Polym. Bull. (2010) 65:45–57
DOI 10.1007/s00289-009-0233-x

ORIGINAL PAPER

Synthesis and characterizations of waterborne polyurethane modified with 3-aminopropyltriethoxysilane

Lai Xiaojuan · Li Xiaorui · Wang Lei · Shen Yiding

Received: 3 July 2009 / Revised: 30 October 2009 / Accepted: 20 December 2009 /

Abstract Waterborne polyurethane (WPU) was prepared by the reaction of isophorone isocyanate (IPDI), polyether polyol (PTMG1000), dimethylol propionic acid (DMPA), and trimethylol propane (TMP) and 3-aminopropyltriethoxysilane (APTES) as coupling agent. The films of the WPU were prepared by casting emulsions on Teflon surfaces. The structure of the polyurethane (PU) was characterized by Fourier transform infrared spectrometer (FT-IR), thermogravimetry (TG), X-ray diffraction (XRD), and differential scanning calorimeter (DSC). The mechanical properties and solvent absorption of the cast films were also measured quantificationally. FT-IR indicates that –NH_2 of APTES reacted with –NCO of PU prepolymer. TG analysis indicates that APTES can improve thermal stability of PU. XRD and DSC show that crystallinity of PU decreased with the increase of w(APTES). It was found that greater mechanical properties of WPU were obtained when chemical networks were formed between PU and APTES. As the mass fraction of APTES increases from 0% to 10%, water absorption decreased from 17% to 8%, ethanol absorption decreased from 46% to 30%. The particle size increases with increase of w(APTES).

Keywords Polyurethane · Silicane · Crosslinking · Films

Introduction

A waterborne polyurethane (WPU) is a binary colloidal system with water as dispersant. The polyurethane (PU) can be dispersed in an aqueous medium since the PU prepolymer contains ionic pendant group along the polymeric backbone. With the environmental regulations prohibiting volatile organic compounds (VOC), WPU

L. Xiaojuan (✉) · L. Xiaorui · W. Lei · S. Yiding
College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology,
Xi'an, China
e-mail: 3578466@163.com

has received increased attention recently because they are non-toxic, apyrous, and do not pollute the air [1–3]. WPUs have already been developed and studied in wide range of applications such as adhesives and coating materials [4–7]. However, some inferior properties of waterborne PUs such as low mechanical strength, solvent, and chemical resistance restrict utility for high performance applications of WPU to some extent. It is important to modify WPU by various methods to improve the solvent and chemical resistance, thermal and mechanical properties of the WPU.

The use of the sol–gel process to prepare highly intermingled organic–inorganic hybrid polymer networks is of current scientific interest since it offers the possibility of tailoring the properties of the materials by variation of the relative composition of the inorganic and organic phases [8–10]. Depending on the desired application, polymers with different mechanical properties can be obtained because of their versatility in the formulation variables. Additionally, because of the hybrid character, they present superior thermal and weathering resistance, and more excellent abrasion than traditional polymers [11–14].

The aim of the present work is to prepare water-based PU with hybrid polymer networks using functionalized silanes coupling agents by the sol–gel process. 3-Aminopropyltriethoxysilane (APTES) is an organofunctional alkoxysilane monomer that can undergo both the sol–gel polymerization of the alkoxy groups and the reaction with NCO functionality in the prepolymer to form a hybrid network with covalent bonds between organic and inorganic phases.

The modified WPU emulsions and the solidified films of the WPU were prepared. The modified WPU were characterized by Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA) instruments, and X-ray diffraction (XRD). Finally, the effects of APTES content on mechanical properties and water absorption were studied.

Experimental

Materials

Isophorone isocyanate (IPDI) was vacuum distilled before use. Poly(tetramethylene glycol) (PTMG; 1000 g/mol) was dried and degassed at 80 °C under vacuum for 3 h. 2,2-Bis(hydroxymethyl)propionic acid (DMPA) and trimethylol propane (TMP) were dried at 50 °C for 48 h in vacuum oven. Dibutyltin dilaurate (DBTDL) was used as received. APTES was used as a coupling agent. 1-Methyl-2-pyrrolidone (NMP) and triethylamine (TEA) were dried over 4 Å molecular sieve before use. IPDI and PTMG were obtained from Bayer (Germany). DMPA, TMP, and DBTDL were purchased from Sigma–Aldrich (USA). APTES and NMP were purchased from Shengzhen, P. R. China.

