

Structure and Properties of Polyurethane/Nanosilica Composites

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ABSTRACT: Nanosilica particles were directly introduced into polyester polyol resins through *in situ* polymerization and blending methods, then cured by isophorone diisocyanate (IPDI) trimers to obtain nanocomposite polyurethanes. FTIR and TGA analyses indicated that more polyester segments had reacted with silica particles during *in situ* polymerization than during the blending method, accompanied by higher T_g and more homogeneous dispersion of nanosilica particles in the polymer matrix from *in situ* polymerization. Maximum values in T_g , tensile properties, macro-

hardness, abrasion resistance, and UV absorbance were obtained when the particle size of silica was about 28 nm. The polyurethane/nanosilica composites obtained by *in situ* polymerization generally had better mechanical properties than those by the blending method except for some unexpected macrohardness at relatively high silica content. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1032–1039, 2005

Key words: polyurethane/nanosilica composites; coatings; mechanical properties; nanocomposites; dispersions

INTRODUCTION

Organic–inorganic nanocomposites combine the advantages of organic polymers (flexibility, ductility, dielectric strength, etc.) and those of inorganic materials (rigidity, high thermal stability, UV-shielding property, and high refractive index, etc.).^{1–9} Moreover, they usually contain some special properties of nanoparticles and consequently can be widely used in many fields such as plastics, rubbers, coatings, inks, and so forth.

Generally, there are two typical kinds of organic–inorganic nanocomposites, depending on the strength or level of interaction between organic and inorganic phases: one involving physical or weak phase interaction (e.g., hydrogen bonding, van der Waals forces) and another possessing a strong chemical covalent or ionic–covalent bond between the organic and inorganic phases. The typical preparation method, for the

second kind of organic–inorganic nanocomposites, is the so-called sol–gel technique. There are many nanocomposite polymers, especially containing nano-SiO₂ or nano-TiO₂, prepared by sol–gel approach, and investigated by focusing on how the nanoparticles influence mechanical, thermal, and optical properties, and so on, of the nanocomposite polymers, and the relationship between structure and properties.^{10–15}

This article reports on a recent investigation of silica particles obtained from the sol–gel process, with different size and surface groups, that were directly embedded into polyester polyol by *in situ* polymerization or a blending method, then cured by isophorone diisocyanate (IPDI) trimer to give polyurethane/nanosilica composites. The objective of this study was to investigate how processing, particle sizes, and surface groups influence the structures and properties of nanocomposites. FTIR, TGA, DMA were used to characterize the interactions between organic and inorganic phases; TEM was used to observe the morphologies of silica particles in the organic matrix. The mechanical and optical properties measured included tensile properties, macrohardness, abrasion resistance, and ultraviolet–visible (UV–vis) properties.

EXPERIMENTAL

Materials

Tetraethylorthosilicate (TEOS, SiO₂ content 28.5 wt %), absolute ethanol (99.7%), and ammonia solution

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TABLE I
Basic Properties of Silica Sols and Their Corresponding Nanocomposite Polyurethanes

| Silica sol | Particle size (nm) | Amount of OH groups ($\times 10^{-3}$ mol-OH/g) | Samples from the resins by <i>in situ</i> polymerization blending method | |
|------------|--------------------|--|--|---------------------|
| S1 | 14 | 0.82 | TU1-4 | BU1-4 |
| S2 | 28 | 1.3 | TU2-4 | BU2-4 |
| S3 | 66 | 1.25 | TU3-2, TU3-4, TU3-8 | BU3-2, BU3-4, BU3-8 |
| S4 | 103 | 1.02 | TU4-4 | BU4-4 |
| S5 | 154 | 0.88 | TU5-4 | BU5-4 |
| S6 | 260 | 0.8 | TU6-4 | BU6-4 |

(25–28% ammonia content,) were purchased from Shanghai Chemical Agent Company of China. Phthalic anhydride (98%), adipic acid (99%), 1,4-butanediol (98%), neopentyl glycol (98%), 4-methyl-2-pentanone (96%), and dibutyltin dilaurate (99%) were supplied by Bayer AG (Leverkusen, Germany). The crosslinking agent VESTANAT T 1890E, an isophorone diisocyanate (IPDI) trimer (solids content: 70%; NCO: 12%), was supplied by Degussa AG (Düsseldorf, Germany). All the ingredients were used as received.

