

EFFECT OF SILICA NANOPARTICLES ON PROPERTIES OF WATERBORNE POLYURETHANES*

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Abstract Waterborne polyurethane composites containing silica nanoparticles are synthesized successfully via the *in situ* polymerization. The structure, thermal stability, surface hardness, tensile strength, UV-Vis absorbance, dynamic mechanical properties and chemicals resistance of the resulting composites are investigated by FTIR, TEM, TGA, UV-Vis, DMA and chemicals soakage measurements. Results show that polyurethane molecules and silica nanoparticles are linked with covalent bonds. As a result, physical properties of polyurethane composites, such as thermal stability, surface hardness, weather and chemicals resistance are all improved when an appropriate concentration of silica nanoparticles are incorporated.

Keywords: Nanosilica; Waterborne; Polyurethanes; Property.

INTRODUCTION

Polyurethane materials are one of well-documented polymeric systems. They have gained widespread acceptance because of their overall balance of properties, such as high impact and tensile strength, abrasion resistance, toughness and excellent resistance to chemicals and solvents^[1, 2]. However, the conventional polyurethane has severe pollution on the environment in the course of production and application due to the evaporation of organic solvents. Thereupon, attention has been paid to waterborne polyurethanes (WPU)^[3, 4].

On the other hand, nanoparticles have quite active behavior due to their high specific surface area and activation energy^[5, 6]. Consequently, the stronger interaction between nanoparticles and polymers can occur when nanoparticles are incorporated into polymers. Many properties of polyurethanes, such as heat and radiation resistance, mechanical and electrical properties, *etc*^[7, 8], can be improved dramatically by introducing nanoparticles. For instance, the tensile strength, the elongation, the hardness and the scratch resistance of the polyurethanes increase when silica nanoparticles are included^[9–11]. Polyurethanes containing silica nanoparticles have been widely studied, and many satisfied conclusions have been gained^[12, 13], however, more researches need to be investigated about the effect of silica nanoparticles on properties of polyurethanes, especially for waterborne polyurethanes. In this study, a waterborne polyurethane composite containing silica nanoparticles was synthesized by *in situ* polymerization. The effect of silica nanoparticles on properties of the polyurethanes, such as the thermal stability, surface hardness, UV-Vis absorbance and chemicals resistance, *etc*, was investigated in detail.

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EXPERIMENTAL

Materials

Silica nanoparticles with a mean size of 40 nm and a specific area of 640 m²/g, was provided by Mingri Nanomaterials Co., Ltd (China). Isophorone diisocyanate (IPDI), reagent grade (Bayer Company). Polyesterdiol with a number-average molecular weight (M_n) of 850, was synthesized in our laboratory. 2,2-Dimethylol propionic acid, used as a hydrophilic chain extension agent (HA), 1,1,1-tris(hydroxyl methyl) propane, used as a cross-link agent (CA) and dibutyltin dilaureate (DBT) were all purchased from Sinopharm Group Chemical Reagent Co., Ltd. Triethanolamine (TEOA), ethylene diamine (EDA), *N*-methyl-2-pyrrolidone (NMP) and acetone were provided by Tianjin Chemical Co., Ltd. (China).

Preparation of NH₂-modified Silica Nanoparticles

Silica nanoparticles were modified with 3-aminopropyltriethoxysilanes (ATES) to introduce NH₂-groups before use, and the detailed modification method is described as follows^[14]: ATES (0.25 mol per 100 weight parts of silica) together with silica was added into toluene, and the dispersion was kept at 35°C for 8 h. Then the free ATES molecules were separated by a centrifugation/redispersion procedure. The separation process was repeated for three times. Finally, the NH₂-modified silica nanoparticles were obtained by drying at 80°C for 2 h.

