ELSEVIER

Polymer 42 (2001) 8379–8385

polymer

www.elsevier.nl/locate/polymer

Polymethylmethacrylate–montmorillonite composites: preparation, characterization and properties

Nehal Salahuddin[a,*], Mohamed Shehata[b]

[a]Department of Chemistry, Faculty of Science, Tanta University, Postal No. 31527, Tanta, Egypt
[b] Department of Dental Materials, Faculty of Dentistry, Tanta University, Tanta, Egypt

Received 31 August 2000; received in revised form 27 February 2001; accepted 26 March 2001

Abstract

The objective of this work was directed to solve a problem of polymerization shrinkage in acrylic resin polymethylmethacrylate (PMMA) material. Organophilic montmorillonite (claytone) was added up to 1% by weight to one commercial type of PMMA powder to form PMMA–MMT composite. Acrylic specimens were processed by the conventional heat curing method following manufacturer's instructions. Thermogravimetric analysis data indicates that polymer–clay composites exhibit significant increase in thermal stability with very small amount of inorganic content. The morphology of the composites was verified using scanning electron microscopy revealing the absence of large mineral aggregates. Interlamellar spacing was measured from wide angle X-ray diffraction. The $d(001)$ spacing of clay was expanded to 18 Å in claytone and the intensity of the peaks is progressively reduced with increasing the concentration of polymer in the composites samples. Warpage and linear dimensional change measurements were achieved using 'traveling microscope' and one way analysis of variance was employed to compare results. The results indicated that there was a significant decrease of warpage and linear dimensional changes between PMMA specimens and that of PMMA–MMT composite materials.

Keywords: Polymethylmethacrylate; Polymer–clay composites; Montmorillonite

1. Introduction

Dimensional stability of dentures during processing and in service in the mouth is of considerable importance as regard to fit and satisfaction to the patient. Generally, if the denture is properly processed, the original fit and the dimensional stability of various denture base plastics are good. There may be some dimensional changes during processing and in storage [1].

All acrylic resin structures receive some internal strains during processing, which may be released in the form of warpage when placed in service. The severity of this change, no doubt, depends upon the processing manner as well as on the shape and form of the structure and also on the chemical nature of the resin [1].

One of the problems met with denture base processing is that during polymerization of heat-cured acrylic resin, there is a considerable degree of internal strain produced primarily by the different thermal coefficients of expansion of the components of the denture and the mold, although, thermal contraction is the principal factor in strain production and warpage of dentures. Polymerization shrinkage and internal stresses in the material on cooling as the material is confined within the mold, both contribute to inaccuracy of fit of acrylic dentures [2,3].

The minimum amount or lake of warpage occurring in the denture resins leading to presence of minimum space between the base and the oral tissues, which is one of the principle factors in denture retention and its fitness to the oral tissues. New materials and methods of processing denture bases are introduced from time to time for use in making complete denture prostheses. The primary aim is to find a material or technique that may be used in processing dentures as good as or better and in less time than dentures made with the usual processing techniques [2,4].

Zero shrinkage and expandable polymer concrete systems have been developed by dispersing in different raw polyester resins and silane coupling agent controlled amounts (0.1, 0.2% by weight) of the hydrated mineral montmorillonite (MMT) in the form of very fine powder. This mineral interacts with the resin during the cure, giving rise to an increase in volume. Depending on the amount of MMT added and cure temperature systems that show zero shrinkage or expansion are obtained upon curing [5]. More recently, the swelling characteristics of montmorillonite have been manipulated to effect shrinkage control of epoxy compounds [6].

* Corresponding author.
E-mail address: snehal@dec1.tanta.eun.eg (N. Salahuddin).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00253-1

Clay minerals constitute a common class of particulate fillers for the plastics in industry. Since the early work, there has been growing interest in the properties of complexes of organic molecules with smectite silicate minerals (montmorillonite). This interest may be attributed to a remarkable level of inherent activity of this class of minerals, related to an oddity of their crystalline structure, which comprises two dimensional crystalline regularity (layers or lamellae) superposed without any regularity except for a constant separation and held together by relatively weak forces. MMT are hydrous alumina silicate minerals whose lamellae are constructed from an octahedral alumina sheet sandwiched between two tetrahedral silica sheets. Although hydrophilic, the ability of montmorillonite to absorb certain organic materials is well known. However, when MMT is saturated with organic cations such as quaternary alkyl ammonium ions, the ability to adsorb organic materials is improved even from aqueous solutions, thereby exhibiting a more organophilic nature [7]. All recent developments suggest that MMT, when properly treated, may be used in the advancement of novel clay polymer compounds [8–11].

