

CHARACTERIZATION OF NOVEL PROPRIETARY POSTERIOR COMPOSITE MATERIALS

By

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**A thesis submitted in conformity with the requirements
for the degree of Master's of Science
Graduate Department of Dentistry
University of Toronto**

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Master's of Science, 2000

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Abstract

Packable composites have been introduced by various manufacturers of dental resin composites as 'improved' restorative materials simulating the favorable handling properties of amalgam through variations in resin composition, particle distribution and/or content of the incorporated fillers. In addition to the quality of packability, the materials are claimed to have superior physical and mechanical properties and are said to demonstrate a reduction in polymerization shrinkage as compared to universal use resin composites. To verify these claims independently, the aim of this thesis was to characterize these new materials and determine whether the alterations made to the resin composites were made at the expense of any other physical or mechanical parameter. An attempt was made to define the concept of 'packability' and establish a standard for the future testing of packable restorative materials. Lastly the materials were tested for changes in adaptation to tooth structure and gap formation on simulated clinical restorations.

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INTRODUCTION

And

OVERVIEW

The continuing debate on the safety of dental amalgam, a restorative material which contains mercury, and the public interest in aesthetic, non-metallic restorations, has fueled the research on alternative restorative materials for the functional posterior teeth. Despite the controversy surrounding dental amalgam, its clinical record remains unmatched and it continues to be the standard of care for conventional restorations involving the chewing surfaces. Any replacement or alternative material must fulfil the mechanical and biological requirements of the posterior dentition where teeth are subjected to high stresses from chewing.

Resin composites were introduced to the dental profession in 1962 as esthetic restorative materials for anterior teeth. Hailed initially as a possible substitute for silver amalgam in posterior teeth, early clinical trials proved disappointing due in particular, to the inability of the material to withstand occlusal wear, problems with microleakage, sensitivity, and intra oral insertion difficulties.

Due to the gradual evolution of technical material developments and improvements in clinical techniques, resin composites can now be routinely used in the posterior dentition in appropriate situations. Composite resins however do not exhibit the self-sealing properties{**Going RE, 1960**}, the long-term excellent wear resistance and good clinical handling properties that are routinely associated with amalgam{**Roulet JF, 1988**}. Compared with amalgam, the placement of posterior composite resins is far more technique sensitive and time consuming and the occlusal surface of the restoration cannot be hand carved. The consequences of saliva contamination during placement are more serious in a composite restoration as compared to amalgam restorations{**Mair LH, 1998**}. In addition, the achievement of tight interproximal contacts is a significant clinical problem with composite resins and can be a major contributor to food impaction and local periodontal problems. Composite resin restorations are associated with a greater incidence of post-operative sensitivity and their longevity is markedly less than that of silver amalgam{**Mjör IA et al, 1998**},{**Collins CJ et al, 1998**}.

Development and Classification of Resins Composites

A 'composite' is defined as a combination of two chemically different materials with a distinct interface separating the components and having improved properties which could not be achieved by any of the components acting alone {**Smith DC, 1985**}. The concept of a resin composite for use as an improved dental restorative material over silicate cement and reinforced poly-methyl methacrylate (PMMA) was introduced by Bowen in 1962 for the restoration of anterior teeth. Resin composites in dentistry comprise materials composed of a high molecular weight organic matrix containing a varying percentage of inorganic filler particles. The original dimethacrylate monomer for the organic matrix was given the acronym BIS-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane and was synthesized by the reaction of bisphenol A and glycidyl methacrylate and later synthesized from the diglycidyl ether of bisphenol A and methacrylic acid {**Bowen RL, 1962**},{**Bowen RL, 1965 (b)**}. Polymerization of this monomer occurs through the carbon-carbon double bonds of the two-methacrylate groups. The resin matrix of current composites contains complex high molecular weight methacrylates such as BIS-GMA or UDMA (urethane dimethacrylate), with the addition of diluent monomers such as TEGDMA (triethylene glycol dimethacrylate). In the development of dental composites, Bowen showed that an increased inorganic filler fraction increased the mechanical properties of modulus of elasticity and strength while it reduced setting contraction and thermal expansion {**Bowen RL 1956**},{**Bowen RL, 1963**}, {**Bowen RL, 1964**}. Filler particles in the composite vary according to the manufacturer and include colloidal silica, silica glasses containing barium or strontium and silicates such as lithium aluminum silicate {**Soderholm K-JM, 1985**}. The organic phase and inorganic filler particles can be micro-mechanically linked but are predominantly chemically bonded by use of a silane coupling agent added to the surface of the glass filler {**Bowen RL et al, 1976 (a)**},{**Bowen RL et al, 1976 (b)**}.

Traditional composites were 'macrofilled'; these composite materials contained filler particles usually quartz, with the mean size of the filler particles averaging between 8-14 μm and an inorganic filler loading of 61-65% by volume {**Willems G et al, 1992**}. The high volume of filler particles contributed to the high compressive strength, stiffness and dimensional stability of the material compared to unfilled materials {**Smith DC,**

1985}. Early macrofilled materials were however not polishable and surface deterioration occurred intra orally due to the wear disparity between the hard filler and the softer matrix allowing particle dislodgment and an increased susceptibility to staining. Individual products revealed distinct differences due to their particular composition. For example quartz, being extremely hard, had the potential of causing abrasion to the teeth in opposition to those restored with a quartz containing composite {Phillips RW, 1996 (d)}. Other drawbacks to quartz include a lack of radiopacity and a coefficient of thermal expansion much higher than that of tooth structure, the latter contributing to instability of true tooth-restoration adhesion{Soderholm K-JM, 1985}.

Microfilled composites using silica powder filler were developed in an attempt to overcome the problems associated with macrofilled composites. Currently, microfilled composites contain colloidal silica as the inorganic filler particles with a mean particle size 0.04 μm and a filler loading of 18-45% percent by volume{Willems G et al, 1992}. Due to the greater surface area per unit volume occupied by the microfine particles that must be wetted by the resin matrix resulting in increases in viscosity these resins cannot be heavily filled{Craig RG, 1980}. The resin matrix may also include pre-polymerized particles of composite highly loaded with colloidal silica particles that are incorporated into the resin to increase filler content to improve the physical properties while maintaining acceptable handling properties. The microfilled materials provide a smoother surface finish and enamel-like lustre for more esthetic anterior restorations. However, their physical properties are inferior to the macrofilled composites, they are radiolucent and they cannot be used in stress bearing areas. The larger amount of resin as compared to the inorganic filler content results in greater water sorption, a higher coefficient of thermal expansion and decreased elastic modulus. The weak bond between the filler particles and the resin matrix due to the absence of silane facilitates chipping of the restoration after curing{Phillips RW, 1996 (d)}.

Hybrid composites were developed in an attempt to combine the advantages of the macrofilled and the microfilled materials. The filler normally comprises a combination of colloidal silica(0.04 μm) and reduced-size glass particles with a mean size of 1-3.6 μm . The mean particle distribution in the composite resin approaches 60-71 % by volume{Willems G et al, 1992}. The filler component of the composite resin has been

shown to directly determine the physical and mechanical properties of composite materials {Willems G et al, 1992}. Willems et al found that commercial examples of these 'ultrafine compact filled composites' with mean filler particle sizes ranging from 1-3 μ m and content averaging 60-71 % by volume were satisfactory materials for the restoration of posterior teeth. Such materials exhibited compressive strength values (>390 MPa), values of Young's modulus (>21000 MPa) and Vickers hardness (>110 kg/mm³) values higher than dentin (dentin values-300MPa, 18.500MPa and 60kg/mm² respectively). Testing in vivo demonstrated that these materials displayed attrition wear rates of 110-149 μ m over a three year period similar to human enamel on molar teeth (122 μ m) {Willems G et al, 1993 (b)} which tends to wear more than the premolars {Lambrechts P et al, 1989}.

Hybrid composite resins contain elements to enhance the radiopacity at least equal to that of human enamel {Roulet JF, 1988}. This property is essential in diagnosing caries under existing restorations at future recalls. It ensures visibility of restoration contour including the presence of restoration overhangs, voids and inadequate marginal contours, which can cause detrimental periodontal effects. Barium is one of the most common elements used to enhance the radiopacity of composites. Other elements include strontium, zirconium, zinc, ytterbium and lanthanum {Willems G et al, 1991}. In addition current composite resins contain several components to enhance the durability and effectiveness of the material. A photoinitiator-activator (camphoroquinone-amine) aids in polymerization of the resin, additives improve color stability, inhibitors like hydroquinone inhibit polymerization while in storage, and lastly, pigments and opacifiers like titanium dioxide and aluminum oxide are present in trace amounts to achieve an acceptable match to the color of the tooth {Phillips RW, 1996 (d)}. Providing polishability for all anterior restorations, these highly filled materials are those also currently used for restoration of posterior teeth in appropriate situations and are often referred to as 'universal resin composites'.

Requirements of Resin Composites as Posterior Restorative Materials

Composite resins are esthetic materials that are available in a variety of shades, tints and opacities that provide an excellent match to tooth structure. Composite resins also possess several other potential advantages as restorative materials. The tooth preparation for a resin restoration can be more conservative, composite resin restorations do not readily transmit temperature changes inherent in the oral cavity and in addition, they offer the potential to seal the margins of the restoration via bonding agents. However, as posterior restoratives these materials need to meet the following requirements: {Roulet JF, 1988}. The material should:

1. Have a wear resistance equivalent to amalgam.
2. Provide an impermeable marginal seal and ideal marginal adaptation.
3. Demonstrate a radiopacity greater than enamel
4. Demonstrate predictable longevity
5. Be dimensionally stable
6. Allow technically simple working procedures
7. Allow quick and exact finishing procedures without tooth destruction.
8. Be esthetic

Similarly, the Council on Dental materials, Instruments and Equipment, of the American Dental Association {ADA Council on Dental Materials, Instruments and Equipment, 1989} specifically recommended that posterior composite restorations demonstrate the following characteristics. The material should

1. Have a good resistance to wear and abrasion.
2. Permit precise adaptation to the cavity margin.
3. Provide adequate resistance to degradation by water and other solvents.
4. Be radiopaque.
5. Have reasonable handling characteristics.

Wear Resistance

Excessive wear of composite resin materials has been a consistent problem until comparatively recently and has prevented absolute acceptance of this material for the restoration of posterior teeth {Dogan IL, 1983}, {Eames WB et al, 1974}. It has been suggested that filler size, content and area occupied by the filler particle within a composite resin formulation have the potential to influence the pattern and the rate of wear of the material, and that the greater the filler particle size, the greater is the potential for wear. {Jaarda MJ et al, 1993 [References 1-7]}. Great efforts have been made to develop new composites by experimenting with different filler materials and through downsizing the filler particles using a varied particle distribution to maximize filler content and minimize exposed organic matrix. This effort, together with improved bonding between the resin matrix and the filler particles, has resulted in posterior composites with improved wear properties {El-Mowafy OM, 1994 (b)}. Willems et al evaluated the performance of five posterior composite resins in vivo and found that the ultra fine compact filled materials exhibited attrition wear rates, ranging from 110-149 μ m at the end of three years, comparable to enamel on human molars and premolars {Willems G et al, 1993 (b)}. Wear rates are affected not only by filler particle size. Wear differs when the restored teeth are either premolars or molars, molars exhibiting more wear than premolars and first molars exhibit more wear than second molars {Sturdevant JR et al, 1986}, {Wilson NHF et al, 1991}. A number of studies have demonstrated the wear of more recent hybrid composites to be comparable to amalgam in moderate sized restorations {Johnson GH et al, 1992}, {Robinson AA et al, 1988}.

Wear does not only occur on the occlusal surface of the restoration, but on interproximal surfaces as well. Although many quantitative methods have been developed to investigate the occlusal wear of posterior restorations, few measuring techniques and little clinical data is available on the approximal wear in posterior composite restorations {Wang JC et al, 1989}.

The most current American Dental Association guidelines for acceptance of posterior composites states that, for full acceptance, the mean abrasive wear of the material should not exceed 100 μ m at four years in the unrestricted category, and 175 μ m

in the restricted category{**ADA Council on Dental materials, instruments and equipment, 1989**}. Many of the currently used posterior composite resins meet this criteria but it should be emphasized that wear is a complex phenomenon, the length of the reported studies was not longer than five years and complex restorations were not evaluated. Longer-term studies are needed to fully evaluate the performance of the posterior composite resins in vivo with a greater variety of clinical situations. Such studies are essential to test the observations obtained in short term studies, to test the life span of the restoration in comparison to other well proven materials, as well as to identify and study modes of clinical failure.

With this discussion of wear in mind it is evident that any new composite structure, such as the recently introduced 'packable composites', needs to be evaluated for wear characteristics. Analysis of filler content, size and distribution may provide some initial information but clinical studies will be necessary to fully evaluate the wear of these materials in an in vivo situation.

Polymerization shrinkage

Polymerization shrinkage is one of the biggest disadvantages of composite resin restorative materials; it is inherent to most dental polymer systems and occurs while curing the material. The process of polymerization shrinkage tends to pull the material away from the margins of the cavity. Hybrid composite materials demonstrate a linear shrinkage of 0.4-1.2% and a volumetric shrinkage of 1.3-3.5% {**Lambrechts P et al, 1987**} resulting in a tendency for gap formation at the margins of the restoration ranging from 5-29 μ m {**Brannstrom M, 1985**}. Polymerization shrinkage is responsible for many of the disadvantages associated with the use of composite restorative materials, most significant of which is microleakage that is evident clinically as staining around the margins of the restoration, post operative sensitivity and recurrent decay{**Eick DJ et al, 1986**}. The vast majority of in vitro microleakage studies reveal gaps and leakage on margins in dentin due to polymerization shrinkage combined with thermal instability. Opdam et al investigated the effects of restoration technique and adhesive systems on 48 Class I restorations placed in vivo which were subsequently evaluated post-extraction{**Opdam NJ et al, 1998**}. Their patients reported postoperative sensitivity in

14 % of all restorations. Interestingly they did not observe any microleakage into dentin but detected microleakage in enamel in 38% of the restorations despite established enamel conditioning and bonding procedures utilized. Enamel bonding is accepted as a clinically reliable procedure, hence the finding of enamel leakage in Opdam's study was interesting and is evidence of dimensional instability.

Composite Resins: Handling Characteristics and Clinical Placement

It is widely acknowledged that the use of resin composites in all but the simplest clinical restorations at the back of the mouth is more challenging than the use of silver amalgam. Resin composite materials are also recognized to be more technique sensitive {Roulet JF, 1988}. The tendency for these materials to stick to placement instruments, the polymerization contraction, the difficulties involved with ensuring marginal integrity and tight proximal contacts plus the necessity for contouring procedures using rotary instruments all point to the difficulties experienced by clinicians.

a. Moisture Contamination

Composite resins are required to be placed in teeth with a rubber dam in place because they are very susceptible to moisture contamination. This restricts the use of composites to areas in the oral cavity where moisture control can be ensured by the use of the rubber dam {Leidal TI, 1985}. The success of a composite restoration depends on the bond to tooth structure and moisture contamination during placement will negate this bond. Although also requiring good moisture control, silver amalgam is less moisture sensitive due to its ease of packability and self sealing abilities {Grossman ES et al, 1986}.

b. Incremental vs. Bulk Filled Restorations

It is generally accepted that to maximize curing depth and minimize the stresses associated with polymerization shrinkage, composite resins are required to be placed in increments no greater than 2mm {Roulet JF, 1988}. Since photo-activated composites tend to contract towards the external light source, this incremental application of the composite resin as opposed to bulk placement, decreases the overall setting contraction by reducing the bulk of composite cured at one time. In addition, the ratio of bonded to

unbonded surface area is decreased, which helps to relieve the stress developed at the bond between the tooth and the composite{Hilton TJ, 1996}. The issue of whether incremental curing reduces shrinkage has been questioned {Versluis A et al, 1996}, {Jedrychowski JR et al, 1998}. Bulk curing the material for depths greater than 2mm reduces chairside time, but raises the question of whether bulk-fill ensures adequate polymerization throughout the depth of the cured material and secondly whether bulk curing extends the probability of increased porosity within the cured material. Incorporation of voids into a restoration can contribute to stress concentrations and slow crack growth with a resultant decrease in clinical durability of the material{Braem M et al, 1998}.

Opdam et al viewed SEM sections of teeth that were filled using the bulk fill and incremental technique{Opdam NJ et al, 1998 (a)}. Their study consisted of Class I composite resins that were inserted in vivo and later extracted. Epoxy resin replicas were made of sections of the teeth were made and viewed under the SEM. They found that bulk filled restorations contained significantly more voids as compared to restorations that were filled using an incremental technique. These voids were present either between the composite/adhesive layer or between the adhesive/dentin interface. Some manufacturers of new high viscosity 'packable' composites state that their materials can be inserted in bulk to a depth of 5mm, a depth it is claimed ensures adequate curing of the material {Caulk Dentsply, 1998}, {Jeneric /Pentron, 1998}. This has not been independently verified.

c. Resin Composite Viscosity

Handling of composite resins depends to a large extent on the viscosity of the materials. Materials today are available to the clinician in a wide variety of viscosities. Materials that tend to be less highly filled or contain more diluent monomers demonstrate less viscous characteristics. Because they flow easily, these materials require greater vigilance when being placed in cavity preparations to ensure that they maintain their shape and form. On the contrary, highly filled materials, which are stiffer, need careful attention to ensure that they are well adapted to the cavity walls. Handling characteristics are not easily quantified and little scientific information on material handling is available.

In addition, the definition of this term is challenging as each dentist has his/her own preference in the handling of dental materials and optimum viscosities for particular clinical situations have not been defined.

With reference to handling of amalgam, the term 'packability' is often utilized. No scientific definition exists on packability but the term implies the ability to force a material into all parts of the cavity preparation ensuring an intimate adaptation to the cavity walls. The pressure exerted by the packed material in turn distends the confining circumferential matrix band to achieve and maintain contact with the approximal tooth. The material should be also able to resist slumping when the packing instrument is no longer in contact. Posterior composites lack this packability feature making it difficult to achieve proper approximal contact without considerable expertise{Roulet JF, 1988}. Inadequate inter-proximal contacts can be a major contributor to food impaction and post operative discomfort in the short term which if not addressed can contribute to recurrent caries, local periodontal disease and tooth migration.

High viscosity packable composites are alleged to have handling properties similar to amalgam {Leinfelder KF et al, 1998 (a)}. The manufacturers of one such material states their 'packable' material contains a high density of filler particles that pack to form an 'interlocking particle network' which is able to resist deformation, distend a matrix band and aid in achieving tight interproximal contacts{Caulk Dentsply, 1998}. Another is said to have small glass fibers with a controlled ratio of length to diameter that can impart a packing characteristic similar to amalgam {Leinfelder KF et al, 1998 (b)}. These changed handling properties have not been verified or quantified in independent studies.

d. Restoration Contours

Composite restorations cannot be hand carved prior to light curing which necessitates the use of rotary instruments to carve occlusal morphology and refine proximal contour following polymerization. This creates difficulties in the restoration procedure and is time consuming{Roulet JF, 1988}. In addition, use of rotary instruments can damage surrounding tooth structure, cause chipping of the restoration at the margin, and make the development of accurate occlusal morphology and occlusion difficult.

Clinical Longevity of Posterior Resin Composites

Many studies have evaluated the performance of posterior composite resins in an in vivo setting. It is difficult to gauge an overall performance of these materials due to differences in the clinical procedures and material variations used in these studies. In addition, many of the materials evaluated are no longer used in clinical practice and have been replaced with newer materials. On the other hand several of these studies have performance evaluations compared with amalgam and are useful in providing us with some longevity data of posterior composite restorations. The following review on longevity of posterior resin composites is based on the long-term evaluation of the clinical performance of resin composites in university-based clinics and general practice situations.

Collins et al, at the Westmead Hospital Dental Clinical School, a teaching hospital in Westmead Australia tested the clinical performance of three different types of composite resins (Heliomolar Radiopaque, Herculite XR and P-30) and reported their findings 8 years after placement{Collins CJ et al, 1998}. Forty-six patients were evaluated out of a group of an original 72. Each of these patients had 4 restorations placed, three out of which were composite resins and the fourth was amalgam. All were placed within the same time period on the posterior teeth. These 46 patients had 161 composite restorations and 52 amalgams, amounting to a total of 213 restorations. At 8 years, 13.7% of the composite restorations and 5.8% of the amalgams failed. Bulk fractures or secondary caries accounted for 76% of the failure of all restorations. Clinical evaluation of the composite restorations revealed only a small number of significant differences among the three composite materials. The fine particle hybrid composite (Herculite XR: mean particle size 0.5-1 μm) tended to show wear around a greater percentage of restorations than the other composites. The combined failure/loss rate at eight years was consistent with the findings of another study{Letzel H, 1989}.

In a ten year assessment of three posterior resin composites and two amalgams, at the University of Liverpool in England, Mair evaluated the clinical performance of Class II restorations using three posterior composite resins (P-30, Occlusin, Clearfil Posterior) and two amalgam alloys (n=30) {Mair LH, 1998}. These were placed by a single

operator, using a standardized placement technique that included moisture control. Immediately after placement, all restorations were evaluated for quality of their contact points, gingival bleeding on probing, and the presence of marginal ledges, gaps or recurrent caries. Addition silicone impressions and epoxy resin replicas of the restorations were made to facilitate an assessment of wear. Reviews took place at 6 months and then at 1,2,3,4,5, and 10 years. In addition, the resin restorations were assessed for cavo-surface marginal staining and general staining, and amalgams were assessed for the presence of tarnish and corrosion. The recall rate at 10 years was 61%. This recall rate was considered incomplete therefore no absolute failure rate was recorded. Although there was no evidence of recurrent caries with all the restorations examined it was found that more than 50% of all the Occlusin restorations examined developed marginal staining between five and ten years. In comparing wear between the resins and the amalgam alloys, it was found that the light cured resins (P-30 and Occlusin) exhibited significantly more wear than the amalgam alloys. although none of the restorations required replacement due to this wear.

In contrast to studies done under well-controlled university conditions, Barnes et al. conducted a study to evaluate the clinical performance of twelve posterior composite resins placed with as standard a placement technique as would be feasible in a general practice setting {Barnes DM et al, 1990}. A total of 61 Class II restorations were placed, 48 of which were evaluated at baseline, and 52 at the end of three years using the modified Ryge criteria for the rating for color, marginal adaptation, anatomic form, cavo-surface marginal discoloration, axial contour, interproximal contact, secondary caries and post operative sensitivity {Cvar JF et al, 1971},{Ryge G, 1980}. Although the number of restorations per brand name of materials used was not specified, and no statistical tests were performed to evaluate the results, the findings were evaluated subjectively. The authors reported higher values for wear at one year and at the end of three years, as compared to the earlier published data of Sturdevant et al {Sturdevant JR et al, 1986}. With the wide selection of posterior composite resins that these authors used, the sample size of the restorations in each category, would be too small to make any definitive comparisons between the various resins. At the end of the three-year period, a considerable number of restorations were negatively rated with respect to marginal

adaptation, secondary caries, post-operative sensitivity and interproximal contacts. Overall, 2% of the restorations failed after one year and 17% failed after three years. This study emphasizes the technique sensitivity of these materials, the need for proper patient selection, and meticulous placement techniques when utilizing composite resin as a restorative material. It also clearly contrasts the difference between carefully controlled university-based clinical studies and the clinical realities of general practice.

Survival rates for posterior composite resins were reported by El Mowafy et al in a meta analysis of 16 published clinical studies reported between 1981 and 1991, conducted for a minimum of three years, and based on well defined inclusion and exclusion criteria{El-Mowafy OM, 1994 (a)}. A comparison of the data at both 3 years and five years revealed that marginal staining, anatomical form and marginal adaptation decreased considerably from 3 years to 5 years. Due to the variations in the reporting criteria, meta-analysis studies may not reflect individual outcome criteria, but are useful in gauging the overall performance of the material. In this study, the overall clinical performance of posterior composite resins was found to be satisfactory up to five years when placed in well-controlled settings. There was a tendency to a downward trend at the end of five years in some categories. Specific problem areas were related to marginal staining, anatomic form and marginal adaptation. Due to the ongoing commercial developments newer, improved posterior composite resins are constantly being introduced to the market requiring ongoing review of clinical data.

Mjor and Moorhead conducted a study among general dentists in Florida to obtain information on the types of restorative materials used for initial placement and replacement of restorations in teeth as well as to examine the main reasons for the replacement of different types of restorative materials and to record the age of failed restorations in Class I and Class II restorations{Mjör IA et al, 1998 (a)}. The responses of twenty-seven clinicians were evaluated. Interestingly there was a slightly higher trend towards the placement of amalgam restoration in the treatment of the initial carious lesion as compared to composite restorations in Class II cavities. Secondary caries was the major reason for the replacement of all old restorations. Statistical analysis revealed no significant association between this reason and any particular restorative material used. Discoloration was the major reason for replacement of composite restorations and

fractures of the tooth the main reason for replacement of amalgam restorations. The calculated mean longevity of amalgam restorations was found to be 15 years and that for composite restorations, 8 years. The difference between the two was highly statistically significant.

The fact that composite resins are being increasingly used as restorative materials, even in Class II restorations, stresses the importance of improved durability of these materials, improved handling and increased longevity.

Introduction of High Viscosity 'Packable' Resin Composites

In an attempt to provide a resin composite with amalgam like handling properties, 'packable composites' have been introduced as alternatives to amalgam for restorative dentistry, with claims made by manufacturers of improved handling properties in particular related to proximal contacts simulating those demonstrated by amalgam. Packable composites differ from conventionally used posterior composites as a result of variations in amount and size of filler particles, or modifications in resin formulation.

The following summary provides a synthesis of purported improvements brought about in packable composites as compared to conventionally used posterior composites as described by one manufacturer {Caulk Dentsply, 1998}.

1. Variations in resin formulation and /or filler characteristics with the following resultant changes:
 - A. Improvements in the physical properties of radiopacity, depth of cure
 - B. Improvements in the mechanical properties of compressive strength, flexural strength, modulus of elasticity and fracture toughness.
 - C. Lower polymerization shrinkage with implications for reduced microleakage.
 - D. Improvements in wear resistance.
2. Improvements in handling characteristics:
 - A. An increase in the viscosity of the material with a resultant improvement in handling properties such as packability, prior to curing. A simulation of the favorable 'packable' qualities of amalgam thereby improving the adaptation of the

material to the cavity walls and enhancing the production of tight interproximal contacts.

B. Bulk cure possible with greater depth of cure.

There is a paucity of research on these novel high viscosity materials that were introduced to the dental market in 1998 without the benefits of published research or clinical trials. The introduction of such new materials often poses a dilemma to the clinician who is presented with diverse options in clinical practice with limited evidence to support the claims made. This dilemma stresses the need for independent research assessing the true advantages and disadvantages of the recently introduced materials. The aim of this study was to evaluate pertinent physical/mechanical properties, handling properties and simulated clinical performance of a range of the new high viscosity resin composites in comparison with currently used universal hybrid composite restorative materials. The resulting data will characterize this group of materials, thus providing useful information for the clinician. The questions that arise from the introduction of these new materials and the review of literature specific to composite resin restorations are:

1. Have the changes in formulation affected the physical/mechanical attributes of currently used composite resin materials?

It is important to determine the effect of the formulation changes on physical or mechanical parameters. It is also of interest to test the manufacturer's claims for superior attributes. The mechanical properties of flexural strength and modulus of elasticity will be analyzed and compared to currently accepted universal composites. Physical properties of radiopacity and hardness of the packable materials relative to the cured depth of the material will be tested to confirm whether the packable composites have the capacity to be cured in bulk. A qualitative description of the filler particles will be made to confirm the changes made to the filler contained in the packable composites. These tests will comprise Part-I: 'Physical and Mechanical Properties of Resin Composites' of this thesis.

2. Can handling properties be scientifically defined and if so, can the changes in handling properties be compared by standard testing?

As handling properties, particularly packability have not been defined, it is important to effectively determine a method for measuring 'packability', which would allow comparison of this property with the gold standard of packability in dentistry i.e. dental amalgam. Such a test would allow quantification and aid in contributing to the future testing of viscosity of dental materials and will comprise Part-II: 'Packability of Resin Composites' of this thesis.

3. Have changed handling characteristics affected the performance of clinical restorations?

Packable materials have an increased viscosity compared to current posterior composites due to their high filler fraction. The question arises as to whether this has affected the clinical performance of the materials. A simulated clinical testing of in vitro microleakage will be used to evaluate whether the increased viscosity is likely to affect the clinical performance of these materials: Part III- 'In Vitro Microleakage of Resin Composites'.

Study Hypotheses

The project hypotheses will relate to the evaluation of the properties and characteristics of the packable composites as follows:

1. The inorganic filler characteristics of the packable composite materials are different from the control composites.
2. The physical attributes of radiopacity and depth of cure by (microhardness profile) of the packable composites is significantly higher as compared to the control composites.
3. The mechanical properties of flexural strength and elastic modulus of the packable composites are significantly higher than the control composites.
4. An enhancement in 'packability' will lead to a reduction in microleakage of clinical restorations as compared to the control composites.

Objectives

1. To characterize and compare the filler particles of the test and control materials.
2. To compare radiopacity of the test and control materials.
3. To utilize microhardness testing of the materials to provide an estimate of depth of cure profiles.
4. To compare mechanical properties of flexural strength and elastic modulus of the packable and control composite materials.
5. To investigate the feasibility of a protocol for testing packability.
6. To compare packability of the test and control materials with dental amalgam.
7. To compare microleakage of the cured materials in simulated clinical restorations.

Part- I

PHYSICAL AND MECHANICAL PROPERTIES OF RESIN COMPOSITES

1.1 Physical Properties

Physical properties are based on the laws of mechanics, acoustics, radiation, atomic structure, thermodynamics, and other phenomena{Phillips RW, 1996 (c)}. Current composite materials contain a mixture of diverse oligomers, monomers, fillers and diluents. The physical properties of the materials are dependent on the type of additive as well as its concentration. In addition, the effects of the oral environment and the handling of the material affect the properties of the material. The purpose of this review is to discuss those physical properties that have obvious clinical relevance and that tend to affect the durability of the restoration.

1.1.1 Influence of Material Composition on the Physical and Mechanical Properties of Composite Resins

a. Resin Content

Most composite resins today are based on the bisGMA resin or bisGMA derivatives. BisGMA (**Figure 1.1**) is a resin of high viscosity and is diluted with diacrylate monomers like EGDMA (ethyleneglycol-dimethacrylate) and TEGDMA (triethyleneglycol dimethacrylate) (**Figure 1.2**) to achieve a viscosity suitable for incorporating fillers {Asmussen E et al, 1998}. Dilution with such monomers however, increases water uptake and polymerization shrinkage. Another group of monomers that have been developed are the urethane dimethacrylates monomers. These monomers have molecular weight (470g/mol) nearly equal to bisGMA (512g/mol) but are less viscous. The most common types which have been used either alone or in combination with bisGMA or TEGDMA are UDMA (urethane dimethacrylate) (**Figure 1.4**) or UEDMA (urethane ethyl dimethacrylate) (**Figure 1.3**). In addition, derivatives of bisGMA have been developed by the selective reaction of the secondary hydroxyl groups of bisGMA to form urethane modified bisGMA resins. Some of these urethane systems are based on oligomers synthesized from bisGMA and hexamethylene diisocyanate (**Figure 1.5**).

These altered monomeric systems were found to be less hydrophilic and demonstrated improved handling and crosslinking characteristics. {Peutzfeldt A, 1997}.

