

Synthesis and Properties of Polyurethane Modified with Aminoethylaminopropyl Poly(dimethyl siloxane)

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ABSTRACT: A series of polyurethanes with different siloxane contents were synthesized, which were based on 4,4'-methylene diphenyl diisocyanate (MDI), poly(tetramethylene oxide) (PTMO), aminoethylaminopropyl poly(dimethyl siloxane) (AEAPS), and butanediol (BD). The chemical compositions, structures, and bulk and surface properties were investigated using an infrared surface quantitative analysis technique (FTIR-ATR), surface contact angle, electron spectroscopy for chemical analysis (ESCA), stress-strain analysis, and dynamic mechanical thermal analysis (DMTA). It was shown that siloxane concentration on the surface region of the elastomers was higher than that in the bulk for a resulting surface enrichment of the siloxane, and the tensile properties of these elastomers were not changed significantly with the AEAPS modification. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2552–2558, 1999

Key words: surface modification; amino siloxane; polyurethaneureas

INTRODUCTION

Polyurethane is a kind of important polymer material that has wide application as foams, elastomers, adhesives, and coatings.^{1–3} Because of its good tensile property, surface-modified polyurethanes are now used in medical devices and prostheses.^{4–6} Recently, the surface-modifying additives have been focused on siloxane. Poly(dimethyl siloxane) (PDMS) systems have several interesting properties including low T_g , low surface energy, biocompatibility, and high thermal and oxidative stability. Thus, appropriate functional oligomers should be good candidates for surface modification of polyurethane.

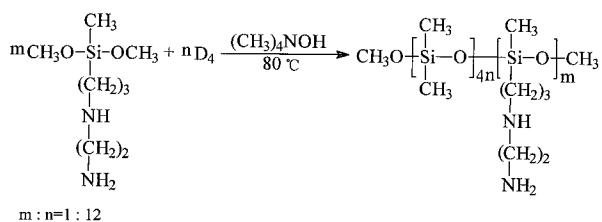
Multiphase segmented siloxane–urethane copolymers have been reported in the literature, which were prepared by primary or secondary amine-terminated siloxane oligomers with diisocyanates and diols.^{7–11} However, because of the

introduction of PDMS into the main chain of polyurethane, the surface-enrichment was restrained by the impediment of the main chain. So in order to meet the need of surface modification, a lot of PDMS must be introduced. Concomitantly, the tensile strength declined swiftly with the increase of the PDMS soft segment.

To overcome some of the limitation of the surface-modifying additives of amino-terminated PDMS, silicones with pendant diamino groups in the side chain are introduced into polyurethane. Because the siloxane chains now lie in the side chain of the polyurethane molecule, the mobility and the surface enrichment of the siloxane chains will be increased. Also, with the existence of a few diamino functional groups in several silicone molecules, the polyurethane chains will be partially branched. Consequently, the tensile strength will not decline as swiftly as that of the former modified products. Thus, only a small amount of silicone is needed to meet the modification. The complicated molecular structure of the modified polyurethane can be briefly seen as duckweed on the surface of the polyurethane.

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Scheme I AEAPS synthesis.

This article reports the synthesis of the polyurethaneurea copolymer containing aminoethylaminopropyl poly(dimethyl siloxane) (AEAPS) via solution polymerization in dimethyl acetamide (DMAc) and toluene, using diphenyl diisocyanate (MDI), poly(tetramethylene oxide) (PTMO, as soft segment), 1,4-butanediol (BD, as chain extender), and a small amount of AEAPS (as the cochain extender because it can be seen as ethylenediamine monosubstituted by polysiloxane). The properties of these polyurethanes were studied by a variety of techniques.

EXPERIMENTAL

Material

Aminoethylaminopropyl-methyl-dimethoxy siloxane was supplied by Witco and used without purification. Octamethylcyclotetrasiloxane (D₄) was distilled before use and dried over 4-Å molecular sieves. MDI was vacuum distilled before use. BD and DMAc were dehydrated over calcium hydride for 2 days and then stripped. PTMO (*M_n* = 1000) was supplied by Aldrich, and used as received; stannous laurate was used as received.