As MMT is composed of stacked silicate sheets, it has a low thermal expansion coefficient, therefore if composites of polymethylmethacrylate–montmorillonite were prepared; problems of thermal expansion might be solved. From this, one can envision the development of polymethylmethacrylate (PMMA) with low shrinkage properties by incorporating an organophilic montmorillonite. The ability of MMT to adsorb MMA molecules should enable their particles to separate and disperse throughout the matrix. The additional free volume development within the clay might reduce the shrinkage or counteract it and the residual stress of the bulk PMMA sample.

The present study exploits the ability of organophilic montmorillonite to reduce the curing shrinkage to minimal to avoid further warpage and dimensional changes that may reduce acrylic denture fitness.

2. Materials, methods and characterization

2.1. Materials

One commercial type of heat-cured acrylic resin PMMA used in dentistry was selected for this work (Super acryl, clear type Spofa Dental, Praha). Weight-average molecular weight of the polymer was measured by laser light scattering method. An air cooled argon ion laser system (uniphase Product model 2013 argon ion laser system consists of a model 2213 head incorporating a 2313 argon ion laser tube, powered by a 2113 power supply) was used as a light source at wavelength 488 nm. ($M_w = 9.5388 \times 10^5$ g/mol, A_2 (second virial coefficient) = 9.51×10^{-5} and radius of gyration (mean end to end distance of molecule) = 1400 Å).

The clay mineral used in this study was organophilic montmorillonite from southern clay products Inc (Gonzales, Texas) under the trade name of claytone APA. It was received as fine particle powder. The $d(001)$ interlayer spacing is 18 Å. The organically modified silicate was produced by a cation exchange reaction between the silicate and dimethyl benzyl hydrogenated tallow ammonium chloride. The percentage of organic content (dimethyl benzyl hydrogenated tallow ammonium chloride) was 24%.

2.2. Methods

2.2.1. Preparation of PMMA/MMT powder mixture

PMMA was mixed with controlled amounts of organophilic MMT in the form of very fine powder. The ratios are shown in Table 1. A mortar and pestle were used for the initial mixing and blending followed by hand tumbling in plastic jar until a uniform mix was achieved.

2.2.2. Warpage test

Forty experimental identical stone casts were poured of pure stone. A double thickness of base plate wax (3 mm) was adapted on each stone model, sealed at the peripheries and then divided into five equal groups (I–V). The waxed up bases were flasked as the usual technique for denture construction. Washing was done in boiling water to remove the wax from the investment.

PMMA/MMT mix (powder) and MMA (liquid) were mixed as recommended by the manufacturer and the resulting dough was packed. Trial closure of the flask was performed to remove the excess dough followed by final closure under pressure. The curing cycle followed the manufacturer's recommendations (74°C for 1.5 h followed by 100°C for 1 h), then they were removed from the water bath and allowed to bench cool before deflasking. Each base

Table 1
Preparation condition and thermogravimetric data of PMMA and PMMA–MMT composites

Sample	%Wt. of clay	PMMA (g)	Organophilic (MMT) clay (g)	%Wt. loss	
				First step	Second step
I	0	20	–	18.64	81.31
II	0.1	19.97	0.03	0.92	98.93
III	0.2	19.95	0.05	0.76	98.87
IV	0.5	19.87	0.13	0.65	98.20
V	1	19.74	0.26	0.90	98.05

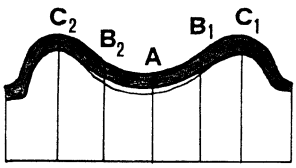

Fig. 1. Illustration for warpage test.

was numbered according to the cast on which it was constructed. Deflasking was carried out carefully to gain all stone casts intact. Polishing was carried out wet to avoid heat generations and the acrylic specimens were reseated in the stone casts and visually examined before testing.

