

INFLUENCE OF SILOXANE CO-SEGMENT LENGTH AND CONTENT OF WATERBORNE POLYSILOXANE-URETHANE COPOLYMERS ON THEIR WATER RESISTANCE, THERMAL STABILITY AND MECHANICAL PROPERTIES*

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Abstract A series of stable waterborne polysiloxaneurethane (WPSUR) dispersions were prepared using amino-terminated polydimethylsiloxane (NS), dimethylolpropionic acid (DMPA), castor oil, polypropylene glycol and toluene diisocyanate. Meanwhile, NS with different molecular weights was synthesized and used as the soft co-segment. Effects of types and contents of soft co-segments as well as chain extenders on the thermal degradation and stability for WPSUR films were examined. Results reveal that WPSUR films exhibit excellent water resistance and mechanical properties as compared with pure polyurethane (PU) films, and the NS soft co-segment possesses a remarkable effect on the second stage (stage II), while the content of the hard segment is propitious to the initial stage (stage I). Moreover, the highest temperature of stage II (T_{2m}) for WPSUR films using NS as soft co-segment is 413°C, approximately being 30°C higher than that of those typical PUs using HDA and APDMS as the chain extenders, respectively.

Keywords: Waterborne; Polysiloxane; Polyurethane; Castor oil; Thermal properties; Water resistance.

INTRODUCTION

As a block copolymer containing polysiloxane and urethane (or polyurethane) segments, polysiloxaneurethane (PSUR) possesses good oxidative stability, satisfactory mechanical, unique dielectric and surface-related and blood contacting properties^[1–6], which has prompted many academic researches in its usage for commercial applications^[7]. The possibility of combining the advantages of polysiloxane (PSI) and polyurethane (PU) has attracted researchers' attention. It is expected that such 'hybrids' would provide better heat resistance and lower temperature flexibility as compared with PU, and better tensile strength and abrasion characteristics as compared with PSI^[8, 9]. It is noted that PSUR can be used in waterproof coatings and finishes for textiles and natural leather^[10–14]. Moreover, there are other potential applications of PSUR, including sealants, adhesives, highly selective gas permeable films, internal mould-release agents, optical and air-spinnable fibres, *etc*^[8].

Various researchers have focused their attentions on modification of waterborne PU by incorporating strong hydrophobic units into these systems with the aim of waterproof performance enhancement^[15]. However, it is difficult to incorporate non-polar polydimethylsiloxane (PDMS) into a polyurethane backbone due to their different solubility parameters^[16–19]. To solve this problem, a second soft segment macrodiol is introduced, acting as an intermediate polarity chemical species between the hard urethane segments and soft PDMS

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segments. Synthesis of polyurethane with multiphase structure by using poly(hexamethylene oxide) (PHMO) and hydroxyl terminated PDMS has been reported^[20, 21]. Dihydroxybutyl terminated PDMS was used to modify the polyurethane-acrylic (PUA) hybrid emulsion, and good water resistance could be gained when PDMS content was higher than 6.5%^[22]. Prepared hydroxyl-terminated PDMS modified PU revealed that domain separation occurred during PU polymerization because of the immiscibility between the hydrophilic and hydrophobic polyols^[23]. A series of hydroxyl-terminated PDMS were synthesized, and effects of PDMS concentration on properties of polyurethane/polydimethylsiloxane hybrid dispersions were studied carefully^[24]. Hydroxyalkyl and hydroxyl terminated PDMS were obtained and used to modify aqueous polyurethanes^[25]. α,ω -Dihydroxypoly[(3,3,3-trifluoropropyl) methylsiloxane] (PTFPMS) was employed to modify waterborne PU, and the water resistance of this polymer was examined^[26, 27]. Besides, there have been some other researches on PDMS modified PU systems^[28]. Segmented poly(dimethylsiloxaneurethane) copolymers (PSUR) were also investigated, and phase-separation and the orientational behavior of segmented PSUR were examined^[29, 30].

It is known that castor oil is endowed with unsaturation and hydroxyl function groups and it can be used in polyurethane preparation. As a polyfunctional alcohol, it can react with polyfunctional isocyanates to form PUs whose morphologies change from rigid foam to elastomers. Moreover, its multi-functional nature can contribute toughness to the structure of PU, and the long fatty acid chain imparts flexibility.