Preparation of silica sols and polyester polyol/nanosilica composites

The silica sol was prepared according to Stöber's method^{16,17} by changing the content of ammonia while keeping other components constant. Polyester polyol was prepared according to Wu et al.¹⁸ Two approaches were adopted to introduce silica particles to form polyester polyol/nanosilica composites: one was the *in situ* polymerization method, in which silica sol was first mixed with the monomers, after which condensation polymerization was carried out using the same procedures and parameters as those for preparing pure polyester polyol resin; another was the blending method, in which silica sol was directly mixed with polyester polyol resin at 160°C for 0.5 h by vigorous stirring. Table I summarizes the particle sizes and hydroxyl values of silica sols.

Preparation of polyurethane/nanosilica composites films

The polyester polyol/nanosilica composite was mixed with IPDI trimer solution in the weight ratio of 0.9/1 and the concentration was adjusted to 60 wt % at appropriate viscosity by adding 4-methyl-2-pentanone at room temperature. Just before application, 0.05 wt % of dibutyltin dilaurate, based on the total weight of the polyester polyol/nanosilica composites and IPDI trimer on solids, was mixed thoroughly with the resin solution. The nanocomposite coatings, with about 45 μm thickness, were prepared by casting the

above mixtures onto glass substrates. The coatings, with about 10 μm thickness, were prepared using a drawdown rod by casting the above solution onto a quartz panel. The coatings were cured at 100°C for 0.5 h then kept at ambient temperature for 2 weeks for further characterization. The prepared polyurethane/nanosilica composites are labeled as TUa-b or BUa-b, where T and B represent silica particles introduced by *in situ* and blending methods, respectively; U represents polyurethane; a represents the introduced silica sol code, and different codes indicate different particle sizes; b represents the silica weight percentage in polyester polyol/nanosilica composite resins before curing by IPDI trimers. For example, the sample TU1-4 indicates the polyurethane nanocomposite prepared by curing polyester polyol/nanosilica composite resin with 4 wt % nanosilica content embedded by *in situ* polymerization, and has silica particle diameter of 14 nm corresponding to silica sol code 1. The samples of the obtained polyurethane/nanosilica composites are also listed in Table I.

Characterization

FTIR

The silica particles, from polyester polyol/nanosilica composite resins, were obtained by diluting the composites with acetone, then centrifuged and washed five times with acetone to remove substances physically adsorbed on the surfaces of silica particles; the washed powders were then dried at 100°C for 2 days. The silica powders were characterized by a Magna-IR[®] 550 FTIR (Nicolet Analytical Instruments, Madison, WI) with 2 cm^{-1} resolution.

Thermal gravimetric analysis (TGA)

The silica powders were analyzed using a TGA Model SDT 2960 apparatus (TA Instruments, New Castle, DE). The measurements ranged from ambient temperature to 600°C with a heating rate of 5°C/min at air atmosphere.

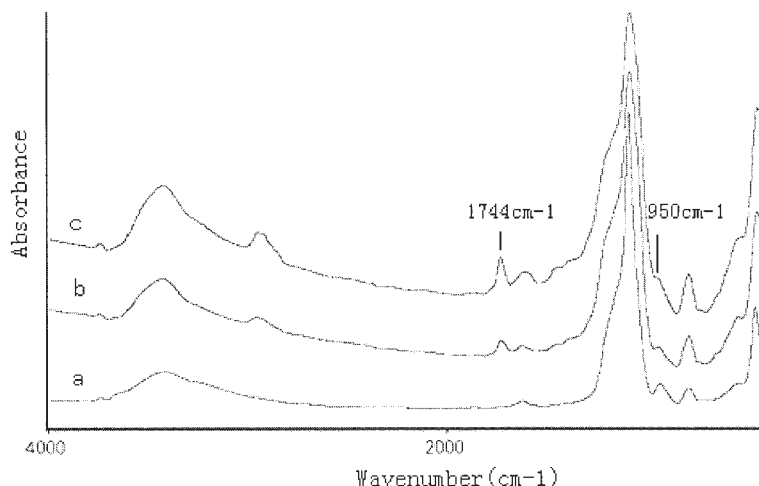


Figure 1 Typical FTIR spectra of silica powders separated from: (a) silica sol, (b) nanocomposite resin by blending method, and (c) nanocomposite resin by *in situ* polymerization.

Transmission electron microscopy (TEM)

The morphologies of silica particles were obtained by a transmission electron microscope (TEM, Hitachi H-600; Hitachi Corp., Osaka, Japan). Samples of the silica particles in the sol, as well as in polyester polyol/nanosilica composite resins, were diluted with ethanol and then dried on copper grids, whereas silica particles in the polyurethane/nanosilica composites were prepared by ultramicrotoming at room temperature, giving sections of nearly 100 nm in thickness. No further staining was used to improve contrast.