Warpage measurements were carried out using the 'traveling microscope' at five fixed points crossing the bases and the stone casts. The least reading was 0.01 mm. The 10th magnification was used. The vertical distance (area of separation between the end of the finished acrylic specimens and the original standard casts) was measured at the five fixed points (Fig. 1).

Results obtained for each group were statistically analyzed and compared with the results of the other groups.

2.2.3. Linear dimensional changes test

Circular brass die was specially fabricated having dimensions 70 mm diameter and 3 mm thickness. Three sharp line grooves A, B and C were made on the surface of the die and another three bisecting cross-lines A′, B′ and C′ were also grooved forming four squares, each one having dimensions of 7.5 mm × 7.5 mm (Fig. 2). A silicon elastomer mold was made of the master die to create a mold cavity. Following the conventional dental laboratory procedures 3 mm thickness wax sheet was softened, adapted and sealed in the silicon rubber mold cavity. Forty wax specimens were then available. Conventional flasking procedures were then followed using the usual water bath technique for denture construction as described in the warpage test. After curing, deflasking was done and the specimens were kept on their stone casts without polishing for measurement procedures (Fig. 3).

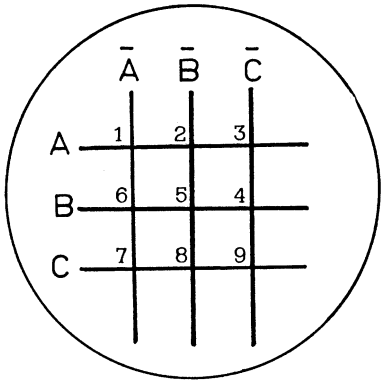

Fig. 2. Illustration for linear dimensional change test.

The mean value (D_1) of 12 linear measurements was recorded for each sample in the five tested groups (I–IV) by measuring the distance between the numbers illustrated in Fig. 2 using traveling microscope. After removal of the acrylic specimens from their stone casts, they were measured as previously described and also the mean value was computed (D_2). Linear dimensional changes for each group were calculated from the following equation.

$$\frac{D_1 - D_2}{D_1} \times 100$$

where D_1 is the mean linear dimensions while specimen still on their stone casts and D_2 the mean linear dimensions after specimen removal from their casts.

The virgin PMMA group was considered as the control group and PMMA–MMT composite specimen groups were compared with each other and with the control one in both warpage (Fig. 4) and linear dimensional change tests. Data were gathered, arranged and compared.

Dimensional changes of rubber base mold (shrinkage), stone model (expansion) and wax specimen (shrinkage) were considered as constant factors for all tested specimens.

2.2.4. Material characterization

Thermogravimetric analysis was carried out under nitrogen atmosphere in the temperature range 20–800°C on a Dupont 990 thermogravimetric analyzer using a heating rate of 20°C/min in order to investigate the thermal stability and the inorganic content of the composites.

X-ray diffraction studies were conducted on specimens cut from the molded samples to examine the interlayer activity in the prepared composite. A Phillips XRG 3100 X-ray generator equipped with a nickel-filtered Cu Kα ($\lambda = 1.5418$ Å). X ray source connected to a Phillips APD 3520 type PW 1710 diffractometer controller was used. The scanning speed was 0.005 2θ S^{-1}. Bragg's law, $n\lambda = 2d \sin\theta$ was used to compute the crystallographic spacing, d.

The morphology of the composite was examined by a Joel JXA-840 scanning electron microscope. The composite specimen was deposited on double scotch tape and examined at the fracture surface. The specimen was coated with gold for improved SEM imaging.

3. Results

In the preparation procedure, the mineral to polymer ratios were 0.1, 0.2, 0.5, and 1% by weight. Thermogravimetric analysis of a cured dried samples of the composites revealed the mineral content Table 1.