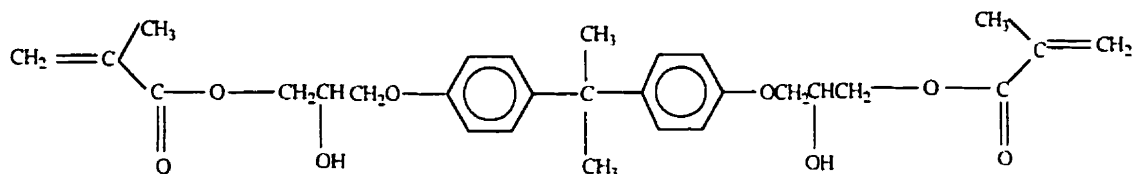


Figure 1.1: (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BisGMA)

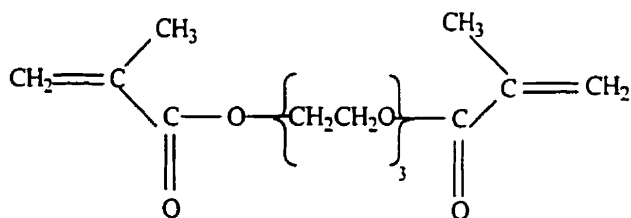


Figure 1.2: Structure of triethylene glycol dimethacrylate (TEGDMA)

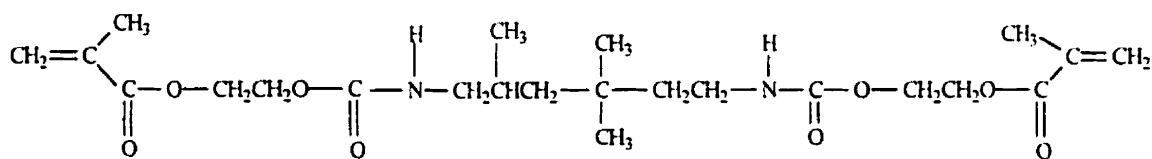


Figure 1.3: Structure of Urethane ethyl dimethacrylate (UEDMA)

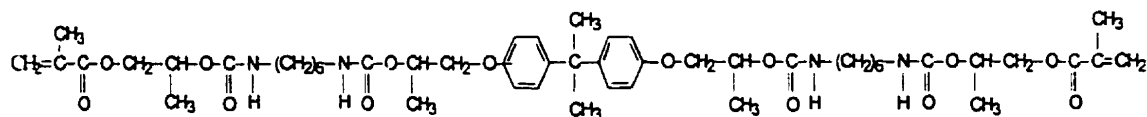


Figure 1.4: Structure of Urethane dimethacrylate (UDMA)

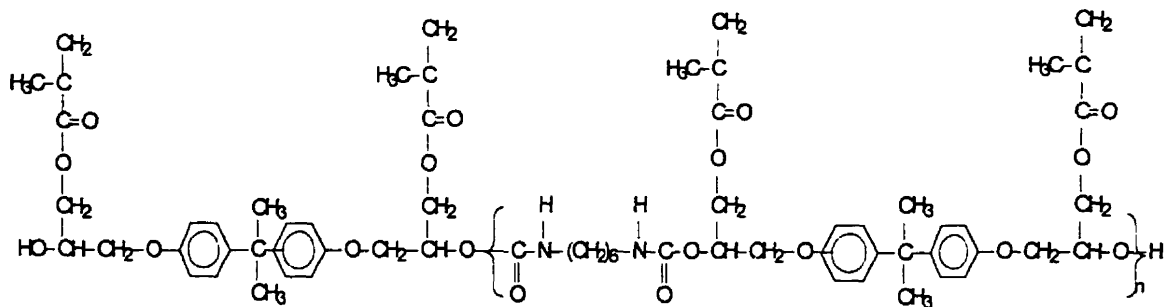


Figure 1.5: Schematic representation of the structure of the urethane modified bisGMA oligomer

The choice of monomer plays a significant role in affecting the properties of the resin composite. In a study conducted by Asmussen to determine the effect of UEDMA, bisGMA and TEGDMA on the mechanical properties of experimental composite resins, it was found that the substitution of bisGMA or TEGDMA by UEDMA resulted in an increase in tensile and flexural strength{Asmussen E et al, 1998}. Similar results were reported by Ferracane et al{Ferracane JL et al, 1986}. This increase in tensile and flexural strength observed by the substitution of bisGMA or TEGDMA by UEDMA was reported to be possibly associated with the ability of the urethane linkage to form hydrogen bonds in the copolymer which would restrict the sliding of polymer segments relative to each other. It was also observed that there was a moderate increase in the modulus of elasticity when bisGMA was substituted with low levels of TEGDMA followed by a relatively steep decline in stiffness as the content of TEGDMA increased. The reduction in the modulus of elasticity was explained by the substitution of the stiffer bisGMA by TEGDMA and the natural flexibility of this molecule, which is related to the ether linkages of the molecule allowing free rotation about the bonds.

Jones et al formulated experimental composite resins of varying proportions of bisGMA/TEGDMA and found that there was a trend of increased modulus with higher proportions of bisGMA and lower modulus with increasing proportions of TEGDMA{Jones DW et al, 1996}.

Beatty et al evaluated the differences in mechanical properties between an aromatic dimethacrylate resin DPMA (diphenyloxymethacrylate) and a urethane

dimethacrylate polymer UDMA (urethane dimethacrylate) {Beatty MW et al, 1993}. They found that the urethane based polymers demonstrated higher compressive and tensile strength and resistance to tooth brush abrasion, but absorbed substantially more water than the aromatic based materials. The high water sorption was attributed to the long aliphatic chains between ring structures (Figure 1.4). In addition, the presence of (O-CO-NH) groups in the repeat unit makes it a potent hydrogen bond former. Normally in the dry state, hydrogen bonds are formed between CO and NH groups of adjacent main chain atoms. The presence of water however, breaks the inter-chain bonds and forms its own hydrogen bonds with the urethane groups, thereby enhancing flexibility and the water uptake potential {Beatty MW et al, 1993}.

These studies demonstrate that varying the proportions of the organic constituents has a significant effect on the mechanical properties of resin composites and thus emphasizes the need for optimization of formulation to achieve a composition at which the restorative material will perform favorably under clinical conditions.

b. Filler Particle Content

The admixing of silanized filler particles into resins forms composite structures with characteristics superior to those of unfilled resins {Braem M et al, 1989}. The type of inorganic filler, filler fraction and distribution and silanization quality has a profound effect on the physical properties and clinical behavior of the resulting resin composite. It has been suggested that filler size, content and area occupied by the filler particles within a composite resin have the potential to influence the pattern and the rate of wear of the material, and that greater the filler particle size, the greater is the potential for wear. {Jaarda MJ et al, 1993 [References 1-7]}.

The mechanical properties of filled resins show a significant correlation with filler fraction {Li Y et al, 1985}. Young's modulus in particular is related to the volumetric filler content of the material: the higher the filler content, the higher the modulus and higher the resistance to deformation {Braem M et al, 1998}. A high filler fraction, although an analogue for high mechanical properties, may not mean an overall improvement in composite performance. Wear resistance should be maximized, yet hardness and stiffness should be optimized to avoid antagonistic cusp wear. Therefore

the relation between filler fraction and mechanical properties deserves detailed consideration.

To study the influence of filler content on mechanical properties, Braem et al prepared an experimental composite resin (BisGMA-62% / TEGDMA-38% by weight) with filler proportions ranging from 0-55.2% by volume {Braem M et al, 1989}. They found a high positive correlation between Young's modulus and volumetric filler content. The same positive result was obtained for their testing of transverse strength, in vitro wear testing, and Wallace Indentation Depth. Although the results cannot be extrapolated to commercially available products, and can be reproduced only if all the parameters that influence the composition of the resin are kept constant, the study clearly reflects the influence of filler content on the properties of the composite resin.

The scanning electron microscope has been used by several researchers to demonstrate filler particle content. The method of examination of filler particles has been both qualitative and quantitative {Willems G et al, 1992},{Jaarda MJ et al, 1993}. In their combined qualitative and quantitative examination of filler particle numbers. Jaarda et al subjected the unpolymerized resin to a washing process by suspension in acetone and centrifugation {Jaarda MJ et al, 1993}. A second centrifugation process following a suspension in chloroform was carried out three times to ensure separation of the particles. The remaining filler particles were suspended in absolute ethanol and smeared on a glass slide and examined under the SEM. They obtained an actual count of the number of filler particles using digital imaging analysis and found significant differences for filler sizes, numbers and the area occupied by the particles among the materials that were studied and originally classified as 'fine particle' composites. All the materials studied were a mixture of various size groupings of filler particles. Filler sizes that were effectively characterized were those that exceeded 1 μ m in diameter. The study showed that the scanning electron microscope could be used as a tool in the selective evaluation of filler particles qualitatively and with other analysis tools quantitatively.

1.1.2 Depth of Cure

The International Standards Organization refers to 'depth of cure' of polymer based restorative materials as being the depth of a surface-polymerized resin specimen below

which uncured resin is no longer present {ISO-4049, 1999}. The evaluation of this 'depth of cure' according to the simplified ISO test involves the scraping of uncured material from the cured specimen and the measurement of the depth of the remaining cylinder of hardened material. At a more detailed level, the degree of conversion of polymer based materials is a measure of the percentage of consumed carbon-carbon double bonds within the matrix of the composite resin {Phillips RW, 1996 (d)}. The polymerization reaction of resin composites can be monitored with a Fourier Transform Infrared spectrometer (FTIR) and the degree of conversion calculated based on measuring the decrease in carbon-carbon double bond (C=C) absorbance of the methacrylate monomers that occurs concomitantly with polymerization. The quantities of remaining unreacted methacrylate groups are expressed as percent of the total amount of methacrylate groups in the unpolymerized materials to indicate the degree of resin polymerization {Ruyter IE, 1985}.

Degree of monomer conversion using an FT-IR (Fourier Transform Infrared) Spectrometer has been used by several researchers as a measure of depth of resin cure and has been reported to be the most sensitive method of assessment of the degree of cure in light activated resins {Chung K-H et al, 1990}, {Ferracane JL, 1985}, {Rueggeberg FA et al, 1993}. The degree of conversion of the resin matrix for posterior composites during polymerization has been found to range from 43.5% to 73.8% {Ruyter IE, 1985}, {Chung K-H et al, 1990}. During polymerization of the resin matrix, a significant proportion of the double bonds of the methacrylate groups of high molecular weight monomers of bisGMA may remain unreacted. This is attributed to the loss of mobility and decreased activity of the polymer radicals in the highly viscous cross linked polymer network after it is formed {Chung K-H et al, 1990}. Unreacted double bonds may also be present from diluents, such as the low molecular weight monomers TEGDMA and UEDMA which are added to the resin to achieve a viscosity suitable for the addition of fillers {Asmussen E et al, 1998}.

In a study to evaluate the correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins Ferracane found, that hardness correlated well to degree of conversion for each individual resin during the initial setting (in the first 5-10 minutes) when approximately 40% of the available carbon

double bonds had reacted. For the same hardness values, the different resins tested exhibited varying degrees of conversion. Maximum hardness values were not correlated with the time period of maximum attainment in degree of conversion. The greatest increase in hardness occurred during a period in which very subtle changes in degree of conversion were taking place{**Ferracane JL, 1985**}. This was explained by the fact that mechanical properties of resins are influenced by the cross linking and network formation taking place during setting and that this network formation occurs after an initial stage of polymer chain propagation when a much greater percentage of carbon double bonds are reacted to form polymer chains than are reacted to cross link existing chains. This study was significant in explaining that in contrast to differing monomer systems, the physical properties of a given system are correlated with the degree of conversion. Secondly, mechanical properties and hardness numbers cannot be used to predict the degree of conversion when comparing different resins of different monomer systems. In a separate study, Ferracane et al showed that for materials with the exact same composition, specimens with increased cure time and a resultant higher degree of conversion demonstrated higher values of flexural strength, flexural modulus and fracture toughness {**Ferracane JL et al, 1998**}.

In another study that supported the findings of Ferracane 1985, Asmussen showed that the quantity of remaining double bonds or the degree of conversion is also affected by the proportion of the different monomers and inhibitors present in the resin. In turn, the mechanical properties of hardness and tensile strength were not entirely dependent on the degree of conversion of the double bonds, but also on the nature of the involved monomer molecules and quantity of inhibitor present{**Asmussen E, 1982**}.

Unlike chemically cured resins, where polymerization occurs uniformly throughout the bulk of the restorative material, light activated or photopolymerized resins, utilize an external light source to initiate polymerization. Light presented to the surface is attenuated through the body of the material restricting the depth of photopolymerization. Light activated resins therefore require adequate intensity and appropriate wavelength of light to ensure adequate depth of polymerization into the material. Depth of cure is dependent upon several variables: these include filler size (only up to a depth of 1mm), resin shade, opacity, light source intensity, duration of exposure;

the latter two factors being the only significant factors influencing cure at depths of 2mm or more {Sakaguchi RL et al, 1992}. The intensity of the light source should range between 400-500mW/cm² {Phillips RW, 1996 (d)}. This intensity decreases rapidly for distances greater than 2mm between the tip of the light guide and the material due to light attenuation, resulting in the cure on the restoration surface being much greater than within the depths of the material {Sakaguchi RL et al, 1992}. The radiant energy spectrum of the curing light source must coincide with the spectral absorption of the photoinitiator in the restorative material. For camphoroquinone, a typical photoinitiator used in dental restorative resins, 85% of the absorption falls between 425 and 490nm {Rueggeberg FA, 2000}.

Measurement of Hardness

Measurements of resin hardness at varying depths have been used as crude indicators of the relative degree of resin polymerization in composite resin specimens of varying thickness' due to the simplicity of the procedure {Swartz ML et al, 1983}. For a specific material, depth of cure assessment by microhardness testing and monomer conversion has shown to correlate well {Caughman WF et al, 2000}.

The term hardness or 'resistance to indentation' of a material is the ability of the surface of a material to resist penetration by a point under a specified load {Phillips RW, 1996 (b)}. The tests most frequently used are known by the names Barcol, Brinell, Rockwell, Shore, Vickers and Knoop and the selection of the test is determined by the material being selected. Both the Brinell and Rockwell tests are known as macrohardness tests and employ a hardened steel ball pressed under a specified load into the polished surface of the material. These tests have not been found to be precise enough for the hardness testing of brittle materials as they make large indentations and give average hardness values over larger areas {Phillips RW, 1996 (b)}.

Vickers hardness test employs a diamond in the shape of a square based pyramid for hardness testing, in a manner similar to that employed in the Brinell test. The square impression obtained by the indentation is measured and the Vickers hardness number is obtained by dividing the load by the projected area of the indentation. In the Knoop hardness test, a diamond-indenting tool is employed. Its shape causes elastic recovery of

the material along its shorter diagonal when the tool is removed after making the elongated diamond indent. The hardness value or KHN is obtained by dividing the load by the projected area and is virtually independent of the ductility of the material. Both the Vickers and Knoop hardness tests employ loads less than 9.8N and the resultant indentations obtained are small. They are therefore capable of measuring the hardness of very thin objects. The load used in this test may be varied over a range so that hardness values for both hard and soft materials may be obtained {Phillips RW, 1996 (b)}.

Research reports indicate that hardness has been used as a measure of depth of cure in several studies {Hansen EK et al, 1993},{Ferracane JL, 1985},{Asmussen E, 1982},{Rueggeberg FA et al, 1993}. Most of these studies are similar in method to that described by Li et al and differ with respect to thickness of the specimen and time between testing periods {Li Y et al, 1985}. Li et al used hardness testing as an indicator of depth of cure when they examined the properties of two composites of varying volumetric content but with constant filler sizes of 2 μ m and 15 μ m respectively. Each group consisted of three specimens. The specimens were fabricated by inserting the resins into brass rings, 7mm in diameter and 2.3 and 4mm high supported on a glass plate. The plate was topped by a Mylar strip and a glass plate, to which pressure was applied to extrude the excess resin. The resin was cured for 60 seconds and immediately after, three Knoop indentations were made using a 200-gram load on each of the top and bottom surfaces of the specimens. These measurements were repeated at 24 hours and seven days. Hardness values were compared at the top and the bottom for the 4mm specimens only, as the thinner specimens showed little differences in hardness between the top and bottom surfaces. Their results showed that, hardness ascertained at 24 hours was significantly more than that measured immediately and thereafter hardness remained relatively constant even up to 7 days. Hardness at the bottom of the specimen was always less than that measured at the top of the specimen. No statistical analysis was performed, but they claimed that depth of cure as measured by hardness for the composites with the 15 μ m filler was 'somewhat better' than that for 2 μ m fillers. They did not however specify, whether the specimens were stored away from light between immediate testing and the 24-hour testing. Secondly, the chances for hardness measurements being made on the filler particles are more for the resin with the 15 μ m

filler particles than the 2 μ m particles, hence perhaps the higher hardness numbers measured.

1.1.3 Radiopacity

Restorative materials need to demonstrate a radiopacity greater than enamel. This property facilitates a confirmation of the form and contour of the restoration and the visualization of marginal adaptation, voids and interfacial gaps. It helps to confirm the proximal contacts with adjacent teeth, enhances the detection of restoration overhangs, which can cause detrimental periodontal effects and is essential to distinguish secondary caries under existing restorations.

Hybrid composite resins contain radiopaque glass fillers with elements such as barium to enhance the radiopacity at least equal to that of human enamel {**Roulet JF, 1988**}. However radiopaque fillers are more susceptible to hydrolysis of the silane bond between the resin and the filler which could lead to greater material degradation {**Soderholm K-JM, 1983**}. A balance between filler particles, resin matrix and additives is crucial for optimizing the properties of the resin.

The importance of radiopacity was demonstrated by Opdam et al who evaluated the margin quality of 144 Class II composite resin restorations post-extraction, which were placed in vivo in 72 teeth {**Opdam NJM et al, 1998 (b)**}. The restorations were placed using a posterior composite after etching and bonding procedures following which the teeth were extracted five to seven weeks after placement and the restorations were evaluated radiographically. Epoxy resin replicas were appraised using a scanning electron microscope to assess the margins. Although not detected radiographically the replicas indicated that several of the restorations were either underfilled or overfilled, thereby reinforcing the need for restorative materials to demonstrate adequate radiopacity.

Willems et al investigated the radiopacity of fifty-five composite materials by measuring the optical density of the radiographed film image using a transmission densitometer against an aluminum step wedge {**Willems G et al, 1991**}. The aluminum standard curve of optical density was plotted as a function of equivalent aluminum thickness. The optical density of the specimen (1mm in thickness) was then transformed

into an equivalent aluminum thickness d_{al} by linear interpolation from the curve and expressed as a percentage of the aluminum radiopacity using the formula:

$$\frac{d_{al}}{d_s} \times 100 = \text{radiopacity in percent Al}; \text{ where } d_s \text{ equaled the specimen thickness.}$$

The ISO Standard {ISO-4049, 1999} exists to ensure all commercial materials meet certain minimum property standards and provides a standard technique for use by researchers to study the radiopacity of resin based materials. Applying the standards ensures that the tests are carried out in a consistent manner and allows for comparison between studies utilizing the same methodology. The results can be expressed in diverse ways. Bouschlicher et al determined the relative radiopacity of dentin, enamel and twenty resin composite materials and expressed the results in terms of the material aluminum equivalent {Bouschlicher MR et al, 1999}. The optical densities of the materials and an aluminum step wedge were read from radiographic images using a transmission densitometer. A linear regression of the logarithm of normalized optical density and Al mm thickness was plotted ($r^2 = 0.9953$). The Al equivalent (mm) was calculated from the linear regression equation of the log of normalized optical density and Al mm thickness obtained from the step wedge.

The ISO stipulates that the radiopacity of the material should be equal to or greater than that of the same thickness of aluminum and shall be no less than 0.5mm of any value claimed by the manufacturer {ISO-4049, 1999 [section 5.5]}. The ISO also states that if specimen thicknesses are known then the optical densities of the material and the step wedge can be directly compared requiring only one specimen of each material.

1.2 Mechanical Properties

Mechanical properties are physical properties defined by the law of mechanics that is, the physical science that deals with energy and forces and their effect on bodies {Phillips RW, 1996 (b)}. An important mechanical property is the strength of the material, which is the stress necessary to cause fracture or a specified amount of permanent deformation. The relationship of stress to strain is represented by the 'Stress/Strain Diagram' (Figure 1.6)

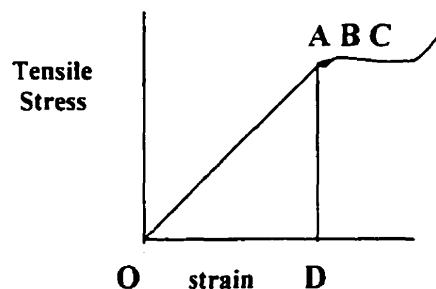


Figure 1.6: Tensile Stress/Strain diagram

In Figure 1.6, between points O and A, stress is proportional to strain, thus obeying Hooke's Law. The slope of the linear portion is a measure of the rigidity of the material and is termed the *modulus of elasticity*. Materials with a higher modulus are deemed more rigid and those with a lower modulus are deemed more flexible. Point A, the *proportional limit*, is the maximum stress at which stress is proportional to strain. Point B, the *elastic limit*, is the maximum stress, which a material can endure without undergoing permanent deformation. This means a material when stressed beyond the proportional limit behaves elastically on removal of the applied load and undergoes no permanent deformation. Point C, the *yield point* describes the point where there is a rapid increase in strain without a corresponding increase in stress, or the point where plastic deformation occurs {Combe EC, 1992}. Strength can also be described by the following properties shear strength, compressive strength, tensile strength and flexural strength each of which is a measure of stress required to fracture a material under

different means of loading{Phillips RW, 1996 (b)}. Shear stresses represent the slide of one portion of a body over another, compressive stresses denote a shortening load. tensile stresses symbolize stretch and flexural forces are combination of compressive, tensile and shear stresses{Phillips RW, 1996 (b)}.

The nature of brittle materials such as composite resins restricts the type of strength tests it can endure. They have a tensile strength that is markedly lower than the corresponding compressive strength because of the inability to plastically deform. The stress/strain plot is a straight line with little or no plastic region{Combe EC, 1992}. Composite resins are brittle materials which when used as dental restorations, are usually subjected to a combination of compressive, tensile and shear forces. The strength of such materials is better determined by the 'flexural strength test' or a three-point flexure of the material where the superior surface is subjected to compressive forces and the inferior surface to tensile forces. In addition to flexural strength, a whole range of tests of a dynamic nature can be used to characterize the resin composites under study. An example of such a test is 'fracture toughness' which is a measure of the energy required to propagate a crack and is a more precise measure of the fracture resistance of brittle materials that are susceptible to surface flaws{Phillips RW, 1996 (b)}.

In his extensive review on the physical properties of composite restorative materials Braem{Braem M et al, 1998} indicated that restorative materials with a low Young's modulus had a lower resistance to deformation and are more prone to deform extensively under occlusal loading. This results in strain development in the resin matrix and in subsequent crack formation. This phenomenon is partly compressive on the surface of the restoration and partly tensile beneath the surface. Microfilled composites exhibit generalized material fatigue in areas of high function because of their low modulus values. Highly filled resins on the other hand deform very little under function. Cracks that do occur move through the matrix phase and along the perimeter of the filler particles resulting in a more localized destruction and in a crack retarding mechanism. Under heavy function, these cracks propagate and weaken the matrix phase and may connect with the surface causing a pitted character. When Young's modulus is too high, the material may demonstrate an almost brittle nature that cannot withstand repetitive impact forces{Braem M et al, 1998}. This work emphasized the need for materials to

demonstrate a modulus of elasticity similar to the material it will replace namely dentin. It also stressed the need for mechanical testing apparatus to deliver a load cycle that is both compressive and tensile in nature.

1.2.1 Flexural Strength

Flexural strength is an important mechanical property related to materials used in dentistry; this property gives us an insight into the failure potential of the material under a combination of applied forces. Stresses imposed to determine the strength potential can be measured as being either compressive, tensile or shear. Flexural forces which are produced by bending can produce all three types of stresses in a structure and deemed a useful way to determine the strength of brittle materials.

The test of flexural strength of composite materials has been used by many researchers. Asmussen and Peutzfeldt tested the flexural strength of experimental composite materials that varied in their contents of bisGMA, TEGDMA and UEDMA {Asmussen E et al, 1998}. Unpolymerized material was applied in molds that were 10mm in length and 2mm in height and width. The molds were covered on both sides with a clear matrix strip and irradiated with a visible light curing unit on each of the two matrix covered sides. The specimens were placed in water at 37⁰C for 1 week. The specimens were polished and then subjected to testing in a universal testing machine 'Instron' at a crosshead speed of 1mm/min with 6mm between the supports until they fractured. Flexural strength was calculated using the formula: *Flexural Strength (S) = (3cF)/(2ba²)*, where 'a' and 'b' were the heights and widths of the specimens respectively, 'c' the distance between the supports and 'F', the force at fracture {Asmussen E et al, 1992}.

Ferracane et al tested the flexural strength, modulus, fracture toughness and hardness of controlled composition composite resin specimens that were aged in deionized water at 37⁰C for 1 day, 6 months, 1 year and 2 years before testing {Ferracane JL et al, 1998}. For flexural strength testing, bar shaped specimens of cured resin were produced (25 x 2 x 2)mm in a split steel mold. The specimens were cured from the top and bottom in a triad light cured unit and stored in water as previously stated. Following the required period of storage, the bars were tested in flexure using a

three point bend test with a span of 20mm and a cross head speed of 0.254mm/min. following the specifications set out in the ISO standards 4049. They found that in general there were no long term reductions in flexural strength as a result of aging in water, with the exceptions of those composites that had a cure time of 25 seconds or lower (degree of conversion 60-55%). Hardness was reduced for most of the tested composites after 6 months but many returned to their original levels at 2 years. Long term aging in water caused a reduction in fracture toughness independent of composition but there was no reduction in modulus of elasticity.

A standard flexural strength test for resin composites exists in the ISO Standards NO. 4049 for polymer-based filling, restorative and luting materials{ISO-4049, 1999 [Section 7.11]}, which was utilized in this study.

1.2.2 Modulus of Elasticity

Another important mechanical property that reflects the elastic or reversible deformation behavior of dental materials is the elastic modulus. It represents the ratio of stress to strain, which means that lower the strain for a given stress the higher the value of the modulus. In other words, it is a measure of the stiffness or rigidity of a material{Phillips RW, 1996 (b)}. This is an important property to consider, as a restorative material with a low modulus will deform more under masticatory forces and be subject to early material fatigue {Braem M et al, 1998}. A material with a modulus of elasticity not compatible with tooth structure will be unable to provide the support at the tooth enamel interface to protect the enamel rods from fracturing under repeated functional stresses{Jones DW et al, 1996}. Young's modulus cannot be described as the only property relevant to describe fatigue sensitivity of composite materials. The behavior of composite materials is the sum of the interaction of several properties relative to tooth structure {Willems G et al, 1992}. Young's modulus however is a convenient way to characterize new materials and to provide a comparison with that of tooth structure {Braem M et al, 1998}. The modulus of elasticity values for enamel and dentin range from 46-48 GPa and 12-14 GPa respectively depending on the form of the tooth be it an incisor, bicuspid or molar{Phillips RW, 1996 (b)}.

Static and Dynamic Elastic Modulus

Determination of the elastic modulus can be made either by static or dynamic methods. The *static* method involves the determination of the modulus from tensile strength, compressive strength or flexural strength tests. The elastic modulus is calculated from the formula E (elastic modulus) = Stress/Strain.

Asmussen and Peutzfeldt {Asmussen E et al, 1992} determined the mechanical properties of modulus of elasticity and flexural strength of monomer mixtures UDEMA and HEMA containing fillers to which had been added bifunctional ketones. Modulus of elasticity was tested with specimens using the data obtained from the flexural strength testing. In the measurements of flexural strength, a chart paper speed of 500 mm/min. was used and the relationship between the applied force and the movement of the crosshead which was approximately linear, was recorded. Straight lines were fitted by hand to the curves on the chart paper and the slopes of these lines calculated. Modulus of Elasticity was calculated from the formula: *Modulus of Elasticity (E) = $(\alpha c^3) / (4ba^3)$* , where ' α ' is the slope of the straight line relationship between the force and deflection of the specimen, ' c ' the distance between the supports (6mm) and ' a ' and ' b ' the height and width of the ground specimens respectively.

The *dynamic* method of determining the elastic modulus is based on the velocity, at which sound travels, which can be readily measured by ultrasonic longitudinal and transverse wave transducers and appropriate receivers. Since the magnitudes of longitudinal and transverse waves depend on the elastic moduli, the measurements of the propagation velocities and absorption of ultrasound can be utilized for determining elastic constants. This method has the advantage of ease of use on very small samples and produces a very small variation and scatter in the data {Jones DW et al, 1996}. Jones and Rizkalla compared dynamic and static methods of elastic moduli determination and found that that the values produced by the dynamic method were higher {Jones DW et al, 1996}.

A static method using data from the flexural strength testing was utilized in this study to calculate modulus of elasticity.

1.2.3 Aging of Materials

The harsh oral environment subjects dental restorative materials to different types of stress and it has been hypothesized that water sorption into the material causes a softening of the polymer resin component by swelling the network and reducing the frictional forces between polymer chains, thereby leading to a decrease in mechanical properties. In vitro once the polymer network becomes saturated with water, the complex appears to stabilize with no further reduction in properties {Ferracane JL et al, 1998}.

Many researchers have demonstrated a reduction in the physical properties of tensile strength {Fujishima A, 1988}, flexural strength, elastic modulus and fracture toughness of composites {Drummond JL et al, 1998} after storage in water for extended periods of one or more months. Ferracane et al {Ferracane JL et al, 1995} demonstrated with composite materials of a controlled composition, that the degree of cure, filler volume and percentage of silane significantly influenced the initial properties of the composite. Aging of the material in water for 6 months and up to 2 years months caused a significant decrease in fracture toughness for most of the composites tested. Hardness and flexural strength were reduced upon soaking for 6 months, however these changes appeared to stabilize and return to almost the original levels after the 6-month time period unless the materials were poorly cured.

In the oral cavity, the additive effects of saliva including salivary enzymes and dietary solvents may present a more detrimental effect than water on the mechanical properties of composite resins {Freund M et al, 1990}, {Bean TA et al, 1994}. However, testing mechanical properties of the aged packable composites will provide some insight into the susceptibility of the material to undergo degradation in vivo.

1.3 Materials and Methods

1.3.1 Materials

The six packable composites used in the testing of the physical and mechanical properties in this project were those commercially available in North America at the time of the study and include all of the following materials in Shade A:

- Alert (Jeneric Pentron)
- Prodigy Condensable(Kerr)
- Pyramid Dentin (Bisco)
- Solitaire (Heraeus Kulzer)
- Surefil (Caulk Dentsply)
- P-60 (3M)

These materials were tested against control composites Z100 (3M) and Spectrum TPH (Caulk Dentsply) that have been used in clinical practice for several years and Z250 (3M), a new universal resin composite. The control composites Z100 and Spectrum TPH were the most commonly used composite restorative materials in a survey of 54 dental schools in North America {Mjör IA et al, 1998}

Table 1.1: Resin Matrix of Composite Materials: Manufacturers Data

Alert	Polycarbonate dimethacrylate resin + ethoxylated bisphenol A dimethacrylate (PCDMA70%; bisEMA-30%)
Prodigy Condensable	bisGMA +TEGDMA+EBDMA (ethoxylated bisphenol A dimethacrylate) HEMA+RCA additive (poly hydroxy carboxylic acid amide)
Pyramid Dentin	Ethoxylated bisphenol A dimethacrylate resin + triethylene glycol dimethacrylate (EBDMA+TEGDMA)
Solitaire	Vitroid Polyglass monomers-not bisGMA or TEGDMA resins
Surefil	Urethane modified bis-GMA
P-60	Urethane dimethacrylate + Bisphenol A polyethylene glycol diether dimethacrylate [UDMA + bis-EMA (6)]
Z250	Urethane dimethacrylate +Bisphenol A polyethylene glycol diether dimethacrylate [UDMA + bis-EMA (6)]
Z100	bis-GMA diluted with TEGDMA
Spectrum	Urethane modified bis-GMA

Table 1.2:Chemical Composition, Size and Distribution of Fillers: Manufacturers Data

Composite Resin	Filler Type	Filler Size: (μm)	Volume %
Alert	Glass microfibres: BaBoAlSi; SiO ₂	60-80 in length; 6-8 in diameter. Not given	62
Prodigy Condensable	BaAlBoSi; fumed SiO ₂ ; ZnSiF ₆	0.6 Not given	62
Pyramid Dentin	Ba glass; St. glass	Average:2	71
Solitaire	SiO ₂ :30%; AlFISi:5%; BaAlBoFISi: 26%	2 to 20	90
Surefil	BaFlAlBoSi glass &; Si fume	Average: 0.8	58
P-60	Zirconia/Silica	0.01 to 3.5; Av: 0.6	61
Z250	Zirconia/Silica	0.01 to 3.5; Av: 0.6	60
Z100	Zirconia/Silica	0.04 to 3.5	66
Spectrum	Ba glass, SiO ₂	0.04 to 5	57

1.3.2 Filler Particle Size

An analysis of filler particle size was carried out using SEM photomicrographs. Cylindrical specimens were fabricated 2.5mm in length and light cured for 60 seconds. The surface was polished to 600 microgrit and the specimens were mounted on SEM aluminum stubs. The specimens were sputter coated with 3nm of platinum in a Polaron ES-100 SEM coating unit and examined with a Hitachi S-2500 scanning electron microscope at an operating voltage of 20kv. SEM views were taken using backscatter electron imaging at 300X and 3000X magnification to qualitatively compare filler particle sizes.

1.3.3 Flexural Strength

Sample Preparation

Ten test specimens of each material measuring 25mm in length by 2mm in width by 2mm in height were prepared according to the ISO Standard 4049 {ISO-4049, 1999 [Section 7.11]} by compacting the composite samples in teflon molds between two glass microscopic slides. Pressure was applied to the two slides with clamps and the material was cured for 60 seconds in a Triad light cure unit (Triad 2000- Dentsply/York Division). Following polymerization, five specimens of each material were stored in distilled water at 37⁰C for 24 hours and the other five were stored under the same conditions for 3 months. Following the stipulated time period, both groups of specimens were tested according to the following protocol.

