

## Effect of Incorporation of Nanoclay on the Properties of Heat Cure Denture Base Material: An *In vitro* Study

### Abstract

**Purpose:** The aim of the study was to evaluate the effect of incorporation of organically modified nanoclay in 1%, 3%, and 5% by weight on the flexural strength, surface hardness, and linear polymerization shrinkage of heat cure denture base material. **Materials and Methods:** One hundred and twenty specimens of heat-polymerized acrylic resin were fabricated. The specimens were divided into four groups ( $n = 10$ ) coded I to IV. Group I was the control group (unmodified acrylic resin specimens). The specimens of the remaining three groups were reinforced with nanoclay (organically modified montmorillonite) nanoparticles to achieve loadings of 1%, 3%, and 5% by weight. The resulting nanocomposites were subjected to mechanical testing and were characterized using X-ray diffraction, scanning electron microscope, and transmission electron microscope. **Results:** The statistical analysis showed that there was no significant increase in flexural strength within and between the groups. The most significant increase in surface hardness was observed between Group I (control) and Group II (1% nanoclay). Linear polymerization shrinkage of the specimens showed a significant decrease in the control and all the experimental groups. **Conclusion:** Addition of 1 wt% nanoclay to polymethyl methacrylate heat cure denture base material could enhance the surface hardness and reduce the linear polymerization shrinkage of the resin. However, there was no significant increase in flexural strength of the resulting nanocomposite.

**Keywords:** Linear polymerization shrinkage, nanoclay, nanocomposite, polymethyl methacrylate, surface hardness

### Introduction

Over the centuries, a variety of materials have been used for denture construction. Polymethyl methacrylate (PMMA), since its introduction in 1930, has dominated the denture base arena for over 85 years. To date, up to 95% of dental prosthesis are composed of PMMA which is due to several reasons such as esthetics, ease of processing, stability in the oral environment, biocompatibility, and easy for patients to maintain oral hygiene. However, few important disadvantages are poor strength properties, low abrasion resistance, and polymerization shrinkage.

Polymer nanotechnology represents a new field of nanoscience. Polymer nanocomposite attracted great attention, especially because of their unexpected hybrid properties that are synergistically derived from the two components. Recently, much attention has been directed toward

the incorporation of inorganic nanoparticles into PMMA to improve its properties. Nanofillers such as clay, silver, zirconium oxide, and calcium carbonate have been incorporated into PMMA in order to bypass the shortcomings of PMMA.<sup>[1]</sup>

Organically modified montmorillonite (OMMT) is one of the nanomaterials incorporated into polymer because of its excellent biocompatibility and esthetics. The nanosized clay has been used to derive nanocomposites with high hardness, tensile, fatigue, and impact strength. However, there are insufficient data evaluating the flexural strength and polymerization shrinkage of the resulting nanocomposite. This study was designed to evaluate the effect of incorporation of organically modified nanoclay in 1%, 3%, and 5% by weight on the flexural strength, surface hardness, and linear polymerization shrinkage of heat cure denture base material. The null hypothesis was that there would be no effect on incorporation of the nanofiller on the properties of heat cure denture base material.

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## Materials and Methods

Organophilic montmorillonite (Cloisite 30B Nanoclay, Southern Clay Products, India) was added in 1, 3, and 5% by weight to one commercial type of PMMA powder (Orthoplast Heat Cure Denture Base Material, India) to form PMMA-MMT nanocomposite. One hundred and twenty specimens of heat-polymerized acrylic resin were fabricated. The specimens were divided into four groups ( $n = 10$ ) coded I to IV. Group I was the control group (unmodified acrylic resin specimens). The specimens of the remaining three groups were reinforced with nanoclay (OMMT) nanoparticles to achieve loadings of 1%, 3%, and 5% by weight.

Metal stainless steel dies were prepared as per (ADA) American dental association specification no. 12 for denture base resins (1999) in specified length, width, and thickness, respectively. These dies are used for mold fabrication which is used to pack acrylic resin for specimen fabrication.