Thermogravimetric analysis curves (Fig. 5) seem to indicate an increase in heat stability of the composite. It is interesting to note that the polymer itself was found to be degraded at 100°C and the composite is resistant to degradation at this temperature. These results seem to indicate

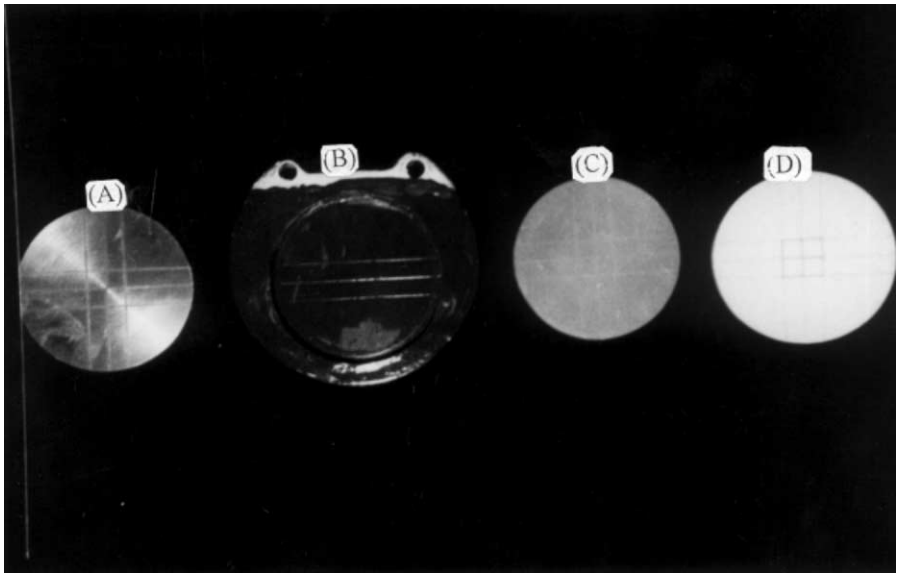

Fig. 3. (A) Brass mold. (B) Silicon elastomer mold. (C) Wax pattern specimen. (D) Acrylic (composite) specimens.

that while the external polymer is destroyed the inserted polymer retained between the lamellae of the crystallites or between primary particles resists degradation. It appears that the stability of the inserted polymer is due not only to its particular structure but also to the steric factors restricting the thermal motion of the segments sandwiched between the MMT particles. The unzipping of the chains begins when the temperature is high enough to bring about this motion. The degradation of all composites (II–V) occurs in two steps, the first step at the temperature range 20–200°C with weight loss lower than 0.9% and the second step at the temperature range 200–450°C (Table 1).

Wide-angle X-ray diffractometer (WAXD) was used to determine the absorption of PMMA by observing changes in the 001 spacing (*d* spacing) of the MMT layers. Fig. 6 shows typical WAXD traces of claytone and composites (II–V), which indicated that the interlayer spacing of MMT (9.6 Å) was increased to 18 Å in claytone due to the presence of long chain ammonium chloride between the layers. WAXD of composites contain peak characteristic of the pristine organosilicate (18 Å) but the intensity and the sharpness of the diffraction peaks corresponding to the pristine organosilicate is progressively reduced as the polymer concentration increase in the sample.

SEM examination of the fracture surface of the compression molded specimen (IV) (Fig. 7) did not reveal the inorganic domains at the maximum possible magnification. The absence of MMT particles indicates that the agglomerate is

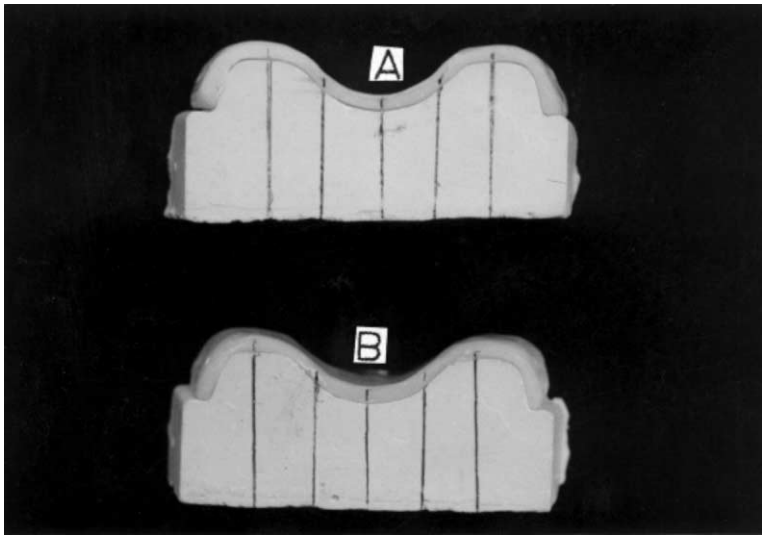

Fig. 4. (A) Control specimen with the vertical separation between acrylic specimen and the model. (B) PMMA–MMT specimen with least separation between the acrylic plate and the model.

