

Preparation of an Ultraviolet-Curable Water-Borne Poly(urethane acrylate)/Silica Dispersion and Properties of Its Hybrid Film

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ABSTRACT: An organic–inorganic hybrid material was prepared through the addition of nanometer fumed silica partly modified by dimethyl dichlorosilane into a water-borne poly(urethane acrylate) (PUA) anionomer. A PUA/silica hybrid film was made via ultraviolet curing. The mechanical properties of the hybrid film were studied. The tensile strength, elongation at break, pendulum hardness and the glass-transition temperature of the hybrid material

increased with increasing content of silica. Scanning electron microscopy showed an asymmetrical distribution of modified silica in PUA. Atomic force microscopy demonstrated that silica particles could make the surface of the film smooth. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1347–1352, 2004

Key words: polyurethane; polyacrylate; silicas; dispersion

INTRODUCTION

Nowadays, nanometer technology is attracting the interest of many researchers because of the possible improvement that it offers in the properties of materials. Many researchers have studied organic–inorganic hybrid polymeric materials containing dispersed particles with diameters of 1–100 nm.^{1–6}

Ultraviolet (UV) radiation is a well-accepted technology for the fast curing of polymeric materials,^{7–9} whereas waterborne coatings are new safe materials that can reduce environmental pollution.^{10–12} The combination of these two technologies is becoming a trend in the development of UV coatings. Many methods have been found to improve the mechanical properties of such coatings.^{13,14} One is nanometer technology. With this technology, an inorganic nanometer phase is added to the coating, and chemical or hydrogen bonds form between the inorganic and organic phases; this improves the properties of the coating.

In this study, nanometer silica modified by dimethyl dichlorosilane (DMCS) was incorporated into a poly(urethane acrylate) (PUA) UV coating, and an

aqueous dispersion of the hybrid polymeric material was obtained. The morphology and properties of the paint film were investigated.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI; 80/20), available from Shanghai Gaoqiao Petrochemical Co., was used without further purification. Poly(neopentylene glycol adipate) (P746; Functionality (F_n) = 2, number-average molecular weight = 2000), supplied by Yiantai Synthetic Leather Co., was dewatered at 110°C and 1–2 mmHg until no bubbling was observed. The hydrophilic monomer dimethylol propionic acid (DMPA; Shanghai Kangda Co.) was dewatered at 70°C and 1–2 mmHg for 24 h. Hydroxyethyl methacrylate (HEMA) was distilled before it was used. The crosslinker trimethylolpropane triacrylate (TMPTA; Eternal Co.), triethylamine (TEA; Shanghai Kangda), *N*-methyl pyrrolidone (NMP; Shanghai Kangda), and the photoinitiator 2-hydroxy-1-4-[(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959; Ciba Specialty Chemicals) were used as received. DMCS and fumed silica were acquired from Degussa Co. and Shanghai Huaming Co., respectively.

Synthesis of the PUA/modified fumed silica hybrid polymeric film

The structure of the fumed silica was as follows:

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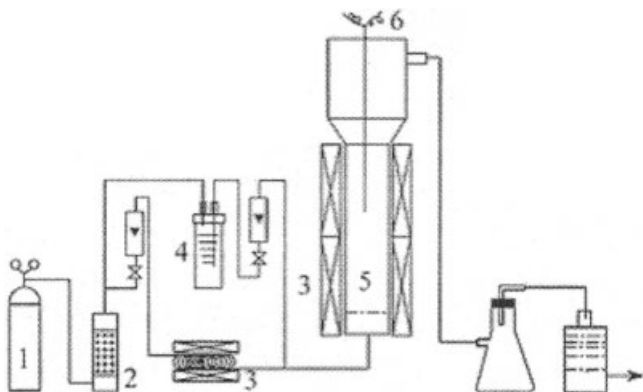
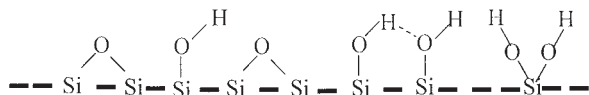
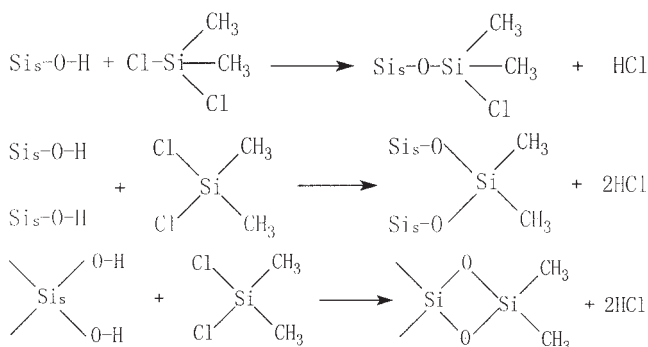


