

# Polymethyl Methacrylate/Montmorillonite Nanocomposite Beads through a Suspension Polymerization-derived Process

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**ABSTRACT:** Polymethyl methacrylate (PMMA) polymer beads with montmorillonite (MMT) were prepared using a suspension polymerization method for applying acrylic bone cements. The polymer beads were characterized by X-ray diffraction and transmission electron microscopy to examine MMT dispersion. The change in the shape and size of the polymer beads due to the preparation conditions, such as stirring speed, degree of polymerization, and concentration of polyvinyl alcohol (PVA) as a suspension stabilizer, and MMT contents, etc. was observed by scanning electron microscopy and particle size analysis. The prepared polymer beads were composed of polymer-intercalated nanocomposites with partially exfoliated MMT layers. The size of

the polymer beads was decreased by increasing the stirring speed. The bead size was decreased with increasing the degree of polymerization and the concentration of PVA molecules. MMT addition into the monomer portion increased the size of the corresponding polymer beads. The bead size was slightly reduced by adding of styrene to the MMA solution. The incorporation of PMMA into monomer portion enlarged the bead size. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2340–2349, 2005

**Key words:** acrylic bone cement; biomaterials; particle size distribution; polycarbonates; nanocomposites; suspension polymerization

## INTRODUCTION

Acrylic bone cements consist of self-curing poly(methyl methacrylate) (PMMA), which are prepared by mixing a liquid component with a solid component. The liquid component is a monomer, typically methyl methacrylate (MMA), which also contains a polymerization activator such as *N,N*-dimethyl-*p*-toluidine (a tertiary amine) and an inhibitor such as hydroquinone to prevent spontaneous polymerization of the monomer. The powder part consists of small spherical polymer beads (approximately 50  $\mu\text{m}$  in diameter) such as PMMA beads, a small amount of a free-radical initiator such as benzoyl peroxide (BPO), and a mineral powder such as barium sulfate or zirconium dioxide, which acts as a X-ray opacifier.

The acrylic bone cements are widely used to fix joint prostheses. Since the work by Charnley in the early 1960s, there are approximately 10 million patients with cemented joint implants.<sup>1</sup> Moreover the cements have been successfully used in vertebroplasty to reinforce the vertebral bones of patients with osteoporosis.

The main advantages of the cements lay in the excellent primary fixation, the fast mechanical augmentation, the load distribution between the implant and the bone, and the fact that the cement allows a fast recovery of the patient. However, 10 to 45%<sup>2,3</sup> of patients who received the cemented joint implants require revision surgery, mainly due to cement fracture.

Various attempts have been made to improve the mechanical properties of the bone cements. The incorporation of reinforcing fibers such as carbon fibers, polymeric fibers, and metallic fibers has been reported.<sup>4–7</sup> However, the flow characteristics of the resulting fiber-reinforced cements are severely compromised, which has led to studies of particulate-filled bone cements. Mixtures with hard particles as reinforcements, such as glass beads and hydroxyapatite, have been examined.<sup>8–12</sup> Alumina particles chemically modified with  $\gamma$ -(trimethoxysilyl)propylmethacrylate were previously examined for use as a radiopacifying filler to simultaneously enhance the mechanical properties and reduce the production of debris and wear particles.<sup>13,14</sup> Other studies have explored ABS rubber particle and polyethyl methacrylate mixtures as a means of enhancing the toughness.<sup>15–17</sup>

Polymer nanocomposites with organophilic montmorillonite (MMT), smectic clay, have been studied extensively because these composites are more effec-

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tively reinforced than conventional ones.<sup>18–20</sup> In such nanocomposites, the polymer molecules are intercalated between the clay layers and/or the clay layers are exfoliated into the polymer matrix. Therefore, the clays and matrix polymers are incorporated in nanometer dimensions. The interfacial effect between the clay layers and the matrix polymers is a key factor leading to the high stiffness and modulus.

This study prepared polymer beads of an organophilic MMT/PMMA nanocomposite via a suspension polymerization method as a substitute for PMMA beads in bone cement to enhance its mechanical properties. This study examined the effect of the preparation conditions on the bead size, such as the stirring speed, suspension–stabilizer concentration, and MMT contents. The bead size is important for bone cement because it affects the properties of the dough stage of the bone cement, such as viscosity and flow. Among the many reports concerning the encapsulation of inorganic particles in polymeric beads, some studies have examined the suspension polymerization process. Abboud et al.<sup>14</sup> reported the encapsulation of chemically modified alumina in PMMA, and Cooper and Vincent<sup>21</sup> examined the synthesis of silica-filled PMMA beads.

## EXPERIMENTAL

### Materials

The organophilic MMT used in this study was purchased from Southern Clay Products and was synthesized by an ion-exchange reaction between  $\text{Na}^+$ -MMT and dimethyl hydrogenated tallow 2-ethyl-hexyl ammonium. The modifier concentration was 95 mEq in 100 g of MMT. The MMT was thoroughly dried before it was mixed with the other ingredients. Methyl methacrylate (MMA) and styrene (St) were purchased from Junsei Chemicals. Benzoyl peroxide, as an initiator, and polyvinyl alcohol (PVA, 88% hydrolyzed), as a suspension stabilizer, were obtained from Aldrich Chemicals.