Dynamic mechanical analysis (DMA)

DMA measurements were carried out on a DMA 242 (Netzsch-Gerätebau GmbH, Bavaria, Germany). The samples were quickly cooled to -50°C and equilibrated at that temperature for 3 min, after which they were heated to 120°C at a frequency of 10 Hz with a constant heating rate of $5^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

Tensile properties

Tensile properties were acquired by an Instron model DXLL 1000-20000 machine (Shanghai, China). The dumbbell-shape specimens for tensile tests were cut from the molded polymer films according to Die C of ASTM-D412t, and testing carried out at a crosshead speed of 200 mm/min. A 20-mm benchmark and the original cross-sectional area were used to calculate their tensile properties. The tensile strength and elongation at break were automatically calculated by the computer connected to the Instron. The average of at least five measurements for each sample was reported, and the experimental error was about $\pm 10\%$.

Abrasion resistance

Abrasion resistance was determined on a round glass board according to GB1768-79. A 120 rubber abrasive wheel was used. The abrasion resistance was evaluated by the average value of five weight losses after 200 cycles of rubbing. Experimental error was about $\pm 10\%$.

Macrohardness

Macrohardness was determined using a pendulum hardness tester according to Chinese National Standard GB/T1730-93. Times, varying from 5 to 2° for the pendulum on the glass, with and without polymer films, were designated t and t_0 , respectively. The ratio of t/t_0 is regarded as macrohardness. Experimental error was about $\pm 10\%$.

Ultraviolet-visible spectra (UV-vis)

The UV-vis absorbance spectra of the nanocomposite films, cast onto quartz panels with about $10\ \mu\text{m}$ thickness, were determined on a UV-vis spectrophotometer (Hitachi UV-3000, Japan) in the range of 200–700 nm wavelength light.

RESULTS AND DISCUSSION

Interactions between colloidal silica particles and polyester polyol resins

The colloidal silica particles from polyester polyol/nanosilica composite resins were scanned by FTIR spectroscopy. Figure 1 displays their representative spectra and the spectrum of the silica particles from silica sol for the sake of comparison.

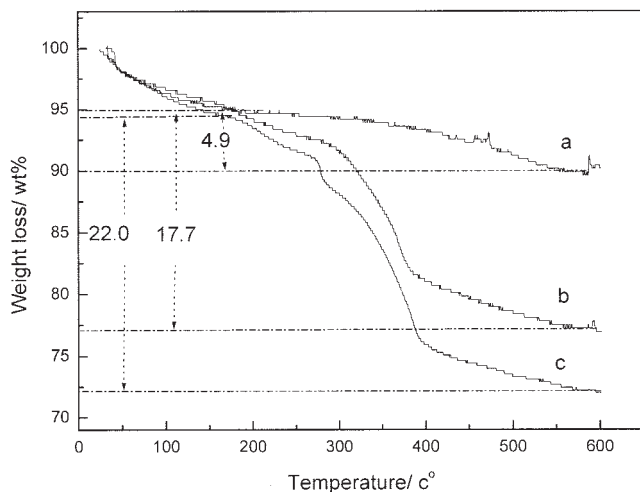


Figure 2 Typical TGA curves of silica powders separated from: (a) silica sol, (b) nanocomposite resin by blending method, and (c) nanocomposite resin by *in situ* polymerization.

Compared with the FTIR spectrum of the silica particles from silica sol, a new absorbing peak at 1744 cm^{-1} belonging to the C=O group is observed in the spectra of the silica particles separated from the nanocomposite resins prepared by both *in situ* polymerization and the blending method, indicating that monomer, oligomer, or polymer of polyester polyol may have been adsorbed on colloidal silica particles through hydrogen and/or chemical bonds. The absorbing peak at 950 cm^{-1} , attributed to the Si—OH group, means that some silanol groups still remain. The relative intensities of this peak, for the silica particles from the nanocomposite resins by *in situ* polymerization, are higher than those by the blending method, suggesting that more polyester segments have adsorbed on silica particles during *in situ* polymerization than during the blending method. Correspondingly, the free silanol group content at silica particles is relatively higher in the blending method than in *in situ* polymerization.

