

# Using Organic Montmorillonite to Reinforce the Structure and Flexural Property of Denture Base Nanocomposites

Zhi-An Li,<sup>1,2</sup> Lijian Liu,<sup>1</sup> Qun Xiao<sup>2</sup>

<sup>1</sup>Key Laboratory of Biomedical Polymer, Ministry of Education, Department of Polymer Science, College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, People's Republic China

<sup>2</sup>Key Laboratory of Oral Biomedical Engineering, Ministry of Education, School and Hospital of Stomatology, Wuhan University, Wuhan 430079, People's Republic China

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**ABSTRACT:** The denture bases nanocomposites were prepared by adding organic montmorillonite (OMMT) into poly(methyl methacrylate) matrix. The resulting composites were characterized by XRD, TEM, and ISTRON 3365 flexural strength testing systems. One-way analysis of variance and Tukey's test were used to compare the difference in flexural strength and flexural modulus. The results showed the formation of exfoliated-intercalated and intercalated denture base nanocomposite when the content of OMMT was 3 wt % and 5 wt % in the powder of denture base resin, respectively. The maximum ultimate flexural strength was observed in denture base nanocomposite

containing 3 wt % of OMMT and flexural strength decreased with further increases of OMMT content. The flexural modulus of denture base nanocomposite increased continually with OMMT content increasing from 1 wt % to 10 wt %. Significant difference in both flexural strength and flexural modulus was observed between the nanocomposites with 3 wt % OMMT and controls ( $n = 5$ ,  $P < 0.05$ ). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3548–3553, 2009

**Key words:** nanocomposite; denture base resin; flexural strength; montmorillonite

## INTRODUCTION

Poly(methyl methacrylate) (PMMA) has been commonly used as a denture base material due to its unique combination property. However, when PMMA denture bases were used by patients, repeated chewing stress from mouth action and impact force from accidental drop might result in brittle fracture or cracks of the bases.<sup>1</sup> Further improvements in the mechanical property of PMMA denture base material are still needed.

To improve the mechanical property, a variety of fibers such as glass fibers,<sup>2–6</sup> woven glass fibers,<sup>7–9</sup> carbon fibers,<sup>10</sup> aramid fibers,<sup>11,12</sup> and ultra high-molecular weight polyethylene fibers<sup>13,14</sup> were used to improve the strength and roughness of PMMA denture bases. The incorporation of metal wires,<sup>14–18</sup> glass fiber sheet,<sup>19</sup> and glass flake<sup>20</sup> was also investigated. Unfortunately, the disadvantage of metal wires and nets, carbon fibers and aramid fibers is poor esthetics. The ultra high-molecular weight polyethylene fibers do not adhere to PMMA matrix.<sup>21</sup> Good esthetics could be achieved when glass fibers, woven glass fibers, and glass flake were used as

reinforcement, but it is very difficult to incorporate them accurately into denture resin<sup>22</sup> under tension because the oral shape is complex and the dentures are custom-made. Recently, more attention has been paid on clay-polymer matrix nanocomposites, which include nanoscale clay dispersion (typically 1–100 nm) in a matrix, especially on clay-PMMA matrix nanocomposites.<sup>23–28</sup> Because of the strong interfacial interaction between nanoscale clay and polymer matrix, the mechanical property of the nanocomposites was significantly improved. In addition, nanocomposites also showed lower thermal expansion coefficient and high solvent resistance than conventional composites. These advantages of clay-polymer make it promising in application as dental prosthodontics materials, but a few studies have focused on it. Salahuddin and Shehata<sup>29</sup> reported that the warpage and line dimension changes of denture base significantly decrease when organic montmorillonite by modified dimethyl benzyl hydrogenated tallow ammonium chloride was added into powder of denture base resin. However, the structure and mechanical properties of this denture base composite were not further investigated.

In this study, organic montmorillonite (OMMT) from modified cetyltrimethylammonium bromide was dispersed into the PMMA matrix to improve the structure and flexural strength of the PMMA

Correspondence to: Z.-A. Li (lizhian2001@yahoo.com.cn).

