

Preparation and Properties of Waterborne Polyurethane/Nanosilica Composites: A Diol as Extender with Triethoxysilane Group

Gang Wang,^{1,2} Guozhang Ma,¹ Caiying Hou,¹ Taotao Guan,^{1,3} Lixia Ling,² Baojun Wang³

¹Shanxi Research Institute of Applied Chemistry, Taiyuan 030027, China

²Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, China

³Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, China

Correspondence to: G. Ma (E-mail: maguozhang@hotmail.com)

ABSTRACT: Waterborne polyurethane (WPU) was prepared from toluene diisocyanate, polypropylene glycol, 2,2-bis(hydroxymethyl)propionic acid and a diol containing triethoxysilane group as the chain extender which was synthesized via Michael addition between 3-triethoxysilylpropylamine and 2-hydroxyethylacrylate. Different amounts of nanosilica were incorporated into the WPU to prepare WPU/nanosilica composites. The results showed that the particle size of the emulsions increased and their viscosity decreased first and then increased with increasing the amount of nanosilica. Incorporation of nanosilica into WPU enhanced the water contact angle and thermal stability of the composites films, meanwhile, their tensile strength and hardness increased first and then decreased. However, increasing the amount of nanosilica resulted in reduction in the elongation at break of the films. It suggested that nanosilica was anchored into the side chain of WPU due to the condensation process between the triethoxysilane group in the side chain of WPU molecular and the silanols group on the surface of nanosilica. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40526.

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INTRODUCTION

Waterborne polyurethane (WPU) has been widely used in a variety of fields such as coatings, adhesives and associated thickeners due to its unique properties in environmental friendly nature, good process abilities and versatile structure–property relationships.^{1–6} However, the films of WPU always exhibit low mechanical strength and thermal stability, and these inferior properties restrict their application. To improve these properties, WPU has always been reinforced by nanosilica, nanoclay or other nanosized materials.^{7–10} Among these modification, incorporation of nanosilica into WPU has attracted much attention due to the synergetic effect between nanosilica and polyurethane, which are expected to produce novel and desired performances. In addition, nanosilica has many advantages, including high hardness, relatively low refractive index, excellent chemical stability, low price and commercial availability from different sources.^{11,12}

Interfacial interaction between WPU and nanosilica is the decisive factor for the properties of WPU/nanosilica composites. Because the interactions between WPU and nanosilica are often physical or weak phase interaction such as hydrogen bonding

and Van der Waals bonding, incorporating nanosilica into WPU always leads to unstable emulsion, nanosilica aggregation and poor mechanical properties.^{13–15} In recent years, sol–gel process and *in situ* polymerization have been developed to prepare WPU/nanosilica composites to solve these problems.^{9,13–16} By these means, strong chemical covalent or ionic–covalent bonds between the WPU and nanosilica are achieved.^{15,17–19} As a consequence, nanosilica shows uniform dispersion in WPU matrix and good compatibility with WPU polymers, which guarantee its capability to obtain the desired properties of modified WPU. To our knowledge, there are few studies about the diol containing triethoxysilane group as chain extender to prepare WPU or WPU/nanosilica composites.^{20,21}

In this work, we synthesized a diol containing triethoxysilane group via Michael addition reaction as the chain extender in preparation of WPU. The triethoxysilane group was designed in the side chain of the polymer, followed by introducing different amounts of nanosilica into WPU to prepare WPU/nanosilica composites. It is expected that the properties of WPU/nanosilica composites can be improved by the condensation between triethoxysilane group in the side chain of WPU and silanols group on the surface of nanosilica.

Table I. Formulation of the Synthesis of WPU/Nanosilica Composites

Sample	Nanosilica/g	TDI/g	PPG/g	DMPA/g	HEA-Si/g	TEA/g	H ₂ O/g
WPU	0.0	11.8	30.0	2.5	4.53	2.83	113.8
WPUSi0.2	0.2	11.8	30.0	2.5	4.53	2.83	114.3
WPUSi0.4	0.4	11.8	30.0	2.5	4.53	2.83	114.8
WPUSi0.6	0.6	11.8	30.0	2.5	4.53	2.83	115.2
WPUSi0.8	0.8	11.8	30.0	2.5	4.53	2.83	115.7
WPUSi1.0	1.0	11.8	30.0	2.5	4.53	2.83	116.2

EXPERIMENTAL

Materials

Polypropylene glycol (PPG, $M_n = 2000$) was obtained from Jiangsu Zhongshan Chemicals Industry, China. Toluene diisocyanate (TDI) was bought from BASF, Germany. Nanosilica with an average particle size of 200 nm, a specific surface area of 460 m²/g and silanol group content of 1.9 mmol/g was obtained from Zhejiang Hongcheng Materials, China. The 2,2-bis(hydroxymethyl)propionic acid (DMPA), 1,4-butanediol (BDO), ethylene diamine (EDA), triethylamine (TEA), *N,N*-dimethylformamide (DMF), 3-triethoxysilylpropylamine (APTES), 2-hydroxyethyl acrylate (HEA) were laboratory grade chemicals. All of the reagents were used without purification.

