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Effect of the diisocyanate and chain extenders on the properties of the cross-linked polyetherurethane elastomers

S. Oprea

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Abstract Polyurethane elastomers with potential for applications in damping bearings were synthesized with 1,6-hexamethylene diisocyanate, 4,4′-methylenebis-(phenylisocyanate), poly(1,4-butane)diols (Terathane 1400), 1,4-butane diol 1,6-hexane diol and glycerin chain extenders. The glass-transition temperatures of the materials ranged from −42 to −75 °C and were higher for polymers based on 4,4′-methylenebis-(phenylisocyanate) and with higher hard segment (HS) contents. The tensile strengths of the materials were 20–55 MPa and the tensile moduli were 30–134 MPa. These increased with increasing HS content. Interchain cross-linking improves thermal stability, which was measured by thermogravimetric analysis and differential scanning calorimetry. The structure and amount of HS used causes a significant variation in the properties of cross-linked elastomers.

Introduction

Higher damping is associated to mechanical stability, thermal and sound isolation, just to cite some consequences, and can provide more comfortable environment. Damping is the most sensitive indicator of all kinds of molecular motions displayed by a polymer in solid state and can be correlated to many transitions, relaxation processes, structural heterogeneities, and to the morphology of multiphase and cross-linked systems [1].

Polymers can absorb mechanical energy and convert this energy partially into heat through viscous deformation [2].

Generally speaking, these polymers often have cross-linked structures (either chemical cross-linking [3] or physical cross-linking) which determine their permanent shapes. Many researchers have studied the damping behavior of polymeric IPN's and it has been shown to be dependent on cross-linking density [4–11], intensity of specific interaction [6, 12, 13], morphology or phase domain size [4, 6, 10–13], and combinations of them [4, 12]. 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 [14, 15] with the data of the amounts of each reactant.

In this study, polyurethane (PU) elastomers based on poly(1,4-butane)diols (Terathane1400), 1,6-hexamethylene diisocyanate, 4,4′-methylenebis-(phenylisocyanate), and glycerin, 1,4-butane diol or 1,6-hexane diol as chain extenders were synthesized. The networks have been prepared by end-linking a mixture of the bifunctional chains with trifunctional cross-linker at off-stoichiometric ratios. We varied systematically the hard to soft segment ratio in the PU component, and for each specific PU composition their thermo-mechanical properties were compared to find the optimum combination.

S. Oprea (✉)
"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Grigore Ghica Voda No. 41-A, 700487 Iasi, Romania
e-mail: stefop@icmpp.ro

Experimental

Materials

All raw materials used in the investigation are listed in Table 1. They were used as received without any further purification. The polyols and short diols were dried under vacuum at 120 °C for about 2 h prior to use.

Preparation of PUs

All the cross-linked PUs systems presented in the work are synthesized according to the prepolymer method. In this process, isocyanate-terminated prepolymers are obtained by reaction of difunctional, hydroxy-terminated polyether 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 average hard segment (HS) composition was controlled by the molar ratios of poly(ether)-diol/MDI/diol and triol used in the synthesis, which was varied from 1/2/1 (22% HS), 1/3/2 (32% HS). The OH diol/OH glycerin ratio used was 1/1 in the each of the synthesized PU samples.

Practically, the synthesis of PUs was performed in a 1-L 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, polyether diol was reacted with a diisocyanate at 80 °C for 1 h to yield a prepolymer that was mixed in the second step with chain extenders at 80 °C for 10 min. 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 PU sheets thus prepared were used for the determination of mechanical and physical properties and for the resistance study.

