus depended upon the mixing time.

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Are encapsulated anterior glass-ionomer restoratives better than their hand-mixed equivalents?

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ABSTRACT

Objectives: The performance of encapsulated anterior GI restoratives were compared with their hand-mixed equivalents for the range of powder to liquid mixing ratios routinely encountered clinically. The clinically induced variability of powder to liquid mixing variations of an anhydrous GI restorative formulation was also compared with conventional GI restorative formulations that contained a polyalkenoic acidic liquid.

Methods: Mean compressive fracture strengths, mean elastic moduli and mean total volumetric wear were determined for the encapsulated anterior GI restoratives mechanically mixed in a Capmix™ or Rotomix™ machine and the hand-mixed GI restoratives prepared with powder contents reduced from that recommended by the manufacturer (100%) in 10% increments to 50% for a constant weight of liquid. Multiple comparisons of the group means were made using a one-way analysis of variance (ANOVA) and Tukey's multiple range tests employed at $P < 0.05$.

Results: For the encapsulated GI restoratives, the mean compressive fracture strength, mean elastic modulus and *in-vitro* wear resistance were significantly increased compared with their hand-mixed equivalents prepared with powder contents below that recommended by the manufacturers. The conventional GI restoratives resulted in a linear deterioration ($R^2 > 0.95$) of the mean compressive fracture strength and mean elastic modulus with powder content compared with the bi-modal deterioration for the anhydrous GI restorative.

Conclusions: Encapsulated anterior GI restoratives outperform their hand-mixed equivalents for the range of powder to liquid mixing ratios routinely encountered clinically such that they are advocated for use in clinical practice. Anhydrous GI restorative formulations are more susceptible to clinically induced variability on mixing compared with conventional GI restorative formulations that contained a polyalkenoic acidic liquid.

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1. Introduction

Glass-ionomer (GI) luting cements were introduced to the dental market in 1972¹ following their development at the Laboratory of the Government Chemist by Wilson and Kent in 1968². Today the range of applications of GIs has expanded to

include cavity liners and bases³ and restoratives⁴ by increasing the proportion of reinforcing glass particles in the GI to counteract the masticatory forces routinely encountered in the oral environment. GIs have found wide acceptance in the dental community⁵ due to their chemical adherence to calcified tooth structures⁶ and their release of fluoride that

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has been claimed to be therapeutic.^{7,8} During the development of GIs over the last 30 years, strength testing methodologies including compressive,^{9,10} bi-axial flexure,^{11,12} three-point flexure,^{13,14} diametral tensile^{10,15} and shear punch,^{16,17} in conjunction with elastic modulus determination^{18,19} and *in-vitro* wear resistance assessment^{20,21} have been reported extensively in the dental literature. These developments have meant that the size and reactivity of the glass particles^{2,22} and the molecular weight,^{23,24} type²⁵ and concentration^{26,27} of the polyalkenoic acids in the GI systems available today have been optimised. As a result, two presentational forms have been employed by manufacturers, namely, a separate glass powder and polyalkenoic acidic liquid that set by an acid-base reaction² or a blend of glass powder and vacuum-dried polyalkenoic acid (anhydrous)^{2,28} where the acid-base reaction² is initiated on mixing with distilled or deionised water.

Hand-mixing has been reported to introduce operator-induced variability due to the inaccurate dispensation of the powder and liquid constituents using scoop and dropper bottle systems.²⁹⁻³³ The volume of powder dispensed utilising a scoop can vary due to the powder packing density achieved on filling the scoop²⁹⁻³² and dropper bottles frequently dispense uncalibrated volumes of the liquid³³ due to variations in the angle at which the bottle is held and the pressure applied to squeeze a drop.²⁹⁻³³ The variations in the powder to liquid mixing ratios utilised in clinical practice are further exacerbated when scoop and dropper bottle systems are not utilised and the constituents are mixed by 'eye' to the operators' desired consistency.³⁰ As a result, the functional characteristics normally associated with hand-mixed luting cements prepared at the manufacturers' recommended powder to liquid mixing ratios are rarely achieved in clinical practice.^{29-32,34}

Encapsulation provides consistent mixes prepared to the manufacturers' powder to liquid mixing ratio where the mixing technique and times are standardised. The vibratory action of the conventional mechanical mixing machines (CapmixTM; 3 M ESPE, Seefeld, Germany) has been reported to incorporate increased porosity into some encapsulated luting cements^{35,36} and GI restoratives^{37,38} compared with their hand-mixed equivalents. Mechanical mixing utilising a combination of rotational and centrifugal action (RotomixTM; 3 M ESPE, Seefeld, Germany) was introduced and the manufacturers' claimed that encapsulated products had reduced porosity compared with conventional vibratory action and the resultant mixes were more homogenous. Authors employing scanning electron microscopy,³⁸ X-ray microfocus

computerised tomography³⁶ and stereological methods^{4,37} have reported that mechanical mixing in the RotomixTM reduced the porosity of some encapsulated GIs^{4,36-38} compared with the CapmixTM mixing machine.

