

Moisture-Cured Polyurethane/Polysiloxane Copolymers: Effects of the Structure of Polyester Diol and NCO/OH Ratio

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ABSTRACT: Moisture-cured polyurethane is one of the commercially important polymers, which is widely used in sealants, coatings, and reactive hot-melt adhesives. A series of moisture-cured polyurethane/polysiloxane (PUSR) copolymers were successfully prepared using a two-step solution polymerization procedure. Both amine-terminated polysiloxane (PDMS) and polyester diol were together used as mixed soft segments to react with 4,4'-diphenylmethane diisocyanate (MDI), and the alkoxy silane was used as end-capping agents. The effects of structure variation of building blocks such as the polyester diol structure and

NCO/OH ratio on the properties and morphology of PUSR copolymers were studied. The tensile properties, dielectric behavior, thermal stability, surface, and water-repellency properties were investigated. The results showed that the properties and morphology of PUSR copolymers were greatly affected by the variations in molecular architecture. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3644–3651, 2008

Key words: moisture-curing; polysiloxane; polyurethane; morphology; solvent polymerization

INTRODUCTION

The most desirable properties of polyurethane/polyurea (PU/PUR) are tailor made, and thus it easily prepared many different properties and microstructure PU/PUR through changing their molecular chain structure.¹ Particularly, PU/PUR is multiblock copolymers consisting of soft and hard segments. The soft segments are in a rubbery state leading to the flexibility and the elasticity, and the hard segments are in a crystalline state or an amorphous glassy state acting as fillers and physical crosslinks through hydrogen bonding. Moisture-cured PU/PUR shows good mechanical and weathering properties, especially because it is very convenient to use. Therefore, it is widely used in reactive hot-melt adhesives, sealant productions, and high-performance coatings.^{1–3} However, the conventional PU/PUR exhibits lower thermal stability and water resistance properties, which limit their applications in some fields.

Polydimethylsiloxane (PDMS) polymers have many interesting properties, which arise mainly from its natural structure composed of inorganic Si—O band and organic graft CH₃ group. The properties of PDMS include high thermal and oxidative stability,

good blood compatible properties, low surface energy, a wide service temperature range (T_g , -123°C), but poor mechanical properties and abrasion resistance.⁴ To combine the advantages of both polysiloxane and polyurethane, the preparation of PU and PDMS copolymer is very attractive. Recently, some researchers have given reports related to PU/PDMS copolymers. The results showed that PU/PDMS copolymers exhibited good gas separation,⁵ thermal stability,⁶ biocompatibility,⁷ surface hydrophobic,² and better mechanical property.⁸ However, these previous studies mainly concentrated on the thermoplastic polyether system and few comprehensive studies on moisture-cured PU/PDMS copolymers based on the polyester system.

In the preparation of PU/PDMS copolymer, the phase separation was the main problem due to the great difference in solubility parameters between the nonpolar PDMS and the highly polar urethane segments. To improve the compatibility and processability, polyether diol was often used to replace part of PDMS to become mixing soft segments.^{9,10} In addition, proper solvent was also important in successful synthesis of such copolymer.^{2,11,12} In this study, the crosslinking PU/PDMS copolymers were prepared using a moisture-curing technique. Both primary amino alkyl terminated dimethylsiloxane and polyester diol were used together as mixing soft segments, which reacted with 4,4'-diphenylmethane diisocyanate (MDI) in the mixing solvent of 1,4-

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dioxane and methylbenzene (volume ratio by 2 : 1). 3-Aminopropyl-triethoxysilane (γ -APS) and aniline-methyl-triethoxysilane (AMS) were used as the end-capping agents. The structure and property of PUSR copolymers were investigated by thermogravimetric (TGA), tensile testing, and contact angle analysis. The effects of the polyester diol structure and NCO/OH ratio on the properties and morphology of the copolymer were studied.