Measurements

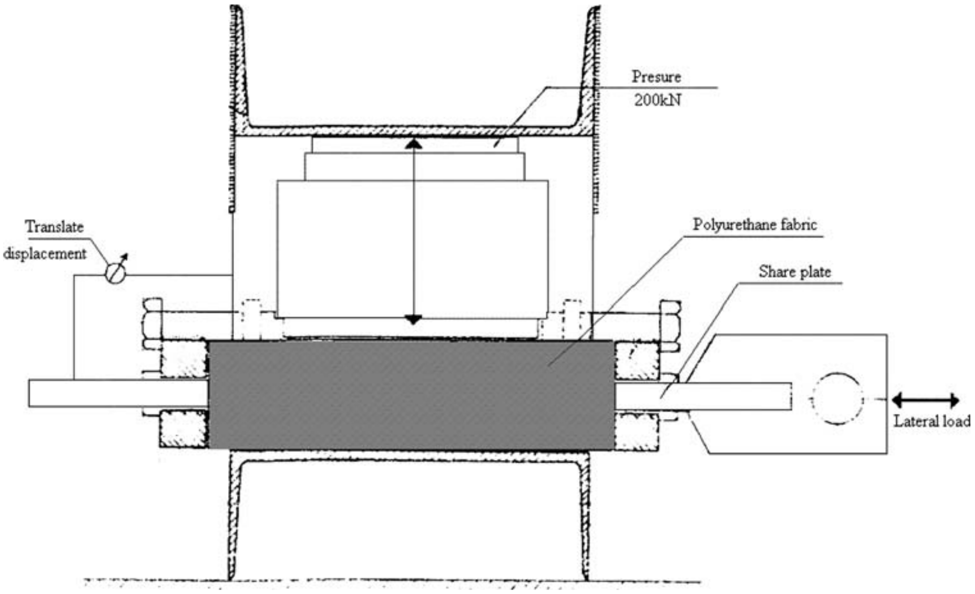
Infrared spectroscopy (FT-IR) was done using a VERTEX 7 Instruments equipped with a Golden Gate single-reflection ATR accessory, spectrum ranging from 600 to 4,000 cm^{-1}.

The *thermal stability* of PUs was performed on a DERIVATOGRAF Q-1500 D apparatus (Hungary). The

Table 1 Materials used to obtain polyether-urethane elastomers

Designation	Mol. wt.	Melting point (°C)	Boiling point (°C)	Density (g/mL)	Refract. index
1,4-butane diol (BD)	90.12	16	230	1.017	–
1,6-hexane diol (HD)	118.1	38	250	–	
Glycerin (Gly)	92.9		182	1.261	1.4740
4,4′-methylenebis-(phenylisocyanate) (MDI)	250.14	42–44	152–156/0.2–0.3 mm	–	–
1,6-hexamethylene diisocyanate (HDI)	168.2	–	255	1.040	1.4520
Poly(1,4-butanediol) Terathane 1400	1,400	33–36	–	1.000	–

Fig. 1 Shear test system



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 was 30–700 °C.

The *thermal transition* behavior 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 glass transition temperature (T_g).

Stress–strain measurements were performed on dumbbell-shaped samples cut from obtained PU sheets using a TIRA test 2161 apparatus (Germany), equipped with a 1 kN 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.

Shearing properties were determined using a loading system which is shown in Fig. 1. Test piece (section, 250 × 250 mm^2; thickness, 40 mm) and axial force: 0–100 kN, temperature 20 °C. Number of cycles is at least five times. During testing the force was applied normally to the plane, operating a crosshead speed of 250 mm/min.

Results and discussion

Any alterations in the chain extender and prepolymer structure cause substantial changes in the resins' chains, leading to modifications in the materials mechanical properties, such as flexibility and rupture stress.

The HS structure and content of the formulation were tested in order to find out the structure–property relationship of the chain extenders-based PUs.

Cross-linked PU based on polyether (Terathane1400) leads to cross-linked PUs with Shore A hardness about 50–75. That may be classified as soft-grade PUs. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

The role of chain extenders nature and molecular weight and the type of diisocyanate groups can also be seen from Table 2. All these elastomers have similar properties; however, the use of 1,6-hexamethylene diisocyanate resulted in an increase of Shore A hardness and a slight change in softening and glass transition temperature.