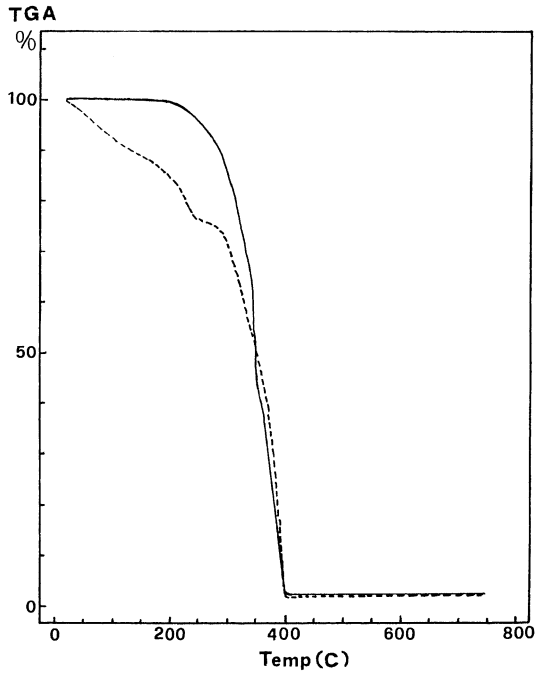

Fig. 5. Thermogravimetric analysis of PMMA(- - -) and PMMA–MMT composites IV (—).

broken down to a size (submicron) that cannot be seen at this magnification.

3.1. Warpage test

Table 2 shows the mean values of the warpage (amount of separation or vertical spaces) for the five tested groups measured at the five predetermined reference points. In all tested groups, it was evident that a space was created between the acrylic experimental bases and their original casts after processing (Fig. 4). All casts showed the greatest mean spaces at the point A, which represents approximately the center of the palate and point C showed the lowest separation as it represents the crest of the ridges.

It was evident that the total mean values of the vertical separation for group I (virgin PMMA) gave the highest recorded value and there was a gradual descending order of the amount of separation from group I up to group V. This means that the amount of MMT percentage up to 1% led to a significant decrease in warpage. There was a significant difference between the control and that of composite groups. *F* ratio (357.813) means that this is highly significant at 0.01 level.

Fig. 6. X-ray diffraction patterns of claytone and the resulting composites with different ratios of MMT.

3.2. Linear dimensional changes

Table 3 shows the percentage values of linear dimensional changes. Comparing the five groups it was found that there was a descending order of linear polymerization shrinkage up to 1% clay. There was also a significant difference between the control and that of composites (*F* ratio = 151.937). The variance for the test groups with a significance level of 0.01.

4. Discussion

Industrially, clays are used as fillers and reinforcement in polymer systems such as elastomers, polyethylene, polyvinylchloride and other thermoplastics and as coating agents for various types of papers. All things being equal, the

Table 2
Warpage test results

Experimental groups	I (control) clay free	II (0.1% clay)	III (0.2%)	IV (0.5%)	V (1%)
X ± SD	0.56 ± 0.03	0.26 ± 0.02	0.18 ± 0.03	0.14 ± 0.03	0.09 ± 0.01

