

Polymer/Silica Nanoscale Hybrids Through Sol–Gel Method Involving Emulsion Polymers. I. Morphology of Poly(butyl methacrylate)/SiO₂

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ABSTRACT: In this article, we report on an approach of using an emulsion polymerized polymer in preparing organic–inorganic nanocomposites through a sol–gel technique. By mixing a polymer emulsion with prehydrolyzed tetraethoxysilane transparent poly(butyl methacrylate)/SiO₂, nanocomposites were prepared as shown by TEM, AFM, FTIR, and XPS results show that there is a strong interaction between polymer latex particles and the SiO₂ network. Comparison of the emulsion method with a traditional solution method shows that nanocomposites can be prepared by both methods, but there is some difference in their morphology and properties. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 446–454, 2002

Key words: organic–inorganic nanocomposites; sol–gel method; latex; poly(butyl methacrylate); latices; polyesters; silicas

INTRODUCTION

The desire for state-of-the-art materials gives rise to the development of organic–inorganic nanocomposites (OINCs) with unique properties not shared by conventional microcomposite counterparts. Nanocomposites can commonly be obtained by either sol–gel methods or intercalating a polymer, or a monomer followed by polymerization, into layered silicates. Much effort has been centered on the sol–gel process in synthesizing the inorganic part of the OINCs.^{1–8}

Hybrid organic–inorganic sol–gel materials can be prepared by two approaches: Organic molecules can just be embedded into an organic material or vice versa. Alternatively, the organic and inorganic grouping can be linked by stable chemical bonds. The latter approach has been a research hot point in recent years. The essence of

the sol–gel process involves the hydrolysis and condensation of metal alkoxides in the presence of a cosolvent to form ramified three-dimensional SiO₂ networks as solvent-swollen gels. The solvents are to prevent liquid–liquid phase separation during the initial stage of the hydrolysis reaction and to control the concentrations of the silicate and water that influence the gelation kinetics. Solvents commonly used are water, alcohol, THF, and DMF, among others. This leads to drawbacks in applications, since the organic solvent vapor concentration has to be controlled for environmental, health, or security reasons. The tightening of worldwide environmental legislation has encouraged us to try polymer latex using emulsion polymerization involving no organic solvents but, instead, environmentally benign water.

Recently, studies on multiporous materials have gained much attention.^{9–15} One of the methods to prepare the multiporous materials is to use polymer latex particles as the template.^{13–15} To obtain multiporous materials, the polymer will be eliminated by calcination. This method can be taken as a good method to prepare organic–inorganic composites. Therefore,

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we have studied the sol-gel method involving emulsion polymers and investigated the difference between the emulsion method and the conventional method using a polymer solution. The preparation of inorganic-organic composites through polymer latex or emulsion polymerization has been reported. Inorganic sol particles such as silica sol or alumina sol are used as seeds added into the emulsion polymerization system to prepare an inorganic-organic composite coating with a core-shell structure¹⁶ or as a reinforcing agent to improve the properties of the resulting materials.¹⁷ The emulsion method as reported here is different from the above-mentioned method; it is a type of sol-gel process to prepare organic-inorganic hybrids through polymer emulsion. The inorganic component comes from the inorganic precursor prehydrolyzed under an acid condition. Therefore, the morphology of the resulting materials by the two methods will be quite different.

Here, we report on a novel avenue in preparing OINCs, trying to gather information on the film-formation process and morphology and properties of the poly(butyl methacrylate) (PBMA)/SiO₂ hybrids thus formed. The morphology and the glass transition of the hybrids by the new emulsion method and the traditional solution method were compared.

EXPERIMENTAL

Materials

The polymer component, PBMA, was synthesized by emulsion polymerization at 80°C. Butyl methacrylate (A.R.) was distilled under reduced

pressure under nitrogen and kept in a refrigerator before use. The initiator potassium persulfate (A.R.), the surfactant sodium dodecylsulfate (A.R.), and the buffer sodium bicarbonate (C.P.) were used as supplied. The metal alkoxide used was tetraethoxysilane (TEOS; C.P.). The PBMA latex particle size was 72.8 nm (measured by a LS particle-size analyzer).