Preparation of WPU dispersions

A 500-mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer and condenser with drying tube was used as reactor. The reaction was carried out in a constant temperature oil bath. PTMG, IPDI, and DMPA were mixed and the reaction mixture was subsequently stirred in the presence of DBTDL for 2 h at 70 °C to obtain NCO-terminated prepolymer. Then TMP was added to the flask and reacted for 2 h at 80 °C. After cooling the reaction mixture to room temperature, 3-aminopropyltriethoxysilane as a coupling agent and NMP were added and reacted for 30 min, then TEA was fed into the reactor and mixed thoroughly for 1 h to neutralize DMPA unit in PUs. Since the water addition rate is a critical parameter to obtain a stable emulsion, distilled water was added dropwise at a constant flow rate to the flask under vigorous magnetic stirring. After all of the distilled water had been dropped into the flask, WPU emulsion modified with 3-aminopropyltriethoxysilane was obtained. The sol–gel process is occurred at this step. APTES can undergo a variety of reactions during the preparation of a hybrid by a sol–gel route. Hydrolysis of ethoxy groups in PU gives silanol groups which can subsequently condense with silanol groups on another PU molecule to form siloxane. The Si atom in APTES is trifunctional in terms of reactive ethoxy groups and is therefore able to form a three-dimensional chemical bonding between PU molecules. The resulting product was a WPU emulsion with a solid content of about 30%.

The overall reaction scheme is shown in Scheme 1. The scheme for the sol–gel process of WPU is summarized in Scheme 2.

Preparation of WPU films

Films were obtained by casting the aqueous dispersions onto Teflon surfaces and allowing them to dry at room temperature for 5 days and then at 60 °C for 12 h. After demoulding, the films were stored in a desiccator to avoid moisture. Composition of WPU dispersions is summarized in Table 1.

Mechanical property tests

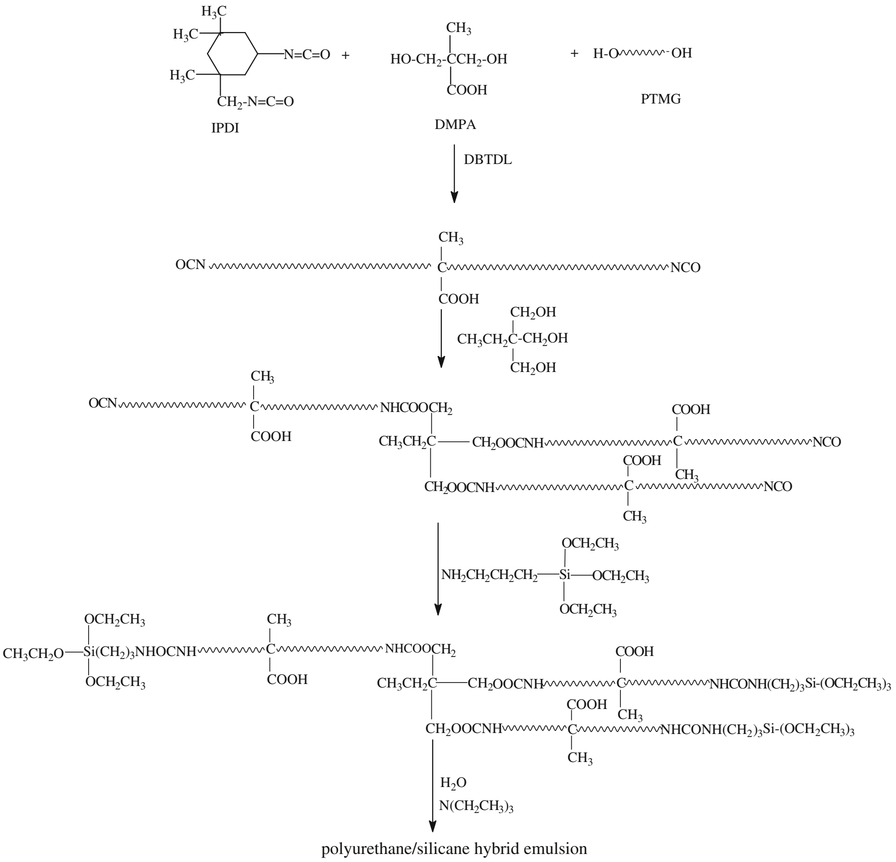
Mechanical property test was done using a Tinius Olsen Series 1000. The specimens were elongated at 500 mm/min. The standard tensile test was performed according to ASTM D-412.

