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Alkoxysilane Functionalized Polyurethane/Polysiloxane Copolymers: Synthesis and the Effect of End-Capping Agent

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Summary

A series of moisture curable polyurethane/polysiloxane (PUSR) copolymers with different end-capping agents were prepared based on amine terminated polysiloxane (PDMS), poly-1, 4-butylene adipate glycol (PBA), 4, 4′-diphenylmethane diisocyanate (MDI). The copolymers were characterized by Fourier transform infrared (FT-IR) spectroscopy, thermogarvimetric (TGA), X-ray diffraction (XRD), dynamic mechanical thermal analysis (DMTA), X-ray photoelectron spectroscopy (XPS), surface contact angle and stress–strain measurement. Compared with conventional moisture curable PU, the PUSR copolymer showed the better thermal stability and surface properties due to the forming of Si-O-Si crosslinking network and the enrichment of siloxane chains on the surface of films , and the tensile strength was not obviously damaged. DMTA results suggested that micro-phase separation was formed in the PUSR copolymer. It was found that the PUSR copolymer with mixed alkoxysilanes as end-capping agents showed better compromised properties than that with single alkoxysilane.

Introduction

Polyurethane (PU) materials have a wide application because of their excellent properties including good mechanical properties, abrasion and chemical resistance [1, 2]. However, poor water resistance and thermal stability limit their applications in some fields. On the other hand, polysiloxane (PSi) materials have high thermal and oxidative stability, good blood compatible properties, low surface energy and a wide service temperature range (T_g, -123°C), but lower mechanical property and abrasion resistance [3, 4]. It is possible to prepare the PU/PSi copolymers which would have better thermo and water resistance than PU while the mechanical and abrasion characteristics are little damaged.

Moisture curing PU systems have a wide variety of high durability application for coating, sealant and adhesive [5-7]. The moisture curing polyurethane is prepared based on the reaction between isocyanate group and water. Adhikari investigated the effect of solvent on mechanical properties of moisture-cured PU. The results showed tensile strength of PU was increased by solvent treatment for organic solvents penetrated inside the PU hard segments and affected hydrogen bonds [8]. Kozakiewicz studied moisture-curable NCO-terminated polysiloxane-urethanes (PSUR) and reported that the coating properties of PSUR were similar to standard PU dispersions. The relationship between the degree of phase segregation and mechanical properties of the samples was obtained by TEM and SAXS studies [6, 9].

The functional siloxane can also have a moisture curing process. It has been employed as PU termination agents replaced isocyanate cure chemistry with alkoxysilane cure chemistry [10-13]. Under appropriate moisture and catalyst, the alkoxy end-groups can hydrolysis followed by condense to form a stable silicone oxide (Si-O-Si) cross-linking networks. The curing process was depicted in Eq. (1)-(3) [14].

$$\begin{aligned}
&\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \longrightarrow \equiv\mathrm{Si{-}OH} + \mathrm{ROH} && (1)\\
&\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} && (2)\\
&\equiv\mathrm{Si{-}OR} + \mathrm{HO{-}Si}\equiv \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} && (3)
\end{aligned} \qquad (\mathbf{1})$$

The curing process was affected by many factors, such as pH, temperature, solvent and concentration. Brinker and Schener summarized the effects of these factors on the hydrolysis and condensation processes, and concluded pH played the key role [15]. Lam investigated the curing mechanisms of alkoxysilane-terminated macromonomers [16]. Soucek prepared alkoxysilane-terminated PU moisture-curing coating and found that the adhesion was enhanced due to the increasing cross-linking density [12].

It is noteworthy that only few published papers dealt with alkoxysilane functionalized polyurethane/polysiloxane (PUSR) system, while isocyanate moisture-curable PUSR system and siloxane terminated PU alone are well known and widely used. The former system was not friendly to the environment for the toxicity of free NCO in air, while the latter can not include the advantages of polysiloxane such as water and heat resistance. Moreover, there is no report about the relationship between properties and structure of alkoxysilane functionalized PUSR.