Organic/Inorganic Nanocomposites Preparation

Hybrid preparation by the emulsion method is as follows: The polymer emulsion was diluted to 1 wt % (solid content) before mixing with prehydrolyzed TEOS. All prehydrolyzed TEOS solutions had a mol ratio of TEOS:H₂O of 1:3, and nonionic water containing 0.17M HCl was used. After the emulsion and the prehydrolyzed TEOS solution were mixed and shaken, the resulting solution was immediately cast into a PTFE mold and dried at 35°C in an oven or at room temperature. The reference hybrids were prepared by the traditional solution method, whereas the dried polymer prepared by the emulsion polymerization was dissolved in THF and the solution was made to mix with prehydrolyzed TEOS. Samples for AFM were dropped onto a piece of mica. All the samples were dried at 35°C in a vacuum before characterization.

Measurements

All AFM experiments were conducted under ambient conditions with a commercial scanning probe microscope NanoScope IIIa (Digital Instruments, Inc). The morphology observation was performed in the contact mode with an etched silicon nitride cantilever (spring constant of 0.06 N/m). All AFM images were shown without any image processing except flattening.

FTIR spectra were obtained using a Bio-Rad FTS-135 spectrophotometer with 4 cm⁻¹ resolution. Samples for FTIR were prepared by casting the solutions directly onto CaF₂ discs at room temperature and heating several minutes under heating lamps to drive off the solvent, except that the PBMA in the THF solution was cast onto KBr discs. A differential scanning calorimetry (DSC) DSC-7 instrument was used in measuring the glass transitions of the hybrid at a heating rate of 20°C/min over the range -60-150°C under a N₂ atmosphere.

Transmission electron microscopy (TEM) was performed on thin sections using a JEOL JEM 2010 transmission electron microscope. The sam-

The theory value of the Si content on the surface of the PBMA/SiO₂ (70/30) sample was calculated as follows:

	Butyl Methacrylate (C ₈ H ₁₄ O ₂)	SiO ₂
Molecular weight	142	60
Weight (g)/100 g sample	70	30

$$\therefore \text{mol number of C} = 8 \times \frac{70}{142} = 3.944$$

$$\text{mol number of O} = 2 \times \frac{70}{142} + 2 \times \frac{30}{60} = 1.986$$

$$\text{mol number of Si} = 1 \times \frac{30}{60} = 0.5$$

$$\therefore \text{Si mol \%} = \frac{0.5}{3.944 + 1.986 + 0.5} \times 100\% = 7.78\%$$

ples were microtomed with an LKB Ultratome III perpendicular to the coating direction.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG ESCALAB MK II spectrometer using an $\text{AlK}\alpha$ exciting radiation from an X-ray source operated at 10.0 kV and 10 mA. The constant analyzer energy (CAE) mode was chosen with a pass energy of 50 eV. The pressure in the analysis chamber was around 10^{-6} Pa.

RESULTS AND DISCUSSION

Film-forming Process

The new emulsion method to prepare OINCs is characterized by using polymer latex as the source of the polymer. It is natural that the film-formation process of polymer latex is related to that of the hybrids. Some authors^{18–20} suggested that the polymer latex film-formation process consisted of four distinct stages separated by three transitions. The first stage corresponds to the wet initial state. With the evaporation of water, the second stage appears in which the particles first come into contact with each other, forming a close-packed array with water-filled interstices. In the third stage, the particles deform and compact; during the transition, the interstitial water is continuously lost. The mechanism by which particle deformation and water loss are linked is still the subject of debate. Stage III indicates a dense array in which individual particles retain their identity. Finally, diffusion across particle–particle boundaries, leading to a homogeneous, continuous material (with no internal solid–solid interfaces), defines the fourth stage. This transition from stage III to stage IV can only occur above the T_g of the polymer. The scheme of the film-formation process of the hybrids based on polymer latex as described in ref. 21 and envisioned in our experiments is depicted in Figure 1. It is worth mentioning that, to achieve good dispersion, we tried to control the latex particle's size below 100 nm in our emulsion polymerization.