Method

A three-point bend test was carried out on a Model 4301 Instron uniaxial servo-mechanical testing machine (Instron Corporation, Canton MA). The test machine consisted of a 1 KN capacity load sensor mounted in a movable crosshead (Figure 1.7). Rotary encoders connected to the machine's crosshead drive system relayed measures of position to the machine's central processing unit and measures of force were relayed to the machine's central processing unit via the load sensor. The apparatus consisted of 2 rods (2mm in diameter), mounted parallel with 20mm between the centers, and a third

rod or the central stylus (2mm in diameter) centered between and parallel to the other two, so that the three rods in combination could be used to give a three point loading to the specimen. The central stylus of the three-point bend test fixture was attached to the load sensor and the two lower supports were attached to the base of a water bath and placed directly beneath the central support. A temperature controller kept the water bath at 37 C during testing.

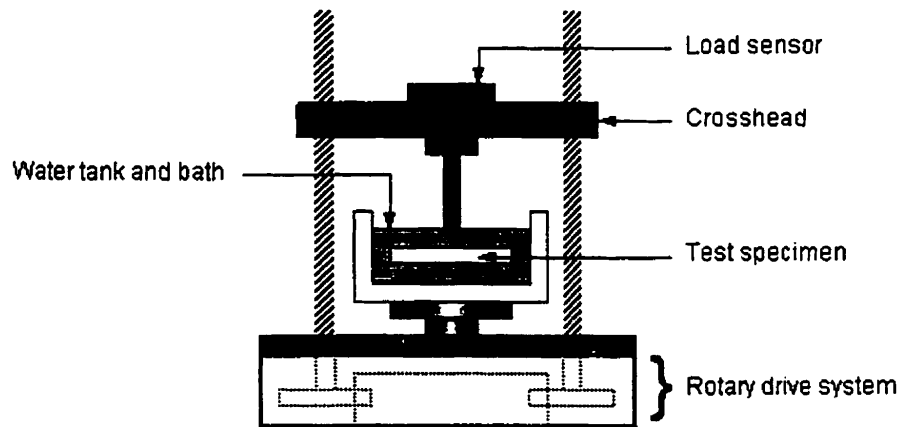


Figure 1.7: Flexural Strength Test Apparatus

The specimens were placed on the lower supports of the three-point test fixture. The crosshead was lowered until the central stylus was positioned just above the specimen. The load signal was zeroed (balanced) to compensate for the weight of the stylus. The crosshead was then lowered at a speed of 0.75 mm/min until the specimen failed. The maximum load supported by the specimen prior to failure was captured electronically by the Instron's central processing unit. A chart plotter recorded the load-deformation profile. Flexural strength was calculated using the rationale described below and the 24 hour and 3-month data was subjected to statistical tests using ANOVA and Scheffe's test to compare differences between groups of materials.

Rationale for test methodology used

It is customary to determine the flexural strength of brittle materials from the three-point bend test (Figure 1.8).

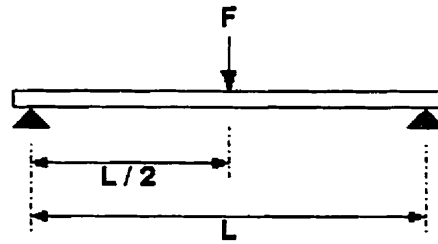


Figure 1.8: Beam theory: Rationale for flexural strength

When a test specimen is subjected to three-point bending, a tensile stress is generated in the lower surface of the specimen and a compressive stress generated in the upper surface. Since the tensile strength of a brittle material is typically much less than its compressive strength, specimen failure commences on the tensile (lower) surface of the specimen. The tensile strength of the specimen (σ_{ts}) is related to the breaking force (F_{max}):

$$\sigma_{ts} = \frac{FLH}{8I} \quad \text{[a]}$$

Where 'L' is the distance between the supports on the tension surface (20mm). 'W' is the width of the specimen, 'H' is the thickness of the specimen between the tension and compression surfaces and 'I' is the second moment of the area of cross-section of the specimen. For specimens with rectangular cross-sections.

$$I = \frac{WH^3}{12} \quad \text{[b]}$$

where 'W' is the width of the specimen. Substituting for 'I' in [a] for rectangular cross-sections,

$$\sigma_{ts} = \frac{3FL}{2WH^2} \quad \text{[c]}$$

1.3.4 Modulus of Elasticity

Another important material property that can be derived from the three-point bend test is the Stiffness Modulus. The stiffness of the material may be defined as the rate at which the stress is increased with respect to an increase in strain. The Stiffness Modulus of the specimen (E) was determined from the flexural strength data by calculating the change in force (ΔF) per unit change in deflection of the center of the specimen (ΔY):

$$E = \Delta F / \Delta Y \times L^3 / 4WH^3 \quad (d)$$

The 24-hour and 3-month modulus data was then subject to statistical tests, ANOVA and Scheffe's test to check for differences between groups.

1.3.5. Radiopacity

Radiopacity testing of the materials was carried out in accordance with the ISO Standard 4049 {ISO-4049, 1999 [Section 7.14]}. Three readings were made on one specimen of each material.

Sample Preparation

One specimen disc of each material 1.0mm (+/- .01mm) in thickness (Shade A) was made using an elastomeric mold, clamped under pressure and cured in a 'Triad' light cure unit for one minute. The specimens were polished using 180, 220, 320 and 400 grit sandpaper in sequence to ensure a smooth finish. The specimen was measured at the end of the polishing sequence to verify that the thickness remained at the critical tolerance of 1 +/- .01mm.

Method

The specimens were positioned on an occlusal x-ray film, (EO 42P, Ekta Speed Plus), along with an aluminum step wedge with a thickness range 0.5 to 13.5mm (with a 1mm increasing thickness of each step) and a 1mm longitudinal section of bovine tooth (comprising enamel and dentin) cut using a micro-slicing machine (Accutom. Struers) (Figure 1.9). The film was exposed for 0.37 milliseconds, with a dental x-ray machine (Belmont-Takara Phot-X), at 70 kV and 10 mA at an object to film distance of 400 mm.

The film was processed in a standard automatic processor Dentex 9000, using a Kodak RP-X-omat developer and Signal fixer. The optical density was verified, to ensure that the region between the specimen and the wedge had an optical density between 1.5 and 2 in accordance with the ISO specifications. Three readings of optical density of each material specimen were obtained using the same photographic densitometer Macbeth TD: 504. A graph was plotted between the entire step wedge thickness (0.5-13.5mm) and its optical density values (**Figure 1.23**). From this graph, the optical density values of the specimens were used to determine the aluminum thickness equivalent values. According to the ISO standards, this value of the aluminum thickness equivalent or the radiopacity of restorative resins were expected to be higher than that for the same thickness of aluminum.

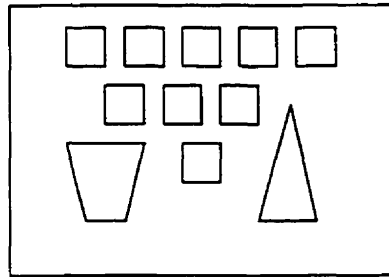


Figure 1.9: Schematic of material specimens on the occlusal film, along with the tooth specimen (bottom left) and the step wedge (bottom right)

1.3.6. Microhardness Profile

The purpose of this test was to determine, whether the new packable composites had the capacity to be cured in bulk as stated by some manufacturers. This was achieved, by comparing the hardness values of the materials at varying depths within the cured specimens. The details are described below.

Sample preparation

Three samples of each material (Shade A1) were prepared in 6mm deep split cylindrical molds. The mold was filled with the material between two glass microscopic slides and clamped under pressure. Each specimen was cured using a light cure unit (Max-Caulk

Dentsply) for 40 seconds. The intensity of the curing light was continually checked with a radiometer to ensure that the reading remained between 400-500mW/cm². The specimen was then de-molded, the uncured material scraped using a scalpel blade, and the specimens stored in dark bottles in distilled water for 24 hours until they were mounted. The specimens were mounted with dental stone in Teflon[®] molds and were polished with 600-grit carbimet paper to ensure a metallographic finish, necessary for a sharp indentation. These were shielded from light in a sealed and dry opaque container for 24-48 hours until the start of the microhardness testing.

Microhardness Testing

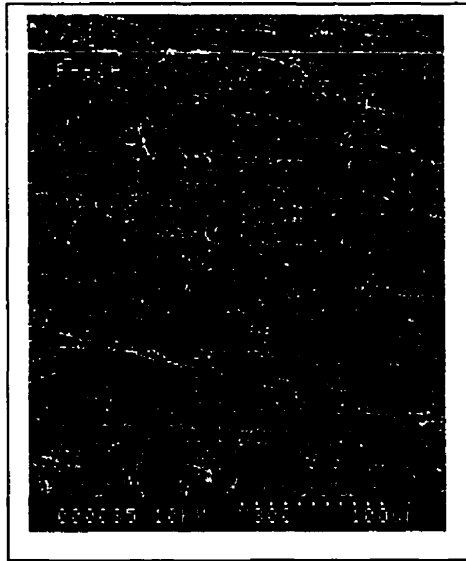
Microhardness testing refers to a static indentation test with loads up to 1kg. This load is applied without friction or impact. The method used in this project involved the Knoop indenter, which is a diamond ground to pyramidal form that produces a diamond shaped indentation having an approximate ratio between long and short diagonals of 7:1. The pyramid shape employed has an included longitudinal angle of 172⁰ 30' and an included transverse angle of 130⁰ 0'. The depth of the indentation is about 1/30 of its length. The Tukon Model 300 microhardness tester automatically calculates the KHN or Knoop hardness number after the long diagonal has been measured. The Knoop hardness number represents the applied load divided by the unrecovered projected area of the indentation.

Method

The mounted specimen was fixed on the precision mechanical stage of the hardness tester and a series of tests were performed with a load of 200 grams with the machine calibrated at 0.4272 for this load. Each indent was viewed with a dry parfocussed lens of 20x and the Knoop hardness value was calculated. The indentations were made from the top of the specimen to the bottom, at a distance of 333µm apart, determined from the center of each diamond indent. This was done to ensure that hardness values could be read at each 0.333mm. The length of each indent was automatically read as the 'Knoop Hardness Number' (Figure 1.10) based on the indentation. The test was performed for all three

specimens for each group of material and the results were then compared statistically using ANOVA and Scheffe's tests.

Figures 1.10: Indent made by Knoop Hardness Tester on a resin sample. Arrows indicate the length of the indent.



1.4 Results

1.4.1 Filler particle Sizes: (Figures 1.11-1.19)

Filler particle size and particle distribution of many of the packable composites were distinctly different compared to the control materials. This was particularly true for the packable composites Alert, Solitaire, Surefil and Pyramid. These materials appeared to be densely filled with a random dispersion of very large filler particles between very small sized particles. The packable composites P-60 and Prodigy showed similar particle sizes and particle size distribution as compared to the control composites Spectrum and Z100 and the new universal material Z250.

a. Alert

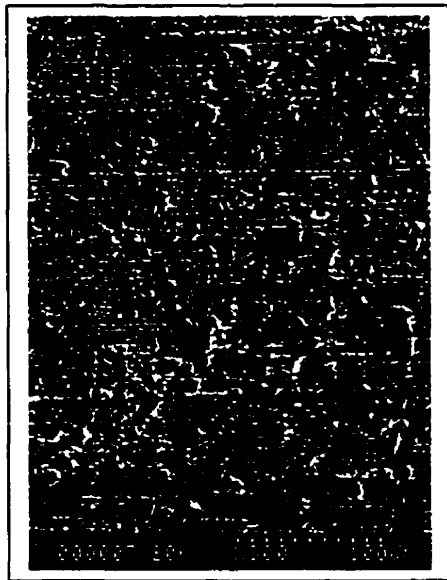


Figure 1.11A: 300X



Figure 1.11B: 3000X

Figures 1.11A and 1.9B: Packable Composite 'Alert'.

Specimen surface (**Figure 1.11A**) at 300X showing particle distribution, with dense concentration of fillers randomly interspersed within the sample. At 3000X

(Figure 1.11B) surface of specimen showing large filler particles approximately 20 μ m in length and 7 μ m in diameter with smaller submicron particles within the resin matrix.

b. Prodigy Condensable

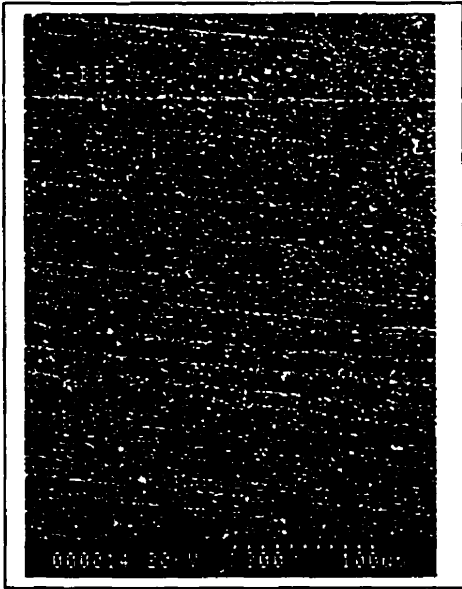


Figure 1.12A: 300X

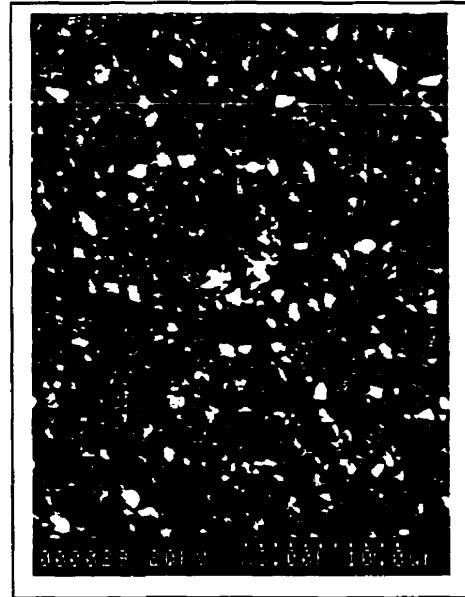


Figure 1.12B: 3000X

Figure 1.12A and 1.12B: Packable Composite 'Prodigy'.

Specimen surface (Figure 1.12A) at 300X showing a dense but uniform distribution of particles throughout the sample. At 3000X (Figure 1.12B), surface of specimen showing standardized filler particles not exceeding 2 μ m in diameter with submicron particles within the resin matrix.

c. Pyramid Dentin

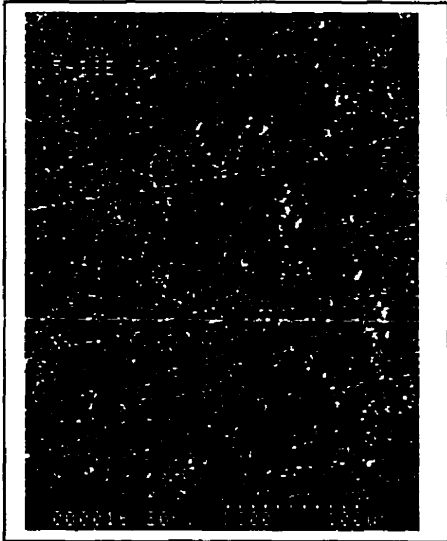


Figure 1.13A: 300X



Figure 1.13B: 3000X

Figures 1.13A and 1.13B: Packable Composite 'Pyramid Dentin'.

Specimen surface at 300X (**Figure 1.13A**) showing a range of particle sizes. At 3000X (**Figure 1.13B**), surface of specimen showing a generalized distribution of particles approximately 4-5 μm with submicron particles in the matrix. The center of specimen with possibly a large void in the resin, approximately 8 μm in length and 5 μm in width previously occupied by dislodged filler particle.

d. Surefil



Figure 1.14A: 300X



Figure 1.14B: 3000X

Figure 1.14 A and 1.14B: Packable composite 'Surefil'.

Specimen surface at 300X (Figure 1.14A) showing a variation of filler particle sizes. Isolated large particles exceeding 20 μ m in diameter interspersed between smaller particles between 1-10 μ m in diameter. At 3000X (Figure 1.14B), a large filler particle (15 μ m) is seen surrounded by smaller filler particles and submicron particles, which appear randomly distributed in the matrix.

e. Solitaire

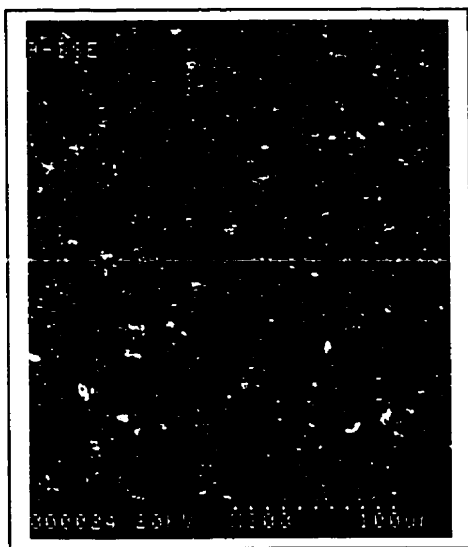


Figure 1.15A : 300X



Figure 1.15B : 3000X

Figures 1.15A and 1.15B: Packable Composite 'Solitaire'.

Specimen surface at 300X (**Figure 1.15A**) showing uniform distribution of isolated particles, which appear black throughout the sample. At 3000X (**Figure 1.15B**), these large particles $10\mu\text{m}$ in length and $6\mu\text{m}$ in diameter are seen surrounded by a dense distribution of submicron particles.

f. P60

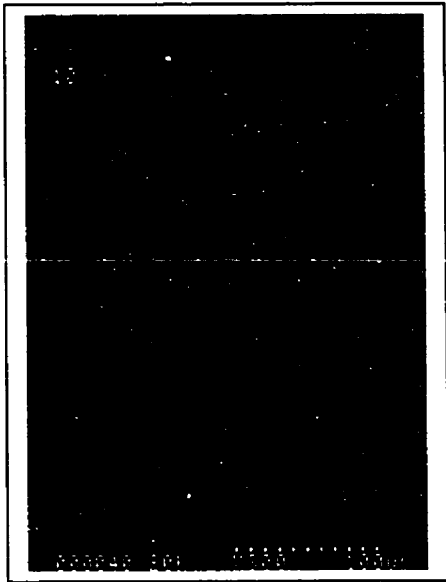


Figure 1.16A: 300X

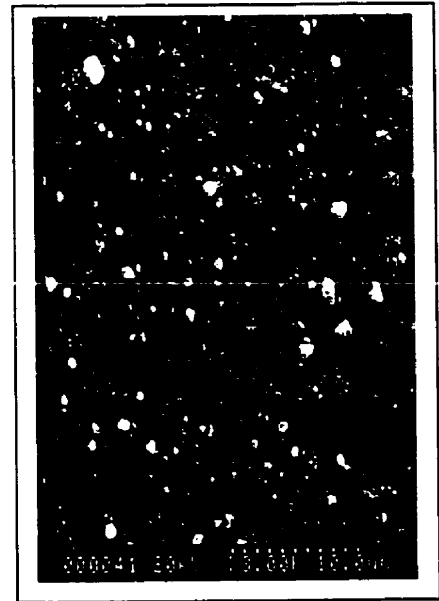


Figure 1.16B:3000X

Figures 1.16A and 1.16B: Packable Composite 'P-60'.

Surface of specimen at 300X (**Figure 1.16A**) shows a uniform distribution of small sized irregularly shaped particles. At 3000X (**Figure 1.16B**), surface of specimen showing a regular distribution of filler particles 1-3 μ m in diameter and submicron particles throughout the matrix.

g. Spectrum

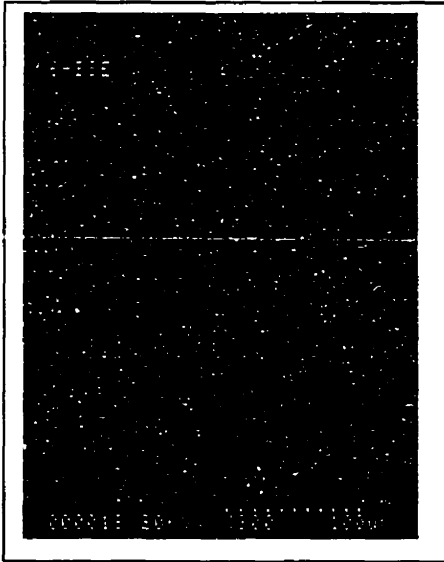


Figure 1.17A: 300X



Figure 1.17B: 3000X

Figures 1.17A and 1.17B: Control Composite 'Spectrum'.

At 300X (**Figure 1.17A**), surface of specimen shows a uniform distribution of small sized irregularly shaped particles. At 3000X (**Figure 1.17B**), surface of specimen showing a uniform distribution of filler particles with size 1-2 μ m in length with submicron particles.

h. Z100

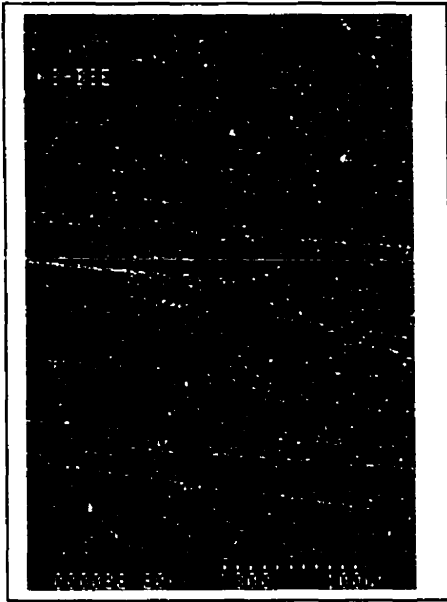


Figure 1.18A: 300X

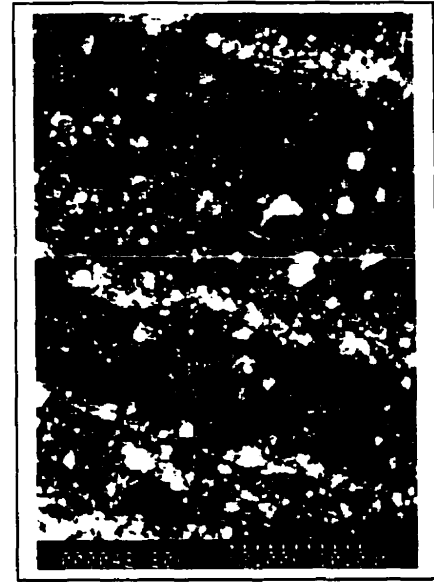


Figure 1.18B: 3000X

Figures 1.18A and 1.18B: Control Composite Z100.

Specimen surfaces at 300X (**Figure 1.18A**) shows a uniform particle distribution. At 3000X (**Figure 1.18B**), surface showing a regular distribution of filler particles with a rounded outline, with a maximum size of $1\mu\text{m}$ in diameter and submicron particles.

i. Z250

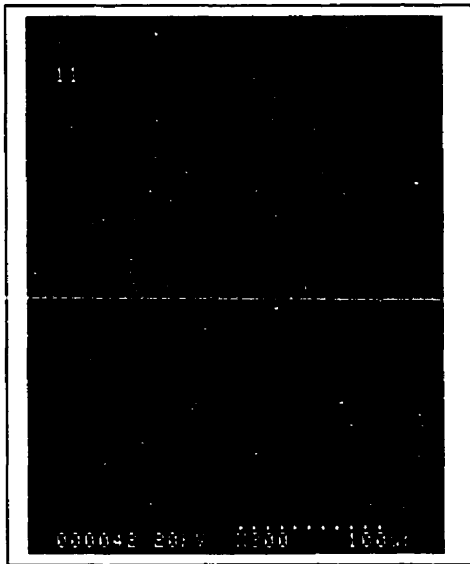


Figure 1.19A: 300X

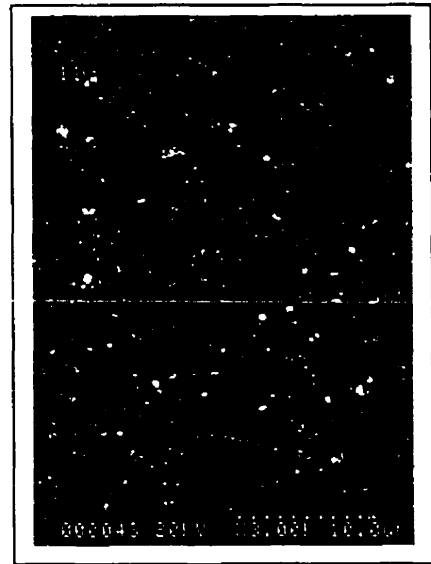


Figure 1.19B:3000X

Figure1.19A and 1.19B: Non Packable Composite Z250.

Surface specimen at 300X (**Figure 1.19A**) shows a uniform distribution of fine particles. At 3000X (**Figure 1.19B**), surface of specimen showing a regular distribution of rounded filler particles, 1-3µm in diameter and submicron particles throughout the matrix

1.4.2 Flexural strength Testing

Results of 24-hour flexural strength testing are depicted in Tables 1.3 & 1.4 and Figure 1.20. Comparison by ANOVA revealed significant differences in flexural strength among groups ($P=0.0001$). Scheffe's test was used to analyze for significant differences among the composites. The control materials represented the middle range of values of flexural strength. With the exception of the packable composite Solitaire, the other packable materials were not significantly different from the two controls. Among the packable materials tested, P-60 had the highest flexural strength and was significantly higher than the packables Prodigy, Pyramid and Solitaire. The latter three however were not significantly different from each other. With the exception of Prodigy, Pyramid and Solitaire, all the other materials met the ISO Standard 4049 requirement for minimum values of flexural strength for polymer based restorative materials of 80MPa.

Table 1.3: One Factor ANOVA [X₁: composite Y₁: flexural]

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	16426.94755	2053.368444	10.02903
Within Groups	36	7370.729477	204.742485	P=.0001
Total	44	23797.677027		

Analysis of Variance Table.

Model II estimate of between component variance = 369.725192

Table 1.4: Flexural Strength: 24-Hour Testing (MPa)*

Group	Count	Mean	Std. Deviation	Std. Error
P-60	5	101.08	14.51	6.49
Surefil	5	85.13	10.07	4.50
Z100	5	84.22	20.69	9.25
Spectrum	5	84.03	11.76	5.26
Alert	5	82.82	10.49	4.69
Z250	5	80.25	15.44	6.90
Prodigy	5	62.21	15.63	6.99
Pyramid D.	5	60.43	17.21	7.70
Solitaire	5	31.73	8.67	3.88

*Values connected by lines are not significantly different

1.4.3 Modulus of Elasticity Testing

Results of 24-hour modulus of elasticity testing are depicted in Tables 1.5 & 1.6 and Figure 1.21. Comparison by ANOVA revealed significant differences in the modulus of elasticity between the groups ($P=0.0001$). The control materials Z100 and Spectrum showed substantially different results and were represented approximately among the highest and lowest values respectively. Scheffe's analysis revealed that the packable and control materials were not significantly different from each other. Solitaire had the lowest modulus of elasticity and was significantly lower than Alert, P-60, Z100 and Surefil, however it was not significantly different from the control composite Spectrum. The analysis also revealed that Z-250, Pyramid, Prodigy, Spectrum and Solitaire had values of modulus not significantly different from each other.

Table 1.5: One Factor ANOVA [X₁: composite Y₁: modulus]

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	152.303434	19.037929	8.423691
Within Groups	36	81.361659	2.260046	P=.0001
Total	44	233.665093		

Analysis of Variance Table

Model II estimate of between component variance =3.355577

Table 1.6: Modulus of Elasticity: 24 Hour testing (GPa)*

Group	Count	Mean	Std. Deviation	Std. Error
Alert	5	6.78	2.64	1.81
Z100	5	6.77	1.27	.57
P-60	5	6.75	1.10	.49
Surefil	5	5.93	1.56	.70
Z250	5	5.02	1.51	.67
Pyramid D.	5	4.61	2.03	.91
Prodigy	5	4.24	.68	.30
Spectrum	5	2.99	1.07	.48
Solitaire	5	1.06	.20	.09

*Values connected by lines are not significantly different

1.4.4 Three Month Flexural Strength Testing

The results of the three-month testing of the packable and control composites are presented in Tables 1.7 & 1.8 and in Figure 1.20. ANOVA tests revealed significant differences among the groups ($P=0.0001$). Scheffe's test revealed that at the three-month testing of flexural strength, the materials reflected a similar trend to what was displayed at the 24-hour testing period in that there were no significant differences in flexural strength between the controls and they were not significantly different from the packable materials except for Solitaire. The control composites at the three-month testing however showed the highest values for flexural strength. P-60 and Z-250 appeared to have dropped in values with respect to the other materials but were not significantly different from them. The test also showed that Solitaire was not significantly different from P-60 and Z-250. ANOVA test for repeated measures revealed a significant interaction between material and the time factor implying that the results were not entirely dependent upon time as a factor affecting the response. An unpaired t-test between each group of material revealed that the flexural strength at the 3 month testing period was significantly lower than at the 24 hour period for P-60 and Z-250 ($P=0.0016$ and $P=0.0421$ respectively).

Table 1.7: One Factor ANOVA [X_i: composite Y_i: flexural]

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	13349.631417	1668.703927	7.2903
Within Groups	36	8240.173587	228.893711	P=.0001
Total	44	21589.805004		

Analysis of Variance Table

Model II estimate of between component variance = 287.962043

Table 1.8: Flexural Strength 3- Month Results (MPa)

Group	Count	Mean	Std. Deviation	Std. Error
Spectrum	5	93.80	17.20	7.69
Z100	5	80.37	23.27	10.40
Alert	5	79.95	9.35	4.18
Pyramid D.	5	79.38	10.36	4.63
Surefil	5	77.98	20.03	8.96
Prodigy	5	73.08	14.32	6.40
Z250	5	62.67	5.11	2.28
P-60	5	55.97	15.90	7.11
Solitaire	5	31.43	11.94	5.34

*Values connected by lines are not significantly different

1.4.5 Three-Month Modulus of Elasticity Testing

Results of the three-month testing of the modulus of elasticity are depicted in Tables 1.9 & 1.10 and Figure 1.21. ANOVA tests showed significant differences among the groups ($P=0.0001$). Scheffe's test revealed that at the three-month testing period the control composites Z100 and Spectrum were in the top and middle ranging of the range of values respectively and were significantly different in their mean values. All the packable materials were within the range of values of the two control materials. Alert had the highest modulus, but was not significantly different from Z100. The packable composites Alert and Surefil were significantly higher than the control composite Spectrum but not from Z100. Solitaire had significantly lower mean values for modulus as compared to Alert, Z100, Surefil and Z250. ANOVA test for repeated measures revealed a significant interaction between material and the time factor implying that the results were not entirely dependent upon time as a factor affecting the response. An unpaired t-test between each material at 24 hours and 3 months revealed that except for P-60 ($p=0.0026$), which decreased in modulus after three months there were no significant differences in modulus between the two time periods.