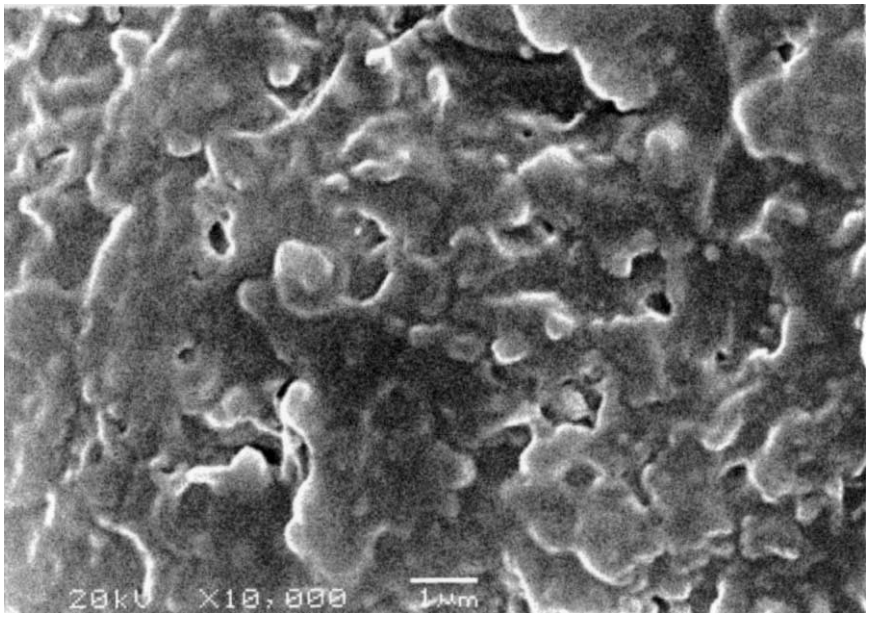

Fig. 7. Scanning electron microscopy of PMMA–MMT composite (IV).

efficiency of filler in improving the physico-mechanical properties of a polymer system is primarily determined by the degree of its dispersion in the polymer matrix. Because clay surfaces are essentially hydrophilic, raw or untreated clay is not readily dispersible in or rapidly wet by the organic phase. To make the mineral organic phases mutually compatible it is often necessary to render the clay surface organophilic prior to blending or compounding the filler with the polymer. Montmorillonite is a hydrated alumino-silicate with the general formula: $(Na_{0.7}Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4{\cdot}nH_2O$. It has a laminar crystal structure that includes up to four layers of semiordered water between the metal-oxide layers of the basic crystal. The interlayer water is bound to the mineral via coordination sorbed cations or through hydrogen bonds with the oxygen of the silicate layers.

It is widely believed that maximum clay swelling in the composite is to be conferred on MMT-polymer intercalates if the Na^+ ion in montmorillonite exchanged with organic cations with long chain of hydrocarbon. For example researchers concluded that organophilic montmorillonite ((stearyltrimethylammonium–MMT)$CH_3(CH_2)_{17}N(CH_3)_3^+$)–MMT) is the best for the preparation of quaternary ammonium montmorillonite–polystyrene complex. The high intercalation of styrene into this organophilic-MMT may be explained by the greater hydrophobic nature of long chain alkyl groups in the interlayer space and van der Waals forces between styrene and the hydrocarbon chain [12].

In another publication by Toyota et al. nylon 6-clay hybrid, which contain isolated silicate layers was prepared. Organophilic montmorillonite (ω-amino acid-MMT) with C-atom 11 or more are intercalated inclined relative to the layers of MMT, stretched and arranged with their longitudinal axes perpendicular to the MMT plate in the presence of ϵ-caprolactam leading to MMT being swollen as large as possible [13].

Based on these findings, organophilic montmorillonite with long chain hydrocarbon was chosen to prepare MMT–PMMA composite to demonstrate the swelling of the clay layers in PMMA. During curing the resin interact with the organophilic MMT creating expansion, which counteract resin shrinkage.

All tested sectional acrylic plate specimens exhibited some degree of warpage, which was represented as increase in the vertical dimension spaces between the acrylic plates and the stone casts. Immediately after deflasking, the sectional plates were well adapted on the models and these vertical spaces were created after removal of the plates, polishing and reseating on their casts. The virgin (control) specimens gave the highest warpage values, which were significantly higher than those of other groups. It is noted that increased montmorillonite percentage leads to a decrease in warpage value.

