

Effect of Chemical Crosslinking on the Structure and Mechanical Properties of Polyurethane Prepared from Copoly(PPO–THF) Triols

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ABSTRACT: Copoly(PPO–THF) (oxypropane–tetrahydrofuran) diol and triol were synthesized by cationic copolymerization of PPO–THF in the presence of 1,4-butanediol (BD) or 2,2'-dihydroxymethyl butanol (DHMB). The results of proton nuclear magnetic resonance verified the chemical structure of the obtained diol and triol. The amounts of the end hydroxyl group for the obtained triol and diol were measured by the end group analysis method. Linear (B-series) and crosslinked (T-series) polyurethanes were prepared from the diol and triol, respectively. The weight ratio of hard segment in the soft domain was calculated with Fourier transform infrared spectroscopy. Differential scanning calorimetry technology was used to investigate the structure of hard domains in B- and T-series polyurethanes. Mechanical properties studies of B- and T-series polyurethanes were carried out. Higher ultimate strength of T-series polyurethane than that of the B-series one was discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2163–2169, 1998

Key words: copoly(PPO–THF) diol and triol; polyurethane; domain structure; chemical crosslinking; mechanical properties

INTRODUCTION

Segmented polyurethane block copolymers composed of incompatible hard and soft segment often formed the following microphase-separated structures: hard segment phase, soft segment phase, and interface phase.¹ At ambient temperature, hard and soft segment phase are in the glassy state and elastic state, respectively. In both domains, crystallization may take place.² Many factors, such as chemical structure,³ stoichiometric ratio between the two segments,⁴ molecular weight and distribution of the segment and macromolecules^{5,6} and processing history,^{7,8} influence the morphology of polyurethane.

The mechanical properties of polyurethane are also affected by many factors, such as chemical structure,⁶ molecular weight distribution of the segment,^{5,9} processing history,¹⁰ and the chemical crosslinking.^{11–13} When the molecular weight of polyurethane was high enough, its mechanical properties were determined mainly by the morphology of the hard domain and the stress crystallinity of the soft segment phase. The enhancement of the hard segment phase cohesion due to either hard domain crystallinity or ionic aggregation resulted in a significant increase of the ultimate tensile strength and Young's modulus of poly(dimethylsiloxane)–polyurethane polymers.¹⁴ It was also found that the crystallinity style, that is, a straight state or a coiled and/or folded state, also have significant effect on the mechanical properties of polyurethane.¹⁵ For polyurethanes prepared from polyester or poly(tetrahydrofuran)

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Table I Composition and Hydroxyl Values of Copoly(PPO-THF) Diol and Triol

Sample	Monomer in Feed (Mol)				Composition THF/PPO (Mol) ^a	Hydroxyl Value (KOH mg/g) ^b
	PPO	THF	BD	DHMB		
Copoly(PPO-THF) diol	11.2	22.3	1	0	1.40	70
Copoly(PPO-THF) triol	16.9	34.0	0	1	1.35	72

Note: Polymerization was performed at 0°C for 6 h.

^a Determined by NMR.

^b Determined by the end group analysis method.¹⁸

(THF), the mechanical properties were improved greatly by stress crystallinity of soft segment.

The properties of polyurethane can be modified by the crosslinking reaction. Random crosslinking initiated by peroxides led to poor mechanical properties,^{11,16} and the chemical crosslinks in the hard segment using short triols as chain extensors lowered its crystallinity in comparison with linear diols; the ultimate tensile properties were always reduced. The crosslinking in the hard domain can also be realized by using short diols having function groups as chain extenders, such as diacetylene diols, and then exposing to heat or radiation.¹² The properties of the obtained polyurethane were improved. Meanwhile, it is of interest that the tensile strength, elongation at break, and tear strength of the polyurethanes were improved simultaneously after the chemical crosslinking in the soft segment occurred by using the block copolymer of poly(oxypropylene-oxyethylene) (PPO-EO)-capped triol instead of the poly(PPO) diol.¹⁵

In this report, copoly(oxypropylene-tetrahydrofuran) (PPO-THF) triols and diols were prepared. Then, polyurethanes prepared from copoly(PPO-THF) triol or diol were prepared. The structure and mechanical properties of these polyurethanes were determined, and the effect of chemical crosslinking in the soft segment on the structure and properties were discussed.