In the film-formation process of polymer latex, the minimum film-forming temperature (MFT) is one of the main factors in determining the properties of the resulting film.^{22,23} Generally, the MFT is near the T_g of the polymer. If the T_g of the latex polymer is below room temperature (i.e., if the operation temperature exceeds the MFT), the particles will deform to produce space-filling Wigner–Seitz cells, yielding a transparent and void-free film. Otherwise, particles will not form

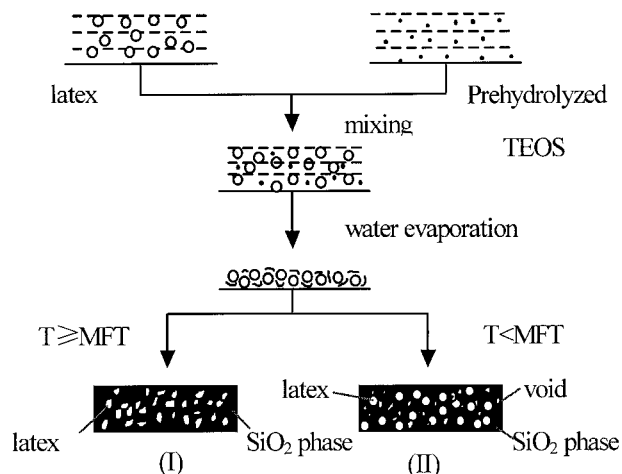


Figure 1 Representation of the film formation.

and voids and surface roughness develop during the film-forming process and a transparent film is not formed. Thus, polymers manipulated at different MFTs involve different film-formation processes, and the properties and morphology of the resulting films should be entirely different. The MFT is certainly also a main factor in the case of the hybrids using polymer latex. In the present case of the polymer PBMA (T_g 33°), the parent PBMA and the PBMA/SiO₂ hybrid transparent films should be formed and were indeed at 35°. For samples dried at room temperature, lower than the MFT of the polymer PBMA, the final hybrids are opaque and this will not be discussed further. Although all hybrid film by the emulsion method cast at 35° are transparent, qualitative differences are apparent between their morphology with respect to the size of the phase heterogeneity and sharpness of the polymer/SiO₂ interface. TEM results of PBMA/SiO₂ (90/10 and 70/30) are shown in Figures 2(a) and 3(a). For the system with a lower SiO₂ content, PBMA/SiO₂ 90/10, the phase heterogeneity is only slight and the PBMA/SiO₂ interface is unclear. When the SiO₂ content reaches 30%, the PBMA latex particles are evenly dispersed in the SiO₂ matrix with a clear phase interface. The range of small smooth patches is below 100 nm. This image [Fig. 3(a)] is quite similar to (I) in Figure 1. This shows that our conception of the film-formation process is reasonable.

Morphology

TEM images of the PBMA/SiO₂ hybrids of different compositions by emulsion and solution methods (Figs. 2–5) show that there is a difference in

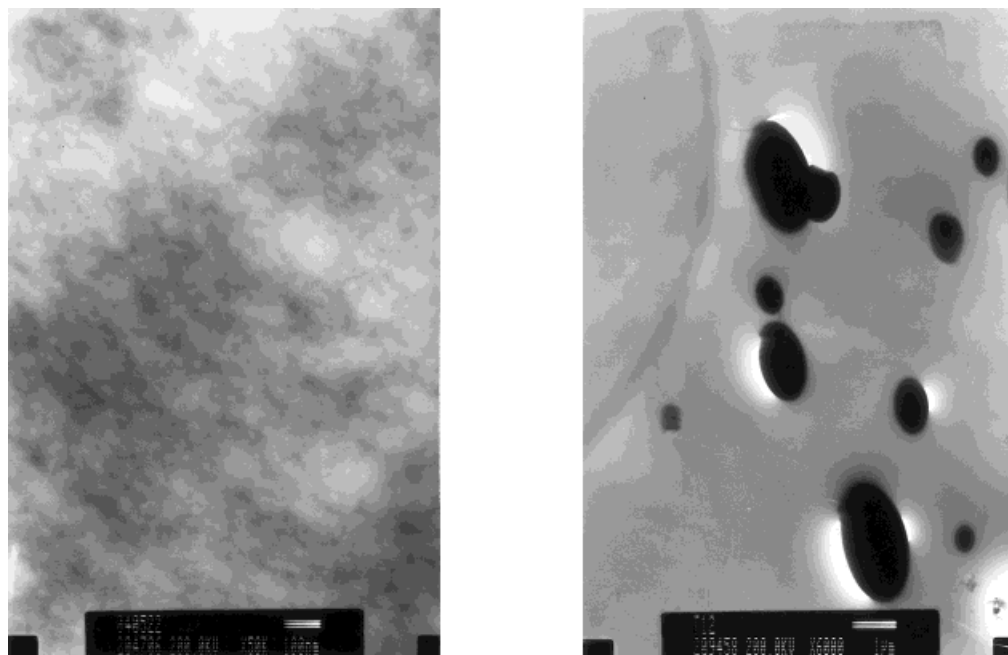


Figure 2 TEM images of PBMA/SiO₂ (90/10) hybrids: (left) by emulsion method; (right) by solution method.