Synthesis of a Diol Containing Triethoxysilane Group

HEA (23.2 g, 0.2 mol) was introduced into a 100 mL four-necked round bottom flask equipped with a reflux condenser, a drop funnel and a nitrogen gas inlet. APTES (22.1 g, 0.1 mol) was added slowly into the flask below 15°C under nitrogen atmosphere for 1 h and the solution was stirred vigorously. After addition, the reaction was continued at 25°C under stirring until the peak at 1637 cm⁻¹ for vinyl groups disappeared as determined by FTIR. The viscous light yellow oil was obtained, named HEA-Si.

Preparation of WPU/Nanosilica Composites

The formulation of the synthesis of WPU/nanosilica composites was indicated in Table I. In a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, thermometer, condenser and a nitrogen inlet, PPG was dried at 120°C under vacuum for 1 h to remove the moisture. After PPG was cooled down to 70°C, TDI was added into the flask and the reaction was carried out in nitrogen atmosphere at the same temperature until the NCO value reached to theoretical value. Then, DMPA in 3 mL of DMF was charged into the flask and the reaction proceeded at 75°C for 30 min followed by the addition of the HEA-Si at 55°C. After reaction for 1 h, TEA was added and reacted for another 30 min at 50°C to form salt and 10 g of acetone was added to reduce the viscosity of the reaction mixtures. Different amounts of nanosilica dispersed in water by ultrasonic was added to accomplish the dispersion by phase inversion process under vigorous stirring. The WPU/nanosilica composite emulsion with about 30 wt % solid content was obtained as long as the acetone was removed under low vacuum at room temperature.

Preparation of the Films of WPU/Nanosilica Composites

The films of WPU/nanosilica composites were prepared by casting the emulsion into a Teflon mould and allowing a slow

evaporation of water at room temperature for 4 days, and the films about 1 mm thick were obtained after it was kept at 60°C for 8 h to remove the residual solvent.

Measurement

FTIR spectra were recorded using a Nicolet 360 Fourier-transform infrared spectrometer (USA). The liquid sample was coated on the KBr pellet and the water-based composite film was formed on the copper ring at room temperature before measurement. Fourier transform infrared spectroscopy (FTIR) spectra were collected with a resolution of 4 cm⁻¹ in the range of 400 and 4000 cm⁻¹ and 32 scans was used to reduce the noise.

¹H-NMR spectra of sample was performed on a DRX-300 nuclear magnetic resonance (Bruker, Switzerland) using CDCl₃ as a solvent and TMS as a reference.

X-ray diffraction (XRD) pattern of the sample was obtained with a Rigaku D/max2500 X-ray diffractometer (Japan), using Cu K α radiation of wavelength 1.54 Å as the X-ray source.

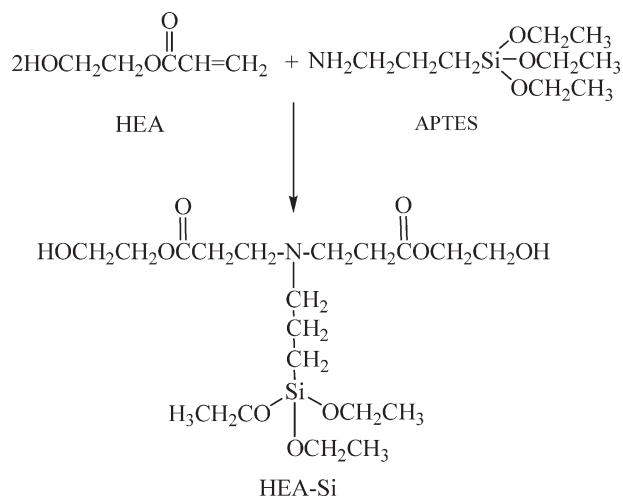
The particle size and the size distribution of emulsion were measured in a Berttsize2000 Laser particle size distribution analyzer (Dandong Bettersize Instruments, China) after a small amount of emulsion was diluted in the deionized water tank at 25°C.

The viscosity of emulsion was determined by NDJ-79 rotation viscometer (Shanghai Scientific Instrument, China) at 25°C with the spindle speed of 600 rpm.