### Preparation of polymer beads with montmorillonite

The polymer beads with the organophilic MMT were prepared by suspension polymerization that was performed in a 500-mL baffled round flask equipped with a two-bladed Teflon impeller and a digital controller to manage the stirring rate and temperature. MMT was dispersed in monomer via ultrasonication at 25°C for 1 h. BPO (2 wt % based on monomer) was added to the MMT/monomer mixture with constant stirring. The monomer mixture was slowly added to the reactor with a PVA aqueous solution as a dispersion medium with constant stirring at 80–82°C, which was

then maintained for 6 h. The polymer beads were gained by centrifugation and thoroughly washed several times with distilled water, and then dried in a vacuum oven at 60°C.

### Characterization of polymer beads

The dispersion of MMT in the polymer beads was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD analysis was performed in a diffractometer (D/MAX-IIIB, Rigaku Corp.) equipped with a rotating-anode generator system using  $\text{Cu-K}\alpha$  radiation. The XRD patterns were recorded within the range from 1 to 10° with the diffraction angle  $2\theta$ . TEM (JEM-2010, JEOL Ltd.) was performed by applying an acceleration voltage of 120 kV to clarify the nanostructure. An ultrathin film for TEM observation was prepared using the following method: The polymer beads were embedded with epoxy resins in an embedding mold and cured at 60°C for 24 h. The above sample was microtomed with a diamond knife and then observed by TEM without staining.

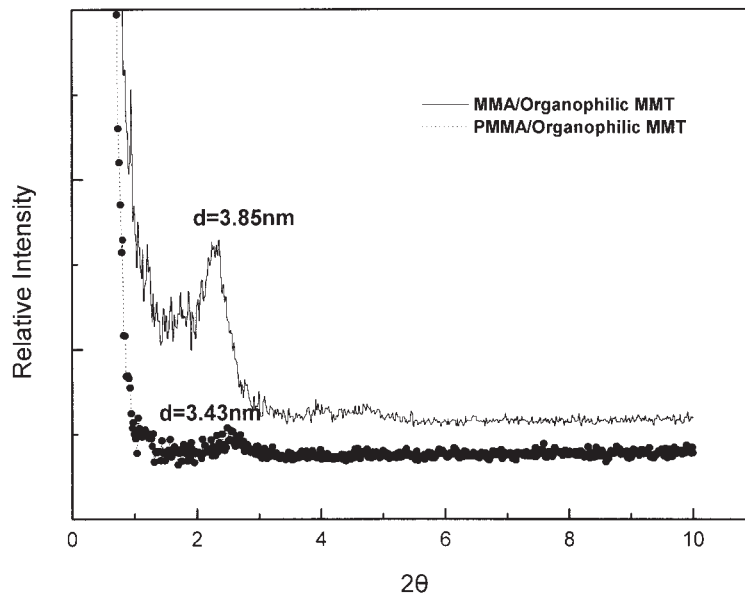
The polymer beads were dissolved in THF, and the PMMA section was filtered using a syringe filter with a pore size of 0.45  $\mu\text{m}$ . The PMMA molecular weight was estimated from gel permeation chromatography (GPC, Waters 2690). Thermogravimetric analysis (TGA, TA Instruments, TGA 2950) was performed to determine the amount of MMT in the polymer beads.

The morphology of the polymer beads was examined by scanning electron microscopy (SEM, JEOL JSM-6700F, JEOL Ltd.) after the polymer beads had been coated with platinum. The particle size and distribution of the polymer beads were measured using a particle size analyzer (BI-DCP, Brookhaven Instruments Ltd.).

## RESULTS AND DISCUSSION

### Characteristics of the polymer beads

Figure 1 shows the XRD patterns of the MMT/MMA monomer mixture and the corresponding polymer beads ranging from 1 to 10°. The mean interlayer spacing of the (001) plane for the organophilic MMT was estimated to be 1.86 nm. The interlayer spacing in the monomer mixture was 3.85 nm, suggesting that the monomer molecules were intercalated into the interlayer space of the MMT. The spacing of the corresponding polymer beads was 3.43 nm, which was 0.4 nm lower than that of the monomer mixture. It was believed that the reduction of the interlayer distance was caused by volume shrinkage via polymerization. A reduction in the intensity of the Bragg diffraction peak of the polymer beads was observed, which indi-



