

Preparation of Silicon Dioxide/Polyurethane Nanocomposites by a Sol–Gel Process

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ABSTRACT: Aqueous emulsions of cationic polyurethane ionomers, based on poly(ϵ -caprolactone glycol) as soft segment, isophorone diisocyanate as hard segment, 3-dimethylamino-1,2-propanediol as chain extender and potential ionic center, and hydrochloric acid as neutralizer, were mixed with tetraethoxysilane to prepare silicon dioxide–polyurethane (SiO₂/PU) nanocomposites by a sol–gel process during which the inorganic mineral is deposited *in situ* in the organic polymer matrix. The sizes and distributions of

the particles were measured by dynamic light scattering, and the structure and morphology of the nanocomposites were observed by transmission electron microscope and FTIR spectrum. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2013–2016, 2004

Key words: polyurethanes; nanocomposites; sol–gel; self-organization; TEM

INTRODUCTION

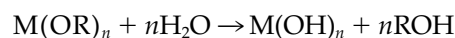
In recent years, nanostructured inorganic–organic composites have attracted increasing interest of researchers.^{1–3} Even though conventional composites have been widely used in diverse areas such as transportation, construction, electronics, and consumer products, it is difficult for them to attain a synergistic property from the individual components. Composites that have more than one solid phase with a dimension in the 10- to 100-nm range^{4,5} are defined as nanocomposites. They exhibit improved performance properties compared with those of conventional composites because their unique phase morphology by layer intercalation or exfoliation maximizes interfacial contact between the inorganic and organic phases and enhances interfacial properties. Inorganic–organic nanocomposites greatly improve the thermal, mechanical, barrier, and even the flame-retardant properties of the polymers.⁶

Inorganic–organic nanocomposites can be prepared by directly blending organic materials with inorganic nanoparticles or by a sol–gel process with a metal alkoxide such as tetraethoxysilane (TEOS) for the silicon dioxide (SiO₂)–polymer system. The most commonly used inorganic nanoparticles are SiO₂, TiO₂, ZnO, and CaCO₃, for example. Of these, nanosilica was first produced and studied in a number of polymer systems. For instance, Chang et al.⁷ introduced it into a poly(methyl methacrylate) matrix.

It has been well established that the introduction of SiO₂ into a polymer matrix can effectively improve the polymer's properties such as abrasion resistance, shock absorption, surface hardness, modulus, and so on. However, it is difficult for nanosilica particles to be dispersed directly in the water phase without a surface pretreatment such as graft modification by an organosilane coupler.^{8,9} Even though they can be dispersed temporarily, the nanosilica particles gather together in larger aggregates finally because of their high surface energy.

In this work, the SiO₂/polyurethane (PU) nanocomposites in which cationic polyurethane was presented in a form of a microemulsion were developed to reduce the surface energy of nanosilica. To our knowledge, there is no information in the literature about the preparation and physical properties of water-based cationic polyurethanes modified by nanosilica.

Since the 1970s the sol–gel process has been used for the deposition of inorganic minerals *in situ* in an organic polymer matrix.^{10,11} Starting materials for the sol–gel process are metal alkoxides, M(OR)_n, and a small amount of acid or base as catalyst. Metal alkoxides are hydrolyzed, and metal hydroxides, M(OH)_n, are formed. The reaction is shown as follows:



where M = Na, Ba, Cu, Al, Si, Ti, Ge, V, W, ···; R = CH₃, C₂H₅, C₃H₇, C₄H₉, ···; M(OH)_n are reactive and three-dimensional networks with –O–M–O–M– linkages, formed by polycondensation of M(OH)_n with M(OR)_n or M(OH)_n.¹²

The diagrammatic sketch of micelles formed by cationic polyurethane ionomers in water is shown in

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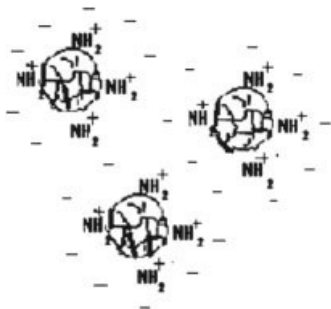


Figure 1 Diagrammatic sketch of micelles formed by cationic polyurethane ionomers in water.