In general, insertion of suitable polysiloxane segments into polyurethane chains facilitates improving water resistance of films, because polysiloxane is hydrophobic, and films of self-emulsification waterborne polyurethane with hydrophilic groups have poor water resistance. If the length of the polysiloxane segment is too short, WPSUR films would possess poor water resistance. On the contrary, the polysiloxaneurethane could hardly disperse in water uniformly if the segment length of polysiloxane is too long. It is believed that the concentration of carboxyl groups is important for water dispersion and water resistance of films. Some researches concerning the effect of carboxyl concentration on waterborne polyurethane were reported previously, and it was confirmed that WPSUR could disperse well in water with a proper concentration of carboxyl^[31].

It is noted that few published patents have involved application of WPSUR in water proof coatings and finishes for textile. In addition, there have been few papers related to synthesis of amino-terminated PDMS modified PU and the properties-structure relationship of WPSUR. The objective of present article is to synthesize a novel high-activity soft co-segment *i.e.* NS and polymerized WPSURs, and to probe their properties. Improvement of water resistance, thermal degradation and stability of the films are expected by ascending the siloxane segment length and content.

EXPERIMENTAL

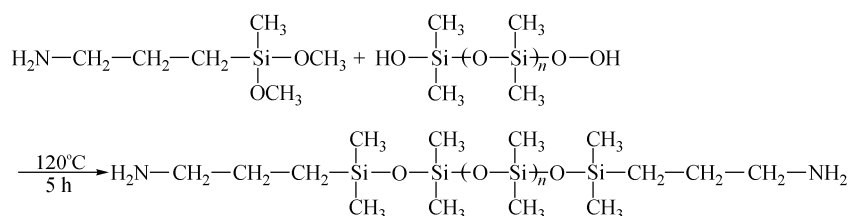
Materials

Castor oil (Acid# 4) and polypropylene glycol (PPG, OH# 105–117, $M_n = 1000 \pm 70$) were supplied by the Third Petrochemical Factory, China. The samples were dried under reduced pressure at 110°C for 1h before use. Dimethylol-propionic acid (DMPA) was purchased from Alfa Aesar Co., USA. 1,4-Toluene diisocyanate (TDI), triethylamine (TEA), hexamethylene diamine (HDA) and acetone were supplied by Shanghai Chemical Agent Co., China. Hydroxyl-terminated polydimethylsiloxane (OH# 4.1 and 3.0) was supplied by Wuxi Quanli Chemical Co., Ltd. China. 3-(2-Aminoethylamino) propyl dimethoxymethyl silane (APDMS) was purchased from Yingcheng Diamond New Material Chemical Co., China. All these materials were standard laboratory reagents and were used as received, except triethylamine, which was treated with 0.4 nm molecular sieves for over 1 week before use. Amino-terminated siloxane (NS) with different molecular weights was prepared in our lab.

Sample Preparation

Scheme 1 presents the illustration of preparation for amino-terminated polysiloxane. The reaction was carried out in a 500 mL four neck round-bottom flask, fitted with a mechanical stirrer, a nitrogen inlet, a thermometer

and a reduced pressure setup. As shown in Scheme 1, hydroxyl-terminated polydimethylsiloxane (PDMS) and aminopropylmethyldimethoxysilane reacted with predetermined quantity at 120°C for 5 h. Methanol was then removed under low reduced pressure. The reaction was ended when the measured amount of methanol reached the calculated value.



Scheme 1 Illustration of reactive equation for amino-terminated polysiloxane (NS)

The polymerization of WPSUR was carried out in three steps. First, NCO-terminated prepolymer was synthesized. A calculated quantity of dried castor oil, polypropylene glycol, DMPA and acetone (20 wt% in the prepolymer) were charged into a 500 mL round bottom flask with a mechanical stirrer, a nitrogen inlet, a condenser and a thermometer. The reagents were stirred until a homogeneous mixture was obtained. TDI was then added into the flask and stirred at 60°C until NCO value reached the theoretical value. Secondly, the temperature was then cooled down to room temperature at which NS reacted with the prepolymer. Thirdly, fine WPSUR dispersion was obtained by slowly adding TEA and water to the solution. The dispersion was then further stirred for 1 h at an agitation speed of 600 r/min. Acetone was removed under reduced pressure. Table 1 lists the composition of WPSUR with different soft co-segments.

Table 1. The composition of WPSUR with different soft co-segments and chain extenders (mmol)

Raw material	HDA	APDMS	NS-840	NS-1300
PPG	42.5	42.5	42.5	42.5
Castor oil	11.1	11.1	11.1	11.1
DMPA	49.1	51.4	60.8	70.3
TDI	132.7	135	144.5	153.3
Chain extender	30	30	30	30
TEA	49.1	51.4	60.8	70.3

^a The carboxyl concentration is 2.5 wt%.