Figure 2 illustrates typical TGA curves of the silica particles from sol and nanocomposite resins. The weight loss before 200°C is attributed to the evaporation of substances physically adsorbed on the surfaces of silica particles. The weight loss in the temperature range of $220\text{--}600^\circ\text{C}$ can be attributed to the thermal decomposition of chemical-bonded groups such as hydroxyl, ethoxy groups, and polyester segments on the surfaces. The order of weight loss is: c (22.0%) > b (17.7%) > a (4.9%), also indicating that both *in situ* polymerization and the blending method cause some polyester segments to bond chemically to silica particles, and the former method produces more polyester segments chemically bonded to silica particles than the latter.

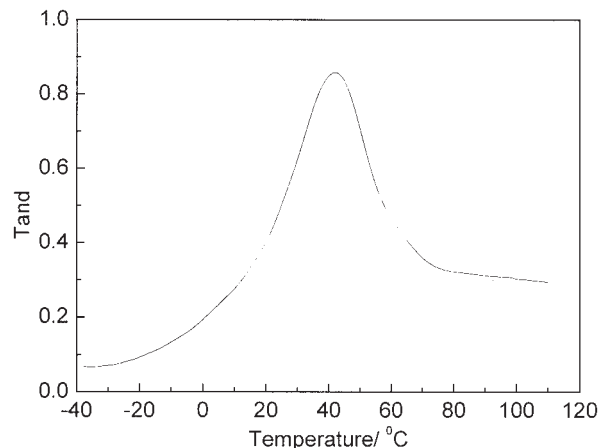


Figure 3 Loss $\tan \delta$ curve of pure polyurethane film as a function of temperature.

Glass-transition temperatures of polyurethane/nanosilica composites

Loss $\tan \delta$ curves of polyurethane films, as a function of temperature, can be obtained by DMA measurement. Figure 3 shows the DMA curve of pure polyurethane. The $\tan \delta$ peak, at around 42°C , that reflects the micro-Brownian segmental motion of amorphous polyester segment is defined as the glass-transition temperature (T_g). Figure 4 illustrates the effects of silica particle size and preparation method on the T_g values of nanocomposite polyurethane films. As the silica particles are introduced, the T_g values of polyurethane/nanosilica composites clearly increase compared with pure polyurethane, no matter which silica particles or preparation approaches are used; the T_g values of polyurethane/nanosilica composites first increase then decrease as the particle size increases. The maximum T_g values occur at silica particle sizes

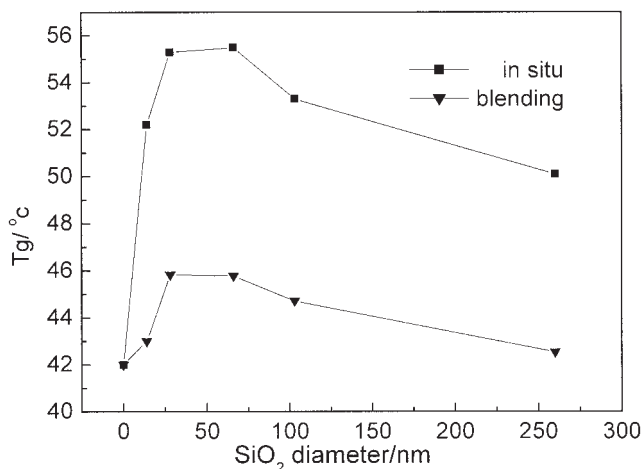


Figure 4 Effect of silica particle size on the T_g of polyurethane/nanosilica composites with 2.25 wt % SiO_2 content.