**TABLE I**  
The Component of PMMA/O-MMT Mixture Powder

	Control	I	II	III	IV
PMMA (g)	100	99.0	97.0	95.0	90.0
O-MMT (g)	0	1.0	3.0	5.0	10.0

denture base nanocomposite without declining the esthetics and handling of denture base resin.

## MATERIALS AND METHODS

### Preparation of organic montmorillonite

Twenty parts (by weight) of montmorillonite-sodium ( $\text{Na}^+$ -MMT) (300-mesh, powder) obtained from Lingan montmorillonite Co. (Hangzhou, China.) was dispersed into 400 parts of distilled water.<sup>24</sup> The suspension was obtained by vigorously stirring the mixture and pH of the suspension was adjusted to 4 using an HCl solution. Ten parts of cationic exchanger cetyltrimethylammonium bromide obtained from Shanghai chemical Co. (Shanghai, China) was added to the suspension. The resulting mixture was stirred for 4 h at 85°C and filtered. The deposition was repeatedly washed using distilled water until free bromide ions were removed completely, i.e., when the filtrate showed a negative reaction to a 0.1M  $\text{AgNO}_3$  solution. The purified deposition was vacuum dried until a constant weight was reached. The final organic montmorillonite product (OMMT) was ball-milled and sieved 200 mesh for next procedures.

### Preparation of experimental denture bases

The organic montmorillonite was mixed with poly(methyl methacrylate) powder ( $M_n = 350,000$ ; 120 mesh) obtained from Dongfanhong chemical (Chongqing, China.) in various mixture ratios as described in Table I. The dough for molding was prepared by completely mixing 2.0 g OMMT/PMMA powder with 1 mL methyl methacrylate (MMA) (from Mitsubishi Chemical Company, Tokyo, Japan). Molding was implemented by pressing the dough into a dual-column. Each column has a dimension of 64.0 mm  $\times$  10.0 mm  $\times$  3.0 mm ( $L \times W \times H$ ). The molded bases were placed in a water bath and processed by heating the water to 100°C within 1 h and kept boiling for 2 h. After cooling down, the bases were polished with 200#, 400#, and 800# silicon carbide paper under lubrication of running water. Their final dimensions were 64.0 mm  $\times$  10.0 mm  $\times$  3.0 mm, with tolerance of  $\pm 0.05$  mm. Five samples were prepared for every composition described in Table I. As shown in Figure 1,

the final samples had a favorable appearance and transparency.

### X-ray diffraction analysis

X-ray diffraction (XRD) analysis was performed using a Rigaku D/max- $\gamma_A$  analyzer at room temperature (Cu  $K\alpha$  radiation,  $\lambda = 0.154178$  nm, scanning range: 0.7°–10°, scanning rate: 2°/min).

### Transmission electron microscopes examination

Using an ULTRACUT-U from LEICA Co. (Bensheim, Germany), a 60–80 nm thick section of specimen was cut from each sample and analyzed with transmission electron microscopes (TEM). The microstructure image analysis to these specimens was implemented using a JEM2011 TEM from JEOL Co. (Tokyo, Japan) with a 200 kV acceleration voltage.

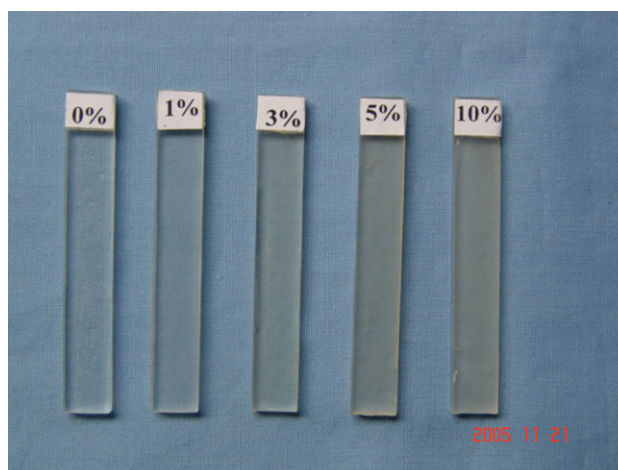
### Measurement of flexural properties

The flexural strength and flexural modulus were measured using a universal testing machine (INSTRON 3365). A 3-point loading method recommended by ISO1567-1999 was used with 5 mm/min cross-head speed and 50 mm span length. The flexural strength ( $F_s$ ) and the flexural modulus ( $E$ ) were calculated from eqs. (1) and (2), respectively.