The aim of the current study was to compare the performance of encapsulated anterior GI restoratives with their hand-mixed equivalents for the range of powder to liquid mixing ratios routinely encountered clinically in terms of mean compressive fracture strength, mean elastic modulus and mean total volumetric wear. The hypothesis examined was that the mean compressive fracture strength, mean elastic modulus and mean total volumetric wear of the encapsulated GI restoratives would be significantly increased compared with their hand-mixed equivalents prepared with powder contents that are routinely employed clinically. In addition, it was hypothesised that an anhydrous GI would be more susceptible to operator-induced variability on hand-mixing than GI formulations containing a polyalkenoic acidic liquid element.

2. Materials and methods

The performance of encapsulated anterior GI restoratives (KetacTM Fil Plus AplicapTM and Fuji II Capsule) were assessed (Table 1). The capsules were tapped to loosen the powder, activated for 2 s to rupture the membrane separating the powder and liquid constituents, placed into the capsule holder of either a CapmixTM or RotomixTM mechanical mixing machine and vibratory mixed for either 10 s or 8 s with 3 s of centrifuging, respectively in accordance with manufacturers' instructions. The capsules were placed in the appropriate applicator to facilitate the extrusion of the GI restorative plastic mass.

The hand-mixed equivalents of the encapsulated GI restoratives (KetacTM Fil Plus and Fuji II) and a hand-mixed anhydrous GI restorative (ChemfilTM Superior) were also assessed (Table 1). The hand-mixed control groups for KetacTM Fil Plus, Fuji II and ChemfilTM Superior (Kf100, F_{II}100 and Cf100, respectively) were prepared in accordance with the manufacturers' recommended powder to liquid mixing ratios (Table 1). A glass-slab was placed on a balance accurate to 0.001 g (Sartorius Expert, Sartorius AG, Goettingen, Germany) and the appropriate weight of GI liquid and powder was placed onto the glass-slab. The GI powder was separated into two equal parts, half the powder was hand-mixed with the liquid for 20 s, using a non-corrodible stainless

Table 1 – The encapsulated (E) and hand-mixed (H) anterior GI restoratives investigated including the manufacturers' details, shade, lot number and powder to liquid mixing ratios used.

Product name	Manufacturers' details	Shade	Lot number	Powder content (g/g) of liquid					
				100	90	80	70	60	50
Ketac TM Fil Plus Aplicap TM (E)	3M ESPE, Seefeld, Germany	A2	277249	3.2	n/a	n/a	n/a	n/a	n/a
Fuji II Capsule (E)	GC Europe, Leuven, Belgium	22	0610201	2.7	n/a	n/a	n/a	n/a	n/a
Ketac TM Fil Plus (Kf) (H)	3M ESPE, Seefeld, Germany	A2	266794	3.2	2.9	2.6	2.2	1.9	1.6
Fuji II (F _{II}) (H)	GC Europe, Leuven, Belgium	22	0611091	2.7	2.4	2.2	1.9	1.6	1.4
Chemfil TM Superior (Cf) (H)	Dentsply DeTrey, Kanstanz, Germany	L (2)	0608001031	7.4	6.7	5.9	5.2	4.4	3.7

steel spatula, the remainder added and hand-mixed for a further 20 s in accordance with manufacturers' instructions. Specimen groups were also prepared with 90% (Kf90, F_{II}90 and Cf90), 80% (Kf80, F_{II}80 and Cf80), 70% (Kf70, F_{II}70 and Cf70), 60% (Kf60, F_{II}60 and Cf60) and 50% (Kf50, F_{II}50 and Cf50) of the recommended powder content for a constant weight of liquid (Table 1).

