Properties of Polyurethane Elastomers Obtained with Various Chain Extenders

STEFAN OPREA*, VERONICA OPREA[1]

[1] "P. Poni "Institute of Macromolecular Chemistry, 41 A Aleea Grigore Ghica Drive, 700487, Iasi,Romania

[2] Medical Bioengineering Dept. of University of Medicine and Pharmacy, Iasi, Romania

Polyurethane-elastomer material was synthesized with an aim to determine the influence of the polyurethane chemical structure as well as of the length of the linear chains between cross-linking points on properties in such systems. Polyurethane elastomers were obtained from polyurethane prepolymers with a mixture of the diol or/and glycerin. The polyurethane prepolymers were synthesized from 4,4'-diphenyl methane diisocyanate and polyesters with molecular weight of about 2000. These polymers had improved properties and have formed flexible films with well stress-strain properties. This effect was explained by the formation of hydrogen bonds between urethane groups, independent of the polyurethane linear chain length, physical networks, which control the molecular mobility. By contrast, the chemical nature of the cross-linker precursors strongly influences the mechanical properties and glass transition. We report the synthesis of the cross-liked polyurethane elastomers and study its properties, the influence of the nature and length of the hydrocarbonate chain of the various micro glycols on the thermal and mechanical characteristics. The chemical cross-linking process decreases the soft segment crystallinity and increases stress properties. Investigation of these properties showed that the elastomers could be tailor made in order to fulfill industrial needs.

Keywords: polyurethanes, cross-link, chain extenders, mechanical properties, thermal behavior

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties [1]. PUs can be tailored to meet the highly diversified demands of modern technologies such as coatings, adhesives, fibres, foams and thermoplastic elastomers.

Linear segmented PU elastomers can be considered as block copolymers, which consist of soft segments formed by polymer glycol and hard segments based on diisocyanate and chain extender. The properties of these PU elastomers are strongly dependent on the molar mass and polymolecularity of the soft segment component [2], as well as on the chemical structure of all the components [3-6].

As far as the PU networks are concerned, one of the important factors used for changing their properties is the type of cross-linking agent. In such systems two kinds of networks can be present: physical and chemical. The physical network results from the H-bonds linking the carbonyl and amine groups of adjacent chains [7]. The physical network density influences strongly the material properties [2]. Chemical network parameters depend on the cross-linker's nature.

The influence of several network parameters such as the average length of the PU chains between cross-links (regulated either by the length of the starting macrodiol or by the number of repeating macrodiol–diisocyanate units)[2], the coordination number (regulated by a partial chemical modification of the hydroxyl chain ends) [8], and the pseudo-generation [9] of the cross-linking agent was investigated. These works showed that in such polyurethane networks, the parameters strictly affecting the global chemical network architecture (namely the coordination number and generation of the cross-linker, and the length of the connecting PU chains) had only a very weak influence on molecular dynamics, as long as the physical network formed by hydrogen bonds was not affected itself [8]. In contrast when the overall H-bond ''concentration'' was varied in a significant way, i.e. by varying the PU connecting chains through changing the nature of the starting micro-diol. This suggests that the modification of the physical network can be the most efficient way of tailoring the properties of these materials.

The presence of cross-linking bonds can limit the chain segmental motion and fine dispersed domain phase can be set by its actuation, and at the same time, also coarse dispersed phase can be formed after copious cross-linking bonds resulting in drastic reduction of intermolecular interaction. Compared to conventional random cross-linking, the end-linking method has the great advantage that one can evaluate the structural parameters such as the numbers of elastic chains, cross-links, and dangling chains in the resulting networks on the basis of a nonlinear polymerization theory[10,11] with the data of the amounts of each reactant.

Physical properties of polyurethanes depend on the raw materials used for their synthesis. The hard segments act as physical cross-links and, as a consequence, the physical [12], mechanical [13-15] and adhesive [16] properties depend on the degree of phase separation between hard and soft segments and interconnectivity of the hard domains.

In this study, polyurethane elastomers based on poly (ethylene adipate) diol, 4,4'diphenyl methane diisocyanate, and glycerin, 1,4-butane diol as chain extenders were synthesized. The networks have been prepared by end-linking a mixture of the bifunctional chains with trifunctional cross-linker or only trifunctional cross-linker at off-stoichiometric ratios. We varied systematically the hard segment structure in the polyurethane component, and for each specific polyurethane composition their thermo-mechanical properties were compared to find the optimum combination.

