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Synthesis and characterization of cross-linked poly(esterurethane)s for elastomeric bearings

Summary — Cross-linked poly(esterurethane) elastomers (PEURs) have been synthesized in a two-step synthesis. In the first step poly(ethylene adipate) diol was reacted with 4,4’-diphenylmethane diisocyanate, then the obtained prepolymers were chain extended with bifunctional precursor (1,3-propane diol or 1,5-pentane diol) chains and a trifunctional cross-linker (glycerine) at stoichiometric ratios, resulting in a series of cross-linked products with various hard segment (HS) of various structure and content. Their thermal and mechanical properties were determined. Due to phase separation and cross-linked hard segments, propane diol based polyurethane exhibited high mechanical properties. The replacement of propane diol with pentane diol had a negative effect on these mechanical properties. The described cross-linked PEURs possessed strain/shape recovery properties.

Key words: poly(esterurethane)s elastomer, cross-linking, mechanical properties, thermal behavior, shearing stress deformation, shape recovery.

OTRZYMYWANIE I CHARAKTERYSTYKA USIECIOWANYCH ELASTOMERYCZNYCH POLI(ESTROURETANÓW) PRZEZNACZONYCH NA ELEMENTY NOŚNE

Streszczenie — Usieciowane elastomeryczne poli(estrouretany) (PEUR) otrzymywano w wyniku dwuetapowego procesu obejmującego syntezę prepolimeru w reakcji diolu na podstawie poli(adypinianu etylenu) (PEA, c. cz. 2000) z 4,4’-diizocyjanodifenylometanem (MDI) i następnie przedłużanie łańcucha tego prepolimeru z zastosowaniem 1,3-propanodiolu (D) bądź 1,5-pentanodiolu (PD) z jednoczesnym sieciowaniem przy użyciu gliceryny (Gly) (tabela 1). Uzyskano w ten sposób próbki PEUR (D1—D3 oraz PD1—PD3) różniące się zawartością oraz budową segmentów „twardych” i twardością (tabela 2). Scharakteryzowano widma IR tych produktów (rys. 2 i 3), ich właściwości cieplne (rys. 4, tabela 3) oraz przebieg krzywych rozciągania (rys. 5). Szczegółowo przeanalizowano zachowanie się PEUR w próbach odkształcania pod wpływem sił ścinających (warunki *quasi-statyczne*, amplituda 5 lub 50 kN, rys. 7—10). Zastąpienie D przez PD znacznie pogarsza właściwości mechaniczne produktów. Opisywane usieciowanie PEUR poddane działaniu naprężeń odkształcających mają zdolność powrotu do pierwotnego kształtu.

Słowa kluczowe: poli(eterouretany), elastomery, sieciowanie, właściwości mechaniczne, właściwości cieplne, naprężenie inicjujące, powrót przekształceniowy.

The availability of urban land for the construction of noise and vibration-sensitive structures is becoming limited. These new constructions generally situated above or in close proximity to existing railway lines, major roads and other “noisy” infrastructure.

The acoustic vibration and seismic isolation of a building requires the support of a comprehensive system of isolating bearing pads designed to operate under specific operating criteria.

Underground railway tunnels generate ground-borne vibration that can propagate into buildings. Bearings are also commonly used in the rail industry to prevent damage resulting from high impact loads on the rail support system.

High damping is associated with mechanical stability and thermal as well as sound isolation, providing 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 partially convert it into heat through viscous deformation [2].

Polyurethane elastomers are lightweight, easy to process and possess high strain/shape recovery ability which are required properties for application as damping materials. The physical and mechanical properties of polyurethanes depend on the starting materials used for their synthesis, the degree of phase separation between hard and soft segments and on the interconnectivity of the hard domains [3—8]. The hard segments act as physical cross-links which improve mechanical properties [9—13]. Most conventional polyurethanes are based either on polyester- or polyetherpolyols, 4,4'-diphenylmethane diisocyanate as an isocyanate component and 1,4-butanediol as a chain extender [14]. The development of soft polyurethanes (having a hardness of about 70—85 Shore A) has been reported where the main focus was on the polyol components [15].