Synthesis

AEAPS used in this modification was synthesized according to refs. 12 and 13, with D₄ : aminoethylaminopropyl-methyl siloxane = 12 : 1 (Scheme I). The average amine content was 0.5 mmol/g siloxane, and the average MW was 3700.

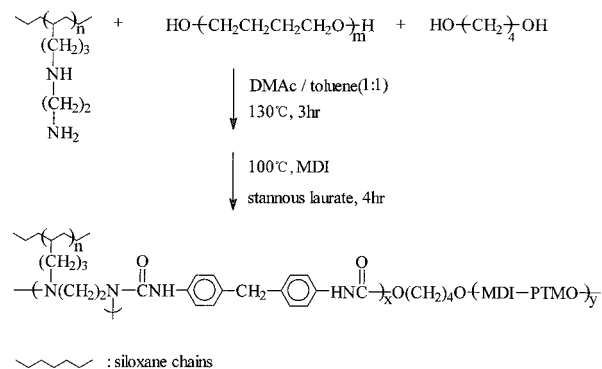
PTMO, BD, and AEAPS (0, 1, 3, or 6 wt %) were added to a four-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a thermometer and a trap. Then the DMAc/toluene (1 : 1) solvent was added into the flask to

form 20 wt % solution. The solution was heated to 130°C under reflux of toluene for 3 h to remove trace water present in the solution. The solution was then cooled to 100°C and MDI was added to the solution, followed by 0.5 wt % of catalyst stannous laurate (Scheme II). The temperature was maintained for 4 h. The solution was then precipitated into methanol/water (1 : 1). The polymer was filtered and dried in a vacuum oven at 80°C for 24 h. Then the polymer was dissolved in DMAc to form film at 60°C for 24 h and then put into a vacuum oven at 75°C for 24 h.

Characterization

Transmission infrared spectroscopy (TX-FTIR) was performed on films cast onto NaCl salt plates from a 5 wt % DMAc solution. The films were thoroughly dried under vacuum at 60°C for at least 48 h before transmission spectra were collected at 4-cm⁻¹ resolution using a Nicolet 170SX FTIR spectrometer. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was performed on films that were formed in a Ploy(tetra-fluoroethylene) disc from a 5 wt % DMAc solution. The films were dried in air at 60°C for 24 h and then under vacuum at 60°C for 24 h.

The water contact angles were measured using a Rame-Hart NRL contact angle goniometer. The surface was equilibrated with double-distilled water for 24 h before the collection of the surface-water-air static captive bubble contact angles. The data was collected after 1 min as one drop of double-distilled water was added on the surface of the films used for ATR-FTIR analysis. A minimum of three measurements were used to calculate the average contact angle.



Scheme II Synthesis of AEAPS-modified polyurethanes.

The electron spectroscopy for chemical analysis (ESCA) spectra were obtained using a V.G. Scientific ESCALAB MK-II spectrometer equipped with a monochromatic $\text{AlK}\alpha$ X-ray source. ESCA analysis was done at a nominal photoelectron take-off angle of 45° , and the depth of analysis for these samples was ≈ 100 Å. The relative atomic percent of each element at the surface was estimated from the peak areas using atomic sensitivity factors specified for the V.G. ESCALAB MK-II. All the binding energies (BEs) used for analysis were C_{1s} : 285 eV; Si_{2p} : 103 eV; N_{1s} : 400 eV; O_{1s} : 533 eV.

The Young's modulus, tensile strength, and ultimate elongation were determined on a table model Instron testing machine. The samples were stamped out of solution cast films (0.4 ± 0.05 mm) using an ASTM 1708 standard die, dried under vacuum for a minimum of 48 h before testing. The samples with gauge length of 1 cm were tested at room temperature using a crosshead speed of 5 cm/min.

Dynamic mechanical thermal analysis (DMTA) of the polymers was obtained at 110 Hz, using a microprocessor-controlled Rheovibron DDV-II. Solution-cast films were cooled to -150°C and then heated at a rate of $2^\circ/\text{min}$ until the samples became too compliant to test.