In the preparation of alkoxysilane functionalized polymers, the alkoxysilane played a key role in the properties of products since it governed the cross-linking kinetics [17]. In this paper, alkoxysilane functionalized PUSR copolymers were synthesized and characterized. Especially, the effect of alkoxysilane as end-capping agent on the properties and morphology of PUSR copolymers was studied. This alkoxysilane functionalized PUSR copolymer may be expected to be used as potential environmental protection materials, such as coatings, sealants and reactive hot-melt adhesives.

Experimental

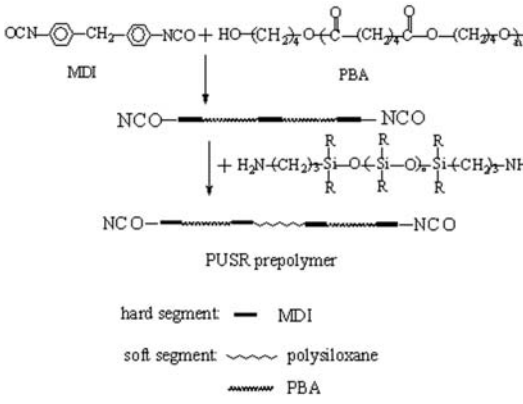
Materials

Amine terminated polysiloxane (PDMS, BY-853) was kindly provided by Dow-Corning and dried for 48 h under vacuum before use, 4, 4′-diphenylmethane diisocyanate (MDI) was used as received, poly-1, 4-butylene adipate glycol (PBA, M_n: 2000) was dehydrated for 3 h under 120°C. The 3-aminopropyl-triethoxysilane (γ-APS) and aniline-methyl-triethoxysilane (AMS) were used as end-capping agents.

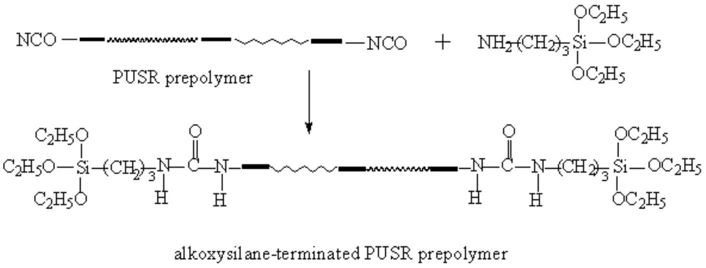
Dibutyltin dilaurate (DBTDL) as a catalyst was used without further purification. 1, 4-dioxane and methylbenzene were dried before use.

Polymerizations

Alkoxysilane functionalized PUSR copolymer was prepared via a two-step reaction, which was shown in Scheme 1. The soft segments in all samples were based on 10% PDMS and 90% PBA.



Step 1: Preparation of isocyanate-terminated PUSR prepolymer



Step 2: Preparation of alkoxysilane-terminated PUSR prepolymer

Scheme 1 Synthesis of alkoxysilane functionalized PUSR copolymer

Step 1: Preparation of isocyanate-terminated PUSR prepolymer

To obtain isocyanate-terminated PUSR prepolymer, the polyester diol and amine terminated PDMS were reacted with MDI with the molar ratio of NCO/ (OH +NH_2) = 2. The percent of PDMS in soft segments was 10%. 40 g molten PBA was weighted into a three-necked round-bottom flask equipped with a mechanical stirrer, a dropping funnel and a nitrogen inlet. After PBA was degassed for 1 h at 90°C under vacuum, 11.25 g MDI was quickly poured into the flask and reacted with PBA for 2.5 h at 90°C under nitrogen. Then the reaction mixture was cooled down to room temperature (25-30°C) and a certain mixing-solvent (1, 4-dioxane and toluene, 2:1 V/V) was added to get a diluted solution (about 40 wt %). 4.4 g PDMS was added dropwise to prevent a quick reaction and kept another 1 h under room temperature. After the reactions, the percent of free NCO in prepolymer was measured using standard di-n-butylamine back-titration method [18].

