

Effect of Nanosilica on the Properties of Polyester-Based Polyurethane

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ABSTRACT: Polyester-based polyurethanes with embedded nanosilica particles were prepared. The viscosity of polyester resins without and with nanosilica was determined by rheoviscometry. The morphology and mechanical and optical properties of the polyurethane coatings were studied intensively with a transmission electron microscope, a pendulum hardness tester, a scanning probe microscope, an Instron testing machine, an abrader and an ultraviolet-visible spectrophotometer. The viscosity of the polyester resins increased as the nanosilica content increased. Nanosilica could basically be dispersed into the polyester and its

polyurethane on a nanoscale. The addition of a small amount of nanosilica increased the hardness, abrasion resistance, and tensile properties of the polymer films. However, these mechanical properties could be worsened at higher nanosilica contents. The ultraviolet-visible spectra showed that the absorbance and reflection of ultraviolet-visible light by the polyurethane films increased as the nano-SiO₂ content increased, especially at wavelengths of 290–400 nm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 189–193, 2003

Key words: polyurethanes; silicas; coatings; nanocomposites

INTRODUCTION

In the past decade, material scientists have shown great interest in organic-inorganic nanocomposites because their applications can dramatically improve material properties in engineering plastics, enhanced rubbers, coatings, and adhesives.^{1–3} The improvements include heat resistance, radiation resistance, and mechanical and electrical properties, usually resulting from the synergistic effect between organic and inorganic components.

The properties of nanocomposites strongly depend on the organic matrix, the nanoparticles, and the way in which they were prepared. Many researchers have studied organic-inorganic nanocomposite systems to better understand the mechanisms and to improve traditional organic materials. The studied organic matrices include epoxy resin, polystyrene, polyacrylate, and nylon, whereas the inorganic phases are usually clay, layered silicates, and nanoparticles such as SiO₂, TiO₂, ZnO, and CaCO₃,^{1,4–7} among which nanosilica is the first produced nanoparticle. It has been reported that nanosilica can increase the hardness and scratch resistance of a coating and keep the coating clear at the

same time.^{8,9} Nanosilica has enhanced the tensile strength and elongation of polyurethane elastomers; however, the modulus and hardness are lower than those of a corresponding microsize filled polyurethane.¹⁰ Because the surface properties, particle size, and dispersibility of nanoparticles are so diversified and nanoparticles tend to aggregate in the organic matrix on account of their high surface energy, it is very difficult to predict the properties of newly prepared nanocomposites.

In this study, polyester-based polyurethanes with embedded nanosilica were prepared. The viscosity of the polyester resins without and with nanosilica, the dispersion, and the mechanical and optical properties of the polyurethanes with embedded nanosilica were investigated with rheoviscometry, transmission electron microscopy (TEM), hardness testing, scanning probe microscopy, abrasion, an Instron testing machine, and ultraviolet-visible (UV-vis) spectrophotometry.

EXPERIMENTAL

Materials

Nano-SiO₂, with a mean size of 10 nm and a specific area of 640 m² g⁻¹, was purchased from Shanghai Bona Weilai New Material Co., Ltd. (Shanghai, China). The monomers phthalic anhydride (PA; 98%), adipic acid (HD; 97%), neopentyl glycol (NPG; 98%), and 1,4-butanediol (BD; 98%) and the solvent butyl acetate (98%) were purchased from Shanghai Chemical Reagent Co. (Shanghai, China).

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The catalysts dibutyltin dilaurate (98%) and *para*-toluenesulfonic acid (*p*-TSA; 97%) and the crosslinking agents Desmodur N-3300 [an isophorone diisocyanate (IPDI) trimer; solid content = 70%, NCO = 12%] and Resimene 747 [hexakismethoxymethyl melamine (HMMM)] came from Bayer Co. (Germany) and were used as received.

Synthesis of the polyester resins

Two polyester resins were synthesized with HD, PA, NPG, and BD and were designated resins A and B, respectively. No PA was used during the synthesis of resin A, and the molar ratio of hydroxyl groups to carboxylic (anhydride) groups was kept at 1.4/1, whereas PA was used for the preparation of resin B, and the molar ratio of hydroxyl groups to carboxylic (anhydride) groups was kept at 1.3/1.