RESULTS AND DISCUSSION

Polymer Synthesis

Only a small amount of AEAPS was used for this modification based on the following consideration. Because of the higher activity of hydrogen in diamino groups than that in the hydroxyl group, diamino groups would react first with diisocyanates. Although the crosslinking activity of ethylenediamino declined significantly after the monosubstitution of polysiloxane, it still could be used to crosslink with the three remaining activate hydrogen. Simultaneously, the number of the diamino groups was not only one (average number) in every siloxane chain; a few siloxane chains might have two or more diamino groups. Consequently, if much AEAPS was used, crosslinkage would result. From the perspective of reaction kinetics, the reaction rate was directly proportional to the reactant concentration. The reaction rate of the diamino group was slower than that of the hydroxyl group, because the concentration of a small

amount of the diamino group was significantly lower than that of the hydroxyl group. In the process of the reaction, AEAPS could still be seen as a chain extender, and the possibility of crosslinking was thus lowered to the minimum. Due to the good surface enrichment capacity of the siloxane chains in the branches of the polyurethane, only a small amount of AEAPS could reach the target of surface modification. After the synthesis, the copolymer could be dissolved with DMAc. This meant that the product had not crosslinked to a large extent. A series of analysis also showed that the addition of a small amount of AEAPS could give good surface modification.

In the synthesis of the AEAPS-containing polyurethane, solvent selection is very important. This is mainly due to the large difference between the solubility parameter of nonpolar AEAPS and the high polar urethane segment, which may result in macrophase separation during polymerization.^{13–15} The solvent system, DMAc/toluene (1:1) was found to be good for AEAPS-containing polyurethane synthesis in the sense that homogeneous solution was maintained throughout the polymerization process.

We failed to get ideal AEAPS-modified polyurethane via two-step polymerization. The gel would be formed as soon as AEAPS was added to the solution before the addition of BD. Because of the high activity of hydrogen in the amino group, AEAPS, after being added, would crosslink with the excess MDI to form a gel before AEAPS was dispersed to the solution. If AEAPS was added after the addition of BD, AEAPS would lie at both ends of the molecular chain as a terminated group. This would promote the macroscopic phase separation of AEAPS and polyurethane.

Infrared Spectroscopy

A typical FTIR-TX spectrum of AEAPS-modified polyurethane is shown in Figure 1. The absorption bands around 3320 cm^{-1} (urea N—H stretching) and 1630 cm^{-1} (H-bonded urea C=O) confirmed the formation of the urea linkage. The peaks at 3300 cm^{-1} (urethane N—H stretching), 1710 cm^{-1} (H-bonded urethane C=O), and 1110 cm^{-1} (C—O—C stretching) showed the formation of the urethane linkage. The peaks at 1260 cm^{-1} [CH_3 in Si— CH_3 (sym. bending)], 1080 cm^{-1} (Si—O—Si stretching), 803 cm^{-1} (CH_3 —Si rocking) showed the incorporation of AEAPS into the copolymer.

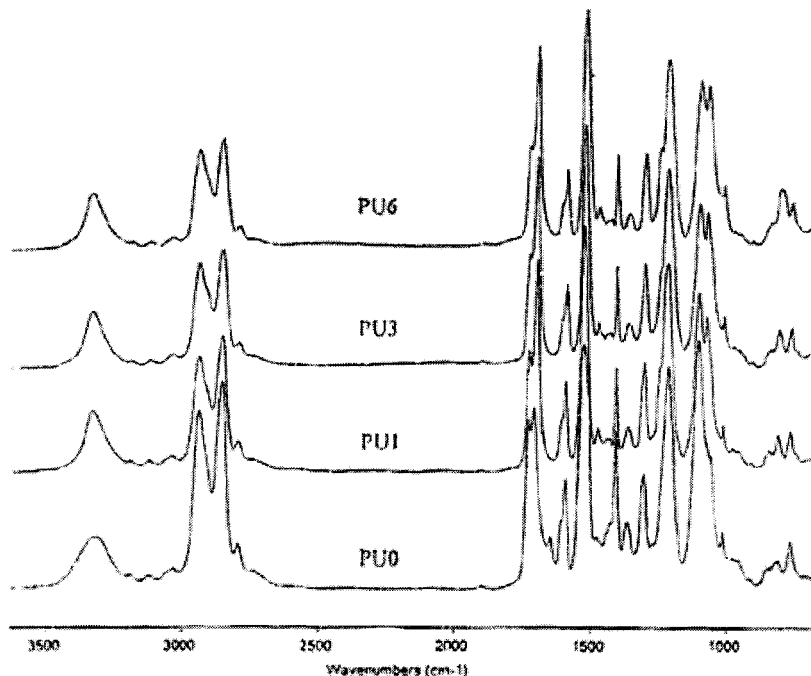


Figure 1 TX-FTIR spectra of AEAPS-modified polyurethanes.