Measurements and Characterization of Properties

Nuclear magnetic resonance (NMR) analysis

¹H-NMR spectrum was obtained from an ARX 500 NMR spectrometer (Bruker, Switzerland) using chloroform-d as solvent and tetramethylsilane (TMS; $\delta = 0$) as internal standard. Then about 400–500 μL D₂O was added into the NMR tube, and oscillated for 20 min for amino hydrogen/deuterium (H/D) exchange.

Fourier transform infrared (FT-IR) analysis

FT-IR spectra were recorded on a VECTOR 22 spectrometer (Bruker, Germany). The diffuse reflectance spectra were collected with a spectra diffuse reflectance accessory and were presented in transmittance mode. The resolution for all the infrared spectra was 4 cm^{-1} , and there were 32 scans for each spectrum. A KBr disc was used as a reference material to produce a background diffuse reflectance spectrum.

Gel permeation chromatography (GPC) analysis

Size exclusion chromatography (SEC) was performed on a gel permeation chromatography (Waters 1525/2414, USA), and THF was used as the eluent with a flow rate of 1.0 mL/min at 25°C. A set of monodisperse polystyrene standards covering molecular weight range from 100 to 4000 was used for molecular weight calibration.

Particle size analysis

The particles sizes of WPSUR were measured at 25°C on a 90 Plus/BI-MAS light scattering ultra-fine particle analyzer (Brookhaven Instruments Corporation, Germany). Each sample was diluted to a required concentration with distilled water before analysis.

Water resistance test

The water contact angles of the films were tested on a contact angle instrument (DSA100, KRUSS, Germany). Films with thickness of 1–2 mm were prepared by casting the WPSUR dispersion into a polypropylene dishware, followed by drying at 40°C for 3 days. The resulting films were then heated overnight in an oven at 60°C and 267–400 Pa. Water swelling tests of the films were performed with de-ionized water, and dry films were weighed (w_0) and then immersed into the de-ionized water to prepare swelling films for 1, 3, 7 and 13 days respectively. The resulting films were taken out, and the excess de-ionized water on the film was wiped off with a paper cloth. Then the weight of the films was measured. The degree of swelling (D_s) was calculated by the equation^[32]

$$D_s (\%) = (w_s - w_0) / w_0 \quad (1)$$

in which w_s represents the weight of the swollen film.

Thermogravimetry analysis (TGA)

Thermal degradation and stability of the polymers were evaluated on a thermogravimetric analyzer (SDT Q600, TA, USA). All tests were measured from room temperature to 600°C with a heating rate of 10 K/min. The nitrogen flow rate was calibrated at 120 mL/min.

Mechanical property test

The tensile strength and elongation at break of the films were measured on a universal testing machine (CMT 4204, Shenzhen SANS Test Machine Co. Ltd., China) at room temperature. The films for mechanical tests were prepared under the same conditions as the films for water resistance measurements. The samples were prepared according to standard GB/T 528–1998. The gauge length was 2 cm, and the crosshead speed was 500 mm/min. At least five samples were tested and the average value was taken.

The storage stability

The high-temperature stability of WPSUR dispersions was tested by the deposition of dispersions after being placed in an oven at 60°C for 40 h. For freeze-thaw stability measurements, the dispersions were subjected to a number of testing cycles in which the samples were frozen at –30°C for 18 h and then allowed to thaw at room temperature for 6 h. At least five cycles were performed for each sample to observe whether any precipitation appeared or not. The stability of WPSUR dispersion was expressed by the recycle times of the freeze-thaw test.

RESULTS AND DISCUSSION

Structure Characterization for NS

Figure 1 shows the FT-IR spectra of PDMS and NS-1300. It can be seen that the monomer exhibits an absorption band at 3296 cm^{-1} , which is ascribed to OH stretching vibrations, and this band disappears in the spectrum of NS-1300. There is an absorption band at 3317 cm^{-1} for NS-1300 which is assigned to NH stretching vibrations, indicating that the hydroxyl group is consumed fully during polymerization reaction. Figure 2 gives ^1H -NMR and amino hydrogen/deuterium (H/D) exchange spectra of NS-1300. There is a blunt resonance peak at δ ca. 1.58 responsible for the amino group, and it disappears in the H/D exchange spectrum. There is a resonance peak at δ ca. 3.46 induced by the resonance of methoxyl group. There is a resonance peak at δ ca. 1.2, which is associated with the hydroxyl of PDMS remanent in the NS synthesis reaction. These results indicate that hydroxyl groups are transformed into amino groups in the NS synthesis reaction.

