

CLAY NANOCOMPOSITES WITH DENTAL RESIN

THESIS

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By

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INTRODUCTION

Dental fillings are used in every dentist office throughout the world. A filling is a material that is placed in the hole of a tooth, formed to the shape of the tooth, hardened, and finally shaped through grinding and polishing to restore the original function of the tooth. They are mainly used to stop pain associated with cavities and prevent the loss of the tooth. In many cases they also serve aesthetic functions to match the natural color of the teeth.

1.1 Tooth Structure

A tooth has a relatively simple structure (Figure 1) (1). The top of the tooth, which contacts food in the mouth and is visible above the gum (gingiva), is called the crown. At the gumline level, there is a region called the neck. This is found between the root and the crown. Below the gumline lies a region of the tooth called the root. Incisors and canine teeth have one root, while molars and premolars have two roots per tooth.

The white coating on the surface of the crown is called enamel. The purpose of the enamel is to protect the dentine (below the crown) from the external environment. Enamel is tightly packed in numerous rows of calcium hydroxy phosphate (apatite) crystals within a protein matrix structure. This

makes it the hardest substance of the human body. {Spiller, 2000 #26} The enamel is formed during development of the tooth. Once the enamel is mature, it is no longer considered to be a living tissue.

Dentine is an elastic and compressible component of the inner tooth that is present beneath the crown. It is not brittle like enamel, and its structure is similar to that of bone. Dentine is a living tissue that has tubules inside that extend to the tooth's central nerve within the pulp. It is covered with a layer of cementum instead of enamel. Cementum attaches to the periodontal membrane and provides movement to the tooth within the tooth's socket. It bonds the jawbone to the tooth's root.

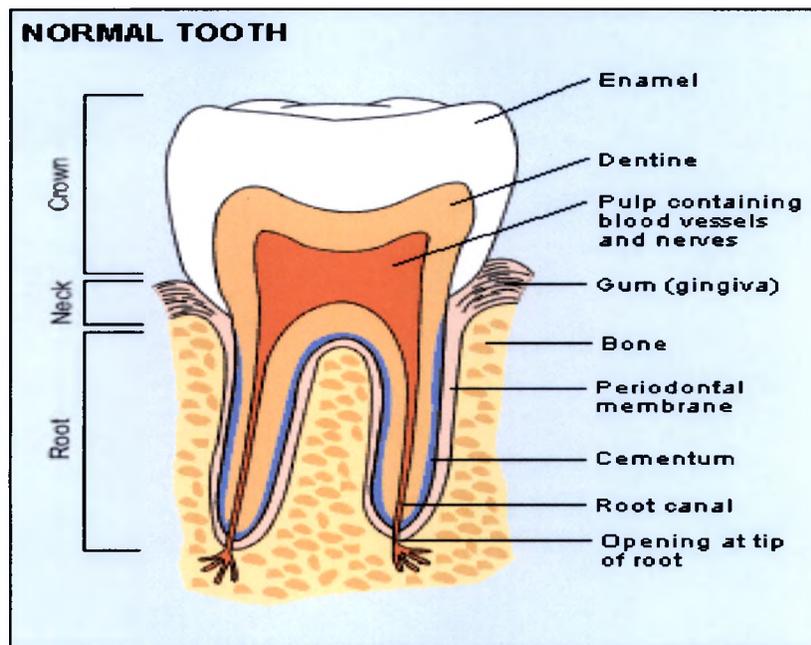


Figure 1. Structure of a tooth (2).

The central chamber located inside the tooth is called the pulp. It is made of soft tissue and supplies nutrients to the tooth via blood vessels. It also supplies nerves that enable one to decipher hot and cold sensations. White blood cells are carried through lymph vessels within the pulp to kill unwanted bacteria. The root canal is an extension of the pulp within the tooth's root and connects to the surrounding tissue through the opening at the tip of the root. The tooth's nerve and blood supply enter the pulp from the surrounding tissue through an opening in the cementum.

1.2 Restorative Materials

When there is a cavity (carie) through the tooth's enamel, fillings are needed. If a filling is not used, the tooth will degrade further eventually leading to the pulp where serious pain can result. There are two different types of restorative materials used in fillings, indirect and direct. When a composite is applied to the tooth, then carved to match the rest of the tooth, it is called a direct filling. Indirect fillings are made in a lab and bonded to the patient's tooth by the dentist. Both types of materials have disadvantages.

There are several types of direct restorative materials (*I*). Amalgam (silver) is a mixture of mercury and silver alloy powder that hardens as a solid metal filling at mouth temperature. There is currently no proof mercury, which can leak from the fillings, has a negative physical effect on the body due to the

low concentration (*I*). Although its overall durability is good, there is moderate leakage around the filling. Leakage happens when there is a tiny hole or crack in the filling exposed to the mouth's environment. Bacteria and other unwanted substances can work their way into the hole resulting in pain and/or infection sometimes leading to tooth decay. Amalgam fillings are however, widely used due to their low cost. A second type of fillings, which are made up of composites are mixtures of a submicron glass filler and an acrylic resin that self-harden in the mouth to form a solid tooth-colored form. When the composite is bonded properly to the tooth, there is little leakage, but the site where the filling is formed must be carefully protected from moisture in the mouth for the filling to have the desired properties. With composites, there is a high dependency on the ability of the filling to adequately bond to the underlying tooth for it to be effective. A third type of filling material is made up of glass ionomers. These contain a self-hardening mixture of metal powder, fluoride, and an organic acid that is able to release the fluoride. There can be moderate decay near the filling yet low leakage with this form of filling. However, when placed on chewing surfaces, these fillings exhibit high wear, and like the composite fillings, conditions at the site of formation must be carefully protected from moisture during the procedure. Direct filling materials also include resin ionomers (compomers), which are a mixture of a submicron glass filler with a fluoride containing glass powder and an acrylic resin which is able to release fluoride when it solidifies. Like the composites and ionomers, formation of compomers must be protected from moisture. Once formed, compomers have a low

resistance to fracture but exhibit high wear when placed on the chewing surfaces of teeth.

Indirect restorative materials (3) have many of the same problems as direct fillings and also require increased patient cost and a larger number of office visits for treatment. In addition, formation of all of the indirect restorative materials involve multiple step methods that require highly accurate clinical and laboratory processing. They provide good biocompatibility, although some patients show allergenic sensitivity. Indirect materials include all-porcelain (ceramic) fillings, which are very brittle and prone to fracture upon impact or tension. The extent of how brittle the porcelain will be is dependant on the ability of the filling to bond to the underlying tooth. Porcelain is highly resistant to wear as long as the filling stays smooth. If the surface becomes rough, it may wear down opposing teeth. Ceramic fillings are the only type of filling that exhibit low thermoconductivity. In addition to the ceramics, indirect materials include gold and base metal alloys. Gold alloy fillings contain a mixture of gold alloy, copper, and other metals. They show a high resistance to fracture and little to no leakage but still have a problem with recurrent decay. Base metal alloys are alloys of non-noble metals with a silver appearance. These fillings share the same strengths and weaknesses as the gold alloy fillings. Both the gold alloy and base metal fillings do not mimic the natural color of teeth.

Composites tend to have better physical properties with a higher proportion of filler and less resin. Even when the composite has an ideal proportion of inorganic filler particles, they still exhibit shrinkage as a result of

hardening. Also, they have a stiffness lower than that of the anchoring tooth, and the thermal expansion coefficient is higher than the tooth's crown (4). These coefficients need to match so that under heat, the tooth and the composite can expand and contract to the same degree. There has however, been success in dealing with problems of bonding the dental composite resins to dentin and enamel (4).

1.3 Material Attributes, Structure, & Problems

Shrinkage is a critical downfall of restorative materials. Plastics shrink when they transform from a liquid to solid state. Composites have been created to minimize shrinkage by using densely concentrated glass particles as fillers (5). The glass does not shrink, and the contraction caused by the hardening of the acrylic matrix is minimized by the glass particles occupying a large volume fraction. Even as the contraction of the acrylic matrix is minimized, there is still microscopic shrinkage (6). A major effect of shrinkage is an accumulation of fluid inside the filling. When bonding techniques are utilized, the vertical wall of the matrix can be pulled together creating an increased sensitivity to cold. There are techniques available to combat the sensitivity to cold, but this requires a second visit in order to fix the problem (7).

An additional cause of shrinkage results from the photochemical curing process (8). When a filling is light cured, there is usually shrinkage directed towards the light source. The light is directed towards the top of the tooth, so

when it shrinks towards the light, it pulls away from the cavity (8). This creates a tiny void between the bottom of the filling and the surface of the tooth. As a result, over time the void accumulates liquid, which cause hydrostatic pressure within the dentinal tubules resulting in an increased sensitivity to pressure (9). Dental tubules are structures by which the enamel communicates with the surrounding oral tissue. The only way to fix this problem is to redo the filling. These light-cured fillings utilize bisphenol A diglycidylether methacrylate (BIS-GMA). Under oral conditions, these groups polymerize rapidly by a free radical chain reaction. This resin is the hardening binder for a wide variety of inorganic fillers. It is used for all different sizes and distributions of fillers as well as fillers with varying degrees of radiopacity, which measures the ability of the material to pass x-rays or other radiation.

Methacrylate resins are used by a large majority of dentists as a direct tooth-colored restorative material. Before BIS-GMA was used, silicate cements were utilized as restorative materials (3). A major problem with silicate cements was that they were subject to acidic degradation. On average, they would last between four and five years before needing to be replaced (7).

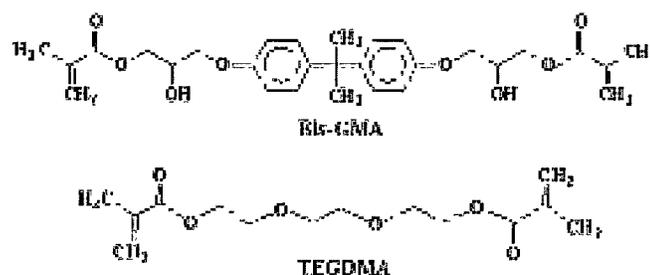


Figure 2. Structures of Bis-GMA and TEGDMA (10).

BIS-GMA is a liquid that is very viscous and honey-like. It is diluted with a low viscosity monomer to improve the handling qualities. Tri-ethylene glycol dimethacrylate (TEGDMA) is commonly used to lower the viscosity. When these two compounds are combined, they form a useful system for dental fillings. BIS-GMA limits the shrinkage while enhancing resin reactivity, and TEGDMA functions to increase resin conversions to the hardened compound which is initiated by means of light curing (12).

