

Preparation of Polymer/Silica Nanoscale Hybrids through Sol-Gel Method Involving Emulsion Polymers. II. Poly(Ethyl Acrylate)/SiO₂

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ABSTRACT: Poly(ethyl acrylate) (PEA)/SiO₂ hybrids with different compositions were prepared under different casting temperatures and pH values. Their morphology as investigated by transmission electron microscopy (TEM) shows that samples with different compositions have different morphologies. When the SiO₂ content is lower, PEA is the continuous phase and SiO₂ is the dispersed phase. At higher SiO₂ content, the change in phase morphology takes place, and PEA gradually dispersing in the form of latex

particles in SiO₂ matrix. Change in phase morphology depends mainly on the time the sol-gel transition occurs. At suitable casting temperature and pH value, PEA/SiO₂ in 95/5 and 50/50 hybrids with even dispersion was obtained. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3532–3536, 2002

Key words: organic-inorganic nanocomposites; sol-gel method; morphology; latex poly(ethyl acrylate)

INTRODUCTION

Hybrid organic-inorganic materials have been developed during the past two decades or so^{1–5} as intimate combinations of these dissimilar materials not constrained by classical material compromises. The sol-gel process under mild conditions offers an efficient and convenient approach to the synthesis of organic-inorganic composite material nanoscales in domain sizes^{6–12} or approaching molecular level.^{13,14} Originally, the sol-gel reaction was used to prepare pure ceramic precursors and inorganic glasses at relatively low temperatures. The reaction is usually in two steps: hydrolysis of metal alkoxides to produce hydroxyl groups, followed by polycondensation of the hydroxyl groups, and residual alkoxy groups, to form a three-dimensional network.

There are many different synthetic techniques used in the sol-gel process to generate organic-inorganic hybrid materials: (1) *In situ* formation of inorganic network in the presence of a preformed organic polymer. To obtain optically transparent materials, conditions need to be identified under which the organic

polymer will not phase separate during both the gel forming and the drying processes. The most important adjustable parameter in controlling polymer solubility is the cosolvent used. Solvents commonly used are alcohol, THF, and DMF. Introduction of covalent bonds between the inorganic and organic phases is more suitable to reduce phase separation. (2) The infiltration of a polymerizable organic monomer into formed oxide gels to be polymerized *in situ* by thermal or irradiation method. (3) Simultaneous formation of both organic polymer and inorganic matrix, whereby transparent organic-inorganic hybrids can be prepared containing organic polymers that would normally be insoluble in typical sol-gel solutions. The above three organic-inorganic synthetic techniques are distinguished by the sequence of formation of the organic and inorganic components.

For most synthetic techniques, we can see that organic solvent is indispensable in the preparation of organic-inorganic hybrids. However, how to avoid the use of organic solvents is an important task at present. We previously described a new sol-gel method of synthesizing PBMA/SiO₂ and poly(methyl methacrylate) (PMMA)/SiO₂ hybrids by an *in situ* sol-gel process by using emulsion polymers.^{15,16} The replacement of organic solvent with water results in a more environmentally friendly method of preparing organic-inorganic hybrids. Though hydrogen bonding between the hydroxyl groups in the SiO₂ network and the SO₃ group of the surfactant aids in getting domain size in nanoscale, materials from the PMMA system

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are still nontransparent, because in this new method, the glass transition temperature (T_g) has a great influence on the transparency of the resultant materials. Because T_g of PMMA is much higher than the casting temperature (room temperature), PMMA latex particles cannot deform to produce space-filling Wigner-Seitz cells during the film forming process. Voids and developed surface roughness result in nontransparent films.

Though organic-inorganic nanocomposites prepared by the sol-gel process have attracted a great deal of attention during the past decade, very few studies were devoted to investigating the mechanism of phase separation.¹⁷⁻¹⁹ The change in morphology in the system by the emulsion method, especially, was not reported. In this article, we prepared transparent PEA/SiO₂ hybrids, and the influence of the SiO₂ content, the casting temperature, and pH value on the morphology of the materials were investigated.