Table 1.9: One Factor ANOVA [X_i: composite Y_j: modulus]

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	233.356114	29.169514	19.542481
Within Groups	36	53.734351	1.492621	P=.0001
Total	44	287.090465		

Analysis of Variance Table

Model II estimate of between component variance =5.535379

Table 1.10: Modulus of Elasticity 3-Month Results (GPa)

Group	Count	Mean	Std. Deviation	Std. Error
Alert	5	9.24	1.22	.55
Z100	5	7.41	2.48	1.1
Surefil	5	4.36	.79	.35
Z250	5	4.36	1.12	.50
Spectrum	5	4.04	.87	.39
Pyramid D.	5	3.82	.59	.26
P-60	5	3.64	1.17	.52
Prodigy	5	3.10	1.16	.52
Solitaire	5	.99	.29	.13

*Values connected by lines are not significantly different

Figure 1.20: Comparison of Flexural Strength of Packable and Control Composites at 24-Hours and 3-Months

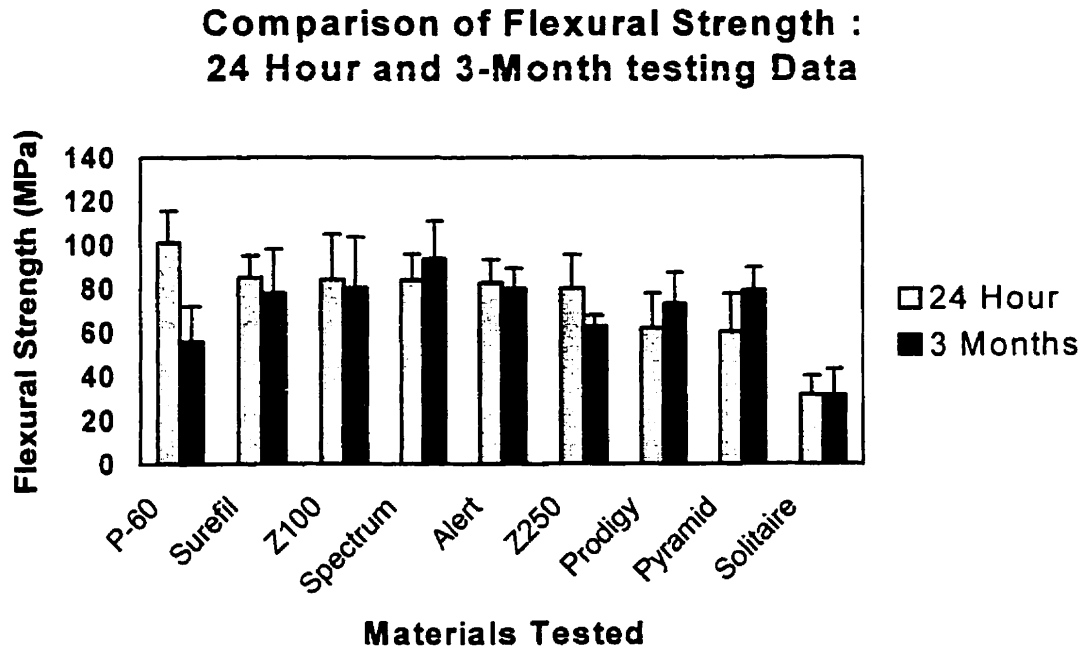
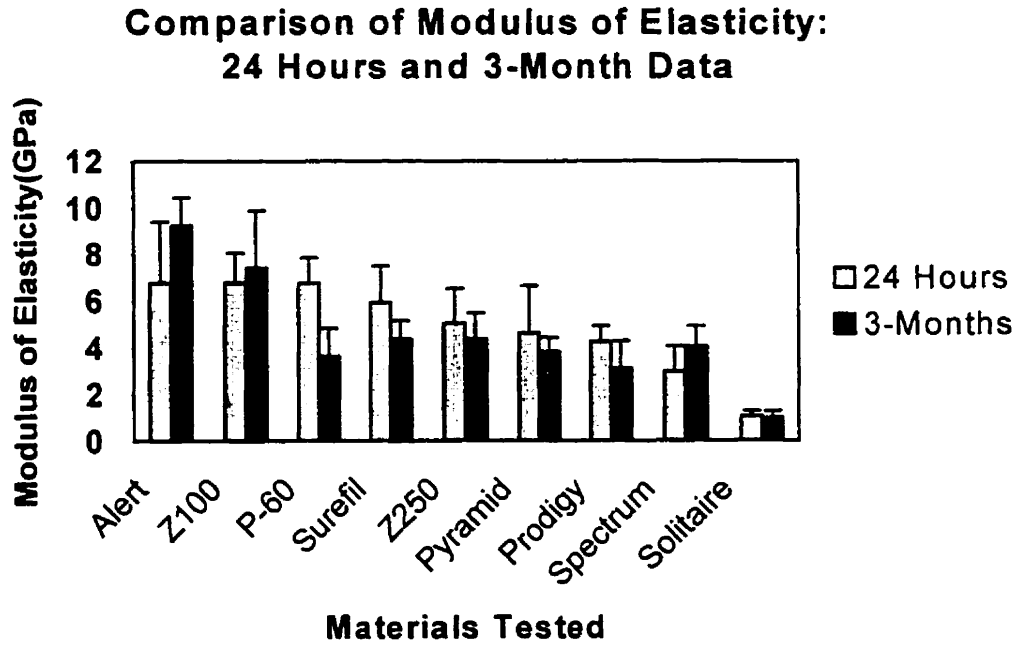


Figure 1.21: Comparison of Modulus of Elasticity of Packable and Control Materials at 24- Hours and 3-Months



1.4.6 Radiopacity Test Results

Results of radiopacity testing of materials is depicted in Tables 1.11 & 1.12 and Figure 1.22. ANOVA tests revealed significant differences between groups ($P=0.0001$). With respect to radiopacity, the control composites Spectrum and Z100 and the tested composites Z-250, Prodigy, P-60 and Surefil were all significantly more radiopaque than enamel and dentin. All the materials tested were significantly higher in radiopacity compared to dentin, but the packable composites Solitaire, Alert and Pyramid were significantly lower in radiopacity than enamel. The optical density of 1mm of Aluminum was determined at 1.55 (Figure 1.23). The radiopacity of all the materials were expressed as aluminum thickness equivalents as was determined from the graph in figure 1.23. Figure 1.22, demonstrates that at a thickness of 1mm, Solitaire and Alert had radiopacity values lower than Aluminum at an equivalent thickness and failed to meet the ISO Standard-4049 requirement for radiopacity.

Table 1.11: One Factor ANOVA [X₁: composite Y₁: Optical Density O.D.]

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	10	.297497	.02975	446.245455
Within Groups	22	.001467	.000067	P=.0001
Total	32	.298964		

Analysis of Variance Table

Model II estimate of between component variance = .009894

Table 1.12: Radiopacity Test Results

Group	Mean O.D.	Std. Deviation	Std. Error	Equivalent Al. Thickness
Z100	1.38	.01	.006	2.1
Spectrum	1.37	.01	.008	2.1
Z250	1.40	.01	.003	1.9
Surefil	1.39	.01	.003	1.9
P-60	1.40	.01	.003	1.9
Prodigy	1.41	.01	.003	1.8
Enamel	1.44	0	0	1.7
Pyramid D.	1.52	.01	.006	1.2
Alert	1.57	.01	.005	0.9
Solitaire	1.58	.01	.003	0.75
Dentin	1.66	0	0	0.55

Figure 1.22: Radiopacity of Materials Expressed as Equivalents of Aluminum Thickness

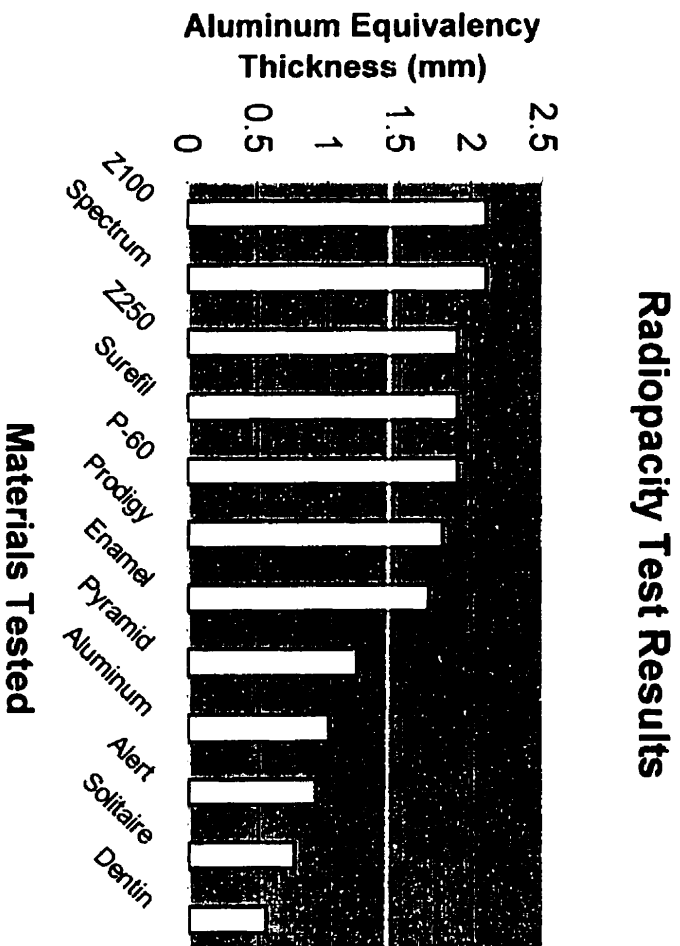
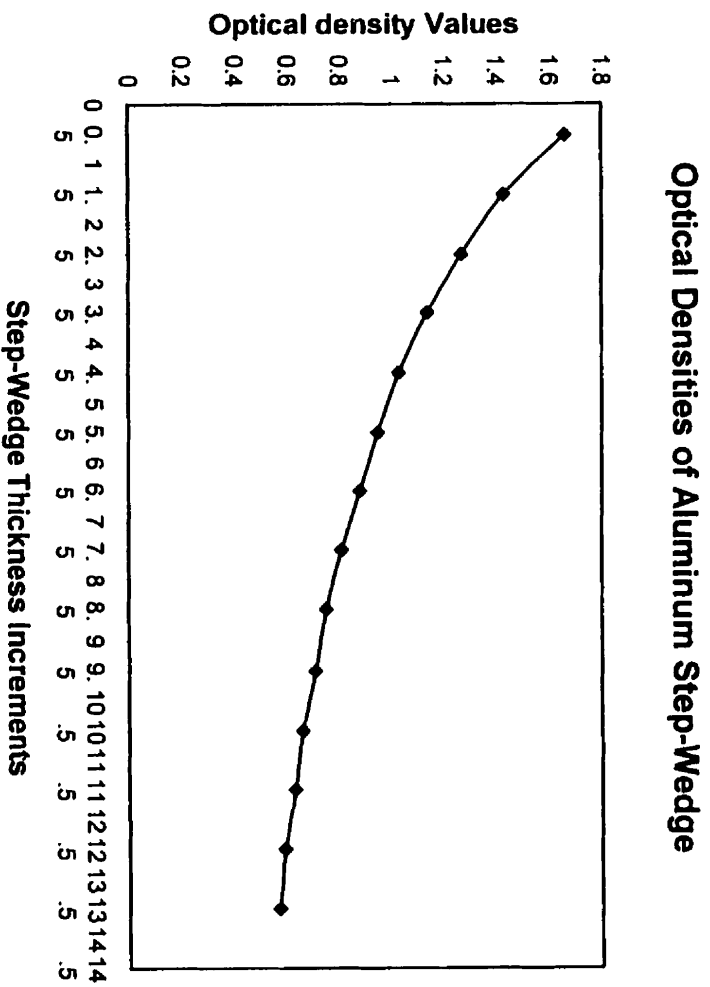


Figure 1.23: Optical densities of Aluminum Step Wedge Increments



1.4.7 Microhardness Testing Results

Results of the microhardness testing of all the materials are presented in Figure 1.24. All materials tested provided hardness data to a depth of at least 2.6mm. Solitaire failed to cure beyond 2.6mm depth. Spectrum, Z100 and Surefil failed to cure beyond 3mm. Pyramid and Prodigy cured to a depth of 3.6mm, but failed to cure beyond this depth. Alert cured to a depth of 4mm. P-60 and Z-250 cured to a depth of 4.3mm.

Figure 1.24 demonstrates the comparison of the depth of cure for all the materials. At a depth of 0.3 mm from the top surface of the specimen until a depth of 2mm, none of the packable composites were significantly different in hardness from the control materials. With respect to the control materials, the mean hardness values of Z100 were more in the upper range of hardness values and Spectrum in the lower range. With respect to the packable materials, Solitaire appeared consistently less hard than most of the other materials but appeared to be within the range of hardness values set by the control materials. This trend of Solitaire was reflected throughout its entire depth of cure. Surefil appeared to be one of the hardest materials up to a depth of 2mm after which the hardness values fell within the middle range of values until it could no longer be effectively tested beyond a depth of 3mm.

Hardness Relative to Cured Depth

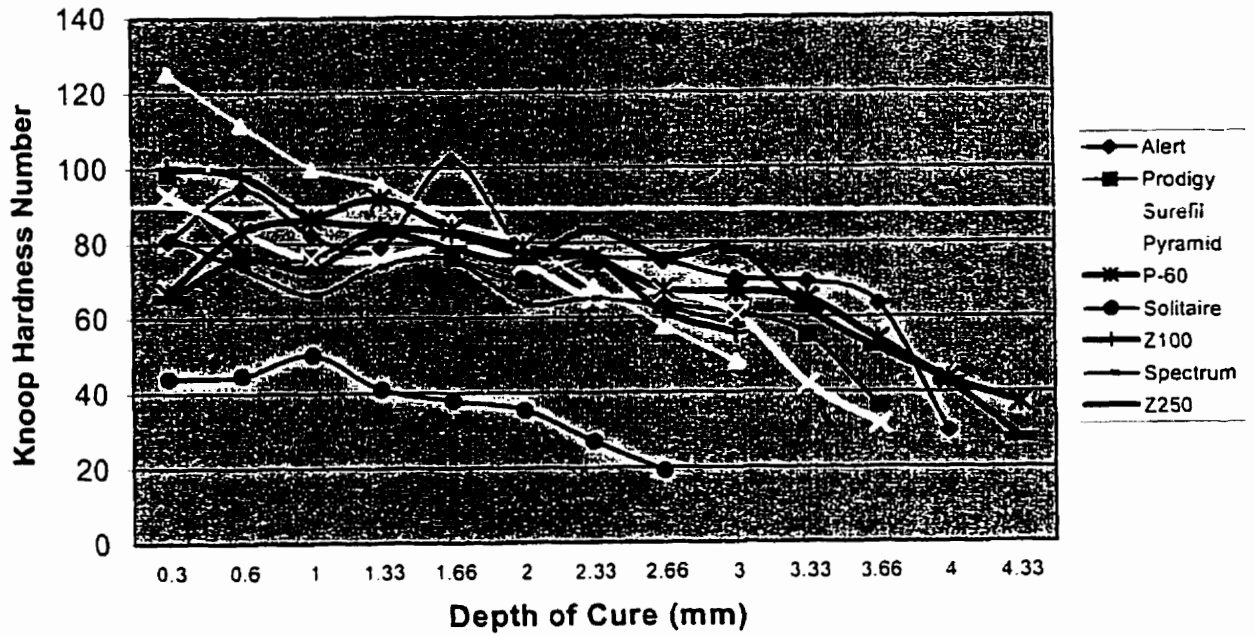


Figure 1.24: Comparison of Cured Depth of Packable and Control materials Relative to Hardness

Profile of Cure of Individual Materials

a. P60

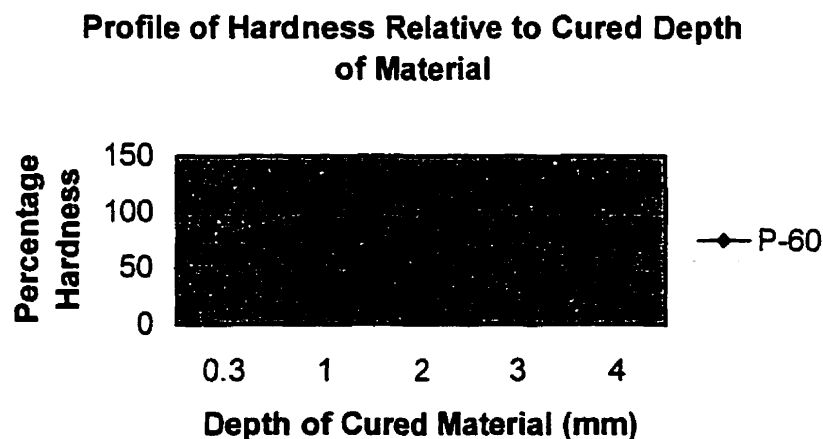
Table 1.13 and Figure 1.25 depict the profile of hardness of P60. The material tested for hardness to a depth of 4.3mm. The maximum hardness was recorded at 1mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of the maximum hardness value at approximately 2.6mm of material thickness (calculated from Appendix1).

Table 1.13: Hardness Profile for P-60

Material Thickness (mm)	KHN*
0.3	66.77
1	86.7
2	78.83
3	66.93
4	43.4
4.3	37.2

* Knoop Hardness Number

Figure 1.25: Percentage of Hardness of P60 Relative to Cured depth of Material



b. Z250

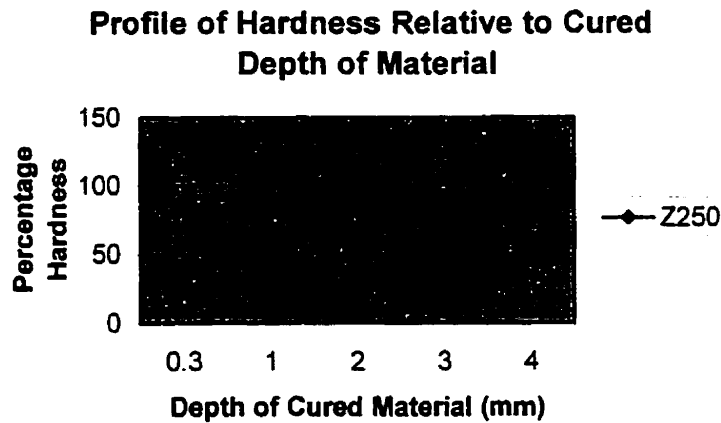
Table 1.14 and Figure 1.26 depict the profile of hardness of Z250. The material tested for hardness to a depth of 4.3mm. The maximum hardness was recorded at 1mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of the maximum hardness value at approximately 3.3mm of material thickness (calculated from Appendix1).

Table 1.14: Hardness Profile for Z-250

Material Thickness (mm)	KHN*
0.3	65.33
1	73.17
2	75.1
3	77.93
4	42.63
4.3	27.57

* Knoop Hardness Number

Figure 1.26: Percentage of Hardness of Z250 Relative to Cured depth of Material



c. Alert

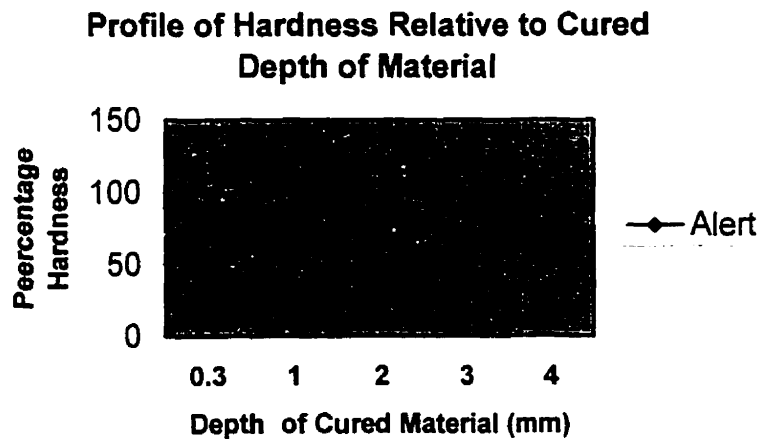
Table 1.15 and figure 1.27 depict the profile of hardness of Alert. The material tested for hardness to a depth of 4.0mm. The maximum hardness was recorded at 1mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of the maximum hardness value at approximately 3.3mm of material thickness (calculated from Appendix1).

Table 1.15: Hardness Profile for Alert

Material Thickness (mm)	KHN*
0.3	80.67
1	82.1
2	77.93
3	70.37
4	29.63

*Knoop Hardness Number

Figure 1.27: Percentage of Hardness of Alert Relative to Cured depth of Material



d. Prodigy Condensable

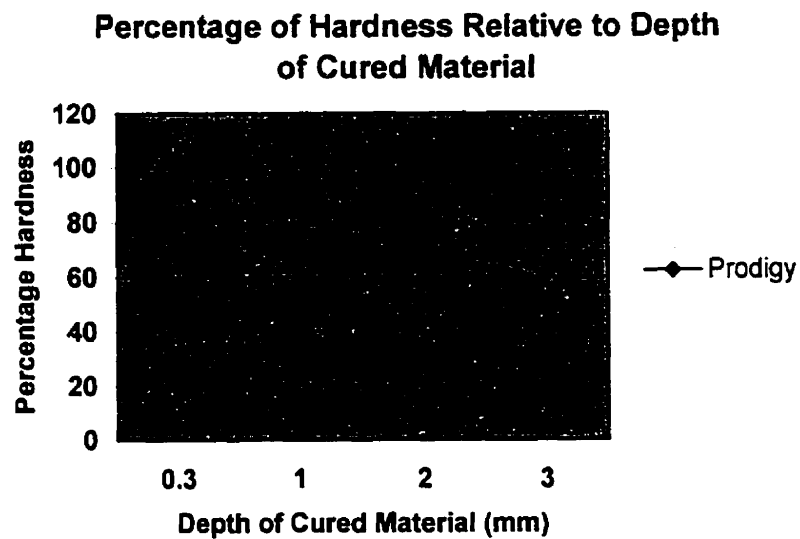
Table 1.16 and figure 1.28 depict the profile of hardness of Prodigy. The material tested for hardness to a depth of 3.6mm. The maximum hardness was recorded at 1mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of this maximum hardness value at approximately 2.3 mm (calculated from Appendix 1).

Table 1.16: Hardness Profile for Prodigy C

Material Thickness (mm)	KHN*
0.3	98.6
1	76.3
2	70.1
3	61.03
3.6	36.3

* Knoop Hardness Number

Figure 1.28: Percentage of Hardness of Prodigy Relative to Cured depth of Material



e. Pyramid

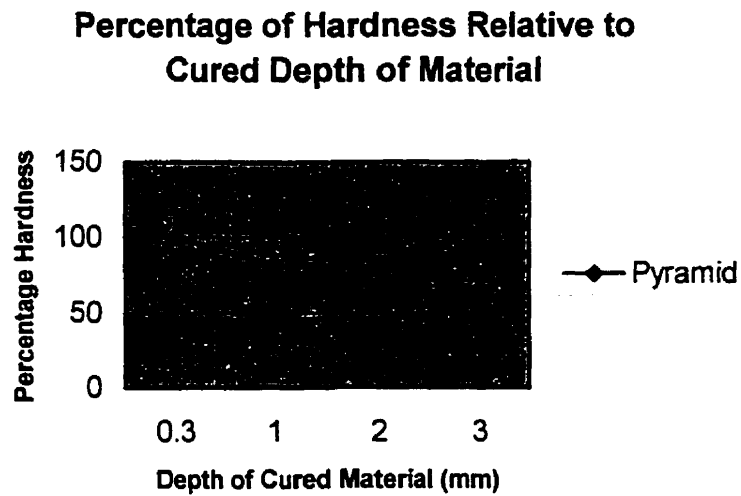
Table 1.17 and Figure 1.29 depict the profile of hardness of Pyramid. The material tested for hardness to a depth of 3.6mm. The maximum hardness was recorded at 0.333mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of this maximum hardness value at approximately 2.0 mm of material thickness (calculated from Appendix 1).

Table 1.17: Hardness Profile for Pyramid

Material Thickness (mm)	KHN*
0.3	92.87
1	75.9
2	74.47
3	60.5
3.6	31.5

* Knoop Hardness Number

Figure 1.29: Percentage of Hardness of Pyramid Relative to Cured depth of Material



f. Spectrum

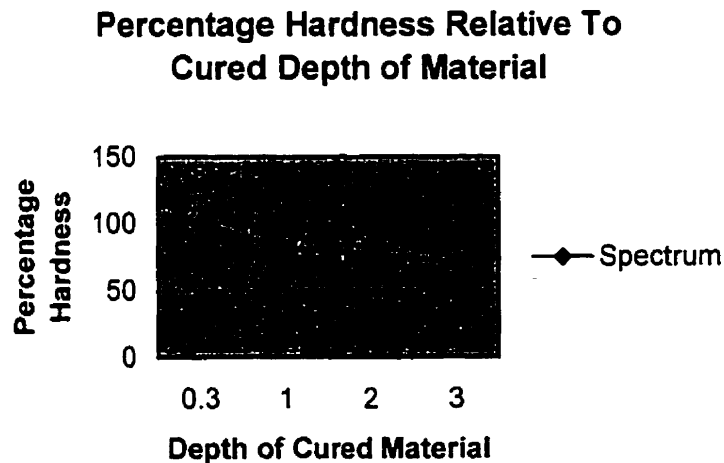
Table 1.18 and Figure 1.30 depict the profile of hardness of Spectrum. The material tested for hardness to a depth of 3.0mm. The maximum hardness was recorded at 0.333mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of the maximum hardness value at approximately 2.0 mm of material thickness (calculated from Appendix1).

Table1.18: Hardness Profile for Spectrum

Material Thickness (mm)	KHN*
0.3	82.3
1	66.37
2	63.8
3	57.83

* Knoop Hardness Number

Figure 1.30: Percentage of Hardness of Spectrum Relative to Cured Depth of Material



g. Z100

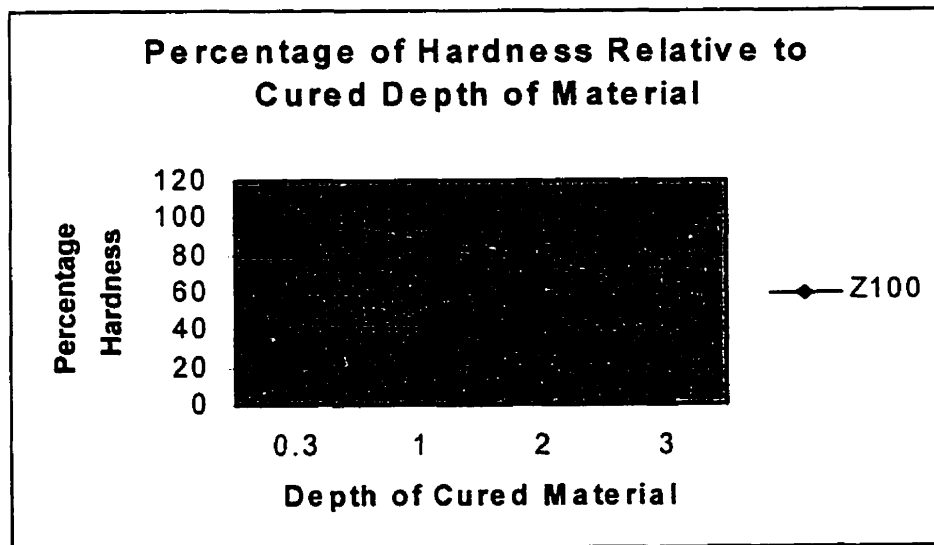
Table 1.19 and Figure 1.31 depict the profile of hardness of Z100. The material tested for hardness to a depth of 3.0mm. The maximum hardness was recorded at 0.333mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of this maximum hardness value at approximately 2.0 mm of material thickness (calculated from Appendix1).

Table 1.19: Hardness Profile for Z100

Material Thickness (mm)	KHN*
0.3	100.13
1	86.97
2	77.1
3	55.8

* Knoop Hardness Number

Figure 1.31: Percentage of Hardness of Z100 Relative to Cured Depth of Material



h. Surefil

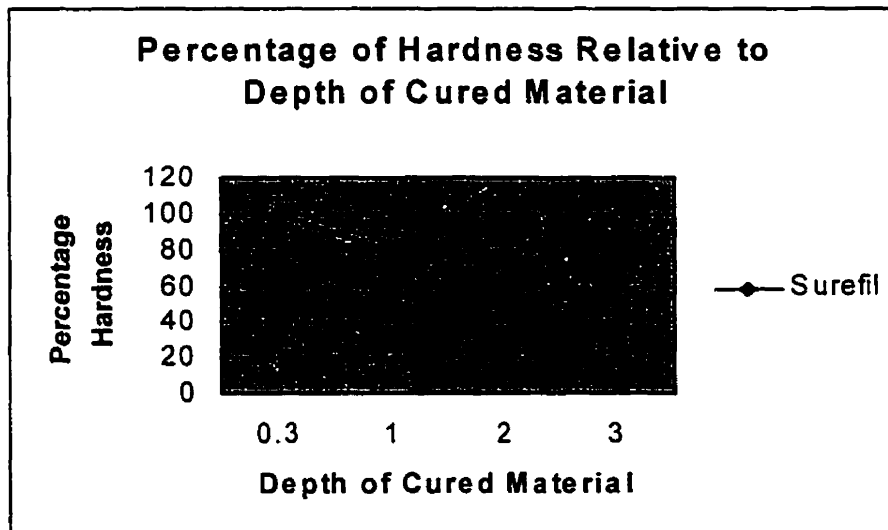
Table 1.20 and Figure 1.32 depict the profile of hardness of Surefil. The material tested for hardness to a depth of 3.0mm. The maximum hardness was recorded at 0.333mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of this maximum hardness value at approximately 1.3 mm of material thickness (calculated from Appendix 1).

Table 1.20: Hardness Profile for Surefil

Material Thickness (mm)	KHN*
0.3	125.3
1	100
2	80.23
3	48.16

* Knoop Hardness Value

Figure 1.32: Percentage of Hardness of Surefil Relative to Cured Depth of Material



i. Solitaire

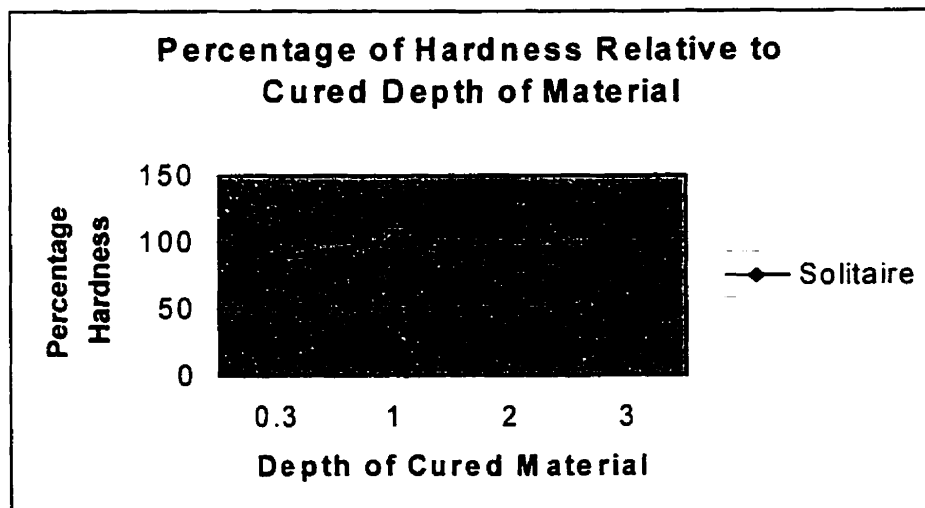
Table 1.21 and Figure 1.33 depict the profile of hardness of Surefil. The material tested for hardness to a depth of 2.6mm. The maximum hardness was recorded at 1mm from the surface of the specimen. The hardness values dropped to 75% (H-75) of this maximum hardness value at approximately 1.6 mm of material thickness (calculated from Appendix1).

Table 1.21: Hardness Profile for Solitaire

Material Thickness (mm)	KHN*
0.3	44
1	50.17
2	35.27
2.6	19.13

* Knoop Hardness Number

Figure 1.33: Percentage of Hardness of Solitaire Relative to Cured Depth of Material



1.5 Discussion

Packable composites have been introduced to assist in the development of more appropriate alternatives to amalgam. They were designed to provide more amalgam like clinical handling with further claims made to their superior physical and mechanical properties. Current composite resins in dental practice have fallen short of being ideal restorative materials due to their demonstrated polymerization shrinkage and resistance to ease of handling by the clinician. However they do demonstrate appropriate physical and mechanical properties and have been effective in providing adequate wear resistance when appropriately selected for use. The first part of this study compared some pertinent physical and mechanical properties of the new 'packable' composites with composites that are in current use. The question asked was whether the formulation changes made to provide 'packability' had been at the expense of an important physical or mechanical parameter, which could affect clinical performance. Filler sizes were scrutinized under the SEM and the physical properties of radiopacity and depth of cure of the materials were appraised separately. The mechanical properties of flexural strength and modulus were evaluated along with a re-testing of these same properties after subjecting the materials to an aging process.

In general, it was found that the filler particle sizes of the packable composites were comparable with those stated by each material manufacturer. Some of the materials had very large filler particles (Surefil, Solitaire, Pyramid, Alert- **Figures – 1.14,1.15,1.13,1.11**), scattered within the resin matrix. Large inorganic filler particles impair surface finish and polishability and raises concerns about potential wear{**Willems G et al, 1993 (b)**}. A quantitative evaluation of the average filler particle sizes and the area occupied by these filler particles becomes important and necessitates further investigation to predict the potential wear characteristics of these materials. The voids in Pyramid could be explained as being either inherent in the material or containing pre-polymerized polymer filler particles. Voids in a material may reflect that the filler particles are not well bonded to the matrix, which raises concerns related to a possible deterioration of properties because of this lack of bonding. In support of this, it has been

reported that resin composites whose filler particles were not properly bonded to the resin matrix demonstrated more wear than those well bonded. In addition an effective bond was found to be necessary to maintain the integrity of the filler particles and prevent leaching when exposed to water{Soderholm K-JM, 1985}. These concerns however, were not applicable to the measured mechanical properties in this study for Pyramid because the material did not demonstrate any reduction in the latter upon exposure to water.

Testing of physical and mechanical properties can be performed using either static or dynamic tests where the applied stress is either constant or fluctuating respectively. Dynamic tests like fracture toughness and flexural fatigue, which may be more appropriate in simulating the stresses endured by a restorative material during mastication, are more difficult to perform. The static physical tests stipulated by the International Standards Organization although not considered entirely appropriate relative to the clinical performance of restorative materials are relatively easy to perform. These tests are a useful guide in providing a broad characterization of the materials being tested and can reveal materials that are less than a stipulated minimum standard.