IR spectroscopy

FT-IR spectra of the polymers were used to confirm the formation of PUs. Formation of the polymer was confirmed by the disappearance of the isocyanate stretching band at 2,200–2,300 cm^{-1} (Figs. 2 and 3).

The FT-IR spectra of the elastomers exhibited the bands typical for PUs: –NH, (free and bonded) at 3,280–3,340 cm^{-1}; CH_2– at 2,850–2,970 cm^{-1}; C=O in bonded urethane group at 1,710–1,720 cm^{-1}; C=O free urethane group at 1,706 cm^{-1}; 1,540 cm^{-1} (Amide I), and 1,500 cm^{-1} (Amide II) occurred in PU, displaying the formation of urethane bonds in the sheets.

A few interactions among the polymeric chains are responsible for the shift of transmittance peak: (1) hydrogen bonding between NH group and carbonyl group of HS; (2) dipole–dipole interaction between carbonyl groups of HSs; (3) induced dipole–dipole interaction between aromatic rings of HS.

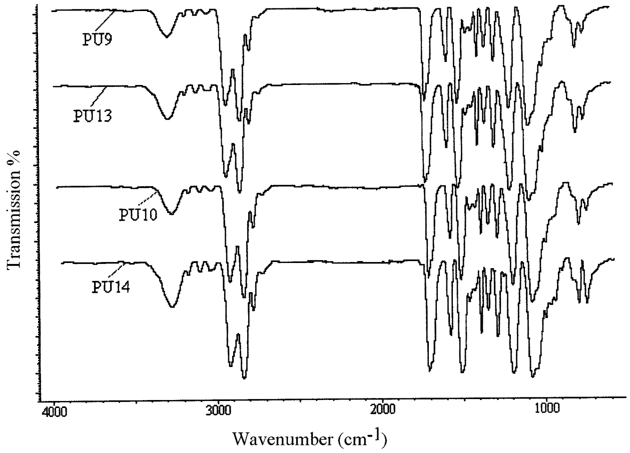


Fig. 2 IR spectra of PU samples synthesized with MDI

Table 2 Formulations and hardness of the PUs obtained

No.	Designation samples	Rate polyether/ diisocyanate/chain extenders	Diisocyanate	Chain extenders glycerin+	Hardness Shore A
1	PU9	1:2:1	MDI	BD	63
2	PU10	1:2:1	MDI	HD	65
3	PU11	1:2:1	HDI	BD	53
4	PU12	1:2:1	HDI	HD	65
5	PU13	1:3:2	MDI	BD	72
6	PU14	1:3:2	MDI	HD	75
7	PU15	1:3:2	HDI	BD	76
8	PU16	1:3:2	HDI	HD	73

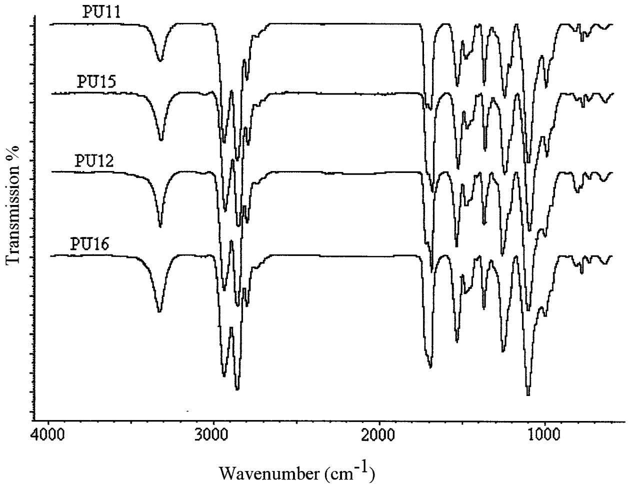


Fig. 3 IR spectra of PU samples synthesized with HDI

It suggests that HSs get more aggregated to form domains in the PUs block copolymer as HS content increases. Such domain formation has a significant influence on the mechanical and thermo-mechanical properties of PU, such as maximum stress, tensile modulus, and elongation at break.