- i. Flexural strength: Bar-shaped specimen with 65 mm × 10 mm × 2.5 mm
- ii. Surface hardness: Bar-shaped specimen with 30 mm × 30 mm × 3 mm
- iii. Linear polymerization shrinkage: Bar-shaped specimen with 65 mm × 10 mm × 2.5 mm. A linear indentation is made which is connected by the intersection of a point half the width (0.5 mm) and 5 mm from both ends of the specimen, measuring about 55 mm.

OMMT was incorporated into PMMA by *in situ* suspension polymerization [Table 1]. Nanoclay nanofiller is added to the monomer using Probe Sonication apparatus at 120 W, 60 KHz for 3 min. Modified monomer is mixed with polymer until dough stage is formed. Acrylic resin specimens were processed by compression molding technique and polymerized using short curing cycle (74°C for 2 h and then at 100°C for 1 h). After polymerization, the flasks are allowed for slow bench cooling for 30 min and then immersed in water bath for 15 min at room temperature before deflasking. The specimens are trimmed and polished using routine finishing and polishing techniques. The resulting nanocomposite was then subjected to mechanical testing which was analyzed in accordance with ADA, American Society for Testing and Materials (ASTM), and (ISO) International Organization for Standardization standards.

Flexural strength was analyzed using universal testing machine (Instron 3365, UK) by three-point loading test. The distance between the centers of support is 50 mm. A load of 1 Newton is applied on the center of the specimen with a crosshead speed of 0.5 mm/min. The maximum load before fracture is measured. The flexural strength of the specimen is calculated using the standard relation. The measuring unit (S. I unit) is Mega-Pascal (MPa).

$$S = \frac{3LP}{2WT^2}$$

S = Flexural strength

P = Maximum load before fracture

L = Distance between supports

W = Width of the specimen (10 mm)

T = Thickness of the specimen (2.5 mm)

Surface hardness was determined using Shore D durometer (Instron, USA). The instrument consists of a blunt-pointed indenter 0.8 mm in diameter that tapers to a cylinder 1.6 mm. The indenter is attached to a scale that is graduated from 0 to 100 units. The method is to press down firmly and quickly on the indenter and record the maximum reading as the Shore D hardness. Measurements are taken directly from the scale reading. Five measurements should be taken on different areas of each specimen, and an average of five readings is calculated.

Linear polymerization shrinkage was analyzed by taking linear measurement of the indentation made in the specimen using a digital vernier caliper (Aerospace, India) using the relation:

$$\text{Polymerization Shrinkage (\%)} = \frac{D_1 - D_2}{D_1}$$

$D_1$  – Linear dimension before polymerization

$D_2$  – Linear dimension after polymerization

A specimen from each group other than the control group was characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), and wide-angle X-ray diffraction (XRD) for the purpose of studying the microstructure of PMMA-OMMT nanocomposite. One-way ANOVA and *post hoc* Bonferroni tests were used for analyzing the data.

## Results

In this study, the comparison of flexural strength, surface hardness, and linear polymerization shrinkage was done between PMMA specimens and PMMA-OMMT nanocomposites in different weight percentages of nanoclay [Table 2]. The highest flexural strength was recorded by Group II (1% wt nanoclay) which is equal to 72.91 MPa. The lowest mean value was recorded by Group I (control) which is equal to 71.37 MPa. The highest surface hardness was recorded by Group II (1% wt nanoclay) which is equal to 84.50 Shore D Hardness. The lowest mean value was recorded by Group I (control) which is equal to 81.60 Shore D Hardness. The highest linear polymerization shrinkage was recorded by Group I (control)

**Table 1: Proportioning of nanoclay, polymer, and monomer for sample preparation**

Percentage by weight	Nanoclay (g)	Polymer (g)	Monomer (ml)
0	0	16	8
1	0.160	16	8
3	0.480	16	8
5	0.800	16	8

group) which is equal to 2.12%. The lowest mean value was recorded by Group I (1% wt nanoclay) which is equal to 0.82% [Figure 1]. The results of one-way ANOVA showed a significant difference between the groups for surface hardness and linear polymerization shrinkage of the nanocomposite [Table 3]. The flexural strength test showed no significant difference between the groups. The *post hoc* Bonferroni tests did not show any significant difference between any of the groups for flexural strength. However, for surface hardness test, there were significant differences only between Group I (control) and Group II (1% nanoclay) and between Group II (1% nanoclay) and Group IV (5% nanoclay). Regarding linear polymerization shrinkage, the *post hoc* Bonferroni tests showed significant differences between the control and experimental groups, but there was no significant difference between the experimental groups.

