

Synthesis and Properties of Polyurethane Modified with an Aminoethylaminopropyl-Substituted Polydimethylsiloxane. II. Waterborne Polyurethanes

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ABSTRACT: A series of polyurethane (PU) emulsions modified with aminosilicone were synthesized, based on 2,4-toluene diisocyanate (TDI), poly(tetramethylene oxide) (PTMO), and dimethylolpropionic acid (DMPA) as a prepolymer which was chain-extended with aminoethylaminopropyl polydimethylsiloxane (AEAPS) in an aqueous emulsion. Their chemical compositions, structures, bulk and surface properties, and emulsion morphologies were investigated using Fourier transform infrared spectrum analysis (FTIR), tensile and surface contact angle measurements, electron spectroscopy for chemical analysis (ESCA), water swellability, an emulsion stability test, and transmission electron microscopy (TEM). It was shown that the PU emulsions were stable and the siloxane chains were enriched on the PU surface. The water resistance of the PU film increased but the bulk tensile properties of the PU film were not changed significantly with a small amount siloxane modification up to 6 wt %. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 295–301, 2001

Key words: aminoethylaminopropyl-substituted polydimethylsiloxane; waterborne polyurethane; prepolymer; emulsion

INTRODUCTION

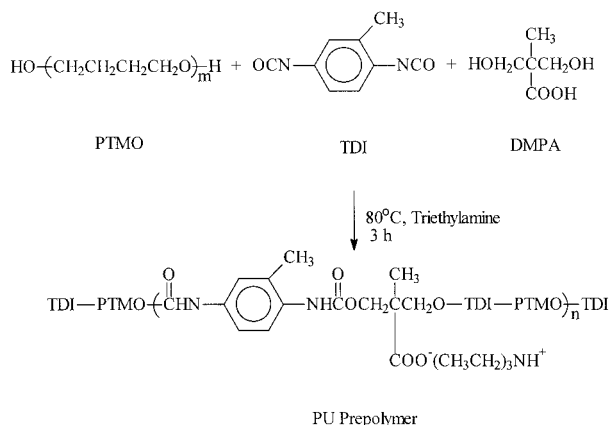
The commercial importance of waterborne polyurethanes (PUs) is increasing, because these systems permit the application of PUs from an aqueous medium. Only water is evolved during the drying process, thus rendering these systems especially safe with regard to the environment. They are nontoxic and nonflammable and do not pollute air or waste water.¹ In the past 50 years, thousands of articles and patents were issued, which kept steady the improvement of the production technology and the quality of waterborne

PUs. Dieterich and colleagues are pioneers in this area.^{2,3} Recently, great efforts have been made to explore various ways of synthesizing and characterizing waterborne PUs.^{4,5}

However, there still exist many problems unsolved in this field, especially the poor water resistance of waterborne PUs, which limits their application. The increasing requirements of good water resistance and surface properties on synthetic material have stimulated the development of modified PUs. Polydimethylsiloxane (PDMS) systems have several interesting properties including a low glass transition temperature, low surface energy, biocompatibility, good water resistance, and high thermal and oxidative stability. Thus, appropriate functional oligomers should be good candidates for the modification of

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Scheme 1 Synthesis of PU prepolymer.

PU_s.⁶ In the synthesis of such PDMS-based PUs by solution methods, solvent selection is very difficult.^{7–10} This is mainly due to the large difference between the solubility parameters of the nonpolar PDMS and the highly polar PU which may result in macroscopic phase separation during polymerization.

To solve this problem, a novel synthetic route was successfully designed as follows: An aminoethylaminopropyl-substituted PDMS (AEAPS) in an emulsion was prepared. Then, the PU prepolymer based on toluene-2,4-diisocyanate (TDI), poly(tetramethylene oxide) (PTMO), and dimethylolpropionic acid (DMPA) was extended and dispersed in this emulsion medium to synthesize a series of silicone pendent PU–urea emulsions as shown (see Schemes 1 and 2). The properties of the emulsions and the desired polymers were studied by a variety of techniques.

