Mechanical and Surface Properties of Polysulfide-Based Polyurea Modified with Aminoethylaminopropyl Poly(dimethylsiloxane)

Yi Wu Quan,[1] Qing Jun Wang,[1] Jiang Ling Fang,[2] Qing Min Chen[1]

[1]*Department of Polymer Science & Engineering, Nanjing University, Nanjing 210093, People's Republic of China*
[2]*Center of Materials Analysis, Nanjing University, Nanjing 210093, People's Republic of China*

ABSTRACT: A series of polysulfide-based polyureas with different siloxane contents were synthesized, and they were based on isophorone diisocyanate, liquid polysulfide oligomer, aminoethylaminopropyl poly(dimethyl siloxane) (AEAPS), and 2,5-diamino-3,6-dimethylmercapto-toluene. The mechanical and surface properties were investigated with attenuated total reflectance Fourier transform infrared spectroscopy, surface contact angles, electron spectroscopy for chemical analysis, and stress–strain analysis. Siloxane was enriched on the surfaces of these elastomers, and the tensile properties of the elastomers did not change markedly with the AEAPS modification. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 584–588, 2003

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INTRODUCTION

Poly(dimethyl siloxane) (PDMS) systems have unique properties, such as low surface energy, low moisture permeability, biocompatibility, and high thermal and oxidative stability. The purpose of incorporating PDMS as part of a polyurethane (PU) structure is to impart such properties to PU. However, PDMS-based PUs exhibit inferior tensile strengths with respect to conventional PU.[1] Therefore, the desirable surface properties of PDMS are what should be imparted to PU, and that proper functionalization of PDMS will keep it at the PU surface and not adversely affect the mechanical properties.

Multiphase-segmented siloxane–urethane copolymers have been prepared by primary or secondary amine-terminated siloxane oligomers with diisocyanates and diols.[2–8] However, because of the introduction of PDMS into the main chain of PU, the surface enrichment was restrained by the impediment of the main chain. For the needs of surface modification, a lot of PDMS had to be introduced. Concomitantly, the tensile strength decreased swiftly with the increase in the PDMS soft segment.

In recent work, a poly(urethane urea) copolymer containing aminoethylaminopropyl poly(dimethyl siloxane) (AEAPS) was synthesized,[9] and amino-terminated PDMS with pedant diamino groups in the side chains was introduced into PU. Because the siloxane chains resided in the side chain of the PU molecule, the mobility and surface enrichment of the siloxane chains were increased significantly. Only a small amount of silicone was needed for the modification. Therefore, the tensile strength did not change markedly.

Liquid polysulfide oligomers cured with metal peroxides have a wide variety of applications in industry, particularly as sealants.[10,11] They exhibit excellent weatherability and good aging properties.[12] Liquid polysulfide oligomers also can react with isocyanates.[13]

This article reports the synthesis of polysulfide-based polyurea copolymers containing AEAPS via solution polymerization in dimethylacetamide (DMAc) and toluene, with isophorone diisocyanate (IPDI), liquid polysulfide oligomer, Ethacure-300 (as a chain extender), and a small amount of AEAPS (as a surface modification material). The properties of these polymers were studied with a variety of techniques.