Compared to conventional random cross-linking, the end-linking method can evaluate the structural parameters such as the number of elastic chains and cross-link density in the resulting networks on the basis of a nonlinear polymerization theory [16].

The high shear stress, to which a material is exposed can lead to serious negative consequences on shear hysteresis phenomenon in linear polyurethanes. This phenomenon is attributed to the disruption of physical cross-links of hard segments directly proportional to the increase in strain, leading to permanent deformation [17]. By chemically cross-linking the polymer, this problem can be avoided.

In this report cross-linked polyurethane copolymers with various hard segment ratios were prepared and their structures and thermo-mechanical properties evaluated in order to achieve an optimum combination.

The aim of this study is to synthesize polymers with good mechanical properties and high resistance to shear suitable for applications as passive isolation bearings in buildings and railway systems. Cross-linked poly(esterurethane)s (PEURs) were synthesized in a two step polymerization process. In the first step, a poly(ethylene adipate) diol (molecular weight 2000 g/mol) was reacted with 4,4'-diphenylmethane diisocyanate; and then the obtained prepolymers were chain-extended with glycerin and 1,3-propane diol or 1,5-pentane diol. The tensile strength, thermal properties and shear hysteresis of these cross-linked polyurethanes, each containing different hard segments were determined.

EXPERIMENTAL

Materials

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

Table 1. Materials used to obtain cross-linked poly(esterurethanes)

Material (symbol supplier)	Mol. wt.	Melting point, °C	Boiling point, °C	Density g/cm^3	Refract. index	Own results
4,4'-diphenylmethane diisocyanate (MDI, Fluka)	250.14	42—44	152—156/ 0.2—0.3 mm			
Poly(ethylene adipate) diol (PEA, Fibrex SA, Savinesti, Romania)	2000	50—55	—	1.175	—	C_{OH} = 56 mg KOH/g
1,3-propane diol (D, Sigma Aldrich)	76.09	-27	214	1.053	—	
1,5-pentane diol (PD, Sigma Aldrich)	104.15		242	0.994		
Glycerin (Gly, Sigma Aldrich)	92.9		182	1.261	1.474	

Polymer synthesis

The synthesis of the different kinds of PEURs were performed in a 1-L glass reactor at normal pressure, under nitrogen blanket and with vigorous agitation. The NCO/OH_{polyol} ratio of all formulations was in the 1.03—1.05 range. Poly(ethylene adipate) diol was reacted with 4,4'-diphenylmethane diisocyanate at 80 °C for 2 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 80 °C for 20 h. Under these conditions, addition of curving catalysts was not necessary. The polyurethane sheets thus prepared were used as samples for the determination of mechanical and physical properties and for thermal resistance studies.

Methods of testing

— Infrared spectroscopy (FT-IR) was performed in a VERTEX 70 Instruments equipped with a Golden Gate single-reflection ATR accessory in a spectrum range of 600 to 4.000 cm^{-1}.

— The thermal stability analysis of PEURs was performed using DERIVATOGRAPH Q-1500 D apparatus (Hungary). The initial sample weight was about 50 mg and the temperature was vamped from 30 to 700 °C at 10 °C/min.

— The thermal transition behavior was studied using differential scanning calorimetry (DSC) measurements in a temperature range of -60 °C to 60 °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 with dumbbell-shaped samples, that were cut from the obtained PEURs sheets. The measurement were done at 25 °C using a TIRA test 2161 apparatus (Germany) equipped with a 1 kN cell at a sample extension rate of 10 mm/min. At least five specimens were tested, and the average value was calculated.

