CHAPTER IV

Preparation and Properties of Dental Nanocomposites

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ABSTRACT

Dental resin/clay nanocomposites were prepared by blending organophilic montmorillonite in urethanedimethacrylate (UDMA) resin with photopolymerization. Two different organophilic clays were used: linear amine modified montmorillonite and long bulky quaternary amine modified montmorillonite. Content of modified clays were varied from 1-16 %wt in pure UDMA resin. The intercalation of resin into the 1 nm clay galleries was investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD spectra show no significant peak at 2θ below 10° at the 1 %wt of octadecyltrimethyl ammonium clay (OCT) while as there is slightly peak occurring in other primary chain amine modified clays dental nanocomposites. That means the successful dental nanocomposites occurred in 1%wt of quaternary amine modified clays; however, with increasing OCT content the distance was reduced and intercalated type nanocomposites were obtained. Dental nanocomposites showed large enhancement of diametral tensile strength (DTS) with only a small amount of the dispersed clay particles in the dental resin matrices. Hardness of the hybrid nanocomposites was comparable with that of resin.

KEYWORDS: **Dental Materials, Nanocomposites**

1. INTRODUCTION

Polymer/organically modified layered silicate (PLS) nanocomposites are a new class of filled polymers with ultrafine phase dimensions. They offer an outstanding combination of stiffness, strength and weight that is difficult to attain separately from the individual components. Additionally, the nanoscopic phase distribution as well as synergism between polymer and the layered silicate result in additional properties, such as flame retardency, enhance barrier properties an ablation resistance, which are not observed in either component [Xie *et al.*, 2001]. Montmorillonite, a representative clay mineral, is composed of unit made up of two silica tetrahedral sheets and an alumina octahedral sheet. Their inter sheet layers include exchangeable metal ions (e.g. sodium ions), neutralizing the net negative charges which are generated by partial substitution of Al^{3+} with Mg^{2+} at the octahedral sites. The number of exchangeable ions within the clay minerals determines the amount of organic guest ions which can be intercalated between the clay layers. For montmorillonite is capable of adsorbing guest cation according to the magnitude of the cation exchange capacity (CEC) which is expressd as milliequivalents of the anionic site per unit gram of the clay [Shichi and Takagi 2000]. The new materials showed dramatic improvement in mechanical properties and physical properties. Numerous other researchers later used this concept for nanocomposites base on epoxies, unsaturated polyester, poly (ε-carpolactone), poly (ethylene oxide), silicone rubber, polystyrene, polyimide, polypropylene, poly (ethylene terephthalate), and polyurethane. Mechanical properties of polymer can be improved by incorporating nanoparticles. However, the nanoparticles cannot be compounded with polymers like conventional particulate fillers, which have been employed in plastics industry on a large scale for many years [Rong *et al.*, 2001]. Xu *et al.* (2001) had applied the nanocomposites approach to biomedical poly(urethane urea)s. Poly (urethane urea) segmented block copolymers are used in a variety of biomedical applications such as blood sacs. Their initial experiments based on a generic Poly (urethane urea) and an alkylammonium-modified montmorillonite, a biocompatible layered filler frequently used in cosmetics, food supplements, and stomach acid – reducing medicines. Increasing in %wt of modified silicate clay, modulus, tensile strength and elongation to break (%) have increased. It concluded that a novel nanocomposite approach for biomedical poly (urethane urea)s have improvement in mechanical properties but reduction in gas permeability. Liu and co-workers (1990) studied NH_3/MMT (0-8 %wt clay adding) for control of polymerization shrinkage in the Bis-GMA resin system. The mean values and standard deviations of compression yield point, compressive strength at fracture, and Knoop hardness of experimental composites are evaluated. The results showed that when increasing in weight percent of NH_3/MMT, the percent volume change approached to zero and keep constant at 4 %wt. The mechanism of cured shrinkage control with both natural and NH_3/MMT utilizes the dilatation of the MMT particles. The resin does not form a continuous phase but is largely confined to the small interstices between the solid particles, which not change in volume. The shrinkage forces developed in these spaces during polymerization are no relieved and give rise to local tensile stresses, which increase as the system cure.

When the internal stress exceeds the cohesive strength of the composites, microcracks may form in the resin. Internal stress may also cause separation of the resin and filler, separation of the composite from the enamel and cracks in the enamel adjacent to the restoration. The filler using in their study were mixture of hydroxyapatite, fluoroapatite and 2 %wt of MMT having a wide range of particle shapes and sizes. The compressive strength of their experimental composites is 32,000 psi. which comparable to the reported for dental composite resins (34,000 to 34,400 psi [Phillip, 1982: Craig, 1989]). It is expected that the compressive strength would be significantly larger if the filler type, content and particle size distribution were comparable to that of reported dental composites because constant volume polymerization shrinkage would eliminate the internal stress. The Knoop hardness that obtained from dental composites with adding NH_3/MMT, hydroxyapatite and fluoroapatite in the range of filler content 0-50 %wt. The NH_3/MMT content was varied from 2, 2.4, 2.8, 3.2, 3.6, 4 %wt. The values obtained for their experimental composites ranged between 18.8 and 25.1 kg/mm^2 for 2 – 4 %wt of clay adding. Increaseing in percent weight of clay adding (4%wt), The hardness decreases. Knoop hardness values generally ranges between 25 kg/mm^2 for Microfilled composite resins and 55 kg/mm^2 for conventional composite resin [Phillips, 1982]. The lower value for their experimental composites were due to the lower filler content as compared to the reported dental composites. This study will focus on the improvement of mechanical properties of dental resin when using the silicate clay compared with the conventional filler system. Acrylate monomer of dental resin is reacted in the presence of clay to yield polymer clay nanocomposites.