To investigate the surface properties and hydrophilicity of the WPU/nanosilica composites films, the water contact angle formed between water drop and the surface of samples was determined by using DSA20 (Kruss, Germany). Results were the mean values of three independent measurements carried out at room temperature.

Thermal stability of the WPU/nanosilica composites film was studied by measuring the weight loss of the films at nitrogen atmosphere using a HCT-1 thermal gravimetric analyzer (Hnven Scientific Instrument, China). Sample ranging from 10 to 15 mg was heated from 25 to 600°C at a heating rate of 10°C/min.

Tensile strength and elongation at break were conducted on a tensile tester (Shengzhen Sans Testing Machine, China) at a crosshead rate of 100 mm/min. All specimens were cut from dry films and the distance between the testing marks was



Scheme 1. The reaction route of APTES and HEA.

25 mm. An average value of three replicates of each sample was taken.

The hardness of the films was measured by using a HT-6510A Shore A hardness tester (LANDTEK, Guangzhou China). The results were the average value of three runs at room temperature.

RESULT AND DISCUSSION

Preparation and Characterization of WPU/Nanosilica Composites

To improve the interfacial action between the nanosilica and WPU, a diol with triethoxysilane group as the chain extender for WPU was designed. Containing —NH_2 group, APTES can undergo Michael addition reaction with —CH=CH_2 groups in HEA quantitatively. Scheme 1 shows the reaction route of APTES and HEA.

Figure 1 shows the FTIR spectra of APTES, HEA, and HEA-Si. In curve a, the peak at 3425 cm^{-1} was ascribed to the vibration of N—H bond. Curve b showed absorption peaks at 3433 cm^{-1} for —OH group and 1637 cm^{-1} for C=C group. After reaction,

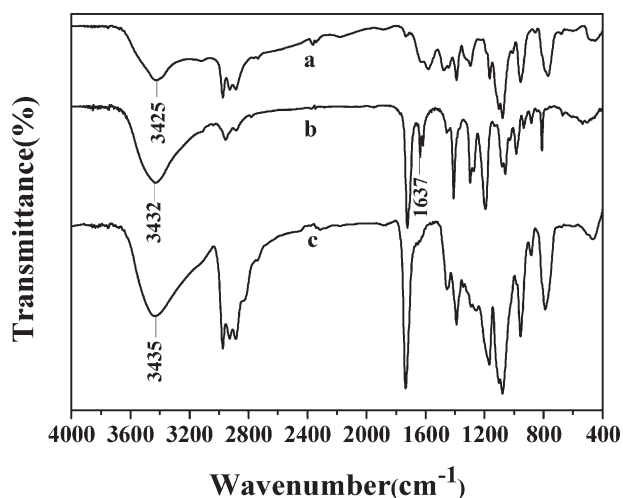


Figure 1. FTIR spectra of (a) APTES, (b) HEA and (c) HEA-Si.

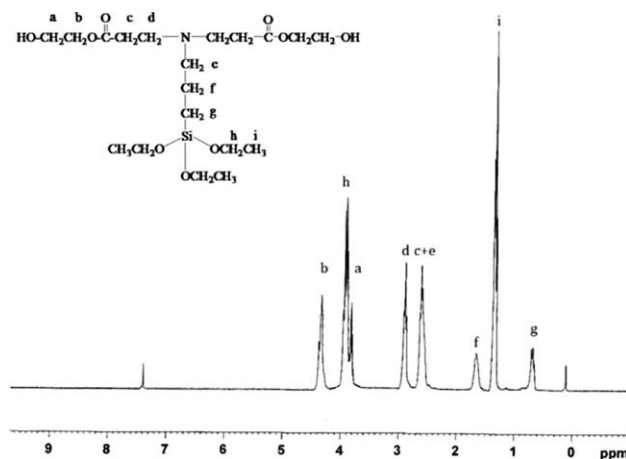
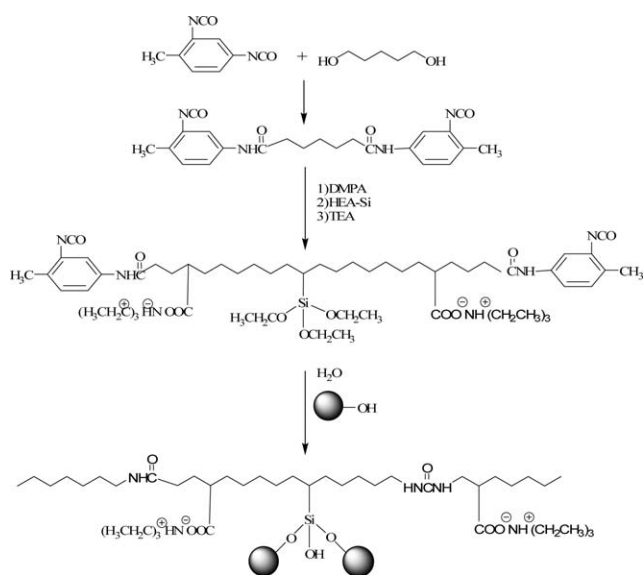


Figure 2. $^1\text{H-NMR}$ spectrum of HEA-Si.

the disappearance of the peak at 1637 cm^{-1} for C=C group and 3425 cm^{-1} for N—H bond was observed in curve c. It illustrated that the reaction took place between APTES and HEA.