Step 2: Preparation of alkoxysilane-terminated PUSR prepolymer

According to the percent of NCO in PUSR prepolymer, the exact amount of alkoxysilane could be calculated with a stoichiometric ratio of NCO/(NH_2+NH) = 1. The prepolymer was reacted with aniline-methyl-triethoxysilane (AMS) for 1 h at 60°C and then reacted with 3-aminopropyl-triethoxysilane (γ-APS) for 1 h at room temperature. No free NCO left in the alkoxysilane-terminated PUSR prepolymer was confirmed by FT-IR.

The catalyst of DBTDL (0.1 wt. - %) was added in the alkoxysilane-terminated PUSR prepolymer which was degassed for 0.5 h under vacuum. It was then poured into a Teflon pan for curing. The moisture-curing process was conducted under stable temperature and humidity conditions (25°C and 50% R.H.) for two weeks. The cured film was dried for 48 h at 60°C under vacuum to remove the solvents.

Pure PU was prepared by the reaction of MDI and PBA for 2.5 h at 90°C with the molar ratio NCO/OH = 2, and its curing was same as the PUSR copolymer curing.

Polyurethane/polysiloxane (PUSR) copolymers are designated as PUSR-X, where X denotes the molar percentage of γ-APS in the end-capping agent. For instance, PUSR-20 refers to a PUSR polymer prepared with a end-capping mixture of 20 mol % γ-APS and 80 mol % AMS. The molar ratios of the end-capping agent used in this study were shown in Table 1.

Table 1 Molar ratios of end-capping agent for PUSR in the series

Sample	PDMS:PBA	γ-APS:AMS(Molar ratio)
PUSR-0	10:90	0:100
PUSR-20	10:90	20:80
PUSR-30	10:90	30:70
PUSR-40	10:90	40:60
PUSR-50	10:90	50:50
PUSR-60	10:90	60:40
PUSR-80	10:90	80:20
PUSR-100	10:90	100:0

Characterization

Fourier transform infrared (FT-IR) spectra: The FT-IR spectra were obtained by a Perkin-Elmer 1000 FT-IR spectrometer with a resolution of 2 cm^{-1}. The diluted solution was cast onto KBr disc and measured. For the cured film, an attenuated total reflection (ATR) attachment with a TaSe plate was used. The film thickness was about 1 mm. The angle of incidence of the IR beam to the sample was 90º.

Thermogarvimetric analysis (TGA): The thermal stability of PUSR copolymers were investigated by a Perkin Elmer 7 Series thermal analysis system from 20 to 800°C at a heating rate of 20°C/min under N_2 flow. The weight of the sample was about 10 mg.

Dynamic Mechanical Analysis (DMTA): DMTA was carried out on a RSA (TA.INSTRUMENTS) with the heating rate of 3°C/min and the frequency of 1 Hz. The operating temperature ranged from -120 to 120°C. For DMTA analysis, the specimens were 20×10×0.7~1.0 mm.

Stress–Strain Measurement: Tensile properties of PUSR copolymers were performed on an Instron 4465 Universal Tester at room temperature, with a crosshead speed of 500 mm/min. The specimens were 20×4×0.7 ~1 mm.

X-ray photoelectron spectroscopy (XPS): XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg/Kα radiation (1253.6 eV) X-ray resource. The take-off angles were 45°. The sample size used was 10×10 mm. The whole spectra (0~1100eV) and the narrow spectra of all the elements with much high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. C 1s of hydrocarbon was taken at 285.0 eV as an internal reference. The spectrometer was typically run about 5×10-8 Pa vacuum.

Contact angle measurement: Contact angles were measured with an OCA 20 Contact Angle System (Dataphysics. Instruments GmbH, Germany). The contact angle of film was measured with water at room temperature. The results were the mean value of five replicates.

X-ray diffraction (XRD): XRD patterns were recorded on a Rigaku D/Max 2000 powder diffractometer equipped with Cu Ka radiation (40 kV, 20 mA) at the rate of 5°/min over the range of 2-50° (2θ).

Results and discussions

In this study, the mixing soft segments of both PBA and PDMS were reacted with MDI with the molar ratio of NCO/ (OH +NH_2) = 2 to prepare the isocyanate terminated PUSR prepolymer, which further reacted with end-capping agents (γ-APS/AMS) to form alkoxysilane functionalized PUSR. This alkoxysilane functionalized PUSR could form tridimensional crossing-linking networks under appropriate moisture and catalyst by the hydrolysis and condensation of ethoxy groups in end-capping agents. During the moisture curing process, only ethanol and water would be produced, which are friendly to the environment.