EXPERIMENTAL

Materials

The AEAPS used in this modification was synthesized according to a procedure described previously[14,15] (the average amine content was 0.5 mmol/g of siloxane, and the number-average molecular weight was 3700). IPDI (supplied by Crendva Speziaichemie, Germany) was used without purification. Ethacure-300 (supplied by Albemarle Corp., United States) was
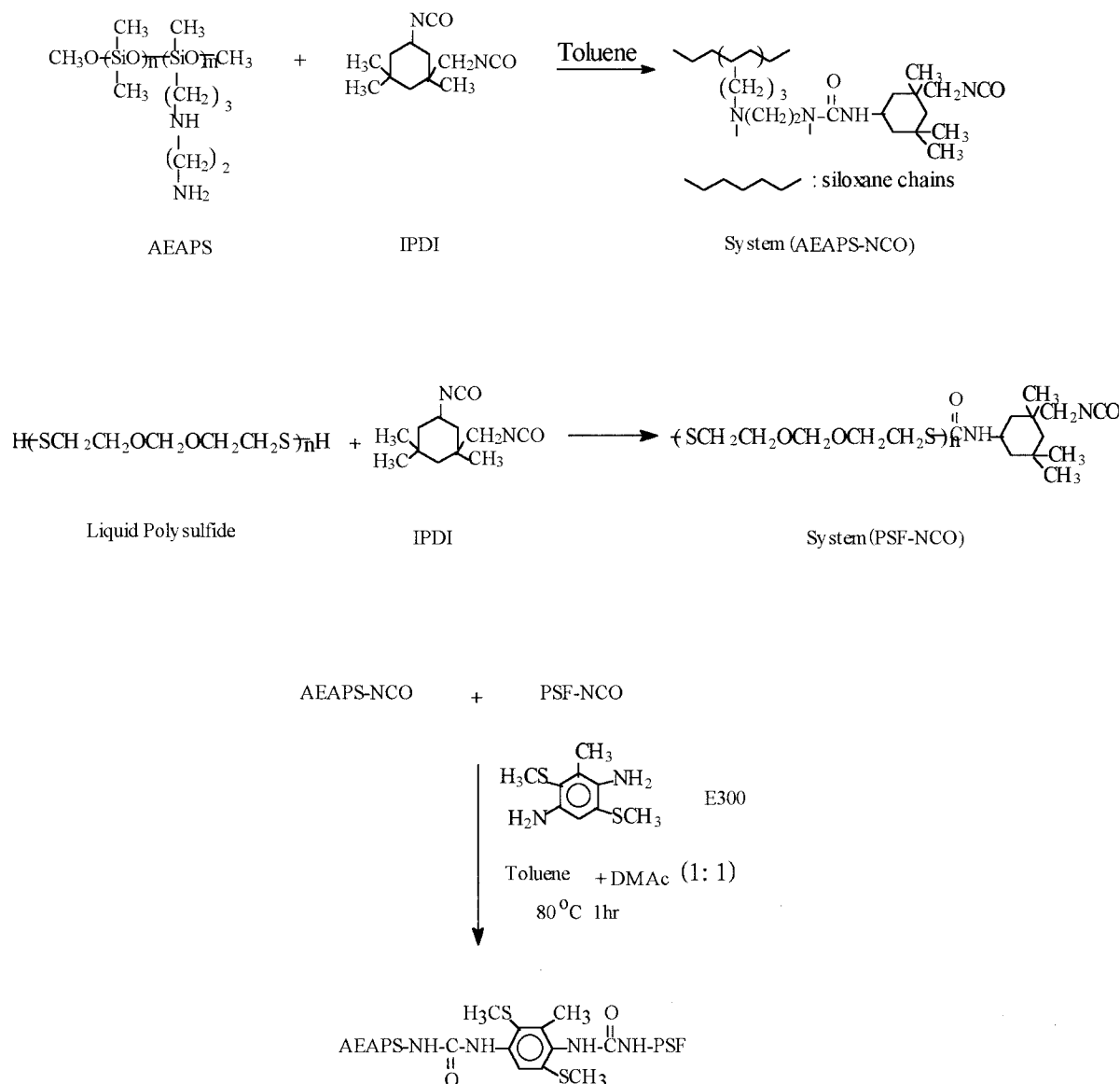
Scheme 1 Synthesis of AEAPS-modified polysulfide-based polyurea.

used without purification. A liquid polysulfide oligomer (SH = 6.2% and number-average molecular weight = 1000 ± 200; supplied by Jin Xi Research Institute of the Chemical Industry, China) was dewatered under vacuum at 100°C for 3 h before use. Toluene and DMAc were distilled before use.

Synthesis

First, the siloxane–urea-linked copolymer was synthesized in solution, with toluene as the solvent. A solution of AEAPS was added slowly to an IPDI solution with stirring at room temperature. The AEAPS–NCO system was reacted at least for 24 h at room temperature before use.

Second, the polysulfide–urea-linked copolymer was synthesized without a solution. The polysulfide and

IPDI were mixed. The PSF–NCO system was stirred at 80°C for 3 h.

In the synthesis of the polysulfide-based polyurea containing AEAPS (1, 3, or 6 wt %; see Scheme 1), AEAPS–NCO, PSF–NCO, and Ethacure-300 were mixed in solutions of toluene and DMAc (1:1 w/w) at 80°C for 1 h. Then, each system was cast onto a ploy(tetrafluoroethylene) disc. The films were dried at room temperature for 48 h and at 60°C for 24 h. All the films were dipped in toluene for 3 h and dried at 60°C for 24 h under vacuum before testing.

Characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed on films with a Nexus 870 FTIR instrument. The incident angle
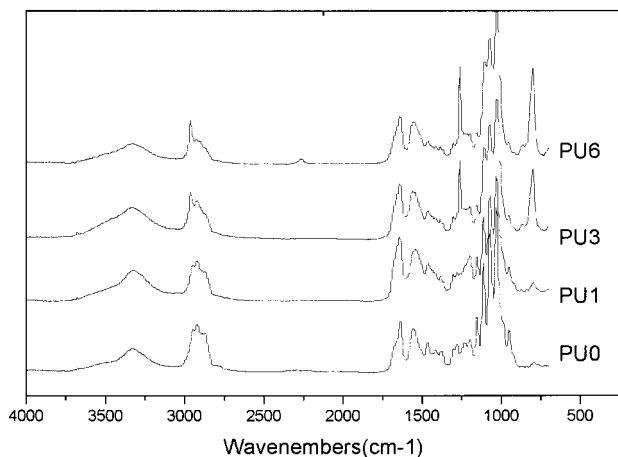
Figure 1 ATR-FTIR spectra of AEAPS-modified polysulfide-based polyureas.

was 60°, and the studied depth of the near-surface region was about 1 μm.

The contact angles were measured with a Rame–Hart NRL contact-angle goniometer. The data were collected after 1 min as one drop of double-distilled water or methylene iodide (CH_2I_2) was added to the surface of the films used for ATR-FTIR analysis. Only the surface formed at the air–solution interface was tested.

The electron spectroscopy for chemical analysis (ESCA) spectra were obtained with a V.G. Scientific Escalab MK-II spectrometer equipped with a monochromatic Al Kα X-ray source. ESCA was performed at a normal photoelectron take-off angle of 45°, and the depth of analysis for these samples was approximately 100 Å. The relative atom percentage of each element at the surface was estimated from the peak areas with atomic sensitivity factors specified for the V.G. Escalab MK-II. The binding energies used for the analysis were 285 eV for C_{1s}, 103 eV for Si_{2p}, 400 eV for N_{1s}, and 533 eV for O_{1s}.

The tensile strength and ultimate elongation were determined on an Instron 4466 testing machine. The samples were stamped out of solution-cast films (0.4 ± 0.05 mm) with an ASTM 1708 standard die. Samples with a gauge length of 1 cm were tested at room temperature at a crosshead speed of 5 cm/min.

RESULTS AND DISCUSSION

Infrared spectroscopy

Four typical ATR-FTIR spectra of AEAPS-modified polyureas are shown in Figure 1. The studied depth of the near-surface region was about 1 μm. With the increase in the AEAPS content in polyurea, the intensities of the peaks at 1260 (CH_3 in Si—CH_3 symmetric bending) and 803 cm^{-1} (CH_3—Si rocking) increased simultaneously. This meant that the near-surface re-

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

Contact angle and surface free energy

The surface–water–air contact-angle measurements were more surface-sensitive and probably responded to the outermost monolayer of the surface. Contact angles on both sides of the profile of a sessile drop were measured, and the results are listed in Table I. The water contact angle increased with increasing AEAPS content, indicating that the surface polarity decreased. Just as expected, polymers modified with AEAPS, a hydrophobic compound, showed increased water contact angles. When the AEAPS content was up to 6 wt %, the value of the contact angle was close to that of the pure PDMS film. This suggests that the low surface energy characteristics of PDMS promote migration to the air–polymer interface to form a predominately PDMS-enriched surface. Also, it shows that the use of a small amount of covalently bonded AEAPS is an effective way of modifying surface properties.