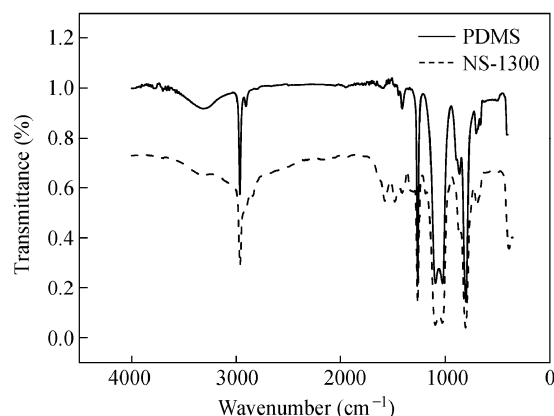


Fig. 1 FT-IR spectra of PDMS and NS-1300

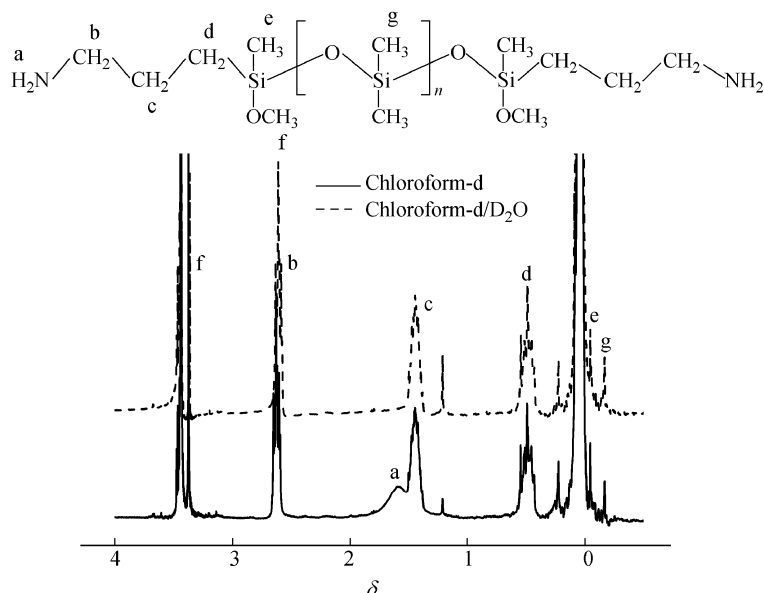


Fig. 2 ^1H -NMR and amino hydrogen/deuterium (H/D) exchange spectra of NS-1300

The M_n of NS-1300 and NS-840 measured by GPC is 1292 and 840, respectively. Their corresponding polydispersity index is 1.3 and 1.16, respectively, indicating that the segment length of NS-1300 is greater than that of NS-840.

Particle Size and Storage Stability

Figures 3 and 4 present the lognormal size distribution of WPSUR dispersions with different NS co-segment lengths and contents. It can be observed that the WPSUR dispersions exhibit narrow particle size, and the particle size increases with the ascending of NS co-segment length and content. The particle size of WPSUR dispersion is primarily dependent on the number of the hydrophilic units, the chemical composition, as well as the electric charge distribution of the particle surface. Besides, the hydrogen-bonding degree of the urea and urethane groups in WPSUR also influences the particle size of WPSUR dispersion. Due to the strong hydrophobicity of the NS co-segment, NS enters into the interior of the particle as far as possible. The hydrophilic parts orient at the polymer-water interface when WPSUR is dispersed into water. As the length and content of NS co-segment increase, both molecular weight and molecular volume of WPSUR increase, leading to the formation of big particles due to enhancement of surface hydrophobicity. Therefore, an increase in particle

size can be obtained with the ascending of NS co-segment length and content.

Excellent high-temperature and freeze-thaw stability is also observed, which is important for waterborne dispersion applied in industries.

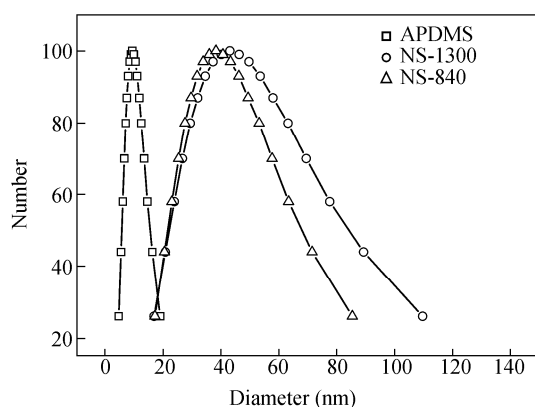


Fig. 3 The lognormal size distribution of WPSUR dispersions with different soft co-segments and chain extenders