BIS-GMA, which is derived from bisphenol-A, is mixed with glass particles and then hardened via UV light. The UV light targets camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) which initiates a chemical reaction that hardens the fluid components of the filling. The free radical reaction occurs in three steps: initiation, chain propagation, and chain termination. First the radicals are created via UV light. The radical products are very unstable. These unstable products are transferred to adjacent atoms rapidly extending the polymer chain until the radical reacts in a way that prevents further propagation. Termination usually occurs when two chains collide preventing further extension of the polymer chain.

When acrylic is used without glass particles, there are huge gaps in the matrix between the filling and the walls of the cavity. This results in leaching of food particles and bacteria into this gap. Another disadvantage of BIS-GMA is its inability of resin to resist wear (11). The resin without glass particles easily breaks and has unfavorable physical properties. In order for this to be improved,

glass filler is added to the resin. Water is part of the tooth's natural environment and leads to lower bonding affinity of the resin while degrading the enamel after a pronounced period of time. The degradation period is dependant on many variables of the oral environment. Because of this, surface active co-monomers (chemical coupling agents) that compete with water for the tooth's surface are needed (13). This lowers the affinity of water for the resin thus reducing the wear on both the filling and the tooth's surface.

The common resin mixture used in dental offices is called GTE. GTE is a generic acronym for the mixture of 37.5% (w/w) bisphenol-A glycidyl methacrylate (bis-GMA), 25% (w/w) triethyleneglycol dimethacrylate (TEGDMA), and 37.5% (w/w) ethoxylated bisphenol-A glycidyl methacrylate (bis-EMA).

Acceptable radiopacity is a necessary ingredient in dental fillings. Radiopacity makes it possible to find secondary caries. It also helps distinguish between the liner/base surrounding the tooth, to detect marginal overhangs, and to radiographically evaluate voids, proper contours, and contacts with adjacent teeth. If a patient has serious facial injuries, fragments from the broken filling can easily be located in the surrounding oral tissue for removal, which in some cases can be lifesaving, as serious infections can occur when filling particles are lodged within the tissue of the mouth along with bacteria. Most current radiopaque dental resin composites use heavy metal glass fillers, which are very prone to hydrolysis. The level of radiopacity is determined in comparison to enamel, dentin, or aluminum. The radiopacity of dentin is nearly equivalent to

that of aluminum. Enamel is about twice as radiopaque as both aluminum and dentin. Various studies have concluded that in order to distinguish from recurrent caries using radiographs, restorative material should be approximately as radiopaque as enamel for optimal contrast (14).

1.4 Clay Nanocomposite Technology

The nanoscale material used in this research is montmorillonite clay. The first recorded scientific use for clays came in the early 1900's through the discovery of the aluminum phyllosilicate Bentonite which W.C. Knight named after Fort Benton, Montana, where it was first discovered. Its early uses were for soap and wagon wheel lubricants when added to an aqueous solution. Bentonite contains mainly montmorillonite. In the Cretaceous Era, volcanos erupted resulting in volcanic ash settling in beds of water. After millions of years, this ash turned into clay. In 1933, a German team of researchers consisting of Hofmann, Endell, and Wilm first determined the structure of montmorillonite. The general chemical formula for the clay is $(\text{Na})_x(\text{Al}_{2-x}\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_{2x}(\text{H}_2\text{O})$. One sodium surface cation (x) results from a magnesium substitution (x) for aluminum (2-x). The exact location and level of substitution varies from site to site (15).

A creation of a nanocomposite with BIS-GMA is be a good potential way to combat the problems of filling shrinkage. A nanocomposite is created by the insertion of particulate matter into a macroscopic sample. Ideally, the

nanoparticles will disperse completely into the polymer matrix. Usually the natural inorganic ions that are used to balance out the negative charge of the clay, are replaced by species that make the clay surface more organophilic which works well when dealing with low polarity polymers. The organic onium “head” attaches to the negative surface of the clay and hydrophobic “tail” extending into the gallery. The tail usually consists of a long carbon chain of around 16-20 carbons which interacts with the resin. When this method is optimized, nanocomposites with less shrinkage, higher thermal stability, lower water uptake, and better mechanical and gas barrier properties are created. They also often exhibit increased tensile strength, modulus, stiffness, and scratch resistance (16).

There are a few different methods of making nanocomposites. One method is to pre-swell the clay along with the polymer in a solvent such as toluene. If the polymer enters the space in the clay, it forms an intercalated nanocomposite (Figure 4A). Once this is formed, the solvent is removed with heat under a vacuum. Another method is in-situ polymerization. The clay is modified with organics and swollen with the monomer/solvent. The monomer is then initiated with some type of initiator such as heat or radiation.

Nanocomposites are most successful in the areas talked about previously when they have a disordered exfoliated structure (Figure 4B). They no longer have the face to face ordering by randomly dispersing the individual clay platelets into the polymer matrix. This leads to an improvement in physical and mechanical properties by maximizing the amount of clay surface (16).

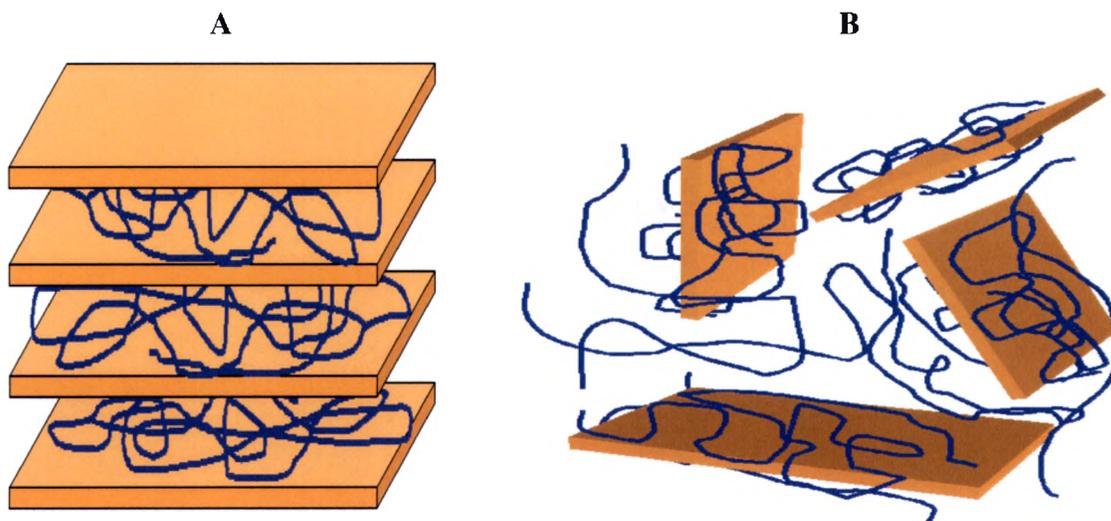


Figure 3. Clay intercalation versus exfoliation.

The thickness of the clay's crystal lattice is about 1 nm. The dimensions vary laterally from 200 Å to a few microns. The clay surface exhibits a partial negative charge due to substitution of Mg^{2+} for Al^{3+} . Both Sodium and Calcium associate with the clay surface, although Calcium's affinity is higher than Sodium's. The volume between the top of the clay and the bottom of the next clay sheet is called the clay gallery. The distance between the bottom of the lower clay sheet and the bottom of the top clay sheet is called its d-spacing. This can be quantified through Bragg's Law and measured through X-Ray diffraction. A theoretical measurement of d-spacing can be obtained through molecular modeling software.

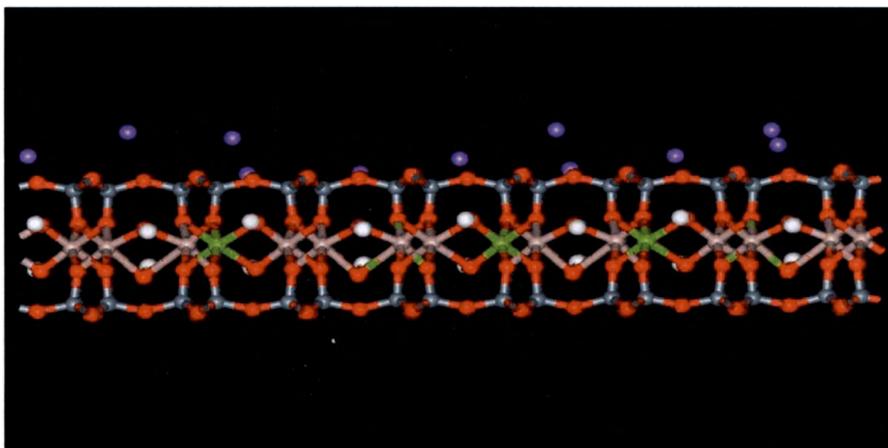


Figure 4. Molecular model of Na⁺ Cloisite.

Southern Clay Products Inc. refines and purifies clays. One clay is known by its trade name, Na⁺ Cloisite. The purification and refinement of the clay takes place at Southern Clay Products, Inc. of Gonzales, Texas. This clay is modified with sodium ions associating with the clay rather than calcium because of its lower affinity for the clay surface.

Cloisite clays are chemically and mineralogically montorillonite in a homoionic form. These clays have been optimized for particle size and purity with a high platelet aspect ratio over 200:1. The total surface area is around 750 m²/gram providing more space for monomer interaction with the surface modifiers. These properties make it optimal for adding barrier and reinforcement to improve the properties of plastics. The range of aggregate particle size is from 2-13 μm with a color of light tan to off-white. Through X-ray diffraction, a basal peak gives a d-spacing value of 11.7 Å in Na⁺ Cloisite. A clay is considered to be dry when it contains less than 2% water within the clay gallery (17).

During the 1940's clay research flourished once it was accepted as a legitimate branch of geology. One of the frontier montmorillonite scientists, Jordan, studied the swelling effects with organic solvents. Once the clay swells, an organic surface modifier can be inserted into the clay gallery via ion exchange with the sodium ions (18). This is necessary when inserting the clay system into a polymer solution since sodium is very hydrophilic. The clay gallery is the area between opposing clay platelets. This is where a monomer or polymer can be inserted to interact with the clay surface. Research of integrating clay systems into polymers was reported first by Blumstein when polymerizing vinyl monomers with unmodified montmorillonite. Later in the 1990's, Toyota showed an exfoliated in-situ nylon-6 nanocomposite for use in a timing belt cover for a Toyota Camry (19). After the physical enhancements exhibited by this polymer were seen, nanocomposite research flourished with a wide variety of polymer systems. After this, nylon-6 degradation was studied through clay nanocomposite technology at the University of Texas (20). Thermoset polymer nanocomposites and other polymers such as polyesters have confirmed the abilities nanocomposites exhibit in a polymer matrix.