Figure 1 Setup diagram of fumed silica modified with DMCS in a fluidized bed reactor: (1) nitrogen container, (2) drying column, (3) heater, (4) DMCS storage tank, (5) fluidized bed reactor, and (6) thermocouple.



The modified fumed silica was prepared according to the following equations:¹⁵



The value of *s* could be varied.

The apparatus for the modification is indicated in Figure 1. Nitrogen was heated to 200°C after being purified and then was mixed with DMCS. Both flowed into a fluidized bed reactor containing the fumed sil-

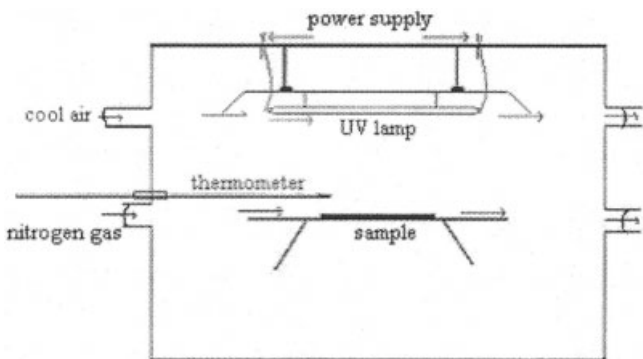


Figure 2 Device used for UV curing.

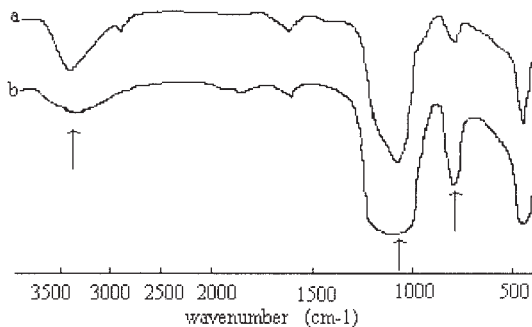


Figure 3 FTIR spectra of silica (a) before and (b) after its modification.

ica. The reaction was carried out at 180–200°C for 0.5 h.

Polyester diol P746 and DMPA were added to a four-necked glass reactor equipped with a stirrer (2000 rpm), a reflux condenser, a thermometer, and a nitrogen gas inlet. TDI and a small amount of NMP were added to the reactor at the ambient temperature. The temperature was raised to 75°C, and the reduction of the amount of —NCO groups during the reaction was examined with an IR spectrometer. When the —NCO content was reduced to 5%, the modified silica was added to the reactor. After 2–3.5 h, HEMA was dropped into the reactor to cap the residual terminal —NCO groups of the polyurethane prepolymer, and the reaction was carried out at 50°C for 7.5 h. The crosslinker TMPTA was added to the reactor. The COOH groups attached to the backbone of the HEMA-terminated anionomer were then neutralized with TEA at 30°C, and the photoinitiator Irgacure 2956 was also added to the reactor. Finally, water was dropped into the reactor under vigorous stirring to form an aqueous dispersion with a solid content of 32%. The