The fractured surface of the specimens following mechanical testing was examined and photographed with SEM. Three specimens, representing the experimental groups, were sputter-coated with gold (JEOL JFC 1600 Auto Fine Coater, Tokyo, Japan) to a thickness of approximately 10  $\mu\text{m}$  in vacuum evaporator to enhance image resolution. SEM observation was conducted at 15 KV using JEOL, JSM-6390, USA. A homogeneous distribution of nanoparticles within the PMMA matrix was observed in specimens reinforced with 1 wt% nanoclay. As the concentration of nanoclay increased to 3 and 5 wt%, the agglomeration of nanoclay particles was seen in some areas within the resin matrix with increasing concentrations of nanoclay [Figure 2].

Wide-angle X-ray diffractometer (X'PERT PRO-PANalytical MPD, the Netherlands) with Cu-K $\alpha$  radiation ( $\lambda = 0.154$ ) at a power of 45 kV  $\times$  30 mA was used for XRD analysis. The sharp peak corresponding to the (001) plane of the nanoclay nanoparticles appears at 4.78°. According to Bragg's equation =  $2 d \sin \theta$ , the d001 (d-spacing) is 18.468 Å. The sharp peak corresponding to the (001) plane of the 1, 3, and 5 wt% MMT appears at 2.44°, 2.38°, and 2.40°, respectively. According to Bragg's equation, the d001 (d-spacing) is 36.17 Å, 36.98 Å, and 36.66 Å, respectively. The results indicate that there is an increase in intergallery spacing of MMT. However, the intensity and concentration of the diffraction peaks corresponding to the experimental groups were progressively reduced when compared with nanoclay nanoparticles which reveal the formation of exfoliated nanocomposites. The PMMA-MMT nanocomposite diffractogram is characteristic for an amorphous polymer [Figure 3].

The microstructure of the nanocomposites was characterized by transmission electron microscopy (TEM), using JEOL-JEM 2100 with 2000 kV accelerating voltage. The samples for TEM were cut into 60-nm thick sections with a diamond knife. The TEM images indicate the formation of exfoliated PMMA/MMT nanocomposites [Figure 4].

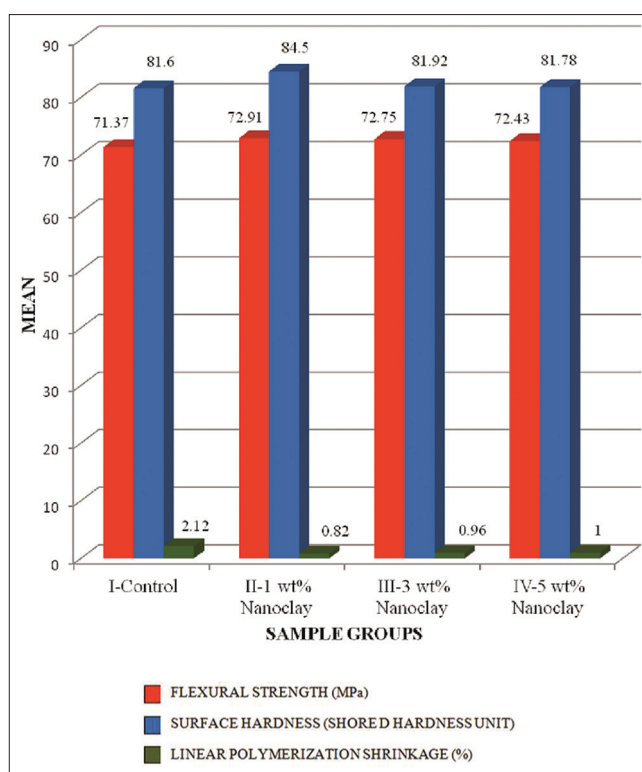


Figure 1: Summary of comparative evaluation of properties of samples in different groups

Table 2: Flexural strength, surface hardness, and linear polymerization shrinkage values of the different samples (mean $\pm$ standard deviation)