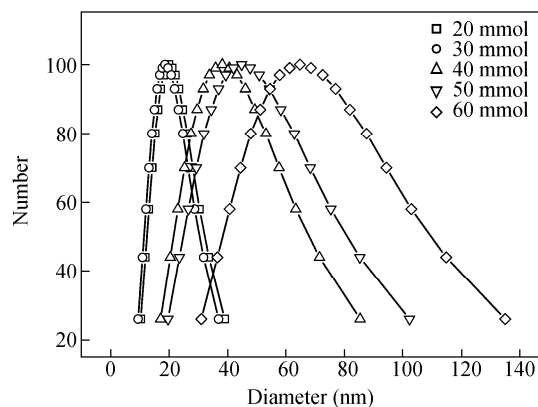


Fig. 4 The lognormal size distribution of WPSUR dispersions with different NS co-segment contents

Water Resistance Properties

Figure 5 shows the degree of swelling (D_s) and water contact angle for WPSUR films with different types of soft co-segments and chain extenders. It is noted that the siloxane content and carboxyl content are fixed at 30 mmol and 2.5 wt%, respectively. Using HDA as the chain extender, WPSUR film is water sensitive and is poor water resistance, while using NS-1300 as soft co-segment, the resulted WPSUR films appear basically waterproof and good water resistance. Moreover, as the siloxane co-segment length increases, WPSUR films possess better water resistance, indicating that the critical surface energy in WPSUR films is low. Figure 6 shows D_s of WPSUR films using NS-1300 as the soft co-segment with various NS co-segment contents. It can be seen that the D_s increases monotonically with the increase of immersion time in water, but decreases with the increase of siloxane co-segment contents. This is because intermolecular interactions between water and the polymer become progressively more unfavorable as more siloxane is added. Therefore, the material becomes more hydrophobic. As the immersion time increases, water molecules penetrate into WPSUR, and D_s increases.

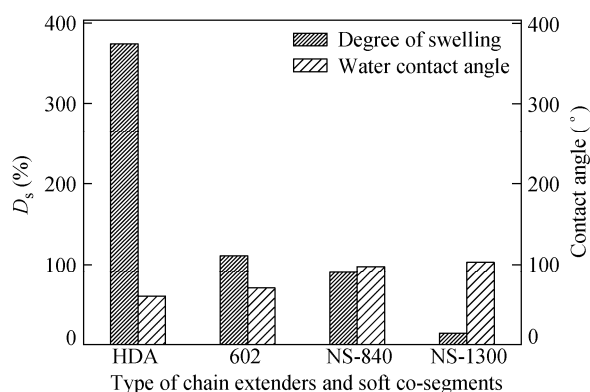


Fig. 5 Degree of swelling (D_s) and water contact angle for WPSUR films with different soft co-segments and chain extenders

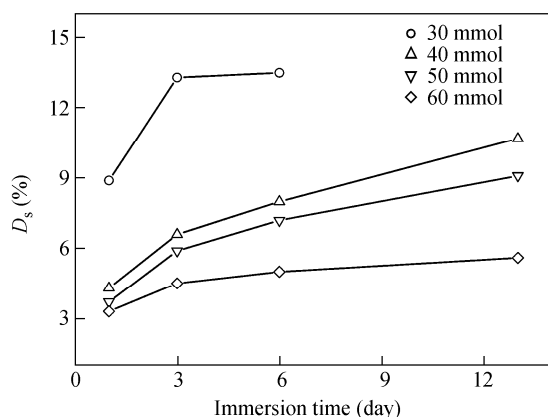


Fig. 6 Degree of swelling (D_s) as a function of immersion time for WPSUR films with different siloxane contents using NS-1300 as the soft co-segment

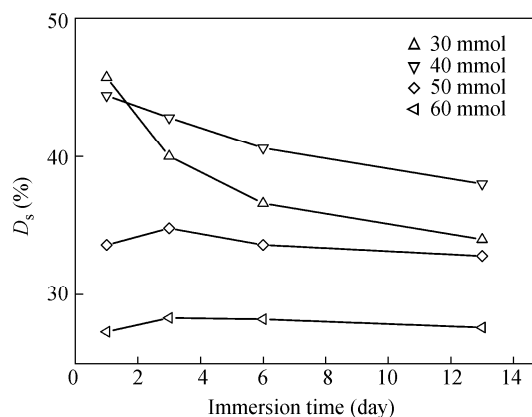


Fig. 7 Degree of swelling (D_s) as a function of immersion time for WPSUR films with different siloxane contents using NS-840 as the soft co-segment