EXPERIMENTAL

Materials

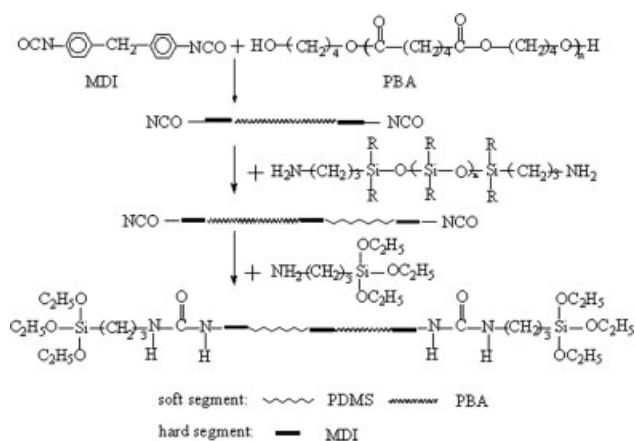
Amine-terminated polysiloxane (PDMS, BY16-853) was kindly provided by Dow-Corning and dried for 48 h under vacuum before use; 4,4'-diphenylmethane diisocyanate (MDI) was used as received; poly-1,4-butylene adipate glycol (PBA, M_n : 2000, 1000), polyethylene adipate glycol (PEA, M_n : 1500), and polyethylene-propylene adipate glycol (PEPA, M_n : 1865, 1500, 1200) were dehydrated at 120°C for 3 h under vacuum before polymerization. The 3-aminopropyl-triethoxysilane (γ -APS) and AMS were used as terminated agents. Dibutyltin dilaurate (DBTDL) as a catalyst were used without further purification. 1,4-Dioxane and methylbenzene were used as the mixing-solvent and dried before use.

Sample preparation

The polyurethane/polysiloxane (PUSR) copolymer was prepared via solution polymerization by a two-step reaction. The synthesis procedure was shown in Scheme 1. The soft segments in all samples were based on 10% PDMS and 90% polyester diol and the end-capping agents were based on the molar ratio of γ -APS/AMS with 1 : 1.

Step 1: Preparation of isocyanate-terminated PUSR prepolymer

To obtain isocyanate-terminated PUSR prepolymer, both the polyester diol and amine terminated polysiloxane were reacted with MDI with the molar ratio NCO/OH (NH_2) = 2. 40-g molten polyester diol was weighted into a three-necked round-bottom flask equipped with a mechanical stirrer, a dropping funnel and a nitrogen inlet. MDI (11.25 g) was quickly poured into the flask and reacted with the polyester diol at 90°C for 2.5 h under nitrogen. The reaction mixture was then cooled to ambient temperature (25–30°C) and a certain mixing solvent (1,4-dioxane/toluene, 2 : 1 V/V) was added to get a dilute solution (about 40 wt %). PDMS (4.4 g) was added dropwise to prevent a quick reaction and kept for another 1 h under ambient temperature. After the reactions, the



Scheme 1 Synthesis of the polyurethane/polysiloxane (PUSR) copolymer.

percent of free NCO in prepolymer was determined by standard di-*n*-butylamine back-titration method.¹³

Step 2: Preparation of alkoxy-silane-terminated PUSR prepolymer

Based on to the content of NCO in the PUSR prepolymer, the exact amount of alkoxy-silane was calculated with a stoichiometric ratio of NCO/ NH_2 (NH) = 1. The prepolymer was reacted with AMS at 60°C for 1 h and then reacted with 3-aminopropyl-triethoxysilane (γ -APS) at room temperature for 1 h. No free NCO left in the alkoxy-silane-terminated PUSR prepolymer was confirmed by FT-IR spectroscopy.

The PUSR copolymers with different NCO/OH ratios were synthesized on 90% PBA (M_n : 2000) and 10% PDMS, and the procedure of preparation was same as shown in Scheme 1.

The reaction product was degassed for 0.5 h and 0.1 wt % catalyst of DBTDL was added. It was then poured into a Teflon pan for curing. The moisture-curing process was conducted under fixed temperature and humidity conditions (25°C and 50% R.H.) for 2 weeks. The cured film was dried at 60°C for 48 h under vacuum to remove the solvents.

Characterization

Thermogravimetric analysis

The thermal stability of PUSR was 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

Dynamic mechanical analysis (DMTA) was carried out on a TA (Q 800) with the heating rate of 3°C/min and the frequency of 1 Hz. The operating tempera-

ture ranged from -120 to 100°C . For DMTA analysis, the specimens were $20 \times 10 \times 0.7\text{--}1.0$ mm.

Transmission electron microscopy

The PUSR films were ultramicrotomed by Reichert-Jung into about 80-nm thick sections. The electron microscopy was taken with JEM-1230EX instruments using an accelerating voltage of 80 kV.