Synthesis of Waterborne Polyurethane (WPU) and WPU-silica Dispersion

WPU-silica dispersion was synthesized according to the following procedure: first, polyesterdiol, HA (2.5 g, 5 wt% of the total solid weight), NMP (10 g, 20 wt%), CA (0.75 g, 1.5 wt%), DBT (0.015 g, 0.03 wt%) and modified silica nanoparticles were charged into a dried three-necked flask with a mechanical stirrer, a condenser and a thermometer. The mixture was heated to 45°C and kept for 30 min under stirring, followed by adding IPDI. Second, the mixture was heated to 70°C and kept at this temperature for 5 h to obtain NCO-terminated prepolymer. The change of NCO value during the reaction process was evaluated using a standard dibutylamine back-titration method^[15]. Third, the prepolymer was cooled to 40°C after the theoretical NCO value was reached. Then TEOA solution in water, which was used as a neutralizing agent, was added under acutely stirring for 20 min. Finally, EDA solution in water was added dropwise to extend the polyurethane chain for 40 min. The resulting WPU-silica was a stable, milk white dispersion with blue light, and its solid content was about 35 wt%. In our experiments, WPU-silica dispersions with contents of silica nanoparticles of 0 wt%, 2.5 wt%, 5.0 wt% and 10.0 wt% were prepared.

Film Preparation of WPU and WPU-silica

The polyurethane film was prepared by casting the synthesized aqueous dispersion onto a polyethylene plate. The film was allowed to dry at room temperature for 3 days, and the residual solvent in the films was removed under an infrared lamp. The thickness of the resulting films was *ca.* 200 μm.

Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded on a Nicolet NEXUS 670 spectrometer, and the KBr pellet technique was adopted.

Transmission electron micrographs (TEM) were conducted with an EM-400T instrument (Philips, Holland). Samples for observation were prepared as follows: dispersions were diluted with deionized water and ultrasonicated at 25°C for 15 min, and then a drop of the diluted dispersion was cast onto carbon-coated copper grids and dried before observation.

Thermogravimetric analysis (TGA) was performed on a ZRP-2P (China) TGA instrument. The temperature ranged from the room temperature to 650°C with a heating rate of 10 K/min.

Pencil hardness of films was measured according to Chinese National Standard Test Procedure as GB6739-86.

Tensile strength was measured with an Instron model DXLL 10000 testing machine (Shanghai, China). The polyurethanes and polyurethane-silica sheets were prepared. The dumbbell specimens (according to Die C of ASTM D 412) were cut from these polyurethane sheets and tested 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 was automatically calculated by the computer connected to the Instron. An average of at least five measurements for each sample was reported, while the experimental error was 10%.

UV-Vis absorbance was recorded using a UV-240 spectrophotometer (Shimadzu, Japan) to evaluate the light absorbance property of films in the wavelength range of 190–700 nm.

Dynamic mechanical properties of the polyurethanes were measured with a DMA242 (Netzsch Inc., Germany) instrument using the two-point bending mode (single cantilever). The experiments were carried out by heating the sample from -30°C to 110°C , using a heating rate of 5 K/min, a frequency of 10 Hz under N_2 atmosphere.

Chemicals resistance of the resulting films was evaluated with tap water, toluene, *n*-butyl acetate and butanone, respectively. Films were immersed in each liquid at room temperature for 24 h. The percentage swelling, which was used to evaluate the degree of the film resistance to chemicals, was determined by measuring the film weight increase:

$$\text{Swelling (\%)} = [(w - w_0)/w_0] \times 100 \quad (1)$$

where w_0 denotes the weight of dried film while w represents the weight of the film at swelling equilibrium.

RESULTS AND DISCUSSION

FTIR Characterization

FTIR spectra of the silica nanoparticles, films of pure polyurethane (without silica nanoparticles) and WPU-silica are shown in Fig. 1. In the FTIR spectrum of silica nanoparticles, the absorption at 3424 cm^{-1} is assigned to the stretching absorbance of Si—OH and $-\text{NH}_2$ groups, and peaks at 956 and 800 cm^{-1} are ascribed to the asymmetric bending and stretching vibration of Si—OH. Meanwhile, the absorption of asymmetric stretching vibration for Si—O—Si appears at $1020\text{--}1110\text{ cm}^{-1}$. In the FTIR spectrum of pure WPU film, the absorption at about 3360, 1646, and 1555 cm^{-1} are assigned to the distortion absorbance of $-\text{NH}$ group (in RCONH), while the strong absorption peak at 1734 cm^{-1} denotes the stretching vibration of $\text{C}=\text{O}$. Meanwhile, the absorptions for stretching vibration of $-\text{CH}$ and $\text{C}-\text{O}-\text{C}$ present at 2952 and $1000\text{--}1100\text{ cm}^{-1}$, respectively. By contrast, in the FTIR spectrum of WPU-silica film, the peak at 3360 cm^{-1} widens as compared to that of the pure polyurethane, indicating that the peak is the overlapping absorption for the stretching vibration of Si—OH in silica nanoparticles and the distortion vibration of $-\text{NH}$ in WPU. The silanol content at the surface of unmodified nanosilica is $0.45\text{ mmol SiOH/g}_{\text{silica}}$ which is evaluated with the titration method put forward by