Thermogravimetric analysis

Representative thermogravimetric data for various copolymers have been reproduced in Table 3. The open-air TGA was used to study some cross-linked polyether urethanes attempting to outline the increase in the thermal stability brought by components from their structure. In order 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 [16, 17].

The MDI-based system can also have more complete microphase separation. The physical cross-links are important for providing dimensional stability and for stopping cold flow in the uncured materials. The effect of restricting segmental motion in a three-dimensional network by chemical cross-link sites is similar to that of microdomain physical cross-links, except that the former is irreversible.

Table 3 Thermal characteristics of PUs obtained

Sample code	Weight losses global (%)	T_i (°C)	T 5% losses (°C)	T_{max} (°C)	T_g (°C)
PU9	97	100	265	350	−47.6
PU10	97	150	300	385	−42.71
PU11	97	100	205	370	−74.38
PU12	96	155	245	365	−74.67
PU13	93	170	320	410	−41.38
PU14	95	175	350	440	−41.67
PU15	96	100	305	450	−71.27
PU16	96	160	265	415	−72.71

Generally, PUs analyzed decomposed in three steps and the temperature which the weight losses were maximum is 260–550 °C increase in flexible chain lead to relative stability, because the possibility of order the molecular chain is high, following a accentuated decompositions. Following the initial degradation in the HSs, the second stage of the degradation was related to the soft segments and started at about 300 °C.

In the DTG curve of PUs, an inflexion is present at about 350–390 °C for PU with a rate of the reagents 1/2/1 and 400–450 °C for PU with a rate of the reagents 1/3/2.

The increase in 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 DSC data of PUs were shown in Table 3. It was evident that the HS structure had influence on glass transition temperature of the cross-linked PU but was less pronounced with the used of 1,6-hexametylene diisocyanate in HSs of PU. The samples with higher percentage of HSs showed rather smaller heat of transition, suggesting that more ordered polymer package was obtained at low percentage of HS.

DSC data support that excess percentage of HS does not always provide well-ordered structure and proper ratio of HS is necessary for ordered structure.

More ordered structure would be expected at low wt.% of HS because HSs are mainly connected by the long and flexible polyether as soft segment contains more polyether than BD or HD. But hindered or restricted alignment of HSs would be made at higher wt.% of HS because the short and less flexible butanediol or hexanediol is the major component.

Mechanical properties

The mechanical behavior of PU elastomers is dependent on the intermolecular interactions between their HSs.

Physico-mechanical analyses evidence the extent of the supramolecular modifications of PUs 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 diisocyanate and/or chain extender molecular weight, as well as variation of chain extenders structure,

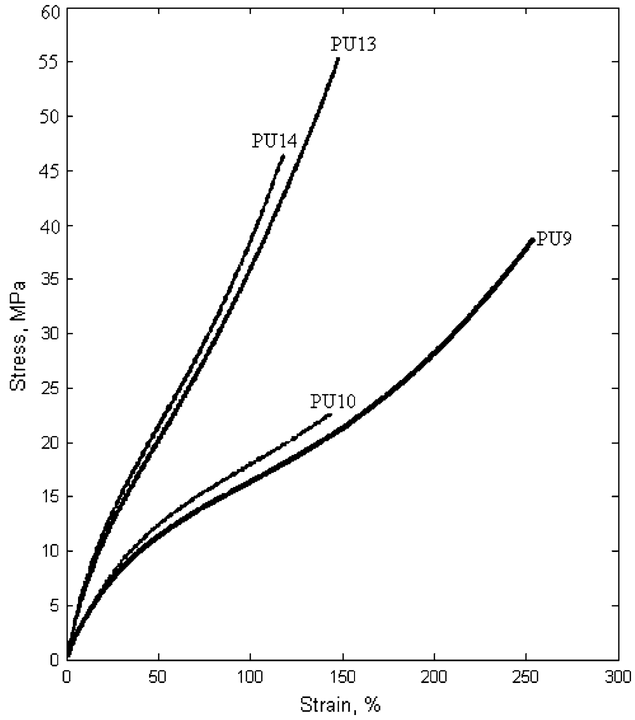


Fig. 4 Stress–strain curves of PU prepared with MDI

leading to modifications of stress–strain, modulus, and elongation [18].