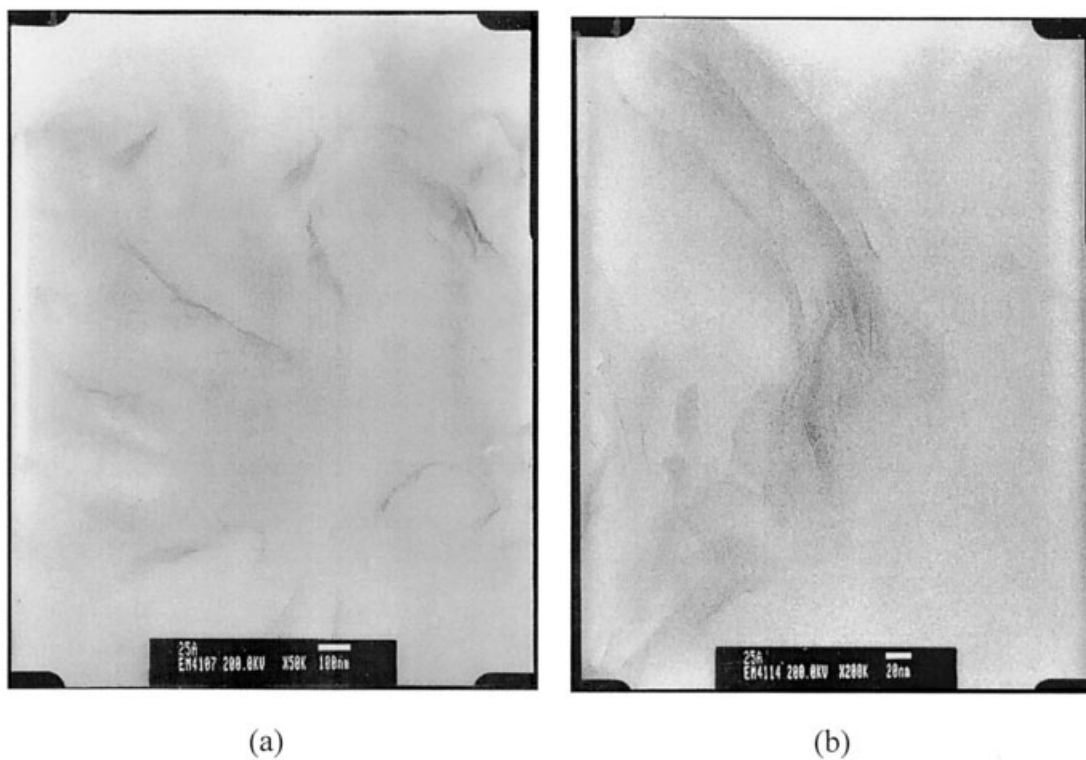
**Figure 1** XRD patterns of MMA/MMT monomer mixture and the corresponding polymer beads.

cates that the MMT layers might have partially exfoliated during polymerization.

Figure 2 shows the TEM micrographs of the MMT/PMMA polymer. The stacked silicate layers with approximately 200–400 nm in length and about 20–40 nm in thickness were randomly dispersed in the PMMA matrix. At higher magnification, exfoliated

layers were also observed. Therefore, it is believed that the polymer beads are composed of polymer-intercalated nanocomposites with partially exfoliated MMT layers.

Table I shows the molecular weights and polydispersity indices of the PMMA from the PMMA/MMT polymer beads. They were not dependent on the



**Figure 2** TEM micrographs of PMMA/MMT polymer bead: (a)  $\times 50,000$ ; (b)  $\times 200,000$ .

**TABLE I**  
Effect of MMT Amount on Molecular Weight of PMMA  
in PMMA/MMT Polymer Beads

Organophilic MMT amount (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
2	144,000	333,000	2.31
4	227,000	638,000	2.80
6	203,000	465,000	2.29
8	208,000	525,000	2.53

amount of the organophilic MMT incorporated. Therefore, the presence of MMT particles in the polymerizing droplets does not appear to affect the reaction kinetics.

The MMT concentration in the polymer beads was determined by measuring the level of weight loss using TGA. The amount of weight loss of the organophilic MMT was 33.91%, which was due to the combustion of the ion-exchanged ammonium compounds. Figure 3 shows the MMT level in the polymer beads with different amounts of the organophilic MMT. The calculated amount of MMT in the polymer blend was converted from the weight loss of the organophilic MMT. The mean deviation between the calculated and measured amount of MMT in the polymer beads was  $15.3 \pm 13.0\%$ , and the measured values were generally lower than the calculated ones. Therefore, a nonnegligible part of the MMT particles would be thrown out of the polymerizing droplets.

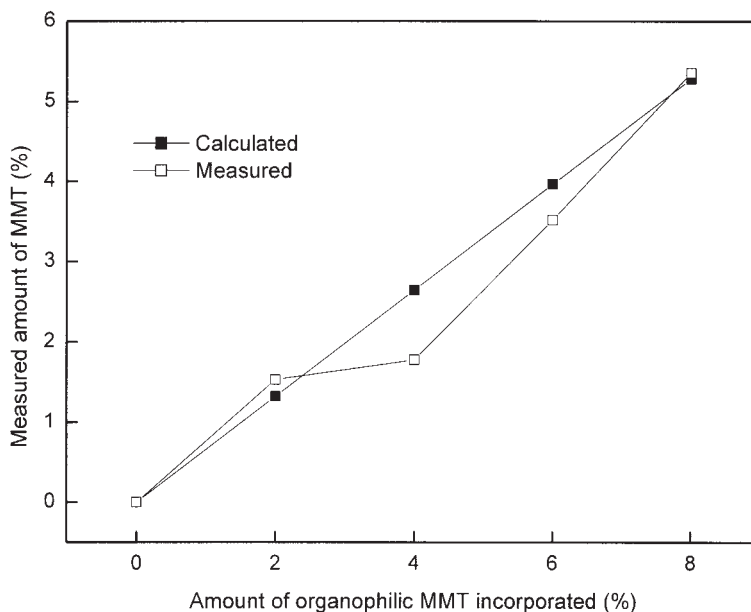
#### Variation of bead size

The void volume of the powder portion of bone cements is dependent on the particle size of the polymer