Four typical FTIR-ART spectra of AEAPS-modified polyurethane is showed in Figure 2. With the increase of the AEAPS content in polyurethane, the intensity of the peaks of 1080 cm⁻¹

(Si—O—Si stretching), 1260 cm⁻¹ (CH₃ in Si—CH₃ (sym. bending) and 803 cm⁻¹ (CH₃—Si rocking) increased simultaneously. This means that the copolymer surface was covered with siloxane

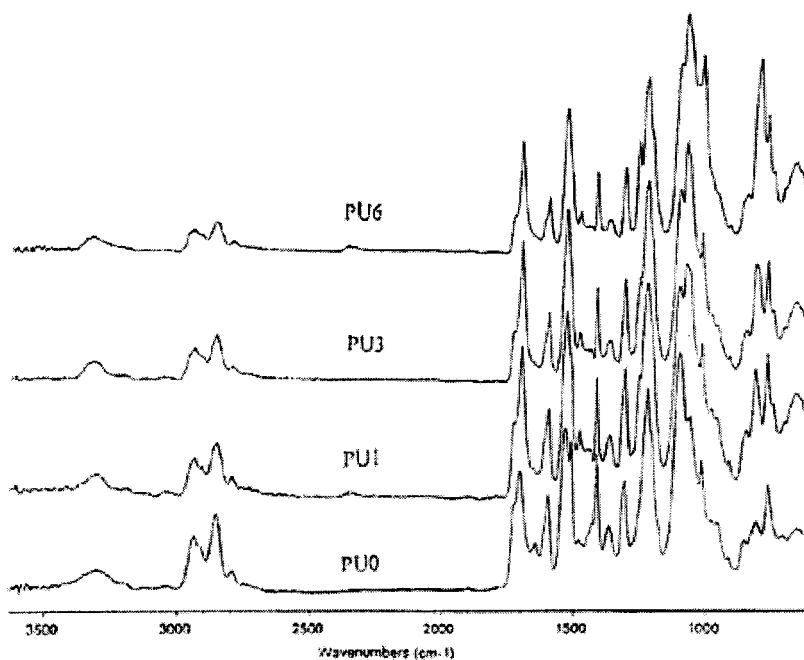


Figure 2 ART-FTIR spectra of AEAPS-modified polyurethanes.

Table I Water Contact Angles of AEAPS-Modified Polyurethanes

Material	AEAPS %	Water Contact Angle (Degree)
PU0	0	65 ± 2.1
PU1	1	94 ± 4.0
PU3	3	98 ± 3.3
PU6	6	101 ± 3.4
PDMS	—	105 ± 2.0

chains, and the content of the siloxane on the surface was increased with the increase of the amount of AEAPS additive.

Contact Angle Analysis

The surface–water–air contact angle measurements are more surface-sensitive, and probably respond to the outermost monolayer of the surface. The contact angle data is presented in Table I. The contact angle increased with increasing AEAPS content, indicating that the surface polarity decreased. Because the surface lay in air (a low-energy fluid), the minimization of interfacial energy was achieved by migration of low-energy chemical groups to the polymer–air interface. Just as expected, polymers modified with AEAPS, a hydrophobic compound, showed a swiftly increased water contact angle. This supported the notion that the siloxane chains have surface activity. When the AEAPS content was up to 3 wt %, the value of the contact angle approximately reached the maximum and near that of the pure PDMS film. This meant that the copolymers surface had been mostly covered with siloxane chains. Also, it showed that the use of a small amount of covalent bonded AEAPS was an effective way of modifying surface properties.