Experimental part

Materials

PU prepolymers were synthesised using polyethylene adipate diol (PEA) macrodiols and pure difunctional 4,4'

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* email: stefop@icmpp.ro

Table 1

MATERIALS USED TO OBTAIN POLYURETHANE ELASTOMERS

Designation	Mol. Wt.	Melting point °C	Boiling point. °C	Density g/cm^3	Refract. index	Obs.
1,4 butane diol (BD)	90.12	16	230	1.017	—	
Glycerin (Gly)	92,9		182	1,261	1.4740	
4,4'diphenyl methane diisocyanate (MDI)	250.14	42-44	152-156/ 0.2-0.3mm	—	—	
Polyethylene adipate diol (PEA)	2000	50-55	—	1.175	—	C_{OH}=56mg KOH/g

diphenyl methane diisocyanate (MDI) as monomers. The chemical structures of these monomers are shown in table 1. As a cross-linking agent the 1,4 butane diol (BD) and glycerin (Gly) was used. The aim of the synthesis presented in this work was to obtain new series of networks, in which polyurethane linear chains are connected by the various chain extenders.

On the other hand, the number of primary –OH functions present in the polyester polymer (that controls the number of PU chains connected to the chain extender) was kept constant throughout this work.

Amounts of ingredients for the synthesis of stoichiometric systems were calculated in accordance with the average numbers of –OH groups in the macrodiol and chain extenders and with the projected length of the PU chains between the cross-linking centres. The end of reaction was determined by FTIR spectroscopy, when the band at 2250–2275 cm^{-1} characteristic of the free diisocyanate –NCO groups completely disappeared.

All chemicals used in this study listed in table 1 were used as received from the suppliers unless otherwise stated. Polyester and chain extenders were checked for the content of moisture and, if necessary, dried under a vacuum until the content of water was below 0.03%.

Preparation of polyurethanes

All the cross-linked polyurethane elastomer (PU) systems presented in the work are synthesized according to the prepolymer method. In this process, isocyanate-terminated pre-polymers are obtained by reaction of difunctional, hydroxy-terminated polyester with an excess of a low molecular weight diisocyanate. Low molecular weight diols are added as so called chain extenders to further couple these prepolymers. The OH diol / OH glycerin ratio used was 1/1 in each of the synthesized polyurethane samples.

Practically, the synthesis of PUs was performed in a liter glass reactor at normal pressure, under nitrogen blanket and vigorous agitation. The NCO/OH ratio of all formulations was 1.03-1.05. In the case of the prepolymer procedure, polyester diol was reacted with a diisocyanate at 80°C for 2 h to yield a prepolymer that was mixed in the second step with chain extenders at 90 °C for 10 minutes. The resulting material was poured into a mold and left to cure at 100°C for 20 h, post-curing of the (PUs) proceeded at laboratory temperature for 7 days. Under these conditions the addition of catalyst was not necessary.

The polyurethane sheets thus prepared were used for the determination of mechanical and physical properties and for the resistance study.

Infrared Spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single reflection ATR accessory, spectrum range 600-4000 cm^{-1}.

The thermal stability of polyurethanes was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was 10°C /min in air atmosphere. The initial weight of the samples was about 50 mg and the temperature range 30-700°C.

The thermal transition behaviour was studied using differential scanning calorimetry (DSC) measurements involving a temperature range of –100 to 50° C on a Perkin Elmer 7 Series DSC, purging with N_2 and chilling with liquid N_2. Runs were conducted on samples of about 10 mg at a heating rate of 10°C/min to observe the glassy transition temperature (Tg).

Stress-strain measurements were performed on dumbbell-shaped samples cut from obtained polyurethane sheets using a TIRA test 2161 apparatus (Germany), equipped with a 1kN cell and an extension rate of 10 mm/min. Measurements were made at 25°C. At least five specimens were tested, and the average was plotted.