Clay exfoliation is optimal for increasing physical properties of clay/polymer systems. Exfoliation is the randomization of the clay platelets within the polymer matrix. There will be little to no apparent diffraction of rays from the clay platelets in an exfoliated system. This is evident through X-ray diffraction, but not totally conclusive as to total exfoliation. Instead of distinct

peaks as a result of an ordered clay arrangement, there will be no peaks of crystallinity.

Normally, in order for an organic polymer to have an affinity for the clay, sodium ions within the clay gallery must be replaced through cation-exchange. Quarternary ammonium salts are introduced to the clay surface achieving a large d-spacing spreading the gallery drastically increasing the chance of exfoliation within the clay system. These salts readily intercalate the clays. Many physical parameters influence exfoliation such as the amount of modifier, processing method and temperature, reactive group properties, pH, etc. Adjustments within these parameters are made for an optimum system.

Quaternary ammonium salts cannot be used for dental composites since they cannot be ingested safely. Lecithin (Figure 5) has a similar structure to other amphiphilic modifiers and is safe for ingestion (21). Lecithin is a phospholipid that is extracted from egg yolk and soybeans by use of hexane extraction. Lecithin is produced by the liver and works to protect cells from oxidation. It is approved by the United States Food and Drug Administration for human consumption. Clay modified with lecithin has a large d-spacing value of 52.8Å which increases the potential of clay exfoliation because the interactions between clay platelets are not as strong.

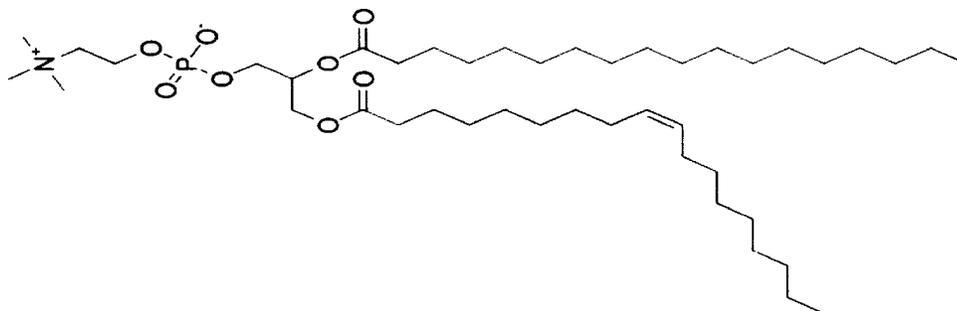


Figure 5. Structure of lecithin (21).

Another way surface modifiers can associate with clay is through ion-dipole bonds. This is a result of a polar molecule binding to an ion such as the sodium ion in the clay through electrostatic interactions. The TEGDMA in the GTE resin could act as the modifier that is attracted to the sodium ions.

1.5 Prospectus of Research

It will be attempted to make nanocomposites with GTE resin and improve the characteristics of dental fillings. Nanocomposites often substantially improve physical properties, producing a substantial increase in tensile strength, modulus, heat distortion temperature, and stiffness. Also, water uptake and gas barrier properties are improved. Tests will also be conducted on the resin-dentin bond and tensile strength.

CHAPTER 2

EXPERIMENTAL

2.1 Clay and Resin Preparation

Southern Clay Products supplied the montmorillonite clay, Na⁺ Cloisite. The clay was used without further purification.

Two organoclay blends were prepared through bulk processing on a Hobart single screw processing mixer, model 4522. The Hobart is powered by a 1725 RPM 15 horsepower electric motor. The mixing environment is maintained through the rotor which operated at 210 RPM. This method was used to create about 250 g of the organoclay. This creates a high shear environment forcing the surface modifier to react with the clay surface.

A 95 meq/100 g clay ratio was chosen for clay studies with lecithin. Lecithin modified clay was made using Cloisite Na⁺ obtained from Southern Clay Products Inc. A water/lecithin emulsion was created for the clay treatment. Water was added to the clay while slowly mixing until beads were formed. The lecithin emulsion was added to the beaded clay and mixed to a thick consistency. The organoclay was then added to the Hobart Processor where it was extruded repeatedly until the clay "strings" were shiny in appearance, the clay was

collected and dried in a 60°C oven overnight. The dried clay was introduced to a coffee grinder. The ground clay was sieved using a 325 mesh US standard copper sieve. The clay particles were collected and stored for use as nanoparticles.

Unmodified clay was used for additional experiments using the TEGDMA component of the GTE resin as a surface modifier. The GTE resin was prepared with 25%, 27.5%, and 30% volume of TEGDMA.

The dental resin, un-photoinitiated GTE was provided by the University of Texas Health Science Center - San Antonio. GTE was prepared using a 1:0.4 mix of camphorquinone and dimethyl amino ethyl methacrylate as photoinitiators. The GTE/photoinitiator ratio was 100:3. The clay was added to the GTE containing a photoinitiator at 5% weight and mixed using a mortar and pestle. The mortar and pestle introduce shear energy to the sample forcing the monomer to enter the clay gallery. The clay/GTE mix was polymerized by a blue light dental gun (Figure 6). The polymerized sample was tested for clay exfoliation on a Bruker X-ray diffractometer.

Clays from Southern Clay Products were also tested on the diffractometer. Cloisite 20A was selected for use in the experiment to test for dispersion with the GTE resin.



Figure 6. Dental Curing Light.

The glass fillers were provided by Kerr Company. The bulk of the material contains barium and zinc. The density of the filler is 2.6564 and was obtained by a mercury porosimeter. The color of the glass fillers is white with the relative consistency of the sieved Cloisite clay modified with lecithin. The filler was mixed into the resin in increments of 50%, 60%, and 75% weight. These percent values represent the weight percent out of the final mass. Clay weight percents between 5% 15% were utilized. These percent values represent the weight percent of the total mass of the resin and clay.

Lecithin-clay samples were sonicated at 22.5 kHz and 40 w for 2-8 minutes. Sonication is the process of introducing sound energy to a sample. This was used to potentially dissociate the intercalated clay platelets from their ordered arrangement.

All samples being prepared for glass filler insertion were mixed in a DAC 150 FV Speedmixer by Flacktek. This mixer spins a high speed-mixing arm in one direction while a basket rotates in the opposite direction. This is also known as a Dual Asymmetric Centrifuge. This enables the mixing to be very fast while creating high shear and eliminating air-bubble production. Prior to adding the glass filler, clay was added to the resin. The clay was incorporated into the monomer by the mortar and pestle method, then it was added to the Speedmixer and mixed at 2000 rpm for 45 seconds. Foundation filler was then added to the resin-clay mix, and mixed at 2000 rpm for 45 seconds in order to introduce the filler into the resin. It was then added to the speed mixer and mixed at 3500 rpm for 50 seconds. This process was repeated after the fused silica was added. Both fused silica and foundation filler, which make up the entire amount of glass filler were always added last.

All samples were hardened via blue light polymerization prior to DMA, shrinkage, and X-ray testing. The fluid un-polymerized samples were hardened in a cast prepared by joining 6 glass slides together (Figure 7). Each slide was connected by using the GTE resin as an adhesive. The top slide is fully transparent in order for proper blue light penetration. Before adding the resin, the distances between slides were measured to ensure precision and uniformity of the resin sample. Since shrinkage occurs, the top side of the sample will not be perfectly flat. Thus, sanding was performed on the non-uniform side. Successively, sandpaper of the following grits were used: 320, 640, 1000, 2000,

then paper. A rough surface is a source of error when tested through Dynamic Mechanical Analysis (DMA).

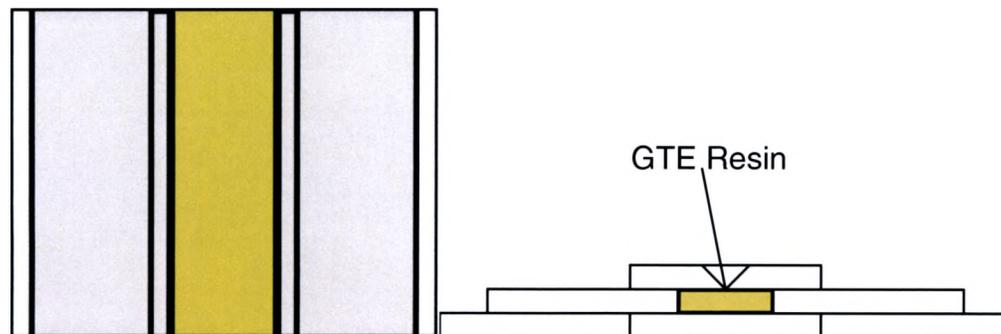


Figure 7. Hexameric slide cast.

All samples with filler and un-filled materials were tested on a volumetric shrinkage analyzer and a dynamic mechanic analyzer to determine the percent shrinkage and elastic modulus.

2.2 X-ray Diffraction

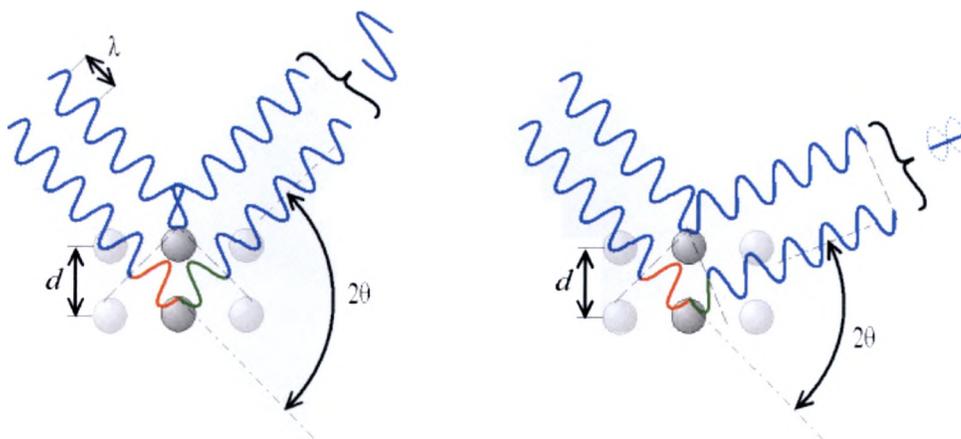


Figure 8. d-spacing calculation within an X-ray diffractometer (5).