ESCA Analysis

The elemental composition data determined by ESCA for the surface of AEAPS-modified polyure-

thane is shown in Table II. ESCA is sensitive to chemical composition in the surface region including several monolayers (≈ 100 Å) below the actual surface layer. Nitrogen was only present in the backbone, while siloxane chains lay in the side chains. As polyurethane was modified with 1 wt % AEAPS, there were a depletion of nitrogen and an enrichment of silicon, indicating that siloxane chains, low-energy groups, migrated to the polymer–air interface, and nitrogen was restricted in the backbone (Table II). With the increase of the AEAPS content, the nitrogen atomic percent in the surface increased, which is contributed to the nitrogen on AEAPS, while the silicon atomic percent increased slightly and approached that of the pure PDMS film, indicating that the polymer surface was covered with nonpolar siloxane chains. When the data of AEAPS-modified polyurethanes were compared to that of polyurethane modified by amine-terminated siloxane oligomers,^{7–11} it is obvious that siloxane chains in the former much more effectively accumulated at the surface than that in the latter, indicating that the mobility to the surface of siloxane chains in side chains was significantly higher than that of siloxane chains in backbones.

Tensile Properties

The data of the Young's modulus, tensile strength, and ultimate elongation is shown in Table III and Figure 3. The Young's modulus and tensile strength of polyurethane increased slightly, but the ultimate elongation decreased after 1 wt % AEAPS modification. This was mostly due to the position of the siloxane chains, which lay in the side chain of polyurethane, not in the backbone. Because the siloxane chains very effectively accumulated on the polymer surface, a greater phase separation resulted, and the Young's modulus increased slightly. When 3 wt % AEAPS was added, the Young's modulus and tensile strength continuously increased, and ulti-

Table II Element Composition Data Measured from the Surface of AEAPS-Modified Polyurethanes

Material	Real Atomic Percent				Theoretical Atomic Percent			
	C	O	N	Si	C	O	N	Si
PU0	77.70	17.90	4.10	0.30	77.86	17.80	4.34	0
PU1	57.40	22.78	0.20	19.62	77.70	17.80	4.32	0.18
PU3	54.63	23.84	1.45	20.08	77.30	17.88	4.27	0.55
PU6	53.57	23.04	2.12	21.27	76.60	18.09	4.20	1.11

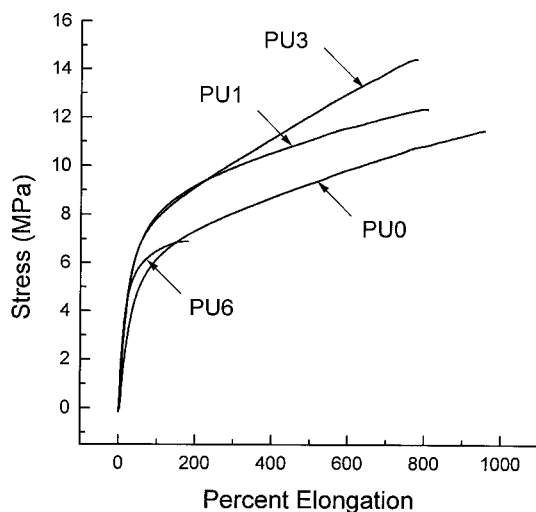
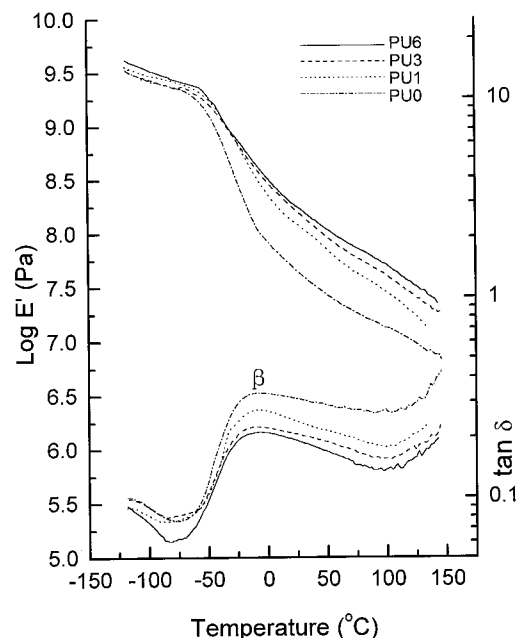
Table III Mechanical Properties