The stress–strain curves representing the various chain extender/diisocyanate ratios, but with a common OH/NCO ratio, are grouped in Figs. 4 and 5.

Increasing the amounts of chain extenders in the PU elastomers, the tensile strength, modulus, glass transition temperature increased but the elongation decreased. These changes are due to the fact that the increase in the amounts of chain extenders resulted in high concentrations of HSs. As a result, with increasing weight percentage of chain extenders, the reinforcement from hydrogen bonding was enhanced and the cohesive energy density also increased.

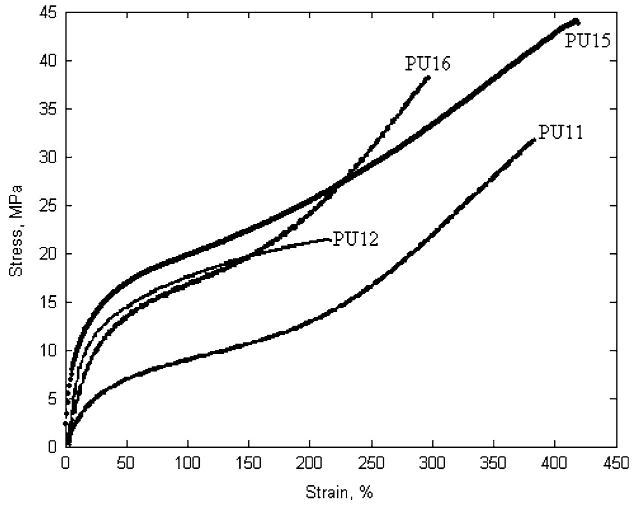


Fig. 5 Stress–strain curves of PU prepared with HDI

The results of physico-mechanical measurements are presented in Table 4, evidencing that increase in the methylenic group number of the chain extenders employed leads to a lower tensile strength.

Overall, there was a greater variation in properties with the chain extender/diisocyanate ratio. This effect is understandable since the former ratio has a more drastic effect on cross-link density. With increasing relative chains of the difunctional curing agent, and consequently a decrease in cross-link density, there was a general decrease in strength and a fourfold increase in elongation. The final elongation is plotted as a function of molecular weight per crosslink.

It is clear that the content of the HS increases and the cross-linking density increases. Varying the chain extenders molecular weight affects the tensile properties of the cross-linked PUs materials.

In segment PUs, the mechanical properties were generally accredited to the result of a pseudo-cross-linking effect resulting from the HS aggregation. The HS domain

Table 4 Tensile properties of PUs obtained

Sample code	E_1 (MPa)	L_1 (%)	FR (MPa)	AR (%)	FM (MPa)	AM (%)	E (MPa)
PU9	8.5	32.68	38.9	257	38.8	257	37.9
PU10	7.9	33.7	20.4	150	20.8	154.5	34.6
PU11	4.3	25.9	27.9	429.4	29.4	429.1	29.7
PU12	9.3	25.1	21.8	210.4	22.5	211	58.3
PU13	13.63	25.9	55.9	148.7	56	148.6	85.8
PU14	12.6	26.2	40.6	117	42.7	116.8	78.2
PU15	12	16.2	44	431	44.7	437	134
PU16	9.15	19.7	35.7	283	35.7	282.9	94

E_1, effective modulus to first transformation of phase; L_1, 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

Table 5 Shear modulus (G) and stiffness (Kh) of cross-linked PUs

Sample	G (daN/cm^2)	Kh (daN/cm)
PU9	132	3,013
PU10	113	1,845
PU11	95	1,115
PU12	193	3,505
PU13	284	4,370
PU14	262	4,013
PU15	442	9,472
PU16	315	6,540

generally exhibits a different degree of order structure, which was considered to be able to reinforce the HS domain and, in the case of these PUs, added a cross-linking effect of the glycerin.