Groups	Flexural strength	Surface hardness	Linear polymerization shrinkage
I (control)	71.37 $\pm$ 6.47	81.60 $\pm$ 2.72	2.12 $\pm$ 1.28
II (1% nanoclay)	72.91 $\pm$ 6.04	84.50 $\pm$ 1.64	0.82 $\pm$ 0.43
III (3% nanoclay)	72.75 $\pm$ 5.38	81.92 $\pm$ 1.95	0.96 $\pm$ 0.50
IV (5% nanoclay)	72.43 $\pm$ 4.06	81.78 $\pm$ 1.99	1.00 $\pm$ 0.50

## Discussion

The material most commonly used for the fabrication of removable dental prosthesis is PMMA. This material is not ideal in every aspect. It is the combination of virtues rather than one single desirable property that accounts for its popularity and usage. Despite its popularity, it is still far from ideal in fulfilling the physical and mechanical requirements of prosthesis. Recent advancements in the field of dental materials and the development of novel forms of denture base materials have enabled acrylic denture base resins to overcome some of these drawbacks. Polymers reinforced with a small amount of MMT clay have attracted research interest in the past decade. The aim of this study was to evaluate the effect of incorporation of organically modified nanoclay in 1%, 3%, and 5% by weight on the flexural strength, surface hardness, and linear polymerization shrinkage of heat cure denture base material.



**Table 3: One-way ANOVA table for flexural strength test, surface hardness, and linear polymerization shrinkage**

Property	Groups	Sum of squares	Df	Mean square	F	P	Significance
Flexural strength	Between groups	21.140	3	7.047	0.235	0.871	Nonsignificant
	Within groups	1078.924	36	29.970			
	Total	1100.064	39				
Surface hardness	Between groups	56.548	3	18.849	4.197	0.012	Significant
	Within groups	161.672	36	4.491			
	Total	218.220	39				
Linear polymerization shrinkage	Between groups	10.894	3	3.631	6.180	0.002	Significant
	Within groups	21.154	36	0.588			
	Total	32.048	39				

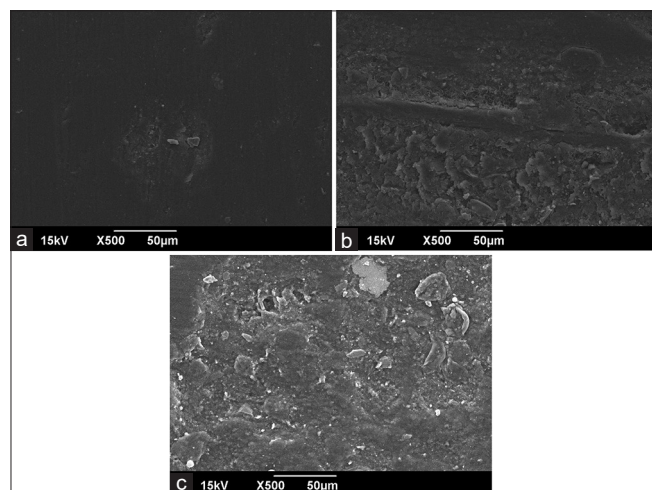


Figure 2: Scanning electron microscope examination of polymethyl methacrylate-organically modified montmorillonite nanocomposite magnification ( $\times 500$ ). (a) 1 wt% of nanoclay. (b) 3 wt% of nanoclay. (c) 5 wt% of nanoclay

Cloisite 3OB (also referred to as organoclay, nanoclay, and OMMT) is a quaternary ammonium salt-modified natural montmorillonite polymer additive. The clay consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers (2:1 ratio). It has been used as an additive in plastics to improve various physical properties, such as reinforcement, heat deflection temperature, coefficient linear thermal expansion, and barrier properties.

Nanoclay is an off-white-colored powder that is not expected to adversely affect the esthetic appearance of the PMMA denture base. It has been reported to be a biocompatible material and has exhibited improved physical and mechanical properties.<sup>[2]</sup> Moreover, it is easily available and has low cost, well-known intercalation/exfoliation chemistry, high surface area ( $750 \text{ m}^2/\text{g}$ ), and high surface reactivity. Accordingly, these particles were selected to improve the shortcomings of PMMA. The method of preparation of PMMA-MMT nanocomposite in this study was *in situ* suspension polymerization which has always been applied in dentures.