D-spacing was identified through X-ray diffractometry. A Bruker D8 Advance Series 2 diffractometer was used for all X-rays. The theory of X-ray diffraction is based on Bragg's Law: $n\lambda = 2d \sin \theta$. The wavelength of the X-ray, λ , is determined from the source and ranged from a few angstroms to 0.1\AA depending on the atom size. N is an integer ($n=1, 2, 3, \dots$) indicating the order of the X-rays when they are constructively in phase. The acute angle between the entering X-ray and the clay is represented by theta (θ).

2.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a method of analysis for a certain material such as its viscoelastic properties. An oscillating force is applied to a sample with the cantilever method, and the displacement is measured. The sample is held under tension as the time-variable force is applied with a continuous increase in temperature. For all experiments, a TA Instrument Q800 analyzer was used. Sample sizes were ~13 mm width, 50 mm length, and 5 mm depth. Readings were taken at 2 points per second. The temperature was increased $10^{\circ}\text{C}/\text{minute}$ starting at room temperature and ending at 175°C . All DMA samples were conducted through the use of a single cantilever apparatus (Figure 9).



Figure 9. Cantilever clamp for DMA.

2.4 Volumetric Shrinkage

Volumetric shrinkage measures the amount of volume loss of a sample. This measurement was obtained through use of a video-imaging device called an Acuvol. The fluid sample is applied to a pedestal, in the form of a droplet. A detector discriminates between the meniscus of the sample and the background. A curing light which emits a beam of 400-515 nm wavelength bandwidth light with the intensity of 300 mW/cm^2 is applied to the sample for 30-45 seconds. This beam is used to polymerize the sample, hardening the material. The point at which the top of the meniscus is recorded in space is the starting value. After curing the material, samples were continuously measured for 30 minutes. After 30 minutes, the samples exhibit no further volume loss. Data are recorded as % loss of the original volume.

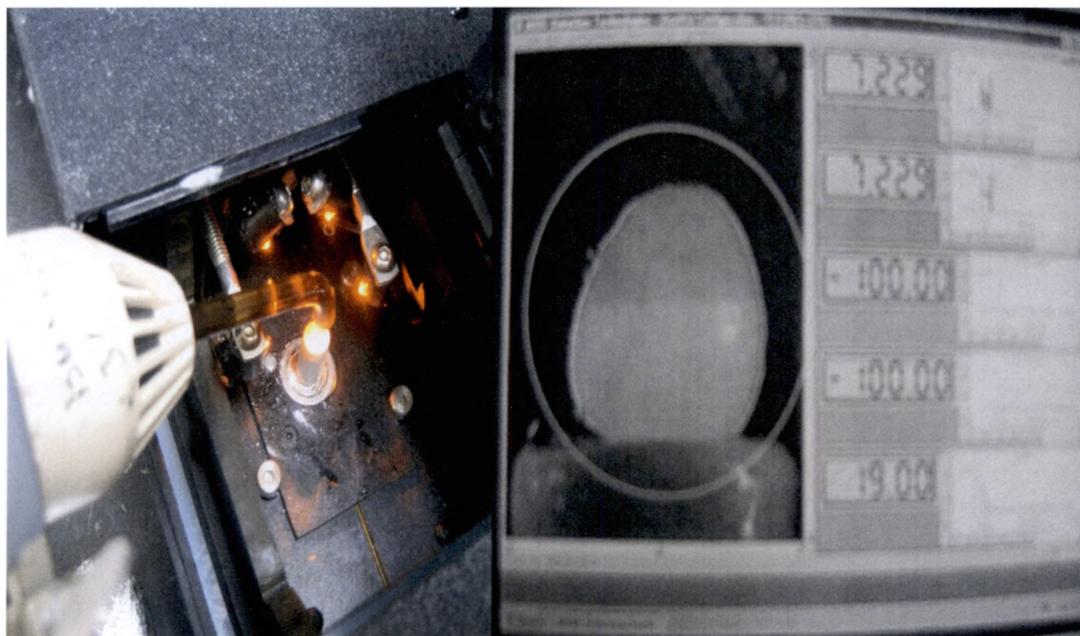


Figure 10. Acuvol shrinkage apparatus and computer readout.

Viscous samples are prepared by a different approach. If the sample has the physical property of being like a paste, the material has to be prepared by hand. The sample was rolled into a ball and formed to fit the top of the pedestal. This method has a higher percent error since gravity has little influence on its physical form. Often the sample can exhibit a rough surface. Samples that undergo this method of volumetric shrinkage analysis have inherent errors. The values or the sample which are sent from the detector to the computer are assumed to be constant forming a perfect arc from the meniscus. If the sample is not constant throughout all dimensions, the calculated values of volume loss will be inaccurate.

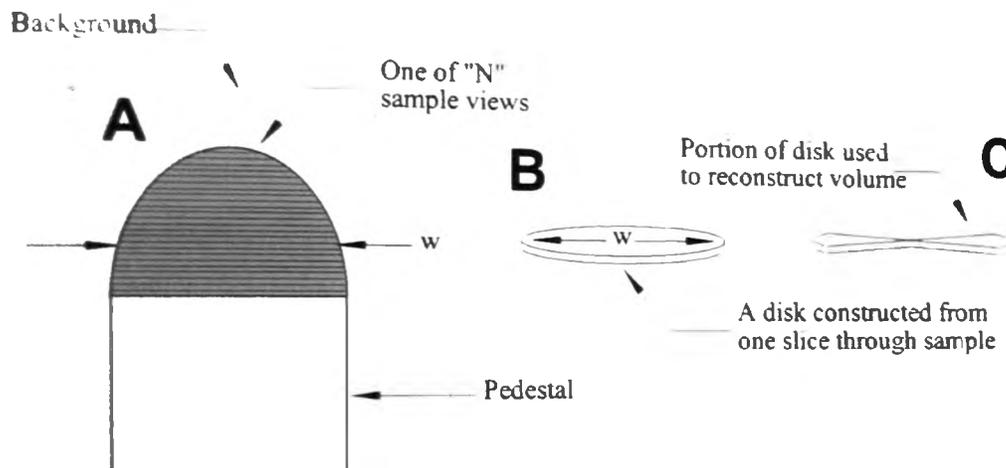


Figure 11. Representation of how samples are analyzed through the Acuvol.

The computer software measures the sample and calculates the volume through the formulas represented below. First, the image is taken from the sample and then converted into numerical measurements. Figure 11 shows how the image is reconstructed. "N" digitized views are reconstructed as the sample is taken through 360° of rotation. Every "n" view is identified by the computer as a separate component which is added together to formulate the total volume. The area of each slice is defined through height "h" and width "w" collectively as "m". For further accuracy, "h" becomes the height of one pixel resulting in a value of "1". The percent change in volume is calculated through the generic calculation given below where "V1" indicates the initial volume calculated by the formula described below. Once the reading is finished, the same calculation is used to calculate the final volume "V2".

$$\mathbf{volume} = \sum_{n=1}^N \sum_{m=1}^M \frac{1}{N} \times h \times \pi \times \left(\frac{w_{mn}}{2} \right)^2 \quad \mathbf{\Delta\%V} = \left| 100 \times \frac{V_1 - V_2}{V_1} \right|$$

Figure 12. Mathematical formula for volumetric shrinkage analysis.

2.6 3-Point Bend

Flexural strength of samples was obtained using an MTS 1125 3-point bend apparatus. Ten samples were prepared. Five samples were GTE resin with filler and no clay. The other five samples contained GTE resin with filler and clay. Force is applied to the material until failure. The force and pressure is given in the computer readout. The 3-point bend apparatus was controlled by Lee Cardenas at The University of Health Science Center-San Antonio.

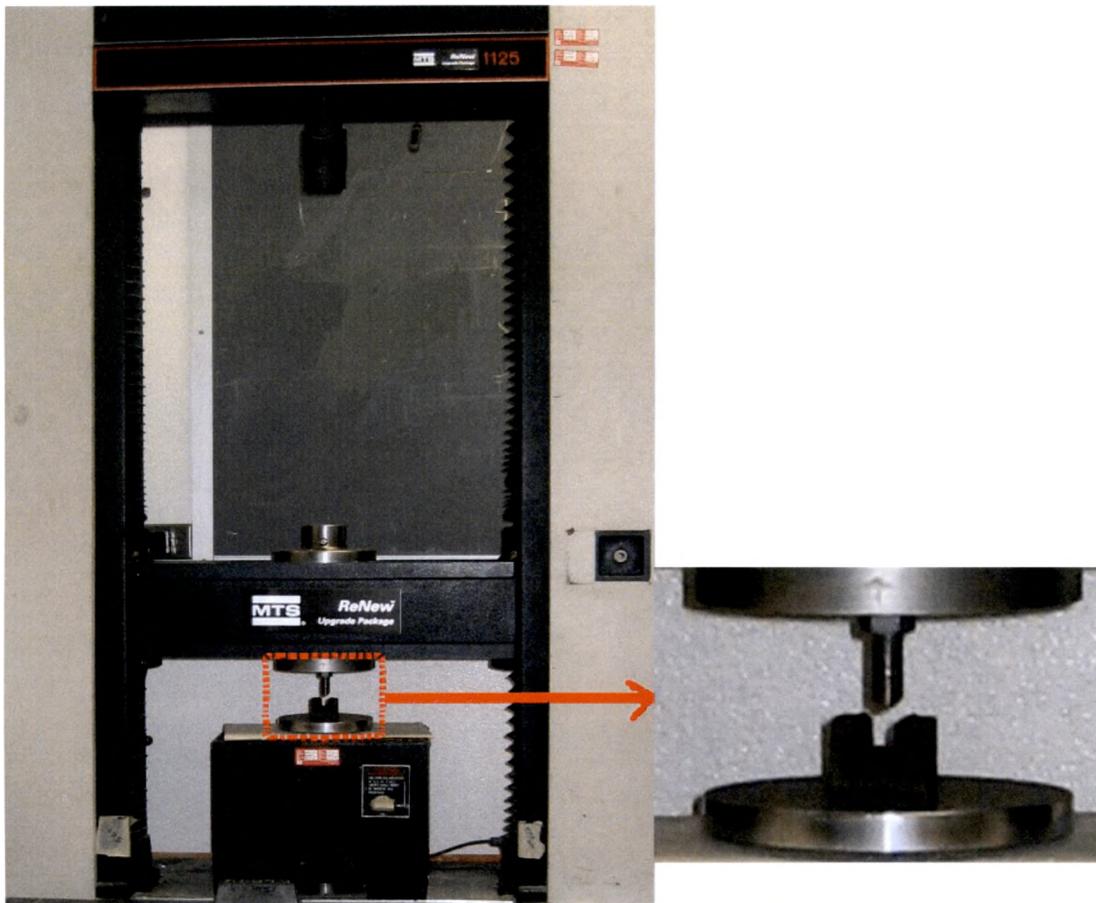


Figure 13. 3-Point bend Apparatus.