EXPERIMENTAL

Materials

Oxypropylene (PPO) (Shanghai Chemical Reagent No. 2 Plant) was distilled after being refluxed over calcium hydride for 24 h, and THF (Shanghai Chemical Reagent No. 2 Plant) was purified by distillation from sodium after refluxed for 48 h. $\text{BF}_3 \cdot \text{OEt}_2$, 4,4'-diphenylenemethane di-

isocyanate (MDI), and 1,4-butanediol (BD) were distilled under reduced pressure just before use. 2,2'-dihydroxymethyl butanol (DHMB) (Tokyo Huacheng Industrial Co., Ltd.) was sublimated under reduced pressure.

Preparation of Copoly(PPO-THF) Diols

Preparation of copoly(PPO-THF) diols was done as follows.¹⁷ THF (3.02 mol), PPO (1.52 mol), and

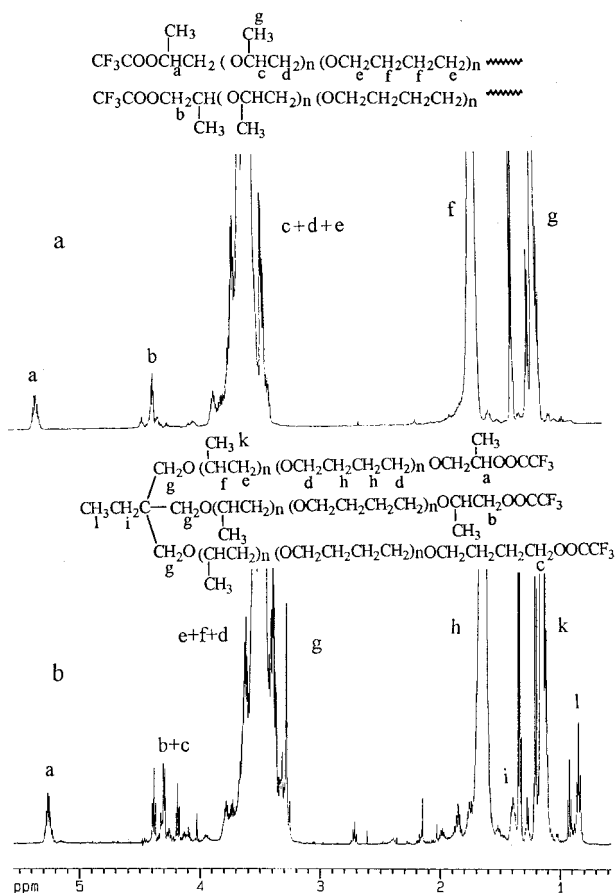


Figure 1 NMR spectra of copoly(PPO-THF) after esterification with (CF₃CO₂)O: (a) copoly(PPO-THF) diol; (b) copoly(PPO-THF) triol.

Table II Chemical Composition of Polyurethane Block Polymers

Sample ^a	Polyether ^b	Mole Ratio			Content of Hard Segment (wt %)
		NCO	OH(BD)	OH(DHMB) ^c	
PU30B	diol	2.5	1.5	1	30
PU30T	triol	2.5	1.5	1	30
PU40B	diol	3.5	2.5	1	40
PU40T	triol	3.5	2.5	1	40
PU50B	diol	5.0	4.0	1	50
PU50T	triol	5.0	4.0	1	50

^a Prepolymerization: 70°C, 2.5 h. After chain extend reaction: 100°C, 24 h.

^b Diol and triol stand, respectively, for copoly(PPO-THF) diol and copoly(PPO-THF) triol in Table I.

^c OH(BD) and OH(DHMB) represent the hydroxyl group in BD and DHMB, respectively.

BD (0.135 mol) were put into a 500-mL flask at 0°C under nitrogen atmosphere while stirring, then $\text{BF}_3 \cdot \text{OEt}_2$ (0.0068 mol) was added. The polymerization was stopped by adding excess distilled water when PPO disappeared in the gas chromatography (GC) measurement. After washing with distilled water, the mixture was purified under 100°C/1 mm Hg for 8 h in order to remove the low-boiling-point chemicals.