$$F_s = \frac{3Fl}{2bh^2} \text{ (Mpa)} \quad (1)$$

$$E = \frac{F_1 l^3}{4bh^3 d} \text{ (Mpa)} \quad (2)$$

Where,  $F$  is the maximum load,  $l$  is the span length,  $b$  is the width of the test specimen,  $h$  is the thickness of the test specimen, and  $d$  is the liner deflection



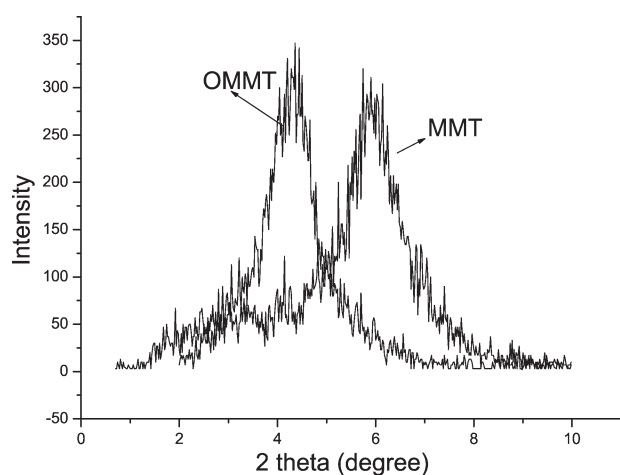
**Figure 1** The photograph of specimens. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

corresponding to load  $F_1$ . Five tests ( $n = 5$ ) were carried out for each composition group (control, I, II, III, and IV). One-way analysis of variance and Tukey's test were used to compare the difference in flexural strength and flexural modulus.

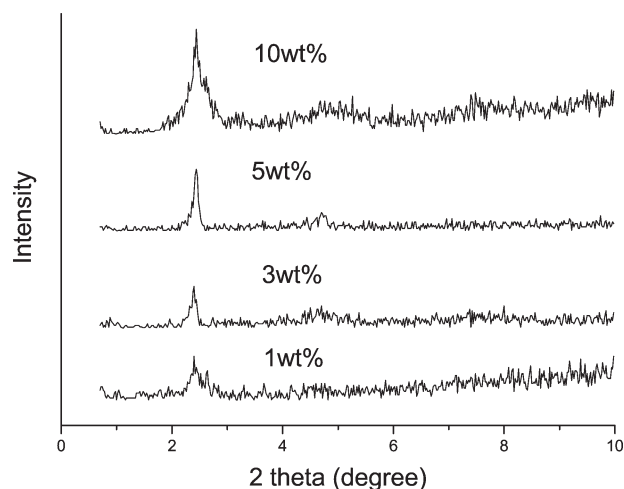
## RESULTS AND DISCUSSION

Montmorillonite (MMT) can be classified as a 2 : 1 layered silicate. Its crystal lattice consists of two-dimensional layers where two silica tetrahedral sheets fuse into an octahedral sheet. These layers self-organize into stacks with a regular Van der Waals gap in between the layers, which is the so-called interlayer or gallery. Isomorphous substitution within the layers generates negative charges that are counterbalanced by cations such as  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . The  $\text{Ca}^{2+}$  or  $\text{Na}^+$  ions residing in the interlayer can be replaced by organic cations such as alkylammonium ions via an ion-exchange reaction. The organic cation input makes the hydrophilic silicate more hydrophobic. As a result, the molecules of monomers and polymers can readily intercalate into the galleries.