2.7 Notched Izod

In order to determine the impact strength of the material, notched izod was used. The sample is held in a cantelever and a pendulum held at a constant potential energy is swung to hit a notched sample. The energy lost from the sample as the pendulum continues on its path is measured by the distance the pendulum travels past the point of impact. Values are reported as the energy lost per unit of the samples thickness. Seven samples were used, and were measured to be ~15 mm width, 50 mm length, and 12 mm in depth. The method was

conducted under ASTM D256. Impact strength is calculated by dividing the energy by the thickness of the sample.

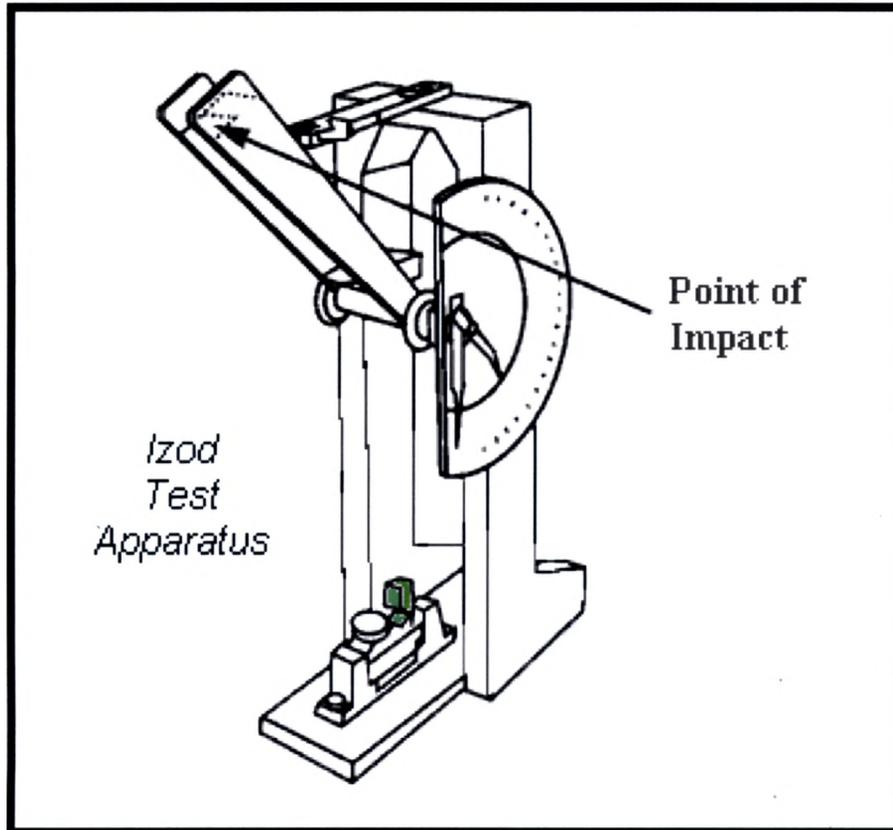


Figure 14. Notched Izod (21).

CHAPTER 3

RESULTS AND DISCUSSION

The discussion is organized into three sections, each aimed at two main goals. First is the development of a material with decreased shrinkage and improved physical properties. There were three main approaches taken. First, analysis of the Cloisite 20 Å clay after incorporation into the dental resin. Here, experiments were conducted to see whether BIS-GMA associated with the quaternary ammonium modifiers. Second, the creation of an ingestion-safe lecithin-modified clay with improved material properties after incorporation into a dental resin was pursued. Third, the formation of a complex with unmodified sodium clay with the viscosity-lowering component of the resin (TEGDMA) via ion-dipole bonding with the exchangeable sodium ions on the clay surface.

3.1 Quaternary Ammonium Modified Clay Results

Initial experiments were conducted to characterize commercial clays prior to insertion of the GTE monomer. Three different clays were characterized by X-Ray diffraction: Cloisite 10 Å, 15 Å, and 20 Å. Each of these clays contains

a different quaternary ammonium surface modifier. D-spacing values for the clays were determined to be 18.3 Å, 31.5 Å, and 24.6 Å, respectively.

A second set of experiments were conducted to assess how well various Cloisite clays interacted with the GTE resin. This information was used to find the most promising surface modifier system. Cloisite 20 Å, which is modified with a hydrogenated tallow showed intercalation of the clay platelets when mixed with the monomer as shown in Figure 13. The d-spacing value of Cloisite 20 Å with GTE resin was 31.5 Å. This increase from 24.6 Å to 31.5 Å is evidence that intercalation occurred. Since the larger d-spacing of the clay with GTE resin indicates that the monomer interacted with the clay's modifiers. This showed promise for the next approach: creating a lecithin-modified clay.

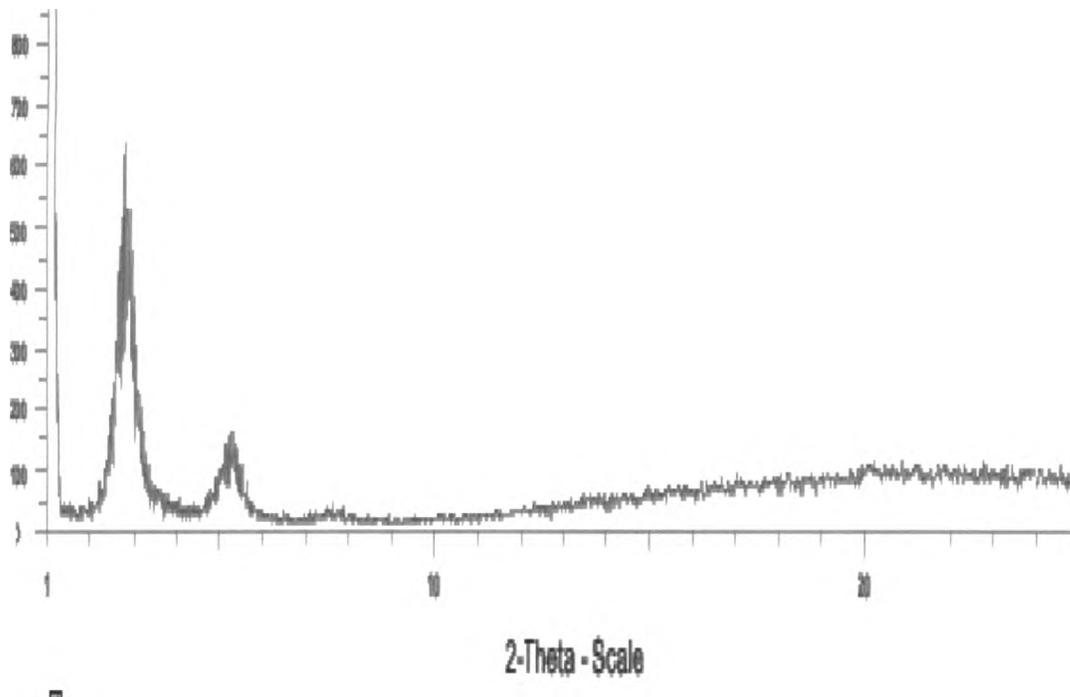


Figure 15. X-ray diffraction pattern of Cloisite 20Å with GTE resin.

3.2 Lecithin-Modified Clay Results

Quaternary ammonium modified clays will intercalate when added to GTE resin, but are not ingestion-safe. An ingestion-safe modifier, lecithin, was then studied. In order to modify Na⁺ Cloisite, an emulsion of lecithin with water was made. Previous experiments using a double boiler apparatus showed that lecithin could not be melted. An emulsion was necessary for the addition of the swollen clay. X-rays were taken of the lecithin-modified clay and compared to the Na⁺ Cloisite clay. The Cloisite-lecithin clay showed significant intercalation with a d-spacing value of 50.4 Å as compared to Cloisite 20 Å value of 24.6 Å. Thus, the lecithin modifier increased the gallery spacing significantly. The X-ray pattern showed four orders for the basal spacing showing significant intercalation. Lecithin was successfully exchanged in the clay modification process through the emulsion method.

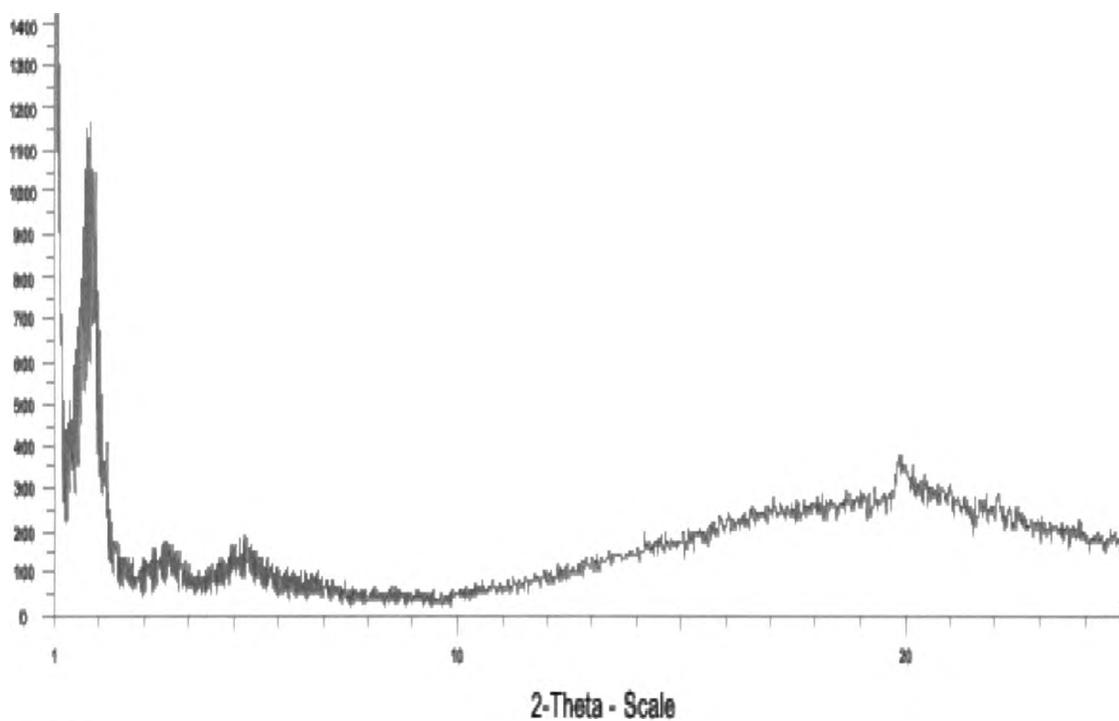


Figure 16. X-Ray of lecithin modified clay with GTE resin before light curing.