Preparation of Copoly(PPO-THF) Triol

Copoly(PPO-THF) triol was prepared by cationic ring-opening polymerization of THF and PPO in the presence of DHMB and $\text{BF}_3 \cdot \text{OEt}_2$ as catalyst using the same procedure as that for preparing copolydiol.

Preparation of Polyurethanes

The weight contents of the hard segment in the polyurethanes were 30, 40, and 50%, respectively. A typical preparation was described as follows: the copoly(PPO-THF) triol or diol was dried under 100°C/1 mm Hg for 5 h while stirring. MDI was added into the triol or diol, and the reaction was carried out at 70°C for 2.5 h under nitrogen. Then, the BD chain extender was added, and, after being degassed, the mixture was poured into heated mold. Meanwhile, a small amount of sample was casted onto the surface of sodium chloride plate for infrared (IR) measurements. The mold was kept at 100°C for 24 h. The samples were taken out from the mold and kept in desiccator for at least one month before measurement.

Measurement

102G GC (Shanghai Analysis Apparatus No. 2 Plant) was used to follow the polymerization pro-

cess. Fourier transform IR spectroscopy (FTIR) was measured on a Bruker Vector-22. The measurements of nuclear magnetic resonance (NMR) were carried out on a Bruker DMX-500 using CDCl_3 as the solvent and TMS as the standard. A Perkin-Elmer DSC-7 was used to measure differential scanning calorimetry (DSC) curves of the samples under nitrogen at a heating rate of 10°C/min. Hydroxyl value was determined by end group analysis method.¹⁸

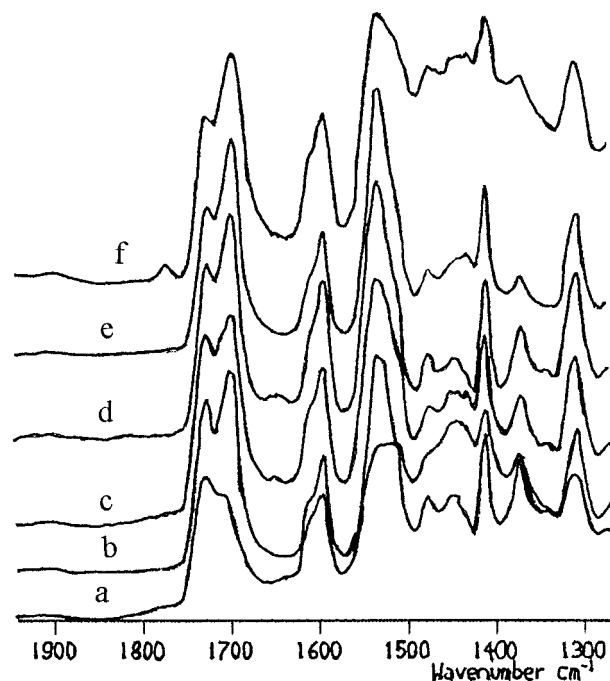


Figure 2 Effect of chemical crosslinking on the carbonyl absorption bands of polyurethanes: (a) PU30T; (b) PU30B; (c) PU40T; (d) PU40B; (e) PU50T; (f) PU50B. Prepolymerization: 70°C, 2.5 h. After chain-extending reaction: 100°C, 24 h. Composition: see Table II.

Table III FTIR Results of Crosslinked and Linear Polyurethane

Sample ^a	Fraction of Hard Segment in Feed (wt %)	Fraction of Hydrogen Bonded C=O (mol %) ^b	Fraction of Hard Segment in Soft Domain (wt %) ^c
PU30B	30	67	12
PU30T	30	58	15
PU40B	40	71	16
PU40T	40	66	18
PU50B	50	81	16
PU50T	50	82	15

^a See Table II.

^b Fraction of hydrogen-bonded C=O(%) = $A_{1703}/(A_{1703} + A_{1733}) \times 100$.

^c The fraction of the hard segment in the soft domain (wt %) = $(1 - x)W(\text{HS})/[1 - x)W(\text{HS}) + (1 - W(\text{HS}))]$, with x as the fraction of carbonyl bonded to hydrogen in the hard segment and $W(\text{HS})$ as the hard segment content, supposing that no soft segment dissolved in the hard segment domain and all of free C=O are located in the soft domain, which is probably not correct for T-series polyurethane.

Mechanical properties were measured on Shimadzu DSC-5000 with a sample size of 0.4×3.0 cm at a constant crosshead rate of 12.5 mm/min. Each value was the average of five measurements.