Figure 7 demonstrates D_s of WPSUR with different co-segment contents using NS-840 as the soft co-segment. It is interesting that this case is different from the case using NS-1300 as the soft co-segment as shown in Fig. 6. D_s almost keeps constant and even decreases monotonically with increase of immersion time of samples in water. D_s for 30 mmol NS-840 content is lower than that for 40 mmol NS-840 content after the first day, which was probably caused by partial dissolution of the film in water while the w_0 remains the same for calculating D_s based on the Eq. (1). This is also confirmed by the weight loss conservation rate of WPSUR films after being soaked in water for 13 days. Table 2 lists the weight loss and conservation rate of WPSUR films.

Table 2. The weight loss and conservation rate of WPSUR films

		20 mmol	30 mmol	40 mmol	50 mmol	60 mmol
NS-840	Weight loss (%)	23.7	11.4	5.3	5.4	1.6
	Conservation rate (%)	72.3	88.6	94.7	94.6	98.4
NS-1300	Weight loss (%)	—	2.5	1.2	4.2	1.0
	Conservation rate (%)	—	97.5	98.8	95.6	99.0

The weight loss and conservation rate is calculated after films being immersed in water for 13 days.

Thermal Degradation and Stability

The thermal degradation of PUs depends not only on the structure of the isocyanate but also on the soft and hard segment contents. Petricic *et al.*^[33] found that the degradation of PU in the initial stage was mainly dominated by the type and amount of the hard segments. Figure 8 presents the thermogravimetry and differential thermalgravimetry curves for WPSUR samples with different soft co-segments with a heating rate of 10 K/min under nitrogen. WPSUR films have two distinct regions of weight loss (Fig. 8a), suggesting that at least two stages of degradation occur for these samples. The second stage (stage II) degradation of WPSUR films using NS as the soft co-segment is more obvious compared with that of WPSUR films using HDA and APDMS as the chain extenders. The stage I and stage II degradation of WPSUR films using NS-1300 as the soft co-segment occurs around 224–334°C and 334–578°C, respectively, reflecting in two peaks around 294°C and 413°C (Fig. 8b). Moreover, curves including the third heat absorption peak at 208°C indicate that the samples perhaps undergo a third stage of degradation, which could be explained by the water loss.

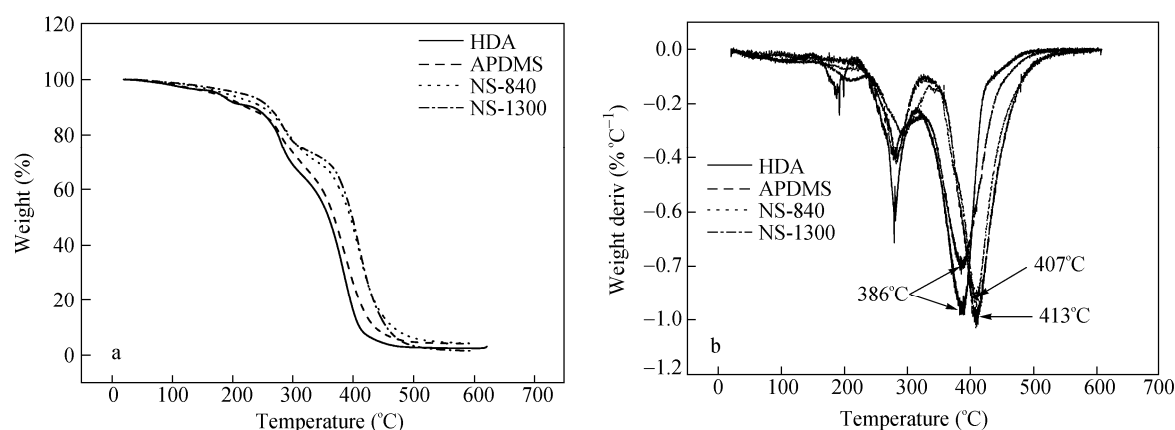


Fig. 8 TGA thermograms for (a) normalized weight and (b) weight derivative against temperature in nitrogen for WPSUR films using different soft co-segments and chain extenders

The degradation process can be qualitatively characterized by the onset and the highest temperatures of stage I (T_{1on} and T_{1m}) and stage II (T_{2on} and T_{2m}). The onset temperature at each stage of degradation reflects that backbone structure of polyurethane is destroyed upon heating. Table 3 lists the characteristic temperatures in each degradation stage for samples with a heating rate of 10 K/min under nitrogen. It is noted that the values of T_{1on} for WPSUR films using HDA and APDMS as the chain extenders are around 224°C and 240°C, respectively. For WPSUR films using NS-840 and NS-1300 as the soft co-segments, T_{1on} exceeds 226°C and 216°C, respectively. The effect of soft segment length on T_{2on} is more significant. The T_{2on} of WPSUR films using NS as the soft co-segment is around 334°C exceeds 314°C and 321°C for WPSUR films using HDA and APDMS as the chain extenders.