the morphology of these hybrids. The micrographs of the PBMA/SiO₂ system with lower SiO₂ (10 and 30%) by the solution method indicate an obvious two-phase structure with SiO₂ particles dispersed in the PBMA matrix. Generally, the

morphology observed during nucleation/growth (NG) phase separation is the droplet/matrix type from the early to the later stages.²⁴ Therefore, it is supposed that an NG mechanism leads to this structure. From Figures 2(b) and 3(b), we can see

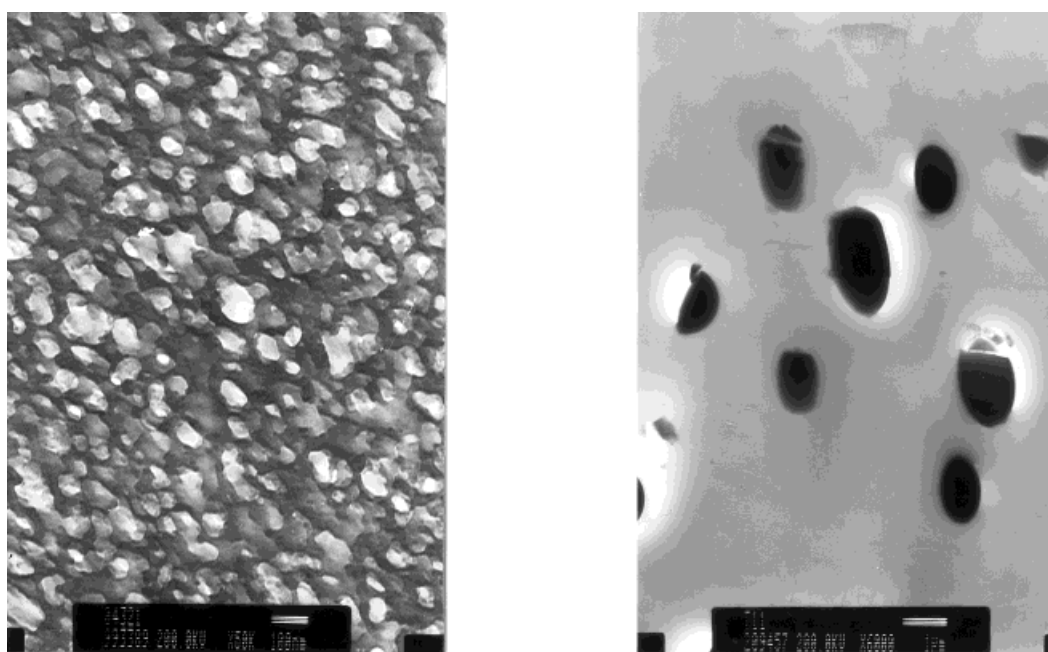


Figure 3 TEM images of PBMA/SiO₂ (70/30) hybrids: (left) by emulsion method; (right) by solution method.