The higher d-spacing value gives more promise of exfoliation since there is more room for the monomer to move into the clay gallery.

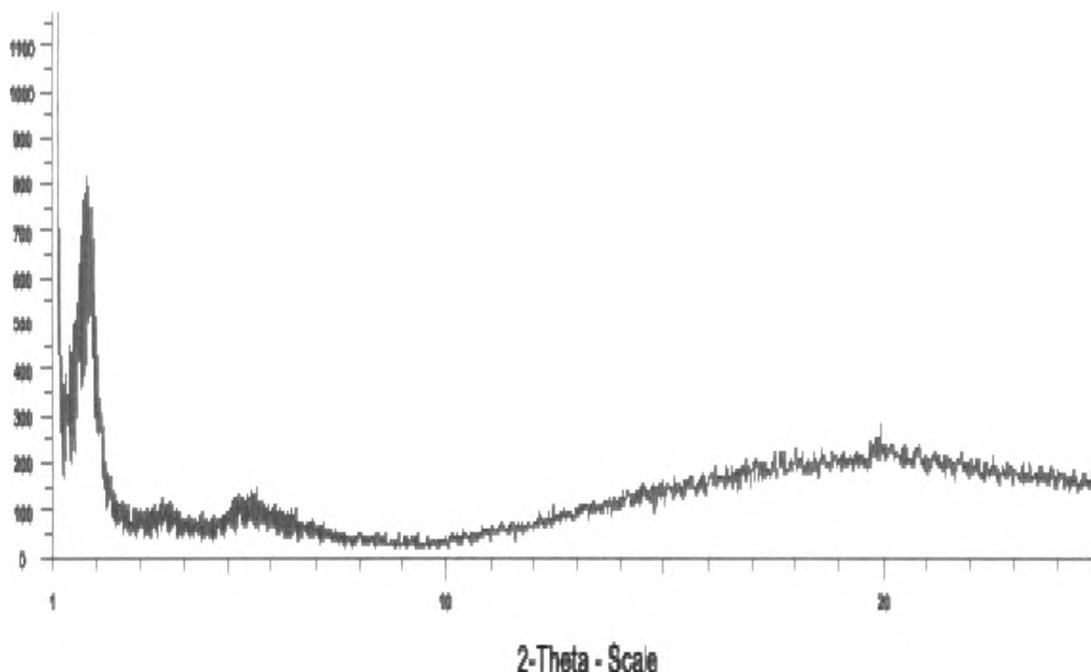


Figure 17. X-ray of lecithin-modified clay with GTE resin after 2 minutes of sonication.

Exfoliation of the clay into GTE resin was first attempted through sonication at 22.5 kHz and 40 w for 2 minutes. X-Ray results show that no exfoliation occurred (Figure 16). The clay still exhibits its original lecithin intercalated form. The resin-clay mixture was then left in the vacuum oven at 60°C overnight and then tested on the diffractometer. After heating in an oven overnight, no apparent exfoliation occurred. Thus, sonication has no apparent effect on clay exfoliation with a lecithin modifier. Under high vacuum, a small portion of the resin-clay mixture hardened to a gel consistency at room temperature.

The resin-clay sample was then subjected to the blue light dental gun in order to polymerize the monomer. X-Ray results showed a smooth curve without

any peaks. Exfoliation occurred via blue light curing (Figure 18). This would indicate that indeed some monomer has intercalated the lecithin treated gallery but only filled in spaces between the lecithin molecules, and did not increase the d-spacing. When resin polymerized, the extension of the monomer broke apart the intercalated clay platelets forming a random order of clay within the entire system {Pinnavaia, 1995 #40}. After the GTE resin and lecithin-modified clay were mixed in a high-speed mixer, there was mild exfoliation due to the high shear forces created (Figure 18). Although, shear mixing is not a necessary step to create exfoliation, it might be helpful to obtain as full an exfoliation as possible. The required step of blue light curing exfoliates the clay quite well.

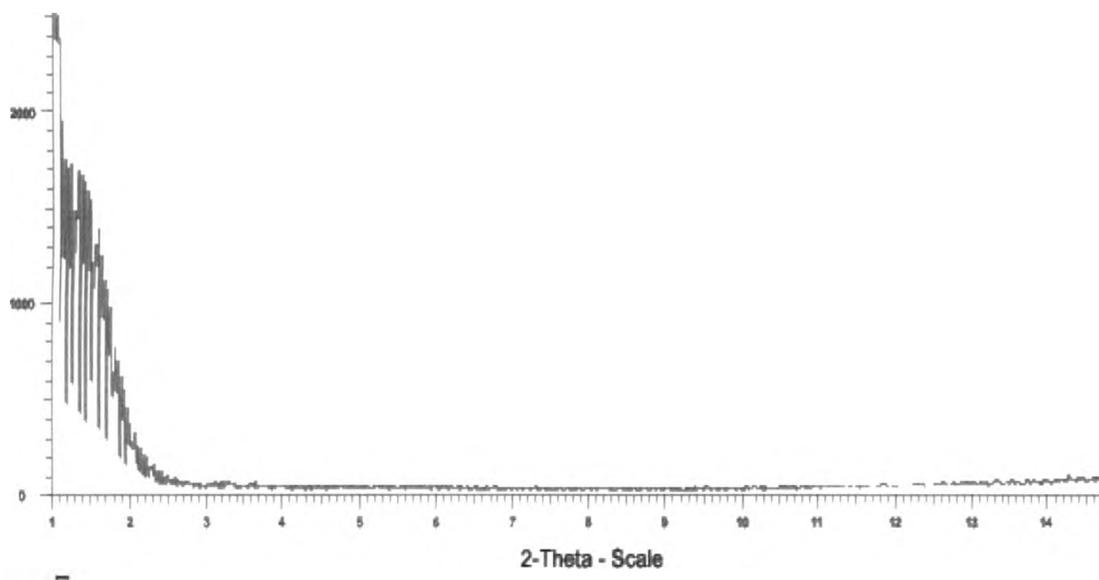


Figure 18. X-ray of lecithin-modified clay with GTE resin after use of a high-speed mixer.

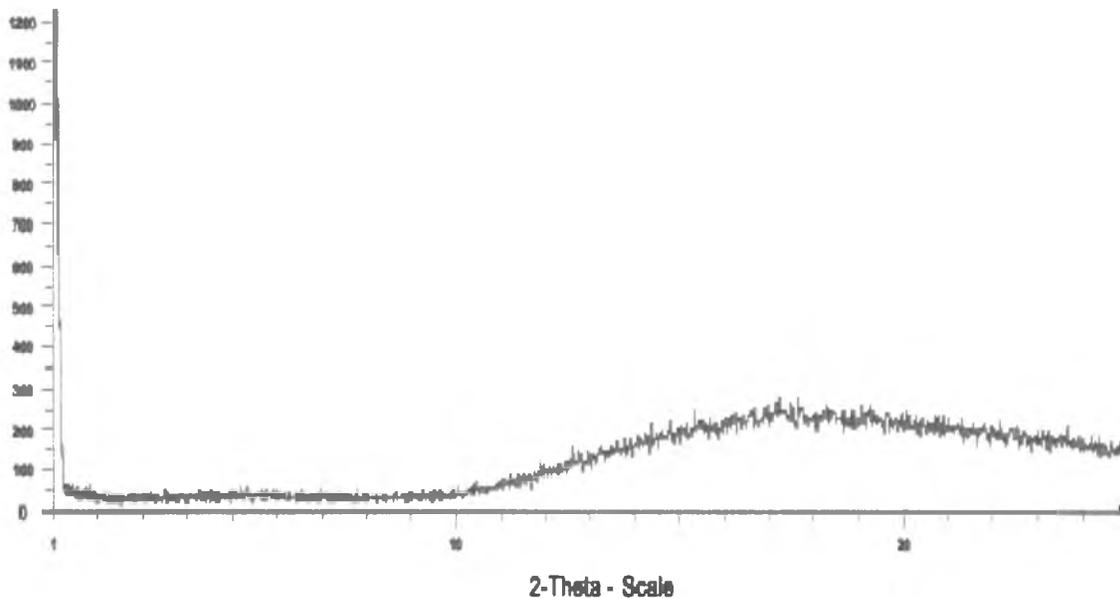


Figure 19. Cloisite with lecithin and GTE resin after light curing.

As previously stated, shrinkage is the number one problem with dental fillings. Since a lecithin-modified clay was produced successfully, shrinkage tests were done on increasing volume percents of clay and resin mixtures, along with pure resin itself. Pure GTE resin had a total shrinkage value of 10.25 %. When the lecithin-modified clay was added, there was a large decrease in shrinkage (see Table 1). A majority of a commercial fillings volume is the glass filler. Increasing amounts of filler was added to the resin-clay mixes and illustrates that the more filler that was added, the less the material shrunk. Likewise, the more clay added to the glass-filled composite, the lower the amount of shrinkage. Clay also had a larger effect on shrinkage than glass (Table 1). It can be seen that the volume percents of shrinkage are much lower than that of glass, but there is a relatively larger decrease in shrinkage with an increased volume of clay.

Table 1. Volumetric shrinkage of samples. Sample composition is based on % volume.