A 500-mL, round-bottom flask equipped with a mechanical stirrer, a thermometer with a temperature controller, an N₂ inlet, a Graham condenser, and a heating mantle was used. All the monomers were first added to the flask. When the flask was heated to around 120°C under a slow stream of N₂, 0.05% dibutyltin dilaurate, based on all monomer weights, was added as a catalyst. When the temperature was raised to 160°C, an esterification reaction occurred, and water began to distill out. The reaction was kept at 150–180°C for 4 h.

Preparation of the nanocomposite films

Nano-SiO₂ was directly dispersed into polyester resins at 70°C for 1 h under vigorous stirring. Then, without any further dilution, the polyester resins without and with nanosilica were mixed with IPDI or HMMM with a 1/1 weight ratio of the resin to the curing agent at room temperature. Just before application, 0.05 wt % dibutyltin dilaurate for IPDI or 0.05 wt % *p*-TSA for HMMM, based on the total weight of the resin and curing agent on total solids, was mixed thoroughly into the solution. Polymer coatings with different thicknesses were prepared by this solution being cast onto Sn-coated ferrous panels with a drawdown rod and dried at 120°C for 30 min or being cast onto glass substrates and dried at room temperature. The nanosilica content in the cured films was only half of that in the polyester resins. Unless otherwise noted, the nanocomposites mentioned in this article were prepared with resin A cured with IPDI.

Characterization of the nanocomposite resins and coatings

The viscosities of the polyester resins were determined with rheoviscometry at 23 °C.

TEM micrographs of the nanocomposite films were obtained with a Hitachi H-600 (Hitachi Corp., Japan)

apparatus. Samples were prepared with an ultramicrotome at room temperature, which gave sections nearly 100 nm thick. No further staining was used to improve contrast.

Macrohardness was determined according to the national Chinese standard GB/T1730-93. The coating film was prepared on glass boards and dried at room temperature for 1 day. The times of swinging from 5 to 2° for the pendulum on the glass with and without a polymer film were designated t and t_0 , respectively, and the ratio of t to t_0 was the macrohardness. The microindentation hardness (MIH) was performed with a modified scanning probe microscope (Nanoscope III, Digital Instruments) equipped with a conical diamond tip. The MIH of the samples was calculated by the division of the normal force by the contact area of the tip and the sample during indentation.¹¹ The abrasion resistance was determined on round glass boards according to GB1768-79. First, the film was rubbed flat for about 100 cycles, and then the initial weight was recorded. For every 200 cycles of rubbing, the abrasive wheel was renewed, and the weight loss was measured, which was used to judge the abrasion resistance. The tensile properties were acquired with an Instron model DXLL 10000 testing machine (Shanghai, China). Polyester resins without and with embedded nanosilica were cured with IPDI and dried for 6 days at room temperature in a mold to form polyurethane sheets about 1.3–1.6 mm thick. The dumbbell specimens (according to Die C of ASTM D 412) were cut from these polyurethane sheets and 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 ultimate tensile strength and elongation were automatically calculated by the computer connected to the Instron. An average of at least five measurements for each sample was reported; the experimental error was ±10%.

A UV-vis spectrophotometer (Hitachi UV-3000, Japan) was used to measure the absorbance and transmittance spectra of the films at wavelengths of 200–700 nm.

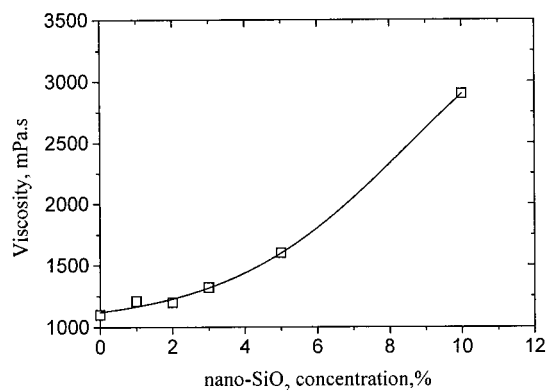


Figure 1 Dependence of the viscosity of the polyester resins on the nanosilica content.