TG analysis

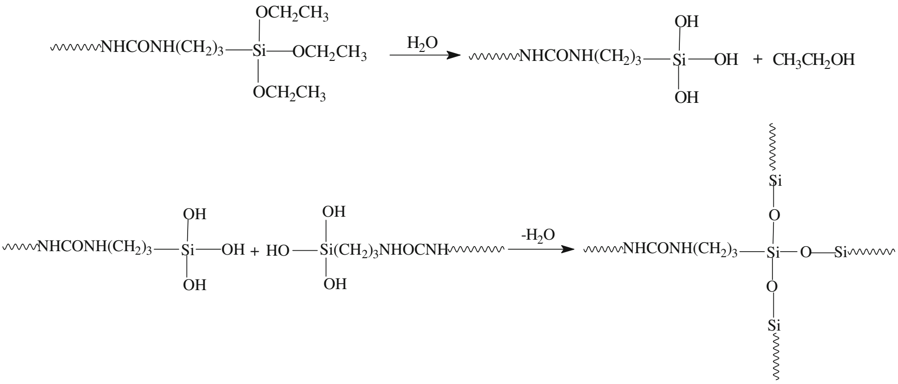
Thermogravimetric experiments were performed on a Germany Netzsch 209 TG analyzer. Film samples about 5 mg were placed in a platinum sample pan and heated from 20 to 650 °C, under N_2 atmosphere, at a heating rate of 10 °C/min.

DSC analysis

The thermal properties were measured with a Germany Netzsch differential scanning calorimeter DSC-204 in a nitrogen atmosphere. All samples of 10 mg were scanned over the temperature range from −50 to 150 °C at a heating rate of 10 °C min^{-1}.



Scheme 1 Reaction scheme of WPU/silicane hybrid emulsion



Scheme 2 The sol–gel process of WPU/silicane hybrid emulsion

Table 1 Composition of WPU dispersions

Designation	IPDI (g)	PTMG (g)	DMPA (g)	TMP (g)	TEA (g)	*w*(APTES) (%)
PU0						0
PU5	15	20	2.1	0.6	1.58	5
PU10						10
PU15						15

Fourier transform infrared spectrometer

A Fourier transform infrared transmission spectrophotometer was used to verify the incorporation between NCO and APTES. Samples for infrared analysis were prepared by drying emulsion directly on KBr pellet. IR spectra were recorded to detect the absorption peaks that are characteristic of the resins during synthetic procedures. Part of the reacting mixture was taken every 0.5 h for IR analysis.

XPS measurement

The study of composition of the WPU was performed using X-ray photoelectron spectroscopy (XPS).

X-ray diffraction (XRD)

Crystallinity determines the flexibility of the molecular chains of polymers. XRD was used to observe the crystallinity of both WPU films. The samples were dried at 40 °C to a constant moisture content in a vacuum oven prior to X-ray scanning with a Rigaku model D/Max-B X-ray diffractometer (Brandt Instruments, Inc., Slidell, LA) with a Bragg–Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional copper target X-ray tube set to 40 kV and 30 mA. The X-ray source was CuK$_\alpha$ radiation. Data were collected from $2\theta = 3°$ to $2\theta = 50°$ (θ being the angle of diffraction) with a step width of 0.02° and a step time of 0.4 s.

Determination of water absorption (WS)

The WPU fims, with a thickness of 0.4–0.8 mm, were cut into circular disks by using a sharp-edged stainless steel die with inner diameter of 20 mm. The samples were dried in vacuum oven for 24 h to determine their dry weight (W_d).Water absorption of the PU membranes was determined by immersing the membranes in a beaker of water at 37 °C. The wet weight with different immersion times (W_t) was determined by wiping off the surface water with a piece of filter paper. The water absorption (WS) of the films was calculated by [15]

$$\mathrm{WS} = [(W_\mathrm{t} - W_\mathrm{d})/W_\mathrm{d}] \times 100. \tag{1}$$

The ethanol absorption was calculated similarly.

Particle size measurement

The particle size of modified WPU emulsions was analyzed by a dynamic light scattering (DLS) (Zeta-plus, Brookehaven Instruments Co.). All samples were first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the emulsion.