EXPERIMENTAL

Materials

PTMO ($M_n = 1000$), supplied by Aldrich (Milwaukee, WI), was dried and degassed at 80°C/1–2 mmHg for 5 h before use. TDI was degassed and purified by vacuum distillation. DMPA (Aldrich) was dried at 100°C for 2 h in an oven. Substituted AEAPS ($M_n = 3000$) was synthesized as described previously.^{7,11} Triethylamine (TEA) and the solvents used in the titrations were dried over 3-Å molecular sieves before use. Nonylphenolpolyethenoxy ether, glacial acetic acid, and ethylenediamine (ED) were used as received.

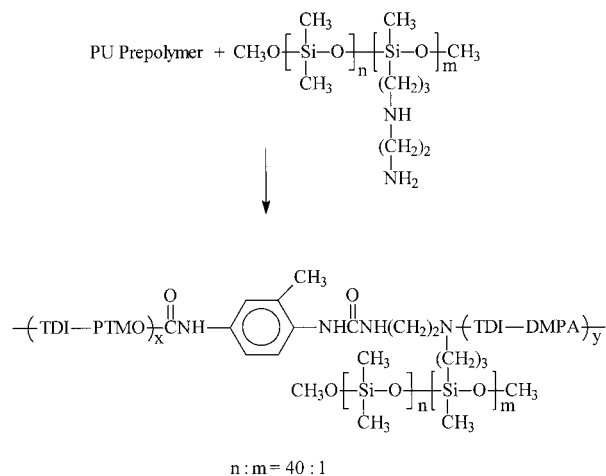
Synthesis

AEAPS Emulsion (15 wt %)

Nonylphenolpolyethenoxy ether, 2.5 g, and AEAPS, 10 g, were charged into a 250-mL three-neck round-bottom flask. While stirring, the mixture was heated to 60°C, followed by dropping 9 g water into the mixture. The mixture was heated to 70–75°C, and 2 g water and 0.2 g glacial acetic acid were added. When the mixture was homogeneous, 75.3 g water was added. Finally, the pH of the emulsion was adjusted to 6–7 by adding 0.1–0.2 g glacial acetic acid.

Prepolymer Synthesis

A 100-mL four-neck dry round-bottom flask equipped with a mechanical stirrer, thermometer, and a reflux condenser with a drying tube and a dropping funnel was used as a reactor. The reaction was carried out in a constant temperature oil bath. Stoichiometric amounts of PTMO (30 g) and TDI (15 g) were charged into the reactor. While stirring, the mixture was heated to 80°C for 1 h, followed by adding DMPA (2.4 g) to the homogenized mixtures. The mixture was heated to 80°C for about 3 h to obtain the NCO-terminated prepolymers. The change of the NCO value during the reaction was determined using a standard dibutylamine back-titration method. Upon reaching the theoretical NCO value, the prepolymers were cooled to 60°C, and the TEA (1.8 g) and acetone (10 mL) were added and stirred for 0.5 h while maintaining the temperature at 60°C (Scheme 1).



Scheme 2 Synthesis of AEAPS-modified PUs.

Table I Properties of AEAPS-modified Polyurethanes

Material	AEAPS Emulsion (g)	AEAPS Content (wt %)	Water (g)	Water Contact Angle (Degree)	Breaking Stress (MPa)	Breaking Strain (%)	Young's Modulus (MPa)	SR (%)
PU-0	0	0	220	62 ± 4	53.6	1036	10.4	53.88
PU-3	10	3	210	74 ± 3	54.5	1054	10.2	18.92
PU-6	20	6	200	78 ± 2	56.1	1168	9.2	14.95
PU94	30	9	190	81 ± 2	39.6	1007	7.1	23.08

Emulsification and Chain Extension

Aqueous dispersions of PU were obtained by adding the prepolymer to varying amounts of the AEAPS emulsion (Table I). ED (2.2 g) dissolved in water was then added to the emulsion, and the chain-extension reaction was allowed to proceed for the next 1 h (Scheme 2). The resulting products were polyurea–urethane dispersions with a solids content of about 20%, which is stable over 6 months at room temperature. The compositions and designations of the synthesized samples are listed in Table I. Films were cast from emulsion on a Teflon plate at 60°C, then stored at room temperature in a vacuum desiccator before further testing.