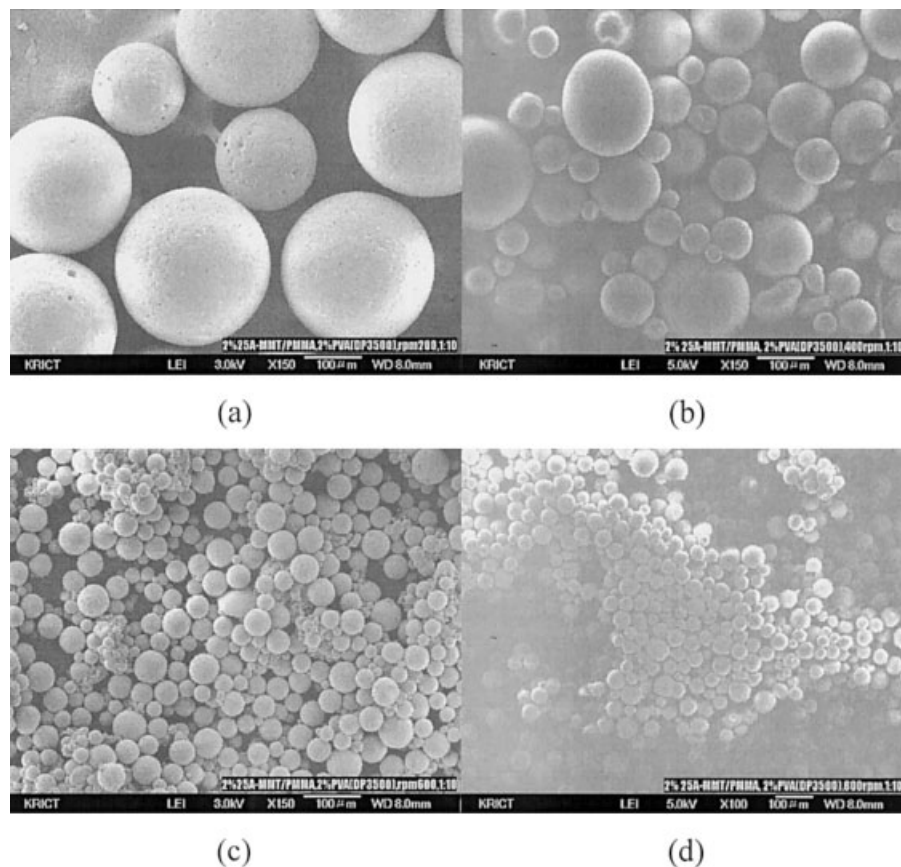
beads used. Therefore, the bead size affects the monomer absorption rate of the powder portion and then the fluidic characteristics of the dough stage, such as the cement viscosity. The optimum fluidic characteristics are important for clinically handling the bone cements. Generally, the mean diameter of polymer beads used in commercial bone cements is 40–60  $\mu\text{m}$ . The factors affecting the size of the polymer beads with MMT, such as the stirring speed, suspension-stabilizer concentration, and MMT contents were observed in this study.

To examine the effect of the stirring speed on the bead size, the suspension polymerization was performed with the MMA monomer mixture with 2 wt % organophilic MMT with a 400 rpm stirring speed in a 2 wt % PVA aqueous solution as the dispersion media. The weight ratio of the monomer mixture and the dispersion media was 1 : 9. The degree of polymerization (DP) of PVA was 3500. Figure 4 shows SEM micrographs of the polymer beads prepared at the different stirring speeds. Figure 5 shows the size of the polymer beads as a function of the stirring speeds. The shape of the polymer beads was spherical and their size decreased as the stirring speed was increased. However, within the experimental region examined, their size did not further decrease at stirring speeds  $\geq 600$  rpm. The bead size distributions at 200 and 400 rpm were bimodal but they were single modal above those speeds (data not shown), which indicated that the larger monomer droplets broke up as a result of the higher stirring speed.

To examine the effect of the PVA molecular weight as a suspension stabilizer on the bead size, the suspension polymerization procedure was carried out in



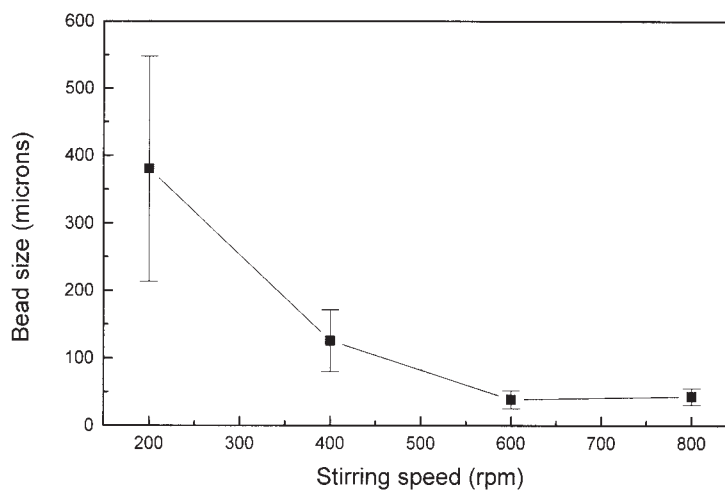
**Figure 3** The variation of the amount of MMT incorporated in PMMA/MMT polymer beads.