Stress-strain measurement

Tensile properties of PUSR were carried out on an Instron 4465 Universal Tester at room temperature, with a crosshead speed of 500 mm/min. The specimens were $20 \times 4 \times 0.7\text{--}1$ mm.

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 under ambient temperature. The results were the mean value of five data.

Dielectric behavior analysis

The electrical volume resistances of PUSR films were measured by ZC-36 megger, Shanghai DiYi Electronic Instrument, China. The charge time is 60 s, and the voltage is 500 V. The dielectric measurements (dielectric permittivity ϵ , dielectric loss tangent $\tan \delta$) were performed with a Q-meter BS-3R (Shanghai, China).

Determination of water absorption

To evaluate the swelling behavior of the polymers in distilled water, the dried polymer films were cut into quadrate shape ($30 \text{ mm} \times 30 \text{ mm}$). The film was immersed in a beaker of water at 37°C . The weight of swollen polymers was measured by wiping off the surface water with filter paper. The water absorption (WS) of the film was calculated by the following equation¹⁴: $WS = [(W_t - W_d)/W_d] \times 100$.

While reaching swelling equilibrium, WS (%) approaches the saturated swelling. W_t and W_d are the weight of polymer swollen in water and dried polymer, respectively.

RESULTS AND DISCUSSION

Tensile properties

The tensile strength and elongation at break of PUSR copolymers with different soft segments were shown in Table I. The mechanical properties of PUSR copolymers were greatly different from the different kinds of the used polyester diols. In the order of PBA, PEA, and PEPA with similar molecular weight, the tensile strength decreased, but the elongation at break increased. It was possible that the degree of crystallization was different in the three polyester diols. PBA had the highest degree of crystallization because it was very easy to crystallize and resulting in the highest tensile strength of PUSR copolymers. PEPA had the lowest degree of crystallization due to the incorporation of propanediol and resulting in the poor tensile strength of PUSR copolymers. In addition, the different tensile properties were also related to the interaction between urethane hard segments with PDMS soft segments.¹⁰ In contrast with PEA and PEPA, PBA with higher hydrophobic was beneficial to better compatibility between high-polar PU hard segment and nonpolar PDMS and then to higher tensile strength.

With different molecular weight of the same polyester diol, the similar results were obtained from PBA and PEPA. The tensile strength of PUSR copolymers decreased, but the elongation at break increased with the increase of PBA or PEPA molecular weight. It was mainly due to the increase of chain flexibility or the decrease of crosslinking density in PUSR copolymers with the increase of the polyester diol chain length.¹⁵ On the other hand, the amount of hydrogen bonds in copolymers also had effect on the tensile properties. The amount of hydrogen bonds was dominated by the amount of urethane groups, which increased with the decrease of molecular weight of polyester diol in PUSR. More hydrogen bonds would improve the tensile strength,

TABLE I
Effects of Polyester Diol Structure on Tensile and Dielectric Properties of PUSR Copolymers

Sample	Tensile strength (MPa)	Elongation at break (%)	Dielectric constant (ϵ)	Dielectric loss ($\tan \delta$)	Resistivity ($\Omega \text{ cm}^{-1}$)
PBA-2000	11.10	178.77	3.81	0.0187	2.49×10^{13}
PBA-1000	16.14	91.04	2.43	0.0122	4.18×10^{14}
PEPA-1865	2.44	202.0	3.44	0.0364	6.64×10^{12}
PEPA-1500	2.77	188.7	3.02	0.0329	2.16×10^{13}
PEPA-1200	6.50	151.6	2.71	0.0275	5.38×10^{13}
PEA-1500	9.57	139.2	2.85	0.0230	5.75×10^{13}

but damage the elongation of the copolymer. In addition, the microphase separation also affected the mechanical properties, and only appropriate microphase is beneficial to higher mechanical properties. In this study, the degree of microphase separation was increased with the decrease of the polyester diol molecular weight (DMTA analysis). The somewhat high-microphase separation in PUSR copolymers probably decreased the tensile property.