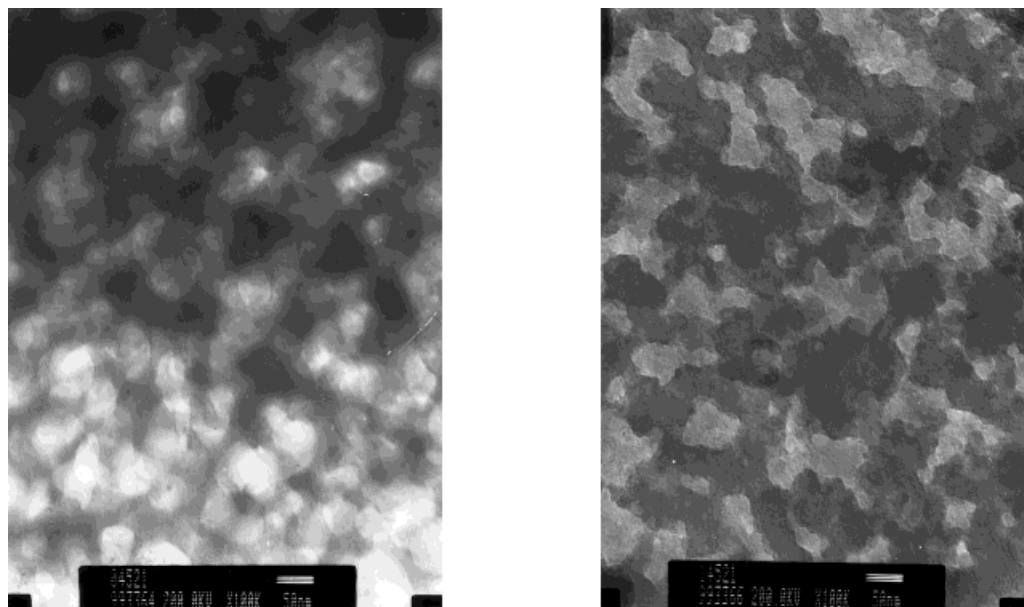


Figure 4 TEM images of PBMA/SiO₂ (50/50) hybrids: (left) by emulsion method; (right) by solution method.

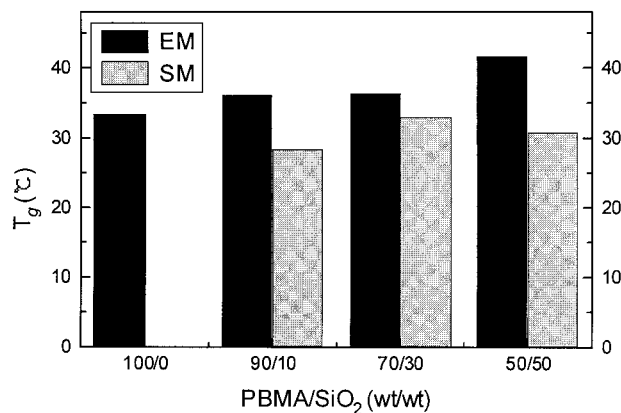
that in the samples by the solution method the particle size is very big, about 2 μm , the degree of heterogeneity is very large, and the interface between the two components is very sharp. Compared to the emulsion method, the degree of their phase separation is much greater. Besides the difference in the degree of phase separation, there is another great difference in the structures of PBMA/SiO₂ 70/30 by the two methods. In the sample by the solution method, the continuous phase is PBMA and the dispersion phase is SiO₂. Instead, for samples by the emulsion method, the PBMA as latex particles is dispersed in the SiO₂ matrix. The difference also exists in the PBMA/SiO₂ 50/50 system (Fig. 4). The two components of the hybrid by the solution method are cocontinuous, while the polymer particles are dispersed in the SiO₂ matrix for the hybrid by the emulsion method.

All these result from the difference in the environment of the polymer chains during film formation. For the solution method, the polymer chains and prehydrolyzed TEOS exist concurrently in the THF solvent, while the polymer chains exist in latex particles for the emulsion method. For the former method, the phase-separation mechanism may be similar to that in the polymer blends.²⁴ Silveira et al. studied the phase-separation mechanism in PMMA/SiO₂ sol-gel systems through the solution method.²⁵ Spinodal decomposition (SD) was confirmed for sys-

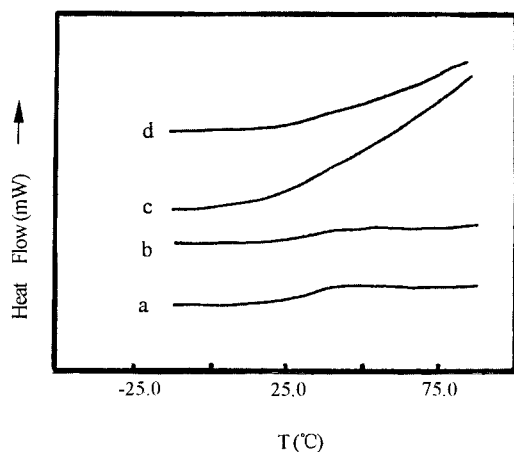
tems with intermediate PMMA/SiO₂ compositions. For systems with a low PMMA content, a typical behavior of nucleation and growth was detected. Therefore, the droplet/matrix structure of the PBMA/SiO₂ (90/10 and 70/30) hybrids by the solution method may be caused by the NG mechanism, and the cocontinuous structure of the PBMA/SiO₂ (50/50) hybrid by the solution method may be caused by the spinodal mechanism. However, for the emulsion method, the polymer chains in the form of latex particles exist in the prehydrolyzed TEOS solution. When the SiO₂ content is high enough, the gel transition of TEOS occurs before fusion of the latex particles, so that the polymer particles are locked in the SiO₂ matrix, forming the structures given in Figures 3(a) and 4(a).