2.1. Compressive fracture strength

Cylindrical specimens (6.0 ± 0.1 mm height, 4.0 ± 0.1 mm diameter) were prepared by a single operator for compressive fracture strength testing by applying the GI restorative plastic mass to a polytetrafluoroethylene (PTFE) split-mould. The split-mould was placed on a PTFE base covered with an acetate strip and aligned with nylon wedges and a locating pin to ensure equal pressure was applied to the mould assembly.³⁰ To minimise the incorporation of air bubbles in the set cylindrical specimens the encapsulated GI restorative plastic mass was extruded slowly from the capsule to provide laminar flow and the nozzle was positioned to one side of the mould. The hand-mixed GI restorative plastic mass was applied to the split-mould using the stainless steel spatula and allowed to flow into the mould to minimise the incorporation of air bubbles.³¹ The filled mould was covered with an acetate strip and a glass-slab and clamped prior to the assembly being transferred to a water-bath maintained at 37 ± 1 °C. After 1 h, the specimens were removed and those that contained defects were discarded. The flash was removed through hand-lapping on P600 silicon carbide (SiC) paper (Beuhler, Lake Bluff, Illinois, USA) using water as a lubricant³⁹ and the specimens were stored in glass containers filled with 50 ml of distilled water at 37 ± 1 °C for a further 23 h prior to testing. The procedure was repeated so that 30 nominally identical cylindrical GI restorative specimens were manufactured for each encapsulated mixing regime and hand-mixed powder to liquid mixing ratio investigated.

The mean specimen diameters were calculated at three points using a digital micrometer accurate to 10 µm (Mitutoyo, Kawasaki, Japan). The compressive fracture strength was determined using a tensile testing apparatus (Instron Model 5565, High Wycombe, England) which applied a compressive load at 1 mm/min to the long axis of each specimen. To mimic the oral environment the specimens were tested 'wet' by placing wet filter paper on the flat ends and the load to failure was recorded. The compressive fracture strength *P* (MPa) was calculated using Eq. (1),

$$P = \frac{4F_f}{\pi d^2} \quad (1)$$

where *F_f* was the load at fracture (N) and *d* the mean diameter of the specimen (mm).

2.2. Elastic modulus

Individual stress/strain plots were derived for each cylindrical specimen tested in compression and the elastic modulus (the ratio of stress to strain below the fracture limit) was determined by calculating the slope of the initial straight portion of the stress/strain plot prior to fracture.

2.3. In-vitro wear resistance

To assess the in-vitro wear resistance, disc-shaped specimens (15.0 ± 0.1 mm diameter, 1.5 ± 0.1 mm thickness) were prepared by a single operator using a Perspex mould positioned on a base plate which was covered with an acetate strip. The encapsulated plastic mass was extruded slowly from the capsule nozzle directly to the centre of the mould whilst the hand-mixed plastic mass was applied directly to the centre of the mould using the stainless steel spatula. To spread the plastic mass evenly within the disc-shaped mould, a second acetate strip was placed on top of the plastic mass and a glass-slab was applied, the assembly secured using a G-clamp and transferred to a water-bath at 37 ± 1 °C. The specimens were removed from the water-bath after 1 h, hand-lapped on P600 SiC abrasive paper and stored in glass containers filled with 50 ml of distilled water at 37 ± 1 °C for 23 h. The disc-shaped specimens were mounted in a two part cold-setting acrylic resin (Varidur 10; Beuhler, Lake Bluff, Illinois, USA) for 45 min to produce cylinders (25.0 ± 0.1 mm diameter, 10.0 ± 0.1 mm height) compatible with the chambers of the wear testing apparatus. The mounted specimens were 'wet' ground on a Beta grinder-polisher machine (Beuhler, Lake Bluff, Illinois, USA) for 30 s with P600 and P1200 SiC abrasive papers at a force of 10 N to provide a surface roughness conducive to wear testing.⁴⁰

The in-vitro wear resistance was determined using the Oregon Health Science University (OHSU) four chamber oral wear simulator⁴⁰ which simultaneously produced abrasion and attrition wear in the presence of a food-like slurry. The mounted GI specimens were secured into individual wear chambers 24 h after the commencement of mixing and a food-like slurry was placed into each chamber. The slurry (1.0 g of ground poppy seeds (Holland & Barrett, Burton-upon-Trent, UK), 0.5 g of PMMA beads (Special Tray, Dentsply DeTrey, Kanstanz, Germany) and 5 ml of distilled water) was identified by De Gee et al.⁴¹ to produce wear rates comparable with those reported in clinical studies. The wear regime consisted of a 20 N sliding abrasion force travelling along a 7 mm path followed by a direct 90 N attrition force applied to each specimen at the end of the 7 mm path using steatite antagonists (10.0 ± 0.1 mm diameter).^{40,42,43} The antagonist was raised at the end of each cycle and returned to the start of the 7 mm path and the wear regime repeated. Each GI restorative specimen was subjected to 50,000 wear cycles at a frequency of 1 Hz (equivalent to 6 months wear in the oral environment)⁴⁰ and eight specimens for each encapsulated and hand-mixed group investigated were tested.