Figure 2 shows the $^1\text{H-NMR}$ spectrum of HEA-Si synthesized from APTES and HEA. The peaks at 4.38, 3.99, and 3.87 ppm were corresponding to the protons of 2-hydroxyethyl (COO—CH_2), oxyethyl ($\text{O—CH}_2\text{—CH}_3$), and hydroxymethyl ($\text{HO—CH}_2\text{—}$) respectively, while the protons on aminomethylene ($\text{N—CH}_2\text{—}$) appeared at 2.93 ppm. The signal located at 2.66 ppm was the peak for the protons of acylmethylene ($\text{CH}_2\text{—COO}$) and 1.41 ppm was the peak for the proton of methyl (—CH_3), meanwhile, the peak at 0.72 ppm belong to the proton of silylpropyl ($\text{Si—CH}_2\text{CH}_2\text{CH}_2$). The $^1\text{H-NMR}$ spectrum of HEA-Si indicated that the diol with triethoxysilane group was successfully synthesized by Michael addition reaction.

WPU/nanosilica composite was prepared according to Scheme 2. Urethane prepolymer was synthesized from TDI, PPG. After extending with HEA-Si and DMPA and neutralizing with TEA,



Scheme 2. Elementary steps for the synthesis of the WPU/nanosilica composites.

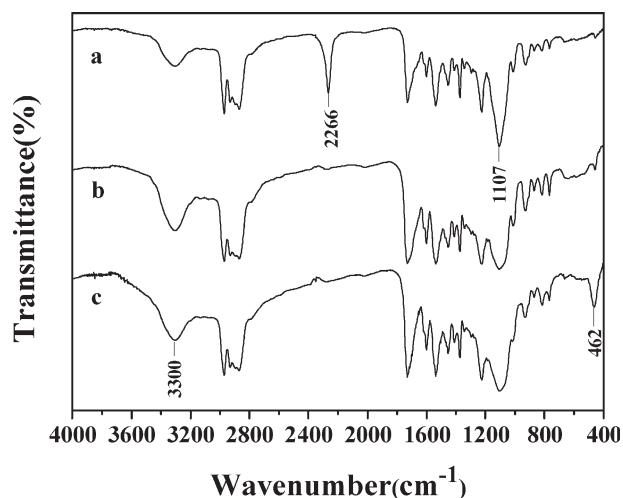


Figure 3. FTIR spectra of a: urethane prepolymer, b: WPU and c: WPUSi0.4.

polyurethane with triethoxysilane groups and triethylammonium carboxylate groups in the side chain was prepared. The triethoxysilane group was easily hydrolyzed in water to form three silanol groups. After nanosilica was incorporated, the condensation reaction occurred between the silanol groups in the side chain of WPU and silanol groups on the nanosilica surface. As a result, nanosilica was anchored onto the chain of WPU.¹⁵

FTIR analysis can give the information about the changes of chemical structure. Figure 3 shows the spectra of urethane prepolymer, WPU and WPUSi0.4. The FTIR spectrum of urethane prepolymer from TDI, PPG showed characteristic absorption peak at 2266 cm^{-1} which is associated with isocyanate group. After extending, neutralizing, and emulsifying, this peak disappeared. Meanwhile, the change of characteristic peak of triethoxysilane groups was also observed before and after incorporating nanosilica. This absorption peak at 1107 cm^{-1} was overlapping with the Si—OH, Si—O—Si, and C—O absorbency. However, compared with the standard absorption peak of about 1730 cm^{-1} for C=O group, the intensity of this peak in the spectra of WPU and WPUSi0.4 became stronger progressively. The reason may be that WPU contained Si—O—CH₂CH₃ or Si—OH group, but these groups transferred to Si—O—Si after incorporating nanosilica into WPU. The peak at 460 cm^{-1} corresponding to Si—O—Si group also confirmed this suggestion.¹³ PU prepolymer showed weak absorption peak at this situation, but this peak became stronger progressively after emulsion and incorporating nanosilica.