Figure 2 is the pattern of MMT and OMMT from modified cetyltrimethylammonium bromide, when cetyltrimethylammonium bromide reacted with  $\text{Na}^+$ -MMT in solutions,  $\text{Na}^+$  ions in the MMT galleries were exchanged by cetyltrimethylammonium ions. The interlayer space of the montmorillonite increased. The shift in the XRD peak toward smaller angle indicates an increase in interlayer space distance (Fig. 2). The interlayer space distance ( $d$ ) is calculated from the observed peak of the angular position  $2\theta$  by Bragg equation  $\lambda = 2d\sin\theta$ . The interlayer space distance of  $\text{Na}^+$ -MMT and OMMT was 1.47 nm ( $2\theta = 6^\circ$ ) and 1.93 nm ( $2\theta = 4.3^\circ$ ), respectively. The slight layer expansion caused by OMMT intercalation resulted in a new basal reflection. The



**Figure 2** XRD patterns of MMT and OMMT.

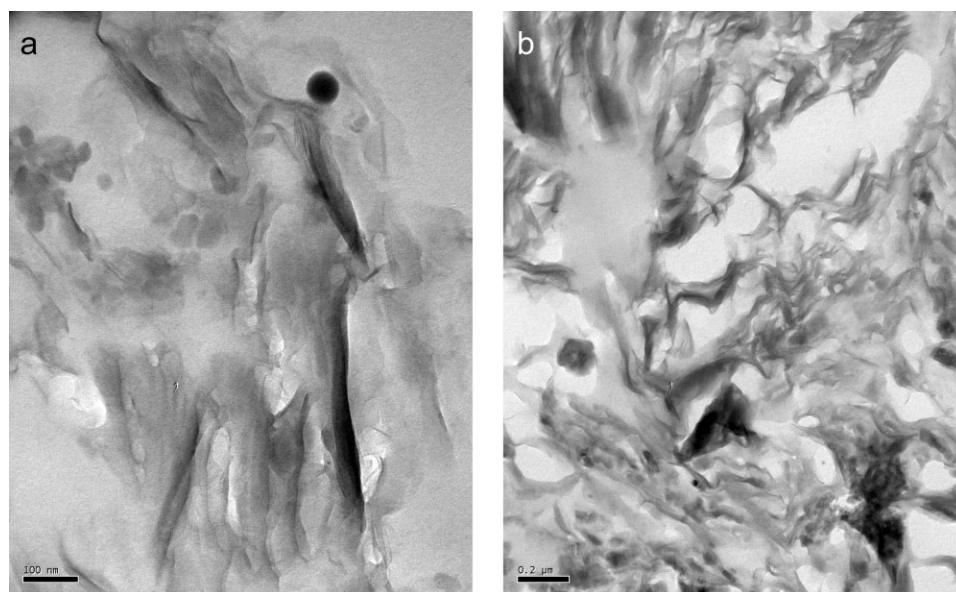


**Figure 3** XRD patterns of denture base nanocomposites.

peak position shifted to 1.93 nm ( $2\theta = 4.3^\circ$ ) from  $\text{Na}^+$ -MMT's 1.47 nm ( $2\theta = 6^\circ$ ), indicating that MMT became organophilic and its basal space increased.