Results and discussion

FT-IR spectroscopy

FT-IR spectroscopy is widely used for identification of polymers because of its sensitivity to minor variations in polymer structure. In addition, the technique is rapid and non-destructive. The FT-IR spectra of APTES, PU prepolymer before and after capping with APTES, and PU film are shown in Fig. 1. The absorption peak at 3310 cm^{-1} indicates the N–H stretch in PU. The peaks at 2980–2850 cm^{-1} are associated to C–H stretch of $CH_{3'}$ $CH_{2'}$ CH. The characteristic absorption peaks at 1690 cm^{-1} is the C=O carbonyl stretchings of urethane. 3400 cm^{-1} in APTES was the N–H stretch of $-NH_2$. The absorption peak at 953 cm^{-1} is associated to the absorption peak of $-OCH_2CH_3$ in APTES, which disappeared in FT-IR spectra d because of the hydrolysis of ethoxy groups of APTES. The absorption peak of the NCO group (2270 cm^{-1}) of PU prepolymer (b) disappeared in (c) and (d) during the reactions of NCO groups with APTES on one terminal. The results indicate that NCO groups of the PU prepolymer have completely been reacted with the amine groups in APTES. The characteristic absorption peaks at 1100 cm^{-1} of (d) was due to the asymmetric vibration modes of Si–O–Si formed by the sol–gel reaction [15]. The absorption peak at 1200 cm^{-1} was due to the symmetric deformation of Si–O–Si. The characteristic absorption peaks of (d) at 1100 cm^{-1} is stronger than (c), it can be inferred that the asymmetric vibration of Si–O–Si and C–O–C are interactional.

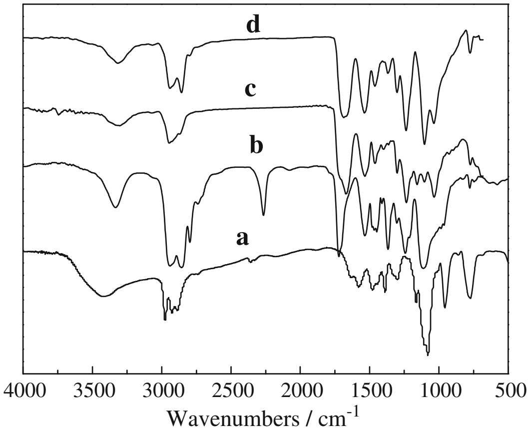


Fig. 1 IR spectra of APTES, polyurethane prepolymer and polyurethane modified with APTES. (*a*) APTES, (*b*) PU prepolymer, (*c*) PU prepolymer with APTES, (*d*) PU10 films

Table 2 XPS results of the WPU films

Element	Concentration (%)			Si Concentration (%)	
	N	O	C	Theoretical	Experimental
PU0	5.37	10.23	73.01	0	0
PU5	5.42	10.78	71.87	0.60	0.61
PU10	5.46	11.27	70.83	1.14	1.15
PU15	5.49	11.73	69.86	1.65	1.63

XPS analysis

Table 2 shows results of XPS analysis of the WPU films. From the XPS analysis, it is found that concentration of N, O, and C is accordant with the amount of the materials used in formulation. The experimental content of Si element is close to the theoretical content. We can conclude that the APTES as coupling agent is successfully introduced into the WPU backbone.

Thermogravimetric analysis

In order to examine the effect of APTES on the thermal stability, TGA was carried out and results are shown in Fig. 2. The thermal stability of PU is generally not high, especially above their softening temperatures [16], and the degradation mechanism is very complex due to the variety of products formed in the process [17]. Usually, at a low heating rate, the degradation process results in differential weight loss (DTG) curves with several peaks, which indicates the complexity of the degradation. Those peaks correspond to the temperatures at maximum rate of weight loss in the corresponding step. Temperatures of 10%, 30%, and 50% weight loss are shown in Table 3.

Fig. 2 TGA thermograms of WPU with APTES

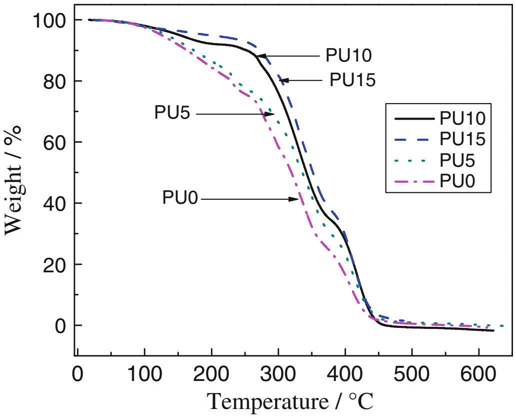


Table 3 Effects of APTES on the heat resistance of WPU films

Designation	$T_{0.1}$ (°C)	$T_{0.3}$ (°C)	$T_{0.5}$ (°C)
PU0	163.22	274.46	319.41
PU5	173.73	288.98	335.98
PU10	252.61	311.62	341.87
PU15	272.45	322.25	351.72