Figure 4 shows the X-ray diffraction curves of WPU, WPUSi0.4, and WPUSi1.0. The WPU had a peak at $2\theta = 20^\circ$ which was assigned to diffraction caused by the crystalline of the hard segment in the macromolecule.^{11,22} However, the incorporation of nanosilica decreased the intensity of this peak. The magnitude of the decrease was similar for WPUSi0.4 and WPUSi1.0, but the width of the peak for WPUSi1.0 was slight larger than that of WPUSi0.4. WPU was prepared with TDI and extended with DMPA and HEA-Si as hard segments which showed crystalline when the film formed. As shows in Scheme 2, nanosilica anchored into the side chain of WPU by reaction of the silanol

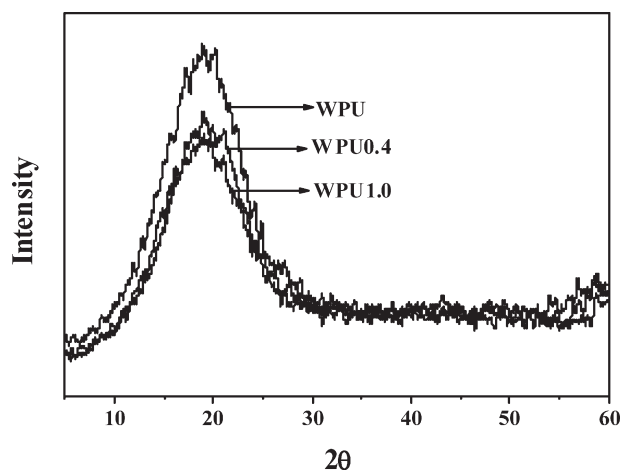


Figure 4. XRD curves of WPU/nanosilica composite films.

group on the surface of nanosilica and triethoxysilane group in side chain of WPU. The nanosilica inhibited the ordering of hard segments into crystals. The increase in the amount of nanosilica led to reducing the crystal degree of WPU/nanosilica composites.²³

Influence of Nanosilica on the Properties of the WPU/Nanosilica Composite Emulsion

Figure 5 shows the particle size and the size distribution of the WPU/nanosilica composites emulsions with different amounts of nanosilica. The average particle size of WPU emulsion was 243 nm. However, the average particle diameter increased and the size distribution of the composite emulsion became broader with an increase in the amount of nanosilica. The reason was that the nanosilica anchored into the chain of WPU by condensation process led to the increase in the particle size and size distribution of composites.^{15,23}

The viscosity of WPU/nanosilica composite emulsions with different amounts of nanosilica is given in Figure 6. It was interested that the viscosity of the composites emulsion decreased firstly and then increased with increasing in the amount of

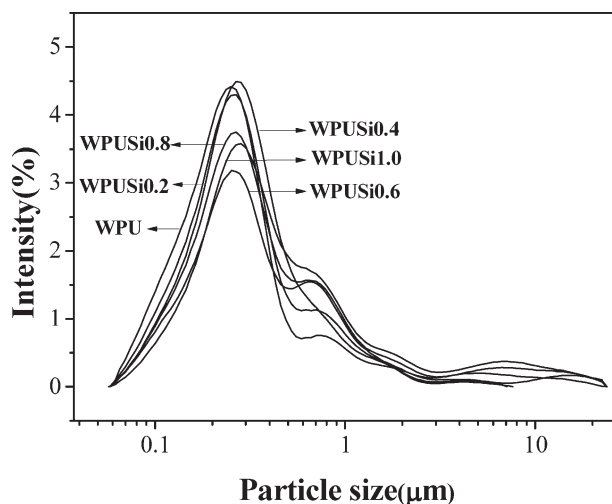


Figure 5. The particle size distribution of the WPU/nanosilica composite emulsions.

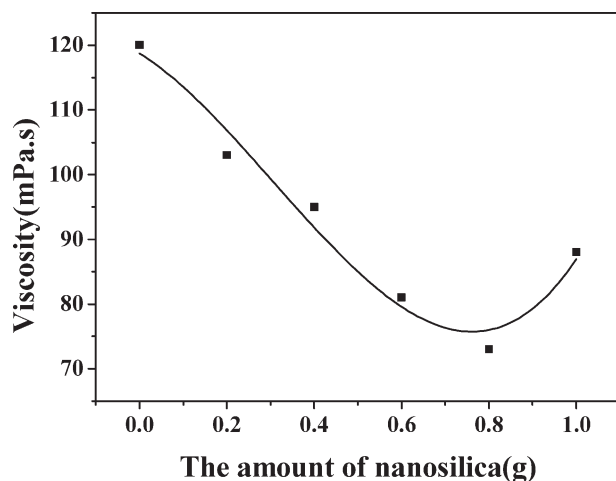


Figure 6. The viscosity of WPU /nanosilica composite emulsions.

