

# Synthesis and Properties of Self-Crosslinkable Polyurethane–Urea with Silsesquioxane Formation

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**ABSTRACT:** Based on the typical two-step polyurethane–urea synthesis, a new series of self-crosslinkable polyurethane (PU)–urea formulations, consisting of poly(tetramethylene oxide) and 4,4'-diphenyl methane diisocyanate, and extended by ethylenediamine (EDA)/aminoethylaminopropyltrimethoxysilane (AEAPS), were prepared. FTIR, ESCA, WAXD, DSC, and mechanical properties of samples were recorded. The results show that the self-crosslinkable polyurethane–urea could be crosslinked by hydrolysis of the

trimethyloxysiloxane group to form the silsesquioxane structure. These structures represent a kind of nanosize, cagelike, chemical crosslink site as well as filler, which affect the properties of PU. The morphology, varied with different ratios of EDA/AEAPS, was also discussed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 190–195, 2004

**Key words:** crosslinking; polyurethanes; silsesquioxane; mechanical properties; synthesis

## INTRODUCTION

It is well known that polyurethane–urea is an (AB)<sub>n</sub> type segmented copolymer. The unusual properties of these materials have been attributed to the formation of a microphase-separated domain structure consisting of “hard”-segment-rich and “soft”-segment-rich domains.<sup>1</sup> The soft-segment domains are rubbery at service temperatures, whereas the hard-segment domains are glassy. The latter are thought to act as thermally labile physical crosslink sites and as filler material. This thermal lability allows polyurethanes to be processed as thermoplastic materials, yet yields mechanical behavior like that of rubbers.

The strong industrial interest in polyurethane–urea polymers has spurred ongoing investigations into their structure–property correlations. In the last few decades, many investigations have been carried out on this versatile polymer. Polyurethane–urea itself is widely used in almost every segment of industry and much higher requirements on this polymer are identified. Thus, functional polyurethane–urea formulations continue to emerge in response to new demands.<sup>2,3</sup>

On the other hand, studies on silsesquioxane have been ongoing in the last half century and the interest continues to increase, especially in the field of organic–inorganic hybrid materials.<sup>4</sup> The excellent thermal

stability, weatherability, oxidative stability, and chemical resistance of these materials have led to wide-ranging uses such as protective coatings, adhesive-related materials, and so on. In recent investigations, hydrogels with silsesquioxane formations have been used as biocompatible materials, for example, as contact lenses.<sup>5</sup>

In the modification studies of polyethylene (PE), the self-crosslinkable PE with a pendant trimethoxysilane group has been commercially produced for a long time. As a crosslinking agent, multi-methyloxysilane has proved to be effective. Consideration of these products led us to synthesize the self-crosslinkable polyurethane–urea.

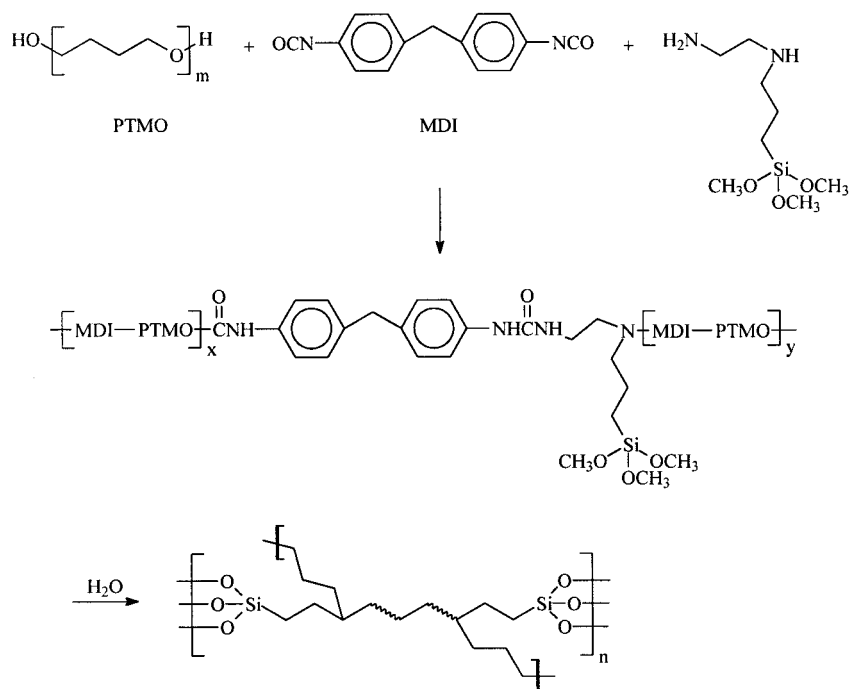
In this study, using a typical two-step solution polyurethane synthesis, a series of novel self-crosslinkable polyurethane–urea formulations, extended by aminoethylaminopropyltrimethoxysilane (AEAPS) and/or ethylenediamine (EDA), were studied.