Table 3. Characteristic temperatures of samples in TGA curves^a

Code	T_{1on}^b (°C)	T_{1m}^b (°C)	T_{2on}^b (°C)	T_{2m}^b (°C)
HDA	224	280	314	386
APDMS	240	278	321	386
NS-840	226	283	334	407
NS-1300	216	294	334	413

^a At a heating rate of 10 K/min and under nitrogen atmosphere;

^b The onset and maximum temperature of the first stage, T_{1on} and T_{1m} , the same for the second stage, T_{2on} and T_{2m}

Considering the onset temperatures of degradation at stage I and stage II, the T_{2on} of typical PU could be increased using NS as the soft co-segment. Therefore, the temperature resistance is related to the soft segment length, while the content of the hard segment is propitious to the initial stage. At the temperature corresponding to the peak of the weight derivative (DTG) curve at each degradation stage, the degradation of the sample is the fastest. This temperature determines the thermal stability of those samples at each degradation stage. Table 3 indicates that the T_{2m} values of WPSUR films using NS as the soft co-segments are higher than those of the typical PU samples, which implies that the soft co-segment length has no obvious effects on T_{1m} . Although T_{1on} of WPSUR films using HDA and APDMS as the chain extenders exceeds that of WPSUR films using NS as the soft co-segment, T_{1m} , to some extent, depends on the soft co-segment length and content. Moreover, T_{2m} clearly reflects the temperature resistance effects of NS. On the other hand, T_{2m} of WPSUR films using NS-1300 as the soft co-segment appears at 413°C, approximately 30°C higher than those of WPSUR films using HDA and APDMS as the chain extenders. Compared the thermal stability of samples at stage I and stage II, it seems that the effect of the soft co-segment length on T_{1m} and T_{2m} is similar to that for WPSUR samples using NS as the soft co-segment.

It was found that the T_{1on} ascended with the increase of soft segment contents, and T_{2on} ascended with the increase of hard segment content^[33]. However, our work here proves that the thermal degradation and stability of WPSUR films are related to the contents of the hard segment at stage I, and soft segment at stage II. It is accepted that chemical or physical processes can improve the thermal degradation and stability, and aromatic imide or PmIA facilitate enhancement of the thermal stability for typical PU^[34–36].

To examine the effect of soft segment content on the thermal degradation and stability properties of WPSUR films, the content of NS is varied from 25 mmol to 60 mmol for NS-840, and from 20 mmol to 60 mmol for NS-1300, with 20 wt% polymer and 15 wt% castor oil. Figure 9 demonstrates TGA thermograms of WPSUR films, and Fig. 10 shows the normalized weight as a function of temperature for WPSUR films with different co-segment contents. Comparing the effect of NS content and length at stage II, the soft co-segment plays a similar role in WPSUR degradation.

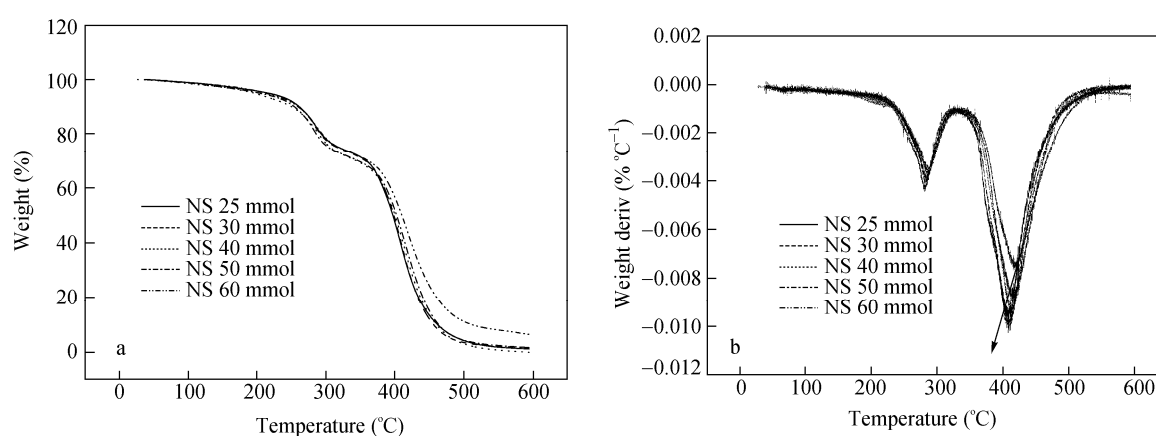


Fig. 9 TGA thermograms for (a) normalized weight and (b) weight derivative against temperature in nitrogen for WPSUR films using NS-840 as the chain extender with different siloxane content