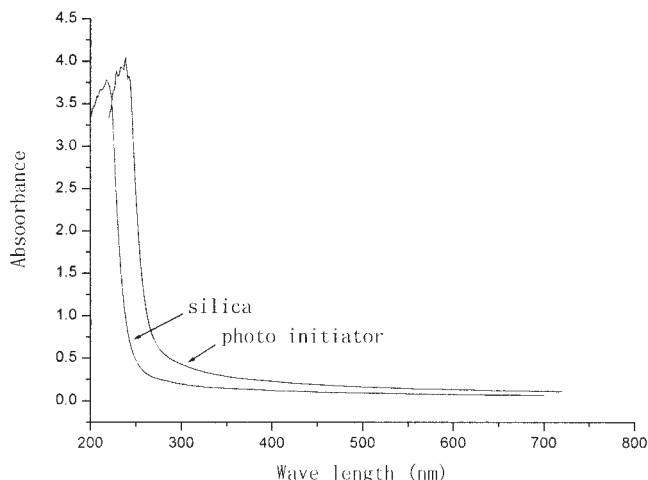


Figure 4 Ultraviolet-visible spectra of the modified silica and photoinitiator.

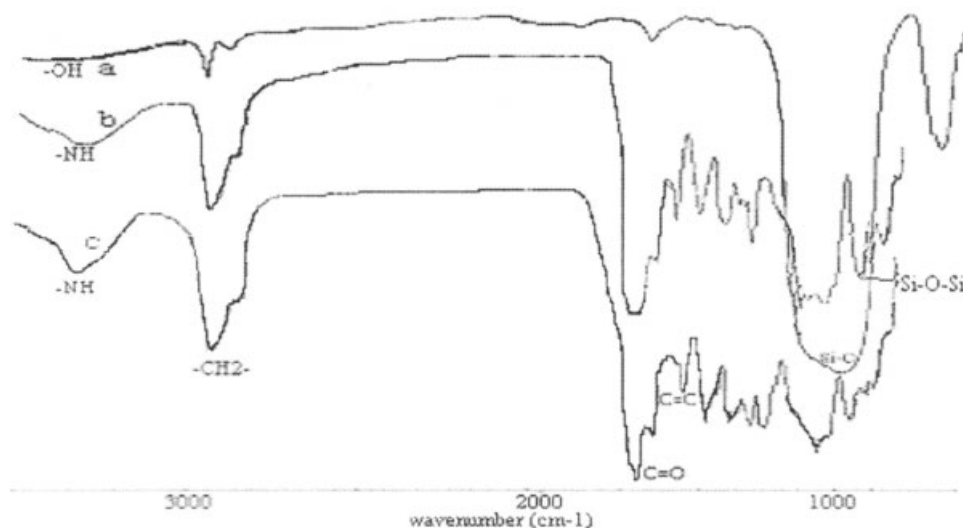


Figure 5 FTIR spectra of (a) the modified silica, (b) PUA film, and (c) PUA/silica (4%) hybrid film.

aqueous dispersion was poured onto a polytetrafluoroethylene plate and cured under a UV lamp. The device is shown in Figure 2.

As shown in Figure 2, the influence of the heat of the lamp on the curing could be avoided because the UV lamp (1 kW, maximum wavelength = 365 nm) was cooled by air. The influence of the oxygen in the air was eliminated by the induction of nitrogen gas. The thickness of the cured film was about 0.1 mm.

Measurement and characterization

The number of —OH groups of the modified silica was measured by sodium hydrate titration (number of hydroxyl groups = $\{(6.02 \times 10 \div 10^4) \times [\text{consumed volume of } 0.1N \text{ NaOH (mL)} \div 2]\} \div \text{area of silica } [(\text{m}^2/\text{g}) \times 10^{18}]$). The size of the modified silica was examined with a Coulter LS photon spectrometer. The pH value of the aqueous solution containing the modified silica, with a concentration of 4%, was determined with a PHS-3D pH meter. IR spectra were recorded in the attenuated total reflection (ATR) mode with a Nicolet 460 Fourier transform infrared (FTIR) spectrometer. Ultraviolet–visible absorbance spectra were recorded with a Varian Cary 500 instrument. Differential scanning calorimetry (DSC) measurements were performed at a heating rate of 10°C/min