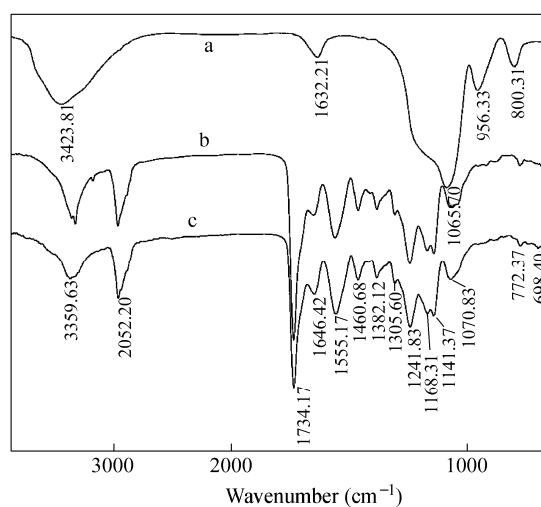


Fig. 1 FTIR spectra of silica nanoparticles (a), pure WPU film (b) and WPU-silica film (c)

Kang^[16]. A small quantity of silanol still exists at the surface of nanosilica after it is treated with ATEs, and the measured silanol content is about 0.10 mmol SiOH/g_{silica}.

Likewise, the intensity of the peak centered at 1070 cm⁻¹ increases slightly as compared to that of the pure polyurethane, demonstrating this peak results from the overlapping vibration absorption of Si—O—Si and C—O—C. The —OH and —NH₂ groups locate at the surface of silica nanoparticles can react with —NCO groups in IPDI molecules in the synthesis process. As a result, the silica nanoparticles are chemically bonded with the polyurethane molecules, which results in the change of absorption for WPU-silica. These results demonstrate that the waterborne polyurethane-silica composites have been synthesized successfully.

Morphology of WPU-silica Dispersion

The morphology of the resulting WPU-silica dispersion was observed with TEM, and the resulting images are shown in Fig. 2. Figure 2(a) shows that silica nanoparticles disperse uniformly with a size of *ca.* 40 nm for the polyurethane dispersion containing 2.5 wt% of nanosilica, and most of silica nanoparticles are well dispersed while a fraction of them aggregates with the increase of the silica content to 5.0% (see as Fig. 2b). However, many silica nanoparticle aggregations present for the WPU-silica containing higher silica concentration (*e.g.*, 10.0% in Fig. 2c), indicating quite severe aggregation happens. Therefore, results indicate that silica nanoparticles can disperse even in WPU-silica dispersion containing lower content of silica, while nanosilica begin to aggregate when nanoparticle content is above 5.0 wt% in WPU-silica dispersion.