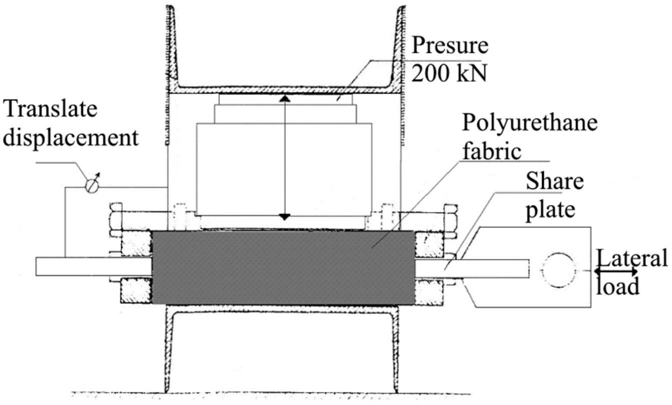

Fig. 1. Shear test system

— Shearing properties (axial force 0—100 kN) were determined at 20 °C using a loading system is shown in Fig. 1, with samples of dimensions 250 × 250 × 40 mm. Force was applied normally to the plane, operating a crosshead speed of 250 mm/min. The tests were repeated at heat five times.

— PEURs hardness was measured in an Instron Shore Durometer using scale-A.

RESULTS AND DISCUSSION

General characteristic and hardness

A series of poly(esterurethane)s was prepared consisting of aromatic hard segments (HS) derived from 4,4′-diphenylmethane diisocyanate and glycerin with 1,3-propanediol or 1,5-pentane diol, and also soft segments of poly(ethylene adipate) diol. The average HS content and composition of were controlled by applying appropriate molar ratios of PEA/MDI/diol and triol used in the synthesis, which varied from 1/2/1 to 1/3/2 and 1/4/3. An equimolar $OH_{diol}/OH_{glycerin}$ ratio was used in each of the synthesized polyurethane samples.

The formulations used and their hardness are shown in Table 2. The average soft-segment length was maintained while the HS was systematically varied.

PEA, MDI and D led to poly(esterurethane)s with Shore hardness in the range of 55—83° A that may be classified as soft grade polyurethanes. Their mechanical properties are comparable to general purpose rubber materials of good quality. By decreasing the HS content, it was possible to prepare PEUR with hardness as low as 55 Shore (sample D1).

Table 2. Poly(esterurethane)s formulations and their hardness

Samples of PEUR designation	Polyester/MDI/ chain extenders ratio	Chain extenders (Gly + D or PD)*)	Hardness Shore A, °
D1	1:2:1	D	55
D2	1:3:2	D	72
D3	1:4:3	D	83
PD1	1:2:1	PD	58
PD2	1:3:2	PD	67
PD3	1:4:3	PD	78

*) The OH diol/OH glycerin ratio was 1/1 in each of the samples.

An increase in HS content resulted in an increase in Shore hardness (Table 2) and a slight change in glass transition temperature. Hard domain formation has a significant influence on the mechanical and thermo-mechanical properties of PEURs, such as maximum stress, tensile modulus, and elongation at break.

IR spectroscopy

FT-IR spectra of the polymers (Figs. 2 and 3) indicated an absence of any residual isocyanate (no absorption at 2270 cm^{-1}). The appearance of a sharp peak at 1730 cm^{-1} is due to the hydrogen bonded carbonyl and the strong absorption at 3320 cm^{-1} is due to the N-H stretching of the formed urethane linkage.

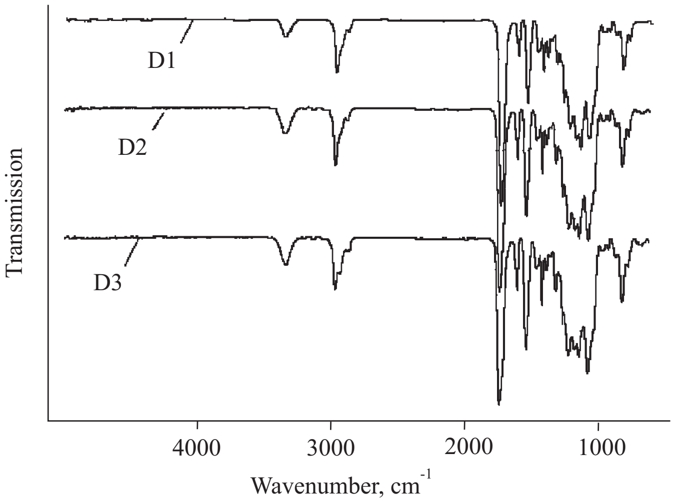

Fig. 2. IR spectra of PEUR samples synthesized with D as a component of chain extender