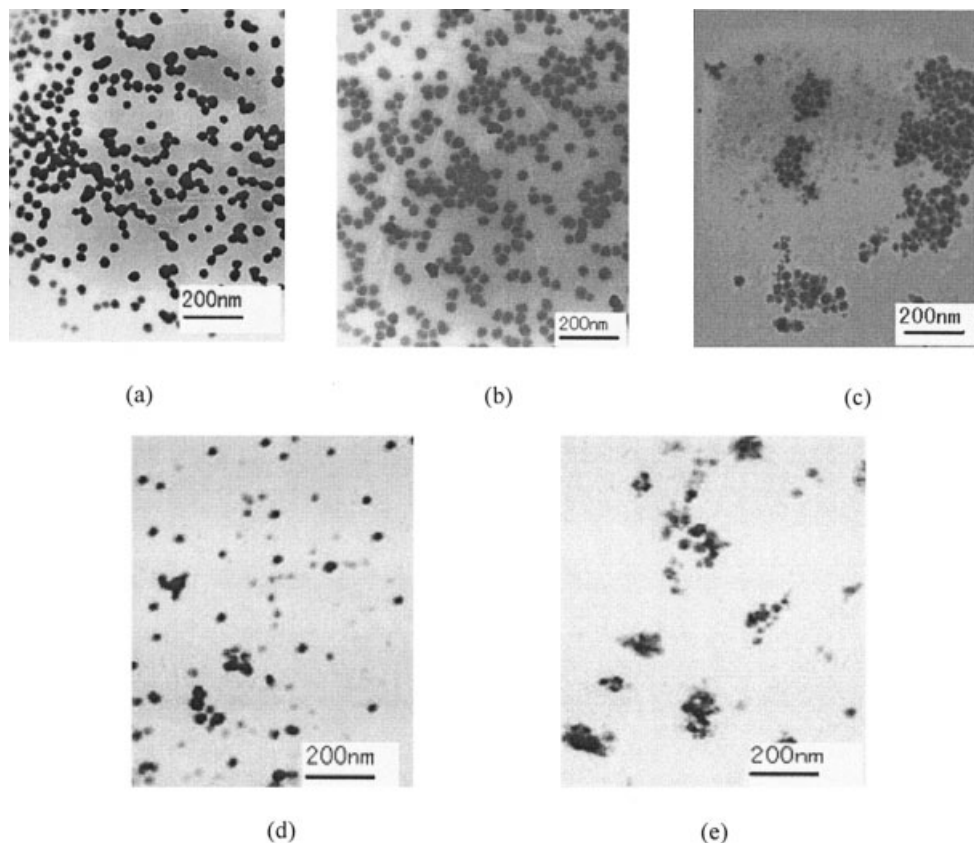


Figure 5 Typical TEM micrographs of the nanosilica particles in silica sol (a), nanocomposite resins prepared by *in situ* polymerization (b) and blending method (c), nanocomposite polyurethanes prepared by *in situ* polymerization (d), and blending method (e).

within the range of 28–66 nm, which is very consistent with the variation of hydroxyl values at the surfaces of silica particles, as shown in Table I. Because the nanosilica with sizes of 28–66 nm have the highest –OH values at their surfaces among these particles, they should have the strongest interaction with macromolecular chains by hydrogen bonding or chemical action between –OH groups of silanol and –OH or –COOH groups from resin molecules at the same mass level, restricting the segmental motion of amorphous polyester molecular chains. Figure 4 also reveals that the polyurethane/nanosilica composites, obtained from *in situ* polymerization, have much higher T_g values than those of their corresponding composites from the blending method because more polyester segments were chemically bonded to silica particles during *in situ* polymerization than during the blending method, as discussed above.

Morphology of nanosilica particles

Typical TEM micrographs, of dispersions of colloidal silica particles in silica sol and corresponding polyester polyol/nanosilica composites and polyurethane/nanosilica composite films prepared by *in situ* poly-

merization and blending methods, are displayed in Figure 5. Basically homogeneous nanosilica particles appear in polyester polyol/nanosilica composite resins prepared by *in situ* polymerization and corresponding polyurethane films [see Fig. 5(b) and (d)],

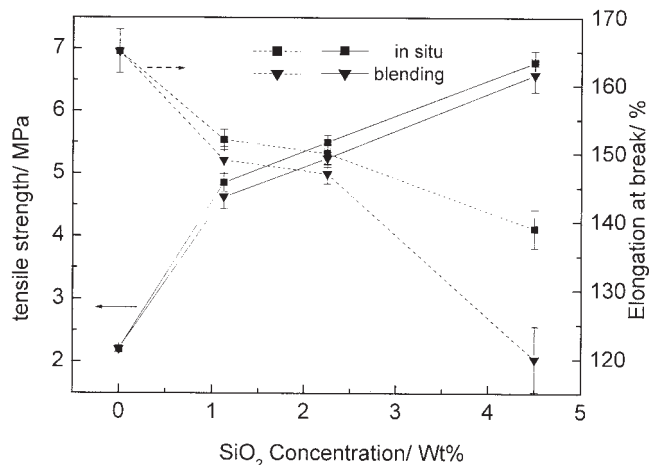


Figure 6 Change of tensile strength and elongation at break of polyurethane/nanosilica composites as a function of silica concentration (silica particle size 66 nm).

whereas some aggregation occurs in polyester polyol/nanosilica composite resins prepared by the blending method and corresponding polyurethane films [see Fig. 5(c) and (e)]. Obviously, this is related to the interaction between nanosilica particles with macromolecular chains. As discussed above, during preparation of polyester polyol/nanosilica composite resins by *in situ* polymerization, some polyester segments were chemically bonded to nanosilica particles. These polyester segments can prevent nanosilica particles from aggregating, whereas by the blending method, very small numbers of polyester segments might be chemically bonded with silica particles, that is, there is less of a protection layer of polyester on the surfaces of nanosilica particles and, thus, free nanosilica particles with relatively more unreacted hydroxyl groups easily promote aggregation through hydrogen bonding.