RESULTS AND DISCUSSION

Syntheses of Copoly(PPO-THF) Diols, Triols, and Polyurethane

Copoly(PPO-THF) diol and triol obtained had similar hydroxyl values and mole ratios of PPO-THF (see Table I). For identifying the end hydroxyl group of diol and triol, excess trifluoroacetic anhydride was added into the NMR tube. After complete esterification of the end hydroxyl group, proton NMR spectra were measured, and the results are shown in Figure 1. The peaks at δ 5.3 ppm and 4.1–4.5 ppm in Figure 1(a) are respectively attributed to methine and methylene groups next to the secondary and primary end hydroxyl groups of diol,¹⁹ which came from ring-opening of PPO in two different directions. In Figure 1(b), the peaks that appeared at 4.1–4.5 ppm correspond to methylene group adjacent to the primary end hydroxyl group obtained from ring-opening of THF and PPO. The new peak at δ = 3.3 ppm, corresponding to the methylene group of DHMB, appeared in Figure 1(b), and the consistency of the integral values at these peaks with the protons of DHMB are evidence that almost all of the hydroxyl group of DHMB took part in the

transfer reaction during cationic polymerization and the copoly(PPO-THF) triol was formed.

Using the copoly(PPO-THF) diol and triol listed in Table I, two series of polyurethanes, linear (B-series) and crosslinked (T-series), were prepared. The compositions of the obtained polyurethanes are listed in Table II. The solubility experiment performed by putting samples in DMF for 48 h showed that T-series polyurethanes were insoluble and that the B-series polyurethanes were soluble. Thus, the former was crosslinked, and the latter was linear.

IR Studies of the Structure of Polyurethane

FTIR was a useful method to investigate the interaction of hard and soft segments in the polyurethane.^{20,21} The peaks at ν = 3420 cm^{-1} is attributed to the free NH stretching vibration, and two types of bonded NH bonds, one bonded to carbonyl groups of hard segment and another to oxygen in the ether group of the soft segment, shifted to higher wave numbers. The quantitative analysis based on this region is difficult.²⁰ Thus, the carbonyl absorption region between 1780 and 1660 cm^{-1} was considered for studying the interaction of hard and soft segments. It was found that the carbonyl peak of urethanes split into the following two peaks: the one at ν = 1703 cm^{-1} resulted from self-association of N—H (and) O=C in the interior of the hard domain; another at 1730 cm^{-1} is related to the free carbonyl group presented in the mixed soft segment domain or at the interface.

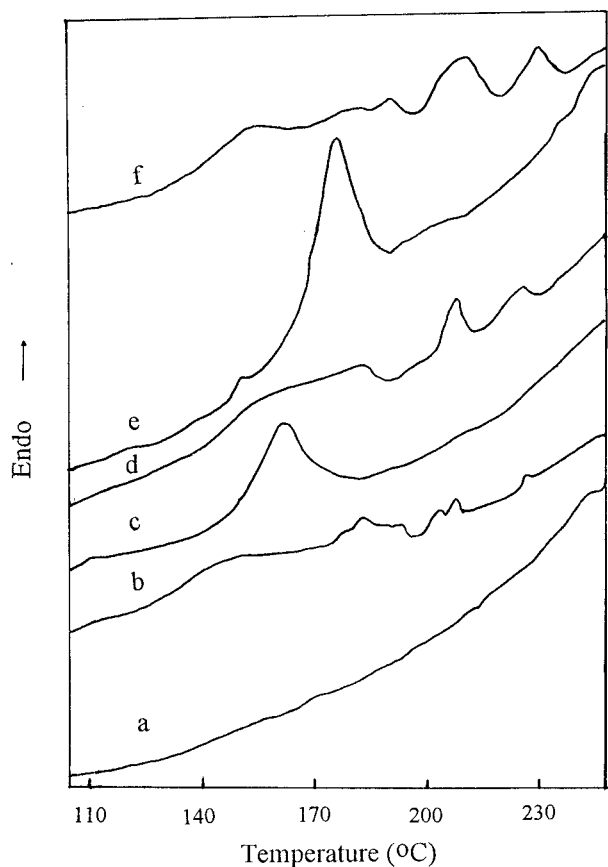


Figure 3 DSC curves of the B-series and T-series polyurethanes, in which (a)–(f) are the same as in Figure 2.