Glass Transition Behavior

Some differences are also seen in the glass transition behavior of hybrids prepared through the emulsion method and the solution method [Fig. 5(a)]. For PBMA/SiO₂ hybrids by the emulsion method, the T_g 's increased slightly as compared to that of the parent PBMA; in contrast, those by the solution method had T_g 's lower than that of the parent PBMA. The difference results from the distinction of the environment in which the polymer and prehydrolyzed TEOS molecules exist during the film-formation process and in the re-



(a)



(b)

Figure 5 (a) Comparison of the T_g of PBMA/SiO₂ hybrids by the emulsion method (EM) and the solution method (SM). (b) DSC curves of hybrids by the emulsion method: (a) PBMA; (b) PBMA/SiO₂ (90/10); (c) PBMA/SiO₂ (70/30); (d) PBMA/SiO₂ (50/50).

sulting samples. The interpretation is that the polymer from the emulsion method is embedded in the latex particles, so it has little effect on the course of condensation with the prehydrolyzed TEOS, and the three-dimensional SiO₂ network is easy to form. The residual oligomer is less. While at the casting temperature near the MFT of the PBMA emulsion, the latex particles in the resulting film deformed slightly but still existed independently. Even if some oligomer was kept in the samples, it had little effect on the T_g of the polymer. In the case of the solution method, the poly-

mer molecules in the solution impede the collision of prehydrolyzed TEOS molecules and impair the formation of the SiO₂ network. The residual oligomers from the sol-gel reaction serve as plasticizers for PBMA, resulting in a decrease in the T_g . Additionally, the DSC results of the samples in the emulsion method indicate that the T_g of the hybrids increased with increasing SiO₂ content, tending to disappear at SiO₂ of 50% (wt) [Fig. 5(b)]. It was also noted that the width of the transition is different for all the samples and the T_g transition became unclear with increasing SiO₂ content. The interpretation is that the mobility of the polymer chains was more and more restricted by the growing SiO₂ network. When the SiO₂ content reached 50% (wt), the mobility of the polymer chain was so restrained that the T_g almost disappeared. The same change occurs to all the samples by the solution method.

Microstructure

AFM was used to observe the microphase structure of hybrids prepared by the emulsion method (Fig. 6). Compared to the hybrid of 90/10 PBMA/SiO₂, it was not hard to find that the latex particle became bigger in the hybrid of 70/30 PBMA/SiO₂. It seems to be an unusual phenomenon because the coalescence and fusion could not be so complete at 35°C that the boundary among the individual latex particles disappears completely. We theorized that since hydrogen bonding can occur between the SO₃ group on the surface of the latex and the OH group in SiO₂ network some parts of the condensation reaction of the hydrolyzed TEOS may take place on the surface of the latex particles so that the latex particles were covered with the SiO₂ network and became bigger.

To prove the existence of the hydrogen bonding, the samples were examined by FTIR (Fig. 7; the data are not labeled in the figure). The broad band around 3400 cm⁻¹ is associated with the stretching of the OH groups; for pure SiO₂, it results from the hydroxyl absorption in the SiO₂ network. For the surfactant, a 3501-cm⁻¹ band is from the detained water. The PBMA/SiO₂ hybrid has a broader OH band [Fig. 7(a)] than that of the surfactant [Fig. 7(b)] and SiO₂ [Fig. 7(c)]. In addition, the SO₃ stretching bands of the surfactant are at 1247 and 1204 cm⁻¹. In Figure 7, they seem to move to a lower wavenumber in the hybrid and overlap with other bands. To further prove their movement, the second derivative curves of the PBMA/SiO₂ (50/50) and the PBMA FTIR curve are shown in Figure 8. From Figure 8, we found