2. MATERIALS AND METHOD

Urethanedimethacrylate (UDMA or UD) were supplied by Esstech Co. (Essington, PA) and were used as received. Camphorquinone and dimethylaminoethyl methacrylate (DMAEMA) were purchased from Fluka. The structure of monomer is shown in Figure 1.

(Figure 1)

The linear amine modified clays: Tetradecylamine modified clay (TET), Hexadecylamine modified clay (HEXA), Octadecylamine modified clay (OC) and quaternary amine modified clays: Hexadecyltrimethyl amine modified clay (HEXT), Octadecyltrimethyl amine modified clay were used as received from the previous work [Thaijaroen *et al.*, 2000].

2.1 Dental resin preparation

Dental resins were prepared by mixing the monomer and photoinitiator (0.2 %wt camphorquinone and 0.8 %wt dimethylaminoethyl methacrylate) using a four-twisted blade turbine on ALC-sL mixer head (variable speed upto 1500 rpm). Prepolymerized dental resin was stirred at 500 rpm for 20 minute at room temperature.

2.2 Dental nanocomposites preparation

The dental nanocomposites were prepared by adding thoroughly organophilic clays into dental resin at 1, 2, 4, 8 and 16 percent by weight. The mixture was further stirred at 500 rpm at room temperature for 2 hours.

2.3 Characterisation

The wide angle X-ray diffraction (XRD) was carried out using a Cu Kα X-ray diffractometer Rigaku D/MAX-2000 series. The radiation source was operated at 30 kV and 30 mA. The standard sample holders were applied to film samples. The experiment was operated in the 2θ ranges of 5-70 degrees at the scan speed 5 degrees/min with 0.02 degrees 2θ-stepwise increment. Transmission electron microscope (TEM) observations of ultrathin microtome cut sections were carried out with JEOL JEM-200CX at an acceleration voltage of 100 kV and 49950X magnifications.

2.4 Diametral tensile strength

The specimens were prepared by pouring the unpolymerized dental resin into a stainless steel mold. Resin disk (3 mm thick by 6 mm diameter) were photopolymerized between glass slide and translucent polycarbonate strip in a dental curing unit (3M Curing Light XL3000) with a light intensity of approximately 300 mW/cm^2 measured by a radiometer for 40 seconds on each side. They were subjected to test in a Universal Testing Machine following the procedure in American Dental Association-Specification No. 27 for Direct Filling Resins. Five specimens for each sample type were tested and their mean values were determined.

The diametral tensile strength (DTS) test was therefore utilized by placing a sample disk vertically between flat grips. Compressive load was applied to failure with a crosshead speed of 10 mm/min, using 25 kN load cell. DTS were determined by the following standard formula (1)

$$DTS = 2f/(\pi dl) \qquad \text{..................(1)}$$

Where f = load at failure; d = specimen diameter; l = specimen thickness

2.5 Microhardness test

The microhardness of the samples was measured using FM-700e Digital Microhardness tester (Future-tech corp. Japan) with 500-gram load, dwell time 15 seconds and 136° pyramidal diamond indenter (Vicker Hardness Scale). The specimens were prepared in the same way as the DTS specimen followed by polishing the surface with 0.3 μm slurry alpha alumina (Imptech, South Africa). The pyramidal shaped indenter was applied on the surface of specimens within dwell time then the force was removed. For the Vickers method, the indentation length of vertical and horizontal axes is measured and averaged. The experiment was repeated five times for each sample set of parameters. The impression length was measured microscopically and the test load was used to calculate a hardness value automatically by the instrument calculation programme.

4. RESULTS AND DISCUSSION

Characterisation of dental nanocomposites

The X-ray diffraction pattern of various type of dental nanocomposites is shown in Figure 2-6.

(Figure 2-6)

The organically modified clay is able to form a nanocomposites with dental resin. The primary alkyl ammonium modified montmorillonite and quaternary ammonium-salt modified were used. There is no peak presented in 2θ range below 10° for OCT

/dental resin nanocomposites while as there is slightly peak occurring in another types of dental nanocomposites. It means that the interlayer spacing between clay galleries has expanded and the dental resin successfully intercalated into clay layer. The shift of peak indicates the formation of an intercalated structure, where as disappearance of the peak, or reduction in its intensity without any shift, indicates an exfoliated structure. It is obvious that OCT has capability to form exfoliated nanocomposites with dental resin for all %wt clay loading because this clay has a higher degree of basal spacing expansion. The bulky group of quaternary ammonium-salted modified clay has higher chance to delaminate in polymer matrix.

TEM micrograph of nanocomposites, the black-thickening line in all Figures represented the clay layers that have expanded throughout the methacrylate resin (grayish).

(Figure 7)

In Figure 7, 1% TET dental nanocomposites the black line stayed closed together that means the clay galleries have less expanded compared with 1% OC dental nanocomposites, Figure 8.

(Figure 8)

The long chain of amine salt has high capability to expand the distance between clay layers. In 1% OCT dental nanocomposites, Figure 9

(Figure 9)

The exfoliated type of nanocomposite is obtained corresponding to the XRD result. The spacing between clay layers is the largest. The 16% OCT dental nanocomposites have much more clay layers mixed with conventional composites (unexpanded clay layers) that stayed very closed together, Figure10.

(Figure 10)

At this condition, the intercalated type of nanocomposites may be obtained. The quaternary amine has the highest ability to expand the distance between clay layers compared with short and long chain amine.