RESULTS

Effect of the nanosilica content on the viscosity of the polyester resins

The viscosities of the polyester resins versus their nanosilica contents are shown in Figure 1. In comparison with the pure polyester resin, the polyester resin containing nanosilica had an increased viscosity. Moreover, the rate of increase, that is, the slope of the curve, increased with the nanosilica content. This was attributable to the fact that more hydrogen bonds between the —OH groups in the polyester resins and nanosilica particles were formed as the nanosilica content was increased.

Dispersion of the nanosilica in the polyurethane films

The dispersion of nanoparticles in an organic matrix affects polymer properties. Figure 2 presents a TEM photograph of a polyurethane film with nanosilica, and it shows that most of the nanosilica particles remained on a nanometer scale in the polyurethane film, although some aggregates could be observed. Figure 3 presents a TEM photograph of the magnified aggregates shown in Figure 2; these aggregates were composed of loose nanosilica particles. The homogeneous dispersion of nanosilica was attributed to the better wettability of HO-terminated polyester molecules with nanosilica.

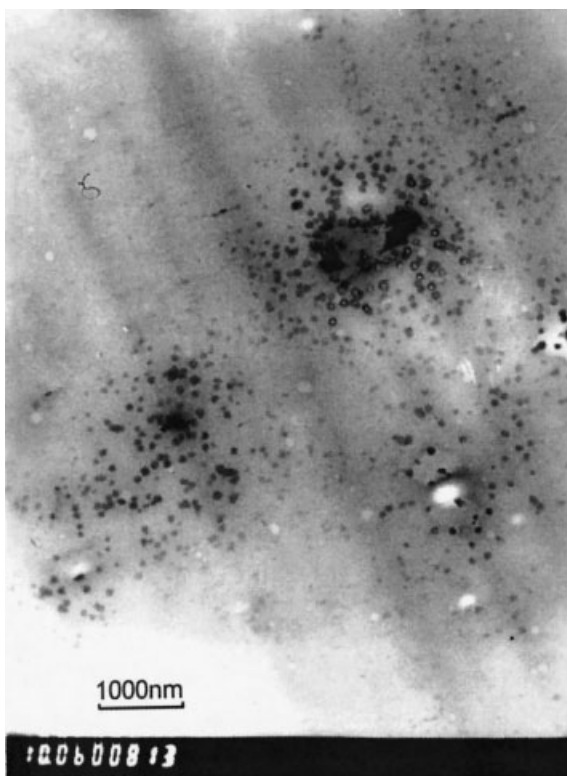


Figure 2 TEM micrograph of the nano-SiO₂/polyester-based polyurethane film.

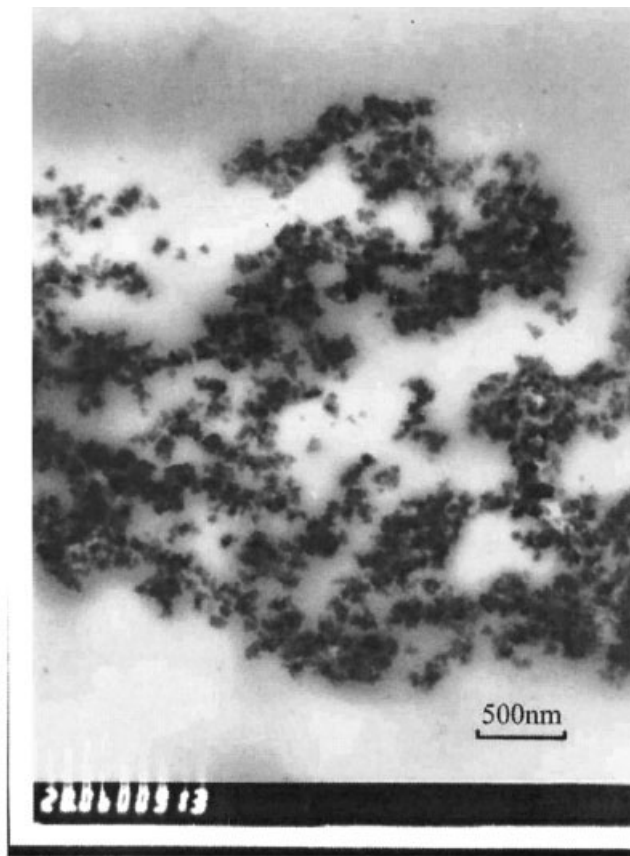


Figure 3 Magnified TEM photograph of the aggregates in the nano-SiO₂/polyester-based polyurethane film.