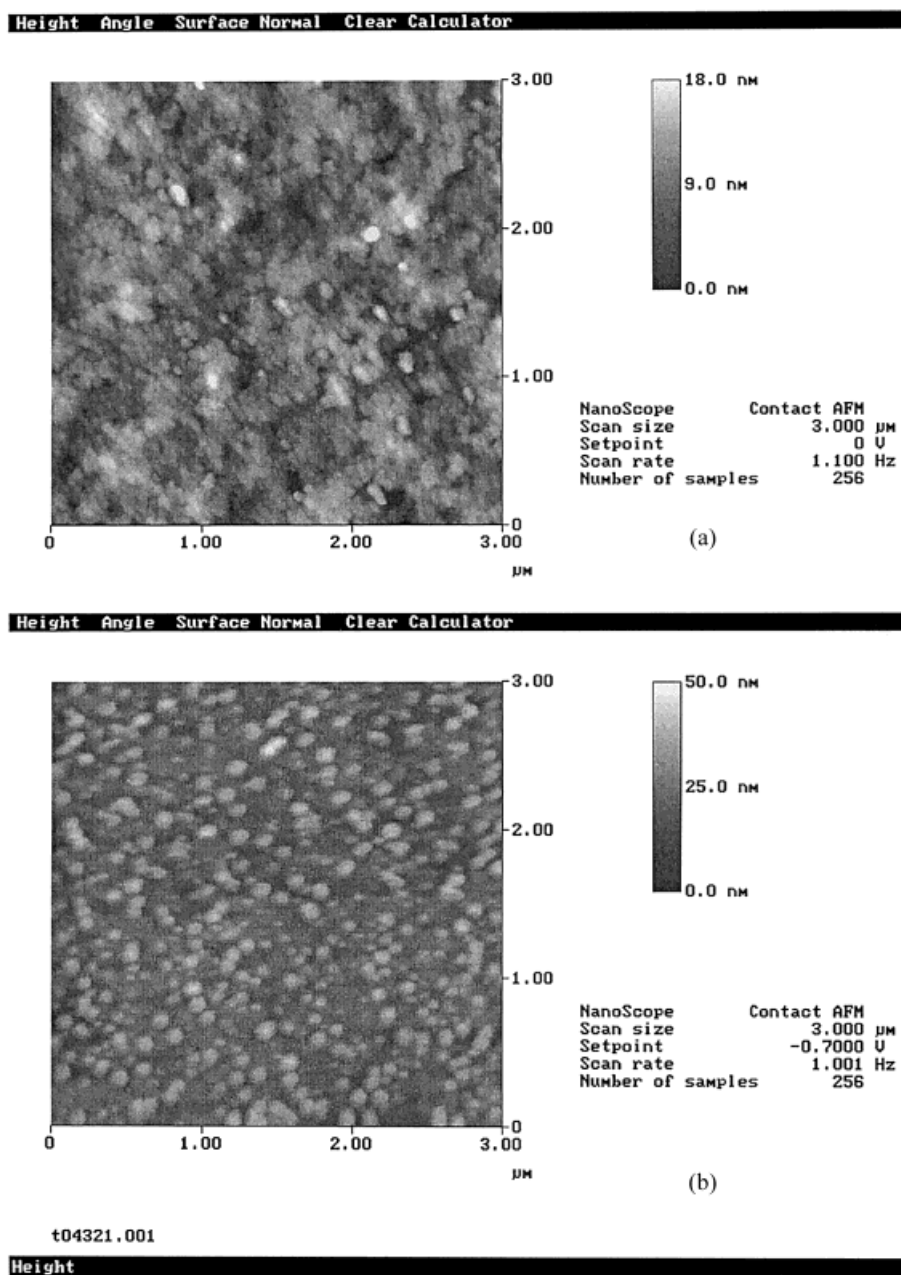


Figure 6 AFM images of (a) PBMA/SiO₂ (90/10) and (b) PBMA/SiO₂ (70/30).

that the peaks in Figure 8(a) almost agree with those of Figure 8(b) except near 1217 cm⁻¹. In Figure 8(a), there is a wide peak between 1225 and 1217 cm⁻¹. We consider that the wide peak comes from the original 1217 cm⁻¹ peak in Figure 8(b) overlapping with the moved 1247 and 1204 cm⁻¹ stretching bands of the SO₃ group. Therefore, it is believed that hydrogen bonding occurs between the SO₃ group and the OH groups in the SiO₂ network as evidenced by its broadening and moving to a lower frequency. Additionally, if the

latex particles were exactly covered with the SiO₂ network, the Si content on the surface of the film would increase.