Shear properties

A common application of rubber in shock and vibration control causes shear. Shear is in effect a combination of tensile and compressive forces acting at right angles to one another.

Assuming that the change in energy and shear modulus was due to the breakdown of intermolecular bonds, this was also considered from molecular weight between cross-links obtained from shear modulus. The maximal shear modulus and maximal stiffness of cross-linked aromatic PU, aliphatic PU is presented in Table 5.

The relaxation of the elastic network is often assumed to be limited to the normal modes relaxation of chain segments between covalent cross-links.

Under normal conditions, however, much more energy can be dissipated during shearing. This loss of energy arises from viscoelastic effects and strain-induced crystallization [19]. It was shown that the shear modulus of cross-linked PUs increases with increasing cross-link density and elasticity modulus.

The permanent deformation is an important parameter since it is directly related to the hysteresis phenomenon. In Figs. 6–9, the hysteresis experiment is shown. The sample is deformed cyclically. It is known that fundamental mechanical characteristics of viscoelastic materials are influenced by temperature, frequency, and shear strain [20]. In this study, cross-linked PU is developed for isolation-based device of buildings. So, it is necessary to investigate fundamental mechanical characteristics and dependencies. Figure 1 shows test piece (section, 250 × 250 mm^2; thickness, 40 mm). The number of cycles is at least five times.

A smooth bilinear hysteretic model which is capable of modeling the behavior depicted in Figs. 6–9 is appropriate for such analyses, as long as the peak shear strain is