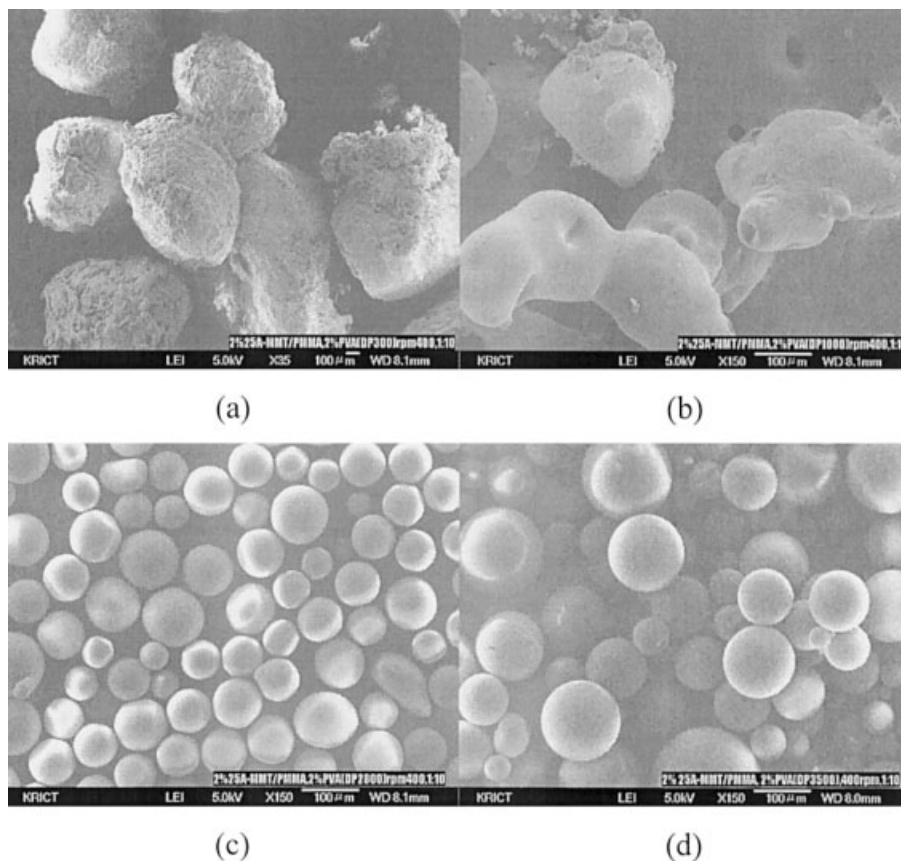
**Figure 4** SEM micrographs of PMMA/MMT polymer beads prepared with different stirring speeds: (a) 200 rpm; (b) 400 rpm; (c) 600 rpm; (d) 800 rpm.

a 2 wt % PVA aqueous solution with a MMA monomer mixture with a 2 wt % concentration of the organophilic MMT. The stirring speed used was 400 rpm and the ratio of the monomer mixture and dispersion media was 1 : 9. The degree of polymerization of the experimented PVA was 300, 1000, 2800, and 3500.

Figure 6 shows SEM micrographs of the polymer beads prepared with different PVA molecular weights. Figure 7 shows the size of the polymer beads as a function of the PVA molecular weight. The size of polymer beads prepared with PVA with a DP of 300 was not indicated because their size was out of the



**Figure 5** Dependence of polymer bead size on stirring speeds.

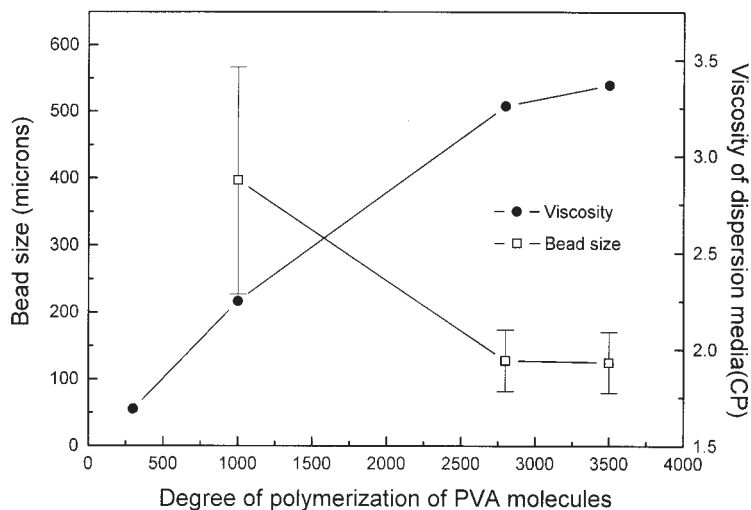


**Figure 6** SEM micrographs of PMMA/MMT polymer beads prepared with different degrees of polymerization of PVA as suspension stabilizer: (a) DP = 300; (b) DP = 1000; (c) DP = 2800; (d) DP = 3500.