## EXPERIMENTAL

### Materials

Poly(tetramethylene oxide) (PTMO;  $M_n = 1000$ ; Aldrich, Milwaukee, WI) was dried and degassed at 80°C / <10 Pa for 2 h before use. 4,4'-Diphenylmethane diisocyanate (MDI) and aminoethylaminopropyltrimethoxysilane (AEAPS) were purified by vacuum distillation. Ethylenediamine (EDA) and *N,N'*-dimethyl formamide (DMF) were dried over a 4-Å molecular sieve for at least 24 h and vacuum distilled before use.

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Scheme 1 Synthesis of crosslinkable polyurethane-urea.

### Preparation of samples

The synthesis of crosslinkable polyurethane-urea is shown in Scheme 1 and a typical preparation was carried out as described.

PTMO dissolved in DMF was charged into a 250-mL dry four-neck round-bottom flask equipped with thermometer, reflux condenser, dropping funnel, and drying tube, followed by stoichiometric amounts of MDI solution in DMF and a drop of stannous octoate [Sn(Oct)<sub>2</sub>] as catalyst. The reaction system was stirred by magnetic stirring for 3 h in an oil bath at 70°C under dry N<sub>2</sub> atmosphere to obtain the -NCO-terminated prepolymers. Then the extenders (AEAPS, EDA, or mixtures with different ratios of AEAPS and EDA) were added dropwise and the reaction continued for about 7–8 h at 90°C to ensure a complete reaction. The polymer solution was kept in a well-sealed bottle away from moisture. The membrane samples of polymers were prepared by casting the polymer solution onto glass dishes and volatilized DMF at about 50°C for at least 72 h; the resulting membranes were extracted with acetone for 24 h in a Soxhlet's extractor and then placed in a vacuum oven for about 1 week to ensure the complete volatilization of solvents. The moisture in air cohydrolyzed with trimethylsilyloxane to form the silsesquioxane crosslink structure.<sup>6</sup>

Using this described method, a series of polyurethane-urea samples with different contents of AEAPS were synthesized and are listed in Table I.

### Equipment and characterizations

FTIR spectra were obtained on a Nexus 870 spectrometer (Nicolet Analytical Instruments, Madison, WI) using the membrane as samples.

The water contact angles were measured using an NRL contact angle goniometer (Ramé-Hart, Mountian Lakes, NJ). The data were collected 1 min after a drop of double-distilled water had been placed on the surface of the film. At least 10 measurements were used and the average contact angle calculated.

Electron spectroscopy for chemical analysis (ESCA), also called X-ray photoelectron spectroscopy (XPS), was obtained using a VG Scientific ESCALab MK-II spectrometer (West Sussex, England) equipped with a monochromatic Mg-K<sub>α</sub> X-ray source. ESCA analysis was performed at a nominal photoelectron takeoff angle of 45°C and the depth of analysis for these samples was 100 Å. The relative atomic percentage of each element at the

TABLE I  
Composition of Self-Crosslinkable Polymers  
and Their Mechanical Properties

Sample	Composition (molar ratio)			
	PTMO	MDI	EDA	AEAPS
AEAPS0%	1	3	2	0
AEAPS25%	1	3	1.5	0.5
AEAPS50%	1	3	1	1
AEAPS75%	1	3	0.5	1.5
AEAPS100%	1	3	0	2