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Ult. Elongation (%)
PU0	17.28	11.23	964.6
PU1	22.23	12.32	806.4
PU3	26.07	14.07	777.3
PU6	31.64	6.92	180.1

mate elongation lowered. These effects could be attributed to the branching of polyurethane molecular chain due to more than one aminoethylaminopropyl group lying in several AEAPS molecular chains. When the content of AEAPS was up to 6 wt %, tensile strength and ultimate elongation decreased greatly, but the Young's modulus increased. The reason for this was that the partial crosslinkage among polyurethane molecular chains occurred with the increase of the diamino group content.

Dynamic Mechanical Thermal Analysis

The results of dynamic mechanical testing are shown in Figure 4. All polymers exhibit a well-developed rubbery plateau region that is characteristic of microphase-separated polyurethane block copolymers. The observed trends in modulus are consistent with those observed in stress-strain testing. The enhancement of modulus with


Figure 3 Stress-strain curves of all AEAPS-modified polyurethanes.

Figure 4 Dynamic mechanical testing results for AEAPS-modified polyurethanes.

AEAPS content was further verified by the increase in the rubbery plateau region with increasing AEAPS content. A possible explanation is that the crosslinkage among the molecules increased. In Fig. 4, peak β moved only slightly with the increase of the AEAPS content, showing that the modification with a small amount of AEAPS did not significantly damage the bulk properties.

CONCLUSION

Branched polyurethane-urea has been synthesized from pedant aminoethyl aminopropyl poly(dimethyl siloxane), PTMO, BD, and MDI. The structure of the copolymer was well characterized via various techniques. The use of a small amount of AEAPS is an effective way of modifying surface properties of polyurethane without dramatically damaging their bulk properties. So the introduction of siloxane chains into the branch of polyurethane will prove to be a useful technique in surface modifications.

REFERENCES

1. Woods, G. *The ICI Polyurethane Book*; New York: John Wiley & Sons, 1990, 2nd ed.

2. Noshay, A.; McGrath, J. E. *Block Copolymers: Overview and Critical Survey*; Academic Press: New York, 1997.
3. Oertel, G. Ed. *Polyurethane Handbook*; Hanser: New York, 1996, 2nd ed.
4. Ward, R. S.; White, K. A.; Hu, C. B. In *Polyurethanes In Biomedical Engineering*; Elsevier Science Publishers B.V.: Amsterdam, 1984.
5. Ward, R. S. *IEE Eng Med Biol Mag* 1989, 8, 2.
6. Okkema, A. Z.; Yu, X.-H.; Cooper, C. L. *Biomaterials* 1991, 12, 3.
7. Yilgor, I.; Wilkes, G. L.; McGrath, J. E. *Polym Prep* 1983, 24, 80.
8. Yilgor, I.; Eberle, J.; Shaaban, A. K.; Yilgor, E.; Steckle, W. P., Jr.; Tyagi, D.; Wilkes, G. L.; McGrath, J. E. *Polym Prep* 1983, 24, 167.
9. Yilgor, I.; Shaaban, A. K.; Steckle, W. P., Jr.; Tyagi, D.; Wilkes, G. L.; McGrath, J. E. *Polymer*, 1984, 25, 1800.
10. Wang, F.; Ji, Q.; McGrath, J. E. *Polym Prep* 1997, 38, 308.
11. White, K. A.; Ward, R. S.; Wolcott, C. A.; Wong, K. *Polym Prep* 1995, 36, 99.
12. Spinu, M.; McGrath, J. E. *J Polym Sci Part A Polym Chem* 1991, 29, 657.
13. Yu, X. H.; Nagarajan, M. R.; Grasel, T. G.; Gibson, P. E.; Cooper, S. L. *J Polym Sci Polym Phys Ed* 1985, 23, 2319.
14. Tyagi, D.; Yilgor, I.; McGrath, J. E.; Wilkes, G. L. *Polymer*, 1984, 25, 1807.
15. Yilgor, I.; McGrath, J. E. *Adv Polym Sci* 1988, 86, 1.