The nomenclature used in this article describes the AEAPS content of the polymer chain. As an example, the designation “PU-3” indicates that the AEAPS content is 3% by weight.

CHARACTERIZATION

A Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet FTIR-170 SX. The water contact angles were measured using a Rame–Hart NRL contact angle goniometer. The data were collected 1 min after 1 drop of double-distilled water had been placed on the surface of the film. A minimum of 10 measurements were used and the average contact angle calculated.

The electron spectroscopy for chemical analysis (ESCA) spectra were obtained using a V.G. Scientific ESCALAB MK spectrometer equipped with a monochromatic AlK α X-ray source. ESCA analysis was done at a nominal photoelectron take-off angle of 45°C 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 spectrometer. The

binding energies (BEs) used were C(1s): 289 eV; Si(2p):107 eV; N(1s): 404 eV; and O(1s): 537 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 emulsion-cast films using an ASTM 1708 standard die and then dried under a vacuum for a minimum of 48 h before testing. The samples (gauge length 1.5 cm) were tested at room temperature using a crosshead speed of 5 cm/min.

The water resistance of the films was studied as follows: A preweighed dry slab (6 × 6 mm in size) was immersed in deionized water at 25°C. After equilibration for 24 h, the sample was blotted with a laboratory tissue and weighed. The swelling ratio (SR) was expressed as the weight percentage of water in the swollen sample:

$$SR = (W_S - W_D)/W_D \times 100\%$$

where W_S is the weight of the swollen sample and W_D is the weight of the dry sample.

The freeze/thaw stability of the emulsions was evaluated as follows: Two milliliters of the emulsion was placed in a sealed weighing bottle. The bottle was first placed in an air oven at 90°C for 5 h, then immediately transferred to a refrigerator at 0°C for 5 h, which concludes a typical testing cycle. At least 10 such testing cycles were performed for each sample to observe whether any system heterogeneity (e.g., phase separation or precipitation) could be detected in response to the temperature.

The morphology of the emulsions was studied by a JEM100-SX transmission electron microscope (TEM). The PU emulsion was diluted and then stained with phosphotungstic acid (PTA) at pH 6.4 and then copper meshes were immersed in it. After drying the meshes at room temperature, the specimens were studied by TEM.

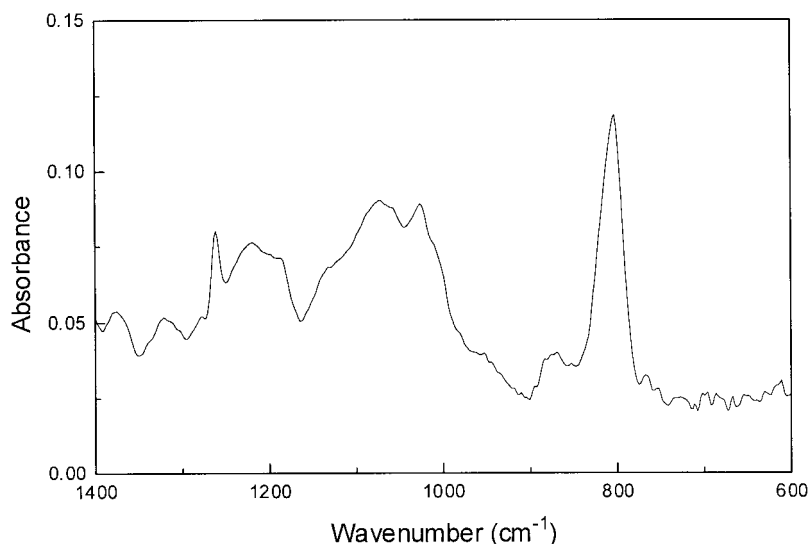


Figure 1 FTIR differential spectrum of PU-0 versus PU-3.