Results and discussion

The following parameters of the formulation were tested in order to find out the structure-property relationship of the chain extenders:

- type of OH groups (primary or secondary) of the chain extenders;
- hardness;

PEA, MDI and BD lead to polyurethanes with Shore A hardness about 70. That may be classified as soft grade

Table 2

HARDNESS OF THE POLYURETHANE ELASTOMERS OBTAINED

Nr.	Designation samples	Rate Polyester/ Diisocyanate/ Chain extenders	Diisocyanate	Chain extenders	Hardness Shore A
1.	PU21	1:2:1	MDI	Gly +BD	56
2.	PU22	1:2:1	MDI	Gly	60
3.	PU23	1:2:1	MDI	BD	72

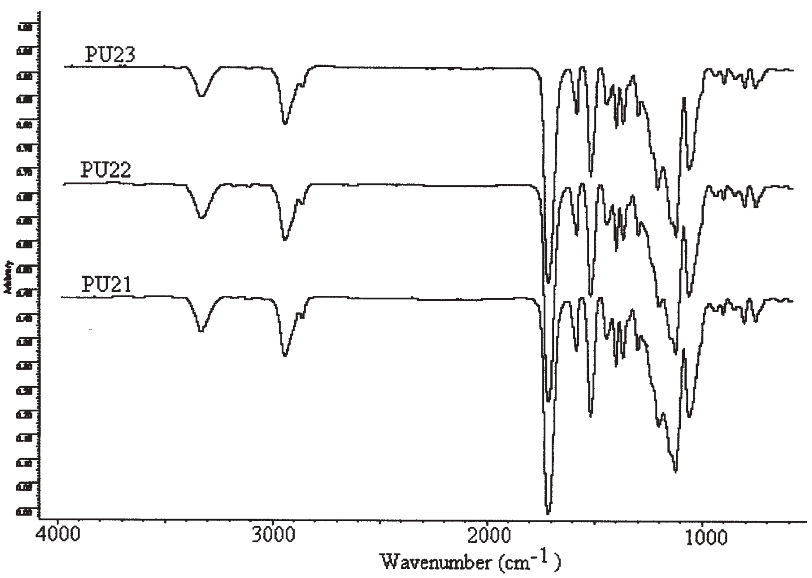

Fig 1. IR spectra of polyurethane elastomers synthesized

PU. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

In an attempt to obtain even softer PU, a series of samples with different hard phase structure was synthesized (table 2, formulations 1-3).

The role of chain extenders molecular structure and of the type of OH groups can also be seen from the table 2. All these elastomers have similar properties however, the use of 1,4 butane diol resulted in an increase of Shore hardness and a slight change in softening and glass transition temperature. A formulation with 1,4 butane diol and glycerin yielded a very soft PU product with hardness 50-55 Shore A, good elongation and relatively high softening temperature.

IR Spectroscopy

Figure 1 shows the IR spectra of the three PU prepared with different chain extenders. The three IR spectra show typical N-H (1550, 3300cm^{-1}), C=O (1720cm^{-1}), C-H (2900cm^{-1}) and C-O-C bands (1050, 1100, 1200cm^{-1}) of polyurethane elastomers.

Formation of the polymer was confirmed by the disappearance of the isocyanate stretching band at 2200-2300 cm^{-1}.

The peak at 1600 cm$^{"1}$ is assigned to the hydrogen bonded C=O stretching, while the peak at 1720 cm$^{"1}$ is for free bonded C=O stretching. Hydrogen bonded carbonyl bands correspond to those groups that are in the interior of the hard segments, whereas the free bands may correspond to those groups in the hard segment domains or in the soft domains or at interface [17].

Usually, the hydrogen bonding among hard segments plus dipole–dipole interaction between carbonyl groups will primarily affect C=O stretching vibration.

The carbonyl stretch peak at 1720–1730 cm^{-1} suggests that more extensive interactions are made not only with the increase of hard segment content but also with the increase in cross-linking, moreover, the later of which is mainly responsible for the increase of the hydrogen bonds in this series. Based on these results of FT-IR spectrum, it was thought that glycerin had already effectively cross-linked which greatly affected the properties of the polyurethane.