nanosilica, and the lowest viscosity was the emulsion of WPU/Si0.8. The reason may be that internal network structure formed by interaction between the silanol groups on the surface nanosilica and triethoxysilane group in the chain of WPU, which consumed the silanol groups in WPU led to reducing the possible crosslinking between WPU. On the other hand, the nanosilica loading led to the increase in the particle size and size distribution, which reduced the number of emulsion particles and the effective volume of the dispersed phase. Hence, the interaction between particle and particle or water molecules became weaker.^{23,24} Therefore, increasing the amount of nanosilica led to a decrease in the viscosity of WPU composite emulsions, but too many content of nanosilica increased the viscosity of the emulsion of WPU because nanosilica has the thickening properties in emulsion.²⁵

Influence of Nanosilica on the Properties of the Film of WPU/Nanosilica Composite

Incorporation of nanosilica can lower surface energy of the WPU film greatly. Water contact angle of the WPU/nanosilica

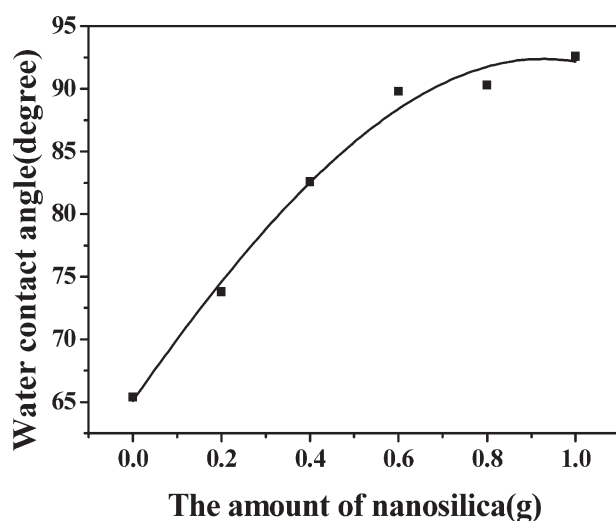


Figure 7. Water contact angle of WPU/nanosilica composite films.

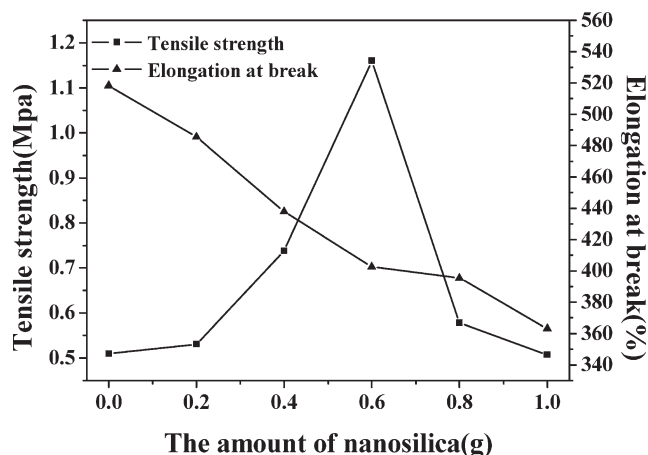


Figure 8. Tensile strength and elongation at break of the WPU/nanosilica composite films.

composite films with different amounts of nanosilica is shown in Figure 7. The water contact angle increased quickly before WPU/Si0.6 and then slowly with increase in the amount of nanosilica. The result showed that nanosilica made a significant impact on surface hydrophobicity of the composite films. This could be ascribed to that the Si atoms migrated to the surface of films, which changed the surface characteristics of the composite materials and led to a lower surface energy.¹⁹ When the amount of nanosilica reached to a certain degree, excessive silica resulted in partial agglomeration of nanosilica particles which cannot reduce surface energy significantly.¹⁸

The tensile strength and elongation at break of WPU/nanosilica composite films were measured and the results are given in Figure 8. The tensile strength of the composite films increased firstly and then decreased with increase in the amount of nanosilica, and the maximum tensile strength was 1.2 MPa when the amount of nanosilica was 0.6 g. However, the elongation at break of the composite films decreased monotonously with increasing the amount of nanosilica. The reason may be due to an increase in crosslinking density of polymer with the