RESULTS AND DISCUSSION

Infrared Spectroscopy

An FTIR differential spectrum of waterborne PU PU-0 and PU-3, which were purified by toluene and hot water extraction separately, is shown in Figure 1. The peaks at 1261 cm^{-1} [CH_3 in $\text{Si}-\text{CH}_3$ (sym bending)], 1072 , 1026 cm^{-1} ($\text{Si}-\text{O}$ stretching), and 803 cm^{-1} (CH_3-Si rocking)¹² can be clearly detected in the spectrum, indicating that siloxane groups had been successfully introduced into the PUs.

Contact Angle Analysis

The contact angle data of waterborne PUs are presented in Table I. It can be clearly observed that the contact angle increased with increasing AEAPS content. The surface water-air contact angle measurements are more surface-sensitive, probably responding to the outermost monolayer of the surface. The contact angle increased, indi-

cating that the surface polarity decreased. Since the surface layer is in air (a low-energy fluid), the minimization of interfacial energy was achieved by the migration of low-energy chemical groups to the polymer-air interface. Just as expected, polymers modified with AEAPS, a hydrophobic oligomer, showed an increased water contact angle. This supported the notion that the siloxane chains have surface activity.

ESCA Analysis

ESCA is sensitive to the chemical composition in the surface region extending several monolayers ($\approx 100\text{ \AA}$) below the actual surface. The elemental composition data determined by ESCA for the surface of AEAPS-modified waterborne PU are shown in Table II. In the molecules of PU modified with AEAPS, nitrogen was present only in the hard segments, while siloxane chains lay in the side chains. As the AEAPS increased, there was depletion of the nitrogen and enrichment of the silicon, indicating that siloxane chains, low-

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
PU-0	62.78	21.97	15.25	0	62.88	21.79	15.3	0
PU-3	62.01	26.38	4.29	7.32	61.19	21.87	14.42	2.52
PU-6	60.44	26.92	3.71	8.92	59.66	21.97	13.63	4.74
PU-9	59.03	26.97	3.47	10.53	58.49	22.05	12.75	6.71

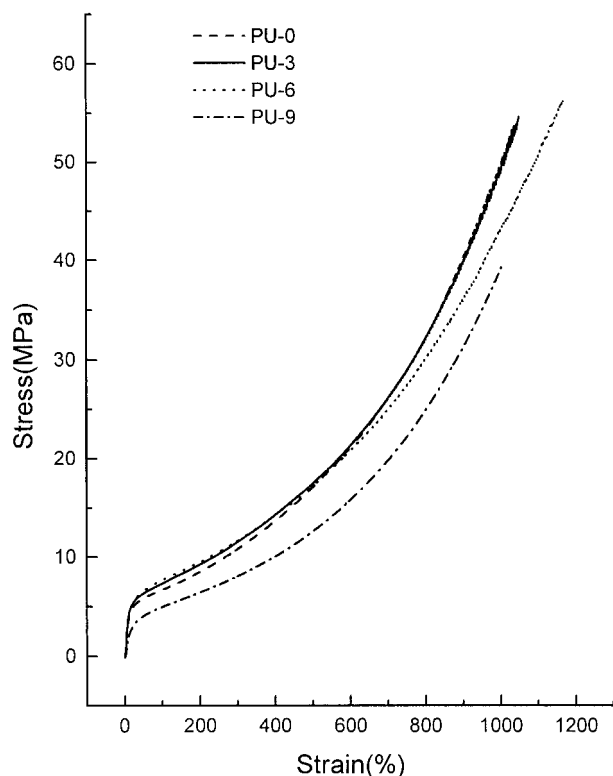


Figure 2 Stress-strain curves of AEAPS-modified PUs.

energy groups, migrated to the polymer-air interface and nitrogen was restricted in the bulk. When the data of PUs modified by the emulsion method were compared to those by the solution method in our previous article,¹⁰ it is obvious that the silicon enrichment on the PU surface in the former is less than that in the latter. It is suggested that the molecular structure of waterborne PU contained polar carboxyl groups as well as the water media of the emulsion and that there existed a competition between the siloxane chain and the carboxyl groups migrating to the PU surface.