Samples (given in % volume)	Volumetric Shrinkage	% Decrease in Shrinkage
Pure GTE resin (control)	10.25	
0.55 v/v % Cloisite/Lecithin + GTE	7.22	29.6
GTE resin with glass filler (32.25 % of total sample) (control)	4.28	
GTE resin with glass filler(46.71 % of total sample)	3.67	14.4
GTE resin with glass filler (53.57 % of total sample)	3.25	24.1
0.91% Cloisite/Lecithin with GTE & filler (32.25 % of total sample)	4.01	6.4
0.91% Cloisite/Lecithin with GTE & filler (46.71 % of total sample)	3.5	18.2
0.91% Cloisite/Lecithin with GTE & filler (54.58 % of total sample)	3.18	25.7
1.09 % Cloisite/Lecithin with GTE & filler	3.1	28.6
1.18 % Cloisite/Lecithin with GTE & filler	3.03	29.2
1.27 % Cloisite/Lecithin with GTE & filler	2.97	30.4
1.37 % Cloisite/Lecithin with GTE & filler	2.91	32.0
1.46 % Cloisite/Lecithin with GTE & filler	2.88	32.7
1.65 % Cloisite/Lecithin with GTE & filler	2.84	33.6
1.84 % Cloisite/Lecithin with GTE & filler	2.8	34.4
2.80 % Cloisite/Lecithin with GTE & filler	2.75	35.7

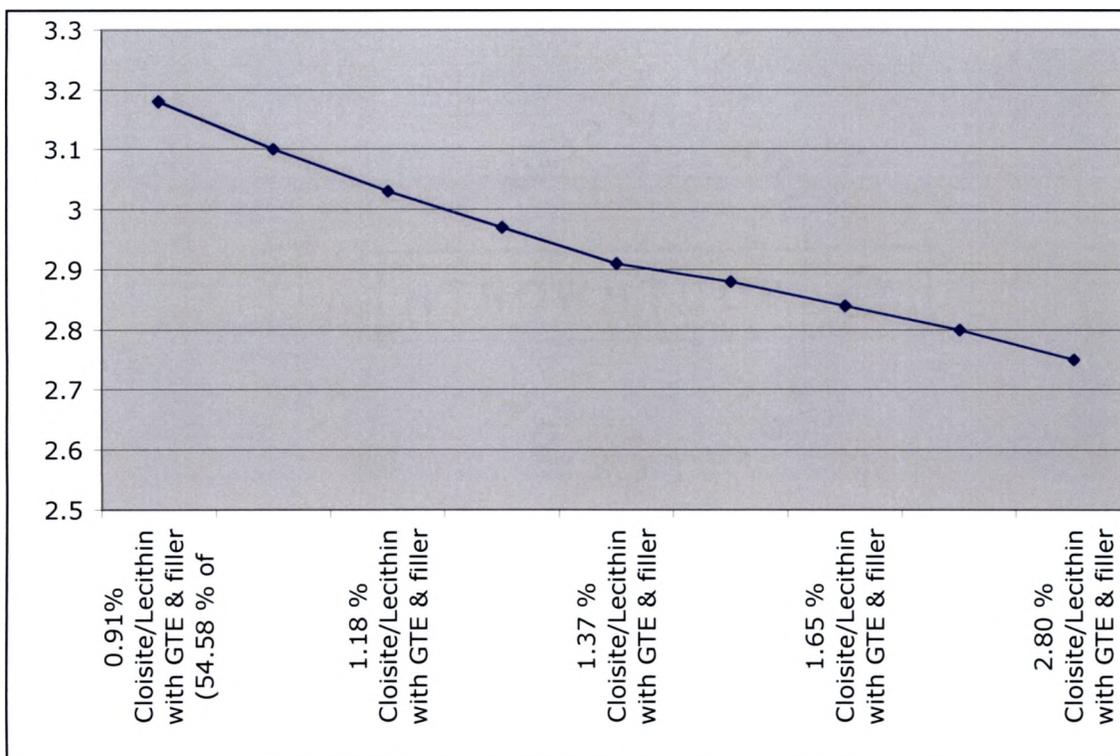


Figure 20. Volumetric shrinkage versus amount of clay added.

There was a large decrease in shrinkage going from 32.25 % to 46.71 % filler. When the amount of filler was increased from 46.71 % to 54.58 %, the amount of decreased shrinkage was even greater. This is likely due to the filler's packing. The more filler-to filler contact, the lower the porosity between particles. When the packing is tight, there is more contact between filler particles with a lower percent volume were the particles are untouched. Porosity depends on the size, shape, and orientation of the particles (23). Arrangement of particles can vary significantly. The loosest cubic packing has a porosity of 47.6 %, while the tightest rhombohedral packing has a porosity of 26.0 % (23). At 46.71 % filler, there was a substantial decrease in shrinkage of 14.3 %, due to the loose arrangement of filler particles. There is still filler to filler contact, but no

substantial amount of packing. At 54.58 %, there is enough volume of filler to have a loose packing arrangement.

Filler addition has effects on the filling's physical appearance and workability. The more filler added, the whiter, or less yellow the material became due to the high brightness of the filler. The limit to the amount of filler that can be added to the resin lies at around 55 %. When filler is added beyond that point, the properties of the material acting as a dental filling diminish. When the amount of glass filler is greatly increased, the filler is unable to mix into the sample. The material becomes unworkable. For proper application to the tooth, a composite has to have a fluid nature. Glass powder will remain outside the sample making it chalky. When trying to form the over-filled sample the material starts to fall apart and crumble. The enamel to filler adhesion also decreases, making the filling easier to fall out.

Different weight percents of clays were tested with a constant 54.58 % glass filler to test the effect of various amounts of clay (Figure 20). The value of 3.25 % shrinkage from the resin without clay was compared against the values of the 0.91 %, 1.09 %, 1.18 %, 1.27 %, 1.37 %, 1.46 %, 1.65 %, 1.84 %, 2.80 % by volume clay-resin mixtures. These samples were tested on the Acuvol to determine percent of volumetric shrinkage. Results are shown in Figure 21. Increasing amount of clay resulted in decreasing amounts of shrinkage. This is due to the clay taking up more volume in the resin. As the amount of filler (glass or clay) is increased, the volume of resin is decreased. There is a near linear decrease in

shrinkage when the amount of clay added to the material is increased: as seen in Figure 20.

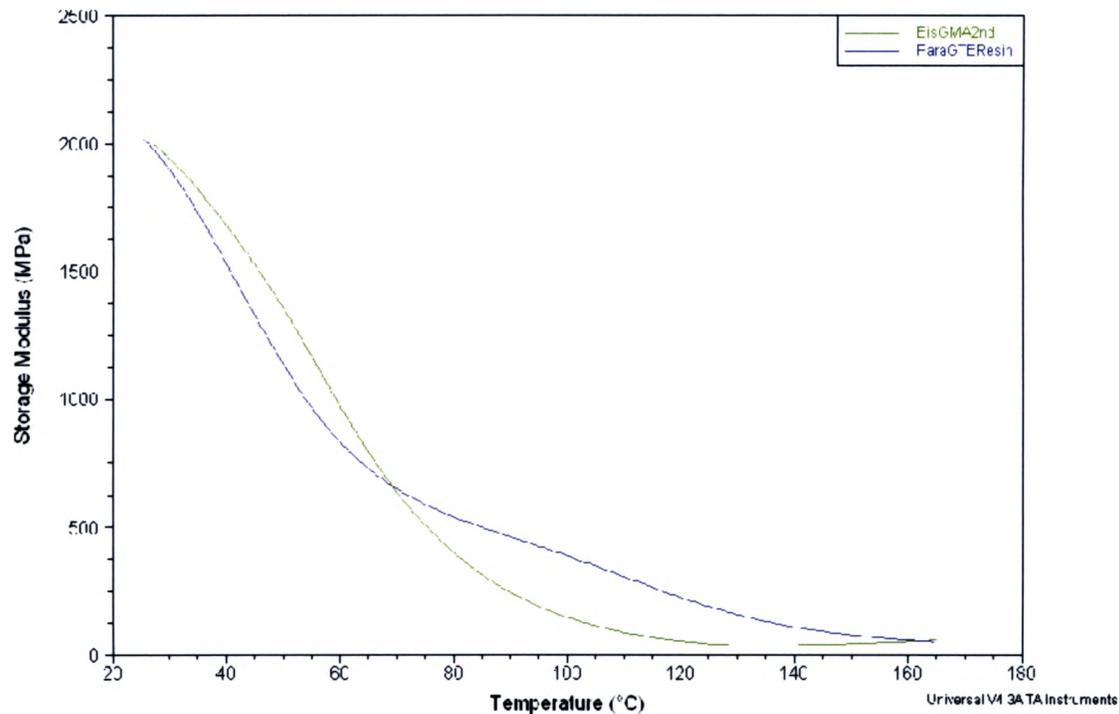


Figure 21. DMAs comparing GTE resin with (blue) and without (green) clay addition.

The second goal, as previously stated, was to improve other physical properties. Storage modulus was obtained through dynamic mechanical analysis. When neat resin was compared to the resin and clay mix, there was no improvement. After filler was added to the GTE resin, the modulus increased significantly. Comparing curves in Figure 21, the storage modulus remained the same at room temperature. There was a slight increase in the GTE-clay sample's storage modulus as the temperature increase from room temperature to 70 °C.

When filler is added to the neat resin, there is an increase in modulus of around 500 %. When clay was added to GTE with filler, the modulus increased by about 50 % (as seen in Figure 22).

Figure 22 shows the improvements in the sample containing clay. The storage modulus is higher in the clay containing sample at temperatures below 84.6 °C. Above 85 °C, the storage modulus declines below the sample without clay. This temperature is beyond what a tooth will encounter under healthy conditions.

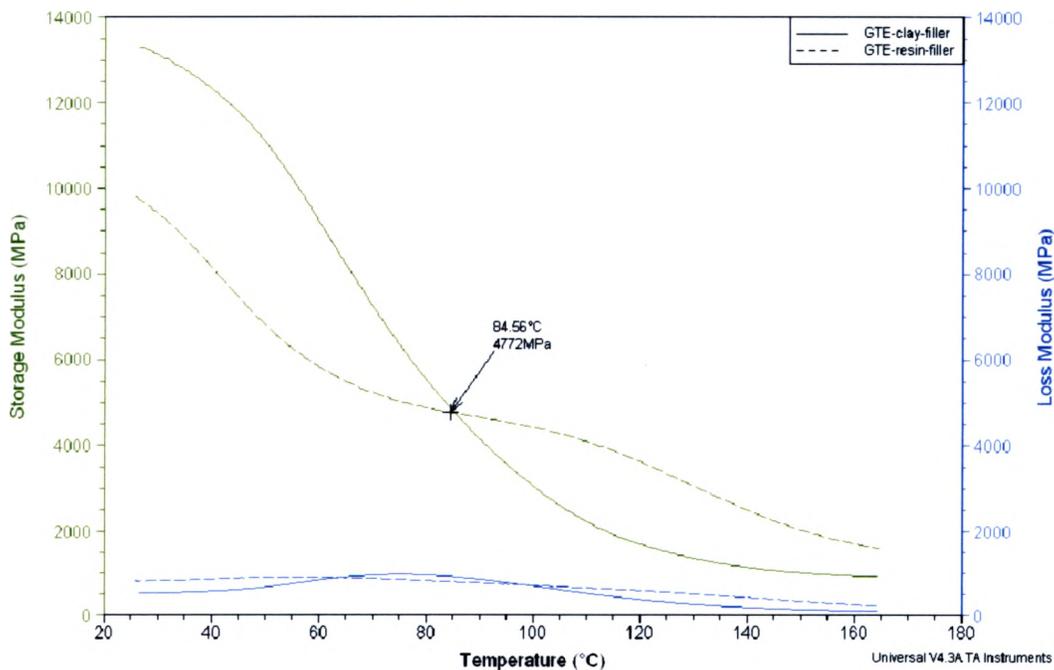


Figure 22. Overlay of GTE with and without clay addition.