Structure Analysis

FT-IR is a convenient instrument to trace the reaction of isocyanate for polyurethane preparation [19]. The FT-IR spectrum for alkoxysilane-terminated PUSR prepolymer represented by PUSR-50 was shown in Figure 1. The characteristic peak at 2260 cm^{-1} (NCO group stretching) was not observed while the peak at 955 cm^{-1} ($Si\text{-}OCH_2CH_3$ stretching) was clearly noticed, indicating that the NCO groups were completely reacted with amine groups. From the absorption peaks at 3320 cm^{-1} (NH stretching), 1730 cm^{-1} (C=O stretching in urethane) and 1640.0 cm^{-1} (H-bonded urea carbonyl group), the formation of both urea and urethane linkage were confirmed. The band at 1530 cm^{-1} was assigned to C-N-H bending [20]. The peaks at 1223 cm^{-1} (CH_3 bending), 1078 cm^{-1} (Si-O-Si stretching) and 785 cm^{-1} (CH_3 rocking) were attributed to the polysiloxane in the copolymer, suggesting the incorporation of polysiloxane into the polyurethane [21].

The alkoxysilane functionalized copolymer was cured under 25°C and 50% R.H. for two weeks. The obtained PUSR films were characterized by ATR-FTIR. The spectrum represented by PUSR-50 was shown in Figure 2. The characteristic peak of $Si\text{-}OCH_2CH_3$ at 955 cm^{-1} was disappeared, which confirmed the moisture curing of

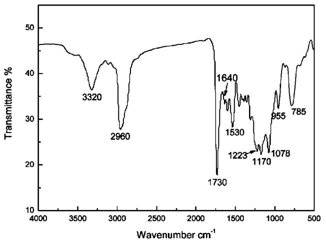


Figure 1 FT-IR spectrum of PUSR-50 prepolymer

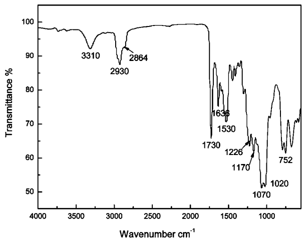


Figure 2 ATR-FTIR spectrum of PUSR-50 film surface

PUSR copolymer was completed. The intensity of peaks at 1070 and 1020 cm^{-1} (Si-O-Si stretching) increased, indicating more Si-O-Si incorporated in the polymer. These changes were resulted from the hydrolysis and condensation of alkoxysilane in the curing process. The band of NH stretching shifted from 3320 cm^{-1} to 3310 cm^{-1}. The band intensity of H-bonded urea carbonyl group increased and the frequency shifted somewhat to the lower wavenumber (1636 cm^{-1}). The assignments of other bands were similar with those in Figure 1. Both the frequency shifts and intensities changes are characteristic of specificity or magnitude of hydrogen bonds [8, 22-23]. The IR band of free N-H stretching is around 3450 cm^{-1} [8]. In Figure 2, the absence of free NH stretching vibration showed hydrogen bonds formed in PUSR copolymers. Comparing with the PUSR prepolymer (Figure 1), both the frequency shifting to lower wavenumber (N-H) and intensity increase of H-bonded urea carbonyl group indicated that the intensity of hydrogen bonds in cured PUSR increased.