Figure 1. According to the conclusion suggested by Lorenz,^{13,14} cationic polyurethane ionomers in water are stabilized because of the electric double layer and solvent effect. Because the soft segment of cationic polyurethane is hydrophobic and the hard segment with NH_2^+ is hydrophilic, the molecular chains of cationic polyurethane can self-organize to micelles when dispersed in water. The hydrophilic groups in the micelles are on the surfaces of particles and hydrophobic groups are crimped into the particles. The micelles make a Brownian motion and positive charges are simultaneous with negative ones, so an electric double layer is formed on the surface and there is a voltage between them. The voltage blocks the aggregation of particles, causing them to act as a surfactant. At the same time, there are hydrogen bonds between the hydrophilic groups and water molecules, and then the particles are surrounded by a layer of water molecules. The solvent effect can also hinder the aggregation of particles.

In this study, to reduce the high surface energy of nanosilica and control its dimension more effectively, the micelles of cationic polyurethane ionomers in aqueous emulsion were used as nanocapsules in which TEOS would precipitate *in situ* in the cationic polyurethane matrix by a sol-gel process, thus allowing SiO_2/PU nanocomposites to be prepared. The microstructure and phase morphology were studied.

EXPERIMENTAL

Materials

Poly(ϵ -caprolactone glycol) (Cp-210, $M_n = 1000$; Solvay Interox, UK), isophorone diisocyanate (IPDI; Nuodex Inc., Japan), 3-dimethylamino-1,2-propanediol (DAH; produced in our laboratory), and tetraethoxysilane (TEOS; Tianjin Chemical Co., China) were used in this investigation. Before use, IPDI was vacuum distilled at 70°C and 0.025 mmHg . Cp-210 was degassed at 40°C and 0.5 mmHg .

Preparation of aqueous emulsion of cationic polyurethane ionomers

A 250-mL round-bottom, four-neck separable flask with a mechanical stirrer, thermometer, and condenser with drying tube was used as a reactor. The reaction was carried out in a thermostat. IPDI (7.33 g) and Cp-210 (10 g) at a molar ratio of 3.3:1 were dissolved in THF solvent, and then the whole solution was heated to 85°C for 3 h with stirring to form a prepolymer. Then 2.38 g of DAH was added to the prepolymer and kept at 85°C for 0.5 h followed by end capping with isopropanol at 60°C for 15 min. Finally, 1.0 g hydrochloric acid and 80 mL distilled water were added to form an aqueous emulsion, after which THF was removed by reduced pressure distillation at 45°C . The final concentration of PU in water was 20% by weight.

Preparation of SiO_2/PU nanocomposites

When the end capping of the prepolymer was finished as described above, a certain amount of TEOS with the ratio of 1–5 : 10 by weight between TEOS and PU was mixed with PU solution at 60°C for 0.5 h, followed by addition of hydrochloric acid, distilled water, and reduced pressure distillation. Then the aqueous emulsions of SiO_2/PU nanocomposites were formed.

Measurement

Energy spectrum scanning on the electrophoresis film of SiO_2/PU nanocomposite was performed by a Philips XL 30 scanning electron microscope (Philips, The Netherlands) and EDAX Phoenix energy spectrum scanning electron microscope. The sample was prepared by putting two iron sheets that acted as electrodes into the prepared SiO_2/PU nanocomposite emulsion. When a voltage of 120 V was charged between the two electrodes, the particles started moving toward the negative electrode and depositing on its surface because of the positive charges on the surface of SiO_2/PU nanocomposite particles in emulsion. The electrophoresis process lasted for 2 min.

Infrared spectroscopic tests on pure PU and SiO_2/PU nanocomposites were performed with a Bio-Rad FTS3000 FTIR spectrometer (Bio-Rad, Hercules, CA). To remove the water, the aqueous emulsions of pure PU and SiO_2/PU nanocomposite were dried in a vacuum oven at 70°C for 24 h. The dried films were coated onto KBr disks.

The morphology of the SiO_2/PU nanocomposite particles was observed by a Philips EM400ST transmission electron microscope. The sample was prepared by depositing the emulsion onto a copper net after being stained by phospho-wolframic acid.