Diametral Tensile Strength (DTS)

The diametral tensile strength of dental nanocomposites is superior than conventional composites. With a rise in filler content, the strength of the nanocomposites decreases. The suitable percent by weight of clay loading is 1%. The DTS of dental nanocomposites nearly equals to DTS of commercial dental composites, Figure 11.

(Figure 11)

Diametral tensile strength of posterior dental composite value ranges between 35 – 40 MPa and DTS of amalgam is 65.7 MPa [Craig and Ward, 1997]. The diametral tensile strength of our experimental dental nanocomposites ranges between 30 – 50 MPa especially in 1-2 %wt of clay adding which is comparable to the reported dental composites. DTS of the exfoliated dental nanocomposites (at 1%wt, we obtained the exfoliated type of dental nanocomposites) are superior to conventional composites (silanized silica filled composites) and CHA filled composites. Since the single silicate nanolayers have been dispersed into the polymer matrix, the exfoliated nanocomposites is more or less microscopically homogeneous relative to the macroscopic homogeneity of conventional composites. Thus each nanolayer of the exfoliated composite contributes to the reinforcement effect. Nanoscale of filler in resin matrix tends to display higher mechanical properties especially diametral tensile strength for urethanedimethacrylate resin. At high loading of alkylamine-modified clay, the DTS decreases due to the effect of excess alkylamine in nanocomposites formation. The excess amine weakens the composites and reduces the benefit derived from exfoliation of the silicate layers. Xu et al. (2000) stated that the diametral tensile strength and toughness of composite first increased, then decreased with increasing filler level. This study suggested that strength and fatigue resistance of conventional composites usually reach a maximum at an intermediate filler level. The optimum of clay loading for dental resin which providing the highest DTS is about 1-2 %wt.

Microhardness of Dental Nanocomposites

Mean value and standard deviations of Vicker hardness of dental nanocomposites are presented in Figure 12.

(Figure 12)

There is no significant different in surface hardness value between each type of modified clay. The VHN of nanocomposites are much lower than those of the conventional dental composites due to the lower percent content of filler and thus less probably of filler to present at the surface of resin. The property of hardness is of major importance in the comparison of restorative materials. Hardness may be broadly defined as the resistance to permanent surface indentation. Vickers hardness test is suitable for testing surface hardness of material and similar in principle to Knoop and Brinell tests except the indenter. Knoop hardness testing has been adapted to use the 136° indenter (not pyramidal shape). Knoop Hardness Number (KHN) of Microfine dental composites ranges between 55-80 KHN (kg/mm^2) and the dentine is about 68 KHN (kg/mm^2) [Craig and Ward, 1997]. The VHN of experimental nanocomposites ranges between 8-20 VHN. It is much lower than those of reported dental composites. Xu et al. (2000) reported the hardness value of the whisker composite at a filler level 79% ranges 1.0-1.2 GPa. This study suggested that as the filler level was reduced, the hardness of the whisker composite decreased. The previous study is consistent with our result showing that the nanocomposite containing the low content of filler loading have lower microhardness than those of conventional or reported dental composites.

Appearance and Color

The prepared prepolymerized composites with silanized silica, CHA and modified clay are shown in Figure 13.

(Figure 13)

The satisfied colors are ranging from gray, white and yellow. The whole prepolymerized dental nanocomposites give grayish yellow which is acceptable for some case. This color is not universal color for all patient's teeth.

4. CONCLUSION

Nanocomposites preparation between ammonium-modified clay and dimethacrylate dental resin is one way for enhancement mechanical properties in nanoscale level. Modified clay with quaternary alkylammonium salt has a high compatibility with dental resin due to the same functional group as the monomer. The successful enhancement of DTS is at 1-2 %wt of clay loading into dental resin. DTS and VHN do not improve with increasing chain length of alkylammonium modify agent due to the side effect between amine group in ammonium salt and urethanedimethacrylate.

The resin can be exfoliated in clay galleries, but the higher concentration of clay and free amine compromise the properties of the matrix by participating in the curing process. Thus, the reinforcing benefit of the nanolayer is diminished.

5. ACKNOWLEDGEMENTS

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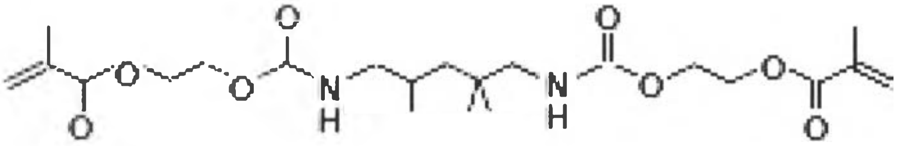