The tear drop shaped wear facets produced were analysed using an optical profilometer (Talysurf CLI 2000, Taylor-Hobson Precision, Leicester, England) consisting of a non-contact 3 mm range chromatic length aberration gauge with a resolution of 0.1 µm (z-direction) at a scanning speed of 2 mm/s. A series of perpendicular traces were performed at 4 µm intervals (y-direction) across the wear facet with measurements taken at 4 µm intervals (x-direction) and a detailed three-dimensional (3-D) representation of the wear facet was generated using the TalyMap analysis software package (Taylor-Hobson Precision, Leicester, England).⁴⁴ The total volumetric wear (mm³) of each wear facet was determined

from the 3-D representation using the non-worn areas around the wear facet as a reference.

2.4. Statistical analysis

Multiple comparisons of the group means of the compressive fracture strength, elastic modulus and total volumetric wear data were made using a one-way analysis of variance (ANOVA) and Tukey's multiple range tests employed at $P < 0.05$. The statistical analysis was used to test the hypothesis that the mean compressive fracture strength, mean elastic modulus and mean total volumetric wear of the encapsulated GI restoratives was significantly increased compared with their hand-mixed equivalents prepared with powder contents reduced from that recommended by the manufacturer. In addition, the hypothesis that the anhydrous presentational form of a GI was more susceptible to operator-induced variability on hand-mixing than GI formulations containing a polyalkenoic acidic liquid element was also examined.

3. Results

3.1. Encapsulated GI restoratives

When the Tukey's test comparisons for the encapsulated restoratives (Ketac™ Fil Plus Aplicap™ and Fuji II Capsule) mechanically mixed utilising the Capmix™ or Rotomix™ machines were analysed ($P < 0.05$), no significant differences in mean compressive fracture strength ($P = 0.990$ and 0.944 , respectively) and mean total volumetric wear ($P = 0.891$ and 0.777 , respectively) were identified (Table 2a and b). A significant increase in the mean elastic modulus was evident for Ketac™ Fil Plus Aplicap™ mechanically mixed in the Rotomix™ compared with the Capmix™ ($P = 0.041$) when the Tukey's test comparisons were analysed (Table 2a) but no such difference was identified for Fuji II Capsule ($P = 0.792$) (Table 2b).

3.2. Hand-mixed GI restoratives

Decreasing the powder content of the GI restoratives from that recommended by the manufacturers (in 10% increments) resulted in a linear deterioration of the mean compressive fracture strength and mean elastic moduli for Ketac™ Fil Plus ($R^2 = 0.96$ and 0.95 , respectively) and Fuji II ($R^2 = 0.99$ and 0.99 , respectively) but not for Chemfil™ Superior ($R^2 = 0.94$ and 0.86 , respectively) (Fig. 1a and b). When the mean compressive fracture strengths with reducing powder content were analysed using the Tukey's test comparisons at $P < 0.05$, significant decreases between successive groups (in 10% increments) were highlighted with the exception of Kf90 to Kf80 ($P = 0.449$), Kf80 to Kf70 ($P = 0.083$) and Kf70 to Kf60 ($P = 1.0$) for Ketac™ Fil Plus, F_{II}90 to F_{II}80 ($P = 0.617$) for Fuji II and Cf100 to Cf90 ($P = 0.877$) and Cf90 to Cf80 ($P = 0.113$) for Chemfil™ Superior (Table 2a-c). Analysis of the mean elastic moduli with reduced powder content, using the Tukey's test comparisons ($P < 0.05$) identified significant decreases between successive groups with the exception of Kf70 to Kf60 ($P = 0.819$) for Ketac™ Fil Plus and Cf100 to Cf90 ($P = 0.651$) and Cf90 to Cf80 ($P = 0.714$) for Chemfil™ Superior (Table 2a-c).