According to the different dispersion ability of clay platelets in a polymer matrix, clay-polymer composites primarily have three types: phase separated (microcomposite), intercalated (nanocomposite), and exfoliated (nanocomposite).<sup>30</sup> After the powder mix with MMA, MMA molecules diffused to OMMT galleries, and this was followed by typical *in situ* polymerization during the heating process, i.e., intercalation polymerization which also released a large quantity of heat. Because the size of PMMA macromolecule chains is much larger than the gallery space of the clay, the MMT interlayer distance may be extended from the growth of PMMA macromolecule chains. Figure 3 is the XRD patterns of PMMA-OMMT denture base composites. For the dental nanocomposites containing 1 to 10% OMMT, the strong plane peaks corresponding to  $d_{001}$  (basal spacing of (001) plane) ( $2\theta = 2.3^\circ$ ) can clearly be seen. Result in two possible types of nanocomposites, one from the partially exfoliated and partially intercalated nanocomposites and the other from intercalated nanocomposites. From Figure 3, after OMMT intercalation, the  $d_{001}$  peak of OMMT shifted to  $2\theta = 2.3^\circ$  from  $2\theta = 4.3^\circ$  as well as the peak intensity enhanced when OMMT increased in the dispersed PMMA matrix. The typical peak intensity of MMT in the PMMA/OMMT nanocomposites is stronger and peak shape is sharper than that of OMMT, indicating that the ordering in the MMT layers was enhanced in the nanocomposites.<sup>24</sup>

TEM images are a useful tool to understand the nanostructure of denture base nanocomposites. Figures 4 and 5 were the TEM photographs obtained from 3% OMMT and 5% OMMT/PMMA nanocomposites, respectively. The bright region represents

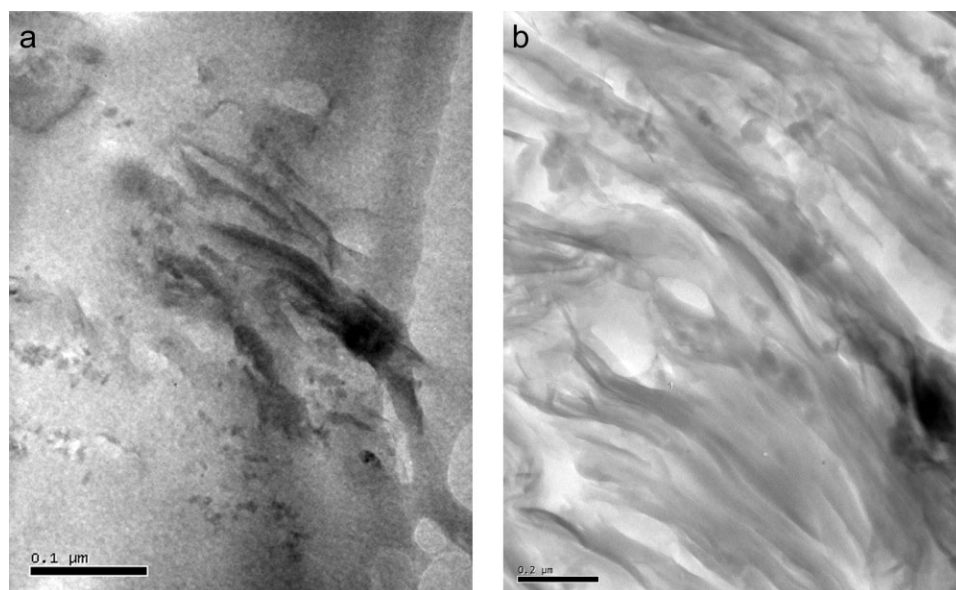


**Figure 4** (a) TEM photograph of denture base nanocomposite of containing 3 wt % OMMT. (b) TEM photograph of denture base nanocomposite of containing 3 wt % OMMT.

the polymer matrix and the dark narrow stripes were resulted from the secondary particles of MMT. The image from 3% OMMT [Fig. 4(a)] reveals the formation of the partially exfoliated and partially intercalated nanocomposites and an oriented collection of parallel silicate sheets with an interlayer spacing of about 3.5 nm interlayer distance. This phenomenon was also observed from XRD analysis ( $2\theta = 2.3^\circ$ ). When OMMT increased up to 5%, the agglomerated clay structures formed and became denser in the PMMA matrix [Fig. 5(a)]. In addition,

Figures 4(b) and 5(b) show that the silicate layers of MMT were of a flexural shape in polymer matrix, suggesting that the nanoscale MMT layers were flexible and could be bent in the polymer matrix. Obviously, the structure of the OMMT-modified PMMA dental base nanocomposites is significantly different from traditional PMMA dental base composites filled with glass fibers that remained straight in the PMMA matrix.<sup>7,31</sup>

Flexural strength is a critical parameter for selecting denture base materials because the denture bases



**Figure 5** (a) TEM images of denture base nanocomposite of containing 5 wt % OMMT. (b) TEM images of denture base nanocomposite of containing 5 wt % OMMT.