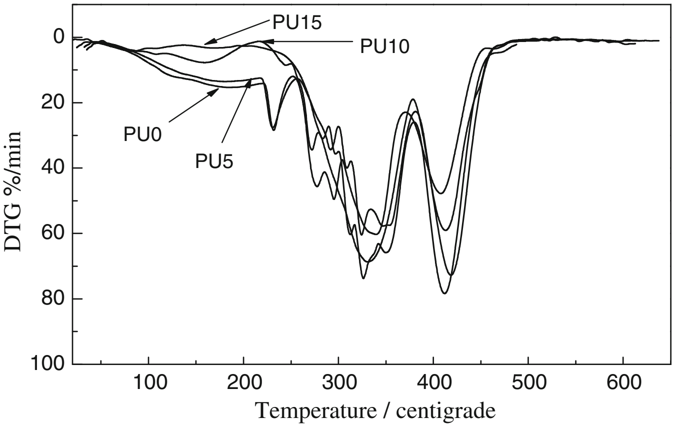


Fig. 3 DTG curves of WPU

It was verified from Table 3 that the thermal stability was influenced by APTES concentration. $T_{0.1}$, $T_{0.3}$, and $T_{0.5}$ of PU5, PU10, and PU15 are higher than PU0, indicating that the addition of APTES enhances the product's thermal stability. Figure 3 shows the behavior of DTG curves for the samples. The curves show that there are different stages of degradation which are not perceptible in TG curves, showing the close relation and mutual influence between degradation process of hard and soft segments. It is shown that the films present three stages and even more degradation-step profile. In general, the first weight loss stage in the temperature range from 25 to 250 °C, results from the vaporization of residual solvent and loss of oligomer and by-products existing in the WPU films. The degradation occurring at around 300 °C might be starting the decomposition of urethane group as the hard segments degradation, while the degradation occurring at around 400 °C might be attributed to the decomposition of the soft segment of PU [18–21].

The weight loss in temperature range from 30 to 600 °C is shown that the thermal decomposition of these WPU films shift toward the higher temperature range than that of PU0, which confirms the enhancement of thermal stability of modified WPU. The modified WPU have an interpenetrated network nature generated in the sol–gel process. The reason limits the segmental movement of WPU, leading to the increase in the thermal stability. In addition, there is Si–O bond in the WPU molecule after reacting with trifunctional APTES and bond energy of Si–O bond is greater than that of C–O bond, which can also improve thermal resistance of WPU.