No linear deterioration of the mean total volumetric wear was evident with reducing powder content (in 10% increments) when employing the Tukey's test comparisons ($P < 0.05$) (Fig. 2). However, analysis of the mean total volumetric wear with reduced powder content using the Tukey's test comparisons ($P < 0.05$) identified significant increases for Kf80 to Kf70 ($P = 0.02$) and Kf60 to Kf50 ($P < 0.0001$) for Ketac™ Fil Plus, F_{II}70 to F_{II}60 ($P < 0.0001$) and F_{II}60 to F_{II}50 ($P = 0.006$) for Fuji II and Cf90 to Cf80 ($P = 0.012$), Cf70 to Cf60 ($P < 0.0001$) and Cf60 to Cf50 ($P < 0.0001$) for Chemfil™ Superior (Table 2a-c).

3.3. Encapsulated versus hand-mixed GI restoratives

The Tukey's test comparisons ($P < 0.05$) highlighted that reducing the powder content of Ketac™ Fil Plus and Fuji II to 70% of that recommended (for a constant weight of liquid) resulted in a significant reduction in the mean compressive fracture strength and mean elastic moduli compared with their mechanically mixed equivalents ($P < 0.0001$) (Table 2a and b). Interestingly, a significant increase in the mean total volumetric wear using the Tukey's test comparisons ($P < 0.05$) was achieved at the manufacturers recommended powder to liquid mixing ratio for Ketac™ Fil Plus and when the powder content was reduced to 90% for Fuji II compared with their mechanically mixed equivalents ($P < 0.0001$) (Table 2a and b).

4. Discussion

4.1. Encapsulated GI restoratives

In the dental literature the Rotomix™ mechanical mixing machine has been reported to have a beneficial effect on reducing the porosity of some encapsulated GIs compared with the Capmix™ machine,^{4,36-38} however, no significant differences in the mean compressive fracture strengths were reported in the dental literature regardless of the mechanical mixing machine employed.^{4,37,38,45} Similarly, in the current study, no significant differences were reported in the mean compressive fracture strengths for the encapsulated anterior GI restoratives investigated (Ketac™ Fil Plus Aplicap™ and Fuji II Capsule) following mechanical mixing in the Capmix™ or Rotomix™ machine. The mean elastic modulus was significantly increased for Ketac™ Fil Plus Aplicap™ when mechanically mixed in the Rotomix™ compared with the Capmix™, however, a significant increase was not evident for the Fuji II Capsule. Prentice et al.¹⁹ showed that progressively increasing the mixing time of an experimental encapsulated GI cement (from 2 to 12 s) progressively increased the mean elastic modulus due to the increased homogeneity of the viscous mix. Dowling and Fleming⁴⁵ also identified the increased mixing time (Rotomix™ (11 s) compared with Capmix™ (10 s)) increased the mean elastic modulus of some posterior GI restoratives (namely, Fuji IX_{CP} Fast Capsule and ChemFlex™ in Caps). Additionally, no significant differences were reported in the mean total volumetric wear for Ketac™ Fil Plus Aplicap™ and Fuji II Capsule following mechanical mixing in either the Capmix™ or Rotomix™ machine in line with Lohbauer et al.⁴⁷ who tested the *in-vitro* wear resistance of encapsulated GI restoratives mixed in either the Capmix™ or Rotomix™

Table 2 - Compressive fracture strength, elastic modulus and total volumetric wear data for the encapsulated anterior GI restoratives (a) Ketac™ Fil Plus Aplicap™ and (b) Fuji II Capsule mechanically mixed with either the Capmix™ or Rotomix™ machine and the hand-mixed anterior GI restoratives (a) Ketac™ Fil Plus; (b) Fuji II; and (c) Chemfil™ Superior prepared using powder contents reduced in 10% increments from that recommended by manufacturers to 50% for a constant weight of liquid (standard deviations are shown in parenthesis). Individual GI restorative group means connected by same letter are not significantly different (Tukey's test comparisons at $P < 0.05$).