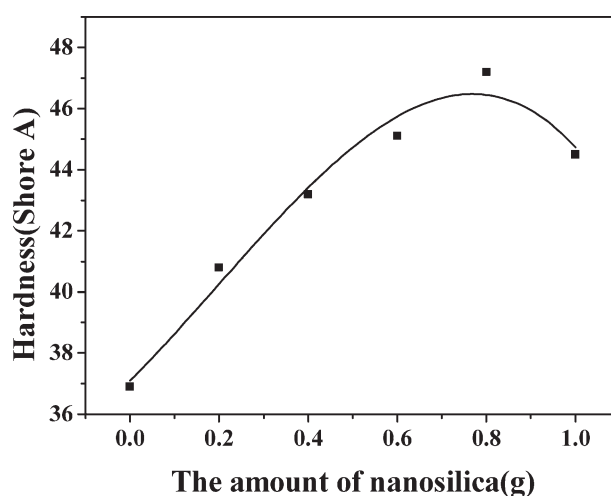


Figure 9. Hardness of the WPU/nanosilica composite films.

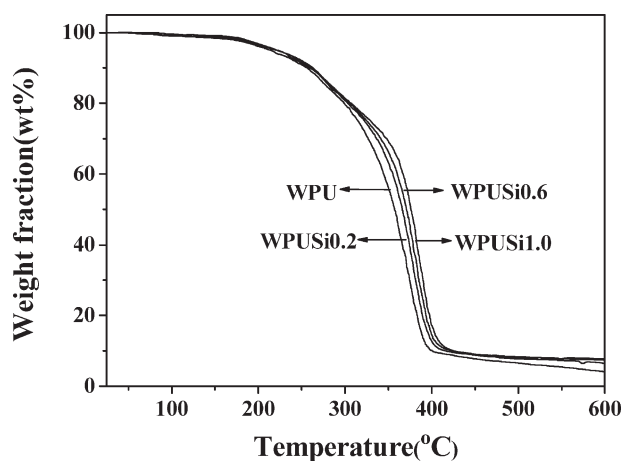


Figure 10. TGA curves of the films of WPU/nanosilica composite.

formation of Si—O—Si linkage through condensation process and the hydrogen bonding between nanosilica and PU.²⁶ These interfacial interactions between the inorganic phase and polymer matrix enable the load transfer from the ductile PU to nanosilica and reduce slippage during stretch,¹¹ which resulted in improved mechanical properties. However, the tensile strength of film decreased when the amount of nanosilica was more than 0.6 g. It may be caused by the aggregation of nanosilica in the films and much bigger particle of emulsion leading to formation of discontinuous films when too many amount nanosilica was used.¹⁵

Figure 9 shows the hardness (Shore A) of the WPU/nanosilica composite films. Compared with the WPU film, the hardness of the WPU/nanosilica composite films were improved greatly, but the improvement degree was different when various amounts of nanosilica were used. The hardness of films increased firstly and then decreased with increase in the amount of nanosilica and the hardest film was WPUSi0.8. The reason was also that crosslinking structure of macromolecule formed and the crosslinking density increased with increase in the amount of nanosilica.^{25,27} However, too many amount of nanosilica led to the aggregation of nanosilica in the films, which reduced the crosslinking density and hardness of the films of WPU/nanosilica composites.¹⁸

To investigate the effect of nanosilica on the thermal stability of the film of WPU/nanosilica composites, TGA was carried out and the results are shown in Figure 10. There was little difference in decomposition temperature of the films of WPU/nanosilica below 300°C, but the thermal decomposition temperature of the film of WPU/nanosilica composite increased with the increase in the amount of nanosilica. The films of WPU always decompose below 300°C owing to the labile urethane and urea bonds.²⁸ Although introducing the triethoxysilane group into WPU and the crosslinking formed between macromolecules, its film had a relatively lower thermal stability than the film of WPU/nanosilica composites. It is because incorporation of nanosilica maintained the crosslink density of hybrid system, and network generated in the condensation process limited the segmental movement of WPU, leading to the increase in the thermal stability.^{12,15,21}

CONCLUSION

To improve the interfacial action organic–inorganic composites, WPU with triethoxysilane group was prepared with a diol as extender which was synthesized based on Michael addition between 3-triethoxysilylpropylamine (APTES) and 2-hydroxyethylacrylate (HEA). A series of WPU/nanosilica composites were prepared by incorporating different amounts of nanosilica in the WPU. It was proposed that nanosilica can be anchored onto the side chain of WPU via condensation process between the triethoxysilane group in the chain of WPU and the silanol group on the surface of nanosilica.

Incorporation of silica can impact the properties of WPU/nanosilica composites greatly. Increasing the amount of nanosilica led to the increase in the particle size of composites emulsion, broadening their distribution, decrease first and then increase in the viscosities of the emulsion. Nanosilica can increase the water contact angle and the thermal stability of the composite films, but decrease their elongation at break. Meanwhile, the tensile strength and hardness of the composites films increased first and then decreased with the increase in the amount of nanosilica.