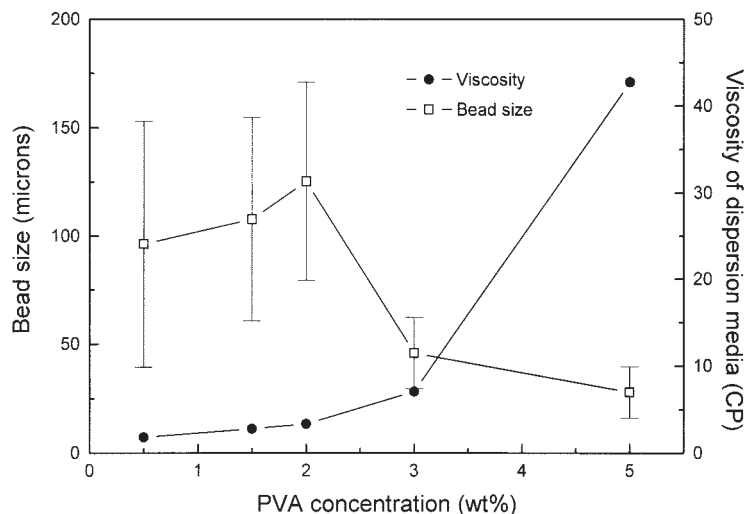
measurement range. The variation of the viscosity of the PVA solution was also measured (Fig. 7).

The polymer beads prepared with the higher-molecular-weight PVA (DP = 2800 and 3500) were approximately spherical, while those prepared with the

lower-molecular-weight PVA (DP = 300 and 1000) had an irregular shape. The bead size decreased as the DP of the PVA molecules increased. The viscosity of the PVA solutions, as dispersion media, did not change significantly with different PVA molecular



**Figure 7** Dependence of the size of polymer beads and the viscosity of dispersion media (PVA solution) on degree of polymerization of PVA molecules.



**Figure 8** Dependence of the size of polymer beads and the viscosity of dispersion media (PVA solution) on PVA concentration.

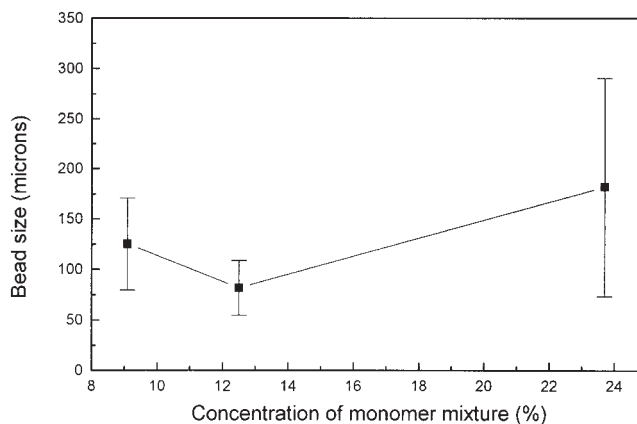
weights. This suggests that, within the experimented range, the solution viscosity may not affect the shape and size of the polymer beads.

The monomer droplets are commonly stabilized by the PVA molecules adsorbed on their surface, which prevents coalescence of the monomer droplets by making a nonadhesive film. The DP and the molar mass of the PVA were reported to affect its ability to act as a stabilizer.<sup>22</sup> The monomer droplets coalesced easily in the dispersion media with a smaller-molecular-weight PVA. This is because the adsorbed PVA layer might be not thick, presumably due to its molecular size, which affects the shape and size of the corresponding polymer beads. Generally, PVA with a moderate degree of hydrolysis (88%) and a relatively large molecular weight ( $> 70,000$ g/mol) acted as a good suspension stabilizer.<sup>22,23</sup>