The mechanical properties of PUSR copolymers are directly related to the amount of the hard segment domains, which are extensively hydrogen bonded with the neighboring chains and depend on the content of NCO groups.¹⁴ The tensile strength and elongation at break of PUSR copolymers with different NCO/OH ratios were shown in Table II. As the NCO/OH ratio increased, there was a reduction of the tensile strength and elongation at break, which was different from the conventional line polyurethane. With the increase of NCO/OH ratio, the free NCO groups in PU prepolymer increased, and more alkoxy silane as end-capping agents was incorporated in the polymer structure to get alkoxy silane-terminated PUSR prepolymer. Alkoxy silane content in the copolymer increased from 7.7% ($R = 1.4$) to 20.88% ($R = 2.4$). It is well known that organosilane has poor mechanical property, and therefore the tensile strength of PUSR copolymer would decrease with the increase of silane content. On the other hand, the crosslinking network was formed by the hydrolysis, and condensation reactions of alkoxy silane which reduce the mobility of the soft segments and block the crystallinity of the hard segments.¹⁶ In higher Si/PU ratio, the greater phase segregation was formed, resulting in the lower tensile strength of silicone-urethane.¹⁷ In this study, the increase of macrophase separation in PUSR copolymers was possible to reduce the tensile properties as the NCO/OH ratio increased (DMTA analysis). Therefore, both the tensile strength and elongation at break of PUSR copolymers decreased with the increase of NCO/OH ratio.

Dielectric properties

The dielectric properties of PUSR copolymers with different polyester diols were shown in Table I. The

dielectric permittivity (ϵ) and dielectric loss tangent value ($\tan \delta$) increased, and the volume resistivity decreased with the increase of PBA and PEPA chain length, which meant that the dielectric properties reduced. Higher hard segment content was in the PUSR copolymers based on lower molecular weight of polyester diol, corresponding to more urethane groups and siloxane crosslinking networks. Polar urethane groups would reduce the dielectric properties while nonpolar siloxane would enhance the dielectric properties. The effect of urethane groups was weaker than that of siloxane, because there were a large number of polar ester groups in the copolymer. The joint effect showed that the dielectric properties of PUSR copolymers were improved on lower molecular weight of polyester diol.

Comparing the dielectric properties of PUSR copolymers based on different polyester diols (with similar molecular weight), the values of dielectric permittivity and dielectric loss were similar while the volume resistivity was increased in the order: PEPA, PEA, and PBA. The volume resistivity of PUSR copolymers based on PBA exceeded $10^{13} \Omega \text{ cm}^{-1}$.

The dielectric properties of PUSR copolymers with different NCO/OH ratios were shown in Table II. With the increase of NCO/OH ratio, the values of dielectric permittivity and dielectric loss decreased, whereas the volume resistivity increased. Organosilicon possess good dielectric property because siloxane chain is with low polarity. As discussed in mechanical properties, more alkoxy silane was incorporated in the PUSR copolymers with the increasing NCO/OH ratio. Hence more siloxane chains from the hydrolysis and condensation of alkoxy silane were in the cured materials. The dielectric properties would improve with the increase of siloxane content.

TGA analysis

Thermal decomposition of PUSR copolymers was investigated by TGA. The TGA curves and data of PUSR copolymers with different polyester diols were shown in Figure 1 and Table III, respectively. The thermal decomposition of PUSR copolymers included two steps, and it was similar with that of poly-

TABLE II
Effects of NCO/OH Ratio on Tensile and Dielectric Properties of PUSR Copolymers

Ratio (NCO/OH) ^a	Alkoxy silane content (%)	Tensile strength (MPa)	Elongation at break (%)	Dielectric constant (ϵ)	Dielectric loss ($\tan \delta$)	Resistivity ($\Omega \text{ cm}^{-1}$)
1.4	7.70	18.59	424.20	3.97	0.0438	9.93×10^{11}
1.6	10.91	17.77	312.37	3.78	0.0421	2.19×10^{12}
1.8	13.31	15.40	217.22	3.81	0.0386	5.12×10^{12}
2.0	16.39	11.10	178.77	3.43	0.0351	2.49×10^{13}
2.4	20.88	5.40	151.03	3.25	0.0187	8.19×10^{13}

^aThe polyester diol was PBA (2000).