Thermogravimetric analysis

A three-step degradation curve was observed in figures 2,3. In the first step, the weight loss is less than 5%. The quantity of gaseous components, mainly water released in this step, is relatively small. Decomposition temperatures of steps 2 and 3 are at approximately 300 and 450°C. The main quantity of gaseous components, e.g., carbon monoxide and methane, is split off in these two steps. Decomposition of step 2 corresponds to urethane-bond (i.e., hard segment) breaking, and step 3 is the polyol decomposition [18].

The decomposition results are shown in table 3. The decomposition temperature of second step and the residue increase are from 240 to 320°C and from 72 to 76, respectively. This was attributed to the increase of cross-linkage, which will increase the intermolecular bonding and hence needs more energy to decompose the membrane.

The open-air TGA was used to study some linear polyester urethanes attempting to outline the increase in the thermal stability brought by components from their structure. To achieve this, the same testing conditions were used for all the copolymer samples being analyzed. The onset (T_i) degradation temperature was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step with the horizontal zero-line of the TG curve [19,20].

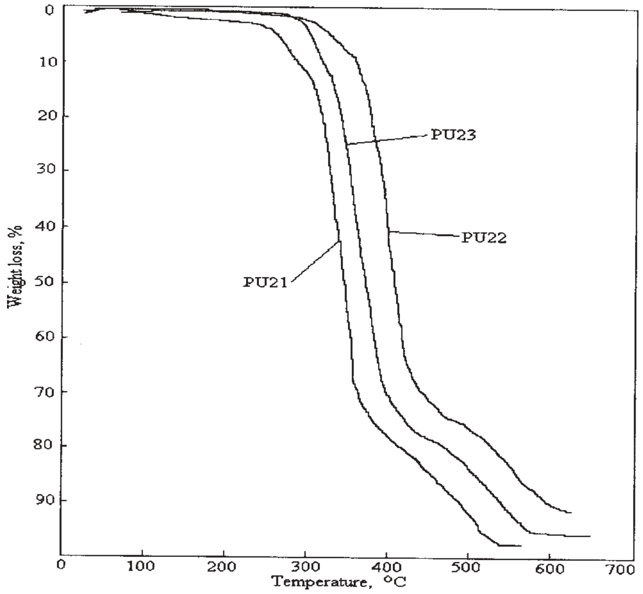

Fig. 2. TG curves of polyurethane elastomers

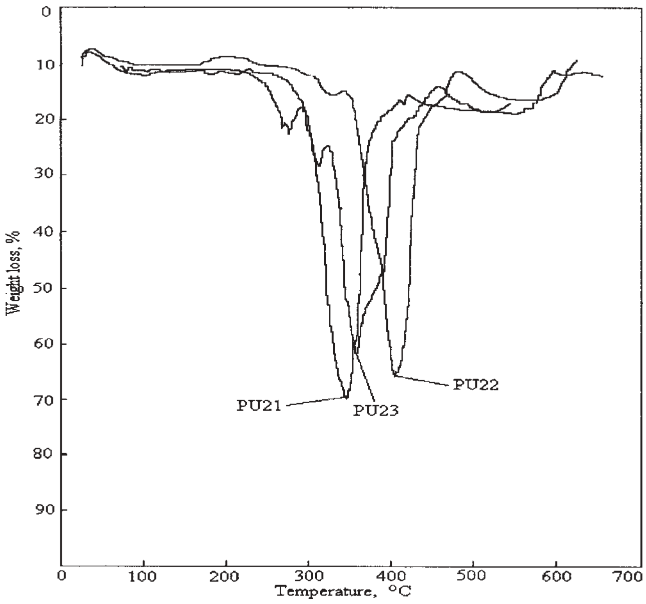

Fig. 3. DTG curves for polyurethane elastomers

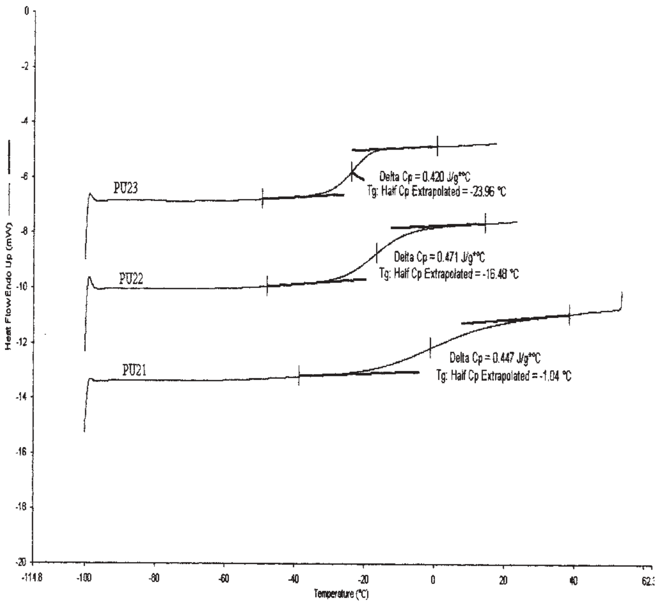

Fig. 4. DSC traces for polyurethane elastomers

Table 3

THERMOGRAVIMETRIC DATA FOR THE POLYURETHANE ELASTOMERS

Sample code	Global	Step I	Step II	Step III	T max, °C
PU21	97	5(100-280)	76(240-380)	16(380-520)	350
PU22	91	4 (120-350)	74(320-470)	13(470-600)	405
PU23	95	4(115-320)	72(270-375)	19(375-480)	370