It has been established that the properties of composite resins are dependent upon the material composition. In general, the monomer constituents and composition affect degree of conversion{Ruyter IE et al, 1981}, viscosity, surface tension and contact angle{Asmussen E, 1977}. It has also been established that certain mechanical properties like compressive strength, modulus of elasticity and wear resistance are dependent upon filler characteristics, particularly filler content and that a correlation exists between filler content and mechanical properties {Braem M et al, 1989}.

In this study, it was seen that although filler characteristics, size and content were different for the packable as compared to the control composites, the 24-hour flexural strength and elastic modulus of the two groups of materials were not significantly different (Tables 1.4&1.6). Prodigy, Pyramid and Solitaire however did not meet the ISO standard 4049 requirement of 80MPa for flexural strength. Solitaire displayed inferior properties in all the mechanical tests performed (Figures 1.20, 1.21,1.22,1.24). The monomer composition consisted of 'polyglass monomers' (an unknown resin whose properties cannot be predicted) as stated by the manufacturer and not bis-GMA or

TEGDMA resins. It is possible that the composition of Solitaire, possibly the monomer constituents render its properties inferior to the other tested materials. The modulus of elasticity being representative of the rigidity of the material is supportive of the fact that the material will not deform under occlusal loading. Modulus of elasticity of the restorative material should generally be equivalent to the tooth tissue the material is going to replace, namely dentin. The modulus of dentin is approximately 18.5 GPa {Craig RG, 1979}. However, the modulus of elasticity in this experiment was not compared with that of tooth tissue. It suffices to know that the modulus of the packable materials is comparatively similar to the control composites, whose modulus of elasticity has been determined elsewhere using a dynamic method and found to be suitable as a posterior restorative material {Willems G et al, 1993 (a)}.

With the exception of P-60 and Z-250, the effect of aging in water for three months showed no significant changes in mechanical properties in the packable and control composites as compared to the properties at 24 hours of testing (Tables 1.8,1.10). ANOVA test for repeated measures indicated a significant interaction between the material and time for P-60 and Z-250. This suggested that the affect of time alone was not sufficient to explain the deterioration in properties. This deterioration was attributed to a factor probably related to the material composition. Due to the wide variations in the formulations it is difficult to identify the most significant compositional factor(s) contributing to the changes in properties during aging, however it is worthy to note that both P-60 and Z-250 contain a urethane dimethacrylate (UDMA) as one of the monomer constituents. A study by Beatty et al demonstrated that urethane dimethacrylate resins (UDMA) although very tough, tend to absorb substantially more water than other aromatic based materials such as DPMA (diphenyloxymethacrylate) {Beatty MW, et al, 1993}. The reduction in properties upon storage in water has been attributed to the flexibility of the molecule as a result of the presence of long aliphatic chains between ring structures (Figure 1.4). In addition, the presence of (O-CO-NH) groups increases the potential for hydrogen bonding with water. In the dry state, hydrogen bonds are formed between C=O and NH groups between adjacent chains. Water, when present, breaks the inter chain bonds and forms its own hydrogen bonds with the urethane groups. In some cases this can plasticize the material and thereby enhances chain flexibility.

Other reasons for a reduction in properties after aging in water have been attributed to the potential break down of silanated bonds between the filler and the matrix {Soderholm K-JM, 1983}. In a material that can promote water uptake, the enhancement of the latter hydrolysis process would be anticipated.

Maximum hardness for most of the materials was recorded at the surface or within 1mm of the surface of the specimen (Figure 1.24). None of the control materials could be tested for hardness beyond 3mm. Based on data reported for current composite resin restorative systems this was expected {Swartz ML et al, 1983}, {Rueggeberg FA, Caughman WF et al, 1993}. All the packable composites could be tested for hardness to a depth of 2.66mm. Hardness has been shown not to be a predictor of absolute degree of conversion when comparing resin composites of differing compositions {Ferracane JL, 1985} but for an individual material, it is a useful indicator of the reduction in cure due to increasing distance from the light source. The thickness of the material at 75% of the maximum hardness value is a fair indicator of the potential depth that the material should be expected to cure to. None of the tested materials demonstrated an H-75 value more than 3.3mm (Tables 1.13-1.21), indicating that none of the materials had a capacity to be bulk cured. Depth of cure is dependent on the composition of the material including the concentration of the photoinitiator in the composite material and its absorption spectrum, and on free radical chain mobility. The materials (P60, Z-250, Prodigy, Pyramid and Alert) that demonstrated a testable hardness at a depth more than 3mm, reflect some similarities in their composition: all of them contain small size filler particles, which average in size between 0.6 and 2 μ m. Alert was the only material that contained in addition to small filler particles, long irregular glass fibers as fillers, the transparency of which possibly enhances the reflectance of light through the resin matrix and conceivably explains the increased depth of cure {Leinfelder KF et al, 1998 (b)}.

The fact that Solitaire was not comparable in hardness to the other tested materials is an indication of its possibly being a softer material. The low depth of testable hardness is possibly indicative of several factors. One of these factors would be inadequate polymerization or degree of conversion of the resin monomer. Although the degree of conversion is not a predictor of the performance in composite resins of different systems, within the same system Ferracane showed conclusively that there was a good

correlation between hardness and degree of conversion during setting {Ferracane JL, 1985}. Secondly, material composition is known to affect degree of conversion in a number of ways. In two independent studies Asmussen and Ferracane demonstrated that monomer composition affected the degree of conversion {Asmussen E, 1982}, {Ferracane JL et al, 1986}. For example, resins composites with a higher content of TEGDMA demonstrated a higher degree of conversion. Unfortunately the reported material composition of Solitaire was rather vague. The manufacturer claimed that the material contained 'vitroid polyglass monomers', and supposedly not Bis-GMA or TEGDMA resins. With an unknown composition it becomes impossible to discuss potential reasons for the low hardness and demonstrates the need for caution with materials of significantly different composition.

The other packable material that cured to a depth of only 3mm was Surefil. Although its other physical and mechanical properties were comparable to that of the control materials, depth of cure was low, and this result was in contrast to its manufacturer's claims of increased depth of cure. Recommended for bulk cure of intra-oral restorations at the back of the mouth, this material may produce significant areas of under cured composite resin, which does not give confidence for restoration longevity.

In the test for radiopacity, the results were far from expected. Although all the packable composites were more radiopaque than dentin, some of the packable composites (Pyramid, Alert, and Solitaire) were not as radiopaque as enamel (Figure 1.22). Radiopacity depends on the type and proportion of radiopaque filler for example barium aluminoborosilicate (BaAlBoSi). The materials Alert and Solitaire, which were found to have a lower radiopacity than the other tested materials contained in addition to BaAlBoSi, a fibrous filler and an amorphous silica (silicon dioxide) respectively, whose proportions was unknown relative to BaAlBoSi. Amorphous silica has the advantage of contributing to a low thermal expansion. However, the disadvantage is its lack of radiopacity {Soderholm K-JM, 1985}.

The assessment of the performance of the physical and mechanical properties obtained in this study is similar to those expressed by Leinfelder et al {Leinfelder KF et al, 1999} in a recent overview of packable composites. The authors summarized the results of the abstracts presented at the 1999 IADR and concluded that none of the

materials studied presented a noteworthy improvement over the properties of the currently used universal composite resins. Indeed this study has revealed some significant shortcomings with regard to manufacturers recommended usage and individual material properties.

An overall assessment indicates that the packable materials with a few exceptions are comparable to the control composites in their physical and mechanical properties. Formulation changes made to the resin content or changes to the filler particles did not result in any significant improvement in the physical and mechanical properties of the new materials, with a few exceptions for specific properties. Specific areas where some of the new materials met with shortcomings were related to deterioration in properties upon incubation in aqueous solution for 3 months, reduction in hardness with increased thickness of material and radiopacity not comparable with tooth enamel. This study indicates that a thorough discernment of material properties and composition is needed before a decision is made to employ new materials in clinical practice.

Part- II

PACKABILITY TESTING

2.1 Packability

Novel posterior composites that have been introduced to the dental profession are being described as 'packable'. No scientific definition exists on packability. The term implies the ability of the operator to feel a positive contact against the material while it is being directed into a prepared cavity in the tooth. The term on its own is meaningless but is used in the context of amalgam use. When silver amalgam is packed into a tooth cavity against an adjacent tooth, the particles get condensed densely and maintain that contact against the tooth until the material solidifies into one compact mass. Composite resins on the other hand need to be packed in increments and cured{**Roulet JF, 1988**}. The material slumps away during its placement allowing development of a gap between the adjacent tooth and the one being restored. This gap is not detectable until the restoration is completed and is a major contributor to food impaction, caries and periodontal disease. This comparison with silver amalgam is one of the biggest drawbacks against the use of composite restorations, particularly in large sized restorations.

The new packable composites are said to contain fillers that are more coarse and textured than those used conventionally in other systems. These particles do not flow over one another when subjected to a load and a considerably greater pressure is required to force the material into the cavity preparation{**Leinfelder KF et al, 1998 (a)**}. Testing of packability is a relatively new concept in composite resin research. No standardized test exists to evaluate material packability. The Caulk Dentsply manufacturing company has used a 'Packability Index' as a measure of packability{**Caulk Dentsply, 1998**}. In this test, a 3.15mm diameter flat-ended metal penetrator was forced into a sample of material contained in a 6.5mm diameter by 4.5mm diameter deep cup at a rate of 200mm/min. The Packability Index was determined by the resistance force in grams measured by an Instron Universal testing machine divided by the area of the penetrator. The test however did not specify the depth the penetrator was forced into the material a relevant point, since force increases with increase in depth of penetration into the material.

Tyas and Jones elected to approximate the clinical use of composites by rapid loading of the material contained in a cylindrical stainless steel mold 8mm in diameter

and 8mm in height{Tyas MJ et al, 1998}. The rod was driven into the composite for 6 seconds at a rate of 24.4mm/min. to a depth of 2.4mm and the maximum load was recorded. Although, the authors graded the packable composites to have a higher value than the non-packable composites, the specimen material was not pre-measured before placing it into the mold. Composite materials being viscoelastic materials may be compressed significantly and hence definitive measurements of materials are necessary to standardize the technique being used.

Vallo et al evaluated the 'workability' of an acrylic bone cement modified by fillers{Vallo CI et al, 1999}. They measured the intrusion capability of their formulation using a procedure outlined in the American Society for Testing and Materials standard F451. An extrusion mold was fabricated from Teflon consisting of a die with four 1mm-diameter holes in the base of the die. Curing dough was forced through the holes in the base of the die and the lengths of the polymer strands discharged from each of the die holes was measured to yield a number proportional to the workability of the cement. The method was suitable for measuring the viscosity of acrylic bone cement, which must flow into cancellous bone as pressure is applied.

2.2 Polymer Rheology

Rheology is the science that deals with the deformation of materials as a result of an applied stress. The most common rheological property is viscosity, which characterizes the material's behavior in steady shearing flow {Instron capillary rheometer system, 1974}. Polymers are classified under the category of 'viscoelastic' materials. These materials exhibit a behavior combination between elastic solid and viscous fluid. In simple terms, a viscoelastic material will not deform instantaneously when non-isotropic stresses are applied. In other words, their response to stress is time dependent. In describing the rheology of the material, polymers are described as "Non Newtonian". This means that polymer systems exhibit a viscosity that decreases with increasing rate of deformation or a non-linear response to stress wherein, the rate of deformation is not directly proportional to the applied stress{Carreau PJ et al, 1997}. Viscoelastic effects of polymeric materials have been studied extensively. It is beyond the scope of this project to describe in detail the different behavioral properties as a result of the

viscoelastic character demonstrated by polymeric systems, therefore the properties relevant to the composite resins used in dentistry will be discussed in the following section.

a. Shear Thinning Behavior:{Vlachopoulos J et al, 1999} Shear thinning is a property of polymer liquids, also known as pseudoplastic behavior. If the rate of shearing is increased. (i.e. made to extrude faster through a die), the viscosity decreases. This reduction of resistance is due to alignment and disentanglement of the long polymer chains.

b. Die swell effect or Extrudate Swell:{Carreau PJ et al, 1997} This phenomenon is the swell of the extrudate or an increase in diameter demonstrated by a viscoelastic fluid as it extrudes from a capillary. This phenomenon can be explained through the presence of stresses created at the wall of the capillary. As the polymeric fluid emerges from the capillary, this internal pressure is released resulting in lateral expansion. Another explanation of die swell is that the long chains of polymers usually align themselves in the direction of flow and upon exiting the die, the polymers realign themselves to their original shape.

c. Elastic recovery:{Carreau PJ et al, 1997} Polymeric fluids are often referred to as 'fluids with memory'. When entering a small capillary die from a large reservoir, the fluid is subjected to a rapid change of shape, and as it emerges from the die, it tends to recover its initial shape. This memory effect is what lends polymers to behave as rubbery materials. This elastic behavior is best described as 'recoil'. For viscoelastic fluids, recoil is only partial and takes a finite time. Viscoelastic fluids are said to have a fading memory, that is they are more affected by recent deformation as opposed to those experienced in the more distant past. Moreover the effect is strongly dependent on the rate of deformation.

d. Stress Relaxation: Stress relaxation is the gradual decrease in stress with time under a constant deformation (strain){Cheremisinoff NP, 1993}. This phenomenon is viewed as the most fundamental manifestation of the viscoelasticity of polymer systems.

e. Influence of Fillers on Rheology of Polymers: The addition of fillers changes the rheology of the resin, thus influencing the properties of the product. Key factors are filler size and shape, filler concentration and the extent of any interactions among the particles

{**Rheometrics Inc., 1990**}. Moreover, particle orientation can further increase this non-Newtonian behavior and cause it to occur at a lower shear rate than for unfilled polymers. The consequences are an increase in viscosity and a decrease in die swell { **Rheometrics Inc., 1990**}.

These phenomena provide us with an insight to the behavior of the composite resins that are used in restorative dentistry. The die swell effect is clearly demonstrated when the material is dispensed from the tube for use. Similarly elastic recovery and stress relaxation are properties that explain why slump of the material occurs when the material is packed against a matrix band during the restoration of the proximal box in a Class II restoration.

2.3 Materials and Method

2.3.1 Materials

The packable composites used in the testing of 'packability' in this project were similar to those tested in Part I of this thesis and include:

- Alert (Jeneric Pentron)
- Prodigy Condensable(Kerr)
- Pyramid Dentin (Bisco)
- Solitaire (Heraeus Kulzer)
- Surefil (Caulk Dentsply)
- P-60 (3M)
- Z-250 (3M) :Non Packable Composite

These materials were tested against control composites Z100 (3M) and Spectrum TPH (Caulk Dentsply) that have been used in clinical practice for several years. These control composites were selected, as they were the most commonly used composite restorative materials in 54 dental schools in North America {**Mjör IA et al, 1998**}

2.3.2 Method

The method of choosing an appropriate viscosity model for non-Newtonian fluids is a complicated one. In chemical engineering, capillary rheometers of various designs have been popularly used for measuring the rheological properties of viscous fluids. These rheometers are sensitive devices and are specific for the materials being tested and could not be employed in this project due to their unavailability. Since handling of composite resins and the properties of the packable composites have been compared to amalgam, the apparatus used for testing the properties of the resins necessitated a dual use for the testing of amalgam and composite resins. Secondly, since handling properties were not features that could be scientifically defined, the test method selected warranted a likening to the clinical managing of amalgam and composite resin to simulate a comparison between the two materials. Of equal importance was the contrast between the packable and non-packable composites. The term 'packable' implies the property of stiffness (resistance to deformation), therefore, the force required to pack the material into a crevice (similar to a cavity), and the resistance of the material to displacement by an applied force were measurements used to quantify this term.

Two test methodologies were devised. A 'displacement' method relatively similar to that used by Caulk Dentsply{**Caulk Dentsply, 1998**} was used to record the maximum force required to displace a known quantity of material that was placed in a confined cylinder with a plunger exerting force upon it. Second, an 'extrusion' method was devised to measure the force required to displace a known quantity of material through a crevice, the size of which was similar to a proximal box in a Class II cavity on a tooth. The resistance of the material was recorded from the Force-Displacement data derived from the Force/Displacement curve. The displacement test was considered a 'reverse extrusion' test and it was anticipated that the results from the two would be similar.

2.3.2.1. Displacement method

A 10-mm high brass cylinder with a 4.77-mm diameter was secured to a stainless steel plate such that the two metal pieces together formed a well. A 0.1 cc pellet of restorative material was measured out in a syringe, placed in the well and compacted with a condenser such that the material was shaped into a cylindrical puck at the bottom of the well (**Figure 2.1**). A brass cylindrical plunger with a 3.15 mm diameter was fixed to the movable crosshead of an Instron model 4301 servo-mechanical materials testing machine equipped with a 1 KN capacity load cell. The well with the compacted material was secured to a platform directly below the plunger and the crosshead lowered until the tip of the plunger was just touching the top of the puck of material. The crosshead was then lowered at a rate of 5 mm/min until the tip of the plunger was 1.5 mm from the bottom of the well. During this controlled rate of descent, a chart recorder interfaced to the Instron machine collected force-position data. The peak force measured during the plunger's descent was recorded.

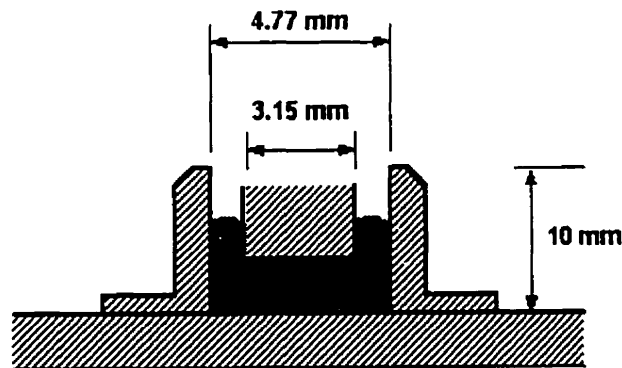


Figure 2.1:Diagram shows plunger (center) being lowered into restorative material (shaded) constrained in a cylindrical well (hatched pattern).

[Diagram not to scale]

2.3.2.2 Extrusion method

A 10-mm high brass cylinder (barrel) 4.77-mm in diameter was secured to a 10-mm thick stainless steel plate such that the two metal pieces together formed a well. In the stainless steel plate, in the center of the bottom of the well, there was a 2-mm diameter hole (capillary) bored 2 mm deep into the plate. Below the 2-mm depth, the hole conically expanded over a depth of 3 mm to a 5-mm diameter hole that traversed the remaining 5-mm of the plate (**Figure 2.2**). A brass cylindrical plunger with a 4.75-mm diameter was fixed to the movable crosshead of the Instron testing machine. A 0.1 cc pellet of restorative material was measured out in a syringe, placed in the well and the latter secured to a platform directly below the plunger. The Instron's crosshead was lowered until the tip of the plunger was just touching the top of the pellet. The crosshead was then lowered at a rate of 5 mm/min until almost all of the material was extruded through the hole in the bottom of the plate. During the plunger's descent, the chart recorder collected the force-position data. The force required to pack the material into the 2mm capillary was recorded as the extrusion force. This extrusion force was used in the determination of the 'Apparent Viscosity' of the tested materials (**Section 2.3.2.3**).

Figure 2.2 shows the five major features of the force-position data. At position "A", the tip of the plunger is just touching the restorative material. While the plunger travels from position "A" to position "B", the material is shaped into a cylindrical puck. From "B" to position "C", the material is starting to be packed into the 2mm crevice. As the plunger travels from position "C" to position "D", there is further packing of the material into the crevice as it approaches the bottom of the crevice. When the plunger travels from position "D" to position "E", the material gets extruded through the well. At and beyond position "E", there is very little material left in the well and a large increase in force is necessary to extrude the remainder since the material has to travel along a path that is virtually orthogonal to the direction of applied force. The peak force required to pack the material into the 2 mm capillary - from position "C" to position "D" on the force-position chart was recorded as the extrusion force.

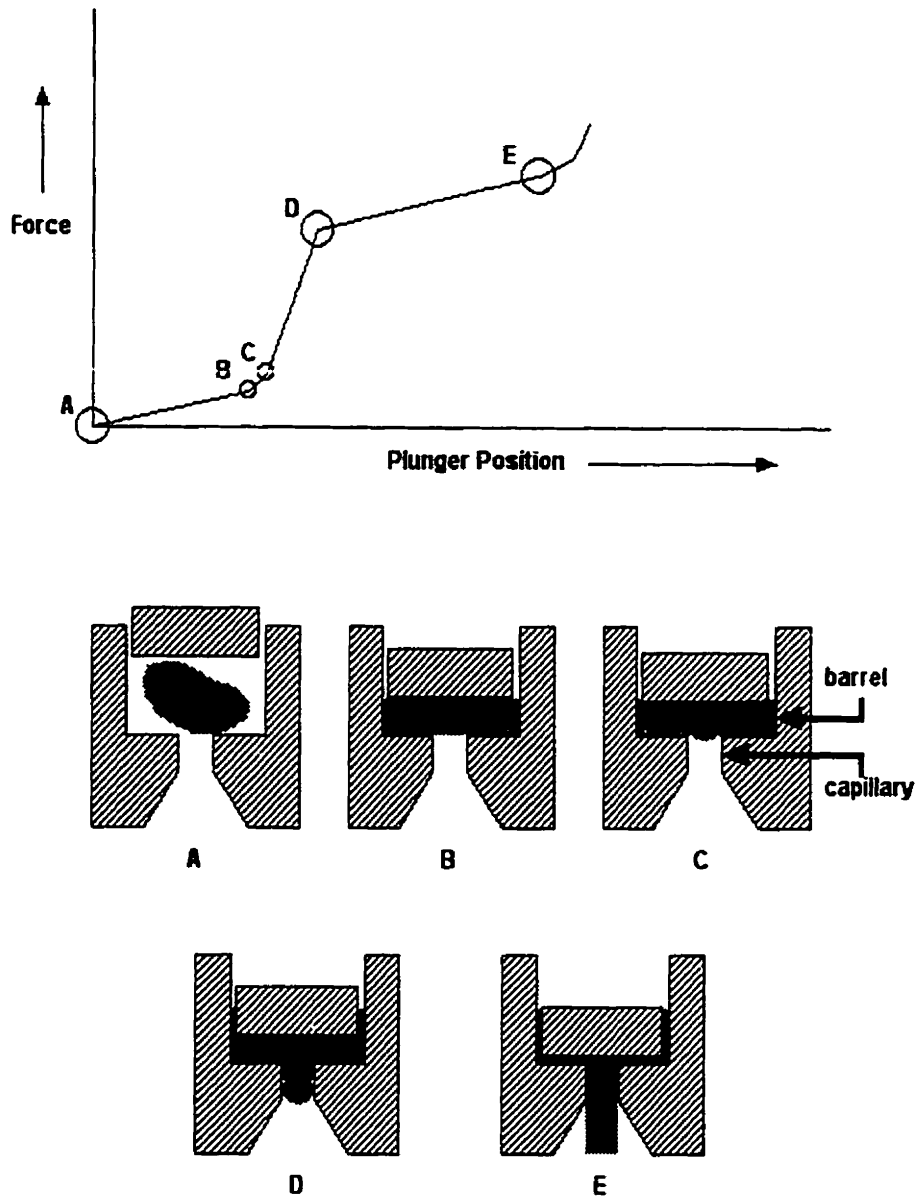


Figure 2.2:Diagram shows the major features of the Force-Position data captured by the chart recorder. The pellet of material (A); is reshaped to a cylindrical puck (B); begins packing into the 2mm crevice (C); completely packed into the crevice before being extruded (D); extrusion through the well (E). [Diagram not to scale].

2.3.2.3. Calculation of Apparent Viscosity

Newton's law of viscosity states that

$$\text{Viscosity} = \text{Shear Stress/Shear Rate} \text{ \{Vlachopoulos J et al, 1999\}}$$

Viscosity is the resistance to flow and is a constant (represented by μ) irrespective of shear rate for Newtonian fluids. Using the extrusion data obtained in Section 2.3.2.2 (Table 2.4), 'Apparent Viscosity' was determined from the basic theory of capillary rheology as follows {Instron capillary rheometer system, 1974}:

$$\text{Apparent Viscosity } (\eta_a) \text{ (Pa S)} = \text{Wall Shear Stress/ Wall Shear Rate}$$

Determination of Wall Shear Stress

$$\begin{aligned} \text{Shear Stress (Pa)} &= \Delta P / 2 L \times R \\ &= \frac{F / A \times R}{2 L} \end{aligned}$$

Where 'L' is the length of the capillary (=2mm); 'R' the radius of the capillary (=1mm); 'A'= $\pi D^2/4$ the cross-sectional area of the plunger and 'F' the mean force required to extrude the material through the die.

Determination of Wall Shear Rate for non Newtonian fluids using the Rabinowitsch correction for capillary rheometers {Instron capillary rheometer system, 1974}

$$\text{Shear Rate (seconds}^{-1}\text{)} = \frac{3n+1}{4n} \times \frac{8V}{d_c}$$

where 'V' is the mean velocity of the polymer flowing through the capillary. The mean velocity is readily calculated from the crosshead speed in mm/seconds (=5mm/seconds) and the ratio of the barrel diameter, d_b (4.77mm) to the capillary diameter d_c (2mm) [Section-2.3.2.2]. The value for 'n' or the power law index is usually experimentally determined from the slope of the force/displacement curve. For polymers, n=1, is a practical number, that was substituted in the following equation

Substituting the value for 'V' in the equation for shear rate, we get

$$\text{Shear Rate (seconds}^{-1}\text{)} = \frac{3n+1}{4} \times \frac{8 \times \frac{5}{60} \{d_b\}^2}{d_c}$$

2.3.2.4 Dynamic Viscosity testing

[Center for Advanced Polymer Processing and Design- McMaster University]

The extrusion test described above is a crude representation of an industrial 'capillary viscometer'. The difference being in the length of the extrusion die. True capillary viscometers employ interchangeable capillaries with various diameters and lengths and various piston speeds to allow a wide range of shear rates to be achieved. A proper selection of length to diameter (L/D) ratio can minimize the effects of entrance, exit and transient losses. Knowing the limitations therefore of the extrusion die (which was only 2mm) used in our experiment, it was necessary to determine whether the resultant viscosities of the materials differed if the test was carried out using an industrial rheometer used routinely for the testing of the rheology of polymer melts. The viscosities of the materials used in this study were tested at the 'Center for Advanced Polymer Processing and Design' (CAPPA-D) at McMaster University in Hamilton, Ontario as described below.

Viscoelastic measurements may be made using a steady test or dynamic test mode. A *steady* test uses continuous rotation to apply the strain and provide a constant shear rate. The resultant stress is then measured when the sample reaches a steady state. In a *dynamic* test, an oscillatory strain is applied to a sample and the resulting stress is measured. Dynamic tests can be made using free oscillations at the resonance frequency of the test material or with a sinusoidal oscillation at a forced frequency chosen from a wide available range {**Rheometrics Inc., 1990**}. The dynamic viscosity (η') measured is virtually identical to the steady shear viscosity (η) measured according to an empirical relation called the Cox-Merz rule, where the frequency of oscillation (rads/sec) corresponds to the shear rate (seconds⁻¹) {**Vlachopoulos J et al, 1999**}.

In industry a variety of instruments are used to measure the viscosity of polymer solutions and melts. The most common types are the rotational rheometers with various fixtures (like the coaxial cylinder, the cone and plate, parallel plate) and the capillary viscometer. Rotational instruments are best used for low shear rates of 10⁻² to 100 seconds⁻¹. For higher shear rates ranging from 10 to 10⁴ seconds⁻¹, capillary instruments are best used. The measurement of viscosity of non-Newtonian fluids is made through 'dynamic viscosity measurements', which makes measurements of material response by

imposition of a sinusoidal stress or strain making use of high oscillatory frequencies up to 500 seconds⁻¹ {Vlachopoulos J et al, 1999}. These measurements are made with rotational rheometers in oscillation mode. Rotational rheometers offer the advantage that they measure the elastic modulus of the material concurrent with viscosity measurements. {Rheometrics Inc., 1990}. In this study, a rotational rheometer with parallel plate fixtures that utilizes low shear rates was used and is described as follows.

Viscosity measurements for the materials were carried out using ARES (Advanced Rheometric Expansion System) parallel plate rheometer (Figure 2.3). This instrument measures the viscoelastic properties of thermoplastic solids and melts, elastomers, and other viscoelastic materials. It is a controlled-strain rheometer, which operates in dynamic, steady and transient test modes. In this study, the measurements were made in 'dynamic mode'.

An oscillatory strain (sinusoidal or other waveform) was applied to the sample and the resulting stress developed in the sample was measured. In addition to measuring the viscosity, the stress signal generated by a viscoelastic material was separated into two components: an elastic stress τ' (tau) which is in phase with the strain, and a viscous stress τ'' which is in phase with the strain rate (90⁰ out of phase with the strain). The elastic stress is a measure of the degree to which a material behaves as an elastic solid: the viscous stress, the degree to which the material behaves like an ideal fluid. The elastic and viscous stresses are related to material properties through the ratio of stress to strain, the modulus. Thus the ratio of the elastic stress to strain is the storage (or elastic) modulus and the ratio of the viscous stress to strain is the loss (or viscous) modulus {Rheometrics Inc., 1990}. The results of the tests are expressed as {Vlachopoulos J et al, 1999}:

G' (elastic or storage modulus)= in phase stress/ maximum strain

G'' (viscous or loss modulus)= out of phase stress/maximum strain.

In this experiment, although the viscous (loss) modulus was obtained, it is not being reported, since viscosity measurements were also determined and these were reported.

Method

A sample specimen ($n=1$) of material 1.5-mm thick was prepared in a concentric metallic disc of diameter 2.5-mm. This sample was then placed in the rheometer apparatus, between two coaxial parallel plates separated by a gap of 1.5mm thus ensuring that the specimen was in contact with the two plates. The upper plate remained stable and the lower plate was oscillated with a frequency ranging from 0.1 to 100 rads/second. The 'Viscosity' measurements and 'Storage Modulus' were obtained from the shear stress at the different shear rates, using the formulas:

1. Viscosity η (Pa S) = $\frac{\text{Shear Stress}}{\text{Shear Rate}}$
2. Storage Modulus G' (Pa) = $\frac{\text{In phase stress}}{\text{Maximum Strain}}$

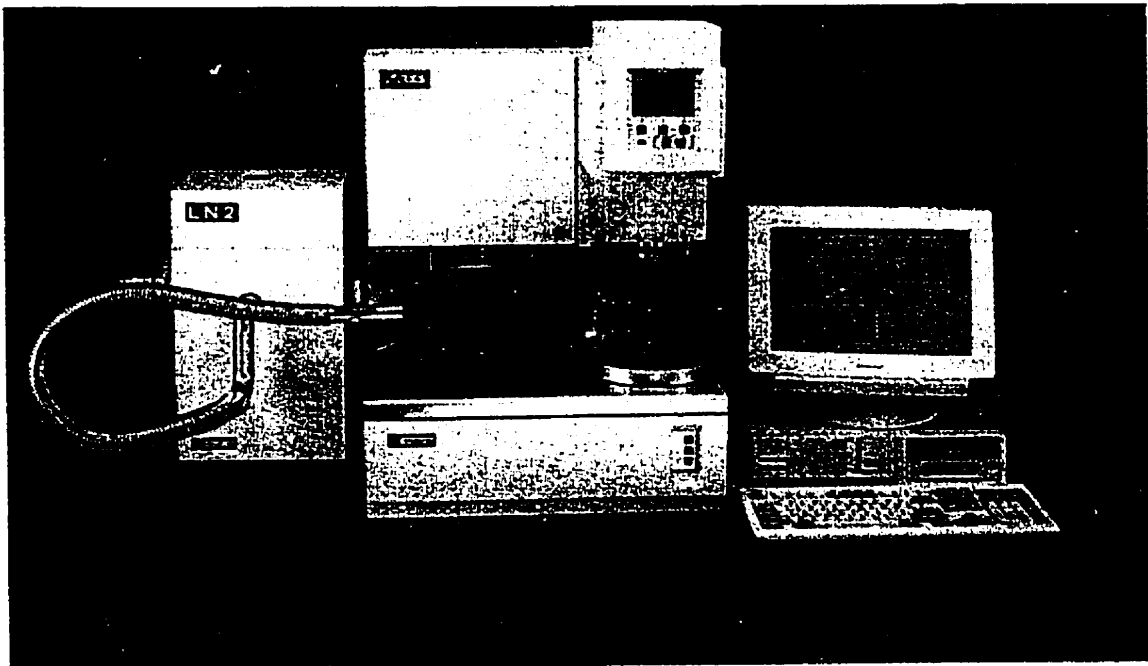


Figure 2.3: Advanced Rheometric Expansion System (ARES)

In addition, to the viscosity testing, a 'stress relaxation' test was performed as described in the following section to further characterize the elastic behavior of the materials **Section-2.3.2.5**).