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REFERENCES

- Król, P.; Król, B.; Stagracyński, R.; Skrzypiec, K. *J. Appl. Polym. Sci.* **2012**, *127*, 2508.
- Steele, A.; Bayer, I.; Loth, E. *J. Appl. Polym. Sci.* **2012**, *125*, E445.
- Aznar, A. C.; Pardini, O. R.; Amalvy, J. I. *Prog. Org. Coat.* **2006**, *55*, 43.
- Rahman, M. M.; Hasneen, A.; Kim, H.-D.; Lee, W. K. *J. Appl. Polym. Sci.* **2012**, *125*, 88.
- Degrandi-Contraires, E.; Lopez, A.; Reyes, Y.; Asua, J. M.; Creton, C. *Macromol. Mater. Eng.* **2012**, *298*, 612.
- Madbouly, S. A.; Otaigbe, J. U. *Prog. Polym. Sci.* **2009**, *34*, 1283.
- Huh, J. H.; Rahman, M. M.; Kim, H. D. *J. Adhes. Sci. Technol.* **2009**, *23*, 739.
- Rahman, M. M.; Kim, H. D.; Lee, W. K. *J. Appl. Polym. Sci.* **2008**, *110*, 3697.
- Zhai, L.; Wang, Y.; Peng, F.; Xiong, Z.; Liu, R.; Yuan, J.; Lan, Y. *J. Mater. Sci. Lett.* **2012**, *89*, 81.
- Choi, H. Y.; Bae, C. Y.; Kim, B. K. *Prog. Org. Coat.* **2010**, *68*, 356.
- Zhang, S.; Liu, R.; Jiang, J.; Yang, C.; Chen, M.; Liu, X. *Prog. Org. Coat.* **2011**, *70*, 1.
- Lee, S. K.; Yoon, S. H.; Chung, I.; Hartwig, A.; Kim, B. K. *J. Polym. Sci. Polym. Chem.* **2011**, *49*, 634.
- Zhai, L.; Liu, R.; Peng, F.; Zhang, Y.; Zhong, K.; Yuan, J.; Zhong, K.; Yuan, J. X.; Lan, Y. *J. Appl. Polym. Sci.* **2012**, *128*, 1715.

14. Yeh, J. M.; Yao, C. T.; Hsieh, C. F.; Yang, H. C.; Wu, C. P. *Eur. Polym. J.* **2008**, *44*, 2777.
15. Wang, L.; Shen, Y.; Lai, X.; Li, Z. *J. Appl. Polym. Sci.* **2011**, *119*, 3521.
16. Chen, J. J.; Zhu, C. F.; Deng, H. T.; Qin, Z. N.; Bai, Y. Q. *J. Polym. Res.* **2009**, *16*, 375.
17. Wu, D.; Xu, H.; Qiu, F.; Yang, D. *Polym. Plast. Technol.* **2011**, *50*, 498.
18. Sun, D.; Miao, X.; Zhang, K.; Kim, H.; Yuan, Y. J. *Colloid Interf. Sci.* **2011**, *361*, 483.
19. Jeon, H. T.; Jang, M. K.; Kim, B. K.; Kim, K. H. *Colloids Surf. A* **2007**, *302*, 559.
20. Sardon, H.; Irusta, L.; Fernández-Berridi, M. J.; Lansalot, M.; Bourgeat-Lami, E. *Polymer* **2010**, *51*, 5051.
21. Xia, Y.; Larock, R. C. *Macromol. Rapid Commun.* **2011**, *32*, 1331.
22. Yang, C. H.; Liu, F. J.; Liu, Y. P.; Liao, W. T. *J. Colloid Interf. Sci.* **2006**, *302*, 123.
23. Mequanint, K.; Sanderson, R. *Polymer* **2003**, *9*, 2631.
24. Athawale, V. D.; Kulkarni, M. A. *Prog. Org. Coat.* **2009**, *65*, 392.
25. Zhang, S. W.; Liu, R.; Jiang, J. Q.; Yang, C.; Chen, M. Q.; Liu, X. Y. *Prog. Org. Coat.* **2011**, *70*, 1.
26. Yeh, J. M.; Yao, C. T.; Hsieh, C. F.; Yang, H. C.; Wu, C. P. *Eur. Polym. J.* **2008**, *44*, 2777.
27. Zhang, L.; Zhang, H.; Guo, J. *Ind. Eng. Chem. Res.* **2012**, *51*, 8434.
28. Gao, X.; Zhu, Y.; Zhou, S.; Gao, W.; Wang, Z.; Zhou, B. *Colloids Surf. A* **2011**, *377*, 312.