EXPERIMENTAL

Materials

The polymer component, poly(ethyl acrylate) (PEA), was synthesized by emulsion polymerization at 80°C. Ethyl acrylate [analytical reagent (AR)] was distilled under reduced pressure under nitrogen and kept in a refrigerator before use. The initiator potassium persulfate (AR), surfactant sodium dodecyl sulfate (AR), and the buffer sodium bicarbonate [chemically pure (CP)] were used as supplied. The metal alkoxide used was tetraethoxysilane (TEOS) (CP). The PEA latex particle size was 76.7 nm measured by a LS particle size analyzer.

Organic-inorganic nanocomposites preparation

The 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 molar ratio of TEOS : H₂O = 1 : 3. Nonionic water containing 0.17M HCl was added. After the emulsion and the prehydrolyzed TEOS solution were mixed and shaken up, the resulting solution was immediately cast into a PTFE mold and dried at 40°C in an oven or at room temperature. For experiments where the influence of pH is investigated, the pH value of the emulsion was adjusted to a prescribed range before mixing with the prehydrolyzed TEOS. All the samples were dried at 40°C in vacuum before characterization.

Measurements

Transmission electron microscopy (TEM) was performed on thin sections by using a Jeol JEM 2010

transmission electron microscope. The samples were microtomed perpendicular to the casting direction with a LKB Ultratome III.

RESULTS AND DISCUSSION

Effect of composition

The PEA/SiO₂ hybrids with different compositions (95/5, 50/50, weight ratio) were prepared in PTFE molds of the same size by air-drying or drying at 40°C the mixed solution of prehydrolyzed TEOS and polymer emulsion. All the mixed solutions are of equal weight and all the resulting samples are transparent; yet, there is a great difference in their appearance. For the 95/5 system, the resulting hybrid is a thin film of the same diameter as the mold, whereas that of the 50/50 system is thicker and smaller. This stems from different forming processes of hybrids of different compositions. When the amount of SiO₂ is quite small and the prehydrolyzed TEOS added into the polymer emulsion is relatively small, the sol-gel transition in the very diluted solution is infinitely extended and the gel state does not occur before the water completely volatilizes and the thickness of the sample is close to that of the pure PEAs. Because there is no chance for a continuous SiO₂ three-dimensional network to form at these dilutions, no shrinkage occurs and an intact film without any cracks can be obtained. At higher SiO₂ content, gelling occurs concurrently with slow volatilization of water, and shrinkage of the gel takes place. The resulting PEA/SiO₂ (50/50) hybrids are smaller, thick discs cracked into two or three parts. Thus, hybrids with different compositions differ in their film-forming processes.

Transmission electron micrographs of the PEA/SiO₂ (95/5) and PEA/SiO₂ (50/50) hybrids are shown in Figures 1 and 2. Though both hybrids are transparent, TEM images reveal that a microscopic heterogeneity exists. Qualitative differences in primary (smallest) particle size, degree of phase heterogeneity, and sharpness of the PEA/SiO₂ interface are apparent. For low SiO₂ ratio samples (Fig. 1), where the rate of gel forming was slower than the rate of water loss, close contact and aging of the latex particles occurred before the formation of the strong SiO₂ three-dimensional network. Under proper conditions, the SiO₂ phase could disperse evenly around the latex particles. The image of Figure 1(b) shows that the boundary between the inorganic and the organic phases is indistinct even at the highest magnification, indicating an intimate mixing of the two phases. For samples with high SiO₂ content (PEA/SiO₂ 50/50, Fig. 2), the PEA latex particles are evenly inlaid in SiO₂ matrix. The sol-gel transition takes place before the water volatilizes completely and there is close contact of the latex particles. During its sol-gel transition, the latex particles lost their ability to move and became fixed in SiO₂ matrix.