Modulus increased with increasing amounts of added clay. Increasing the clay loading only increases the amount of solid substance in the sample. As more clay is added, there is a decrease in the amount of liquid resin. The density

of the clay is the same as the filler, so the relative volume this clay occupies is the same as the volume the filler occupies if quantities were equal. Since the largest decrease in shrinkage resulted from adding the clay without filler, there was a reinforcement effect by dramatically decreasing shrinkage. The reason the sample did not exhibit this property upon filler addition is likely due to a lower amount of liquid volume for the clay to become dispersed. As stated previously, the surface area of clay is much higher than that of glass filler particles. The glass filler surface areas range from 55 m²/gram to 80 m²/gram while clay's surface area is 750 m²/gram. This maximizes the interactions between the clay and the resin. In addition, when the resin is polymerized, the components of the composite shift.

Table 2. 3-point bending results with Cloisite/Lecithin, GTE, and filler.

	<u>GTE resin with filler</u>	<u>GTE resin with filler and Cloisite/Lecithin clay</u>
Peak Load (N)	32 (st.dev 4.7)	24 (st.dev 6)
UTS (Mpa)	133 (st.dev 3.9)	125 (st.dev 6.2)
Modulus (Mpa)	12228 (st.dev 970)	12818 (st.dev 1100)
Energy To Break (N*mm)	9.9 (st.dev 1.7)	7.4 (st.dev 2.3)

From previous DMA results, the modulus of resin with Cloisite/Lecithin clay increased when compared to samples without clay. This did not give any information on how brittle the Cloisite/ Lecithin clay samples were. Standard deviations were high. Therefore, the samples were indistinguishable (Table 2).

3.3 Na⁺ Cloisite Results

In order to reduce manufacturing costs and possibly improve the physical properties of the fillings, unmodified Na⁺ Cloisite was chosen for insertion into the resin. An X-ray was taken of Na⁺ Cloisite added to GTE resin. The cured material showed an intercalated arrangement prior to high-speed mixing. TEGDMA was acting as a surface modifier for the clay through an ion-dipole interaction with sodium. Increased volume of TEGDMA increased the amount of shrinkage (Table 3).

Table 3. Volumetric shrinkage of TEGDMA-modified clay with GTE resin.

Samples (given in % volume)	Volumetric Shrinkage	% Decrease in Shrinkage
GTE resin with glass filler (32.25 % of total sample) (control)	4.28	
0.91 % Cloisite Na+ (25 w/w% of total sample)	2.98	30.4
0.91 % Cloisite Na+ with GTE (27.5 w/w% TEGDMA) & 54.58 % filler	3.18	25.7
0.91 % Cloisite Na+ with GTE (30 w/w% TEGDMA) & 54.58 % filler	3.26	23.4
2.80 % Cloisite Na+ with GTE (25 w/w% TEGDMA) & 54.58 % filler	2.89	32.48

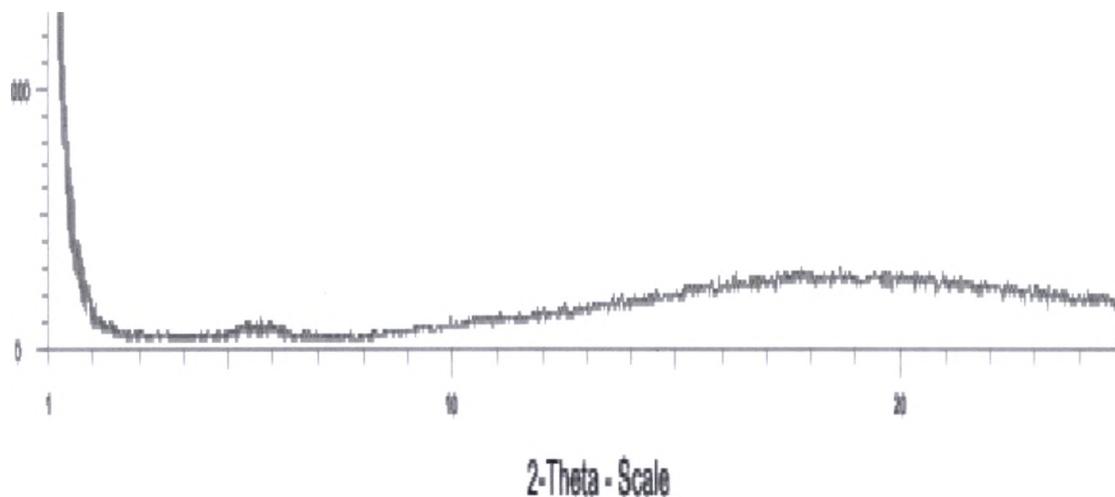


Figure 23. X-Ray of Cloisite Na+ and GTE resin.

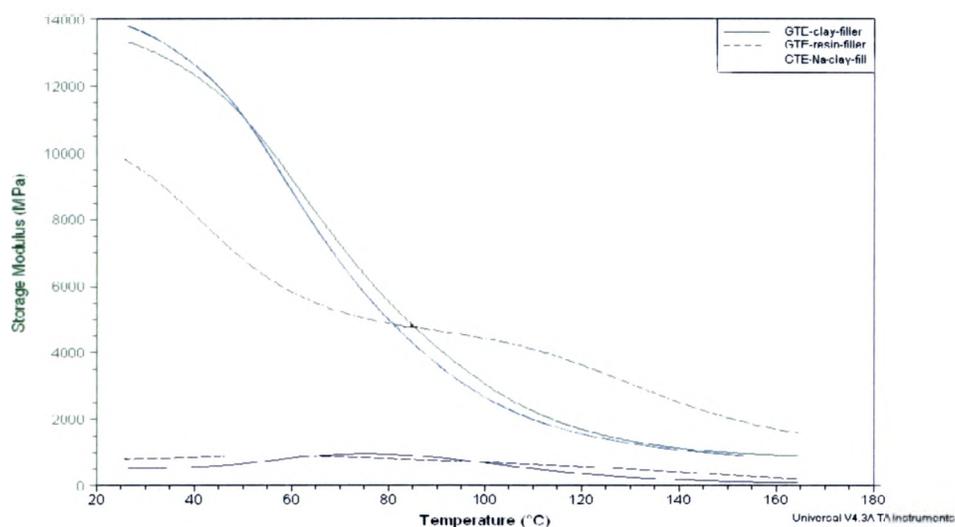


Figure 24. DMA of GTE-lecithin clay-filler (solid green), GTE-Na+clay-filler (solid blue), and GTE with filler and no clay (dotted green).

When compared to Cloisite/Lecithin GTE samples, there was a small increase in storage modulus of about 500 MPa in resin containing Cloisite Na+.

Table 4. 3-point bending results with Na⁺ Cloisite, GTE, and filler.

	<u>GTE resin with filler</u>	<u>GTE resin with filler and Cloisite</u> <u>Na+ clay</u>
Peak Load (N)	32 (st.dev 4.7)	34 (st.dev 4.2)
UTS (Mpa)	133 (st.dev 3.9)	115 (st.dev 8.2)
Modulus (Mpa)	12228 (st.dev 970)	13113 (st.dev 1150)
Energy To Break (N*mm)	9.9 (st.dev 1.7)	7.5 (st.dev 1.6)

Standard deviations for this test were too high to distinguish between samples. Therefore, no increase or decrease can be seen between samples with clay and samples without (Table 4).

This flexural strength apparatus has many sources of error. Because of this, a large number of samples have to be created. The samples are relatively small with the average width and thickness of approximately 1.8 mm, and a length of 25 mm. The method of casting a sample does not effectively eliminate air bubbles. With a smaller sample, an air bubble takes up more area and introduce more error. The computer assumes samples do not contain flaws and measurements are perfectly precise. Air bubbles greatly reduce the sample's modulus decreasing the material's consistency. The samples often break at the locations where the air bubbles are present.

Impact strength was measured through use of the notched izod apparatus. Standard deviations were high. Therefore, samples are indistinguishable (Table 5).

Table 5. Notched Izod test of Na⁺ Cloisite.

	<u>GTE resin with filler</u>	<u>GTE resin with filler and Cloisite Na+ clay</u>
Average Impact Strength	1.12 ft-lb/in (st. dev. 0.5)	2.15 ft-lb/in (st. dev. 0.7)

Radiopacity remained unchanged with addition of clay. By viewing the sample through the Acuvol, the transparency between samples with clay and without clay were not distinguishable. This is due to the low overall percent of clay added. A numerical radiopacity value was not needed since the color and consistency were unchanged, and the clay occupied such a low volume.

4.0 CONCLUSION

Clay nanocomposite techniques were employed in order to lower the shrinkage percent below 1% and increase modulus. At <1, no bacteria or small particles can leach into the fillings. Since shrinkage is the biggest problem with today's dental fillings, it was necessary to learn more and possibly solve this problem. Once shrinkage is decreased to a value below 1%, dental composite science could only benefit from other physical properties in the future.

Volumetric shrinkage was decreased to 2.75%. This was an improvement from the original glass-filled resin without clay, but some dental companies are quoting values under 2%. The exfoliated clay serves as a reinforcement to the polymer system which increases physical properties in most systems including dental fillings, although this research showed shrinkage is decreased to only a small extent.

A promising factor in this research was the 50% increase in storage modulus. Therefore, the sample will be resistant to many external factors such as chewing and demineralization from food. It will take a force greater than 13500mPa to distort the clay filling. The average pressure applied during normal chewing of food is 43mPa depending on the occlusal contact area of the two opposing teeth. High sources of pressure are required for distortion of the material.

One major downfall of this new clay loaded material is its brittleness. Although there was a 50% increase in storage modulus, the sample breaks easier under a low amount of strain. In order to combat this problem, other components could be added to the samples that overcome the brittleness.

Clays have been proven to exfoliate with GTE resin via polymerization. There were not many ingestion safe materials that could be used as surface modifiers that are promising for interaction with the GTE resin. Lecithin was the current best choice for this duty.

Future research can be conducted on other ingestion safe surface modifiers. Exfoliation did not improve the physical property of shrinkage when glass filler was added. This problem can be looked into more thoroughly to possibly find a solution to this problem. Modulus has substantially increased in the clay filled resins. The overall strength of the material has greatly improved. This strength increase does not relate to shrinkage. This was the second goal of the research. An increase in modulus was necessary for dental fillings. It may be useful to employ other techniques to combat shrinkage while maintaining the use of clay nanocomposites for increased modulus.

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