Tensile properties

Figure 6 demonstrates the tensile strength and elongation at break of the polyurethane/nanosilica composites films as a function of silica content. A considerable increase in the tensile strength, for the polyurethane/nanosilica composites even with very low nanosilica content, can be observed regardless of *in situ* polymerization and blending methods; the nanocomposites, obtained by *in situ* polymerization, have higher tensile strength than that of those obtained by the blending method at the same mass level because the former preparation method causes more polyester chains to be chemically bonded to nanosilica particles, and more homogeneous dispersion of nanosilica in polymer matrix than by the latter method. The elongation at break, of polyurethane/nanosilica composites, decreases as the silica content increases, but the extent of decrease is relatively lower compared with the increasing degree in tensile strength.

Figure 7 presents the influence of silica particle size on the tensile properties of the polyurethane/nanosilica composites. The nanocomposites with silica size of 28 nm have the highest tensile strength as well as elongation at break, which is consistent with the change in T_g of these nanocomposites. The polyurethane/nanosilica composites, containing embedded silica particles of 260 nm size, have a relatively high elongation at break, which may be attributable to relatively weak interaction between the silica particles and macromolecular segments.

Macrohardness

The influence of particle size of nanosilica on the macrohardness of polyurethane films is illustrated in Figure 8. Just as observed in the tensile properties, the macrohardness increases with increasing nanosilica content, regardless of the preparation method, and

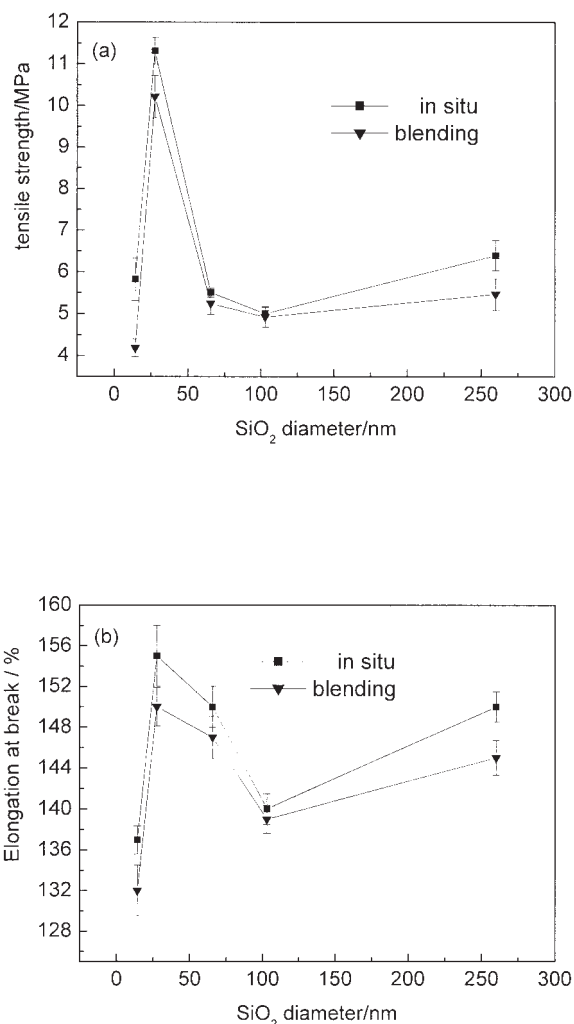


Figure 7 Change of (a) tensile strength and (b) elongation at break of polyurethane/nanosilica composites as a function of particle size (2.25 wt % silica content).