Mechanical properties of the polyurethane films

Hardness

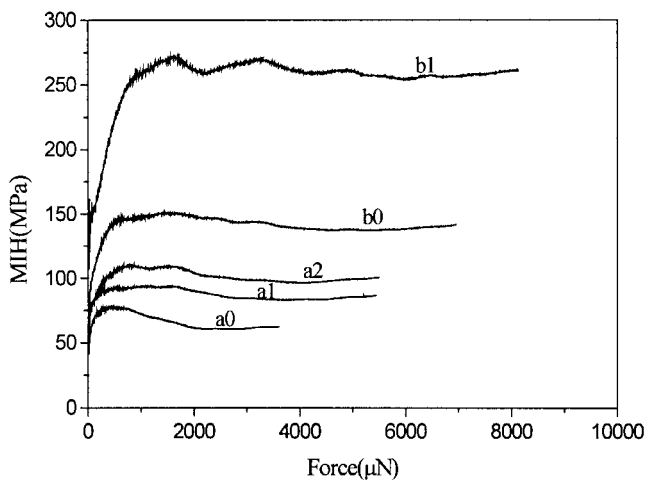
Table I summarizes the effects of nano-SiO₂ particles on the macrohardness of polyurethane films. The data show that the hardness first increased and then decreased as the nano-SiO₂ content increased further, no matter how much the film thickness changed. The MIH of the polyester-based films was measured with a modified scanning probe microscope equipped with a conical diamond tip, and the results are shown in Figure 4. The introduction of a small amount of nano-

TABLE I
Effect of Nano-SiO₂ Content on the Macrohardness of Polyurethane Coatings

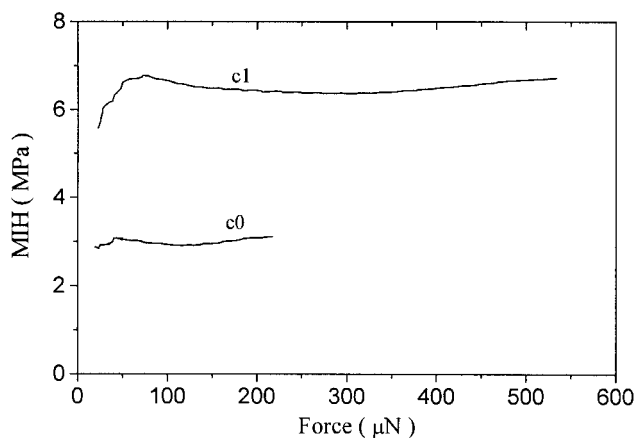
Nano-SiO ₂ content (%)	Macrohardness ^a (#60 drawdown rod)	Macrohardness ^b (#100 drawdown rod)
0	0.48	0.41
1	0.62	0.44
3	0.63	0.34
5	0.59	0.29
10	0.50	0.37

^a The thickness of the films was about 30 μm, and the films were dried for 1 day.

^b The thickness of the films was about 50 μm and the films were dried for 4 days.



(A)



(B)

Figure 4 Effect of the nano-SiO₂ particles on the MIH of the polymer coatings: (A) the polyester resins cured with IPDI (a0 = pure polyurethane from resin A; a1 = polyurethane from resin A with 5 wt % nano-SiO₂; b0 = pure polyurethane from resin B; b1 = polyurethane from resin B with 4 wt % nano-SiO₂) and (B) the polyester resins cured with HMMM (c0 = pure polyester resin A; c1 = polyester resin A with 1 wt % nano-SiO₂).