from –100 to 100°C. The dynamic mechanical properties [by dynamic mechanical analysis (DMA)] were obtained at 1 Hz and at a heating rate of 2°C/min from –100 to 100°C with a Netsch DMA 242 instrument. The appearance of the cross section of the cured polymeric material in the form of a rectangular pole, obtained after the quenching of the stress, was observed with scanning electron microscopy (SEM; JSM-6360LV, JEOL). Atomic force microscopy (AFM) images of the cured film were recorded in the noncontact tapping mode.

RESULTS AND DISCUSSION

Modified silica

The characteristic values of the silica modified by DMCS were as follows: specific surface area = 200 m²/g, primary particle size = 7–16 nm, pH = 5.01, and —OH concentration = 0.351 groups/nm².

In Figure 3, the peak at 3400 cm⁻¹ reveals the absorption of Si—OH; the absorption of Si(CH₃)₂ can be observed at 800 cm⁻¹, and that of Si—O—Si can be observed at 1060 cm⁻¹. After the modification, the peak at 1060 cm⁻¹ became larger, whereas the absorption peak of Si—OH became weaker; the absorption peak of Si(CH₃)₂ became stronger. The variation of the

TABLE I
Change in the —NCO Content After the Addition of Modified Silica

	Content of nanosilica (%)											
	1			2			3			4		
Reaction time (h)	2	3	3.5	2	3	3.5	2	3	3.5	2	3	3.5
Content of NCO groups (%)	4.7	4.7	4.7	4.2	4.2	4.2	4.2	4.15	4.15	4.1	3.9	3.9

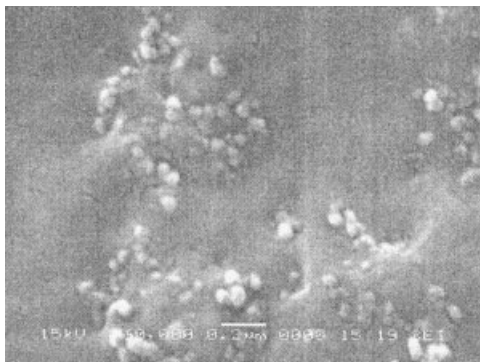


Figure 6 SEM photograph of the cross section of the hybrid material with 2% modified silica.

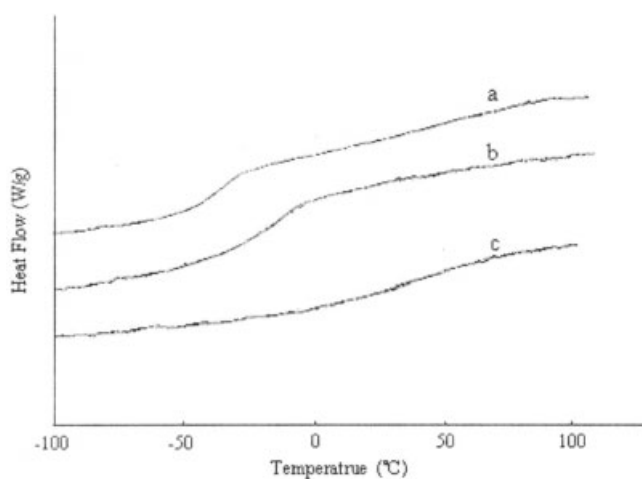


Figure 7 DSC spectra of PUA with various contents of the modified silica: (a) pure PUA, (b) PUA with 2% silica, and (c) PUA with 4% silica ([DMPA] = 3.2 wt %).