there is also a maximum hardness, at about 28 nm silica, which is consistent with the change of T_g and tensile properties of nanocomposites as a function of particle size of nanosilica. Also, the nanocomposite polyurethanes, obtained by *in situ* polymerization, generally have higher hardness than that of those obtained by the blending method at the same mass level because the former preparation method causes more polyester chains to be chemically bonded to nanosilica particles, and more homogeneous dispersion of nanosilica in the polymer matrix than by the latter method. However, at relatively high silica concentration (e.g., >2.25%), the polyurethane/nanosilica composites, obtained from the blending method, have higher degrees of macrohardness than that of those obtained from *in situ* polymerization, as indicated in Figure 9. For an example, at 5.63 wt % silica with 66 nm, the macrohardness is 0.59 for the nanocomposite polyurethane obtained from *in situ* polymerization but

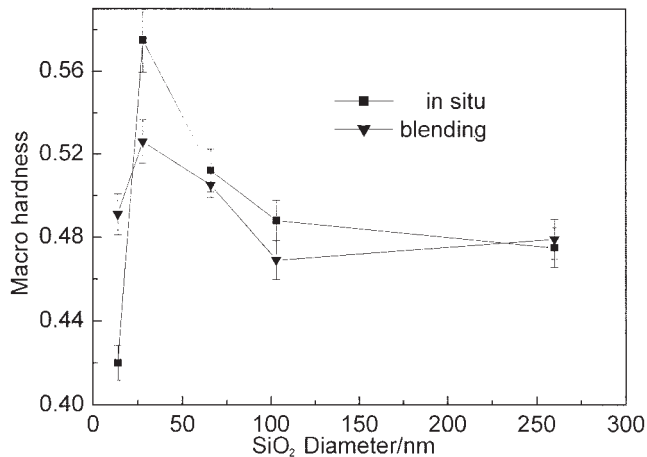


Figure 8 Change of macrohardness of polyurethane/nanosilica composites as a function of silica diameter (silica content 2.25 wt %).

is 0.77 for the polyurethane obtained from the blending method. This is probably because a much higher nanosilica content causes more aggregation during the blending method than by *in situ* polymerization, thus increasing macrohardness.

Figure 10 reveals the effects of content and particle size of nanosilica on abrasion resistance. Obviously, introducing nanosilica into polyurethane can dramatically enhance the abrasion resistance of polymer films no matter which preparation method was used. The higher the nanosilica content, the better the abrasion resistance. The best abrasion resistance is also achieved when the particle size of the introduced nanosilica is about 28 nm. The polyurethane/nanosilica composites, obtained by *in situ* polymerization, possess better abrasion resistance than that of those obtained by the blending method at the same mass

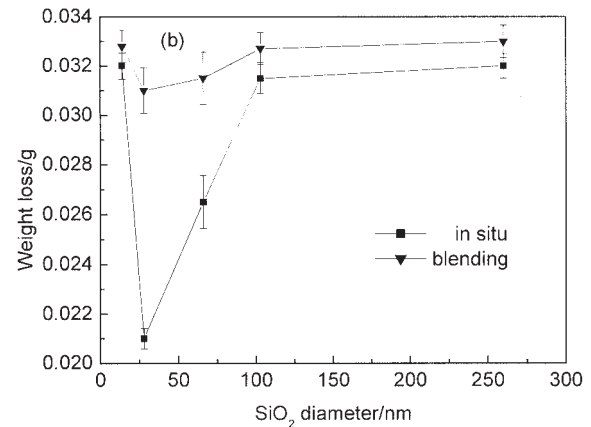
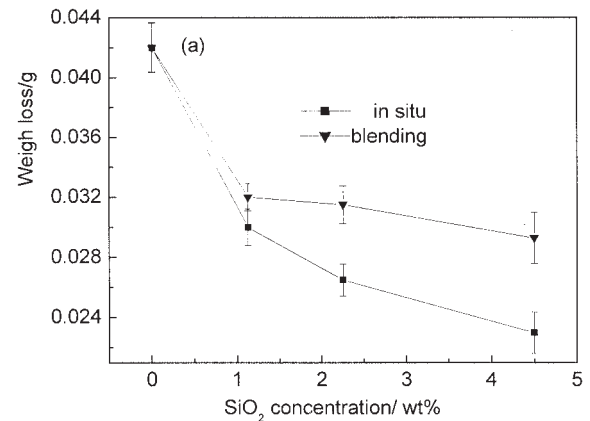


Figure 10 Change of weight loss of polyurethane/nanosilica composites as a function of (a) silica concentration (silica particle size 66 nm) and (b) silica diameter (silica content 2.25 wt %).

level and particle size for the same reasons discussed above.