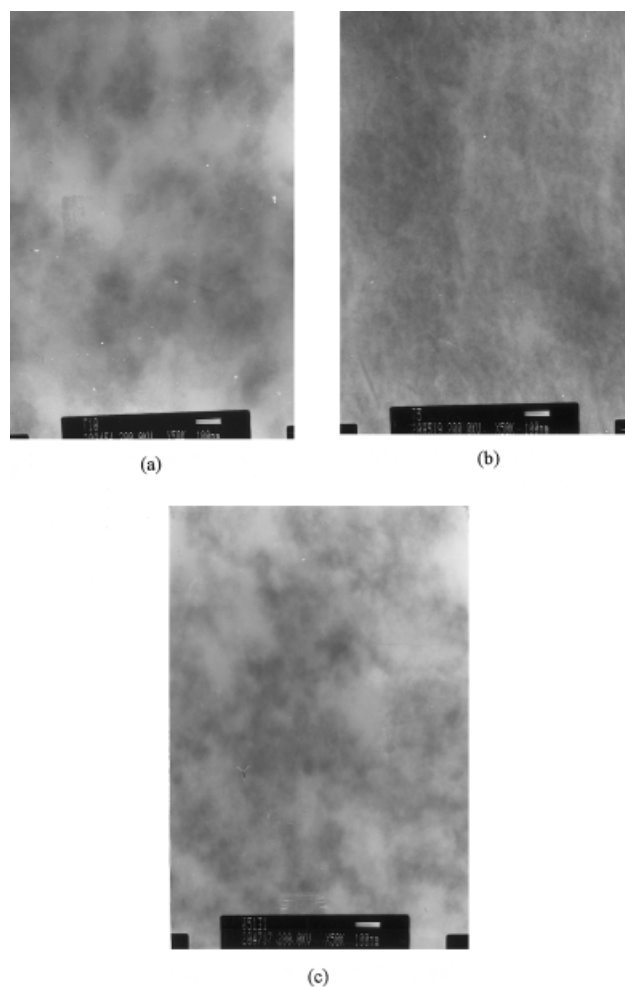


Figure 1 TEM of PEA/SiO₂ (85/5) hybrids at room temperature pH = 6.5 (a), pH = 8 (b), and at 40°C pH = 8 (c).

Therefore, we draw the conclusion that different compositions govern different film formation processes, leading to different morphology of the hybrids. Further discussion will be appear in the last part of Results and Discussion.

Effect of pH value

The hydrolysis of TEOS is most rapid and complete when catalysts are employed.^{20–22} Although mineral acids and ammonia are most generally used in sol-gel processes, many authors reported that mineral acids are more effective catalysts than equivalent concentrations of a base. In this experiment, when the hydrolysis of TEOS was catalyzed by hydrochloric acid, the reaction was fast and stable. Instead, if NH₄OH was employed as the catalyst, the rate of hydrolysis was relatively slow and precipitation was apt to occur. Generally, the pH value was about 2 in solution of a prehydrolyzed TEOS, and the pH value of the resultant mixed solution increased gradually with an in-

crease in polymer content (e.g., pH ~ 3 in a 50/50 system and ~ 6.5 in a 95/5 system).

To investigate the influence of pH on the 95/5 and 50/50 systems, pH values of the mixed solutions were adjusted to three chosen values of 3, 6.5, and 8, respectively, by adding HCl or NH₄OH. In the 95/5 system, under acid conditions, obvious phase separation occurred. It is reasoned that the latex particles are unstable under acid conditions and are easy to agglomerate. On drying, clusters of polymer latex particles were produced. Hydrogen bond interaction between the surfactant on the surface of the latex particles and the SiO₂ network was impaired and phase separation occurred. Under neutral and basic conditions, transparent films were prepared, yet as shown in Figure 1, there is slight difference in TEM images: the pH = 8 sample of PEA/SiO₂ is more uniform than the pH = 6.5 sample. This is because the latex particles are more stable under a weakly basic condition. For the 50/50 system, under acid and weakly basic conditions, transparent hybrids can be obtained, but pores are retained. For this system of higher SiO₂ content, the gel transition appeared ahead of the coalescence and fusion of the latex particles, so the latex particles were evenly inlaid in the SiO₂ matrix. TEM result of sample PEA/SiO₂(50/50), pH = 3, is shown in Figure 2. The gel time was the shortest, when pH was near 6. The mixed solution of PEA emulsion and prehydrolyzed TEOS turned into gel state in about 5 min after the pH was adjust to 6.5. Because the rate of the gel transition was too fast, water was difficult to release and pores were retained. The resultant hybrid was often opaque.