Generally, polyurethanes analyzed decomposed in three steps and the temperature which the weight losses were maximum is 280-450°C increase of flexible chain lead to relative stability, because the posibility to order the molecular chain is high, folowing an accentuated decompositions.

Following the initial degradation in the hard segments, the second stage of the degradation was related to the soft segments and started at about 300°C.

In the DTG curve of polyurethanes, an inflexion is present at about 350°C for polyurethane with BD and glycerin, 370°C for polyurethane with BD and 405 °C for polyurethane with glycerin.

The increase of the temperature maxim indicates a lower rate of diffusion of the degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures. Thus, it is evident that the cross-linking bonds restrict the diffusion of the degradation products from the matrix.

The glass transition temperatures (Tg) of polyurethane elastomers are shown in figure 4. It was evident that the hard segment structure had influence on glass transition temperature of the cross-linked polyurethane. The samples with higher percentage of cross-linked segments showed rather smaller heat of transition as linear polyurethane elastomers, suggesting that more ordered polymer package was obtained at low percentage of cross-linked segment.

DSC data supports that excess percentage of cross-linked segment do not always provide well ordered structure and proper ratio of hard segment is necessary for ordered structure.

More ordered structure would be expected at low wt % of cross-linked hard segment because hard segments are mainly connected by the long and flexible polyester as soft segment. But hindered or restricted alignment of hard segments would be made at higher wt % of cross-linked hard segment because the short and less flexible butanediol and/or glycerin are the major components.

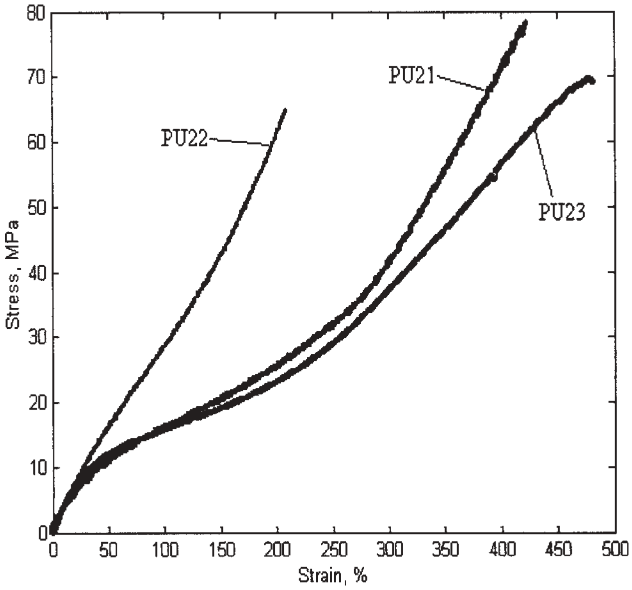

Fig. 5. Stress-strain curves of polyurethane elastomers

The change of Tg of the soft segment has been used as an indicator of the degree of phase separation.