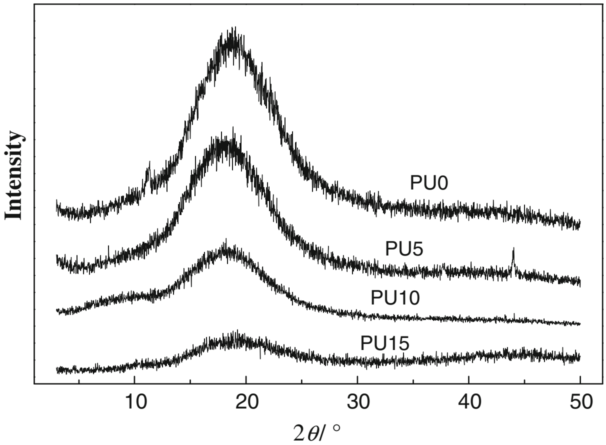


Fig. 4 X-ray diffractograms of WPU with different silica content

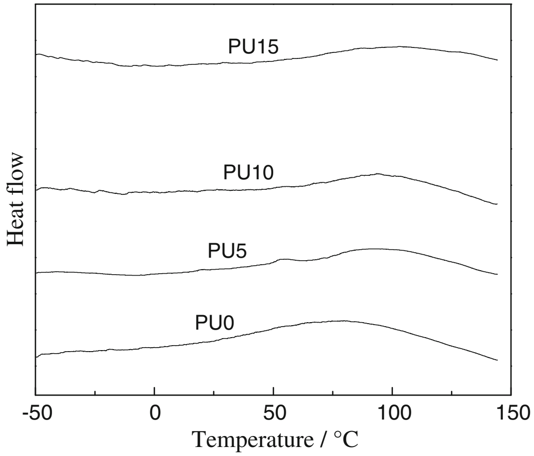
XRD analysis

Figure 4 shows the X-ray diffraction curves for WPU samples with varying the APTES content. For pure WPU, nearly amorphous diffraction peak is seen near $2\theta = 20°$ [22], which is the diffraction peak of the crystalline PU. Crystallinity in PU is commonly considered as ordered structure of chain segment owing to hydrogen bonds occurring in PUs. It is found that the diffraction peaks become weaker as the APTES content increases. While $w(\text{APTES}) = 15\%$, the diffraction peak nearly disappeared, only a broad diffraction peak can be observed. This implies that the crystallinity and orientation of PU chains is significantly disturbed through the addition of APTES. We can conclude that the presence of Si–O–Si seems to disfavor the formation of a more ordered structure. Hydrogen bonds interactions between the soft and hard phases favor ordered structure of chain segment in PU. Nevertheless, hydrolysis of ethoxy groups in APTES and condensation of silanol groups form three-dimensional chemical bondings Si–O–Si, weakening hydrogen bonds in PUs. On the other hand, three-dimensional Si–O–Si reticulation restricts the movement of chain segment, disfavoring the formation of new crystalline structures, so the diffraction peaks become weaker as the APTES content increases. The crystallinity of WPU can also be confirmed by the DSC analysis in Fig. 5.

DSC analysis

Figure 5 shows DSC thermogram curves of PU0, PU5, PU10, and PU15. There is an endothermic peak in DSC thermogram curve of PU0, it is the melting temperature of hard segment crystals in PU. With the increase of APTES, intensity of melting endothermic peaks decreased, which indicated that the crystallinity of PU segments declined with increasing APTES. DSC thermogram curve of PU15 is flat and there is no obvious endothermic peak or exothermic peak.

Fig. 5 DSC thermogram curves



Influence of the APTES weight percent on the mechanical properties

Influence of the APTES weight percent on the mechanical properties of films is shown in Fig. 6. Figure 6 shows that the tensile strength of the WPU films increases generally with increase of APTES, whereas the elongation at break shows the opposite tendency. On the whole, the tensile strength increase from 18 MPa to 28 MPa while *w*(APTES) increases from 0% to 10%. However, the tensile strength will decrease when *w*(APTES) is more than 10%. The excessive APTES is disadvantageous to tensile strength improvement. The Si atom in APTES is trifunctional in terms of reactive ethoxy groups, so the APTES can improve the mechanical properties of PU films by increasing crosslinking density of the polymer. Increasing *w*(APTES) leads to higher cross-linking density between crosslinking points. Excessive crosslink structure of macromolecule leads to the increasing particle size of PU emulsion and PU emulsion will be unstable. Unstable

Fig. 6 Influence of the APTES weight percent on the mechanical properties of films

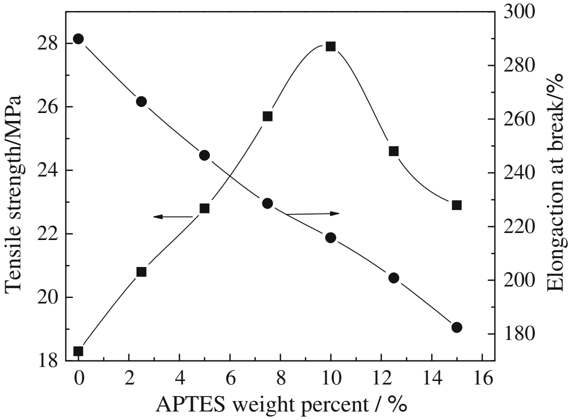
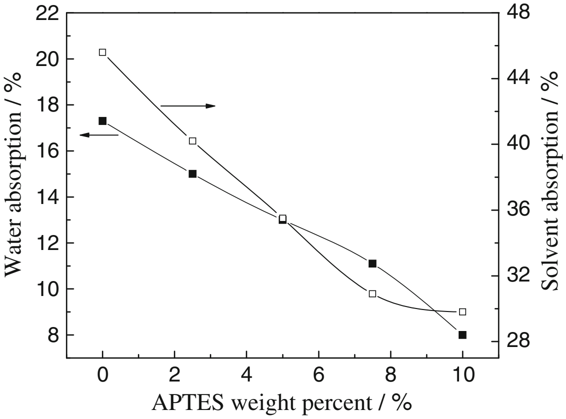


Fig. 7 Influence of the APTES weight percent on the water absorption and solvent absorption of films



PU emulsion is a great disadvantage to the film-forming properties, which results in the decrease of tensile strength.