XPS was used to examine the Si content on the surface of PBMA/SiO₂ (70/30) sample. Three main elements (C, O, and Si) were tested. The XPS results showed that the Si content on the surface was 22.82% (mol), much higher than the theory value of 7.78% (mol)* in the PBMA/SiO₂ (70/30) hybrid. Therefore, we preliminarily deduce that the growth of the particles might come

from the SiO₂ enrichment on the surface of the particles. This shows that a strong interaction exists between the PBMA phase and the SiO₂ phase.

CONCLUSIONS

Transparent PBMA/SiO₂ hybrids were prepared by a new sol-gel method using polymer emulsion. Because the replacement of the traditional polymer solution with polymer emulsion will alleviate pollution, the new method would have better prospective application. From the above results, we deem that the SiO₂ phase is dispersed when the SiO₂ content is below 10% for both methods in the PBMA matrix and the degree of phase separation for emulsion is far less than in the solution method. Therefore, the emulsion method is a better method to prepare PBMA/SiO₂ nanocomposites to replace the conventional solution method. When the SiO₂ content is higher, the emulsion method is also a good method to prepare PBMA/SiO₂ nanocomposites. But the fields in which the materials by the new emulsion method are to be used may be different from the conventional solution method, because the type of the micromorphology in the resulting materials is different. Additionally, there is some difference in the T_g of the samples by the two methods. For PBMA/SiO₂ hybrids by the emulsion method, the T_g 's increased slightly as compared to that of the parent PBMA; in contrast, those by the solution method had T_g 's lower than that of the parent PBMA.

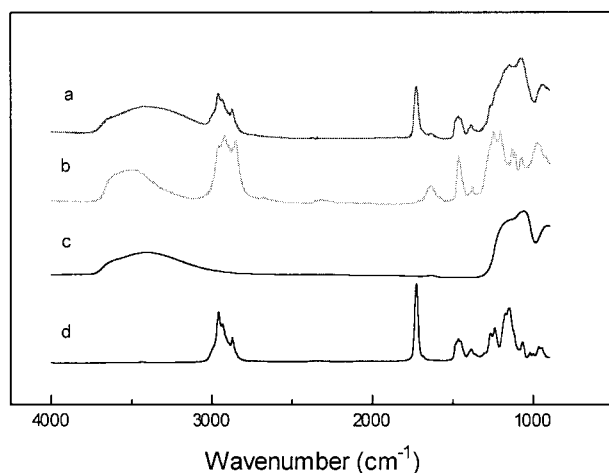


Figure 7 FTIR spectra of (a) PBMA/SiO₂ (50/50), (b) the surfactant, (c) the hydrolyzed TEOS, and (d) PBMA.

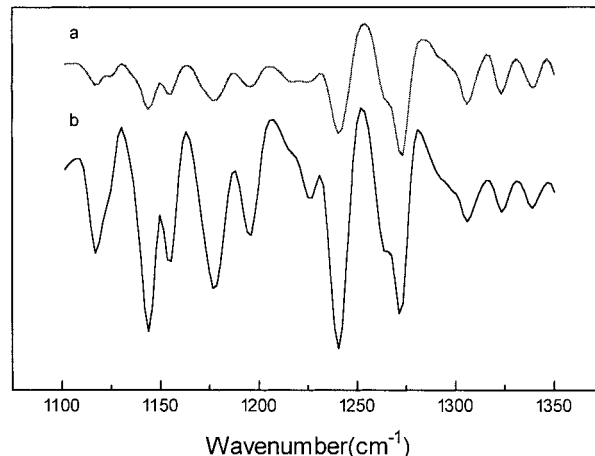


Figure 8 Second derivative results of FTIR curves of (a) PBMA/SiO₂ (50/50) and (b) PBMA.

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