TGA Analysis

The thermal stability of PU was commonly characterized by TGA [24]. The TGA and differential thermogravimetric (DTG) curves of alkoxysilane functionalized PUSR were shown in Figure 3 and 4, respectively. The TGA data were shown in Table 2. The results showed that the decomposition of alkoxysilane functionalized PUSR took place in two stages. The first stage started in the hard segments degradation from 250 to 400°C. The second stage was from the soft segment degradation over 400°C. Generally, the temperatures at maximum decomposition rate (T_{max}) of polymers could present polymer thermal stability. In Figure 4, the T_{max} of PUSR (over 370°C) in the first decomposition stage increased over 45°C in contrast to PU (325°C), indicating that the thermal stability of PUSR was greatly improved. The different T_{max} in the first stage can be attributed to the structure change in the hard segment. The hydrolysis and condensation of alkoxysilane would form cross-linking networks (Si-O-Si) which possess excellent thermal stability [10, 16]. Therefore, both Si-O-Si cross-linking networks and carbamate (–NH-CO-) in hard segments of PUSR could greatly improve the thermal stability of the copolymer. The initial decomposition temperature of PUSR-50 was 366°C (T at 10% weight loss) and much higher than that of PU (320°C), which also suggested its thermal stability was greatly enhanced compared with PU. As discussed above, the decomposition of the polymers in the second stage was governed by the soft segment degradation. The T_{max} data showed the same results because of the incorporation of PDMS with a good thermal stability in the soft segments.

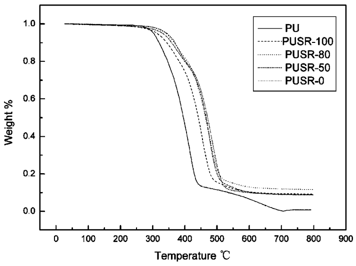


Figure 3 TGA curves of alkoxysilane functionalized PUSR

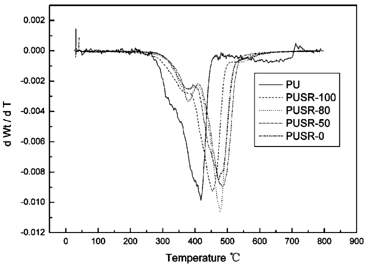


Figure 4 DTG curves of alkoxysilane functionalized PUSR

Table 2 TGA data of alkoxysilane functionalized PUSR

Sample	T (5%) °C	T (10%) °C	T(max) °C	Grayish char %
PU	308	320	325, 417	0.48
PUSR-100	313	344	370, 453	9.25
PUSR-80	331	359	376, 477	8.79
PUSR-50	341	366	378, 473	11.65
PUSR-0	343	369	376, 484	8.94

T (5%), temperature at 5 wt % decomposition of the polymer; T (10%), temperature at 10 wt % decomposition of the polymer; T (max), temperature at maximum decomposition rate of the polymer.

In the PUSR copolymers, the different ratio of end-capping agents also had a great influence on the thermal properties. When the content of AMS varied from 0 to 100, the initial decomposition temperature increased from 313°C to 343°C. Since AMS contained an aromatic group (phenyl), while only aliphatic chain was in γ-APS . With the increasing of AMS in end-capping agents, more aromatic structure was incorporated in the PUSR, thus the thermal stability was improved.

In all cases, the content of the grayish char formed at final temperature (800°C) was higher in PUSR than in PU. It would form silica in the process of organosilicon burning, which would gather the surface of the polymer as a result of protecting the inner organic network. Hence, the property of flame retarding was probably improved by introducing silicon chains in the polymer.

Contact angle analysis

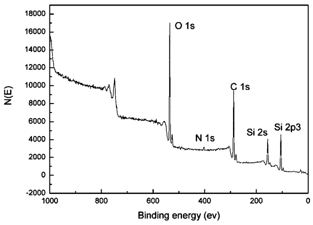
The surface-water-air contact angle measurements are surface-sensitive, and possibly respond to the outermost monolayer of the surface [25]. The water contact angle data of samples were shown in Table 3. The results showed that the contact angles of PUSR were much larger than that of PU. The surface of PUSR was hydrophobic and lower surface polarity, while the surface of PU was hydrophilic. The surface in air would achieve the minimization of interfacial energy by low-energy chemical group's migration to the polymer-air interface [24]. In the PUSR copolymers, the siloxane units possess surface activity and would migrate to the surface of the films, resulting in interface energy decreasing and the contact angles increasing. The contact angles of PUSR approximately reached that of the pure silicon rubber, which indicated the copolymers surface had been covered with non-polar siloxane chains. The contact angles of PUSR with different ratios of end-capping agents were no considerable change since there was the same concentration of PDMS in each PUSR copolymers.