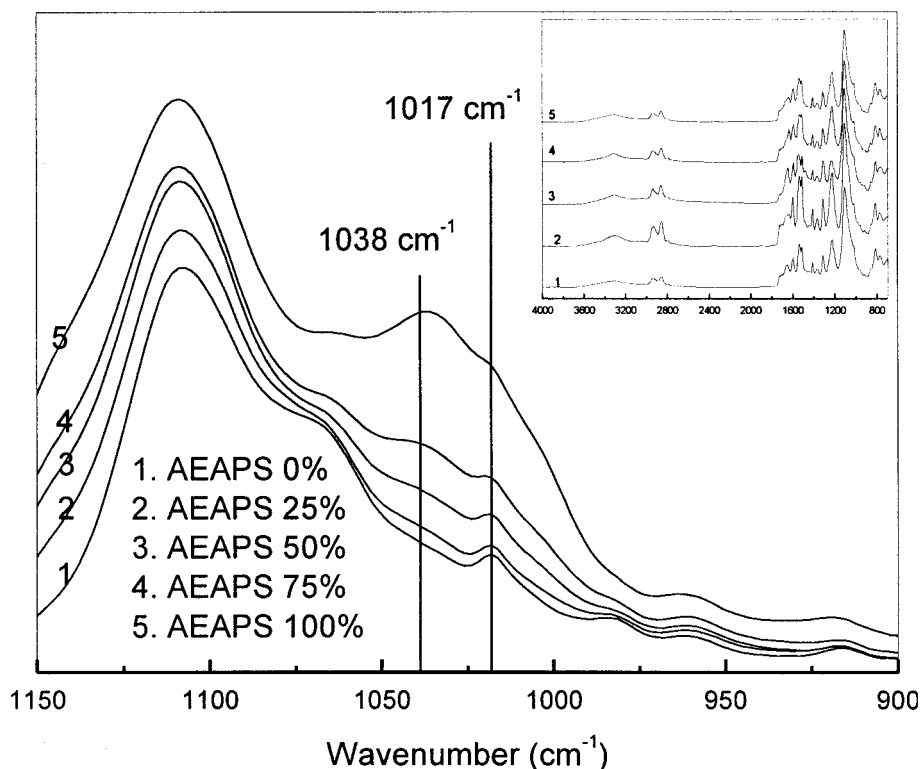


Figure 1 FTIR spectrum of self-crosslinked polyurethane-urea.

surface was estimated from the peak areas using atomic sensitivity factors specified for the spectrometer. The binding energies used were C(1s): 289 eV; Si(2p): 107 eV; N(1s): 404 eV; and O(1s): 537 eV.

The differential scanning calorimetry (DSC) thermograms were recorded at a heating rate of 20°C/min in N<sub>2</sub> atmosphere and at a temperature range from -150 to 100°C with a Perkin-Elmer Pyris 1 thermal analysis system (Perkin Elmer Cetus Instruments, Norwalk, CT). Before the scanning was carried out, the samples were annealed at about 100°C for 10 min to eliminate the remnant stress during the membrane formation.

Wide-angle X-ray diffractions (WAXD) of the polymers were recorded in an ARL X'TRA X-ray diffractometer (Ecublens, Switzerland) using a Cu-K<sub>α</sub> source from 5 to 50°.

The mechanical properties were determined on a table model Instron Series IX Automated Materials testing system with type 4200 interface (Canton, MA). The samples were stamped using an ASTM 1708 standard die and were tested at a crosshead speed of 50 mm/min at room temperature (about 18°C) under 50% humidity.

## RESULTS AND DISCUSSION

### FTIR analysis of polymers

Figure 1 shows the FTIR spectrum of polyurethane-urea with silsesquioxane formation. In the spectrum,

the peaks at 1038 and 1017 cm<sup>-1</sup> wavenumber are characteristic of the Si—O—Si bond. Enhancement of the peaks shows the increase in the amount of AEAPS in agreement with the synthesis. Along with increased amounts of added AEAPS, increased amounts of trimethoxysiloxane group were introduced into the polymers, which cohydrolyzed to form the Si—O—Si bond and provided the crosslinkage of polymers.

In the spectrum, the peaks at 1108 cm<sup>-1</sup> were assigned to the absorbance of C—O—C in the PTMO segment. The peaks at 1540 and 1512 cm<sup>-1</sup> were assigned to the stretching vibrations of —NH—. The broad peaks at about 1640 and 3300 cm<sup>-1</sup> were assigned to the primary amide in the solid state.

Normally, the —NCO group would show a characteristic peak at about 2250 cm<sup>-1</sup>. However, this absorption cannot be found from FTIR spectra of samples, which indicated that the reaction of the —NCO group with the amino group of EDA and/or AEAPS is complete and that the Si—O—Si groups are certainly bonded to the polymer and not just solved in the polymers.