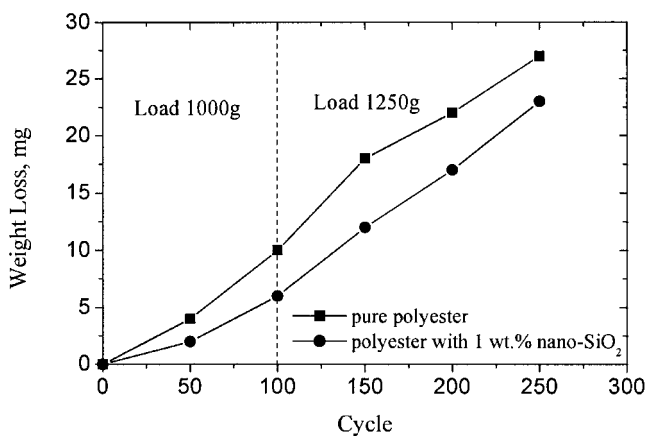


Figure 5 Effect of the nanosilica on the weight loss of the polyester-based polyurethane films.

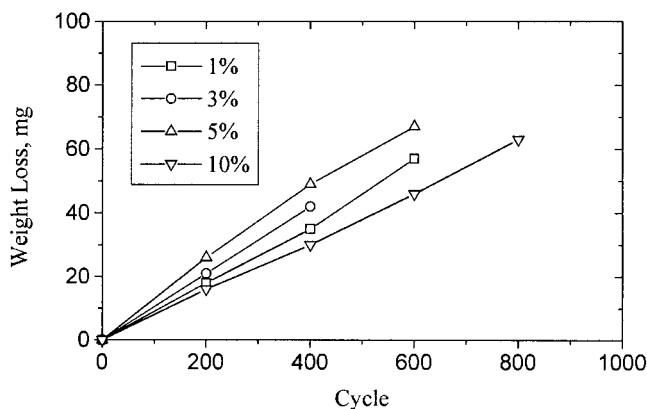


Figure 6 Effect of the nano-SiO₂ content on the weight loss of the polyester-based polyurethanes.

SiO₂ into the polyester resin led to an increase in the MIH, no matter which polyester composition and which type of curing agent were used. The case of resin A cured with IPDI indicated that the MIH increased as the nanosilica content increased, and this was partially consistent with the variation of the macrohardness.

Abrasion resistance

The weight losses of the polyurethane films before and after nanosilica was added are shown in Figure 5, which indicates that polyurethane containing 1 wt % nano-SiO₂ had better abrasion resistance than pure polyurethane. However, the abrasion resistance decreased with an increasing content of nano-SiO₂ until the content reached 10 wt %, as shown in Figure 6. Why the abrasion resistance varied in such a way is not very clear now and should be further investigated.

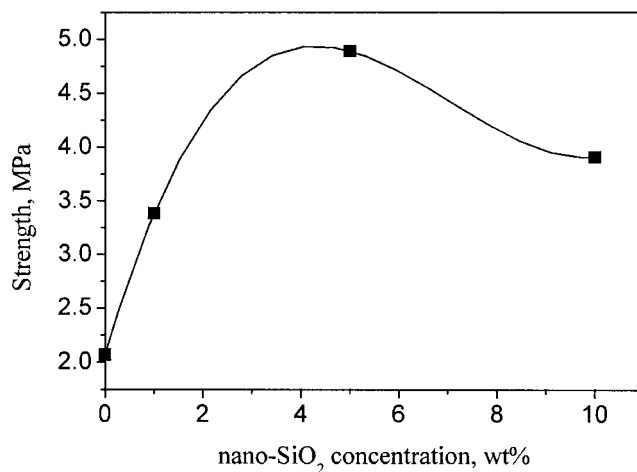


Figure 7 Effect of the nano-SiO₂ content on the tensile strength of the polyester films.