Table 3 Water contact angles of alkoxysilane functionalized PUSR

Sample	γ-APS molar ratio (%)	Contact angle(°)
Pure PU	—	78.0
PUSR-0	0	102.2
PUSR-20	20	103.2
PUSR-30	30	102.5
PUSR-40	40	104.9
PUSR-50	50	106.6
PUSR-60	60	107.2
PUSR-80	80	103.0
PUSR-100	100	102.3
Silicon Rubber	—	105-108

XPS Analysis

The surface elemental composition was measured by XPS to confirm the siloxane chain migrating to the surface of PUSR film. Figure 5 showed the XPS spectrum of PUSR-50 recorded at 45° take-off angles. The elemental composition data determined by XPS for the air-surface of PUSR-50 was C: 49.61 O: 27.86 Si: 21.24 N: 1.39. The molar percent of Si in PUSR-50 was high and almost approached that of pure PDMS (Si: 21.5%), which confirmed that the polymer surface was covered with non-polar siloxane chains. It stemmed from the silico-organic groups with low surface energy, incompatibility with polyurethane and high chain flexibility, which allowed it's migrate to the surface in the formation of film [26]. This result was in good agreement with that from the contact angle analysis. On the other hand, the N concentration in surface was very low, indicating the hard segments of PUSR copolymer were hardly present in the surface.



Atomic molar percent: C: 49.61 O: 27.86 Si: 21.24 N: 1.39

Figure 5 XPS spectrum of air-contacting surface of PUSR-50

Mechanical properties

The tensile strength and elongation at break of alkoxysilane functionalized PUSR were shown in Figure 6. The PUSR with mixed end-capping agents exhibited better tensile strength than that with only γ-APS or AMS as the end-capping agent, and reached the maximum tensile strength at 50% γ-APS in the end-capping agent. The elongation at break of all the PUSR polymers was lower than 250%, and reached the largest with only AMS as the end-capping agent. With increase of γ-APS content, the elongation at break firstly decreased and then kept steadiness when γ-APS content was more than 50%. It is postulated that the mixed end-capping agents is more beneficial to improve the compatibility of the PDMS soft segment and the hard segment, thus strengthen the interactions of soft and hard segments.

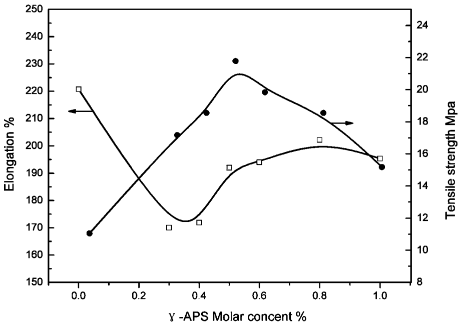


Figure 6 Tensile strength and elongation at break of alkoxysilane functionalized PUSR

The tensile strength and elongation at break of PU were 24 MPa and 593 % respectively. Compared with PU, the PUSR copolymers showed much lower elongation at break. It was mainly due to the higher cross-linking density in PUSR forming by the hydrolysis and condensation of alkoxysilane. The tensile strength of PUSR was slightly decreased due to the incorporation of PDMS, which mechanical properties was poor due to the lower intermolecular force. Moreover, the hydrogen bond between the hard and soft segment in PUSR copolymers would decrease because of the incorporation of PDMS and the forming of cross-linking structure [27]. It is known that the influence of micro-phase separation on the mechanical properties of PU is complicated and appropriate micro-phase separation leads to the enhancement of tensile properties, however, too high or too low micro-phase separation would reduce the strength of polymers. In this study, somewhat high micro-phase separation in PUSR copolymers (comparing with PU) probably decreased the tensile property.

DMTA analysis

Dynamic mechanical relaxation behaviors of PU and PUSR-50 materials were shown in Figure 7. The glass transition (T_g) was identified by a prominent peak in tan δ and a drop in storage modulus (E′) of two orders of magnitude [28]. The main transition in Figure 7 could be attributed to the glass transition of PBA in the soft segment. The T_g of PUSR-50 increased from -32.3°C (PU) to -18.8°C (PUSR-50) because of the higher cross-linking density. Meanwhile, The tan δ peak showed lower amplitude and was broadened, indicating the decrease of the polymer chain motion ability and the increase of phase separation in copolymer.