Figure 1

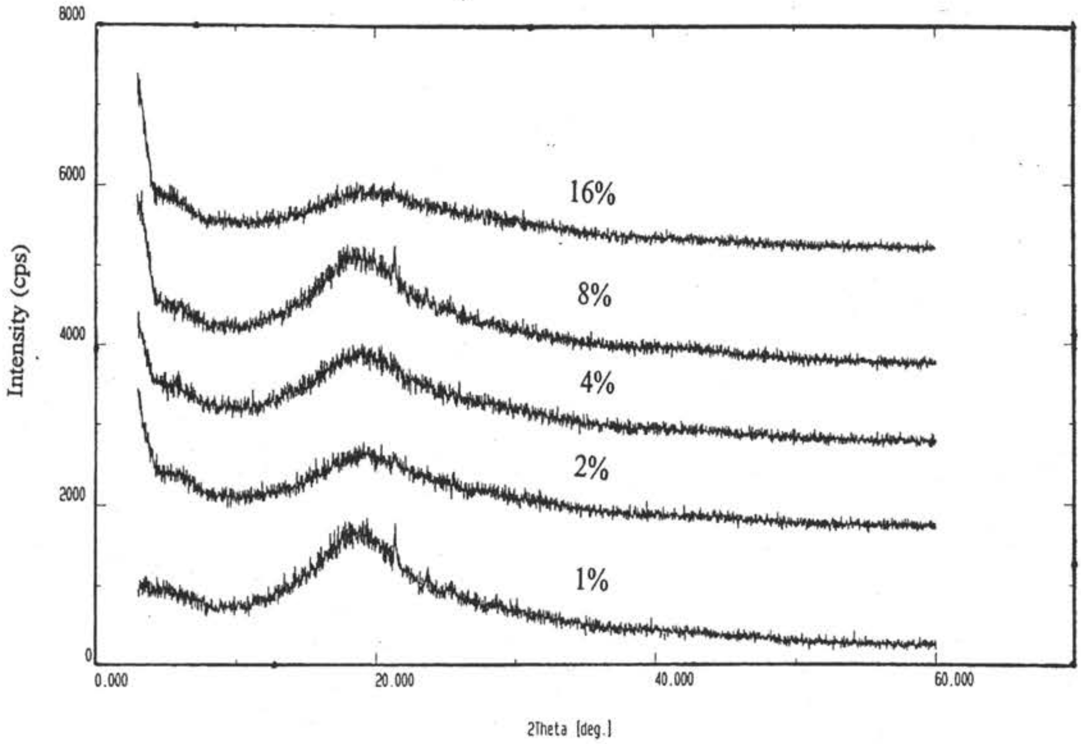
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Figure 2

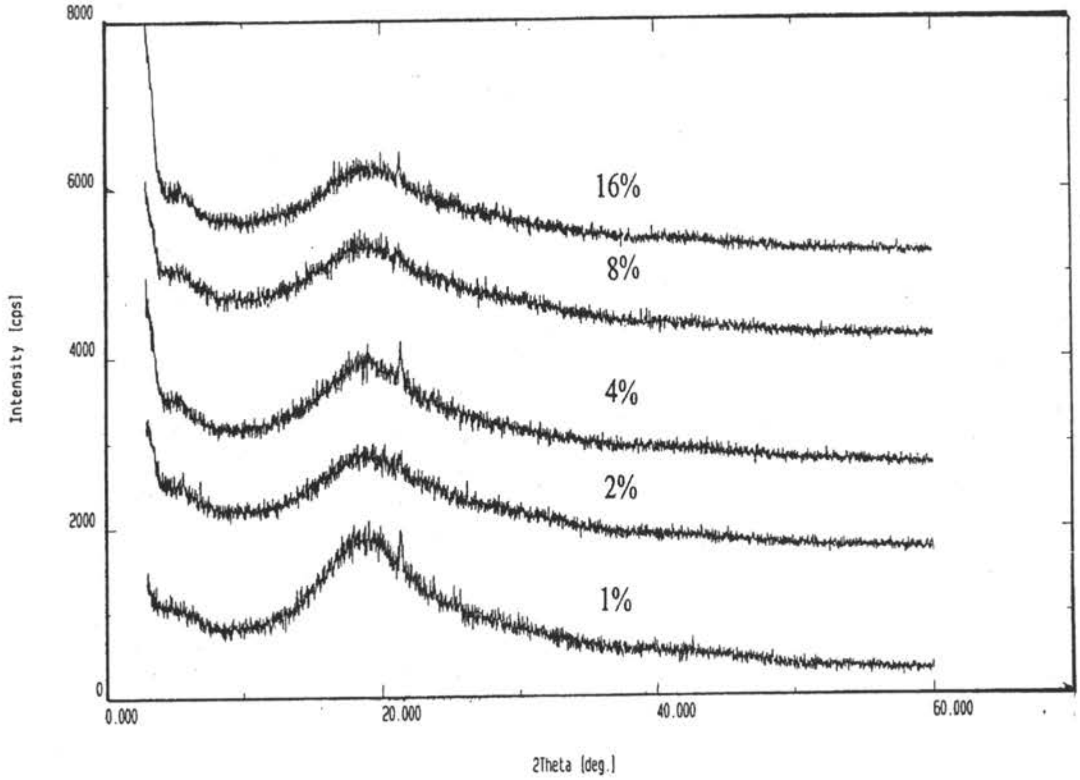
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Figure 3