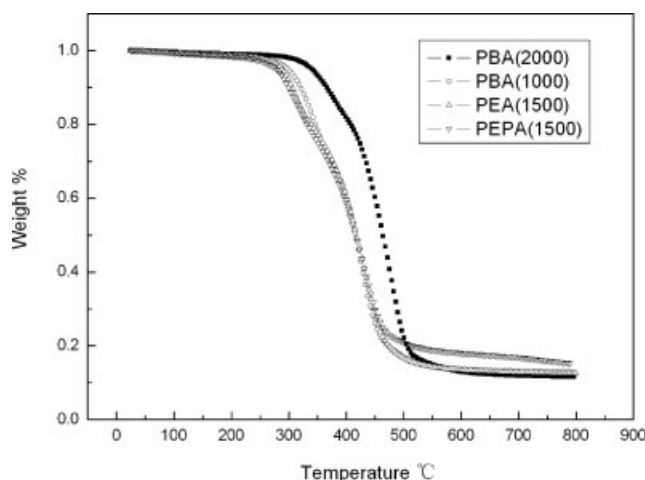


Figure 1 TGA curves of PUSR copolymers with different polyester diols.

urethane.⁶ In the thermal decomposition, the first step started in the hard segments in the range of 250–400°C, and the second step did in the soft segments beyond 400°C. The T_{\max} of PUSR copolymers was higher when PBA or PEA was used as the soft segments than that when PEPA was used as the soft segments. The reason was higher degree of crystal in PBA and PEA than that in PEPA. In all PUSR copolymers, PBA serials copolymers exhibited the best thermal stability. Moreover, the thermal stability of PUSR was enhanced with the increase of the PBA molecular weight. The grayish char contents increased with the decrease of PBA or PEPA molecular weight due to more siloxane incorporated in the PUSR copolymers.

The TGA curves of PUSR copolymers with different NCO/OH ratios were similar with Figure 1, and the data were shown in Table IV. As shown in Table IV, the thermal stability of PUSR copolymers slightly increased with the increase of NCO/OH ratio. The Si—O bond has a high-bonding energy and very low-bond rotation energy; therefore, siloxane polymer possesses good thermal stability.^{18,19} Ther-

TABLE III
TGA Data of PUSR Copolymers with Different Polyester Diols

Sample	T (10%) (°C) ^a	T (50%) (°C) ^a	T_{\max} (°C) ^a	Grayish char %
PBA-2000	346.2	444.5	358.4, 453.1	11.65
PBA-1000	320.8	417.0	344.9, 426.8	12.84
PEA-1500	305.9	417.8	316.4, 436.3	12.59
PEPA-1200	310.4	402.5	313.9, 413.7	16.84
PEPA-1500	299.2	416.0	315.9, 426.8	15.25
PEPA-1865	304.1	406.0	312.1, 406.3	11.08

^a T (10%) (°C), T (50%) (°C), and T_{\max} (°C) refer to the temperature at 10 wt %, at 50 wt %, and at maximum decomposition of the polymer, respectively.

TABLE IV
TGA Data of PUSR Copolymers with Different NCO/OH Ratios

Ratio (NCO/OH)	T (10%) (°C) ^a	T (50%) (°C) ^a	T_{\max} (°C) ^a	Grayish char (%)
1.4	319.5	409.0	343.1, 425.8	4.25
1.6	326.2	415.0	334.3, 429.0	5.35
1.8	330.4	415.0	340.9, 426.7	9.35
2.4	309.0	409.5	325.2, 422.3	9.45

^a T (10%) (°C), T (50%) (°C), and T_{\max} (°C) refer to the temperature at 10 wt %, at 50 wt %, and at maximum decomposition of the polymer, respectively.

mal stability was improved with the increase of NCO/OH ratio or the increase of siloxane chains and crosslinking density in the PUSR copolymers. However, the PUSR copolymer with RCO/OH = 2.4 showed lower thermal stability than the other PUSR copolymers. It probably resulted from the serious phase-separated structure in the copolymer for the excess siloxane. This would be discussed in DMTA analysis. The grayish char at 800°C increased with the increase of NCO/OH ratio, which may be due to the increase of silicate formed in the siloxane pyrolysis.¹¹

DMTA analysis

The DMTA curves of PUSR copolymers based on different molecular weight of PBA were shown in Figure 2. The glass transition (T_g) was identified by a prominent peak in loss factors ($\tan \delta$) and a drop in storage modulus (E') of two orders of magnitude. In Figure 2, the main transition was attributed to the glass transition of PBA in the soft segments. The T_g of PUSR copolymers was obviously increased from -23.8°C (PBA = 2000) to 18.3°C (PBA = 1000) because of the decrease of chain flexibility, but the increase of crosslinking density as PBA molecular weight