### Water contact angle and ESCA analysis

ESCA is sensitive to chemical compositions in the surface region extending several monolayers (≈ 100 Å) below the actual surface. The elemental composition data determined by ESCA for the surface of poly-

TABLE II  
ESCA Results and Water Contact Angle of Samples

Sample	Real atomic percentage (%)				Theoretical atomic percentage (%)				Water contact angle (°)
	C	O	N	Si	C	O	N	Si	
AEAPS0%	62.78	21.97	15.25	≈0	77.17	15.38	7.45	0	68 ± 3
AEAPS25%	65.36	22.07	3.75	8.82	76.30	16.08	7.26	0.36	65 ± 3
AEAPS50%	61.73	22.85	4.69	10.73	75.47	16.74	7.08	0.71	72 ± 5
AEAPS75%	65.31	23.31	3.75	7.63	74.68	17.37	6.91	1.04	56 ± 3
AEAPS100%	63.52	23.74	4.07	8.67	73.93	17.98	6.74	1.35	61 ± 4

urethane-urea with silsesquioxane formation are listed in Table II. From the data of the theoretical and real atomic percentages, silicon was enriched on the sample surfaces, although the enrichment was irregular with added amounts of silicon-containing materials. Compared to the results of our previous studies,<sup>7,8</sup> it is obvious that the silicon enrichment in this series of polyurethane-urea formulations is less than that in those previous investigations. It may be attributable to the fact that the shorter molecular chain restricts the siloxane chain migrating to the samples' surface. Furthermore, the silsesquioxane crosslinking during film formation is another important factor that also greatly limited migration of siloxane chains.

The data from determination of water contact angles also support the same conclusion. Although the water contact angle of samples containing silicon is larger than that of control samples, the variety is random.

It may be seen from Table II that the silicon enrichment of sample AEAPS50% extended by EDA/AEAPS = 50/50 is higher than that of the other samples. This irregularity is in agreement with the results shown in DSC and WAXD analyses, discussed in subsequent sections.

### DSC analysis of polymers

The glass-transition temperatures ( $T_g$ ) of samples were determined using a Perkin-Elmer Pyris 1 thermal analysis system. In general, the  $T_g$  of polyurethane includes the  $T_g$  values of both the soft segment and the hard segment. However, in this crosslinked polyurethane-urea system, there is only the  $T_g$  of the soft segment, determined to be below  $-40^\circ\text{C}$ . Figure 2 shows the variability of glass-transition temperature with the composition of samples.

The  $T_g$  variability of self-crosslinked polyurethane-urea shows a tendency to decrease first and then increase, at temperatures ranging from  $-49$  to  $-65^\circ\text{C}$ . This phenomenon can be explained as the interaction results of the physical crosslink attributed to hydrogen bonds and chemical crosslink caused by the hydrolysis of trimethoxysilane groups in the polymers.

It is well known that the main chains of the linear polyurethane are strongly polar because of the urethane-urea bonds. It is this polarity that gives the strong hydrogen bonding between urea linkages to form the hard-segment-rich domain, which resembles a physical crosslink to provide the size stabilization, rigidity, high modulus, and high tensile stress of polyurethane-urea. Domains enriched with hard segment and soft segment, respectively, are separated normally, a process called microphase separation. Commonly, however, this separation is not very strict and some hard segment may dissolve into the soft-segment-rich domain, causing the phase to be not so pure. Thus the  $T_g$  of the soft segment in the polyurethane-urea system is usually higher than that in a pure polyether. In this polyurethane-urea system extended by EDA/AEAPS the same microphase separation exists. With the increasing of AEAPS content, chemical crosslinkages are introduced that draw out the hard segments dissolved in the soft-segment-rich domain to purify the soft phase, resulting in a decrease of  $T_g$  value of the soft segment in polymers. However, with continuous increases of AEAPS content, there is partial dissolution of the hard segment into the soft-segment-rich domain because of the decrease of hydrogen bonds in the hard domain, and the  $T_g$  increases once again. This phenomenon is very similar to that in polyurethane ionomers: with increasing density of the ionic sites, the  $T_g$  of the soft-segment-rich microphase first decreases, then increases once again.<sup>9</sup>

### WAXD analysis

Figure 3 shows the WAXD pattern of the self-crosslinkable polyurethane-urea. According to this pattern, the samples extended by the mixture of 50% AEAPS and 50% EDA show the greatest crystallinity in the PTMO phase; the samples extended by the mixture of 25% AEAPS and 75% EDA also show some evidence of crystallites, indicated by arrows in Figure 3.