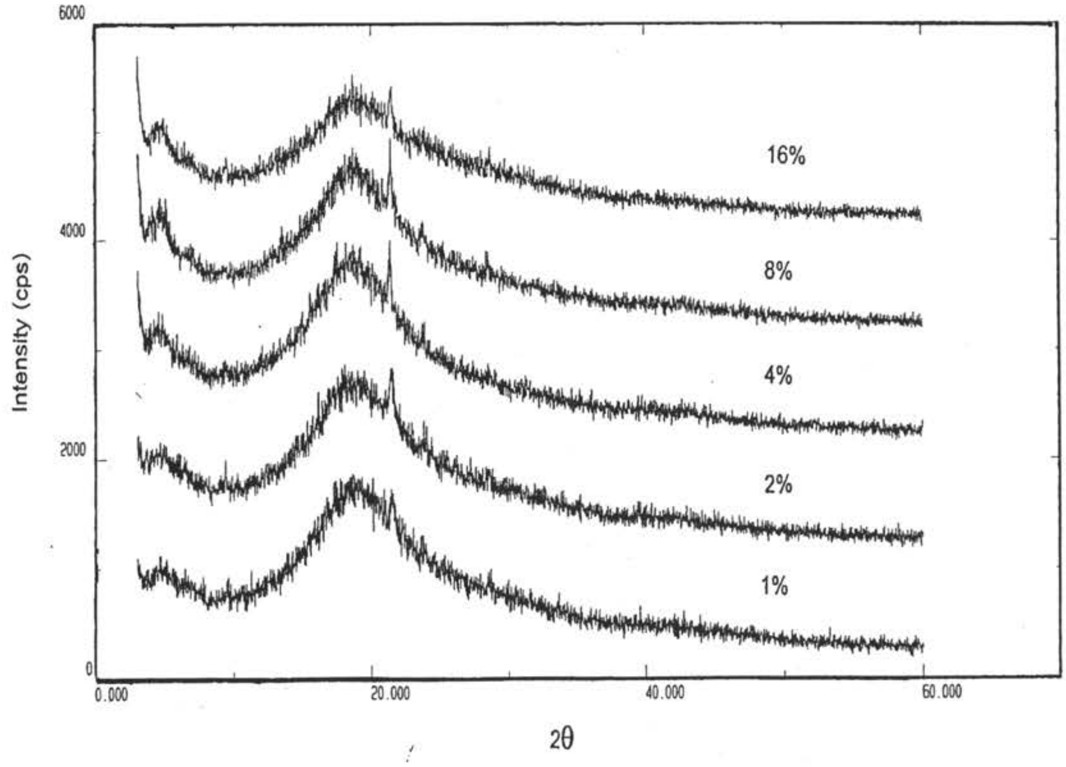
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Figure 4

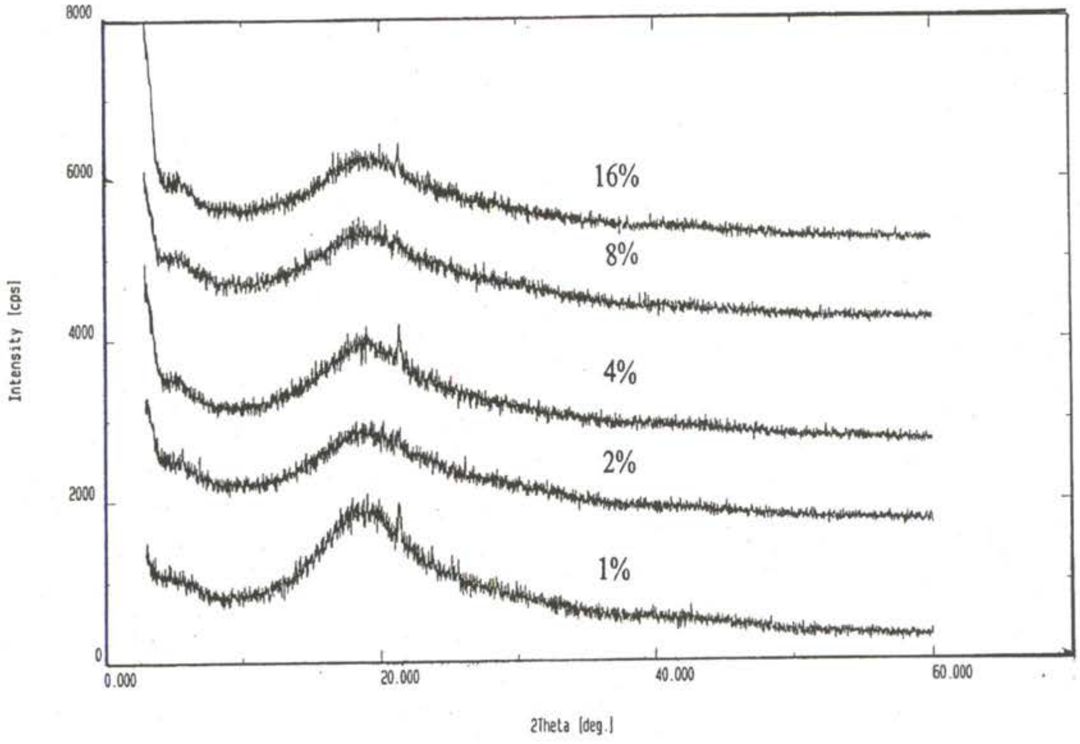
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Figure 5

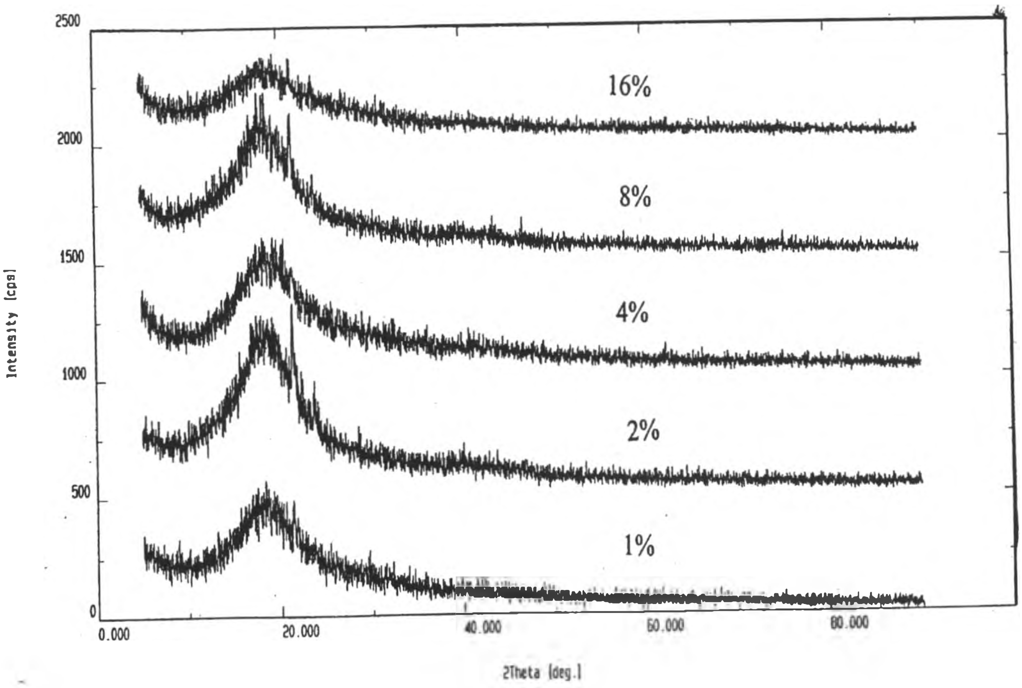
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Figure 6