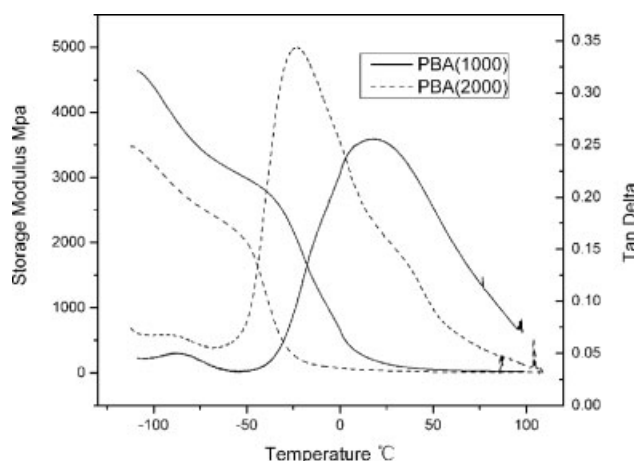


Figure 2 DMTA curves of PUSR copolymers based on different molecular weight PBA.

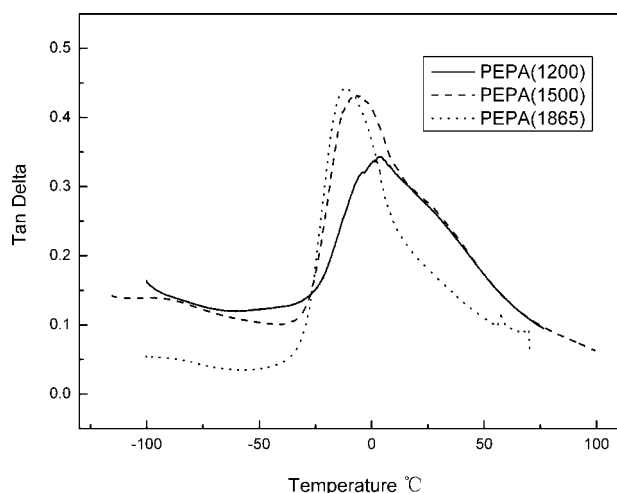


Figure 3 DMTA curves ($\tan \delta$) of PUSR copolymers based on different molecular weight PEPA.

increased. The minor transition peak near -100°C attributed to the T_g of PDMS also shifted to higher temperature with the decrease of PBA molecular weight. The intensity of $\tan \delta$ peak increased with the increase of PBA molecular weight, indicating that the motion of soft segment and the damping ability were improved. The peak of $\tan \delta$ in PUSR on PBA 1000 was obviously broadened, suggesting the increase of phase separation due to more nonpolar siloxane incorporated in the copolymer. Above the glass transition temperature (T_g), the storage modulus for PUSR copolymers had no obvious difference. However, below the T_g , the modulus was decreased with the increase of the molecular weight of PBA. This is due to the increased elastomeric character and the decreased degree of interchain hydrogen bonding.²⁰ This microphase structure of PUSR copolymers was in agreement with the different tensile and thermal properties based on different molecular weight of PBA.

The storage modulus (E') of PUSR copolymers based on different molecular weight PEPA was similar with that of PBA, and the loss factors ($\tan \delta$) curves were shown in Figure 3. As shown in Figure 3, the intensity of $\tan \delta$ peak increased with the increase of PEPA molecular weight, indicating that the motion of soft segment and the damping ability were also improved. Meanwhile, the maximum of $\tan \delta$ peak shifted to the lower temperature, showing that the T_g of PUSR copolymers decreased from 4.1°C to -11.7°C . This may be attributed to the decrease of the hydrogen bonding density and the increase of microphase separation.

The DMTA curves of PUSR copolymers with different NCO/OH ratios were shown in Figure 4. The storage modulus (E') [Fig. 4(a)] was not obviously changed, but the amplitude of the $\tan \delta$ peak [Fig. 4(b)] obviously decreased with the increase of NCO/

OH ratio, indicating that the motion of soft segment hindered and the damping ability decreased. The half-width of the $\tan \delta$ peak increased as the NCO/OH ratio increased. When the NCO/OH ratio was 2.4, the $\tan \delta$ peak sharply broadened, suggesting that the microphase separation in the copolymer was greatly increased. The increasing phase separation degree of PUSR copolymers would result in the decrease of tensile properties. The position of $\tan \delta$ slightly shifted to the higher temperature, which can be evidenced by the increasing T_g of PUSR copolymers from -28.5°C ($R = 1.4$) to -22.1°C ($R = 2.4$). This may be attributed to an increased crosslinking density caused by the hydrolysis and condensation of alkoxy silane in PUSR copolymers with the increase of NCO/OH ratio.