Group	Ketac™ Fil Plus Aplicap™		Ketac™ Fil Plus					
	Capmix™	Rotomix™	Kf100	Kf90	Kf80	Kf70	Kf60	Kf50
(a)								
Compressive fracture strength range (MPa)	95-165	96-173	104-185	95-155	93-142	92-128	88-126	74-109
Mean compressive fracture strength (MPa)	126 (18) ^{ab}	129 (19) ^a	132 (19) ^a	122 (16) ^b	116 (12) ^{bc}	107 (10) ^{cd}	106 (10) ^d	90 (9) ^e
Elastic modulus range (GPa)	3.7-5.1	3.9-5.1	4.5-5.2	4.2-4.9	3.6-4.6	3.5-4.3	3.4-4.3	2.7-3.6
Mean elastic modulus (GPa)	4.4 (0.4) ^h	4.6 (0.4) ^g	4.9 (0.2) ^f	4.7 (0.2) ^g	4.2 (0.3) ^h	4.0 (0.2) ⁱ	3.9 (0.2) ⁱ	3.2 (0.3) ^j
Total volumetric wear range (mm ³)	0.91-1.29	0.91-1.32	1.04-1.54	1.44-2.04	1.60-2.37	1.96-2.99	2.36-3.58	3.24-6.81
Mean total volumetric wear (mm ³)	1.13 (0.15) ^k	1.10 (0.14) ^k	1.35 (0.17) ^l	1.67 (0.22) ^{lm}	1.94 (0.27) ^{lm}	2.41 (0.37) ^{mm}	2.89 (0.48) ⁿ	4.95 (1.18) ^o
Group	Fuji II Capsule		Fuji II					
	Capmix™	Rotomix™	F _{II} 100	F _{II} 90	F _{II} 80	F _{II} 70	F _{II} 60	F _{II} 50
(b)								
Compressive fracture strength range (MPa)	104-153	101-156	109-177	103-152	102-142	91-133	77-121	63-107
Mean compressive fracture strength (MPa)	127 (14) ^{bc}	131 (15) ^{ab}	141 (16) ^a	125 (14) ^{bc}	120 (13) ^c	107 (11) ^d	94 (11) ^e	84 (11) ^e
Elastic modulus range (GPa)	3.7-4.7	3.8-4.8	4.3-5.2	4.0-4.8	3.5-4.6	3.2-4.1	3.0-3.6	2.3-3.1
Mean elastic modulus (GPa)	4.2 (0.2) ^{gh}	4.3 (0.3) ^g	4.7 (0.2) ^f	4.4 (0.2) ^g	4.1 (0.2) ^h	3.7 (0.3) ⁱ	3.3 (0.2) ^j	2.7 (0.2) ^k
Total volumetric wear range (mm ³)	0.91-1.29	0.92-1.22	0.86-1.36	1.00-1.43	0.94-1.71	1.44-2.23	2.24-3.64	3.00-4.76
Mean total volumetric wear (mm ³)	1.08 (0.17) ^l	1.05 (0.13) ^l	1.08 (0.19) ^l	1.21 (0.15) ^{mm}	1.40 (0.27) ^{mm}	1.81 (0.26) ⁿ	2.88 (0.49) ^o	3.59 (0.52) ^p
Group	Chemfil™ Superior							
	Cf100	Cf90	Cf80	Cf70	Cf60	Cf50		
(c)								
Compressive fracture strength range (MPa)	105-165	101-157	92-151	88-127	66-103	54-78		
Mean compressive fracture strength (MPa)	132 (18) ^a	128 (15) ^{ab}	120 (13) ^b	107 (12) ^c	85 (9) ^d	66 (7) ^e		
Elastic modulus range (GPa)	3.8-4.7	3.7-4.6	3.7-4.4	3.4-4.1	2.6-3.4	2.0-2.6		
Mean elastic modulus (GPa)	4.3 (0.2) ^f	4.2 (0.2) ^f	4.1 (0.2) ^f	3.8 (0.2) ^g	3.0 (0.2) ^h	2.3 (0.2) ⁱ		
Total volumetric wear range (mm ³)	1.48-2.08	1.56-2.25	2.80-3.44	3.58-4.49	6.43-8.13	12.45-16.99		
Mean total volumetric wear (mm ³)	1.78 (0.24) ^j	1.91 (0.24) ^j	3.17 (0.28) ^k	3.97 (0.30) ^k	7.12 (0.58) ^l	14.29 (1.56) ^m		