The sample with a high content of glycerin implied that its cross-linked density was high in molecular structure. Comparing the data of PU 21-23, it can be found that cross-linking also affects the thermal property of polyurethane elastomers. The decrease in the melting temperature of

Table 4
TENSILE PROPERTIES OF POLYURETHANES OBTAINED

Sample code	**E_1 MPa**	**L1 %**	**FR MPa**	**AR %**	**FM MPa**	**AM %**	**E MPa**
PU21	8.8	40	78	420	79	420	29.4
PU22	11.8	46	65	200	65.7	201	82.6
PU23	10.3	31	72	477	73	472	50

E_1 – effective modulus to first transformation of phase; L1- elongation to first transformation of phase; FR- tensile stress at break; AR- elongation at break; FM- tensile stress at maximum; AM – elongation at maximum; E- modulus

the soft segment and the melting enthalpy, which is probably because cross-linking increases the miscibility of the soft segment and the hard segment as the crystallization of the soft segment decreases: the more glycerin is used, the less crystallization enthalpy is needed.

Mechanical properties

The mechanical behaviour of polyurethane elastomers is dependent on the intermolecular interactions between their hard segments.

Physico-mechanical analyses evidence the extent of the supermolecular modifications of polyurethanes obtained as a function of their structural modifications.

Stress-strain, modulus and elongation are important for polymer characterization, depending on their structure by varying the polyol and/or diisocyanate molecular weight, as well as variation of chain extenders structure, leading to modifications of stress-strain, modulus and elongation [21].

If the amount of cross-linked hard segments is greater, higher stress and modulus and lower elongations result. Reverse effects occur with more numerous and longer soft segments.

The stress-elongation curves representing the various chain extender, but with a common OH/NCO ratio, are grouped in figure 5. This figure, in essence, shows the change in tensile properties with crosslink density.

The increase of chemical cross-linking leads to a change in morphology and affects the mechanical properties [22].

The existence of three-dimensional restricts the mobility of molecular chain. And the increase of intermolecular attraction of hard-to-hard segments tends to increase tensile property, while the elongation decrease due to the increase of three-dimensional cross-linking between hard segments. It is obvious that lower cross-linking density will increase the elongation and larger cross-linking density then change the elastomer to glassy type and break at lower elongation.

This effect is understandable since the former ratio has a more drastic effect on crosslink density. The final elongation is plotted as a function of molecular weight per crosslink.

The data on the tensile analysis of PUs with various hard segment structures or cross-linking were listed in table 4.

It was found that PU21 have better elongations with more than 400%, while PU22 showed an elongation of about 200%. PU21 showed a higher maximum stress break, while the maximum stress of the sample increases with both a decrease in the cross-linking. The following two reasons maybe explain the results: first, the increase in the physical cross-linking points; second, as chemical cross-linking increases, the mechanical properties of the hard segment also increases, especially when they are in a rubbery state.

Comparing samples of PU21-23, which differ in their degree of cross-linking, it can be found that the PU21 has the best mechanic property, while PU22 has poor mechanical properties. From these results, it was suggested that the degree of cross-linking is also very important to the mechanical properties of polyurethane elastomer and that only suitable cross-linking in PU can lead to better mechanical properties.

Conclusions

The mechanical properties of the polyurethane elastomers were dependent on the combination of the constituents of polymer chains (NCO/OH ratio, type of chain extender).

Depending on the parameters of the formulation, the resulting PU exhibited hardness about 50-75 Shore A , making them prospective materials falling into the category of the soft grade PU.

Longer chain lengths of chain extender produce higher elongations at break and lower mechanical moduli. The cross-linking process increases the urethane domain rigidity and decreases the soft segment crystallinity. These factors enhance the tensile strength of the materials.

The thermal stability is a function of the components present in the formulation.

Polyurethanes show a three-step thermal degradation. The first stage was associated with the hard segment degradation and the second one, with the soft segments. Higher length of the soft segment and the presence of glycerin linkages increased the polyurethane thermal stability.

Chemical modification of the PU chains between the cross-linking points is the most effective method of changing the properties of the PU networks, since in this way one can change the stiffness of the linear PU chains, the structure of the groups involved in molecular relaxation and distribution of the hydrogen bonds.

The low cross-linked PUs has better mechanical properties and the content of the cross-linking has a very significant effect on these properties.

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