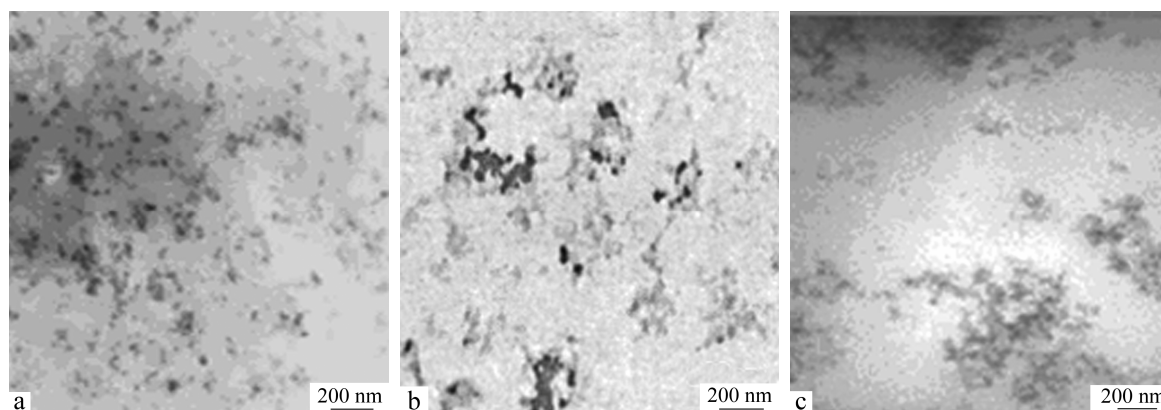


Fig. 2 TEM images of WPU-silica with silica concentration of 2.5% (a), 5.0% (b) and 10.0% (c)

Surface Hardness

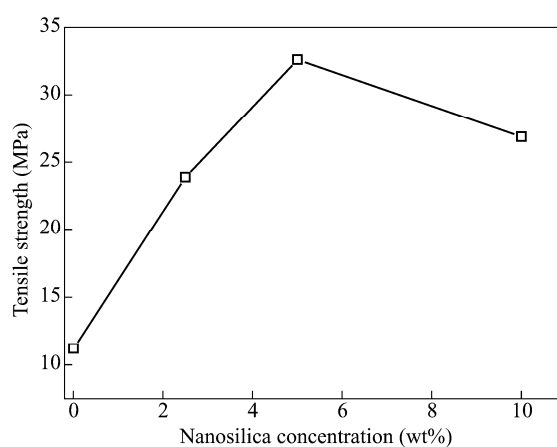
As proved by many researchers, the interaction between silica and polyurethane has distinct influence on mechanical and thermal properties of polyurethane films^[5, 9, 17]. As shown in Table 1, the surface hardness of polyurethane films increases with the increase of silica concentration when the content of silica nanoparticles is below 5.0 wt%. Nevertheless, the surface hardness of the film does not increase any more after the silica content is more than 5.0 wt%. The possible reason that leads to this outcome is deduced as follows: on the one hand, the —OH and —NH₂ groups locate at the surface of silica nanoparticles can react with —NCO groups. Consequently, the silica nanoparticles are chemically bonded onto the polyurethane molecules, and so silica nanoparticles can act as a cross-linker for composites. As a result, the surface hardness of the WPU films is raised. On the other hand, the large specific surface area of the nanoparticles is favorable to enhance the mechanical property of polymers^[18]. When the content of silica nanoparticles is beyond 5.0 wt%, however, more and more silica nanoparticles begin to aggregate, which can result in more phase separation between silica nanoparticles and polyurethanes. Consequently, the mechanical property of the composites is affected.

Table 1. The surface hardness of polyurethane films

Content of silica nanoparticles (wt%)	0	2.5	5.0	10.0
Pencil hardness	HB	2H	3H	3H

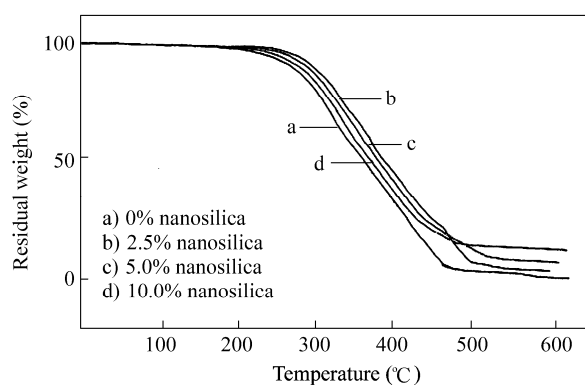
Tensile Strength

Figure 3 demonstrates the effect of nanosilica on the tensile behavior of WPU films. As the nanosilica content increases, the tensile strength increases as well. However, as the nanosilica content continues to increase, the tensile strength decreases. And this is consistent with the results reported by Petrovic *et al.*^[19]. A possible mechanism is as follows: when lower content of nanosilica is used, the chemical bonds between WPU molecules and silica nanoparticles form and the strong interaction between the nanoparticles and polymer molecules is favorable for enhancing the mechanical properties of the polymer. However, when a relatively higher nanosilica content is used, more and more nanosilica particles can possibly aggregate, and this can result in a deterioration of the mechanical properties.