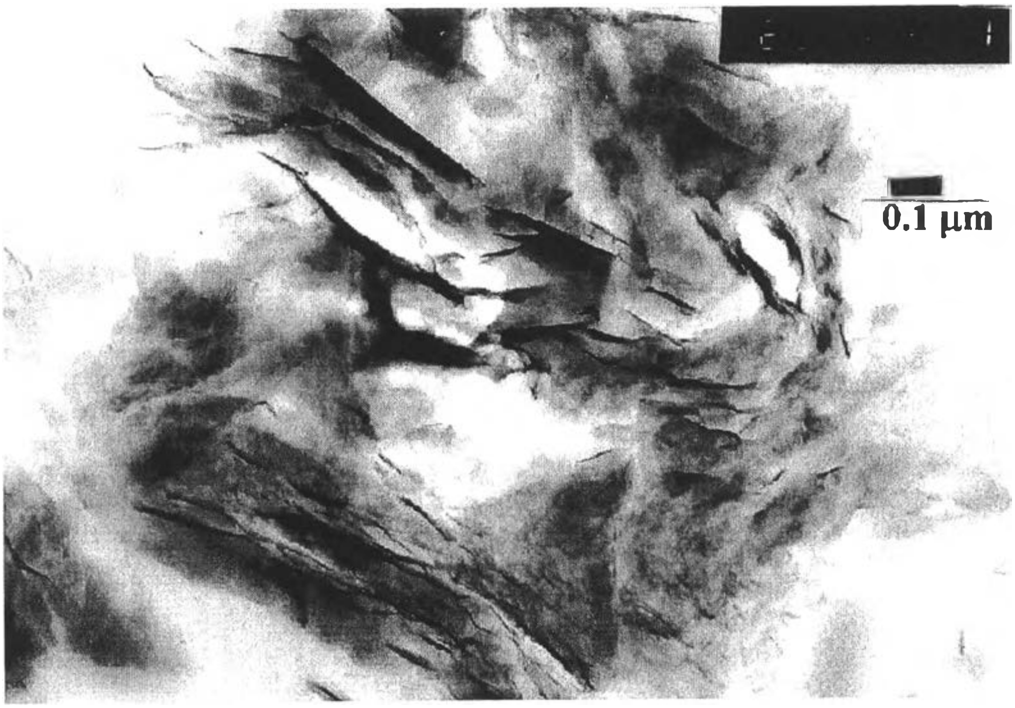


Figure 7

Figure 8

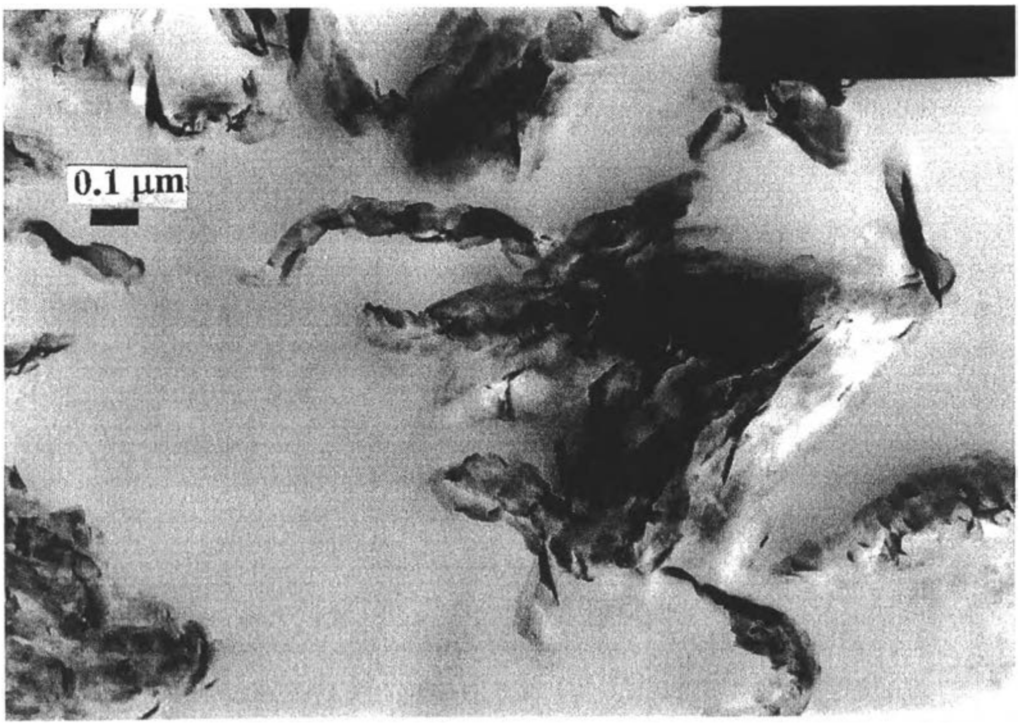