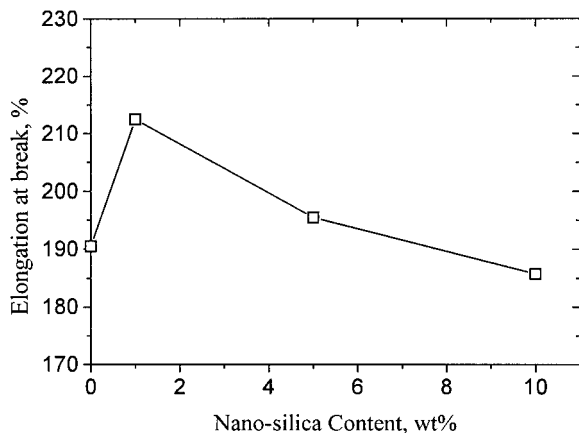


Figure 8 Effect of the nano-SiO₂ content on the elongation at break of the polyester-based polyurethane films.

Tensile behavior

Figures 7 and 8 further demonstrate the effect of nanosilica on the tensile behaviors of polyurethane films. As the nanosilica content increased, both the tensile strength and elongation increased, but as the nano-SiO₂ content continued to increase, the tensile strength and elongation decreased, and this is consistent with the results reported by Petrovic et al.¹⁰ The reason is not completely understood at this time. A possible mechanism is as follows. When a low nanosilica content was used, the strong interaction between the nanoparticles and polymer molecules, due to the large specific surface area of the nanoparticles, was favorable for enhancing the mechanical properties of the polymer. The possible multidimensional hydrogen-bond structure, through HO groups between nanosilica particles and more than two polymer molecules, may also be responsible for the increase in the mechanical properties. However, when a relatively high nanosilica content was used, more and more nano-

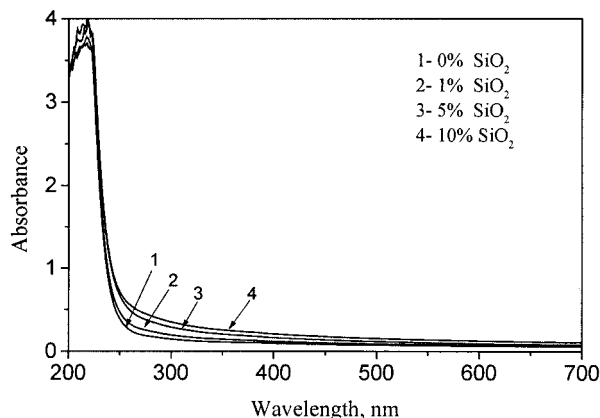


Figure 9 UV-vis absorbance spectra of the polyurethanes containing nano-SiO₂.

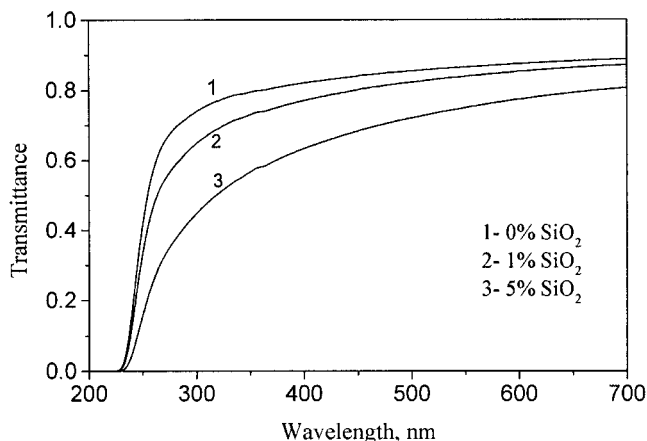


Figure 10 UV-vis transmittance spectra of the polyurethanes containing nano-SiO₂.

silica particles could possibly aggregate, and this could result in a deterioration of the mechanical properties.

Optical properties

Figures 9 and 10 display the UV-vis absorbance and transmittance spectra, respectively, of polyurethane films containing nanosilica. Figure 9 indicates that the absorbance for the polyurethane films at wavelengths of 290–400 nm increased as the nanosilica content increased. Figure 10 shows decreasing transmittance spectra for polyurethane films with an increasing nanosilica content, suggesting that the shielding property of nanosilica for UV light could improve the weatherability of the coating films.

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