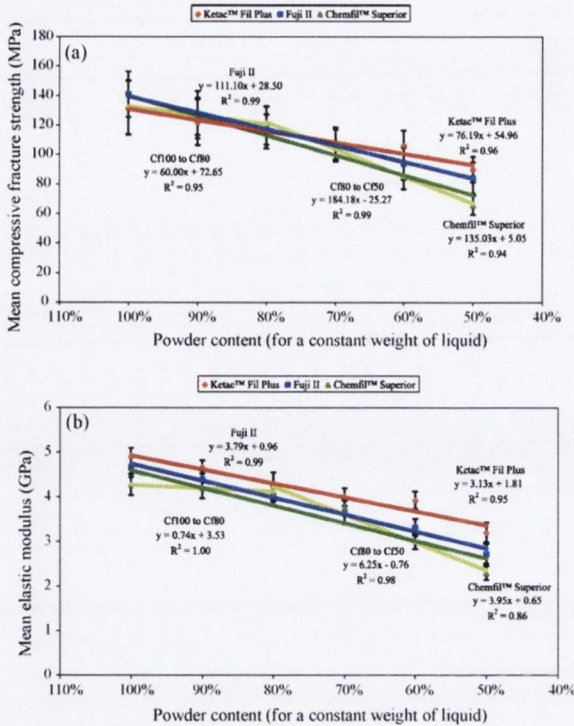


Fig. 1 – (a) A plot of the mean compressive fracture strength versus powder contents reduced from that recommended by the manufacturer (100%) in 10% increments to 50% (for a constant weight of liquid). A linear deterioration of the mean compressive fracture strength was evident for Ketac™ Fil Plus and Fuji II and a bi-modal deterioration observed for Chemfil™ Superior with reduced powder content with two distinct linear regions from Cf100 to Cf80 and Cf80 to Cf50 (standard deviations are indicated by error bars). **(b)** A plot of the mean elastic modulus versus powder contents reduced from that recommended by the manufacturer (100%) in 10% increments to 50% (for a constant weight of liquid) illustrating the linear deterioration of the mean elastic moduli for Ketac™ Fil Plus and Fuji II and the bi-modal deterioration of Chemfil™ Superior from Cf100 to Cf80 and Cf80 to Cf50 (standard deviations are indicated by error bars).

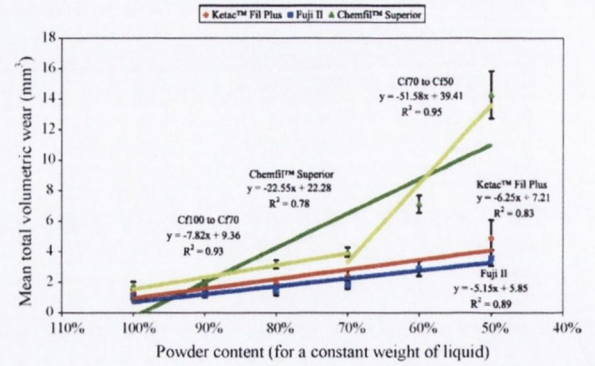


Fig. 2 – A plot of the mean total volumetric wear versus powder contents reduced from that recommended by the manufacturer (100%) in 10% increments to 50% (for a constant weight of liquid) illustrating the non-linear deterioration of the mean total volumetric wear for the three anterior GI restoratives (standard deviations are indicated by error bars). Interestingly, a bi-modal deterioration of the mean total volumetric wear was evident for Chemfil™ Superior from Cf100 to Cf70 and Cf70 to Cf50.

machine using the Academisch Centrum for Tandheelkunde Amsterdam (ACTA) wear machine. When determining mechanical properties (mean compressive fracture strength, mean elastic modulus and mean total volumetric wear), it cannot be assumed that mechanical mixing in the Rotomix™ compared with the Capmix™ will result in the exact pattern of variability for all encapsulated GI restoratives as the overall effects may be influenced by the powder to liquid mixing ratio,^{4,38} initial viscosity of the cement mix,^{4,38} capsule design³⁷ and exit diameter of the nozzle.⁴⁶

4.2. Hand-mixed GI restoratives

Previously, it has been shown that reducing the volume of the reinforcing phase (glass particles) in GI restoratives decreases

the ability of the restoratives to resist crack growth under loading.³¹ As a result, the crack stopping potential of hand-mixed conventional GI restoratives prepared with progressively reduced powder contents (from 100 to 50% in 10% increments) for a constant weight of liquid resulted in a linear deterioration of the mean compressive fracture strength and mean elastic moduli for Ketac™ Fil Plus and Fuji II (Fig. 1a and b). Linearisation was manifested as an R²-value greater than 0.95⁴⁸ when a least squares regression analysis was performed on the data. Interestingly, the compressive fracture strength and elastic modulus data for Chemfil™ Superior were not linear (R² = 0.94 and 0.86, respectively) but bi-modal distributions with two distinct linear regions from 100 to 80% (R² = 0.95 and 1.0, respectively) and 80 to 50% (R² = 0.99 and 0.98, respectively) indicative of differing performance behaviour compared with Ketac™ Fil Plus and Fuji II. Ketac™ Fil Plus and Fuji II had a constant volume of the polyalkenoic acid liquid in the cement mix due to the presentational form whereas Chemfil™ Superior had a progressively reduced acidic component since the polyalkenoic acid element was vacuum-dried and contained within the powder element.^{2,28} Therefore, progressively reducing the powder content would also progressively reduce the proportion of the polyalkenoic acid element resulting in the differing compressive fracture strength and elastic modulus behaviour presented in the current study.