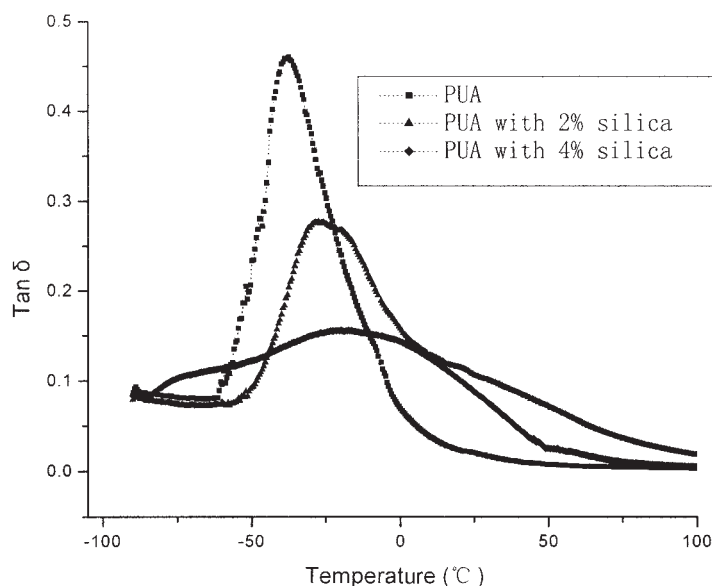


Figure 8 DMA spectra of hybrid materials with different silica contents.

IR spectrum proves that the silica was partly modified by DMCS.

The UV spectra in Figure 4 demonstrate that the peak attributed to the modified silica and the peak attributed to the photoinitiator partly overlapped, and this means that the silica could also absorb UV light. Therefore, the dosage of the silica had to be smaller than a given concentration to avoid a reduction of the effect of the photoinitiator. In this work, the concentration of the photoinitiator was 3% and the curing time was 150 s when the dosage of the silica was less than 4%.

PUA/silica hybrid film

Figure 5 shows IR spectra in the ATR mode for the modified silica, PUA, and PUA/silica hybrid film. The absorption peak of the —OH group of the silica at 3400 cm^{-1} in spectrum a is not found in curve c, whereas the absorption peaks of —NH and C=O of urethane at 3347 and 1735 cm^{-1} , respectively, appear in spectra b and c; this indicates that the —OH groups of silica reacted with the —NCO groups of the polyurethane prepolymer. Moreover, the absorption peak of Si—O—Si at 1060 cm^{-1} in spectrum a is transferred to 1040 cm^{-1} in spectrum c; this may have been caused by C—O—Si that resulted from the reaction between polyurethane and silica. These results prove that chemical bonds were formed between the silica and PUA and that a hybrid PUA/silica polymeric film was obtained.

The concentration of NCO groups in the polyurethane prepolymer after the addition of nanosilica was measured by titration. The results are shown in Table I; they demonstrate the reduction of the concentration

TABLE II
Effect of the Content of the Silica on the Glass-Transition Temperature (T_g) by DSC

Sample	Content of silica (%)	Range of T_g (°C)	T_g (°C)
a	0	-40.98 to -34.48 (6.50)	-37.48
b	2	-31.48 to -20.98 (10.50)	-27.98
c	4	-29.98 to -13.98 (16.00)	-21.98

of NCO groups and prove the reaction between the OH groups on the surface of the nanosilica and the NCO groups.

Distribution of the modified silica in the PUA/silica hybrid material

Figure 6 shows that the particles of the modified silica were distributed in the PUA matrix without evident agglomeration, and their average diameter was 50–80 nm. For this reason, the silica needed to be modified with DMCS.

The polyurethane composed of poly(ester glycol) P746, DMPA (only 3.2 wt %), and TDI should have been a kind of segmented polyurethane consisting of soft segments (polyester diol) and hard segments

(DMPA with TDI); in other words, the macromolecular chain, composed mainly of poly(ester glycol), should have been segmented by DMPA (with TDI). The temperature range of the glass transition should have been narrow if the segmentation was well proportioned; otherwise, the range should have been wider. In this work, however, the PUA macromolecule contained silica, which was bonded in the PUA macromolecule. Figure 7, Table II, and Figure 8 prove that the temperature range of the glass transition became wider with an increasing amount of the modified silica. This means an asymmetrical distribution of the silica in PUA, just as Figure 5 reveals. The reason might be that the functionality of the modified silica was not as definite as eq. (1) showed.