It has been firmly established that there is microphase separation in the polyurethane-urea system. The hard-segment-rich domain is composed of isocya-

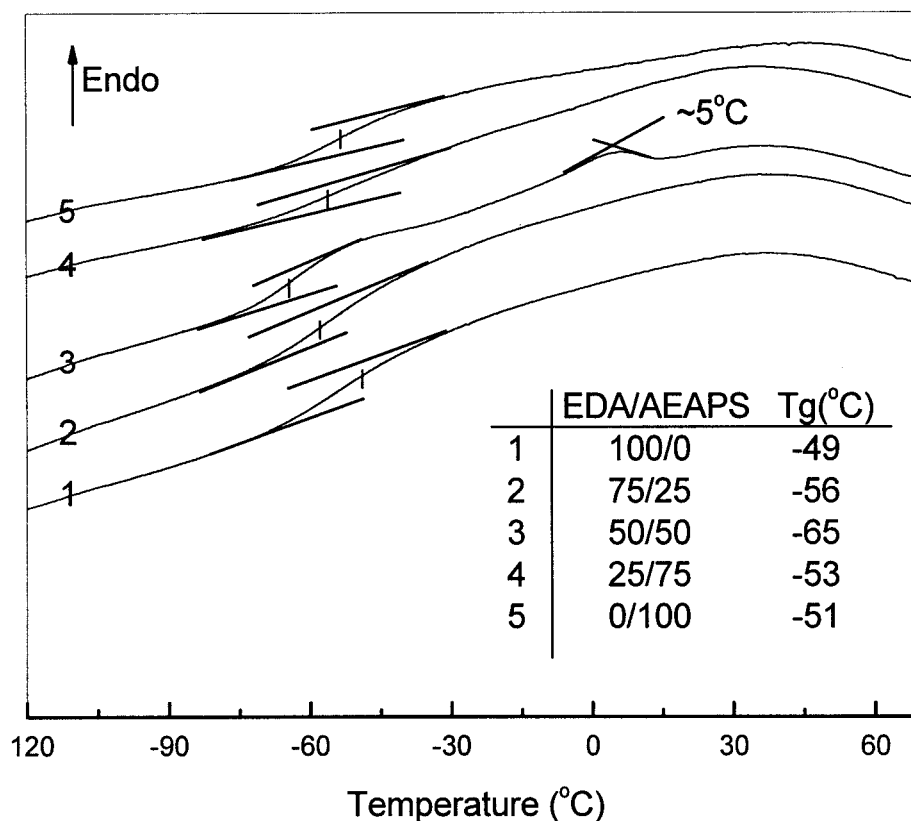


Figure 2 DSC analysis of self-crosslinkable polyurethane-urea.

nate and extender, whereas the soft-segment-rich domain is composed of polyether or polyester. Normally, however, the microphase separation is not so strict. Some hard segments dissolved in the soft-segment-rich domain, which renders the phase not so

very pure. Therefore the crystallization of the soft segment cannot be observed. In the present case, the hard-segment-rich domain is composed of MDI, EDA, and AEPAS, whereas the soft-segment-rich domain consists of PTMO.

There are two kinds of crosslinks in such a hard domain: (1) a physical crosslink caused by hydrogen bonds and (2) a chemical crosslink caused by cohydrolysis of AEAPS and water. As the content of AEAPS increased, the more chemical crosslinks formed; fewer physical crosslinks remained; and the much purer soft segment appeared, leading to formation of the soft segment crystallite, as shown in Figure 3. With further increases of AEAPS content, an increasing number of chemical crosslinks were introduced and a partial hard segment again dissolved into the soft segment, and thus the crystallite of the soft segment disappeared again.

The same evidence can also be seen in the DSC curve of this polyurethane-urea series, shown in Figure 2. Only on the curve of polymer extended by 50% AEAPS and 50% EDA does an endothermic peak appear at about 5°C, which can be explained as the melting peak of the crystal of the soft segment, PTMO. Additional information on this phenomenon is found in the mechanical properties data of the polymers, discussed next.