**TABLE II**  
Flexural Strengths and Comparative Significance of Denture Base Nanocomposites

Test group	Flexural strength (Mpa)		Comparative significance				
	Mean	SD	Control	I	II	III	IV
Control	71.5	3.6	-	S	HS	NS	HS
I	78.4	4.1	S	-	NS	S	HS
II	82.8	2.7	HS	NS	-	HS	HS
III	72.6	2.2	NS	S	HS	-	HS
IV	60.8	4.6	HS	HS	HS	HS	-

SD, standard deviation; HS, highly significant difference ( $P < 0.01$ ); S, significant difference ( $P < 0.05$ ); NS, no significant difference ( $P > 0.05$ ).

must endure various stresses in the mouth, including tensile, compressive, and shear stresses. Three-point flexural testing is often used to evaluate the mechanical properties of denture base materials.

The data in flexural strength, flexural modulus, and their statistical analysis are summarized in Tables II and III. From ISO 1567-1999, the flexural strength and the flexural modulus of PMMA denture base materials are not less than 65 and 2000 Mpa, respectively. The flexural strength cannot meet the demand of ISO 1567-1999 when the OMMT content is over 10%. Group II has a peak flexural strength and significant difference in flexural strength was found between the control group and Group II ( $P < 0.05$ ). The flexural modulus of all OMMT-containing groups is significantly larger than that of the control group ( $P < 0.05$ ). This indicated that the amount of OMMT in PMMA matrix effect on the flexural strength and flexural modulus.

Figure 6 shows the flexural strength of the OMMT-modified PMMA nanocomposites with different OMMT/PMMA ratios. The ultimate strength of the denture base nanocomposite increased with an increase of OMMT. The maximum strength was

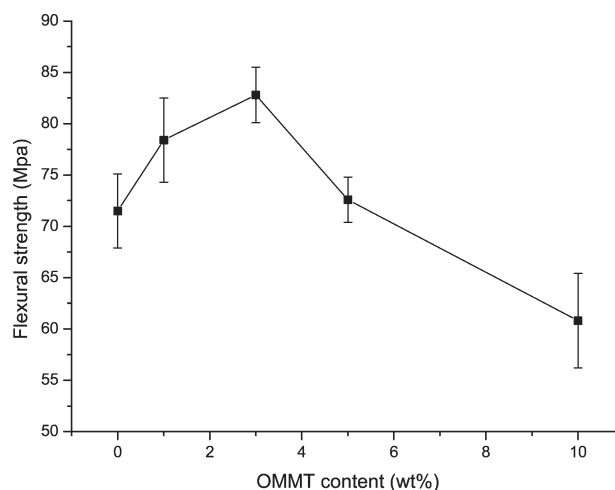
**TABLE III**  
Flexural Moduli and Comparative Significance of Denture Base Nanocomposites

Test group	Flexural moduli (Mpa)		Comparative significance				
	Mean	SD	Control	I	II	III	IV
Control	2384	68	-	S	HS	HS	HS
I	2577	53	S	-	S	HS	HS
II	2748	43	HS	S	-	S	HS
III	2857	62	HS	HS	S	-	S
IV	2989	67	HS	HS	HS	S	-