TEM analysis

Transmission electron microscopy was used to study the morphology of this PUSR copolymer. The PUSR sample was not necessary to stain because of the great difference in electron density between PDMS and PU segments. The representative TEM micro-

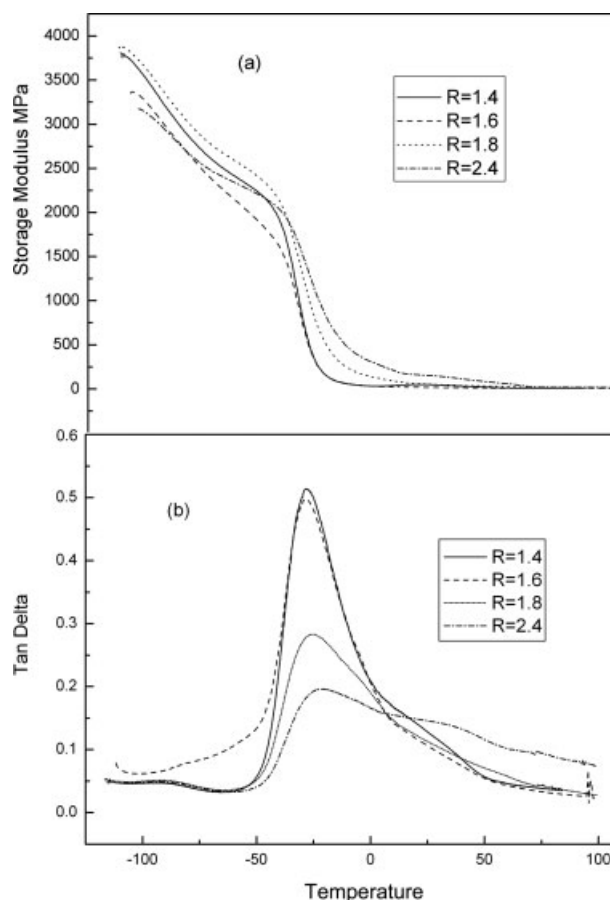


Figure 4 DMTA curves of PUSR copolymers with different NCO/OH ratios. (a) Storage modulus (E') and (b) $\tan \delta$.

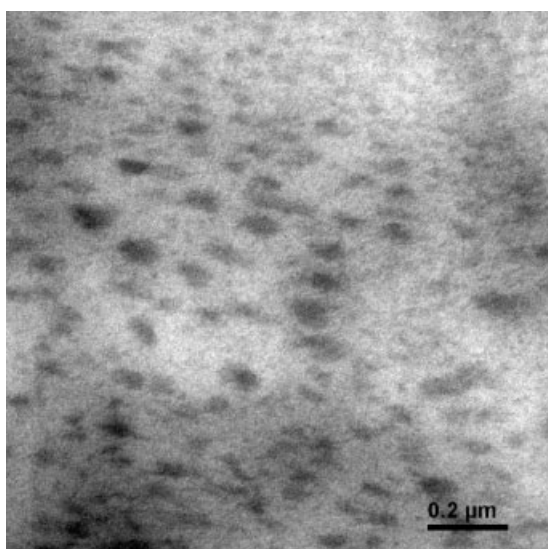


Figure 5 TEM micrograph of the PUSR copolymer.

graph of the PUSR copolymer (PBA = 2000, NCO/OH = 1.8) was shown in Figure 5. Because the thermodynamic incompatibility between the different chemical blocks prevents to form a homogeneous phase, the PU segment and PDMS soft segment cluster into separate domains. In Figure 5, the sample showed obvious two-phase structure. The continuous phase was PU segment, and the darker domain was PDMS segment with ~ 80 -nm size because PDMS with higher electron densities are more resistant to the transmittance of electrons than PU. Similar result was reported by Lee et al.⁵ about PDMS/polyether urethane urea membranes.