**Fig. 3** Tensile strength of polyurethane films with different contents of silica nanoparticles

Thermal Stability

Results from Zoran^[5] showed that silica nanoparticles can act as reinforcing fillers and the thermal property of the polyurethanes can be improved grounded on the large surface area of silica nanoparticles and the strong interaction between silica nanoparticles and polyurethane molecules. Thereupon, TGA technique was used to investigate the thermal stability of the polyurethane films, and results are shown in Fig. 4. It can be found that the polyurethanes containing silica nanoparticles have better thermal stability than pure polyurethane, and the thermal stability of the composites increases with the increase of the silica content when the content of silica is

**Fig. 4** TGA curves of polyurethane films

below 10 wt%. However, the thermal stability is weakened for the WPU-silica with the higher silica concentration, which is due to silica nanoparticles' aggregation and then the phase separation between the polyurethane and silica nanoparticles.

Optical Property

The UV-Vis absorbance spectra for films of WPU and WPU-silica are shown in Fig. 5. It can be found that the absorbance of the polyurethane films at wavelengths of 190–400 nm increases with the increase of the content of silica nanoparticles, indicating that the UV absorbing capability of the WPU-silica increases with the increase of the silica nanoparticles. Consequently, the ability of the weather resistance of the polyurethane film can be improved by introducing the silica nanoparticles. On the other hand, it can be found that the light transmission of the polyurethane films is not affected for all polyurethane composites since the size of nanoparticles is much smaller than the wavelength of the visible light. However, the film gradually whitens upon tension for films containing more than 5.0 wt% of silica nanoparticles, indicating serious phase separation between polyurethanes and silica nanoparticles happens. As a result, the film whitens because the light can not pass through the phase-separated films. Therefore, in order to obtain polyurethane composites with good properties of both weather resistance and light transmission, the ratio of silica nanoparticles incorporated in the WPU should be less than 5.0 wt%.

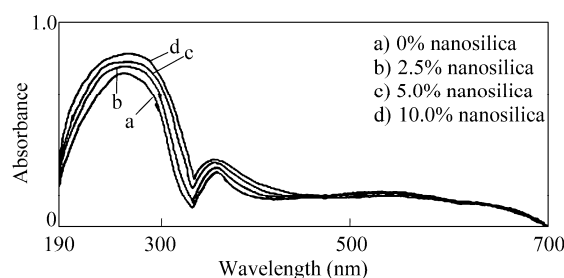


Fig. 5 UV-Vis absorbance spectra of polyurethane films

Dynamic Mechanical Properties

Dynamic mechanical experiments are used to obtain the viscoelastic properties of the polyurethane films. Figures 6 and 7 show the variation of the storage modulus (E') and $\tan\delta$ as a function of the temperature for the WPU films without and with nanosilica, respectively. It can be found that the storage modulus of the WPU gradually increases with the increase of nanosilica content when the nanosilica content is below 5.0%, which

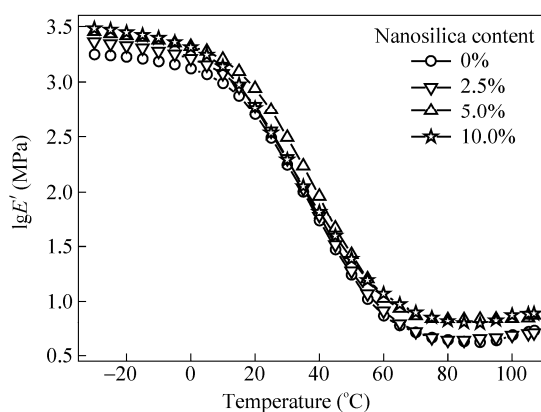


Fig. 6 Storage modulus (E') versus temperature of polyurethane films with different contents of silica nanoparticles