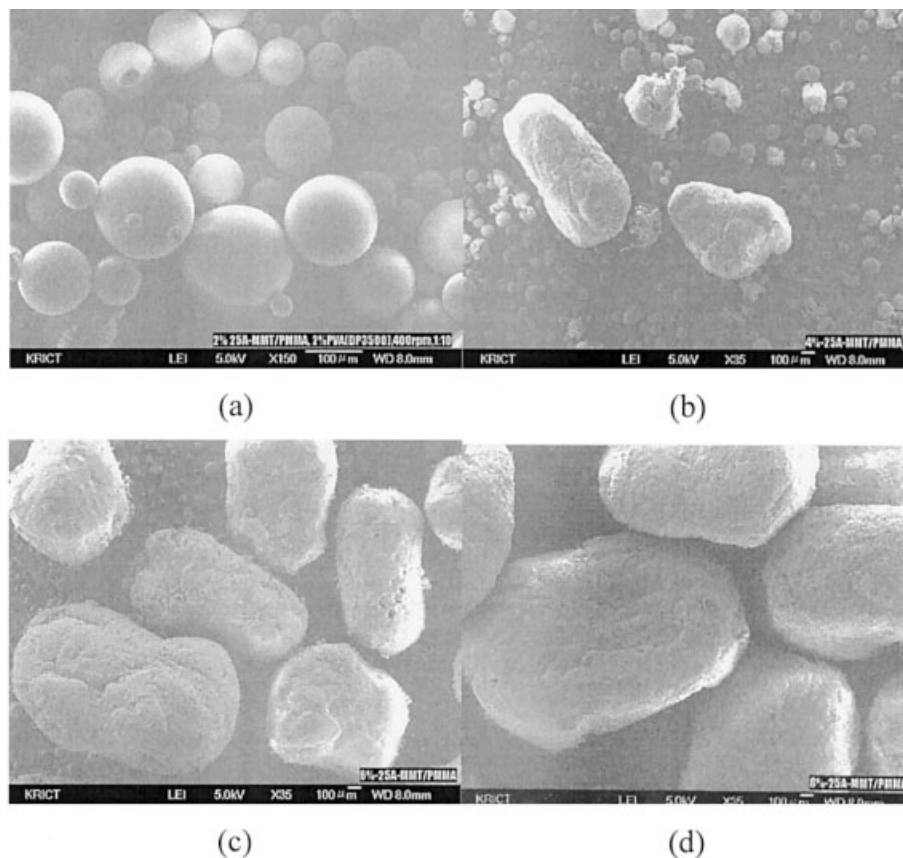
The suspension polymerization was performed using a MMA monomer mixture with 2 wt % organophilic MMT in different concentrations of the PVA aqueous solution to examine the effect of the PVA concentration on the bead size. The stirring speed used was 400 rpm and the ratio of the monomer mixture and the dispersion media was 1 : 9. The DP of the experimental PVA was 3500. Figure 8 shows a plot of the size of polymer beads and the viscosity of dispersion media as a function of the PVA concentration. The size of the polymer beads prepared in the solutions with a PVA concentration  $\leq 2\%$  was similar. At PVA concentrations  $> 3\%$ , the size diminished as the PVA concentration was increased. There was virtually no increase in the viscosity of the dispersion media with a PVA concentration  $\leq 2\%$ , while the increase became larger in the solutions with a PVA concentration  $> 3\%$ . The PVA concentration generally affects the amount of PVA adsorption on the mono-

mer droplets and the surface tension and viscosity of the dispersion media. Within the experimental range, the variation in the surface tension and PVA adsorption was reported to be minimal.<sup>21</sup> Therefore, the surface tension and PVA adsorption rate may not affect the bead size in this polymerization system. Therefore, the variation of the bead size is mainly dependent on the viscosity of the dispersion media.

The suspension polymerization was performed with different ratios of the monomer mixture and dispersion media to evaluate the effect of the ratios on the generation of polymer beads. The concentration of the organophilic MMT in the monomer mixture was 2 wt %, and there was 2 wt % PVA in the dispersion media (DP = 3500). Figure 9 shows a plot of the size of the polymer beads as a function of the concentration of the monomer mixture in the polymerization system. The bead shape was spherical under all experimental



**Figure 9** Dependence of bead size on concentration of MMA/MMT monomer mixtures.

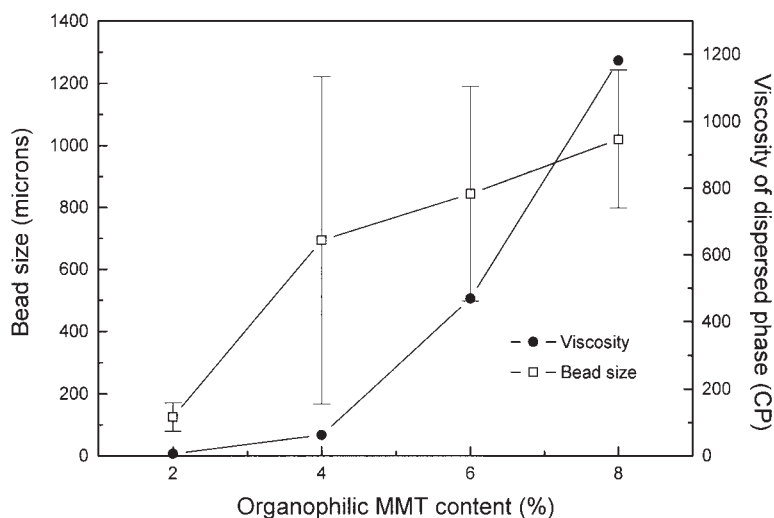


**Figure 10** SEM micrographs of PMMA/MMT polymer beads prepared with different MMT contents: (a) 2 wt %; (b) 4 wt %; (c) 6 wt %; (d) 8 wt %.

conditions examined. At higher concentrations of the monomer mixture (23.7%), the bead size became larger and numerous aggregated beads were found. This may have been caused by the increased collision

rate of the monomer droplets due to the increased concentration of the monomer mixture.

The suspension polymerization was performed with different concentrations of the organophilic



**Figure 11** Dependence of the size of polymer beads and the viscosity of dispersed phase (monomer mixtures) on MMT content.