Effect of the casting temperature

In two previous articles,^{15,16} it was shown that T_g of a polymer is important for both the pure polymer latex

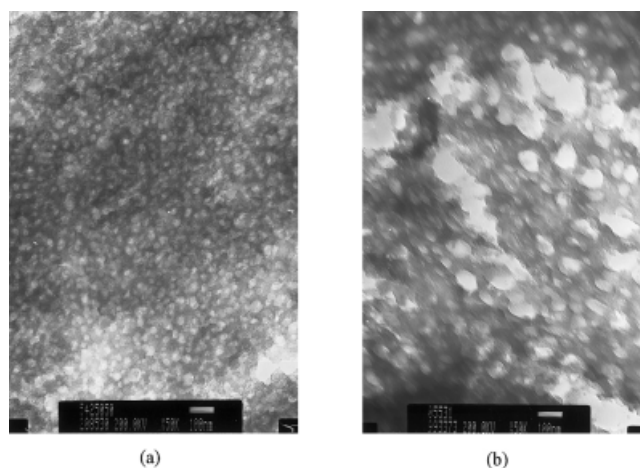


Figure 2 TEM of PEA/SiO₂ hybrids at pH = 3 (a) at room temperature, (b) 40°C.

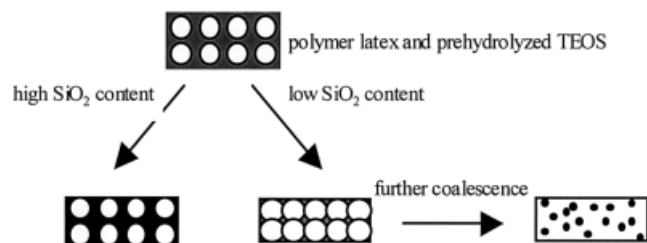


Figure 3 Schematic illustration of morphology in PEA/SiO₂ films with different SiO₂ contents. The particle sizes are not drawn to scale.

and the hybrids by emulsion method. The virgin latex, when applied onto a substrate and subsequently dried below a certain temperature, will result in a film consisting of nontransparent, powdery fragments. The opacity suggests that there are still many residual voids left within the film capable of scattering incident light. However, if it is dried above this temperature, the result will be a homogeneous, transparent film. This apparent critical temperature is called the minimum film-forming temperature (MFT) generally lying near T_g of the polymer. For the PMMA ($T_g = 100^\circ\text{C}$) system,¹⁵ nontransparent hybrid films were obtained at room temperature, although their TEM micrographs revealed that the phase size was <100 nm. For the PBMA ($T_g = 33^\circ\text{C}$) system,¹⁶ transparent hybrid films were obtained at 35°C . Instead, the films were opaque at room temperature. All the results showed that one can prepare transparent hybrids by choosing the polymer with lower T_g and a suitable casting temperature. In this article, hybrids PEA/SiO₂ (95/5 and 50/50) at different casting temperatures were prepared to investigate the effect of casting temperature on the hybrids. At both room temperature and 40°C , transparent PEA/SiO₂ samples can be obtained, even though TEM results show that their morphology is quite different (Figs. 1 and 2). For the PEA/SiO₂ (95/5) system, the dispersion of SiO₂ in PEA is very uniform at pH = 8 at room temperature [Fig. 1(b)], but coalescence of latex particles occurs at 40°C [Fig. 1(c)] with some degree of phase separation or phase heterogeneity. The PEA/SiO₂ (50/50) system had a similar phenomenon [Fig. 2(a) and 2(b)]. This is because the casting temperature has an effect on both the fusion of the latex particles and the gel transition of TEOS. The rising of temperature accelerated the fusion among the particles and the TEOS's gel transition, destroying the interaction of the hydrogen bonds between the latex particles and the SiO₂ network. Therefore, suitable temperature is the premise in preparing hybrids with good dispersion.