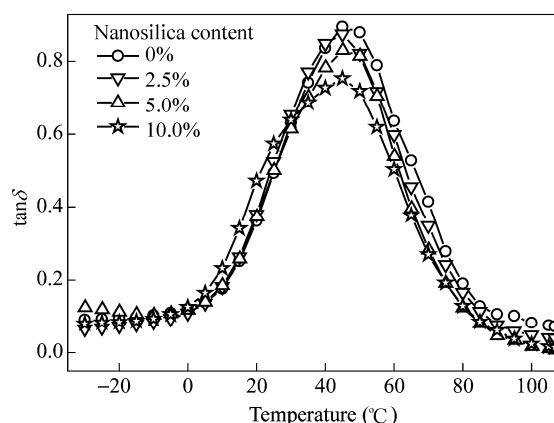


Fig. 7 $\tan\delta$ versus temperature of polyurethane films with different contents of silica nanoparticles

indicates that the higher nanosilica content, the greater interaction happens between the WPU molecules and nanosilica. This further implies that chemical bonding between WPU and nanosilica is essential for better reinforcement of WPU with nanosilica. However, the storage modulus of WPU films decreases when the nanosilica content reaches 10.0%, which mainly results from the aggregation of silica nanoparticles and serious phase separation between silica nanoparticles and polyurethanes.

The T_g of hard segment in WPU films without nanosilica is about 47°C, while the peak temperature varies much in WPU films containing nanosilicas. The T_g of hard segment gradually decreases with increasing contents of nanosilica, indicating that the degree of partial phase mixing between soft and hard segments increases in the presence of nanosilica. With the addition and increasing amount of nanosilica, rubbery plateaus are well defined and increase in magnitude and extend to higher temperatures. The increase of rubbery modulus is an indication of effective reinforcement of WPU by nanosilica.

Chemicals Resistance

Four different kinds of reagents are selected in our experiments to evaluate the chemicals resistance. It can be found from the Fig. 8 that the percentage swelling of the composite films in all four chemicals decreases as compared to that of pure polyurethane. Namely, the chemicals resistant capabilities of the polyurethane film increase after incorporating silica nanoparticles. Generally speaking, the percentage swelling of WPU films in organic solvents decreases gradually with the increase of the content of silica nanoparticles, while that in water increases slightly when the content of silica nanoparticles reaches 5.0 wt%. The reason that leads to this result is that solvents can not infiltrate into the polyurethane molecules due to the increase of the cross-link density. However, the excessive silica nanoparticles reduce the polyurethane strength because of the silica nanoparticles' aggregation and phase separation between polyurethanes and silica nanoparticles. As a result, more Si—O—Si bonds will hydrolyze in water easily. It can also be found that the lowest water absorption ratio is only 1.24 wt% when 5.0 wt% of silica nanoparticles is introduced. It is well known that the water resistance is a troublesome problem which has puzzled the further application of the waterborne polyurethane materials for a long time. So this problem can be solved by introducing of silica nanoparticles. Meanwhile, Figure 8 indicates that the chemicals resistance capabilities decrease one by one from water to toluene, *n*-butyl acetate and butanone.

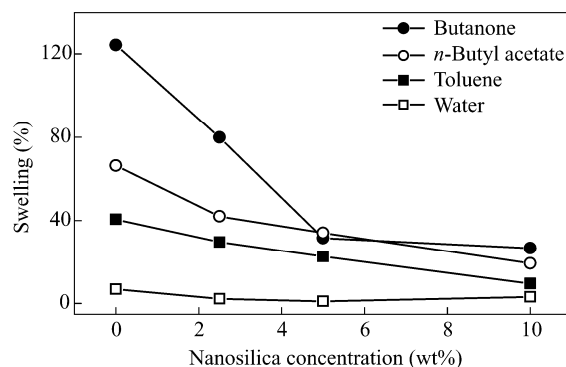


Fig. 8 Effect of silica nanoparticle concentration on chemicals resistance

CONCLUSIONS

A kind of waterborne polyurethane composites containing silica nanoparticles was synthesized successfully by *in situ* polymerization method. Results show that polyurethane molecules and silica nanoparticles link with each other covalently. As a result, many physical properties of the polyurethanes, such as surface hardness, tensile strength, thermal stability, UV light absorbance, dynamic mechanical properties and the chemicals resistance, *etc.*, are improved by the introduction of silica nanoparticles. Meanwhile, results show that the WPU-silica composites have optimal properties when the content of silica nanoparticles is between 2.5 wt% and 5.0 wt%.

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