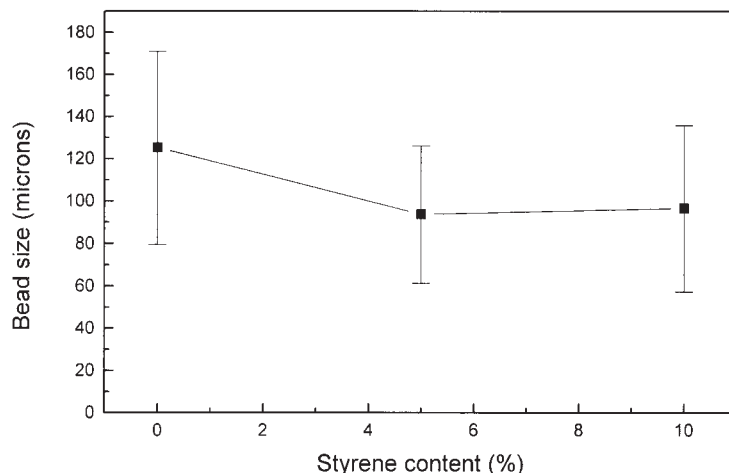


Figure 12 Effect of styrene addition to polymer bead size.

MMT in the monomer to evaluate the effect of the MMT contents on the generation of the polymer beads. The ratio of the monomer mixture and the dispersion media was 1 : 9. The dispersion media was a 2 wt % PVA (DP = 3500) solution. Figure 10 shows SEM micrographs of the polymer beads prepared with 2, 4, 6, and 8 wt % MMT in the monomer mixture. The dependence of polymer bead size and the viscosity of the monomer mixture on the contents of the organophilic MMT was plotted and shown in Figure 11. The polymer beads with 2 wt % MMT were spherical, while the shape was irregular with higher MMT concentrations. The size of the polymer beads and the viscosity of the monomer mixtures increased markedly as the MMT contents became larger. It is believed that the size of the polymer beads is mainly dependent on the viscosity of the monomer mixtures. That is, when the viscosity of monomer mixtures increases,

the monomer droplets are not easily broken up due to the increased shear stress of the monomer mixtures.

Various commercial bone cements include polymer beads with a copolymer of methyl methacrylate and styrene because styrene enhances the fatigue strength of the bone cements due to its hydrophobic characteristics.<sup>24,25</sup> This study examined the effect of styrene on the size of the polymer beads. The suspension polymerization was carried out with 0, 5, and 10 wt % styrene in the monomer mixtures with 2 wt % MMT. The ratio of the monomer mixture and the dispersion media was 1 : 9. The dispersion media was a 2 wt % PVA (DP = 3500) solution. Figure 12 shows the dependence of the bead size on the styrene contents. The size of the polymer beads decreased slightly as the styrene content was increased. This result may be caused by the reduced surface tension of the monomer mixture as a result of the added styrene.

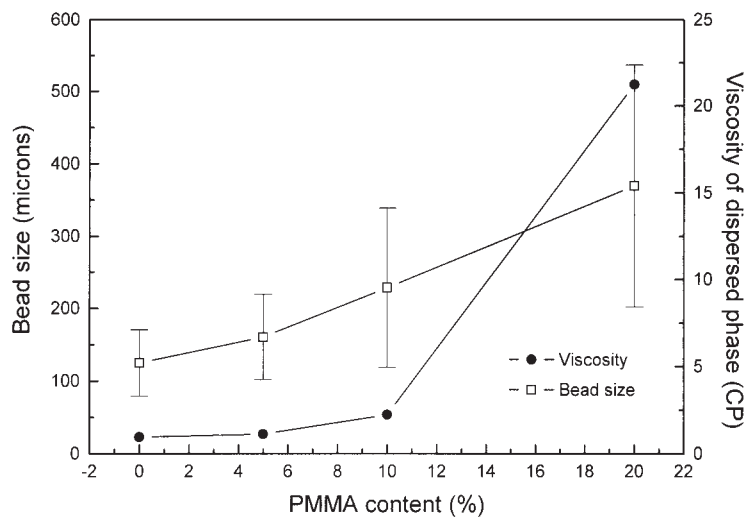


Figure 13 Effect of PMMA addition to polymer bead size and viscosity of dispersed phase (monomer mixtures).

The viscosity of the monomer portion could be used to control the size of the polymer beads prepared by suspension polymerization. In this study PMMA was added to the monomer portion to control its viscosity, and its effect on the formation of the polymer beads was investigated. The suspension polymerization was performed with 0, 5, 10, and 20 wt % PMMA in the monomer mixtures containing 2 wt % MMT. The stirring speed used was 400 rpm and the ratio of the monomer mixture and dispersion media was 1 : 9. The DP of the experimented PVA was 3500. The bead shape was spherical at all experimental conditions (data not shown). Figure 13 shows the changes in the size of polymer beads and the viscosity of the monomer mixtures affected by the PMMA contents. The viscosity of the monomer mixtures gradually increased at PMMA concentrations  $\leq 10\%$ , while, at 20% PMMA, the viscosity increased markedly. The polymer beads also gradually became larger with the increasing viscosity of the monomer mixtures as the PMMA concentration was increased.

### CONCLUSIONS

PMMA polymer beads incorporated with organophilic MMT were prepared and were characterized by XRD, TEM, and SEM particle size analysis. The polymer beads were considered to be in an intercalated state with a partially exfoliated MMT. The bead size was controlled by the preparation conditions such as the stirring speed, the DP, and the PVA, MMT, styrene, and PMMA concentrations, etc.

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