Flexural strength (bending strength or modulus of rupture) is defined as the force per unit area at the instant of fracture

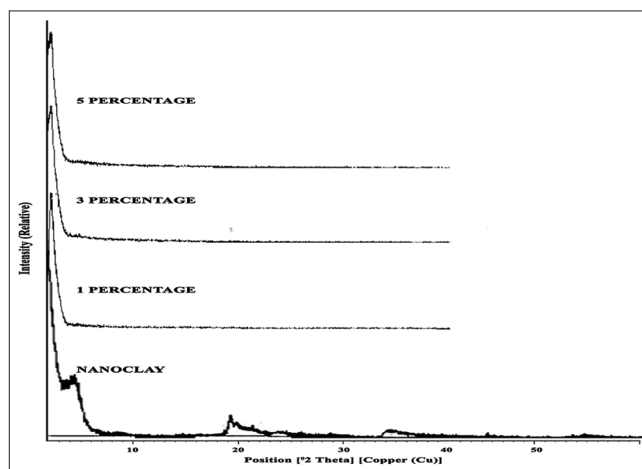
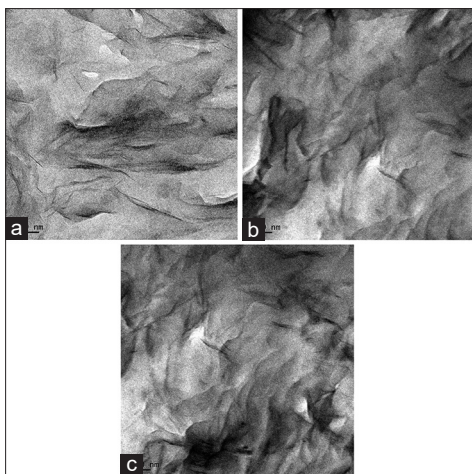


Figure 3: Comparative evaluation of X-ray patterns of organically modified montmorillonite and polymethyl methacrylate-organically modified montmorillonite nanocomposite

in a test specimen subjected to flexural loading.<sup>[3]</sup> The ultimate flexure strength of a material reflects its potential to resist catastrophic failure under a flexural load. An acrylic resin capable of sustaining higher flexure in combination with high resistance to cyclic loading may be less prone to clinical failure.<sup>[4]</sup> According to ISO 1565, flexural strength of acrylic resin, processed and cured with any method, should not be less than 65 MPa.<sup>[5]</sup> The results of this study demonstrated that the mean flexural strength of all specimens tested in the current work was higher than that required by ISO 1565. An important goal in application of fillers to the polymer is improvement in the mechanical properties, and therefore, fillers are commonly called as reinforcement agents.<sup>[6]</sup> The mechanism of the reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher module. When rigid filler is added to the soft polymer matrix, it will carry the major portion of applied load to the polymer matrix under stress conditions, if the interfacial interactions between filler and matrix are adequate.<sup>[7-9]</sup> Therefore, the larger the interface between filler and matrix, and also more strong interfacial interactions, the greater the reinforcement effect will be. Dramatic improvements in the mechanical properties of nanocomposites are achieved even at very lower nanoclay additions.<sup>[10]</sup> Various authors have



**Figure 4: Transmission electron microscopy examination of polymethyl methacrylate-organically modified montmorillonite nanocomposite-magnification (100 nm). (a) 1 wt% of nanoclay. (b) 3 wt% of nanoclay magnification. (c) 5 wt% of nanoclay magnification**

proposed that the addition of nanofillers to the resin matrix can improve the mechanical properties of resin-based materials.<sup>[11,12]</sup> Based on Li *et al.*'s and Adabo *et al.*'s studies, a significant enhancement was observed in flexural strength by addition of small amounts of nanofillers, and then, the strength decreased subsequently by increasing the filler to higher amounts.<sup>[13,14]</sup> In Bowen's study, the results showed that by increasing the amount of nanoparticles more than a particular point, flexural strength will face a significant reduction.<sup>[15]</sup> The results of these studies were in agreement with the present study.