The solid surface free energy was calculated from the contact angle of two liquids, with a method suggested by Owens and Wendt[16] and Wynne and Ho.[17] Each contact-angle value reported in Table I is an average of at least 10 readings:

$$1 + \cos\theta = 2\sqrt{\gamma_s^d}\,(\sqrt{\gamma_l^d}/\gamma_l) + 2\sqrt{\gamma_s^h}\,(\sqrt{\gamma_l^h}/\gamma_l) \quad (1)$$

$$\gamma_l = \gamma_l^d + \gamma_l^h \quad (2)$$

$$\gamma_s = \gamma_s^d + \gamma_s^h \quad (3)$$

where γ_l is the surface free energy of the liquid, γ_s is the surface free energy of the solid, γ_l^d and γ_s^d denote the components due to dispersion forces, and γ_l^h and γ_s^h represent the components due to hydrogen bonding and dipole–dipole interactions. According to the literature,[16] the surface free energies of water and methylene iodide to be used in calculations are as follows: for water, $\gamma_l^d = 21.8$ erg/cm^2 and $\gamma_l^h = 51.0$

TABLE I
Contact Angles and Surface Free Energy of AEAPS-Modified Polysulfide-Based Polyureas

Material	θH_2O (°)	θH_2O (°)	θCH_2I_2 (°)	γ_s (erg/cm)
PU0	52 ± 3.0	52.4	41.5	51.9
PU1	88 ± 4.0	87.5	53.2	33.2
PU3	99 ± 3.0	98.6	69.2	23.6
PU6	102 ± 2.5	102.4	72.2	21.7
PDMS	105 ± 2.0			

TABLE II
Elemental Composition Data Measured from the Surface of AEAPS-Modified
Polysulfide-Based Polyureas

Material	Real atom percentage				Theoretical atom percentage			
	C	O	N	Si	C	O	N	Si
PU0	72.95	19.87	6.75	0.43	74.03	18.94	7.03	0
PU1	59.26	24.23	3.83	12.68	73.70	19.01	6.93	0.36
PU3	58.74	23.45	3.41	14.40	72.99	19.18	6.77	1.06
PU6	58.51	22.61	4.06	14.82	72.13	19.40	6.46	2.01

erg/cm^2, and for methylene iodide, $\gamma_s^d = 49.5$ erg/cm^2 and $\gamma_s^h = 1.3$ erg/cm^2.

The surface free energies of polysulfide-based polyureas modified with AEAPS are listed in Table I. With the addition of AEAPS, the surface free energy of the elastomer decreased rapidly. When the content of AEAPS was 6 wt %, the surface free energy of the elastomer was close to the literature value of 22 erg/cm^2 for PDMS,[16] indicating that the surface of the polymer was almost covered with PDMS. The result showed no difference from that revealed by the water-contact-angle test.

ESCA analysis

The elemental composition data determined by ESCA for the surface of AEAPS-modified PUs are shown in Table II. ESCA was sensitive to the chemical composition in the surface region. Generally, ESCA probed much less than 1% of the total thickness of the sample, and the depth of analysis for the sample was approximately 100 Å. Nitrogen was only present in the backbone, and siloxane chains lay in the side chains. As PU was modified with 1 wt % AEAPS, there was a depletion of nitrogen and an enrichment of silicon, and this indicated that siloxane chains, low-energy groups, migrated to the polymer–air interface and that nitrogen was restricted to the backbone. With the increase in the AEAPS content from 3 to 6 wt %, the content of siloxane increased slowly, indicating that the polymer surface was almost covered with nonpolar siloxane chains. This result was also confirmed with contact-angle and surface free energy tests.

TABLE III
Mechanical Properties of AEAPS-Modified
Polysulfide-Based Polyureas

Sample	Tensile strength (MPa)	Ultimate elongation (%)
PU0	18.1	113
PU1	17.1	100
PU3	17.0	100
PU6	16.6	96

Mechanical properties

The data for the tensile strength and ultimate elongation are shown in Table III. The tensile strength and ultimate elongation decreased slightly after AEAPS modification. This was mostly due to the position of siloxane chains, which lay in the side chain of PU, not in the backbone. The mobility and surface enrichment of the siloxane chains were increased. Because the siloxane chains very effectively accumulated on the polymer surface, phase separation had little influence on the material mechanical properties. When 6 wt % AEAPS was added, the surface of the material was modified, whereas the mechanical properties decreased slightly.

CONCLUSIONS

With AEAPS, the surfaces of polysulfide–polyurea-containing liquid polysulfides, IPDI, and Ethacure-300 were effectively modified. With the addition of PDMS, there was a 100% increase in the contact angle and a 50% reduction in the surface free energy. Because the siloxane chains resided in the side chain of the PU molecule and accumulated on the polymer surface, there was only an 8.3% reduction in the tensile strength and a 15% reduction in the ultimate elongation. The mechanical properties of the polysulfide–ureas were not negatively affected.

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