Tensile Properties

The data of the Young's modulus, tensile strength, and ultimate elongation is shown in Table I and Figure 2. The tensile properties of the PU film which was modified with 3 and 6 wt % AEAPS were similar to those of the PU-0. The siloxane chains very effectively accumulated on the polymer surface; adding a small amount of siloxane did not affect the bulk tensile properties. When the content of AEAPS was up to 9 wt %, the

tensile strength decreased greatly as well as did the ultimate elongation and the Young's modulus decreased, which may be due to the excess siloxane inserting in the bulk of PU, which loosens the packing of the hard segments.

Water-resistance Analysis

As indicated in Table I, the cast films from the emulsions exhibited different swelling ratios in a wide range. It should be noted first that the AEAPS-modified PU samples demonstrated much lower water swelling ratios than those of non-modification PU, because hydrophobic siloxane chains migrated to the surface to prevent the water molecule getting into the bulk. In addition, it was found that PU-9 exhibited a higher swelling ratio than those of PU-6 and PU-3, indicating that the higher content of AEAPS may decrease the water resistance. A possible explanation is that the excess siloxane inserted in the bulk of PU destroyed the compact hydrogen-bonding structure to form a tunnel which makes water easier to get in. A similar result was reported by Philips et al.¹³

Emulsion Stability

Since DMPA was employed in this study, which acted as an internal emulsifier, and there was also a small amount of an external emulsifier in the AEAPS emulsion, the resulting emulsion modified with aminosilicone exhibited satisfactory stability in the whole range of the testing temperatures. No phase separation or material precipitation was detected. This feature might be desirable for their future applications.

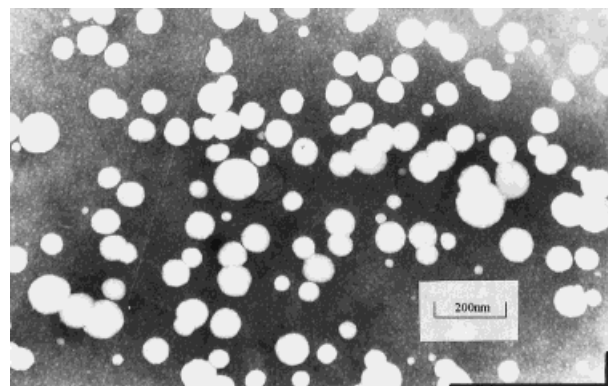


Figure 3 TEM photograph of the emulsion particle of PU-3 (magnification: 50,000 \times).