Hardness is defined as the resistance of a material to plastic deformation, which is typically produced by an indentation force. Hardness is indicative of the ease of finishing of a structure and its resistance to in-service scratching. Finishing and polishing is important for esthetic purposes, and if scratches are present, it can compromise fatigue strength and lead to premature failure of the prosthesis. Shore D hardness test methods were performed in accordance with ASTM D 2240 and (DIN) Deutsches Institut für Normung 53 505 for rubber and hard plastics.<sup>[16]</sup> The surface hardness of 5% Cloisite Nylon 6 is 83 Shore D Hardness. The results of this study demonstrated that the mean surface hardness of Group II specimens (1 wt% nanoclay) tested in the current work was higher than that reported for 5% Cloisite Nylon 6. The other specimens tested showed lower values as compared to 5% Cloisite Nylon 6, but there was a significant increase in surface hardness when compared with the control group. The enhancement of hardness is related to the reinforcing effect of filler particles, as well as to the orientation and high aspect ratio of clay platelets.

Dimensional stability of dentures during processing and during function in mouth is of considerable importance as regards to fit and satisfaction to the patient. 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. Polymerization shrinkage and dimensional change of denture bases during resin polymerization are unavoidable and have been well-documented.<sup>[17]</sup> The PMMA specimens in the control group showed the highest amount of linear polymerization shrinkage. Inclusion of MMT in the composite led to a pronounced decrease in the recorded values due to stacked silicate sheet structure and low thermal expansion coefficient of MMT. The decrease in linear polymerization shrinkage in nanocomposite containing 1 wt% nanoclay correlates with the study made by Salahuddin and Shehata *et al.* in 2001 and Collard *et al.* in 1991.<sup>[18,19]</sup> The swelling characteristics of MMT as well as the interaction of MMT with the resin during cure give rise to an increase in free volume, thereby contributing to a decrease in the linear polymerization shrinkage of the nanocomposite.

In the preparation of a polymer/clay nanocomposite, it is important to know the degree of intercalation/exfoliation and its effect on the nanocomposite properties. SEM, XRD, and TEM are common characterization techniques employed for this purpose.

The SEM provides images of surface features associated with a sample. The purity of the clay and the homogeneity of dispersion of the clay also affect the properties of nanocomposite. The increase in flexural strength and surface hardness of the nanocomposite containing 1 wt% may be due to the homogeneous distribution of nanoparticles within the acrylic resin matrix as seen in SEM examination. The decline in these properties in 3 wt% and 5 wt% may be attributed to the agglomeration of nanoparticles. This finding correlates with the studies made by Ruyter in 1980 and Salahuddin in 2009.<sup>[20,21]</sup>

XRD provides almost quantitative and TEM provides qualitative information about the exfoliation and d-spacing of clay layers in the polymer matrix compared to that in pure clay material. XRD results for organoclay reveal d-spacing of 18.46 Å. The PMMA-MMT nanocomposites with 1 wt% MMT, 3 wt% MMT, and 5 wt% MMT reveal d-spacing of 36.17 Å, 36.98 Å, and 36.66 Å, respectively. The results indicate an increase in the intergallery spacing of MMT. No significant peak was found for organoclay and PMMA-MMT nanocomposites, which means that all nanocomposites obtained from the *in situ* suspension polymerization were exfoliated. It also indicates the formation of an amorphous polymer matrix.

In the TEM micrographs, the darker lines in the brighter matrix show the clay layers because of the presence of heavier elements (aluminum, silicates, and oxygen) in the composition of clay layers compared to lighter atoms (carbon, hydrogen, and nitrogen) present in the polymer matrix or interlayer spacing of clay sheets.

The results indicate that an exfoliated PMMA/MMT nanocomposite has been prepared by *in situ* suspension polymerization.

## Conclusion

Within the limitations of this study, the following conclusions were drawn:

1. PMMA/MMT nanocomposites were successfully prepared by *in situ* suspension polymerization
2. Reinforcement of dentures with 1 wt% nanoclay nanofillers has shown significant improvements in increasing surface hardness and decreasing linear polymerization shrinkage of PMMA-MMT nanocomposite.