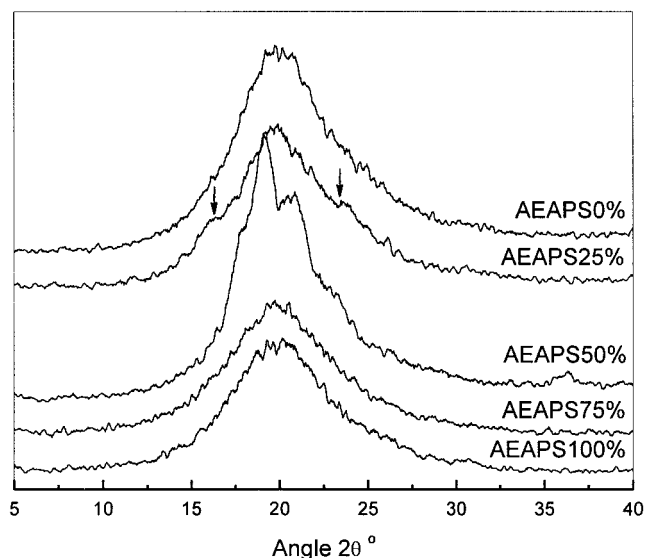


Figure 3 WAXD spectrum of self-crosslinkable polyurethane-urea.

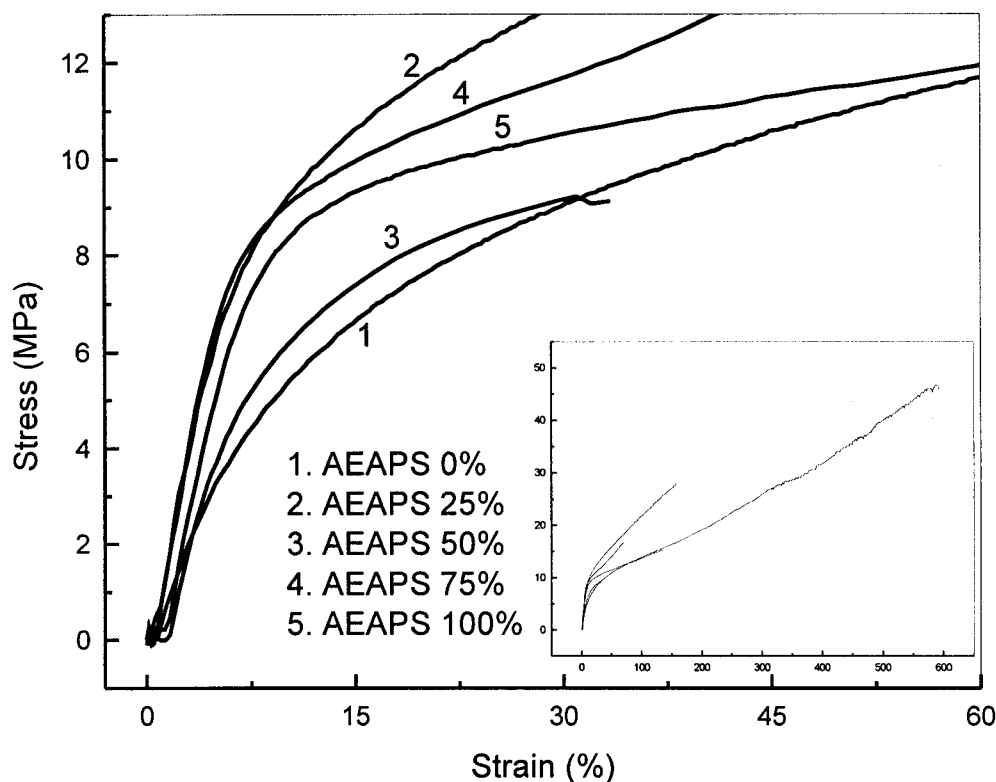


Figure 4 Stress-strain curves of self-crosslinkable polyurethane-urea.

### Mechanical properties

Figure 4 shows the magnified tensile curves of the polyurethane-urea extended by EDA/AEAPS, in which the inset shows the complete pattern. The results from the sample extended by EDA/AEAPS = 50/50 show uniquely poor mechanical properties. This phenomenon matches well the molecular structure of the polymers. As mentioned in DSC analysis, with greater amounts of AEAPS being introduced into the extender, the physical crosslink was destroyed and the chemical crosslink was more firmly established. When the ratio of EDA to AEAPS is 50 : 50, the destroyed physical crosslink and the underforming chemical crosslink lead to remarkably poor mechanical properties. In other samples, the continuous increase of chemical crosslinking leads to improvements in mechanical properties.

Additionally, the sample extended by EDA/AEAPS = 25/75 was subjected to tensile testing again 3 months later under the same conditions. The two re-

sults show no obvious difference, which indicates that the hydrolyzing crosslink had already finished during the film formation.

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