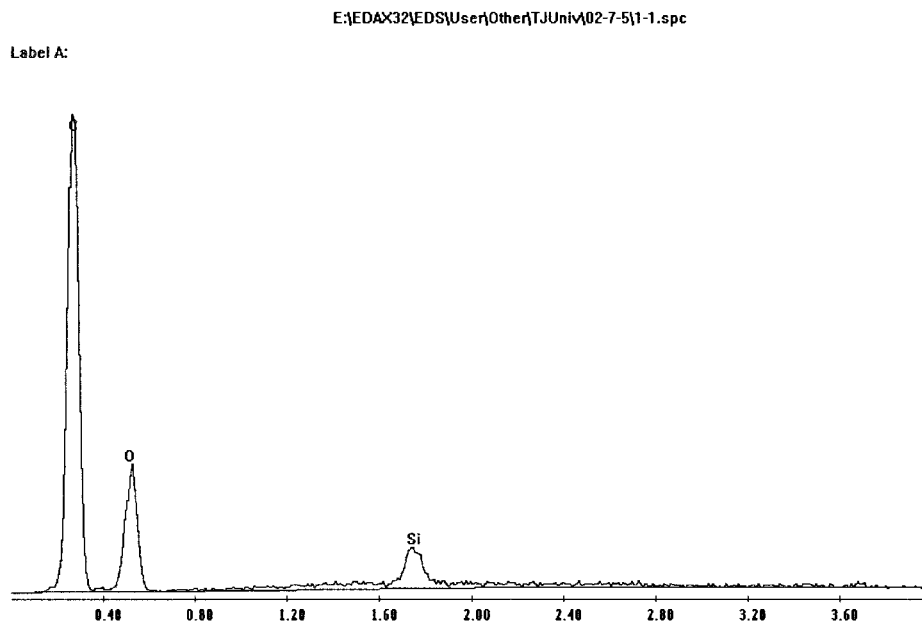


Figure 2 Energy spectrum scanning of SiO₂/PU nanocomposite with the ratio of 1 : 10 by weight between TEOS and PU.

Average sizes and size distributions of the particles in aqueous emulsions were measured by dynamic light scattering (BI9000AL), where an Ar-type laser with wavelength 514.5 nm was used. The samples were first diluted with deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion.

RESULTS AND DISCUSSION

The energy spectrum scanning on electrophoresis film of SiO₂/PU nanocomposites is shown in Figure 2,

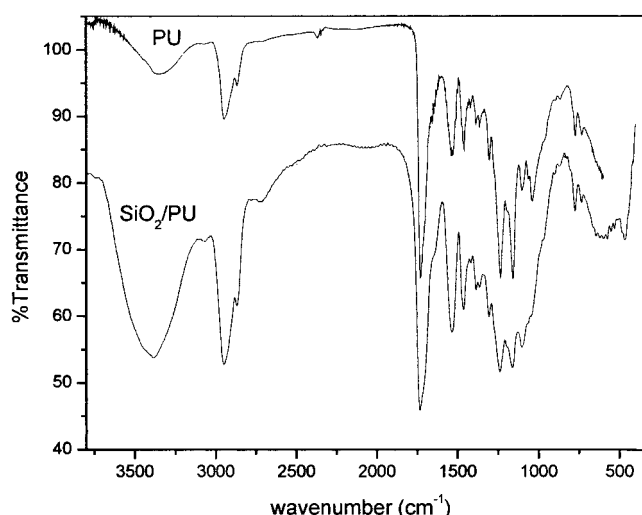


Figure 3 FTIR spectra of pure polyurethane and SiO₂/PU nanocomposite with the ratio of 3 : 10 by weight between TEOS and PU.

from which it may be seen that the silicon element was in the sample in addition to carbon and oxygen. As we know, there were no charges on the surface of SiO₂; thus SiO₂ particles themselves could not move toward the negative electrode automatically during the electrophoresis process except by being encapsulated by cationic polyurethane micelles. Thus we can say that TEOS had precipitated *in situ* in the polyurethane matrix, and then SiO₂/PU nanocomposites could be prepared by this method.