In PUSR copolymers, the T_g around -90.0°C was assigned to the glass transition of PDMS segment, which was at -123°C for pure PDMS. The T_g in PUSR-50 was greatly increased with the increasing of the macro-phase separation between hard and soft segments, resulting from the great different solubility parameter of PDMS and PU [29]. Therefore, complicated microstructure was formed in PUSR copolymers.

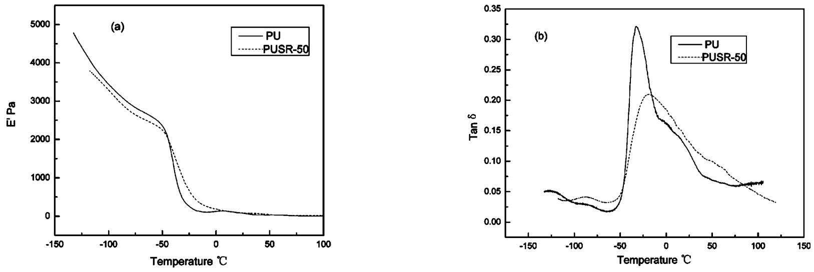


Figure 7 DMTA thermal transitions of (a) E′ and (b) tan δ versus temperature of PU and PUSR-50

In Figure 7 (a), there was no obvious difference in storage modulus above the T_g for PU and PUSR-50, but the storage modulus (E′) of PU was higher than that of PUSR-50 below the T_g since PU had the higher crystallization.

XRD analysis

The X-ray diffraction spectra of PU and PUSR copolymers were shown in Figure 8. It was evident that the crystallinity of PU was larger than that of PUSR copolymers. The crystalline structure is probably due to the uniform chain alignment driven by the hydrogen bonding [11]. In PU, there are stronger hydrogen bond between hard-soft and hard-hard segments, which was beneficial to the crystal formation. While in PUSR copolymers, the hydrogen bond in PUSR would be decreased due to the incorporation of PDMS and the Si-O-Si cross-linking net, resulting in the crystallization was destroyed both in soft and hard domain. In PUSR copolymers, the peak at 2θ=24.2°, attributed to the crystallization of hard domain, was disappeared. This mainly resulted form the Si-O-Si cross-linking structure reducing the mobility of hard segments, thus destroyed the ordered arrangement. The intense peak at 2θ=22.3° assigned to the PBA crystallization in soft domain was obviously decreased in PUSR copolymers and another peak appeared at 2θ=21.7°, which was probably the different crystallite size or crystal perfection of PBA in soft segments.

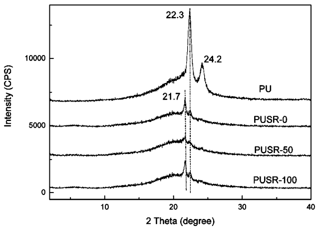


Figure 8 X-ray diffraction spectra for PU and PUSR copolymers

Conclusions

Alkoxysilane functionalized PUSR copolymers were successfully prepared based on amine terminated polysiloxane, poly-1, 4-butylene adipate glycol, MDI and alkoxysilane in a two-step way. Compared with conventional PU, the thermal stability of PUSR copolymers was greatly improved. As for the initial decomposition temperature, it was increased over 30°C. The surface of PUSR copolymers showed hydrophobicity, moreover, it was coved with non-polar siloxane chains. However, the tensile strength of PUSR copolymers was not significantly declined. DMTA and XRD analysis showed the complicated micro-phase separation formed in PUSR copolymers, while the crystallization was somewhat destroyed.

The component of end-capping agent greatly influenced the properties of PUSR materials. The thermal stability of PUSR was increased with the increasing of AMS content in end-capping agents. With a 50:50 molar ratio of γ-APS: AMS as the end-capping agent, the PUSR copolymer showed better comprehensive properties.

In the study, alkoxysilane functionalized PUSR with no free NCO group in prepolymer would be friendly to environment. Therefore, it is believed that such PUSR material would be hopeful for making novel moisture-curing sealants, coatings and adhesives for some special purposes.

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