Because the extinction's coefficients of free and bonded carbonyl groups are almost the same,²⁰ the fraction of carbonyl groups bonded to hydrogen in the hard segment domain and the weight fraction of the hard segment dissolved in the soft

segment phase can be calculated based on the area of these two peaks in Figure 2. The results are listed in Table III. They show that an increase of the hard segment content led to a higher fraction of hydrogen-bonded carbonyl groups and a higher weight fraction of the hard segment dissolved in the soft segment. Comparing FTIR spectra of T-series with that of B-series polyurethanes at the same content, T-series polyurethane contained a lower hydrogen-bonded carbonyl group and a higher free carbonyl group; however, as the hard segment content was 50%, the difference between two series of polyurethanes almost disappeared. The fact indicates that crosslinking by copoly(THF-PPO) triol was unfavorable in the formation of $\text{NH} \cdots \text{O}=\text{C}-$ at the interface of the hard segment domain, especially in the case of the lower hard segment. As the increase of the hard segment, crosslinkage of polyurethane decreased, and the chain length of hard segment increased. This function was reduced.

DSC Studies of the Structure of Polyurethane

The results about DSC studies of the polyurethane samples are shown in Figure 3 and summarized in Table IV.

For the polyurethanes prepared from the same kind of copoly(PPO-THF), DSC studies showed that as the content of the hard segment increased, T_g of the soft segment increased. This is because the weight fraction of the hard segment dissolved in the soft domain increased as shown in Table III for the B-series polyurethane. The soft segment of the T-series polyurethanes had higher T_g than that of the B-series (see Table IV). This resulted

Table IV DSC Results of the B-Series and T-Series Polyurethanes

Sample ^b	T_g (°C) ^c	Endothermic Peak ^a (°C)				ΔC_p (J/g) ^d
		T_1	T_2	T_3	T_4	
PU30B	-50.23	132.75	182.86	204.00	226.84	1.67
PU30T	-36.42	—	—	—	—	—
PU40B	-46.83	141.28	182.79	204.00	221.56	3.16
PU40T	-34.42	161.10	—	—	—	8.14
PU50B	-44.62	144.79	183.40	207.00	226.44	5.58
PU50T	-33.26	175.50	—	—	—	10.24

^a The temperature at the peak.

^b See the footnote of Table II.

^c The midpoint of the glass transition process.

^d For multipeaks, ΔC_p was the sum of that of every peak.

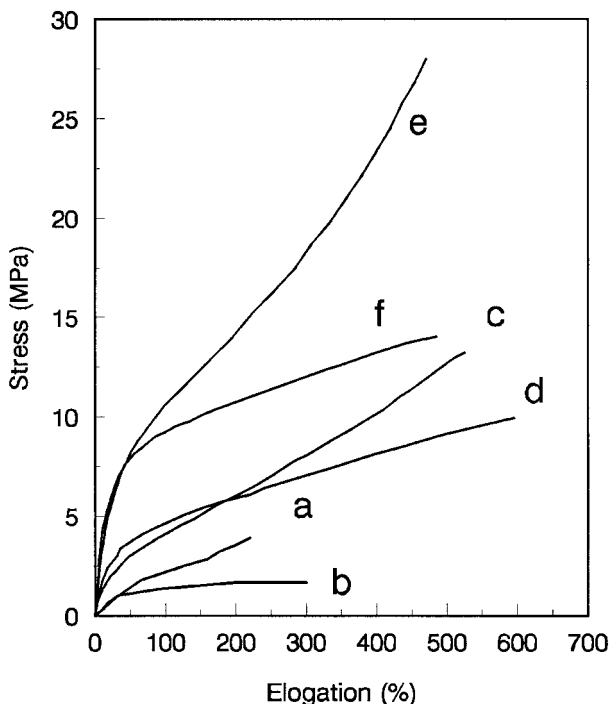


Figure 4 Stress-strain curves of the chemical cross-linked and linear polyurethanes, in which (a)–(f) are the same as in Figure 2.

from the limited chain mobility caused by the chemical crosslinkage.