2.3.2.5 Stress Relaxation

The time dependent elastic response of materials like gum, rubber and silk was first measured by Kolrausch (1863) using a torsional creep apparatus {Macosko CM, 1994}. When the load was removed part of the deformation recovered instantly, other materials recovered with time and in some materials there was a permanent set. Today this time dependent response is called viscoelasticity. {Macosko CM, 1994}.

Stress relaxation is a measure of the viscoelastic properties of polymers and is defined as a decrease in stress under sustained constant strain {Whittington LR, 1978}. When a polymeric liquid is subject to a step increase in strain, the stress relaxes in an exponential fashion. If a purely viscous liquid is subjected to the same deformation, the stress relaxes instantly to zero as soon as the strain becomes constant. An elastic solid would show no deformation {Macosko CM, 1994}.

Stress relaxation measurements were carried out using ARES (Advanced Rheometric Expansion System) rheometer in transient test mode. Stress relaxation tests involve a rapid pre-selected deformation of the material followed by a measurement of the stress required to maintain that strain over time. Stress relaxation of a material is measured at the material's 'linear viscoelastic region'. This region describes where the rheological properties of a viscoelastic region are independent of imposed stress or strain levels. The strain level for the linear viscoelastic region of the materials was measured using the 'Strain Sweep test' and found to be at 4% strain and this level of strain was used in the stress relaxation measurement.

The 'Stress Relaxation' test was carried out over a time range of 0.01 to 1000 seconds by measuring the stresses after the motion had stopped. The stress relaxation modulus $G(t)$ was then calculated by dividing the stress measured as a function of time by the constant strain. {Rheometrics Inc., 1990}.

2.4 Results

2.4.1 Displacement Testing

The results of displacement testing are presented in Tables 2.1 and 2.2 and Figures 2.4 and 2.5. For amalgam, the data collection went beyond the capacity of the machine and the results were recorded at 1000N, which meant that the force required to displace amalgam was well above those for the other materials (**Figure 2.4**). For the two amalgam products, the force values were the same and therefore were just reported as 'amalgam'. ANOVA test disclosed significant differences between groups ($p=0.0001$). Scheffe's tests revealed that the materials were divided into three groups. Alert represented the highest displacement force and was significantly higher than all the other composite groups. Pyramid, Prodigy and Surefil were the second highest group. This group had significantly higher displacement forces than the lowest group represented by P-60, Spectrum, Z-250, Z100 and Solitaire, except for Surefil and P-60, which were not significantly different from each other.

Table 2.1: One Factor ANOVA X_1 : composite Y_1 : Displacement Force

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	9	1.82×10^6	201902.39	35643.63
Within Groups	19	107.63	5.66	$P=0.0001$
Total	28	1.82×10^6		

Analysis of Variance Table

Model II estimate of between component variance = 679702.44

Table 2.2: Displacement Test Results (Vertical lines represent groups not significantly different)

Group	Count	Mean Force (N)	Std. Deviation	Std. Error
Amalgam	2	1000	0	0
Alert	3	49.67	4.51	2.60
Pyramid	3	18.50	3.04	1.76
Prodigy	3	17.17	3.05	1.76
Surefil	3	16.67	5.55	2.05
P-60	3	8.00	0.50	0.29
Spectrum	3	5.17	1.15	0.67
Z250	3	3.83	0.58	0.33
Z100	3	2.00	0.50	0.29
Solitaire	3	1.67	0.38	0.22

Displacement Force Results With Amalgam

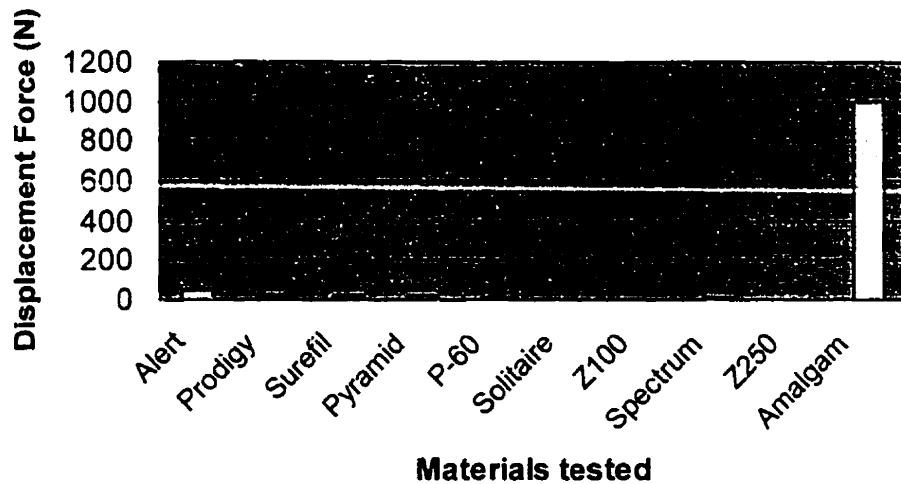
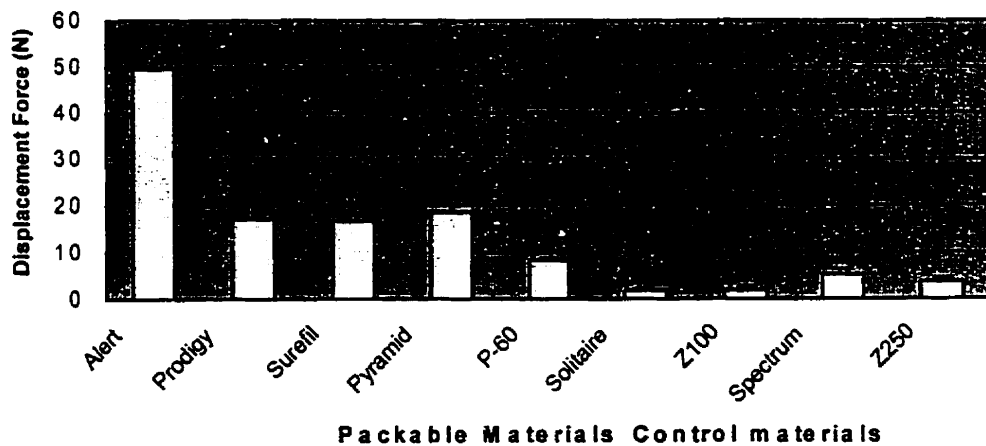


Figure 2.4: Comparison of Displacement Force. Amalgam versus Composite materials

Figure 2.5: Comparison of Displacement Force. Packable Composites and Control Composites

Displacement Force Results Without Amalgam



2.4.2. Extrusion testing

The results of the extrusion testing are presented in Tables 2.3 and 2.4 and Figure 2.6. Amalgam could not be tested using this test methodology, as it was not extrudable through the apparatus. ANOVA tests revealed significant differences between groups ($p=0.0001$). Scheffe's tests disclosed that the materials were divided into three groups Alert representing the material with the highest extrusion force, Prodigy, P-60, Pyramid and Surefil the second group and Spectrum, Z-250, Solitaire and Z-100 the third group. The three groups had significantly different extrusion force values from each other with the exception of Surefil from Group II which was not significantly different from the materials in Group III.

Table 2.3: One Factor ANOVA X_1 : composite Y_1 : Extrusion Force

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	2.3×10^4	2.9×10^3	69.40
Within Groups	18	7.7×10^2	43.19	$P=0.0001$
Total	26	2.4×10^4		

Analysis of Variance Table

Model II estimate of between component variance $=9.8 \times 10^2$

Table 2.4: Extrusion Force Test Results *

Group	Count	Mean Force (N)	Std. Deviation	Std. Error
Alert	3	106.00	17.09	9.86
Prodigy	3	39.33	6.02	3.48
P-60	3	34.50	3.97	2.29
Pyramid	3	33.67	4.04	2.33
Surefil	3	19.00	3.90	2.25
Spectrum	3	8.83	2.26	1.36
Z250	3	8.67	2.52	1.45
Solitaire	3	8.33	2.36	1.36
Z100	3	5.33	0.29	0.17

* Vertical lines represent groups not significantly different

2.4.3 Apparent Viscosity Test Results

Extrusion force data was used to calculate the viscosity of the materials. Data is presented in Tables 2.5 and 2.6 and in Figure 2.7. The ranking of the materials was similar to the extrusion test results. ANOVA tests revealed significant differences between groups ($p=0.0001$). Scheffe's tests disclosed that the materials were divided into three groups. Alert represented the material with the highest viscosity and was significantly different from the other materials. Prodigy, Pyramid, P-60 and Surefil represented the second group, which were not significantly different from each other. These materials except for Surefil were significantly different from the third group with the lowest viscosity values represented by Z-250, Spectrum, Solitaire and Z-100 whose values were not significantly different from each other.

Table 2.5: One Factor ANOVA X_1 : composite Y_1 : Apparent Viscosity

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	1.32×10^{12}	1.65×10^{11}	66.40
Within Groups	18	4.48×10^{10}	2.49×10^1	$P=0.0001$
Total	26	1.36×10^{12}		

Analysis of Variance Table

Model II estimate of between component variance = 5.43×10^{10}

Table 2.6: Apparent Viscosity Test Results (PaS)*

Group	Count	Mean	Std. Deviation	Std. Error
Alert	3	7.87×10^5	1.31×10^5	0.75×10^5
Prodigy	3	2.87×10^5	0.45×10^5	0.26×10^5
P-60	3	2.53×10^5	0.31×10^5	0.18×10^5
Pyramid	3	2.47×10^5	0.31×10^5	0.18×10^5
Surefil	3	1.40×10^5	0.26×10^5	0.15×10^5
Spectrum	3	0.63×10^5	0.06×10^5	0.03×10^5
Z250	3	0.63×10^5	0.21×10^5	0.12×10^5
Solitaire	3	0.60×10^5	0.17×10^5	0.10×10^5
Z100	3	0.40×10^5	0.00	0.00

* Vertical lines represent groups not significantly different

Extrusion Force Results

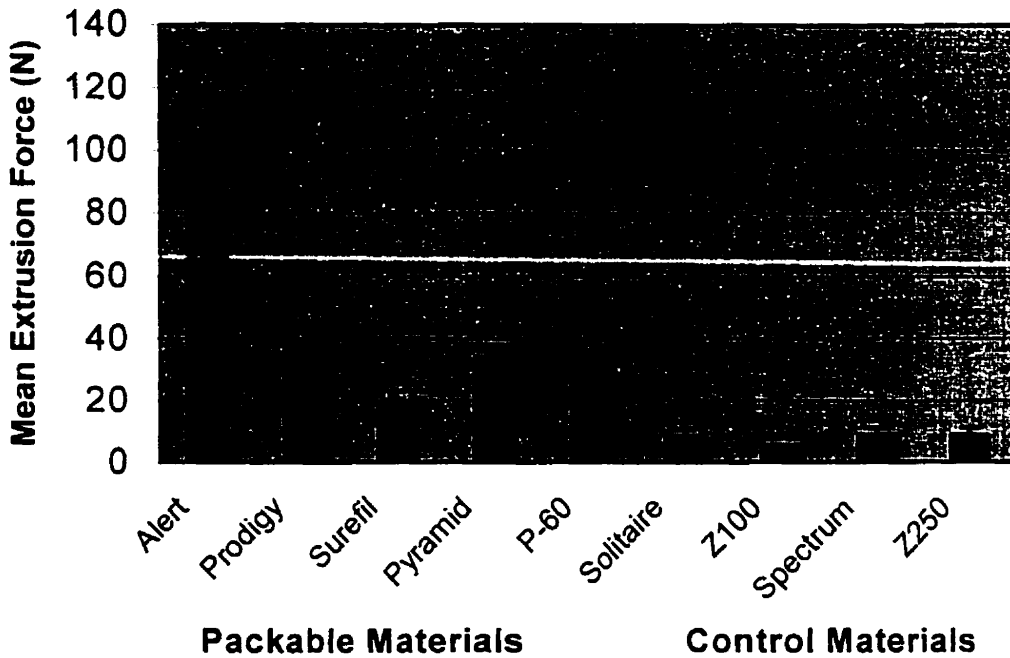
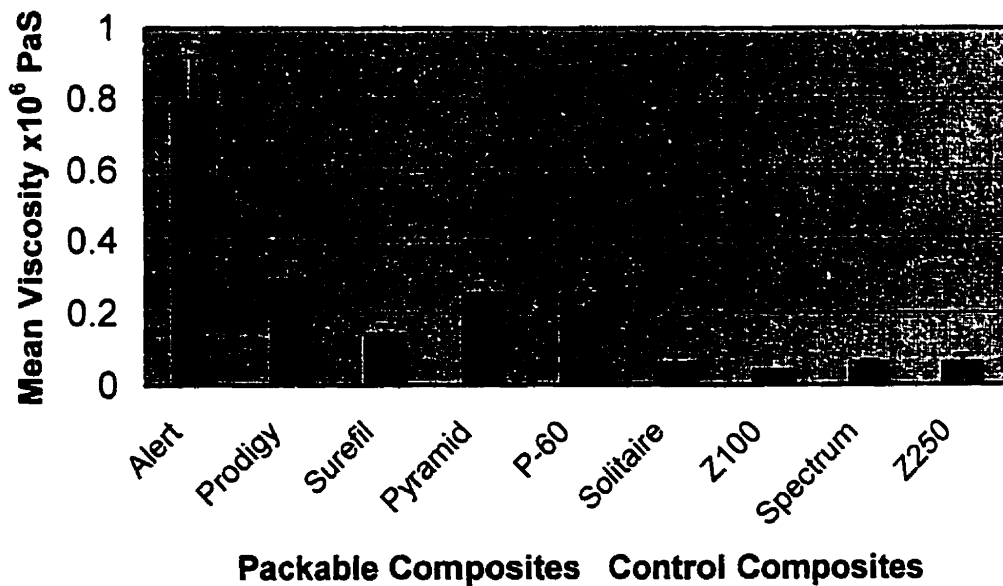


Figure 2.6: Comparison of Extrusion Forces. Packable vs. Control Composites

Figure 2.7: Comparison of Apparent Viscosity Test Results. Extrusion testing

Apparent Viscosity Test Results



2.4.4: Dynamic Viscosity Testing Results

Figure 2.8 depicts the data from the viscosity testing using the ARES rotational rheometer with parallel plate fixtures. Statistical analysis was not done due to the small sample size ($n=1$). The viscosity was measured as a function of frequency. The materials demonstrated a shear-thinning behavior with a decrease in viscosity at increasing shear rates. At 0.1 rads/second, the composites were divided into four groups of low, medium high and very high viscosity. Surefil demonstrated the highest viscosity and was in the same range as Alert (500,000-1,000,000 PaS). Pyramid and Prodigy were in the high range of 300,000PaS. P-60 and Spectrum were in the medium range of 50,000-100,000PaS; and Solitaire, Z100 and Z-250 were in the low range of 2500-6000PaS. At 100 rads/second, the groups demonstrated a decrease in viscosity. They were divided into three groups with Surefil and Alert in the range of 5000-6000 rads/second, Pyramid, Prodigy, Spectrum, P-60 and Z-250 in the range of 500-1000 PaS and Solitaire and Z100 in the low range of 80-100 PaS. P-60 and Spectrum demonstrated similar viscosities of 5000 PaS at 10 rads/second, but at lower shear rates, the viscosity of Spectrum was higher than P-60.

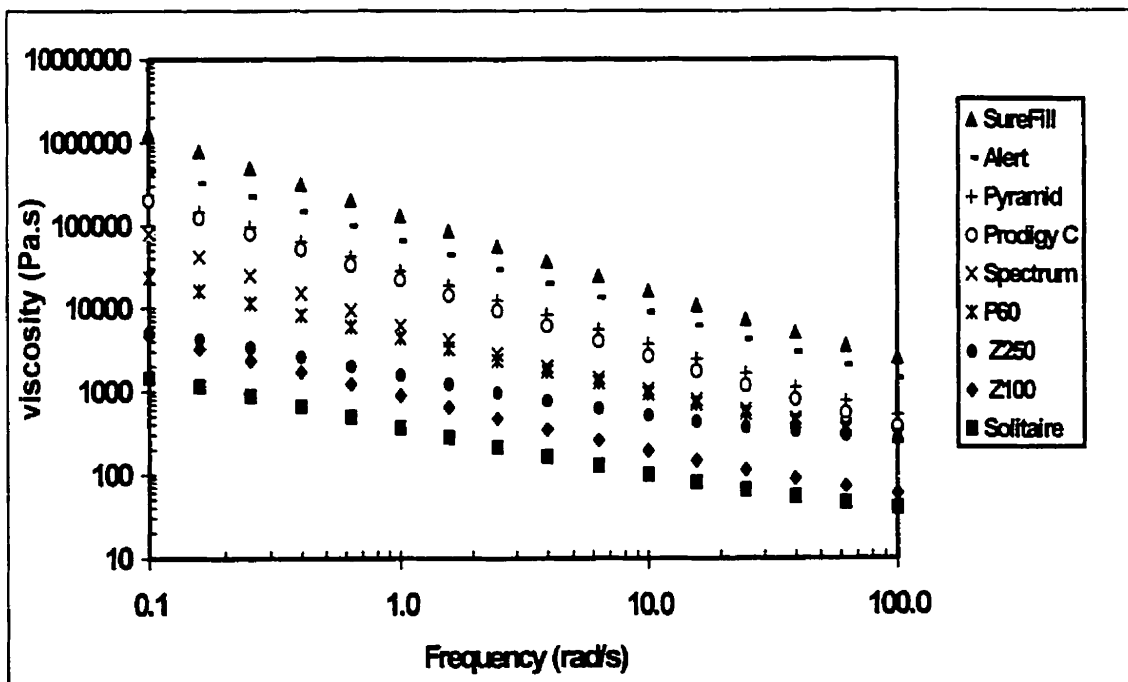
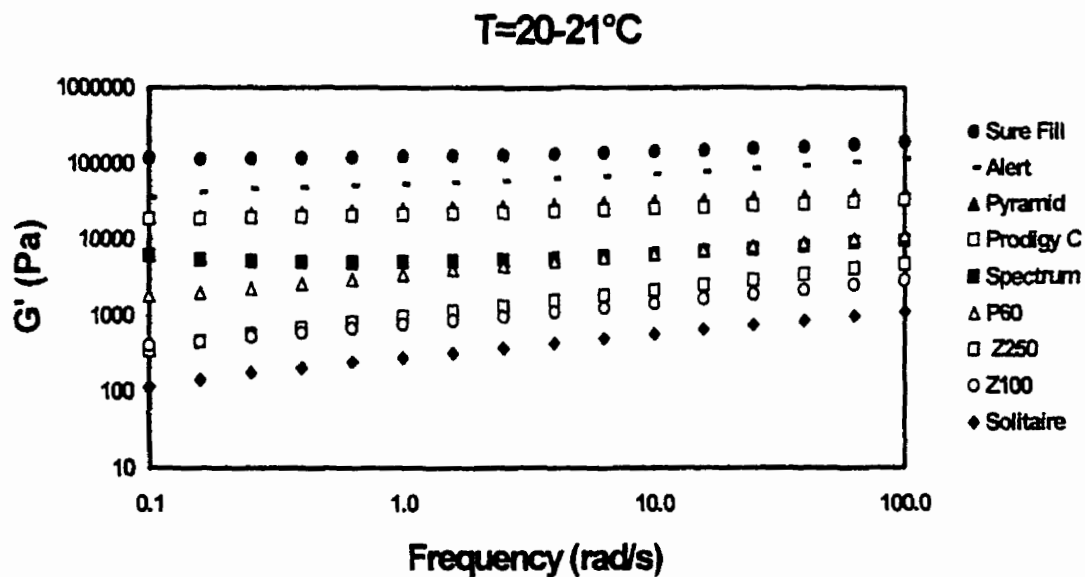


Figure 2.8: Viscosity data obtained from ARES plotted versus the rotational frequency

2.4.5 Storage Modulus

Figure 2.9 explains the elastic behavior of the tested materials. Statistical analysis was not done due to the small sample size ($n=1$). It can be seen from the graph that the materials which are highly viscous have a very high storage modulus. The graph indicates the materials with greater storage modulus (higher G') require more stress to achieve the same deformation as compared to materials with lower G' .

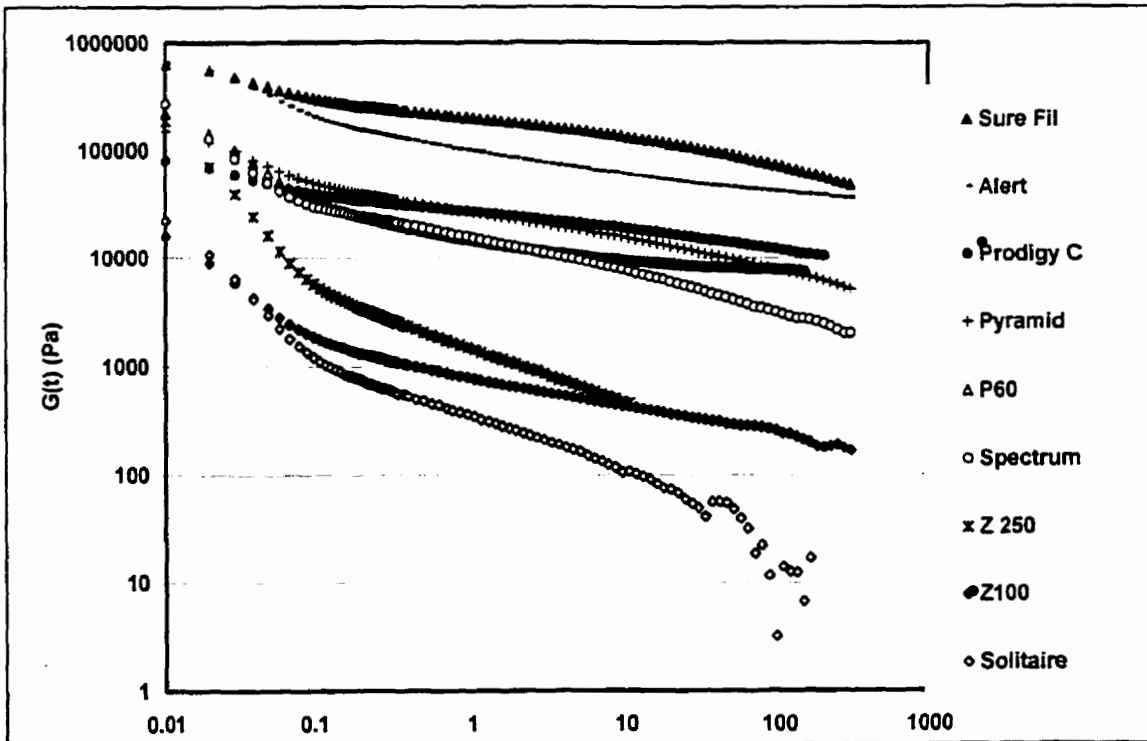
Figure 2.9: The Elastic or Storage Modulus of the materials as a function of frequency



2.4.6 Stress Relaxation Results

Figure 2.10 demonstrates the graph of $G(t)$:the 'Relaxation Modulus' obtained by dividing the stress, measured as a function of time, by the constant strain. Statistical analysis was not done due to the small sample size ($n=1$). Surefil, Alert, Prodigy, P-60 and Pyramid. behave as 'rubber concentrated suspensions'. These materials demonstrate short-time relaxation followed by a decreasing modulus. In contrast, Z250 and Solitaire show 'dilute solution' behavior demonstrating flow when stresses are imposed as visualized by a very short time relaxation.

Figure 2.10: Stress Relaxation Graph demonstrating Relaxation Modulus $G(t)$ as a function of time



2.5 Discussion

Composite resins are well accepted in the practice of restorative dentistry but their utilization has been less than ideal particularly for large restorations in the back of the mouth. They are difficult to place in all aspects of the prepared cavity and the production of anatomic contact areas is unpredictable. Packable composites were recently introduced with the promise of being packable, thus simulating the favorable properties of amalgam. In an attempt to define the term packability, the rheology of the composite resins was studied. Two test methodologies were devised. A 'displacement' method that measured the force required to displace the material and an 'extrusion test' which measured the force required to extrude the material through a narrow channel. In addition, the results of the extrusion test were verified with a standard industrial rheometer, which is routinely used to measure the viscosity of polymeric materials.

It was shown that the displacement forces for amalgam far exceeded by a factor of 20 those for any of the tested resin composite materials in this study (**Table 2.2**). When amalgam alloy is mixed with mercury, a plastic mass is obtained that allows a relative ease of adaptation to the cavity walls. This is followed by setting and hardening of the amalgam as the liquid mercury is consumed in the formation of solid phases (**Phillips RW, 1996 (a)**). The packable characteristics of amalgam are attributed to its irregular alloy particles that offer resistance to condensation when the material is packed into the tooth. In contrast to amalgam, composite resins do not offer this unique alloy condensation process while being packed. The test results categorized most of the packable materials as requiring either a large displacement or extrusion force and the non packable materials as requiring a significantly lower displacement or extrusion force. This implies that the packable materials offer increased resistance or positive contact to condensing instruments when placed as restorative materials. The extrusion test measured viscosity at one shear rate (**Table 2.4**) and therefore provided only a limited definition of material flow character given that the viscosity of these materials is not constant with shear rate (**Figure 2.8**). In industry this is important because the apparent viscosity may change by an order of magnitude over two or three decades of shear rate and it is imperative therefore to determine the apparent viscosity over a range of shear rates which spans the required operating conditions (**Instron capillary rheometer**

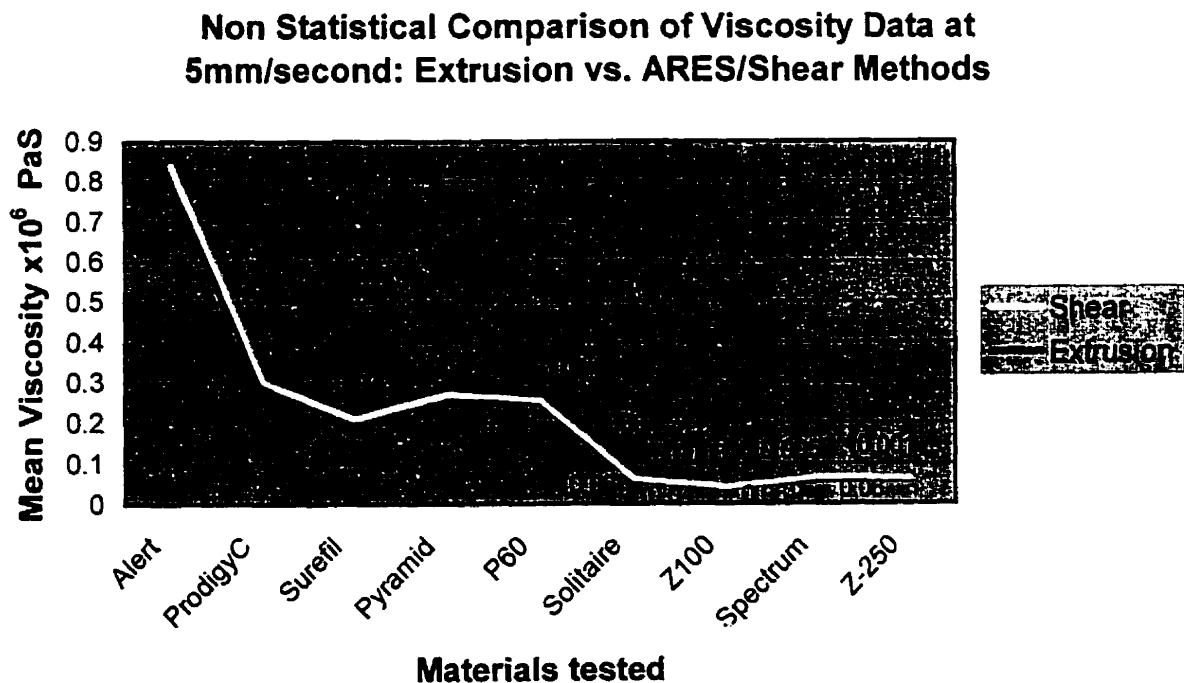
system, 1974}. In dentistry, although not known, the specific shear rates for material insertion in a cavity during the restorative procedure are the only ones with some relevance. As a result a rate of 5mm/seconds was chosen as the most appropriate crosshead speed of the Instron in the extrusion study being representative of material insertion rates during a clinical restoration.

The viscosity data obtained using the ARES parallel plate rheometer indicated that the materials were viscoelastic (**Figure 2.8**), in that they demonstrated shear-thinning behavior and a significant storage modulus G' . The data obtained from the extrusion test was used to calculate the apparent viscosities of the composite materials using the shear stress determined from the extrusion force and the shear rate that was determined from the velocity of the crosshead speed of the Instron and the diameters of the cylinder and capillary (**Section 2.3.2.3**). A non-statistical comparison of the viscosity results obtained by both test methods at a shear rate of 5mm/second is shown in Figure 2.11. It can be seen that the results followed a similar trend. The results obtained with testing using the ARES were (with the exception of Surefil) within a 1-10% range of that obtained using the extrusion method. This variation in the two methods could be explained by the fact that the extrusion method measured not only the viscosity, but also the large entrance and exit effects of the composite material through the extrusion channel. The only difference in results was with regards to Surefil, the values using the extrusion method were lower than those obtained with ARES and would require further investigation to determine the reason for such behavior. The displacement method was representative of a reverse extrusion method, which measured the resistance to flow backwards and therefore demonstrated similar results to the extrusion method for all the materials with the exception of Surefil.

The stress relaxation data gives us an insight to the relaxation behavior of the materials. The data followed the order of the viscosity and storage modulus data, with the same order of groupings. The materials were grouped according to their relaxation behavior into three groups. Surefil, Alert- Group I; Prodigy, Pyramid, P60, Spectrum- Group II; Z100, Z250, Solitaire- Group III. All the materials tested demonstrated stress relaxation. Group I and Group II materials demonstrated short time relaxation followed by a slowly decreasing modulus. This implies that all these materials will be similar to

work with in terms of application but materials with higher values of $G(t)$ would be 'stiffer' and need more stresses to be applied to flow (Figure 2.10). The materials with lower viscosity (Group III) demonstrated 'dilute solution behavior', in that they demonstrated very short time relaxation or 'flow' when stresses are imposed. Such a relaxation, however slight, would tend to cause a relapse of proximal contour prior to photopolymerization therefore the potential for improved proximal contacts during the restorative procedure is questionable. These tests describe the rheological behavior of the materials, however the true significance of the rheological behavior particularly that of stress relaxation in the production of proximal contacts requires a specific study simulating clinical usage. Such a study would need to examine the application procedures of the materials. This would include the preparation of the material before insertion into the tooth cavity, the mode of insertion and, the time lapse between packing of the material and the external polymerization.

Figure 2.11: Non-Statistical Comparison of Viscosity data at 5mm per second



The rheological behavior of the materials is related to the molecular structure of the resins and the physical shape and distribution of the filler particles. The materials tested in this study demonstrate polymeric behavior probably due to the long chain structure of the oligomers, even though they cannot be described as true polymers in the unpolymerized state. Experimentally it has been established that viscosity of a linear polymer chain increases rapidly with chain length and larger structure. The relative motion of the polymer chains depends upon the rate at which the chains can disentangle themselves, and this becomes rapidly more difficult as chain length increases {Hall C, 1989}.

An analysis of resin chemistry and filler particle size and distribution gives us an insight into the rheological behavior. Although the exact composition of the materials could be analyzed by FT-IR (Fourier Transform Infra Red Spectroscopy), mass spectrometry and other methods, this process was considered beyond the scope of this project. Hence an attempt to explain the behavior of the materials was solely done on the basis of the technical data sheets and material safety data sheets (MSDS). A summary of the resin monomers and filler content of the tested materials is presented in Tables 1.1 & 1.2. Although the shear method may have been more accurate, the test utilized only one sample of each material and the results were not analyzed statistically, hence the apparent viscosity results obtained by the extrusion method are used here in the examination of the rheological behavior.

Based on Figure 2.7 and Table 2.6, the materials are categorized into 3 groups (Table 2.7): [Alert- Group I]; [Prodigy, P-60, Pyramid, Surefil- Group II]; and [Spectrum, Z250, Solitaire, Z100- Group III]. These groups are similar in ranking with the viscosity results obtained by dynamic shear testing using ARES except for Surefil. Alert was in the highest viscosity groups in both test methods. This highly viscous material contains a combination of two resin monomers. Ethoxylated bisphenolA (bisEMA) and Polycarbonate dimethacrylate (PCDMA). The molecular weight of these compounds is reported to be 584 and 462g/mol respectively {Jia W, 2000}. The high molecular weight results in a decreased mobility of the monomer chains and exaggerates the difficulties encountered in dis-entanglement of the chains when stresses are imposed {Hall C, 1989}. In addition to the resin, the filler particles in Alert consisted of glass

fibers that ranged from 60-80 μ m in length and 6-8 μ m in diameter and submicron particles of silica. The high viscosity of this material is attributed to the irregular shape of the long glass fiber particles that require to be in alignment to enhance flow. Also the submicron filler particle content which provides a larger surface area will increase material viscosity {**Soderholm K-J.M, 1985**}.