Influence of the APTES on water absorption

Influence of the APTES weight percent on the water absorption and solvent absorption of films is shown in Fig. 7. The water absorption and solvent absorption of films decreases monotonically with increasing APTES mass fraction. As the mass fraction of APTES increases from 0% to 10%, water absorption decreases from 17% to 8% and ethanol absorption decreases from 46% to 30%, indicating the forming of siloxane structure enhances the resistance to water and solvent. The films prepared with higher APTES weight percent exhibited better water resistance, and this may be ascribed to the higher cross-linking density between cross-linking points. Hydrolysis of ethoxy groups in PU gives silanol groups which can subsequently condense with silanol groups on another PU molecule to form –Si–O–Si– linkage. The Si atom in APTES is trifunctional in terms of reactive ethoxy groups and is, therefore, able to form a three-dimensional chemical bonding between PU polymer molecules, leading to the increasing crosslinking density of the polymer and decreasing free volume of the molecular chain, thus the water and ethanol molecules were hard to penetrate into the membranes, therefore the water and solvent resistance increased.

Effects of APTES on particle size

The particle size and distribution of WPU dispersions are shown in Fig. 8. It is found that the particle size of pure PU dispersion (PU0) is just 88.45 nm, and its particle size distribution is also very narrow. However, the particle size increases with increased silane coupling agents addition. When *w*(APTES) increases from 0% to 15%, the dispersions' average size increase from 88.45 nm to 168.1 nm and the distribution width becomes wider. Increasing *w*(APTES) leads to more hydrophobic structure and higher cross-linking density in the macromolecular

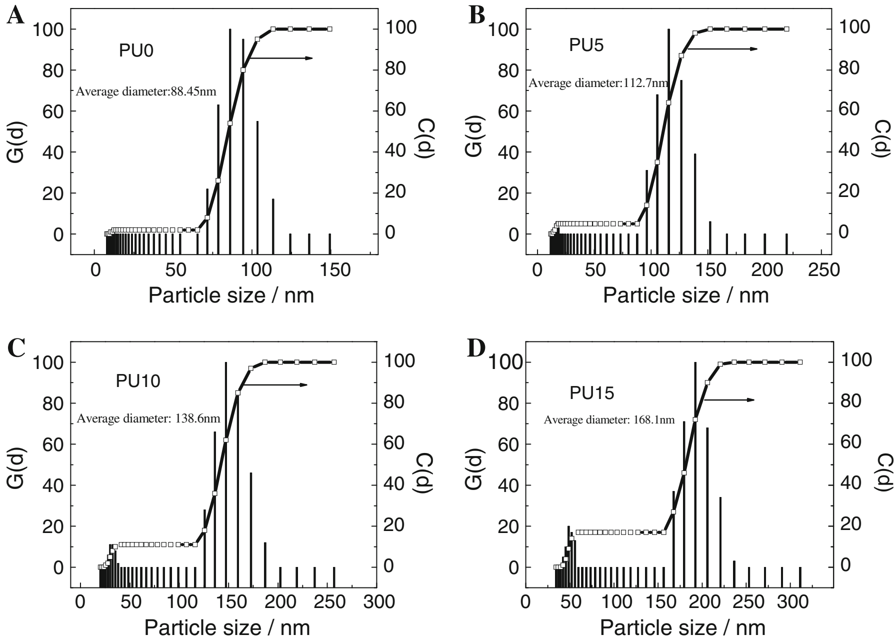


Fig. 8 Particle size and distribution of WPU emulsions

chains, consequently it is difficult to emulsify the PUs with a fixed COOH content and the particle size increases. Increasing *w*(APTES) favors the forming of siloxane structure which enhances the resistance to water and solvent of PU films. However, particle size increases and WPU dispersions will be unstable if the *w*(APTES) continuously increases. Considering the characteristic of water resistance for the formed films, the optimum *w*(APTES) was about 10%.

Conclusion

Waterborne polyurethane (WPU) prepolymer was prepared, which was modified by APTES to form highly crosslinked PU dispersion. The films of the WPU were prepared by casting emulsions on Teflon surfaces. The structure of the PU was characterized by FTIR, TG, XRD, and DSC. As the mass fraction of APTES increases from 0% to 10%, the tensile strength of WPU films increased, water absorption and ethanol absorption decreased. The forming of siloxane structure in the PU enhances the resistance to water and solvent of films. FT-IR indicates that –NH_2 of APTES reacted with –NCO of PU prepolymer. TG analysis indicates that APTES can improve thermal stability of PU. XRD shows that crystallinity of PU decreased with the increase of *w*(APTES). DLS shows that the particle size of WPU emulsion increases with increased silane coupling agent addition.