Figure 9

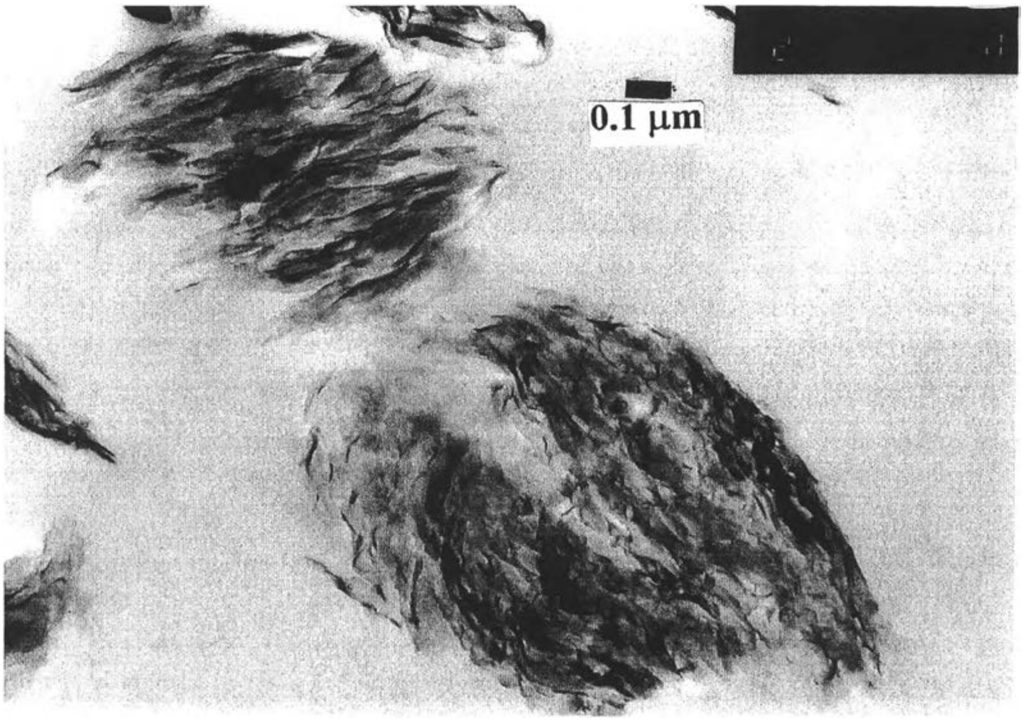
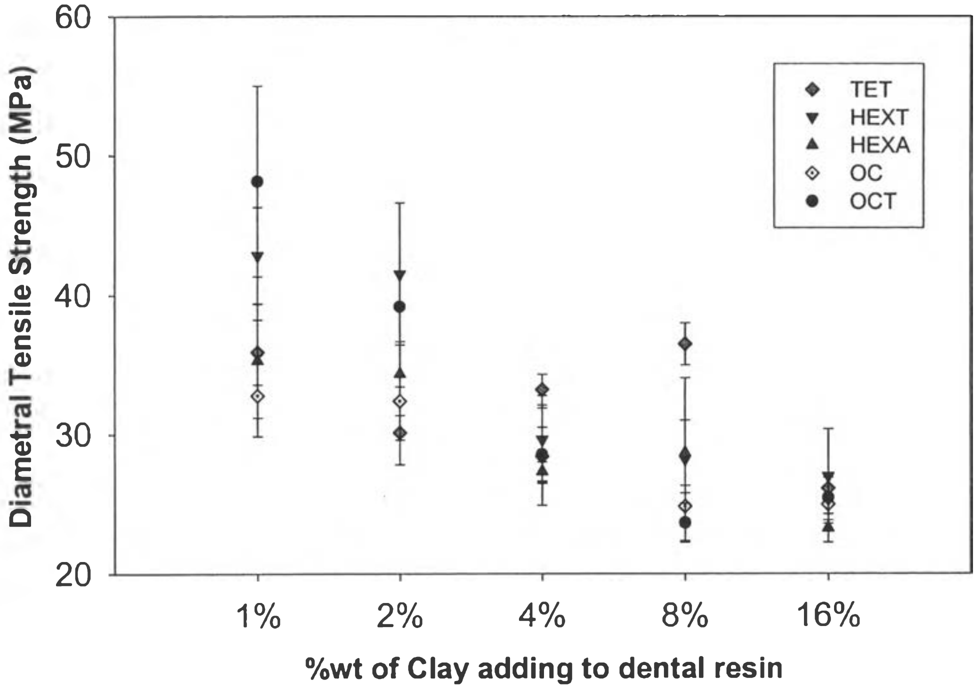