Film-forming mechanism

During the past few years, the use of latex blends has gained more and more attention. Several implicit or

explicit aims in blending large and small latex particles underlie the development of latex blend films. Many studies^{23–25} focus on blends of large and small particles, blends of film-forming and non-film-forming (i.e., hard and soft) particles, and blends with various sizes and hardness to obtain films with ideal properties. Our study in this article, although not on blends of latex, has some points in common. For latex blends, the critical volume fraction of small particles was required to obtain a continuous phase of small particles surrounding the large particles. Below this value, there are not enough small particles to create a continuous phase. The critical volume fraction also exists in our case. Our conclusions for PEA/SiO₂ film with different SiO₂ contents are summarized in Figure 3. When the SiO₂ content is high enough, the sol-gel transition occurs before the complete volatilization of water and also the close contact. The polymer latex particles are then fixed in the SiO₂ matrix. If the SiO₂ content is not high enough, the prehydrolyzed TEOS molecules only exist among the particles, in no way to form continuous SiO₂ networks. After further coalescence of the PEA latex particles, SiO₂ as dispersed phase are evenly dispersed in the PEA matrix. The smaller the size of latex particle, the higher the interfacial area between PEA and SiO₂ phases and the more intimate the mixing of the two phases. The above process can take place under conditions where the latex particles are stable enough in the whole drying process. Under heating or acid condition, the latex particles are unstable and easy to coalesce, leading to a decrease of the interfacial area between PEA phase and SiO₂ phase. Therefore, the size of phase heterogeneity increases under this condition. The process is depicted in Figure 4.

From the above, we can see that the mechanism of phase separation is quite different from that of traditional polymer solution organic-inorganic nanocom-

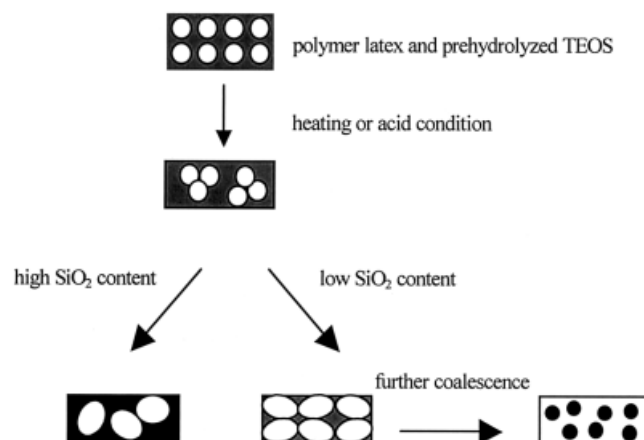


Figure 4 Schematic illustration of clustering of latex particles under heating or acid conditions leading to an increase in phase heterogeneity.

posites. For traditional polymer solution systems, phase separation mechanism is similar to that of polymer blends, i.e., nucleation and growth mechanism and spinodal decomposition mechanism.^{26,27} Generally, the component with higher content is apt to form the continuous phase and the other as dispersed phase. However, for polymer emulsion system, whether PEA can be continuous or not depends mainly on whether the PEA latex particles are in close contact before the sol-gel transition. Instead, it depends on whether the content of PEA is larger than SiO₂.

CONCLUSION

For PEA system with lower T_g (-15°C), transparent PEA/SiO₂ hybrids were conveniently prepared by emulsion sol-gel method. TEM results show that morphology of the resulting materials changes with the SiO₂ content. With increasing SiO₂ content, PEA turned into dispersed phase from continuous phase as the SiO₂ content was lowered. The change in phase morphology depends mainly on the time the sol-gel transition occurs. If the sol-gel transition occurs before the complete volatilization of water and close contact of the polymer latex particles, PEA will be dispersed phase. Instead, PEA will be continuous phase. Additionally, pH value and the casting temperature affect the morphology of the hybrids. On the whole, the pH value should be adjusted from high to low with increasing SiO₂ content. The rise in casting temperature is always detrimental to the morphology for any composition.

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