Effect of the modified silica on the properties of the PUA film

As previously revealed, the glass-transition temperature rose with an increasing dosage of the modified silica; that is, the rigidity of the molecular chain was enhanced by the hard silica particles chemically bonded in the backbone of PUA, and the mobility of the molecular chain was hindered.

Figure 9(a,b) presents AFM photographs of cured PUA films containing 2 and 4% silica, respectively.

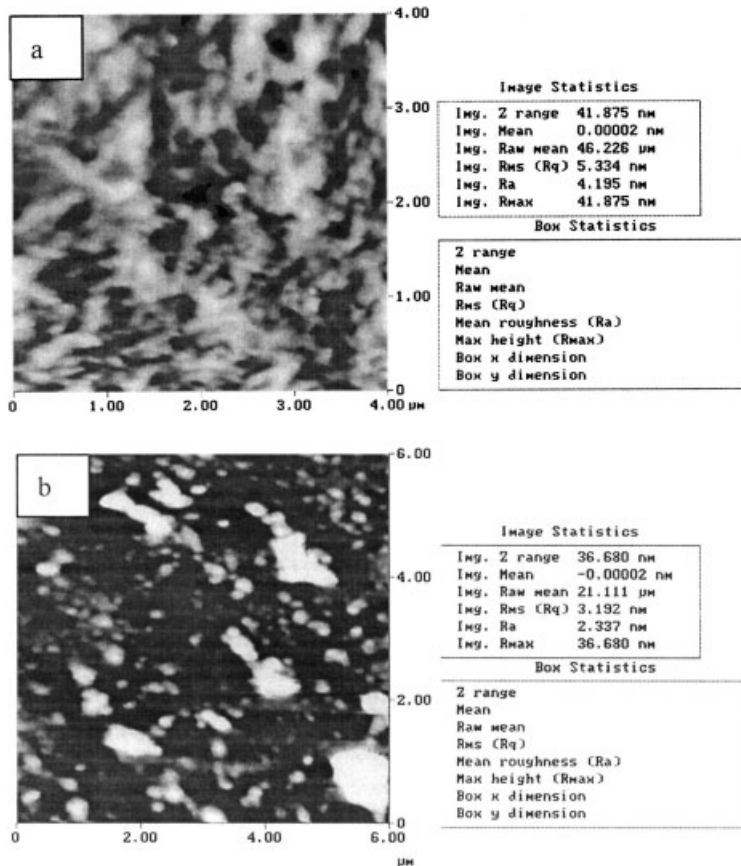


Figure 9 AFM photographs of hybrid films with (a) 2 and (b) 4% modified silica.

TABLE III
Effect of the Silica Content on the Mechanical Properties of the PUA/Silica Hybrid Film

Sample	Silica content (%)	Tensile strength (MPa)	Elongation at break (%)	Pendulum hardness
1	1	14.7	77.3	0.53
2	2	15.2	79.2	0.57
3	3	15.6	81.3	0.58
4	4	16.1	85.2	0.62

The data show that the mean roughness, which was the average vertical deviation of the surface with respect to the center plan,¹⁶ was 4.195 nm for film a and 2.387 nm for film b, whereas the value of R_q (root mean square), which was also a criterion for the roughness of the surface, was 5.334 and 3.192 nm, respectively. These data indicate that a greater dosage of the modified silica led to a smooth surface for the film.

In addition to the aforementioned effect, the mechanical properties, listed in Table III, were improved when the concentration of the modified silica was increased.

CONCLUSIONS

Chemical bonds were formed between partly modified silica and PUA, and a PUA/silica hybrid film was obtained. The particles of the modified silica were distributed in the PUA matrix without evident agglomeration. The greater the content was of the silica, the more asymmetrical its distribution was in PUA.

The rigidity of the molecular chain was enhanced by the hard silica particles. A greater dosage of the modified silica led to a smooth surface for the film. The mechanical properties were also improved as the concentration of the modified silica was increased.

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