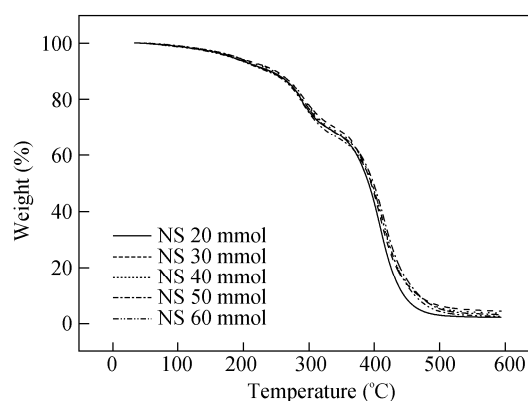


Fig. 10 Normalized weight as a function of temperature for WPSUR films using NS-1300 as the soft co-segment with different siloxane contents

According to the above analysis, it is noted that NS has little effect on T_{1on} , however, more obvious effect on T_{2on} . Hence, using NS as the soft co-segment improves the thermal stability at stage II. The higher the soft co-segment content, the better the thermal stability. Moreover, the effect of the soft segment length on T_{1m} and T_{2m} of WPSUR samples is similar to that of segment contents.

Mechanical Properties

Figure 11 depicts the tensile strength and elongation at break for WPSUR films. It can be found that the values of strength and elongation at break are 3.11 MPa and 189%, respectively, for WPSUR films using NS-1300 as the soft co-segment. WPSUR films using HDA as the chain extender has the highest elongation at break but the lowest tensile strength. On the other hand, the tensile strength of WPSUR films using APDMS as the chain extender are higher than that of WPSUR films using NS-840 as the soft co-segment, while elongation at break is much lower. This can be explained by the larger amount of hard segment, which strengthens the films. WPSUR films using NS-1300 as the soft co-segment has the highest tensile strength, due to enhancement of the morphology-separation and elasticity of WPSUR by increased soft co-segment length.

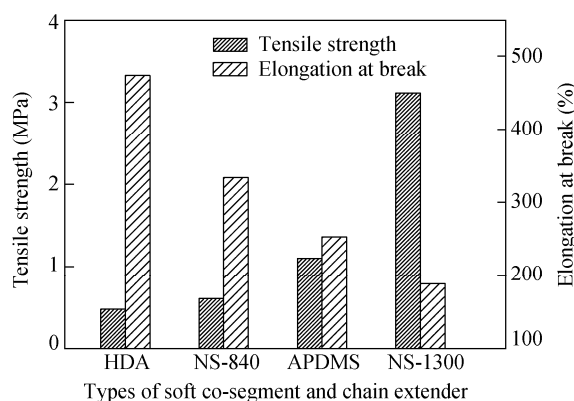


Fig. 11 Tensile strength and elongation at break for WPSUR films with different soft co-segments and chain extenders

CONCLUSIONS

Stable, water-dispersible anionic amino-terminated PDMS modified PU (WPSUR) samples were synthesized and characterized. The particle size of the emulsion increased with increase of polysiloxane content. Experimental results showed that these WPSUR dispersions had excellent freeze-thaw and high temperature stability. Compared with pure PU, water absorption of WPSUR films decreased dramatically with increase of amino-terminated siloxane (NS) soft co-segment length and content, indicating that they have excellent water resistance. Mechanical properties of WPSUR films could be improved by addition of NS. Meanwhile, the samples using HDA and APDMS as the chain-extender appeared more thermally stable than those using NS as the soft co-segment at stage I. The sample using NS-1300 as the soft co-segment exhibited the lowest T_{10n} . However, following this step, these samples exhibited much higher thermal stability than that of PU using HDA and APDMS as the chain-extendors at stage II. T_{2m} of WPSUR using NS-1300 as the soft co-segment was 413°C, approximately 30°C higher than that of typical PU using HDA and APDMS as the chain extenders, respectively.

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