The viscosity of group II is similarly attributed to the resin and filler. All the materials in Group II were highly filled. The filler content ranging from 58-71% by volume. The materials however demonstrated no significant differences in their viscosity. In addition to the resin monomer these resins contain a wide range of filler particle sizes. Manufacturer data provides us with knowledge of average particle sizes, but particle size distribution of the fillers is unknown. It is well known that microfine fillers can enhance viscosity due to their large surface area and therefore the quantity of microfine filler that can be incorporated into the resin is limited {**Craig RG, 1980**}. An SEM analysis of these resins in part I of this thesis (**Figures 1.11-1.19**) demonstrated the presence of submicron sized particles in all of these resins, the content of which if known would help explain the minor variations in the viscosity in this group.

The difference in viscosity between Z100 in Group III and materials in Group II in general may be explained based on resin dilution. The viscosity of undiluted bisGMA is 1200-1500PaS {**Davy KWM et al, 1998**}. When diluted with TEGDMA, the viscosity of BisGMA decreases substantially {**Asmussen E, 1977 (b)**} and can approach 1-2PaS depending on the TEGDMA concentration {**Taylor DF et al, 1998**}. Hence the quantity of TEGDMA incorporated to dilute the resin affects the viscosity and explains the low viscosity of Z100 in Group III compared to higher viscosity materials in Group II.

With reference to pairs of materials from the same manufacturer, for example Caulk Dentsply Surefil and Spectrum are both urethane modified bisGMA resins (**Figure 1.5**) of high molecular weight (mol wt.4900g/mol). The difference between these two materials would depend upon the resin dilution as well as the fillers. Both materials are highly filled: Surefil 58% and Spectrum 57% by volume. Filler particles in Surefil range from submicron particles to 20 μ m and in Spectrum the filler particles range from 0.04 to 5 μ m with submicron particles. The differences in the viscosity can be therefore

attributed in greater part to the differences in the content of the submicron particles and perhaps to the irregular shapes of the filler particles in the more packable material Surefil.

P60 and Z250 were another paired group, which differed in their viscosity but reportedly had the same composition. The resin components for both consisted of BisEMA(6) (**Figure 2.12**) and UDMA resins, (molecular weight 629 and 470 g/mol. respectively) and filler particle sizes and particle distribution were very similar (0.01-3.5 μ m), but the materials differed in filler loading. P60 was 1% more highly filled in volume than Z250. The differences in the viscosity between these two materials has been explained by the manufacturer as being exclusively due to the difference in filler loading between these two materials and the subsequent 5% reduction in the volume of the resin content of P60 causing a higher viscosity {3M,1998}.

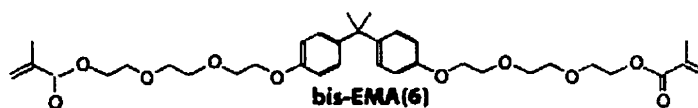


Figure 2.12: Structure of bis EMA (6){3M Dental Products Laboratory, 1998}

The material whose behavior could not be adequately explained was Solitaire. This material contained methacrylate monomers of unknown composition and a light porous filler with a volume content of 90%. SEM samples in Part I of this thesis (**Figure 1.15**) demonstrated the presence of large particles and submicron particles in the resin. In spite of this the material demonstrated the lowest viscosity. Due to the limited information on its components the reason for this behavior could not be explained.

Table: 2.7: Material Ranking based on Apparent Viscosity

	Resin Composite	Mean Apparent Viscosity (PaS)	Material Ranking
1	Alert	7.87×10^5	Group I
2.	Prodigy	2.87×10^5	Group II
3.	P60	2.53×10^5	
4.	Pyramid	2.47×10^5	
5.	Surefil	1.40×10^5	
6.	Spectrum	0.63×10^5	Group III
7.	Z250	0.63×10^5	
8.	Solitaire	0.60×10^5	
9.	Z100	0.40×10^5	

2.6 Conclusions

From the above discussion several conclusions may be drawn. None of the packable materials approached the packing force values demonstrated by amalgam. In general, the materials, which are classified by manufacturers as 'packable' were highly viscous as compared to the 'non-packable' materials. However all the materials demonstrated the rheological property of stress relaxation associated with polymeric materials. It is reasonable to conclude that resin monomer composition along with filler size and particle distribution affects viscosity. Dilution of the resin decreases viscosity. Composites with approximately the same resin composition and similar filler particle size and distribution differ in viscosity if they differ in volume filler loading.

Precise knowledge of material composition is necessary to allow proper interpretation of data. This data together with information as to relevance on clinical behavior of these materials would aid in making a practical selection of restorative materials for use in clinical practice.

2.7 Recommendations

The combined test results provide useful information in helping to characterize the rheology of the composite materials. The limitations of the extrusion test have been identified and include:

1. A modification in the channel length of the apparatus to minimize the entrance and exit effects.

2. Another instrument that could be useful in measuring the viscosity of the materials is the 'capillary extrusion rheometer', that contains two capillary tubes one of length 16mm (or longer) and another one of negligible length. The viscosity of the material that passes through the two tubes is obtained by subtracting the effect of the smaller tube from the larger one, thus compensating for the large entrance and exit effects. {Vlachopoulos J et al, 1999}

3. The test could be repeated using ARES with a larger sample size and the results could then be analyzed statistically.

4. An analysis of the resin and filler composition of the tested materials would provide further insight into the rheological behavior of these materials.

5. A clinical evaluation of the effectiveness of increased viscosity and varied stress relaxation periods of these materials to further determine if these properties are beneficial in providing a restoration with improved proximal contacts.

Part- III

SIMULATED CLINICAL TESTING 'MICROLEAKAGE'

3.1 Overview

The longevity of resin composite restorations and the evaluation of 'failure' of these restorations is most often based upon the detection of staining at the tooth restoration interface {Mair LH, 1998}, as well as the detection of secondary caries {Collins CJ et al, 1998}, {Qvist V et al, 1990}. The success of resin composite restorations is largely dependent upon the long-term intimate adaptation of the restorative materials to the tooth structure and the prevention of the ingress of bacteria into the tooth-restoration interface. The subject of bacterial percolation, bacterial growth and the accumulation of toxins collectively known as microleakage at the tooth restoration interface has been a subject of research mainly because of the deleterious effect of these processes on the etiology of pulpal pathology and caries.

Microleakage at the tooth restoration interface can result from inadequate initial adaptation of the restorative material to the tooth tissue. Marginal defects and/or gaps can also occur as a result of polymerization shrinkage. Adaptation of the material to the tooth surface is dependent upon the viscosity of the restorative material and the adhesive technique used {Opdam NJ et al, 1996}. With regard to polymerization shrinkage, hybrid composites demonstrate a linear shrinkage of 0.4 –1.2% and a volumetric shrinkage of 1.3-3.5% {Lambrechts P et al, 1987}. This shrinkage has been associated with a gap at the margin of the restoration ranging from 5-29 μ m {Brannstrom M, 1985}. The clinical consequences of this gap and the resulting microbial percolation are postoperative sensitivity in the short term and secondary caries over the long term {Eick DJ et al, 1986}.

The following section will review in detail, the implications of gap formation at the tooth-restoration interface and the method used in detection of such gaps. A microleakage study will then be used as an assessment of the presence of interfacial gaps which will compare the behavior of packable and control composites in simulated clinical restorations.

Initial and Secondary Gap formation

Qvist reported an extensive review on gap formation in resin restorations in which he described the process of gap formation as occurring in stages{Qvist V, 1993}.

An *initial gap formation* occurs when the resin material polymerizes and undergoes volumetric contraction. This initial gap is primarily dependent upon the adhesive forces of the material to the tooth as well as the viscosity of the material, which influences the adaptation of the material to the walls of the cavity. Absorption of water into the resin results in hygroscopic expansion, which may compensate for the initial gap formation. This expansion however is dependent upon whether finishing and polishing of the restoration has taken place before closure of the gap occurs as this could cause enamel prism fracture along the periphery of the cavity. In addition, the gap tends to close with enamel and fragmented particle debris, thus obstructing a later closing by hygroscopic expansion{Asmussen E et al, 1972},{Asmussen E, 1977}, {Michem JC et al, 1976}.

Secondary gap formation tends to occur as a result of temperature changes in the oral cavity or repeated mechanical loading {Qvist V, 1993}. Gap formation as a result of temperature change is intermittent and is attributed to the differences in the thermal coefficient of expansion between the resin and enamel or dentin {Nelsen RJ et al, 1952}. Gap formation as a result of mechanical loading has been demonstrated in vitro and is explained as being attributable to a plastic deformation of the restorative material{Jorgensen KD et al, 1976}. A difference in Young's Modulus between the tooth and the restorative material may also contribute indirectly to gap formation. A material with a modulus of elasticity not compatible with tooth structure will be unable to provide support at the tooth enamel interface to protect the enamel rods from fracturing under repeated functional stresses{Jones DW et al, 1996}.

Methods to Minimize Gap Formation

a. Acid Etching of Enamel

The technique of acid etching the enamel was introduced by Buonocore in 1955{Buonocore MG, 1955}. Etching of enamel with 37% phosphoric acid for 30-60

seconds creates a dry, clean highly polar inorganic surface with microporosities. To this surface, hydrophobic bonding agents can be applied to create a micro-mechanical attachment between the resin and tooth surface that provides bond strengths of up to 20 MPa {**Nordenvall KJ et al, 1980**}. More recently, studies have shown that a 15 second conditioning time produces a similar morphologic pattern and equivalent bond strengths on cut enamel surfaces{**Barkmeier WW et al, 1986**},{**Barkmeier WW et al, 1987**}.

b. Dentin Bonding

In contrast to an etched enamel surface, acid conditioning of dentin leaves a sponge-like inorganic structure with a high protein content and low surface energy making the attachment more difficult {**Van Meerbeek B et al, 1992 (b)**}. The first step in successful dentin bonding involves the removal of the smear layer on the tooth surface that is produced by dental instrumentation. Acid conditioning with 32-35% phosphoric acid results in a removal of the smear layer, opens the dentinal tubules, increases dentinal permeability and decalcifies the intertubular and peritubular dentin{**Van Meerbeek B, et al, 1992 (a)**}. A micromechanical attachment between the resin and tooth is dependent upon the diffusion of appropriate hydrophilic primers that permit surface wetting and penetration into the exposed collagen network of superficially demineralized dentin. The primer application is followed by the subsequent penetration of low viscosity adhesive resin into the microspaces between the collagen fibrils and into the dentinal tubules co-polymerizing with the primer to form an intermingled layer of collagen and resin called the 'hybrid layer' {**Nakabayashi N et al, 1982**},{**Van Meerbeek B et al, 1992 (a)**}.

Significant improvements have been made with dentin bonding agents. In contrast to first and second generation dentin bonding agents which demonstrated poor clinical performance and shear bond strengths ranging from of 1-10MPa {**Bowen RL, 1965**},{**Chan DC et al, 1985**}, third generation bonding agents which were introduced in the late 1980's permitted a removal of the smear layer to allow resin penetration into the underlying dentin {**Prati C et al, 1990**}. Although these dentin adhesives were more effective than their predecessors in reducing microleakage at dentin and cementum margins, they did not completely eliminate marginal leakage {**Swift EJ, 1998 (a)**}. The bonding mechanism of fourth generation dentin bonding adhesives is a three-step process

that continues to be in wide use today. This includes conditioning, priming and bonding as three separate steps. Reported shear bond strength values for these materials can approach the typical enamel bond strength of 20MPa. In addition, microleakage studies indicate that they provide a better marginal seal than earlier generation products {Gwinnett AJ et al, 1994},{Holtan JR et al, 1994}.

Fifth generation dentin bonding agents were recently introduced, in an attempt to simplify the process of dentin bonding. These systems continue to require conditioning of enamel and dentin, however they combine the primer and bonding agent into one step that require one or two more applications {Swift EJ, 1998 (a)}. Results of shear bond strength with these new one-bottle adhesives are variable. The new one-bottle adhesives appear to be technique sensitive particularly with respect to the hydrating conditions of the dentin. All current dental adhesives systems are designed to be hydrophilic, containing resin monomers (e.g. hydroxy ethyl methacrylate HEMA) dissolved in acetone, water, ethanol or a combination of these solvents {Swift EJ et al, 1997 (a)}. Bonding to dentin therefore is dependent on the surface being moist to permit resin penetration into the tubules. Studies have shown that the quantity of moisture on the dentinal surface, whether insufficient or excessive may compromise the bonding {Swift EJ et al, 1997 (b)}{Tay FR et al, 1996 (a)},{Tay FR et al, 1996 (b)}.

Swift et al measured the shear bond strength of several one bottle adhesives including Single Bond (3M), One Step (Bisco) and Prime &Bond (Caulk Dentsply) against a conventional 3-step adhesive Scotchbond Multi-Purpose (3M) to varying degrees of moist dentin{Swift EJ et al, 1997 (a)}. The materials were bonded using the said adhesives and Z100 (3M) restorative resin. They found that unlike One Step, Single Bond and Prime &Bond did not demonstrate any significant differences in bond strength to the varying degrees of moistness present on the dentinal surface. They also found that bond strengths for Single Bond and Scotchbond Multipurpose were not significantly different.

Swift et al reported shear bond strengths of several one bottle dental adhesives to enamel{Swift EJ et al, 1998 (b)}. The one bottle adhesive materials they tested included One Step (Bisco), OptiBond Solo (Kerr Corp.), Prime &Bond 2.1 (Caulk Dentsply), Single Bond (3M), Tenure Quik (Den-mat Corp.) and Syntac single Component (Ivoclar

Vivadent). Shear bond strength was tested against Scotchbond Multi-Purpose (3M) which is a conventional 3 step, fourth generation bonding agent. They found that with the exception of Syntac, all the one step adhesives demonstrated enamel bond strengths comparable with the conventional bonding agent.

In an in vitro study comparing the sealing ability of fourth and fifth generation dentin bonding agents, Pilo and Ben Amar found no significant differences in microleakage around Class V resin composite restorations subjected to occlusal and thermal stresses {Pilo R et al, 1999}. Products tested included those by 3M (ScotchBond Multipurpose/SingleBond), Bisco (All-Bond2/One-Step) and Kerr (Optibond FL/Solobond). Kruskal-Wallis 1-way ANOVA revealed that none of the fifth generation dentin bonding agents demonstrated more leakage than their fourth generation counterparts. 3M products demonstrated a superior sealing ability on enamel, while Bisco products were superior in sealing dentin and cementum.

Based on the above review, Single Bond (3M) was selected as the material of choice for use in this experiment because it appeared not to be influenced significantly by different hydrating conditions of dentin (more technique tolerant), provided that the surface was moist, and yet demonstrated comparable shear bond strength values with conventional 3- step bonding agents {Swift EJ et al, 1997 (a)}.

Methods for registration of gap occurrence

Measurements of gap formation at the margin of the tooth-restoration interface can be measured in vivo and in vitro.

Although in vivo studies have been shown to be more clinically relevant, they are more time consuming, expensive and are subject to a number of variables which may be difficult to control {Qvist V, 1993}. Some of the clinical methods rely on visual inspection and probing; as well as the scoring of models and photographs, the marginal penetration of radioactive isotopes or low viscosity fluorescent resin. Light or SEM examination of impressions and models are also used for diagnosing gaps less than 20-30 μm {Qvist V, 1993}.

In vitro methods of gap analysis involve functional and morphological methods that include marginal percolation, penetration of dyes and radioactive isotopes; light and SEM examination of restorations or impressions and models respectively {Qvist V, 1993}.

In vitro simulation of clinical conditions

Restorative materials when tested *in vitro* fail to simulate the dynamic intra oral conditions exemplified by constant thermal changes induced by routine eating and drinking. For this reason, thermocycling is often employed in laboratory experiments to simulate the stresses induced by temperature changes in the oral cavity. The regimens used in thermocycling vary considerably, and are without standardization. This includes variations in both temperature ranges and the number of cycles used {Gale MS et al, 1999 (b)}. Gale and Darvell reported on 130 experiments that utilized thermocycling in tests of shear bond strength, tracer penetration tests and tensile bond strength {Gale MS et al, 1999 (b)}. Most of the studies utilized low temperatures that ranged from 3⁰ to 15⁰ C and high temperatures that ranged from 55⁰ to 60⁰C. Based on the reported literature, they concluded that 'no definitive statement of a relevant regimen could be made', however they suggested that thermocycling regimens should not opt for extremes of temperature as these were not representative of oral temperature variations.

Microleakage studies employing thermocycling procedures have become a common way of attempting to simulate clinical conditions *in vitro*. The intent of these studies is to demonstrate permeability at the interface of the tooth and the restoration. The results of these studies vary considerably, and studies have shown that microleakage measured *in vitro* is not representative of what happens *in vivo* and the reports appear conflicting. Pashley theorized that *in-vitro* studies of microleakage should be regarded as setting a theoretical maximum amount of leakage that may or may not occur *in vivo* for the following reasons {Pashley DH, 1990}.

1. The dynamic nature of the pulp-dentin complex, with the pulp hydrostatic pressure being higher than in dentin, causes dentinal fluid to move through the dentinal tubules in the opposite direction to the bacterial products.
2. Large molecular weight proteins such as fibrinogen may lower the permeability of the dentin by adsorbing to the tubule walls.

3. Sclerosis of dentin can lower dentin permeability over time.

Using a microleakage assessment study Abdalla and Davidson compared the marginal integrity of Class II resin restorations placed in vivo to a similar number of restorations prepared and restored in vitro with the gingival margins in enamel{Abdalla AI et al, 1993}. In both situations the teeth were restored with a variety of composites and dentin bonding agents, but each in vivo group was complemented with a similar in vitro group. The restored teeth in vivo were extracted after 4-6 weeks. The teeth in the in-vitro group were stored in water for 2-3 weeks following a similar restorative protocol followed in vivo. These specimens were thermocycled between 5⁰C and 55⁰C for 500 cycles. They were then subjected to a cyclical loading process supposed to be clinically relevant, where a steel ball was allowed to deliver a force of 12.5kg at 52 cycles /min. for 4000 cycles{Fields HE et al, 1986}. All the in vivo and in-vitro specimens were coated with nail polish 1mm short of the margin of the restorations and stored in dye solution for 24 hours. The teeth were then sectioned and graded for microleakage. Statistical analysis using the Wilcoxon signed rank test showed that the in vivo groups demonstrated more microleakage than the in-vitro groups. The results add to the controversy regarding in-vitro testing of microleakage, particularly as the authors did not mention whether the in vivo restorations were place using a rubber dam. It is well documented that composites are seriously compromised by moisture contamination{Leidal TI, 1985} and the results reported would be significantly dependent upon whether this procedure was employed or not.

In vitro teeth samples are subject to an entirely different set of conditions as compared to those in vivo. Not only in the clinical condition is the outward flow of fluid through the dentinal tubules prominent but the surface tension of in-vitro dentin samples is completely altered as a result of extraction and storage{Abdalla AI et al, 1993}. In vivo, the marginal integrity of resin composites is influenced by the functional stresses imposed by mastication{Qvist V, 1983}, adhesion may also be compromised by a number of intra oral environmental conditions including the possibility of contamination by saliva, gingival fluids and the technical difficulty associated with the placement and finishing of the restoration {Abdalla AI et al, 1993}.

Thus although there is a poor correlation between in vivo and in vitro microleakage studies, in vitro studies can provide some initial information and useful comparison of behaviour of different materials and guidelines as to the theoretical expectations of the material in vivo. Microleakage is dependent upon several factors including adaptation of the material to the tooth surface, the bonding material used and the technique of bonding, polymerization shrinkage of the resins and the thermal stability of the material. Studies continue to show that microleakage into dentin remains a significant problem{**Davidson CL et al, 1997**}.

Packable composites have been recently introduced with claims made to improved handling characteristics of these materials simulating those of dental amalgam. The new materials are claimed by their respective manufacturers to demonstrate lower polymerization shrinkage as compared to conventional universal use resin composite materials{**Caulk Dentsply, 1998**},{**3M, 1998**}. In part I of this thesis, the physical and mechanical properties of these new materials were evaluated. The viscosity of these materials was found to be higher than the universal use materials as demonstrated in Part II of this thesis. Although these materials demonstrate the potential for improved contacts with adjacent teeth, their performance in a clinical scenario with regards to microleakage remains to be assessed. Lambrechts et al reported that with highly filled resin composites, the wetting ability and penetration coefficient of these composites is low and tends to induce void inclusion, poor adhesion and an inadequate marginal seal{**Lambrechts P et al, 1987**}. Opdam et al evaluated the influence of consistency of composite materials and the mode of application on voids and porosities in one hundred Class I adhesive restorations. They found that the thicker consistency composites demonstrated more problems related to voids and wall adaptation than thinner consistency materials{**Opdam NJ et al, 1996**}. Thus the need for evaluation of microleakage of the packable materials, of which many are highly filled, becomes imperative.

There are numerous articles in the literature reporting the microleakage assessment of restorative materials. Most of these studies demonstrate little consistency in the method of experimentation. Gale and Darvell conducted a thorough review of the microleakage studies reported and found that the evaluation of the results was found to be

often vague and not descriptive of the true picture of leakage {Gale MS et al, 1999 (a)}. To avoid repetition of these inconsistencies, it was decided to perform the microleakage experiment in accordance with the ISO Standards. The measurement of microleakage was modified to better describe the microleakage that occurs in dentin.

3.2 Material and Method

3.2.1 Materials

Experimenting with all the packable composites was considered an exhaustive process. therefore the decision was made to test the control composites with their respective packable counterparts. The packable composite Alert, rated the most viscous in the extrusion test (Table 2.4), and was included as well.

Control composites: Z100(3M); Spectrum TPH (Caulk Dentsply)

Packable Composites: P-60 (3M); Surefil (Caulk Dentsply); Alert (Jeneric Pentron)

3.2.2 Method

Due to wide variability in the protocol followed for microleakage reported in the literature, it was decided to follow the ISO guidelines on the 'testing of adhesion to tooth structure'{ISO-11405, 1991}

Pre- Preparation and Storage

Freshly extracted third molar teeth were stored in distilled water immediately after extraction. Using a clinical protocol for asepsis, the teeth were thoroughly cleaned of debris, blood and other organic media and the periodontal ligament was removed with a sharp scalpel blade. Following this they were stored in clean distilled water in a refrigerator at 4⁰C. This was done as recommended by the ISO standards, to avoid any alteration of the tooth substance as may occur with other chemical agents{ISO-11405, 1991}. The storage medium was replaced constantly, to avoid any deterioration. Before tooth preparation, the teeth were inspected for defects such as enamel and dentin fractures and were discarded if found not suitable.

Tooth Preparation

Ten teeth per group were randomly selected, a combined total of 50 teeth in five groups. The cavity preparation and restoration was performed separately for each group. Class V cavities were prepared on each tooth, 3mm in length, 2mm wide and 2mm in depth using a high speed tungsten carbide 245 bur with a water coolant. The cavities were prepared half on enamel and half on dentin to permit microleakage assessment on both tooth margins, ensuring that the depth of the cavity was within dentin. To reduce apical leakage into the pulp which would confound the results, the root apices were sealed with light cure Glass Ionomer cement (Fuji II LC: GC Corporation, Japan) (**Figure 3.1**). The entire tooth was varnished with two coats of nail varnish, except for a 0.5mm window around the preparation. This was done to seal the tubules around the restoration, yet leaving the tooth restoration interface patent. While the nail varnish was drying the cavity was kept moist with water that was inserted into the preparation using a dropper. The prepared cavities were then restored according to a standard protocol as follows.

Tooth Restoration

The prepared tooth cavities were etched for 15 seconds with 35% phosphoric acid (3M-Scotchbond); rinsed and blotted dry, ensuring that the dentin remained moist. This was followed by the application of two coats of 'Single Bond'- (3M) a one step prime and bond resin. Excess resin was dried with an air syringe for 2-5 seconds followed by light curing for 10 seconds. The restorations (Shade A) were placed using a microscope (Bausch & Lomb) under 0.7x magnification and it was ensured that no flash overlapped the margins (**Figure 3.1**). It was also ensured that the restorations were not underfilled. The restorations were cured for 40 seconds as recommended by all the manufacturers and stored overnight in distilled water at 37⁰C. The restorations were not subjected to a finishing procedure to avoid fracture of the enamel prisms around the cavity as well as to prevent debris from sealing the interface between the tooth and restoration{**Asmussen E et al, 1972**},{**Asmussen E, 1977**}, {**Michem JC et al, 1976**}.

The next day, the restored teeth were subjected to a thermocycling protocol as recommended by the ISO standards {**ISO-11405, 1991**}. The teeth alternated in the thermocycling machine (Haake R- Dieselstrasse, W. Germany) between two baths at 5⁰C

and 55⁰C, for a dwell time of 20 seconds each with a resting time for 5 seconds in between each bath at 23⁰C. This was repeated for 500 cycles and took approximately 9 hours and 20 minutes to completion. Following thermocycling, the teeth were stored in 2% methylene blue for one hour, after which they were rinsed under running water and stored in an incubator at 37⁰C. The following day, each tooth was mounted on an acrylic block, (with precautions taken to ensure the other teeth in the group were not dehydrated) and sectioned with a high speed diamond saw (Accutom-Struers) with the restoration parallel to the face of the saw. Three sections were made within each restoration approximately 0.7mm in thickness, and each section was then photographed on one face with a photomicroscope (Wild: Photomakroskop M400) using a magnification ratio 1:10. This cycle was then repeated for the remaining four groups.

Microleakage Assessment

Following the sectioning, and photography of the specimens, and taking into account the loss of specimens due to de-bonding, each section was evaluated according to the assessment criteria (Table 3.1) by two examiners (Drs. D'Souza N. & Tam L.E.) for microleakage. Enamel leakage was evaluated separately from dentin leakage. Enamel leakage was evaluated based on the penetration into the enamel/restoration interface. Dentin leakage was categorized as being parallel to the interface as well as perpendicular to the interface. Dentin leakage *parallel* to the interface referred to the *length or extent* of staining along the interface (parallel direction), from the cavo-surface margin towards the axial wall (Figure 3.2A). The assessment of leakage *perpendicular* to the interface, referred to the *degree of stain* (color) along the dentin composite interface as well as the *depth of stain* penetration from the interface towards the pulp via the dentinal tubules (Figure 3.2B). In this way the interfacial penetration at the dentin/ restoration interface could be evaluated separately from the degree of stain penetration and depth of dentinal tubule penetration relative to the pulp proximity. The assessment parallel to the interface represented the length of the marginal gap, while the assessment perpendicular to the interface reflected the width of the marginal gap and the depth of leakage into the permeable dentin towards the pulp. The non-parametric data was statistically compared using 'Kruskal Wallis' test. This test is a useful way for comparing groups, where more

than two score-measured experimental groups exist. The test assigns a mean rank to each group in order of differences based on evaluation of qualitative data.

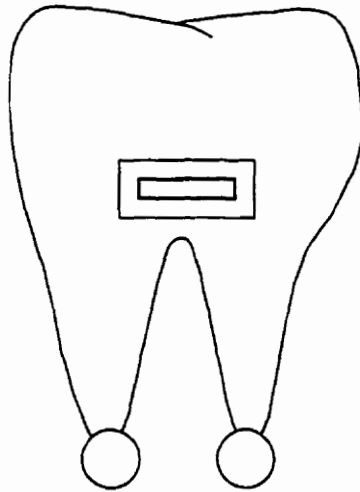


Figure 3.1: Schematic diagram of tooth restoration with the apices sealed, surrounded by a varnish coat except for a 0.5mm window surrounding the restoration

Table 3.1: Criteria for assessment of microleakage

Criteria for Evaluation of Microleakage

Extent of Leakage in Enamel

- 0: No Leakage
- 1: Leakage into Enamel up to 1/3 of its length
- 2: Leakage into Enamel up to 2/3 of its length
- 3: Complete leakage into Enamel up to the Dentin-Enamel Junction.

Extent of Leakage in Dentin (Parallel to the interface)- Figure 3.2A

- 0: No leakage in dentin
- 1: Leakage into dentin less than or up to 1/3 of its length
- 2: Leakage into dentin from 1/3 up to 2/3 of its length, but not extending to the axial wall
- 3: Leakage extending to the axial wall of the cavity
- 4: Significant leakage beyond the axial wall up to the pulp chamber

Degree of Microleakage in Dentin (Perpendicular to the interface)- Figure 3.2B

- 0: No interfacial stain penetration; no tubule penetration
- 1: Faint interfacial stain with no tubule penetration
- 2: Darker interfacial stain with none or slight tubule penetration (<1/3 towards the pulp)
- 3: Distinct interfacial stain with moderate tubule penetration (about 1/2 way towards the pulp)
- 4: Distinct interfacial stain with tubule penetration close or into the pulp (>2/3 towards the pulp)

Figure 3.2 A: Dentin Leakage evaluated Parallel to the tooth -restoration Interface

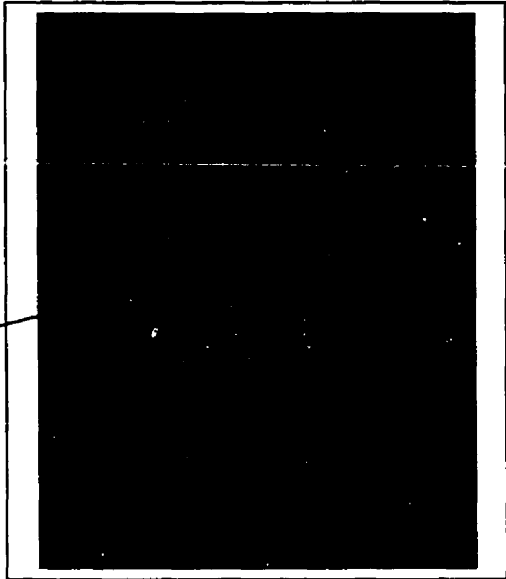
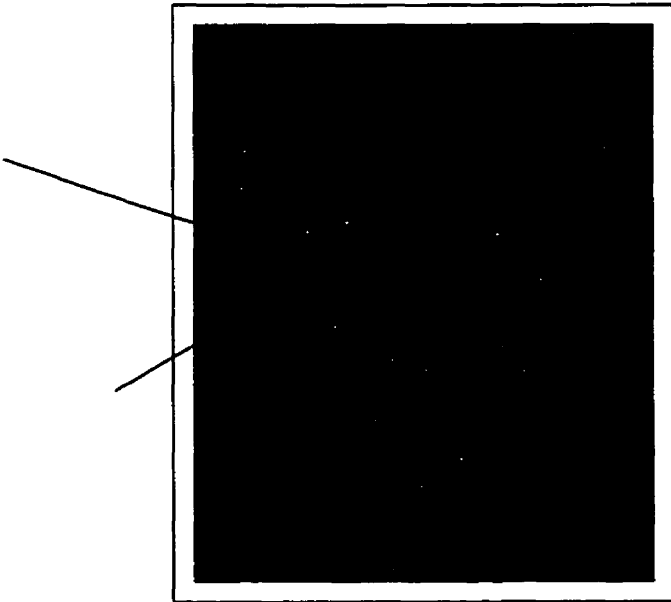


Figure 3.2B: Dentin Leakage evaluated Perpendicular to the tooth -restoration interface



3.3 Results

3.3.1 Enamel Leakage (Tables 3.2, 3.3 & Figure 3.3)

Figure 3.3 depicts the microleakage assessment in enamel for the materials tested. The Kruskal –Wallis test for assessment of enamel leakage is shown in Tables 3.2 and 3.3. There were significant differences among groups ($p=0.0001$). The packable composites Surefil and Alert demonstrated significantly the highest enamel leakage. A pair-wise comparison among the five groups, using the Mann Whitney U test revealed that the mean values for Alert and Surefil were not significantly different from each other. The mean values for enamel leakage of Z100, Spectrum and P-60 were not significantly different from each other.