Table 3
Linear dimensional changes results (%)

Experimental groups	I (control) clay free	II (0.1% clay)	III (0.2%)	IV (0.5%)	V (1%)
X ± SD	0.61 ± 0.44	0.34 ± 0.41	0.30 ± 0.42	0.24 ± 0.27	0.22 ± 0.32

The warpage of acrylic resin plates may be explained by the friction between the walls of the mold and expanding soft resin induce stresses in the polymer, which will persist below glass transition temperature. If the gypsum mold is stressed beyond its proportional limit by the expanding resin, permanent deformation of the mold may occur. During cooling of the flask, stress is induced, since the resin is forced to follow the shape of the cast, inspite of the differences in their thermal coefficient of contraction. These stresses induced in the plastic are relieved when plastics are separated from the casts.

In general, the processing shrinkage that occurs tends to draw flanges of the dentures inward and causes the palatal portion to be caused creating the vertical space at the posterior palatal portion. In another publication by Chen et al. [14], it was stated that due to polymerization shrinkage and release of internal stresses, the peripheral areas of a denture base tend to move inwards elevating the palatal area away from the master casts.

Virgin PMMA specimens showed the highest amount of curing shrinkage as represented by the measured linear dimensional changes. Increase MMT percentage in the composite led to a pronounced decrease in the recorded values.

A considerable number of studies have been made on the dimensional changes occurring during processing and storage of the dentures. In general heat cured dentures immersed in water show a linear expansion in the posterior palatal region of the upper denture of 0.1–0.2%, which partially but not completely compensates for processing of shrinkage of 0.3–0.5%. The net linear change can vary from a shrinkage of 0.1–0.4%. The fit of the denture bases may be related more to glass transition temperature than to water sorption for these materials. In addition to knowing the fit on the model or the percentage of linear dimensional change, it is of interest to know how accurately certain portions of the dentures fit.

An ideal plastic of course, would be one that had no polymerization shrinkage but even if these requirements were fulfilled, thermal dimensional changes would still result from cooling the plastic from molding temperature to room temperature. Sykora and Sutow [15], stated that current denture base materials change dimensionally as a result of polymerization and thermal contractions. In contrast, Yeung et al. [16] concluded that temperature differential is excluded as a reason for the warpage of dentures.

The MMT particles may serve as additional crosslink centers, thus we expect increasing the strength of the system in a manner analogous to the action of carbon black in rubber. Experiments are in progress to measure the strength of these materials.

5. Conclusion

By understanding and controlling the swelling of montmorillonite clay material, the expanding nature of MMT was used in this study to counteract polymerization shrinkage and the resultant residual stress development in polymethyl-methacrylate (PMMA) polymer. Polymerization shrinkage of PMMA in the form of warpage and linear dimensional changes of PMMA was greatly decreased and controlled in PMMA–MMT polymer composites.

6. Recommendation

Further research work is required to investigate the mechanical properties for these composite materials investigated in this study.

References

[1] Peyton FA, Craig RG. Restorative dental materials. 5th ed. St. Louis: C.V. Mosby Company, 1997 (p. 403).
[2] Anthony DH, Peyton FA. J Prosth Dent 1962;12:67.
[3] Osborne J. Mechanics for students. 5th ed. London: Staples Press, 1986 (p. 268).
[4] Goodkind JR. J Prosth Dent 1970;24:662.
[5] Haque E, Armeniades CD. Polym Engng Sci 1986;26(21):1524.
[6] Kelly P, Akelah A, Qutubuddin S, Moet A. J Mater Sci 1994;29:2274.
[7] Theng BKG. Clays Clay Miner 1982;30(1):1.
[8] Usuki A, et al. US Patent 4,889,885; 1989.
[9] Giannelis EP. Appl Organomet Chem 1998;12:675.
[10] Wang Z, Pinnavaia TJ. Chem Mater 1998;10:3769.
[11] Agag T, Koga T, Takeichi T. Polymer 2001;42(8):3399.
[12] Kato C, Kuroda K, Takahara H. Clays Clay Miner 1981;29(4):294.
[13] Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T, Kamigaito O. J Mater Res 1993;8(5):1174.
[14] Chen JC, Lacefield WR, Castleberry DJ. Dent Mater 1988;4:20.
[15] Sykora O, Sutow EJ. J Prosth Dent 1997;77(2):205.
[16] Yeung KC, Chow TW, Clark RK. J Dent 1995;23(4):245.