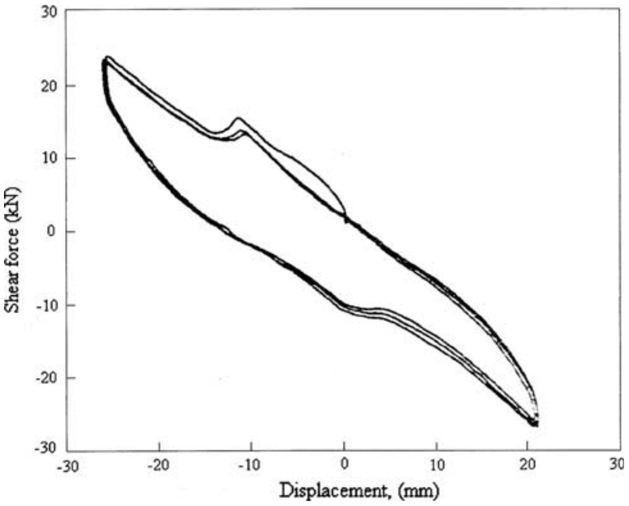


Fig. 6 Hysteresis loops for cross-linked polyurethane PU9

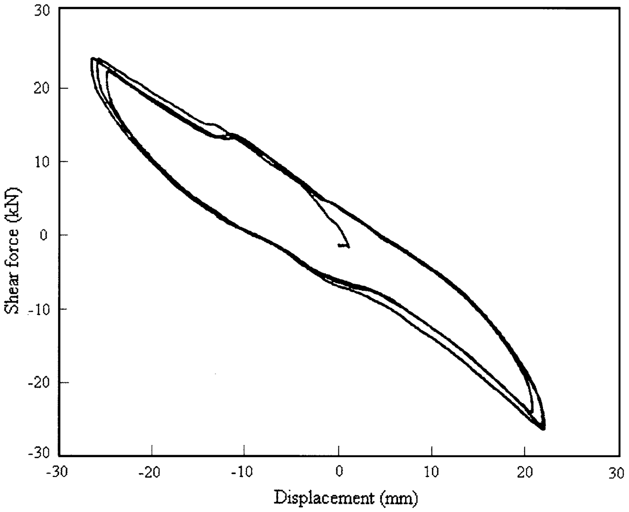


Fig. 7 Hysteresis loops for cross-linked polyurethane PU10

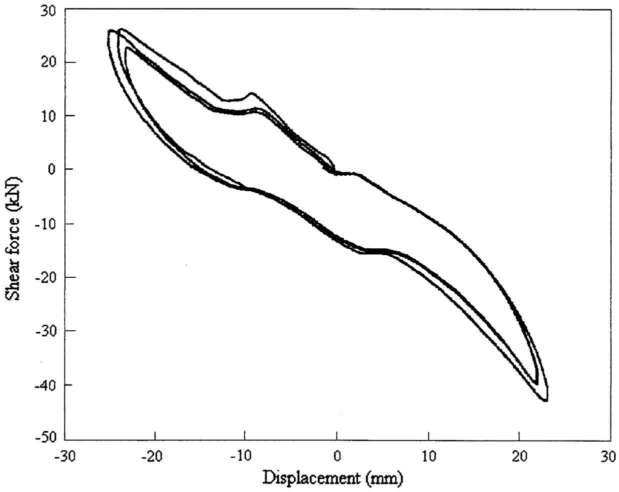


Fig. 8 Hysteresis loops for cross-linked polyurethane PU13

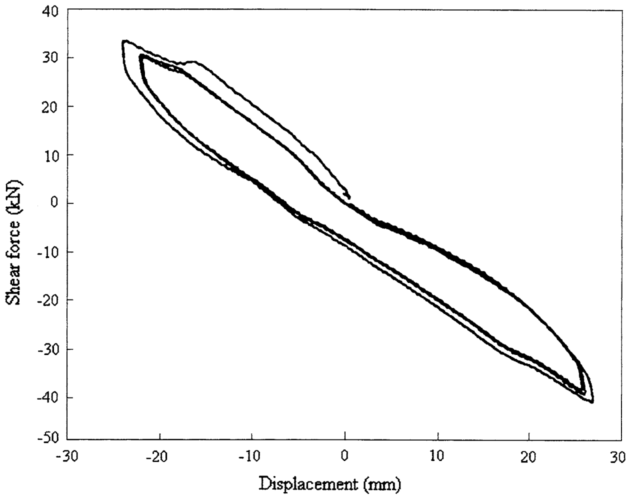


Fig. 9 Hysteresis loops for cross-linked polyurethane PU14

depending on the PU compound. However, at lower peak shear strain the analytical loops have a constant characteristic strength, whereas the experimental loops have a characteristic strength dependent on the shear strain amplitude. Nevertheless, the analytical model will likely produce acceptable results when the design parameters are based on the mechanical properties at a strain corresponding to the design displacement.

From the result of loading test, differences in mechanical characteristics of molded cross-linked PU are depended on shape factor.

Maximum responses are by 1/2/1 formulation and are shown in Figs. 6 and 7.

There are several factors that determine the resistance to shear. In the case of cross-linked polymer, shear strength increases with increasing molecular weight between cross-links. This can be accounted for the fact that shear energy arising from viscoelastic effects depends upon the degree of cross-linking. Additionally, the effect of strain-induced crystallization is more pronounced at high molecular weight between cross-links.

Two opposite effects may be observed. Higher molecular weight, between cross-links, gives rise to strain-induced crystallization but at the same time the concentration HSs decreases which will lower the resistance to shear. The net effect is likely to depend upon the structure of hard and soft segments.

Conclusions

Depending on the parameters of the formulation, the resulting PUs exhibited hardness about 50–80 Shore A, making them prospective materials falling into the category of the soft-grade PUs.

Longer chain lengths between cross-links 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. PUs show a three-step thermal degradation. The first stage was associated with the HS degradation and the second one with the soft segments. Higher length of the HS and the presence of glycerin linkages increased the PU thermal stability. The use of aliphatic diisocyanate structures enables light and color stable PU elastomers to be obtained.

The damping maximization is attributed to a higher strength of interaction between phases, and it is consequence of phase's interfacial cohesiveness and increased interface volume.

It appeared that cross-linking had a large effect upon the shearing modulus of the polymer which increased with increase in cross-linking density.

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