The microdomain structures of the PU and SiO₂/PU were analyzed by FTIR as shown in Figure 3. From Figure 3, the peaks that are characteristic of PU structure may be found in the curves for both PU and SiO₂/PU systems. The detailed description of IR bands in pure polyurethane may be found elsewhere.¹⁵ In addition, there were some other peaks in



Figure 4 TEM image of SiO₂/PU nanocomposite with the ratio of 2 : 10 by weight between TEOS and PU.

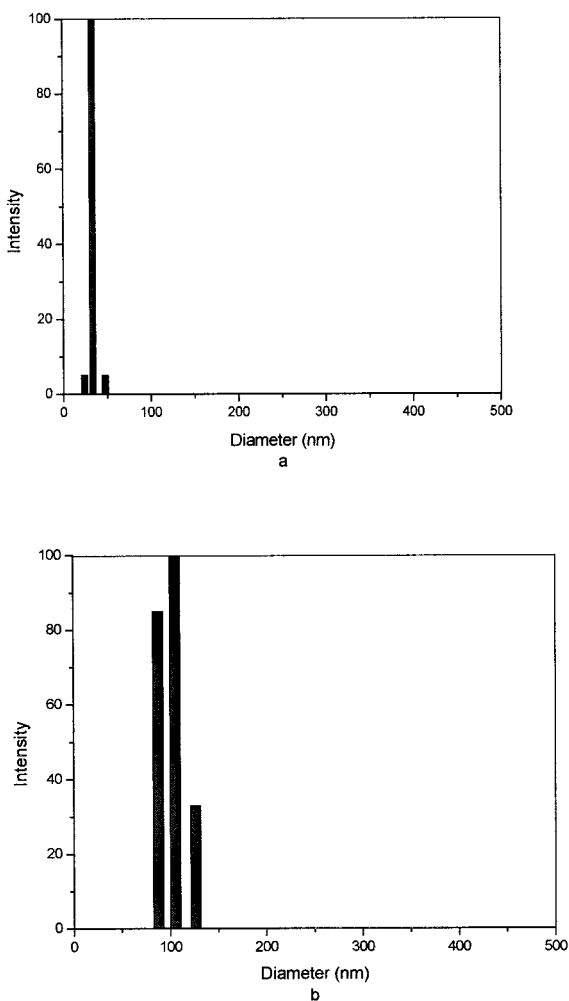


Figure 5 SEM images of (a) PU and (b) SiO₂/PU with the ratio of 5 : 10 by weight between TEOS and PU.

the IR spectra of SiO₂/PU. The peak with a wavenumber of 3384 cm⁻¹ corresponded to O—H stretching of Si—OH, and the peaks at 1100 and 871 cm⁻¹ were attributed to Si—O stretching. It may thus be proved that the structure of PU was been affected by the presence of SiO₂, implying that the SiO₂ did not react with the PU molecules.

Figure 4 is the TEM micrograph of SiO₂/PU nanocomposite colored by phospho-wolframic acid. We can see clearly that the SiO₂/PU nanocomposite particle is approximately round with a diameter of about 90–100 nm.

The particle sizes and distributions of PU and SiO₂/PU measured by dynamic light scattering are presented in Figure 5. The particle size of SiO₂/PU was larger than that of PU, and the distribution wider. The size actually doubled going from pure PU to SiO₂/PU nanoparticles. This is because PU micelles could effectively encapsulate TEOS, supplying micro-reactors for its hydrolysis and polycondensation. The electric double layer and solvent effect would block the aggregation of particles. However, because the nanoparticles were of a loose structure in which there were other materials such as water and alcohol besides SiO₂ particles, the precipitation of TEOS within polyurethane nanocapsules caused the particles to increase in diameter. Even so, both of them were still at the order of nanometer.

CONCLUSIONS

Aqueous emulsions of silicon dioxide–polyurethane (SiO₂/PU) nanocomposites were synthesized from the tetraethoxysilane deposited *in situ* in the cationic polyurethane matrix by a sol–gel process. The structures of PU were not affected by the introduction of the silicon dioxide.

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