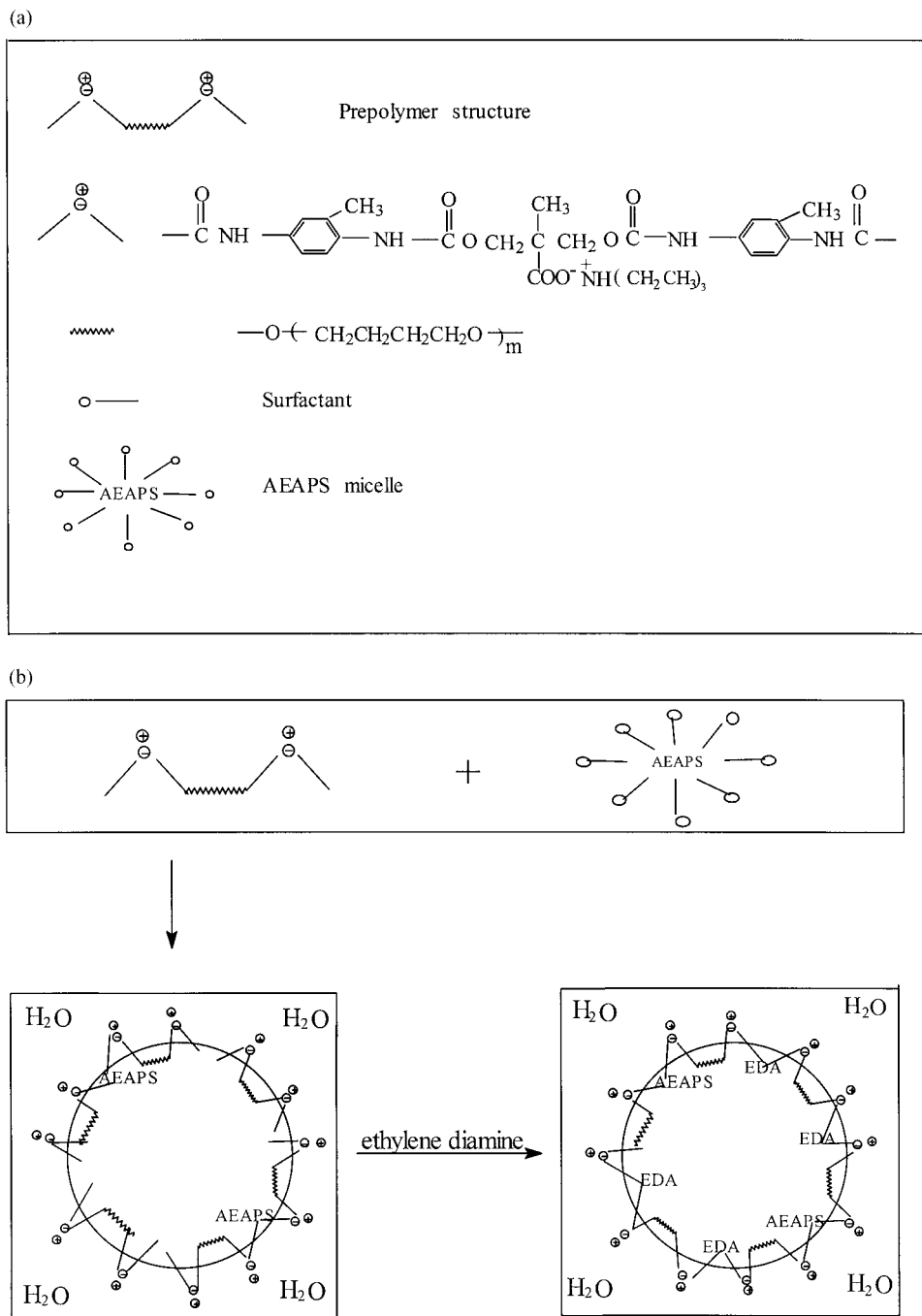


Figure 4 Reaction scheme: (a) chemical structure of the prepolymer; (b) emulsification and chain-extending process.

Particle Morphology and Reaction Mechanism

TEM photographs of the emulsion particle of PU modified with aminosilicone (3 wt %) is shown in Figure 3 (magnification: 50,000 \times). The particles are spherical and the particle-size distribution is similar to the normal PU emulsion. The average particle size is about 40 nm.

To explain the process of particle forming, a reaction mechanism was proposed as follows: The chemical structure of the prepolymer is shown in Figure 4(a). Since neutralized DMPA segments in the middle of the prepolymer possess hydrophilic properties, they could act as an anionic-type internal emulsifier to form prepolymer stable parti-

cles. The terminals of the prepolymer were attached with the remaining isocyanate groups for chain extension. When the prepolymer was added to the AEAPS emulsion, the silicone micelles collapsed while AEAPS reacted with isocyanate groups quickly. At the same time, the PU particles were formed with carboxyl groups stretching to the water. Then, with the ED being added and moving into the PU particles, the isocyanate groups in the particle could continue to react with ED to accomplish the chain-extension procedure. This whole process is also clearly expressed in Figure 4(b). Recently, our research based on a crosslinkable branched aminoethyl aminopropyl PDMS instead of AEAPS is under way.

CONCLUSIONS

1. A series of PU emulsions modified with aminosilicone were successfully prepared by a novel method which will be universal to any other waterborne PUs.
2. The emulsion was stable and the siloxane chains were enriched on the PU surface.
3. The water resistance of the PU film increased but the bulk tensile properties of the PU film were not changed significantly with a small amount siloxane modification (up to 6 wt %).

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