Contact angle analysis

Table V summarized the water contact angles of the air-contacting surfaces of PUSR copolymers with different polyester diols. In Table V, the contact angles of all PUSR copolymers were higher than 105° , which were equal to that of the pure PDMS.²¹ It indicated that the contact angles of PUSR films were independent with the polyester diol, and the hydrophobicity of film surfaces was mainly related to the PDMS content. Siloxane chain in PUSR copolymers was the

TABLE V
Effects of Polyester Diol Structure on Contact Angles and Water Absorption of PUSR Copolymers

Sample	Contact angles ($^\circ$)	Water absorption (%)
PBA-2000	106.3	1.00 ± 0.02
PBA-1000	105.7	1.73 ± 0.05
PEPA-1865	108.8	1.26 ± 0.02
PEPA-1500	106.9	1.63 ± 0.01
PEPA-1200	108.2	1.76 ± 0.02
PEA-1500	108.8	1.75 ± 0.03

only hydrophobic segment and would migrate to the surface due to its surface activity. In all the PUSR copolymers, the contents of PDMS were the same. Therefore, similar contact angles were observed on the surface of PUSR copolymers, and a pure PDMS layer covered on the top of the air-contacting surface. The similar results were reported by Ma et al.¹⁸

The contact angles of PUSR copolymers with different NCO/OH ratios were shown in Table VI. The contact angles slightly increased with the increase of the NCO/OH ratio. The surface contact angle measurement is more surface sensitive, probably responding to the outermost monolayer of the surface.²² The contact angles increase with the increase of the NCO/OH ratio, which may be due to more alkoxy-silane incorporated in the copolymers. Siloxane chain with surface activity would accumulate on the surface resulting in the decreasing interfacial energy and increasing the contact angles.

Water absorption

The WS of PUSR copolymers with different polyester diols were shown in Table V. The aim for testing the WS of PUSR materials at 37°C was to imitate the rational body temperature of the healthy human being. In Table V, the PUSR copolymers based on relatively low-molecular weight of PBA and PEPA absorbed more water. The WS increased with the decrease of the polyester DMTA. The reason was more hydrophilic PU hard segments (urethane groups) or less siloxane chain in the copolymer structure when the lower molecular weight of polyester diol as soft segments. With similar molecular weight polyester diol, the WSs of PUSR copolymers were almost the same. It was indicated that the WS of PUSR copolymers was mainly related with the siloxane chain content, while it was slightly affected by the structure of the polyester diol.

The WS of PUSR copolymers with different NCO/OH ratios was shown in Table VI. The results showed that the PUSR copolymers were with much lower WS than PU. The reason was that siloxane chain in PUSR had surface activity and was prone to

TABLE VI
Effects of Different NCO/OH Ratios on Contact Angles and Water Absorptions of PUSR Copolymers

R (NCO/OH) ^a	Alkoxy-silane content (%)	Contact angles ($^\circ$)	Water absorption (%)
1.4	7.70	101.7	1.07 ± 0.01
1.6	10.91	104.2	0.96 ± 0.03
1.8	13.31	106.1	0.86 ± 0.06
2.0	16.39	106.3	1.00 ± 0.02
2.4	20.88	106.4	1.12 ± 0.03
PU	–	75–78	1.80 ± 0.01

^aThe polyester diol was PBA (2000).

migrate to the surface, thus it became a barrier to prevent the water molecular getting into the bulk.¹⁸ In Table VI, the WS of PUSR copolymers decreased with the increase of NCO/OH ratio because of the increase of hydrophobic siloxane content. However, the NCO/OH ratio increased further, the WS increased instead. This may result from the increase of phase separation in PUSR copolymers, as described in DMTA analysis.

CONCLUSIONS

A series of PUSR copolymers were successfully prepared based on amine-terminated polysiloxane, polyester diol, MDI, and alkoxy silane as the end-capping agent in a two-step way. The effects of polyester diol structure and NCO/OH ratios on the properties and morphology of PUSR copolymers were investigated. The results showed that the properties and morphology of the copolymers strongly depended on polyester diol structure. In the three polyester diols PBA, PEA, and PEPA, PUSR copolymer based on PBA showed better comprehensive properties. With the increase of polyester molecular weight, the thermal stability and water repellency of PUSR copolymers enhanced, but the dielectric properties and tensile strength decreased. The NCO/OH ratio significantly affected the properties and morphology of PUSR copolymers because of the different crosslinking density and siloxane content in copolymers. DMTA analysis indicated that microphase-separated structure formed in the PUSR copolymers, and TEM analysis confirmed this result. The thermal and mechanical behaviors were correlated with their phase-separated morphology. Therefore, polyurethane/polysilane copolymers with different properties

could be achieved by controlling the different molecular structure.

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