Figure 10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50
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Diametral Tensile Strength (MPa)
TET
HEXT
HEXA
OC
OCT
1%
2%
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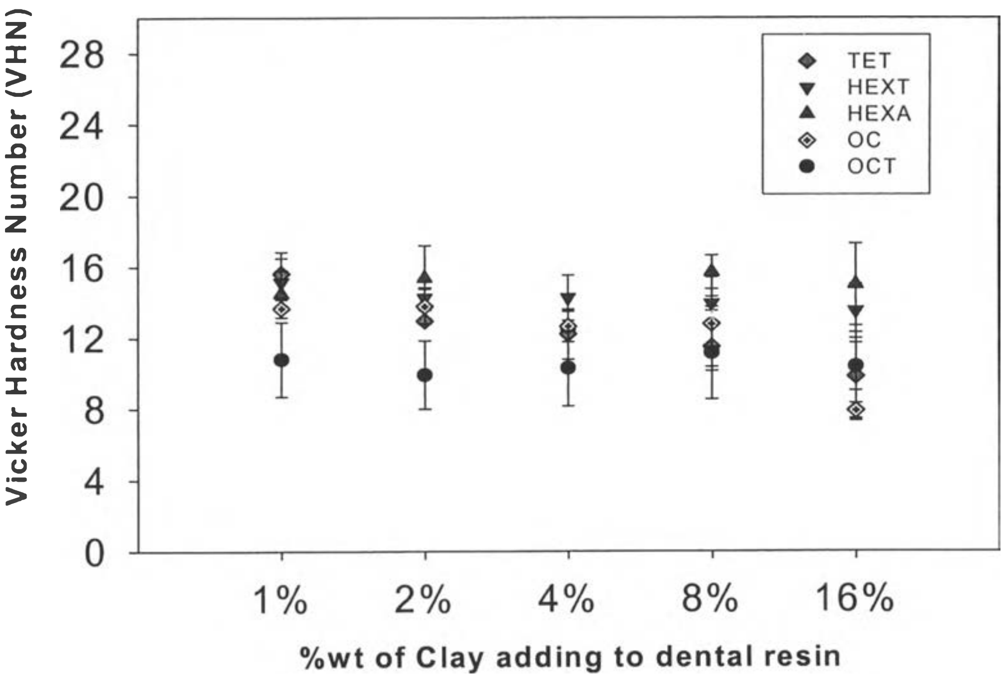
8%
16%
%wt of Clay adding to dental resin

Figure 11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%wt of Clay adding to dental resin

Figure 12

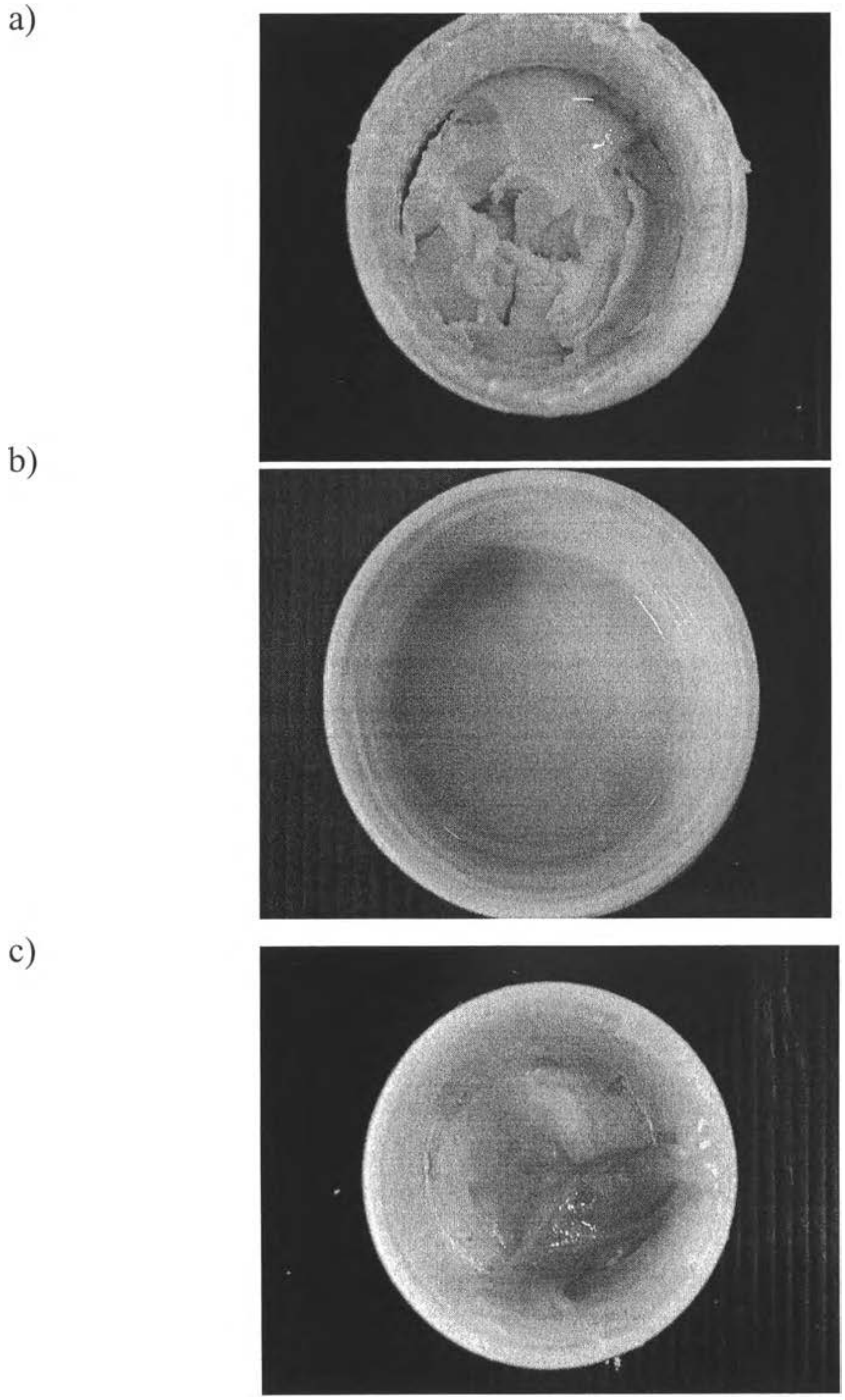

Figure 13