Table 3.2:Kruskal-Wallis: X₁- Material; Y₁- Enamel leakage

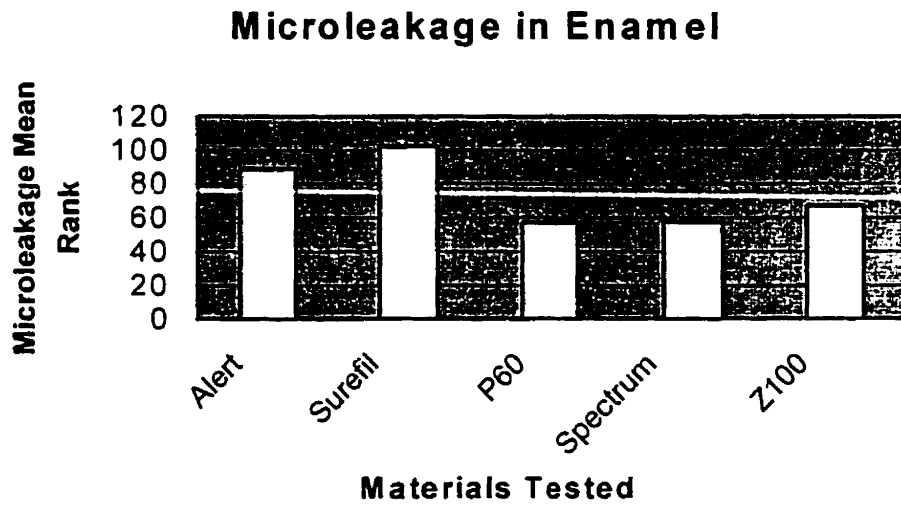
DF	4
Number of Groups	5
Number of Cases	148
H	25.14 p=0.0001
H corrected for ties	27.56 p=0.0001
Number of tied groups	4

Table 3.3:Kruskal-Wallis: X₁- Material; Y₁- Enamel Leakage*

Group	No. of cases	Σ Rank	Mean Rank
Alert	33	2929	88.76
Surefil	27	2759.5	102.20
P60	30	1707.5	56.92
Spectrum	25	1431	57.24
Z100	33	2199	66.64

*Groups represented by straight lines are not significantly different

Figure3.3: Microleakage Assessment of Materials in Enamel



3.3.2 Dentin Leakage Parallel to Interface: (Tables 3.4, 3.5 and Figure 3.4)

Tables 3.4 and 3.5 depict the length of leakage along the restoration/dentin interface. The Kruskal -Wallis test revealed significant differences among the groups ($p=0.0001$). A pair-wise comparison among the five groups, using the Mann Whitney U test, revealed the mean values for Alert and Surefil did not differ significantly from each other. Packable composites Alert and Surefil demonstrated significantly the highest leakage compared to the other materials. Spectrum demonstrated significantly higher dentin leakage than P60 but was not significantly different from Z100.

Table 3.4:Kruskal-Wallis :X₁- Material; Y₂- Dentin Leakage (Parallel to Interface)

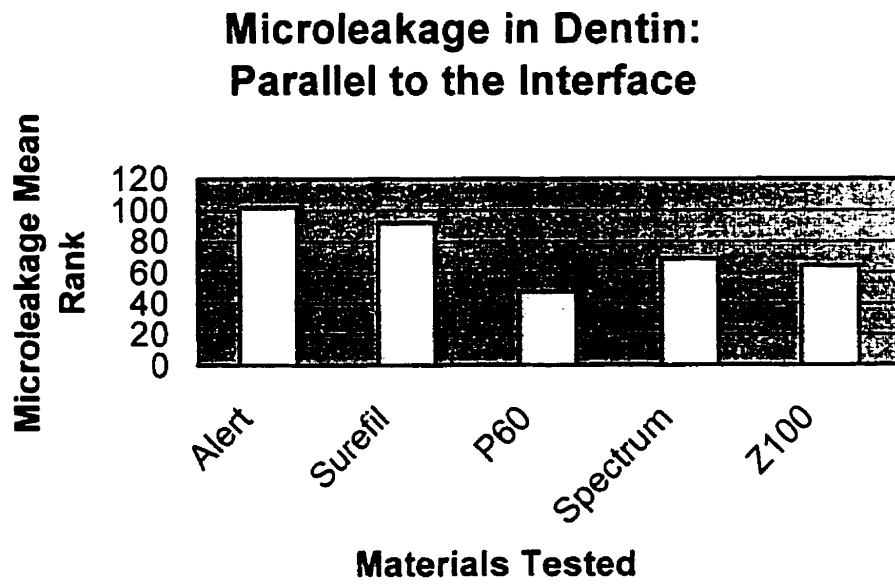
DF	4
Number of Groups	5
Number of Cases	149
H	31.93 p=0.0001
H corrected for ties	41.36 p=0.0001
Number of tied groups	3

Table 3.5:Kruskal-Wallis: X₁. Material; Y₁- Dentin Leakage*

Group	No. of cases	Σ Rank	Mean Rank
Alert	33	3353.5	101.62
Surefil	28	2573	91.89
P60	30	141.5	47.18
Z100	33	2119	64.21
Spectrum	25	1714	68.56

*Groups represented by straight lines are not significantly different

Figure 3.4: Microleakage Assessment of Materials in Dentin: Parallel to the Interface



3.3.3Dentin Leakage: Perpendicular to Interface (Tables 3.6, 3.7 &Figure 3.5)

Figure 3.5 depicts the dentin leakage perpendicular to the interface. The Kruskal –Wallis test revealed that the groups were significantly different from each other ($p=0.0001$). A pair-wise comparison among the five groups. using the Mann Whitney U test revealed that the packable composites Alert and Surefil demonstrated the greatest degree of stain penetration which was significantly higher than the other materials. P60 demonstrated significantly less leakage than Spectrum and Z100; and Spectrum and Z100 were not significantly different from each other.

Table 3.6:Kruskal-Wallis: X_1 - Material; Y_3 - Dentin Leakage (Perpendicular to Interface)

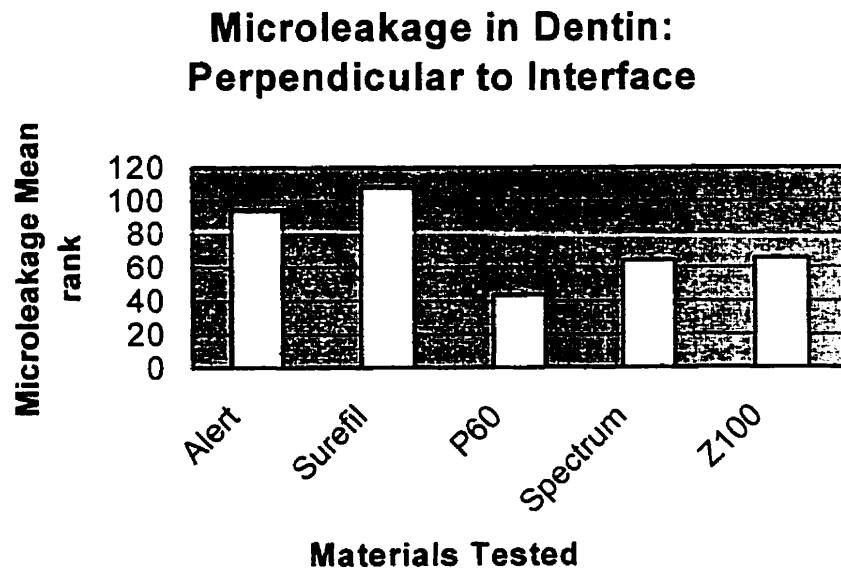
DF	4
Number of Groups	5
Number of Cases	149
H	42.47 $p=0.0001$
H corrected for ties	46.48 $p=0.0001$
Number of tied groups	4

Table 3.7:Kruskal-Wallis: X_1 - Material; Y_3 - Dentin Leakage*

Group	No. of cases	Σ Rank	Mean Rank
Alert	33	3104	94.06
Surefil	28	3024	108
P60	30	1294.5	43.15
Spectrum	25	1594.5	63.78
Z100	33	2158	65.39

*Groups represented by straight lines are not significantly different

Figure 3.5: Microleakage Assessment of Materials in Dentin: Perpendicular to the Interface



3.4 Discussion

All the materials tested demonstrated enamel and dentin leakage. The packable materials (with the exception of P60) Alert and Surefil, which were shown to be highly viscous (Part II of this thesis- **Figure 2.8**), demonstrated significantly more enamel and dentin leakage (both parallel and perpendicular- **Figures 3.3, 3.4& 3.5**), as compared to P60 and the control materials. P60 demonstrated significantly less enamel leakage and dentin leakage, as compared to the other two packable materials and was not significantly different in enamel leakage compared to the control materials (**Table 3.3**). Except for perpendicular dentinal leakage, which was significantly lower (**Table 3.7**), P60 was not significantly different from the control materials with respect to parallel dentin leakage (**Table 3.5**). The control composites were not significantly different from each other with respect to either enamel or dentin leakage as was expected with current universal use composite resins. In this experiment, enamel and dentin leakage was evaluated on the occlusal and gingival walls of the tooth cavity respectively. Dentin leakage was evaluated with reference to the extent of interfacial percolation, independent from the degree (color) of stain and depth of dentin tubule penetration. Dentin leakage in relation to tubular penetration reflects to some extent the sealing capacity of the dentin-bonding agent used as well as the permeability of the dentin tubules. To avoid the possibility of variation and the introduction of additional variables, the same dentin-bonding agent was used for all the composites. The differences in microleakage results between materials using the same bonding agent can therefore be attributed to the differences in the properties of the composite resin material and/or differences in the interaction of the composite resin with the dentin-bonding agent. Parallel dentin leakage reflects a marginal gap either due to poor adaptation of the composite resin to the tooth or as a result of polymerization shrinkage. Both parallel and perpendicular dentin leakage are an indication of a marginal gap at the tooth restoration interface which could be attributed to either polymerization shrinkage{Qvist V, 1993}or a difference in the thermal coefficient of expansion between the tooth and the composite resin material{Nelsen RJ et al, 1952}.

The increased microleakage demonstrated by the very viscous materials Alert and Surefil in enamel and dentin is an indication that materials with a very high viscosity demonstrate a decreased wetting ability to tooth structure or perhaps a tendency for

incorporation of voids at the interface. Opdam et al demonstrated that thicker consistency materials produced more voids and imperfect wall adaptation than composites of a thin and medium consistency, thereby emphasizing a critical consistency to allow proper wetting of the cavity{Opdam NJ et al, 1996}.

An earlier study by Asmussen, that compared the viscosity values of adhesives with different formulations, supported the findings that materials with a higher viscosity demonstrate higher contact angles and higher surface tension values{Asmussen E, 1977}. Although he concluded that viscosity was not a limiting factor in the wetting of the tooth structure, his study utilized unfilled resin monomers as opposed to filled resins, which were used in this thesis.

The significance of the results in microleakage studies although generally accepted is seriously questioned. The term bacterial leakage was introduced by Bergenholtz in 1982 {Bergenholtz G, 1982}, in support of the observation that bacterial occurrence under experimental restorations in otherwise intact teeth was a result of bacterial invasion of the cavity through marginal leakage around the restoration{Qvist V, 1993}. This observation was later confirmed by Qvist, who demonstrated that a gap communicating from the tooth surface to the dentinal portion of the cavity was a necessary requirement for bacterial invasion and growth {Qvist V, 1993}. Therefore to confirm the presence of leakage, the observation of bacterial species under restorations is essential and experimental conditions are required to be carried out in vivo. Secondly, the thermocycling environment in which the experiment is done, is an attempt to mimic the stresses encountered by restorative material intra orally. This procedure has been regarded as being too harsh and not representative of the thermal or mechanical stimuli that can occur in the mouth{Crim GA et al, 1987},{Barnes DM et al, 1993}. Although in vitro microleakage may not be absolutely representative of the in vivo scenario, it provides a "snap-shot" image comparing the response of different restorative materials when exposed to the same experimental conditions.

In an attempt to mimic the packable characteristics of amalgam, several of the packable resins composites contain various formulations that include viscous resin monomers and /or irregular sized particles along with submicron particles that increases the viscosity of the resin. However this increase in viscosity coupled with the physical

nature of the large sized filler particles appears to have contributed to the decreased adaptability of the material at the tooth-restoration interface. This phenomenon was demonstrated with both the materials with large filler particles Surefil (2-20 μm) and Alert (60-80 μm in length). The packable composite P60 was less viscous as demonstrated in part II (**Figure 2.8**) of the thesis and contained filler particles in the range of 0.01 to 3.5 μm (**Table 1.2**). This material demonstrated less microleakage than the other packable materials. The results of this study suggest that materials which are highly viscous and with large filler particles produce inferior surface wetting and inadequate adaptation to the tooth structure resulting in more microleakage. The increased microleakage demonstrated with the use of more viscous composites also suggests that modifications in the bonding technique are needed with viscous materials to ensure a more effective bond between the tooth and restoration. These modifications include the application of a thicker low stiffness adhesive which has been shown to absorb some of the stresses generated in the composite during polymerization and to reduce interfacial leakage {Choi KK et al, 2000}. A second modification includes the use of densely filled adhesives which have been shown to undergo less shrinkage as compared to unfilled adhesives {Labella R et al, 1999}. A third modification includes the use of the 3-step bonding agents over the 2- step bonding agents which have been shown to be particularly sensitive to the hydrating conditions of the dentin.

Thus even though handling properties may be improved through changes in formulation, a reduction in optimal clinical performance negates the advantages of the new materials. The tendency for decreased adaptation and increased void formation increases the potential for gap formation at the tooth restoration interface and exacerbates the likelihood of bacterial percolation{Qvist V, 1993}, post operative sensitivity and a decrease in longevity of the clinical restoration.

3.5 Conclusions

The results of this study support the conclusion that composite resins with very high viscosity demonstrate more microleakage in enamel and dentin than lower viscosity materials most likely due to the decreased wetting action of the higher viscosity

materials. However not all materials with an increase in viscosity demonstrate a decrease in wetting properties. The combination of high viscosity materials with large filler particle sizes appears to be particularly deleterious. The specific influence of viscosity and filler particle size on adaptability at the tooth restoration interface deserves more detailed consideration.

Thus an improvement in the handling properties of packability appear to be at the expense of restoration to tooth adaptation which could decrease longevity of the clinical restoration through the potential for increased bacterial percolation at the tooth restoration interface.

3.6 Recommendations

1. A study of in-vivo microleakage of packable versus non-packable materials would be more relevant in illustrating the differences in microleakage between the packable and non-packable resin composite materials.

2. A study of the wetting action, through surface tension and contact angle measurements of the high viscous materials compared to the low viscosity materials is needed to confirm the theory of decreased wetting action of the packable materials.

3. A comparative analysis of microleakage specimens of both in vivo and in-vitro packable and non-packable resin composites using SEM photomicrographs is needed to characterize the details of the interface microleakage phenomenon.

4. A study utilizing the proposed modifications of the bonding technique is needed to assure a more effective bond between viscous composite resin restorations and the tooth surface.

DISCUSSION

Lack of total acceptance of resin composites as alternative restorative materials to amalgam is due to their inferior clinical performance and unpredictable longevity. This is largely due to clinical insertion problems and material deficiencies such as polymerization shrinkage. The resin based materials are known to be highly technique sensitive and require perfect moisture control, meticulous cavity wall adaptation and specific time consuming techniques to produce a well contoured restoration. The attainment of proximal contacts with adjacent teeth using these soft putty like materials is unpredictable during the restorative procedure. The clinical consequences of inadequate proximal contacts include food impaction, patient discomfort and local periodontal problems. The clinical consequences of inadequate tooth adaptation include marginal gaps and voids. Many of the problems associated with composite restoration longevity are indirectly related to bacterial ingress due to gap formation at the tooth restoration interface. These include microleakage and post operative sensitivity in the short term and secondary caries over the long term.

Packable resin composites were introduced by various manufacturers of dental resin composites as 'improved' restorative materials in an attempt to address the situation by simulating the favorable handling properties of amalgam. These viscosity changes were brought about in the formulation either through changes made to the resin composition, the particle distribution and content of the incorporated fillers or both. Interestingly, several of these new materials contain large irregular filler particles in an attempt to provide a replication of the packing qualities experienced with amalgam during the restorative insertion procedure. In addition to the quality of packability, the materials are claimed to have superior physical and mechanical properties compared to universal-use resin composites and a reduction in polymerization shrinkage. Since these claims had not been verified independently, the aim of this thesis was to characterize these new materials and determine whether the alterations made to the resin composites to introduce a stiffer more packable restorative, were made at the expense of any other physical or mechanical parameter. Secondly, the concept of "packability" was undefined and it was the aim of this thesis to determine an in vitro method for quantifying this property with a view to establish a standard for the future testing of dental restorative materials. Thirdly, the effect of the formulation changes to the resin composites was

tested in simulated clinical restorations for resultant changes in adaptation to tooth structure and gap formation.

Analysis of the physical and mechanical properties revealed that the packable composites represent a disparate group of more viscous composite materials with differences in their physical nature and chemical composition. As a group they demonstrate a wide range of property values and different order of values between materials. The physical and mechanical properties, other than viscosity, of the packable resin composites were within the range of values demonstrated by the control composites and did not demonstrate any clear improvement or advantage over current universal hybrid resin composites. Although individual materials performed well, no one material was clearly superior in all tests and one material demonstrated low values in all tests. Although two packable materials revealed enhanced photopolymerization capabilities, as a group the new materials demonstrated depth of cure values similar to conventional composites indicating that no change in standard clinical polymerization procedure is possible with these materials. None of the packable materials was considered any more suitable for bulk curing than current composites. Specific areas where the new packable materials were not comparable to current universal hybrids related to aging of the materials where specific new materials demonstrated a reduction in properties upon exposure to aqueous solution. The static physical tests stipulated by the International Standards Organization although not considered entirely equivalent to clinical performance of restorative materials are a useful guide in providing a relative characterization of the materials being tested and can reveal materials that are less than a stipulated minimum standard. These tests demonstrated that individual 'packable' materials did not meet the ISO minimum standard for flexural strength and radiopacity.

An analysis of the 'packable' characteristics of resin composites with those of amalgam revealed that the packable qualities of amalgam far exceed those of any tested resin composite. The packable characteristics of amalgam are attributed to its irregular alloy particles that offer resistance to condensation when the material is packed into the tooth. When amalgam alloy is mixed with mercury, a plastic mass is obtained that allows a property of 'positive pack' and relative ease of adaptation to the cavity walls. This is followed by setting and hardening of the amalgam as the liquid mercury is consumed in

the formation of solid phases {Phillips RW, 1996 (a)}. In contrast to amalgam, composite resins do not offer this unique alloy condensation process. The resin composites tested could be categorized into groups by their varied viscosities. Most, but not all, of the materials that were classified as packable by manufacturers demonstrated significantly higher viscosity than the non-packable materials. This implies that these materials offer increased resistance while being adapted to the tooth structure. All the materials tested demonstrated stress relaxation. The materials with higher viscosities demonstrated short time relaxation followed by a slowly decreasing modulus. This implies that these materials will be similar to work with in terms of application but materials with a higher values of $G(t)$ would be 'stiffer' and need continuing stresses to be applied to flow (**Figure 2.10**). The materials with lower viscosities demonstrated dilute solution behavior, in that they exhibited very short time relaxation or 'flow' when stresses were imposed. Such a relaxation however slight would tend to cause a relapse of proximal contour prior to photopolymerization therefore the potential for improved proximal contacts during the restorative procedure is questioned. These tests describe the rheological behavior of the materials, however the true significance of the rheological behavior particularly that of stress relaxation in the production of proximal contacts requires a specific study simulating clinical usage. Such a study would need to examine the application procedures of the materials. This would include the preparation of the material before insertion into the tooth cavity, the mode of insertion and, the time lapse between packing of the material and photo polymerization.

The adaptive capacity of the materials to the tooth structure was tested in simulated clinical restorations. The analysis of this study revealed that the materials that were highly viscous demonstrated a potential for increased microleakage in enamel and dentin, most likely due to the decreased wetting capability to the tooth structure. This finding of decreased adaptability to the tooth structure with materials of higher viscosity has been confirmed in other studies{Chohayeb AA et al, 1989},{Opdam NJ et al, 1996}. One moderately viscous material without large filler particles demonstrated better adaptation to the tooth, suggesting that large filler particles interfere with surface wetting and adaptation. Although microleakage testing in vitro may not be totally representative of what occurs in vivo, these results provide us with an estimation of how different

materials behave when exposed to the same experimental conditions. In contrast to the behavior of packable resin composites, the wetting properties of less viscous resin composites enhances adaptation to the tooth during the restoration insertion procedure.

Thus an overall improvement in material properties and behavior was not found to be the outcome of an improvement in handling characteristics. The new packable materials demonstrated shortcomings in comparison to current universal hybrid materials, indicating that the enhancement of handling properties was made at the expense of several other important parameters. Such changes could prove to be detrimental to the longevity and success that is associated with current resin composites. Although in vitro studies do not provide an accurate picture of the clinical performance of the material in vivo, in vitro research is invaluable in characterizing the gamut of restorative materials available and aids in providing information on the applicability of the material in decision making in clinical practice. Such research also sheds light on the inadequacies of materials that are currently available, thus providing scope for improvement. Of particular concern are new materials with very different handling properties, which will affect clinical usage and which have been introduced for patient care without reliable research and suitable clinical trials.

CONCLUSIONS

1. The 'packable' composites represent a disparate group of viscous composite materials with different physical nature and chemical composition, demonstrating a range of property values and different order of values between materials.
2. The physical and mechanical properties, other than viscosity, of the packable resin composites were within the same range and did not demonstrate any clear improvement or advantage over current universal hybrid resin composites. Although individual materials performed well, no one material was clearly superior in all tests and one packable material demonstrated low values in all tests.
3. As a group the 'packable' composites were significantly more viscous than the non-packable materials tested. However the increased resistance to displacement did not approach that exhibited by silver amalgam restorative material and the clinical advantage would therefore appear to be minor. Despite the potential for increased packability, all the materials demonstrated varying degrees of relaxation after deformation, a property not associated with silver amalgam. Such relaxation would tend to cause a relapse of proximal contour prior to photopolymerization thus the potential for improved proximal contacts during the restorative procedure is questioned.
4. Simulated clinical testing in vitro showed that the materials with the highest viscosity exhibited the most potential for microleakage, thus negating the improvements brought about as a result of the changes in handling properties. Although the limitations of in vitro testing are recognized the results clearly indicate that viscosity changes particularly those associated with large particle inorganic filler content have a negative effect on surface wetting and cavity wall adaptation.
5. This study emphasizes the need for extensive testing and characterization of newly developed materials, including simulated clinical testing, prior to clinical usage. Materials should at least fulfil ISO numerical requirements. Materials which do well

in independent simulated in vitro clinical testing should undergo clinical trials before they become available for patient care.

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APPENDICES

I: MICROHARDNESS TESTING AT VARYING DEPTHS OF THICKNESS ON MATERIALS

1. Hardness Testing: 333 μm (Tables A: I & II)

Table A I: Hardness Testing: Depth of Cure 333 μm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	13559.82	1694.9775	12.060845
Within Groups	18	2529.64	140.535556	P=.0001
Total	26	16089.46		

Analysis of Variance Table

Model II estimate of between component variance = 518.147315

Table AII: One Factor ANOVA X_1 : composite Y_1 : Hardness at 333 μm *

Group	Count	Mean	Std. Deviation	Std. Error
Surefil	3	125.33	8.02	4.63
Z100	3	100.13	10.62	6.13
Prodigy	3	98.6	8.82	5.09
Pyramid	3	92.87	16.69	9.64
Spectrum	3	82.3	20.00	11.55
Alert	3	80.67	.55	.32
P-60	3	66.77	6.91	3.99
Z250	3	65.33	15.12	8.73
Solitaire	3	44	7.38	4.26

*Vertical lines represent groups not significantly different

2. Hardness Testing: 667 μm (Tables B: I&II)

Table BI: Hardness Testing: Depth of Cure 667 μm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	8460.680741	1057.585093	
Within Groups	18	1847.473333	102.637407	P=.0001
Total	26	10308.154074		

Analysis of Variance Table
 Model II estimate of between component variance = 318.315895

Table B II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 667 μm *

Group	Count	Mean	Std. Deviation	Std. Error
Surefil	3	111.67	8.39	4.84
Z100	3	98.13	6.00	3.47
Alert	3	94.5	19.64	11.34
P-60	3	83.13	11.87	6.85
Pyramid	3	82.87	10.43	6.02
Prodigy	3	77.13	7.76	4.48
Z250	3	75.73	4.66	2.69
Spectrum	3	73.57	5.85	3.38
Solitaire	3	44.73	8.11	4.68

*Vertical lines represent groups not significantly different

3. Hardness Testing: 1mm (Tables C I & II)

Table CI: Hardness Testing: Depth of Cure 1mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	4786.514074	598.314259	7.97973
Within Groups	18	1349.626667	74.979259	P=.0001
Total	26	6136.140741		

Analysis of Variance Table

Model II estimate of between component variance = 174.445

Table CII: One Factor ANOVA X_1 : composite Y_1 : Hardness at 1mm*

Group	Count	Mean	Std. Deviation	Std. Error
Surefil	3	100	9.16	5.29
Z100	3	86.97	4.55	2.63
P-60	3	86.7	6.24	3.60
Alert	3	82.1	15.02	8.67
Prodigy	3	76.3	5.81	3.35
Pyramid	3	75.9	6.95	4.01
Z250	3	73.17	11.38	6.57
Spectrum	3	66.37	5.40	3.12
Solitaire	3	50.17	8.04	4.64

*Vertical lines represent groups not significantly different

4. Hardness Testing: 1.33mm (Tables D I&II)

Table D I: Hardness Testing: Depth of Cure 1.33mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	5952.773333	744.096667	8.840208
Within Groups	18	1515.093333	84.171852	P=.0001
Total	26	7467.866667		

Analysis of Variance Table
 Model II estimate of between component variance = 219.974938

Table DII: One Factor ANOVA X_1 : composite Y_1 : Hardness at 1.33mm*

Group	Count	Mean	Std. Deviation	Std. Error
Surefil	3	95.73	2.20	1.27
P-60	3	91.8	7.40	4.27
Z100	3	84.5	13.07	7.54
Prodigy	3	83.63	5.95	3.43
Z250	3	82.6	7.50	4.33
Alert	3	78.77	13.50	7.80
Pyramid	3	75.9	14.85	8.57
Spectrum	3	73.93	4.72	2.72
Solitaire	3	41.03	3.25	1.88

*Vertical lines represent groups not significantly different

5. Hardness Testing: 1.667 mm(Tables E I& II)

Table EI: Hardness Testing: Depth of Cure 1.66mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	6909.580741	836.697593	3.167079
Within Groups	18	4908.8	272.711111	P=.0201
Total	26	11818.380741		

Analysis of Variance Table
 Model II estimate of between component variance = 196.995494

Table E II: One Factor ANOVA X_i : composite Y_i : Hardness at 1.66mm*

Group	Count	Mean	Std. Deviation	Std. Error
Alert	3	101.9	45.85	26.47
Surefil	3	85.77	5.25	3.03
P-60	3	83.67	9.72	5.61
Z100	3	82.47	6.73	3.88
Pyramid	3	79.47	6.59	3.80
Z250	3	78.4	3.78	2.18
Prodigy	3	76.07	4.22	2.44
Spectrum	3	75.63	9.64	5.56
Solitaire	3	37.9	4.00	2.31

*Vertical lines represent groups not significantly different

6. Hardness Testing: 2mm (Tables F I &II)

Table FI: Hardness Testing: Depth of Cure 2mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	4758.060741	594.757593	4.807431
Within Groups	18	2226.893333	123.716296	P=.0027
Total	26	6984.954074		

Analysis of Variance Table

Model II estimate of between component variance = 157.013765

Table F II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 2.0 mm*

Group	Count	Mean	Std. Deviation	Std. Error
Surefil	3	80.23	1.03	.59
P-60	3	78.83	8.50	4.91
Alert	3	77.93	28.91	16.69
Z100	3	77.1	6.83	3.94
Z250	3	75.1	4.88	2.82
Pyramid	3	74.47	6.18	3.57
Prodigy	3	70.1	7.21	4.16
Spectrum	3	63.8	4.78	2.76
Solitaire	3	35.27	4.53	2.62

*Vertical lines represent groups not significantly different

7. Hardness Testing :2.33 mm (Tables G I & II)

Table G I: Hardness Testing: Depth of Cure 2.33 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	6563.642963	820.45537	13.346284
Within Groups	18	1106.54	61.4744	P=.0001
Total	26	7670.182963		

Analysis of Variance Table
 Model II estimate of between component variance = 252.993642

Table G II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 2.33 mm*

Group	Count	Mean	Std. Deviation	Std. Error
Z250	3	83.33	11.47	6.62
Z100	3	76.3	8.49	4.9
Alert	3	76.2	10.60	6.12
P-60	3	75.93	1.96	1.13
Prodigy	3	74.93	1.23	.71
Surefil	3	68.43	9.82	5.67
Pyramid	3	65.17	5.10	2.95
Spectrum	3	65.13	8.97	5.18
Solitaire	3	26.9	5.38	3.10

*Vertical lines represent groups not significantly different

8. Hardness Testing: 2.66mm (Tables H I & II)

Table H I: Hardness Testing: Depth of Cure 2.66 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	8	6806.034074	850.754259	12.182768
Within Groups	18	1256.986667	69.832593	P=.0001
Total	26	8063.020741		

Analysis of Variance Table

Model II estimate of between component variance = 260.307222

Table H II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 2.66 mm*

Group	Count	Mean	Std. Deviation	Std. Error
Z250	3	76.03	5.08	2.93
Alert	3	74.9	16.71	9.65
P-60	3	67.5	10.40	6.01
Pyramid	3	66.53	6.98	4.03
Prodigy	3	64.1	2.69	1.55
Spectrum	3	62.6	4.69	2.71
Z100	3	61.33	9.90	5.71
Surefil	3	57.6	6.09	3.51
Solitaire	3	19.13	1.40	.81

*Vertical lines represent groups not significantly different

9. Hardness Testing: 3mm (Tables I: I & II)

Results for hardness testing at 3mm is presented in Tables 29 and 30. ANOVA tests revealed no significant differences in hardness between groups. Solitaire was unable to be tested for hardness due to inadequate hardness of cured material.

Table I I: Hardness Testing: Depth of Cure 3.0 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	7	1793.199583	256.171369	2.061327
Within Groups	16	1988.4	124.275	P=.1094
Total	23	3781.599583		

Analysis of Variance Table

Model II estimate of between component variance = 43.965456

Table I II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 3.0 mm

Group	Count	Mean	Std. Deviation	Std. Error
Z250	3	77.93	9.31	5.37
Alert	3	70.37	15.29	8.82
P-60	3	66.93	11.73	6.77
Prodigy	3	61.03	6.47	3.73
Pyramid	3	60.5	7.34	4.23
Spectrum	3	57.83	2.67	1.54
Z100	3	55.8	19.02	10.98
Surefil	3	48.16	8.47	4.89
Solitaire				

10. Hardness Testing: 3.33mm (Tables J I & II)

Table J I: Hardness Testing: Depth of Cure 3.33 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	4	1360.202667	340.050667	2.716638
Within Groups	10	1251.733333	125.173333	P=.0911
Total	14	2611.936		

Analysis of Variance Table

Model II estimate of between component variance = 71.625778

Table J II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 3.33 mm

Group	Count	Mean	Std. Deviation	Std. Error
Alert	3	69.4	19.80	11.43
P-60	3	64.87	10.34	5.97
Z250	3	62.03	7.22	4.17
Prodigy	3	55.4	5.56	3.21
Pyramid	3	42	6.60	3.81

11. Hardness Testing: 3.66mm, 4mm, 4.33mm, (Tables K-M)

Table K I: Hardness Testing: Depth of Cure 3.667 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	4	2094.904	523.726	3.599013
Within Groups	10	1455.193333	145.519444	P=.0457
Total	14	3550.097333		

Analysis of Variance Table

Model II estimate of between component variance = 126.068889

Table K II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 3.667 mm

Group	Count	Mean	Std. Deviation	Std. Error
Alert	3	63.57	14.32	8.27
P-60	3	54	5.93	3.42
Z250	3	51.57	13.96	8.06
Prodigy	3	36.3	14.63	8.45
Pyramid	3	31.5	8.83	5.10

Table L I: Hardness Testing: Depth of Cure 4.0 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	2	359.108889	179.554444	2.10221
Within Groups	6	512.473333	85.412222	P=.2033
Total	8	871.582222		

Analysis of Variance Table

Model II estimate of between component variance = 31.380741

Table L II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 4.0 mm

Group	Count	Mean	Std. Deviation	Std. Error
Z250	3	42.63	6.02	3.48
P-60	3	43.4	12.64	7.3
Alert	3	29.63	7.75	4.47

Table M I: Hardness Testing: Depth of Cure 4.333 mm

Source	DF:	Sum Squares	Mean Square	F-test
Between Groups	1	139.201667	139.201667	1.306485
Within Groups	4	426.186667	106.546667	P=.3168
Total	5	565.388333		

Analysis of Variance Table

Model II estimate of between component variance = 10.885

Table M II: One Factor ANOVA X_1 : composite Y_1 : Hardness at 4.333 mm

Group	Count	Mean	Std. Deviation	Std. Error
P-60	3	37.2	14.07	8.13
Z250	3	27.57	3.87	2.23