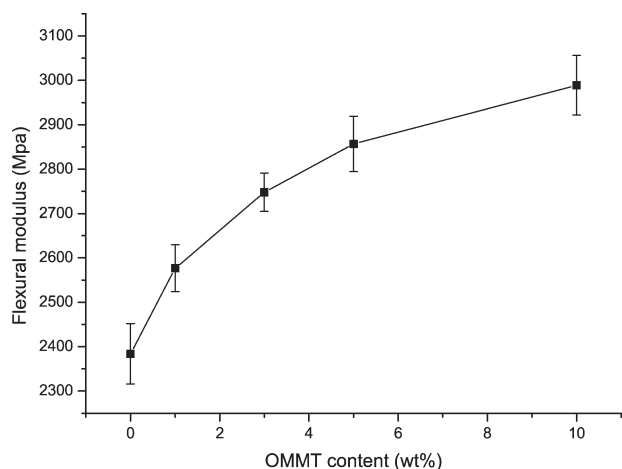
SD, standard deviation; HS, highly significant difference ( $P < 0.01$ ); S, significant difference ( $P < 0.05$ ).

obtained from the 3% OMMT nanocomposites. The ultimate flexural strength of the nanocomposites increased from 71.5 to 82.8 MPa when OMMT increased from 0 to 3%, but further increase ( $>3\%$ ) resulted in a decrease in flexural strength.

MMT is a clay mineral containing stacked silicate sheets  $\sim 1$  nm in thickness and 220 nm in length. The sheet of MMT was uniformly dispersed in the PMMA matrix when OMMT was less than 3%. The exfoliated sheets functioned as short fibers which could absorb the stresses that the base suffered as well as increase the flexural strength of the material. However, further increasing OMMT induced agglomeration and consequently led to the failure of dispersion. From XRD patterns of nanocomposites, the peak intensity versus  $d_{001}$  ( $2\theta = 4.5^\circ$ ) for MMT was found to increase with an increase of OMMT content (Fig. 3). Strong interaction and cross-linking sites were previously observed between MTT layers and PMMA segments.<sup>24,25</sup> The segmental motions of the polymer chains inside the interlayer of montmorillonite were highly restricted by cross-linking reactions. All of these resulted in lower flexural strength. In addition, the study of Fornes and Paul<sup>32</sup> found that silicate sheets of OMMT could serve as nucleating agent at low concentration, 3%, in nylon-6/OMMT nanocomposite but retarded the crystallization of nylon-6 at high concentration around 7%. It may be the one of reasons that cause the flexural strength increase at low concentration (no more than 3%) and the flexural strength decrease further increasing OMMT. The molecular weight of the PMMA matrix also effect on the flexural strength of denture base nanocomposite. But from the view of clay-polymer nanocomposites, some studies<sup>33,34</sup> indicated that in comparison with that of pure PMMA, the molecular weight of the PMMA chains polymerized *in situ* is



**Figure 6** Effects of the OMMT content on flexural strength of denture base nanocomposites.



**Figure 7** Effects of the OMMT content on flexural modulus of denture base nanocomposite.

constant or slightly decreased. The effect of molecular weight of PMMA matrix on the flexural strength is very weak. In short, an agglomeration of MMT sheets and an increase of cross-linking sites result in a lower flexural strength as OMMT content is over 3%.

Figure 7 shows that the modulus keeps increasing when OMMT increases from 1 to 10%. The increase in the flexural modulus was primarily attributable to the high resistance exerted by the organoclay against the plastic deformation, the orientation and the high aspect of the organoclay. Other factors including the cross-linking interaction between MMT sheets and polymer chains as well as the stretching resistance of the oriented backbone of polymer chains in the gallery might also increased the flexural modulus. From Figure 7, when the OMMT content is relatively low, the increase of flexural modulus is more significant. This is because the nanometric secondary particles were easily exfoliated and uniformly dispersed in the PMMA matrix. In this case, the chemical interaction and nanoscale effect play key roles in obstructing the motion of PMMA segments and result in the significant increase in the flexural modulus.

## CONCLUSIONS

This study provided a feasible approach of developing denture base nanocomposites with excellent mechanical properties and operability. OMMT fillers were demonstrated to be effective to reinforce the flexural properties of PMMA matrix dental nano-

composites. The optimal nanocomposites were obtained from the addition of 3% OMMT in the PMMA/OMMT powder. The present PMMA/OMMT denture bases can be potentially used for dental clinics.

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