Acknowledgements We would like to express our great thanks to the National Natural Science Foundation of China (grant number: 50673055) and the Natural Science Foundation of Shaanxi University of Science & Technology (grant number: ZX08-08) for financial support.

References

1. Jang JY, Jhon YK, Cheong IW (2002) Effect of process variables on molecular weight and mechanical properties of water-based polyurethane dispersion[J]. Colloids Surf A 196:135–143
2. Jeon HT, Jang MK, Kima BK (2007) Synthesis and characterizations of waterborne polyurethane–silica hybrids using sol–gel process[J]. Colloids Surf A 302:559–567
3. Madbouly SA, Otaigbe JU, Nanda AK (2005) Thermal-induced simultaneous liquid–liquid phase separation and liquid–solid transition in aqueous polyurethane dispersions. Polymer 46:10897–10907
4. Shimizu H et al (2005) Polyurethane resin water dispersion and aqueous polyurethane adhesive. US patent, US 6881788, 19 Apr 2005
5. Nanda AK, Wicks DA (2006) The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process. Polymer 47:1805–1811
6. Melchiors M, Sonntag M et al (2000) Recent developments in aqueous two-component polyurethane (2K-PUR) coatings. Prog Org Coat 40:99–109
7. Adler HJ, Jahny K, Bettina VB (2001) Polyurethane macromers-new building blocks for acrylic hybrid emulsions with outstanding performance. Prog Org Coat 43:251–257
8. Frings S, Meinema HA, van Nostrum CF, van der Linde R (1998) Organic-inorganic hybrid coatings for coil coating application based on polyesters and tetraethoxysilane. Prog Org Coat 33:126–130
9. Zou J, Shi W, Hong X (2005) Characterization and properties of a novel organic–inorganic hybrid based on hyperbranched aliphatic polyester prepared via sol–gel process. Compos A 36:631–637
10. Rekondo A, Fernández-Berridi MJ, Irusta L (2006) Synthesis of silanized polyether urethane hybrid systems. Study of the curing process through hydrogen bonding interactions. Eur Polym J 42:2069–2080
11. Ni H, Skaja AD, Soucek MD (2000) Acid-catalyzed moisture-curing polyurea/polysiloxane ceramer coatings. Prog Org Coat 40:175–184
12. Ni H, Simonsick WJ Jr, Skaja AD et al (2000) Polyurea/polysiloxane ceramer coatings. Prog Org Coat 38:97–110
13. Xu J, Shi W, Pang W (2006) Synthesis and shape memory effects of si-o-si crosslinked hybrid polyurethanes. Polymer 47:457–465
14. Chen Y, Zhou S, Gu G, Wu L (2006) Microstructure and properties of polyester-based polyurethane/titania hybrid films prepared by sol–gel process. Polymer 47:1640–1648
15. Wang LF, Ji Q, Glass TE et al (2000) Synthesis and characterization of organosiloxane modified segmented polyether polyurethanes. Polymer 41:5083–5093
16. Coutinho FMB, Delpech MC (2000) Degradation profile of films cast from aqueous polyurethane dispersions. Polym Degrad Stab 70:49–57
17. Chang TC, Shen WS, Chiu YS, Ho SY (1995) Thermo-oxidative degradation of phosphorus-containing polyurethane. Polym Degrad Stab 49(3):353–360
18. Marcos-Fernández A, Abraham GA, Valentín JL, San Román J (2006) Synthesis and characterization of biodegradable non-toxic poly(ester-urethane-urea)s based on poly(e-caprolactone) and amino acid derivatives. Polymer 47:785–798
19. Chuang FS, Tsen WC, Shu YC (2004) The effect of different siloxane chain-extenders on the thermal degradation and stability of segmented polyurethanes. Polym Degrad Stab 84:69–77
20. Lee MH, Choi HY, Jeong KY, Lee JW, Hwang TW, Kim BK (2007) High performance UV cured polyurethane dispersion. Polym Degrad Stab 92:1677–1681
21. Chattopadhyay DK, Mishra AK, Sreedhar B, Raju KVSN (2006) Thermal and viscoelastic properties of polyurethane-imide/clay hybrid coatings. Polym Degrad Stab 91:1837–1849
22. Zhang T, Xi K, Yu X, Gu M, Guo S (2003) Synthesis, properties of fullerene-containing polyurethane-urea and its optical limiting absorption. Polymer 44(9):2647–2654