UV-vis spectra

The UV-vis absorbance spectra of the films, as displayed in Figure 11, indicate that introducing nanosilica can clearly increase the UV absorbance of polyurethane films, and the polyurethanes containing nanosilica with 28–66 nm diameter seem to have relatively better UV absorbance than that of those with other particle sizes. There is almost no absorbance above 300 nm wavelength, demonstrating that transparent nanocomposite polyurethane coatings can be obtained with improved weather resistance.

CONCLUSION

Polyester polyol/nanosilica composites were first prepared by *in situ* polymerization and blending meth-

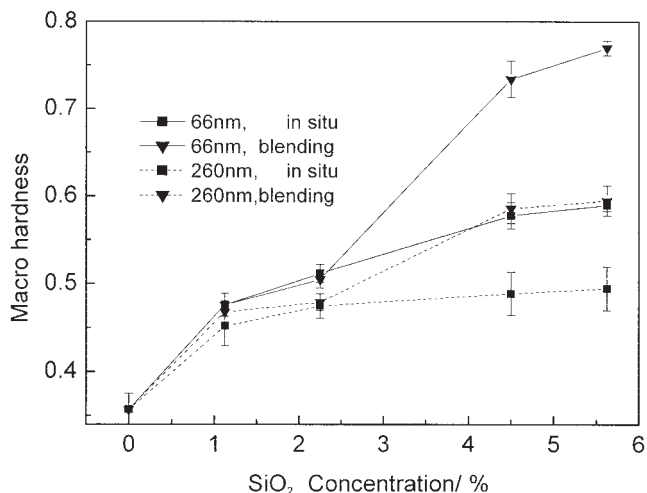


Figure 9 Change of macrohardness of polyurethane/nanosilica composites as a function of silica concentration.

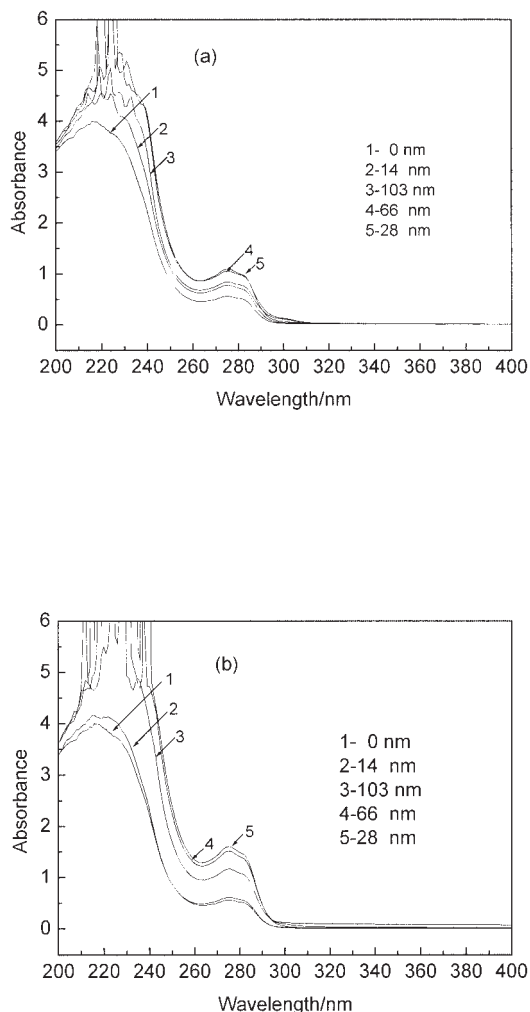


Figure 11 Absorbance spectra of polyurethane/nanosilica composites as a function of particle size embedded by (a) *in situ* polymerization and (b) blending method.

ods, then cured by IPDI to obtain nanocomposite polyurethanes. FTIR and TGA analyses indicate that more polyester segments were absorbed in particles during *in situ* polymerization than during the blending method. TEM showed a more homogeneous dispersion of nanosilica particles in nanocomposite polymers obtained by *in situ* polymerization than that by the blending method, imparting better mechanical properties for the polyurethane/nanosilica composites obtained by *in situ* polymerization than those by the blending method. An exception was for the mac-

rohardness, which had the opposite result at relatively high silica content. The maximum values of T_g , tensile properties, macrohardness, abrasion resistance, and UV absorbance were observed when the particle size of silica was about 28 nm, given that silica particles of this size have the most hydroxyl value at their surfaces.

Based on this study, polyester-based polyurethane coatings, with better mechanical properties and UV-shielding property compared with those of the corresponding pure organic coatings, could be obtained using *in situ* polymerization method or even the blending method.

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