DSC spectra of B-series polyurethanes show four endothermic peaks, which correspond four temperatures: T_1 , T_2 , T_3 , and T_4 . T_1 may be attributed to short-range order of the hard segment. It was observed by many investigators.^{8,22–24} As the hard segment content increased, the longer hard segment resulted in the increase of order degree; thus, T_1 increased. T_2 , (approximately 180°C) on which the hard segment content has little effect (see Table IV), was assigned to the microphase separation transition, which was associated with the microphase coming from the mixing of noncrystalline hard and soft segment.²⁵ T_3 and T_4 are related to the melting of the microcrystalline in the hard-segment-rich domains.^{8,24,26,27} The results came from different crystal structures, domain sizes, or different degrees of order in the crystalline structure.²⁸ In contrast, no peak appeared in Figure 3(a) for T-series polyurethane containing 30 wt % of the hard segment. This indicates that the crosslinking structure of triol reduced the accessibility of the short hard segment distributed in the large soft segment domain; thus, ordered hard segment domain was not easily formed. In 40 and 50 wt %

of hard segment [see Fig. 3(c) and 3(e)], only one large endothermic peak appeared. It is attributed to the melting of the crystalline in the hard domain. The longer hard segments were easily aggregated to form ordered hard segment domain. The longer the hard segment, the larger the hard segment domain formed, resulting in the increase of T_1 . The interesting phenomenon that the heat capacities of the crosslinked polyurethanes were almost double higher than that of linear polyurethanes was observed. Four phase-transition temperatures, T_1 , T_2 , T_3 , and T_4 , in DSC of B-series polyurethane, were the result of random arrangement of linear polyurethane molecules. For T-series polyurethane, as the hard segment was longer than a certain value, the crosslinked structure of triol would favor the ordering arrangement among the soft domains; thus longer, crystalline, hard-segment domains were formed.

Mechanical Properties of Polyurethanes

The stress-strain curves of polyurethanes are shown in Figure 4, and the results are listed in Table V.

It can be seen from Table V that for the same series of polyurethanes, the ultimate stress strength and Young modulus increased, and the elongation at break increased to a maximum at 40 wt % of the hard segment as the hard segment content increased. In comparison with B-series polyurethanes, the T-series had a higher Young modulus, except 50 wt % of hard segment, but less elongation at break. It is interesting to note that the T-series polyurethanes were of higher ultimate stress strength, almost double that of the B-series polyurethanes (see Table V). The reason for this fact is the crosslinking structure of the

Table V Mechanical Properties of Polyurethanes

Sample ^a	Young Modulus (MPa) ^b	Strength at Break (MPa) ^b	Elongation at Break (%) ^b
PU30B	0.8	1.6	300
PU30T	1.5	3.9	225
PU40B	7.2	9.7	620
PU40T	8.2	13.4	530
PU50B	35.0	14.2	471
PU50T	35.0	28.0	426

^a See footnote in Table II.

^b Average value of five measurements for each value.

T-series polyurethane. Probably, the contribution of the higher ordered hard segment in the T-series polyurethane to its higher ultimate stress strength is another reason because the increases of the ultimate stress strength and T_1 relating to the size and crystallinity of the hard segment domains as the increase of hard segment were observed in Tables III and IV. Generally, the increase of hard segment reduced the crosslinkage of the obtained polyurethanes.

CONCLUSIONS

Copoly(PPO-THF) triols were synthesized by cationic copolymerization of PPO and THF in the presence of DHMB. The crosslinked polyurethane was obtained using triols as soft segment. Compared with the linear polyurethanes obtained from diols, the crosslinked polyurethanes had less fraction of the hydrogen-bonded carbonyl at 30 and 40 wt % of hard segment, and almost the same at 50 wt % of hard segment. T-series had a higher ordered hard segment phase than that of the B-series polyurethanes at 40 and 50 wt % of hard segment; meanwhile, the former showed two phase transition temperatures, T_g of the soft segment and the melting temperature of the ordered hard segment. The latter had five phase transition temperatures corresponding to T_g of the soft segment and melting temperatures of the short-range order and different crystalline structures. When the hard segment content was the same, the T-series polyurethanes had slightly lower elongation at break and similar Young modulus compared with B-series polyurethanes. However, the T-series polyurethanes had higher ultimate stress strength, almost double that of B-series polyurethane, which may result from the crosslinking and higher ordered hard segment.

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