Further, processing of PMMA-MMT denture bases seems to be technique sensitive and difficult to fabricate in the dental laboratory. Although improved mechanical properties make nanoclay reinforcement of dentures attractive, further research is needed to address the other mechanical properties as well as the biological effects of these reinforced materials in the long run.

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## Conflicts of interest

There are no conflicts of interest.

## References

1. Wang X, Su Q, Hu Y, Wang C, Zheng J. Structure and thermal stability of PMMA/MMT nanocomposites as denture base material. *J Therm Anal Calorim* 2014;115:1143-51.
2. Zheng J, Su Q, Wang C, Cheng G, Zhu R, Shi J, et al. Synthesis

and biological evaluation of PMMA/MMT nanocomposite as denture base material. *J Mater Sci Mater Med* 2011;22:1063-71.

3. Stafford GD, Bates JF, Huggett R, Handley RW. A review of the properties of some denture base polymers. *J Dent* 1980;8:292-306.
4. Diaz-Arnold AM, Vargas MA, Shaull KL, Laffoon JE, Qian F. Flexural and fatigue strengths of denture base resin. *J Prosthet Dent* 2008;100:47-51.
5. Uzun G, Hersek N. Comparison of the fracture resistance of six denture base acrylic resins. *J Biomater Appl* 2002;17:19-29.
6. Jiang L, Lam YC, Tam KC, Chua TH, Sim GW, Ang LS. Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate. *Polymer* 2005;46:243-52.
7. Tortora M, Vittoria V, Galli G, Ritrovati S, Chiellini E. Transport properties of modified montmorillonite/poly (caprolactone) nanocomposites. *Macromol Mater Eng* 2002;287:243-9.
8. Tortora M, Gorrasi G, Vittoria V, Galli G, Ritrovati S, Chiellini E. Structural characterization and transport properties of organically modified montmorillonite/polyurethane nanocomposites. *Polymer* 2002;43:6147-57.
9. Gorrasi G, Tortora M, Vittoria V, Pollet E, Lepoittevin B, Alexandre M. Vapour barrier properties of polycaprolactone montmorillonite nanocomposites: Effect of clay dispersion. *Polymer* 2003;44:2271-9.
10. LeBaron PC, Wang Z, Pinnavaia TJ. Polymer-layered silicate nanocomposites: An overview. *Appl Clay Sci* 1999;15:11-29.
11. Su S, Wilkie CA. Exfoliated poly (methyl methacrylate) and polystyrene nanocomposites occur when the clay cation contains a vinyl monomer. *J Polym Sci Part A Polym Chem* 2003;41:1124-35.
12. Su S, Jiang DD, Wilkie CA. Methacrylate modified clays and their polystyrene and poly (methyl methacrylate) nanocomposites. *Polym Adv Technol* 2004;15:225-31.
13. Li Y, Swartz M, Phillips R, Moore B, Roberts T. Materials science effect of filler content and size on properties of composites. *J Dent Res* 1985;64:1396-403.
14. Adabo GL, dos Santos Cruz CA, Fonseca RG, Vaz LG. The volumetric fraction of inorganic particles and the flexural strength of composites for posterior teeth. *J Dent* 2003;31:353-9.
15. Bowen RL. Effect of particle shape and size distribution in a reinforced polymer. *J Am Dent Assoc* 1964;69:481-95.
16. Bona AD, Bello YD, Sartoretto SC. Use of standards in papers published in dental journals. *Braz Dent J* 2012;23:471-6.
17. Takamata T, Setcos JC. Resin denture bases: Review of accuracy and methods of polymerization. *Int J Prosthodont* 1989;2:555-62.
18. Salahuddin N, Shehata M. Polymethylmethacrylate-montmorillonite composites: Preparation, characterization and properties. *Polymer* 2001;42:8379-85.
19. Collard SM, Karimzadeh A, Smith LT, Parikh U. Polymerization shrinkage, impact strength and roughness of montmorillonite-modified denture base resins. *Am J Dent* 1991;4:285-90.
20. Ruyter IE. Release of Formaldehyde from denture base polymers. *J Acta Odontol Scand* 1980;38:17-27.
21. Salahuddin N. The effect of polyoxypropylene montmorillonite intercalates on polymethylmethacrylate. *Polym Compos* 2009;30:13-21.