The in-vitro wear resistance of GI restoratives prepared with reduced powder to liquid mixing ratios which are routinely encountered clinically has not been reported previously in the dental literature. The wear resistance of GI restoratives can be attributed to the reinforcing glass particles¹⁴ which inhibit crack growth under loading^{31,34,49} and protect the polymeric matrix from wear.⁵⁰ As a result, when the volume of the reinforcing glass particles in the GI restoratives was reduced

the volume of polymeric matrix exposed to the wear regime of the OHSU was increased which resulted in the increased mean total volumetric wear observed for Ketac™ Fil Plus, Fuji II and Chemfil™ Superior as the powder content was reduced in 10% increments (for a constant weight of liquid). Interestingly, the increase in the mean total volumetric wear with reducing powder content for the anhydrous GI restorative Chemfil™ Superior produced a bi-modal distribution with exacerbated mean total volumetric wear when the powder content was reduced below 70% of that recommended by the manufacturers. Therefore, the hypothesis that an anhydrous GI would be more susceptible to operator-induced variability on hand-mixing than GI formulations containing the polyalkenoic acidic liquid element when determining mean compressive fracture strength, mean elastic modulus and mean total volumetric wear was accepted.

Dowling and Fleming⁴⁵ suggested that employing the elastic modulus in combination with the compressive fracture strength would offer further insight into how GI restoratives performed when prepared with the powder to liquid mixing ratios routinely encountered clinically.^{29,30} In the current study, the mean elastic modulus was identified to be more sensitive to significant differences between successive GI restorative groups prepared with progressively reduced powder contents (in 10% increments) than the non-intrinsic material property (mean compressive fracture strength). Analysis of the mean elastic moduli data for Ketac™ Fil Plus and Fuji II hand-mixed with progressively reduced powder contents highlighted significant differences for nine of the ten groups compared with six groups for the mean compressive fracture strength data. This confirms the findings of Dowling and Fleming⁴⁵ that the use of an intrinsic material property (elastic modulus) offers a further tool to the dental materials scientist in looking at compressive fracture strength data and should be added to the standards armoury.

4.3. Encapsulated versus hand-mixed GI restoratives

Previously, it has been reported that powder contents as low as 37%²⁹ and 34%³⁰ of that recommended by the manufacturer were routinely utilised clinically for GI and zinc phosphate luting cements, respectively. GI restoratives have an increased powder to liquid mixing ratio (2.7/1.0 g/g for Fuji II) compared with GI luting cements (1.8/1.0 g/g for Fuji I) such that more powder has to be incorporated into the liquid resulting in a more viscous mix. As a result, it is postulated that it would be more difficult for operators in a clinical setting to incorporate extra powder into the liquid of GI restoratives and thereby achieve the manufacturers recommended powder to liquid mixing ratio within the specified working time. Therefore, it is suggested by the authors that powder contents below that recommended by the manufacturer would routinely be utilised for GI restoratives in clinical practice and the authors speculate that markedly reduced powder contents (below 50%) would not be uncommon based on the studies on operator induced variability in less viscous luting cements.^{29,30} In the current study, it was identified that the performance in terms of mean compressive fracture strength and the mean elastic moduli of the encapsulated GI restoratives (Ketac™ Fil Plus Aplicap™ and Fuji II Capsule) was significantly increased

compared with their hand-mixed equivalents (Ketac™ Fil Plus and Fuji II) when the powder content was reduced to 70% of that recommended (for a constant weight of liquid). Additionally, the mean total volumetric wear for Ketac™ Fil Plus Aplicap™ was significantly decreased compared with Ketac™ Fil Plus at the manufacturers recommended mixing ratio and for Fuji II Capsule when the powder content of Fuji II was reduced to 90% of that recommended by the manufacturer. Therefore, the hypothesis proposed that the performance of encapsulated anterior GI restoratives, in terms of mean compressive fracture strength, mean elastic modulus and mean total volumetric wear, would be increased compared with their hand-mixed equivalents for the range of powder to liquid mixing ratios routinely encountered clinically was accepted advocating the use of encapsulated GI restoratives in clinical practice.

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