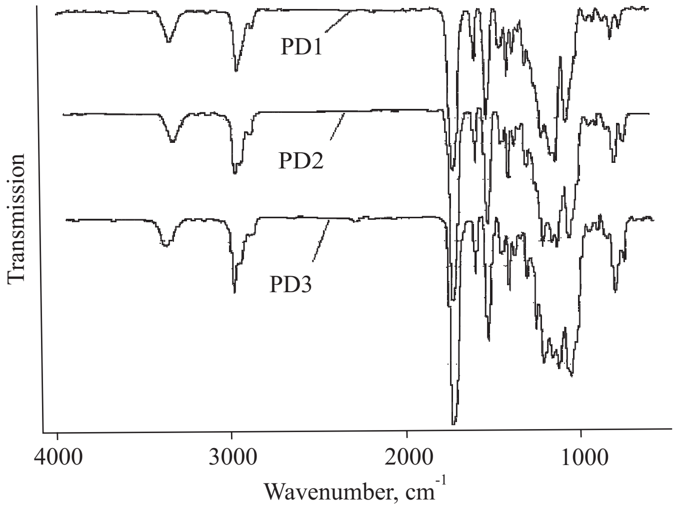

Fig. 3. IR spectra of PEUR samples synthesized with PD as a component of chain extender

The C-O-C stretching at 1370 cm^{-1} is characteristic for ester with the inclusion of polyester in the polymer chain. Similarly the peak for CH_2 stretching appears at 1470 cm^{-1}. The hydrogen bonding among HS coupled with dipole-dipole interaction between the carbonyl groups primarily affects the C=O stretching vibration. The carbonyl stretching peak indicates that an increase of HS content leads to extensive interactions [18]. Such strong interaction among HS will probably lead to phase separation or domain formation [19, 20] and chemical cross-links which is quite desirable in order to obtain a shape memory effect.

Thermostability

Representative thermogravimetric data for various PEUR samples is presented in Table 3.

Table 3. Thermal characteristics of poly(esterurethane) samples

Samples of PEUR designation	Weight losses global, %	T_i, °C	$T_{5\,\%\,\text{losses}}$ °C	T_{max}, °C
D1	95	100	310	350
D2	96	120	340	370
D3	98	120	350	425
PD1	96	115	315	365
PD2	96	120	335	395
PD3	97	125	355	435

One of the objectives of this paper is to compare the thermal decomposition process of the poly(esterurethane) elastomers based on MDI while modifying chain extenders. Open-air TG was used to study some PEUR samples with the aim of outlining the increase in thermal stability caused by the introduction of components into their structure. Purpose all the tested samples were subjected to the same testing conditions. The onset of degradation temperature (T_i) was defined as the initial temperature of degradation, corresponding to the intersection of the tangent drawn at the inflection point of the decomposition step and of the horizontal zero-line of the TG curve.

The tendency to form a hydrogen bond between the carbonyl group in the soft segment and the urethane hydrogen atom in the HS makes the interaction between the soft segment and the hard segment in PEUR stronger.

The physical cross-links are important for providing dimensional stability and for stopping cold flow in the uncured material. Restriction of segmental motion in the three-dimensional network by chemically cross-linked sites results in an effect similar to that of microdomain physical cross-links, except that the former is irreversible [21].

The crystalline polyester domains act as additional physical cross-link sites below their melting temperature.

Maximum weight loss was observed in the 280—570 °C temperature range. An increase in the hard domain content (D1 → D3, PD1 → PD3) led to a relative stability because of the high tendency of chain ordering. In the DTG curve of PEURs, an inflexion is observed at about 350—435 °C (see Table 3).

An increase in the value of T_{max} cause by an increase of HS indicates a lower rate of diffusion of the degraded products as indicated by the lower degradation rate peak exhibited at these temperatures. Thus, it is evident that the cross-linking bonds restrict the diffusion of the degradation products from the matrix.

Thermal transitions

DSC thermograms of cross-linked PEURs are presented in Fig. 4.

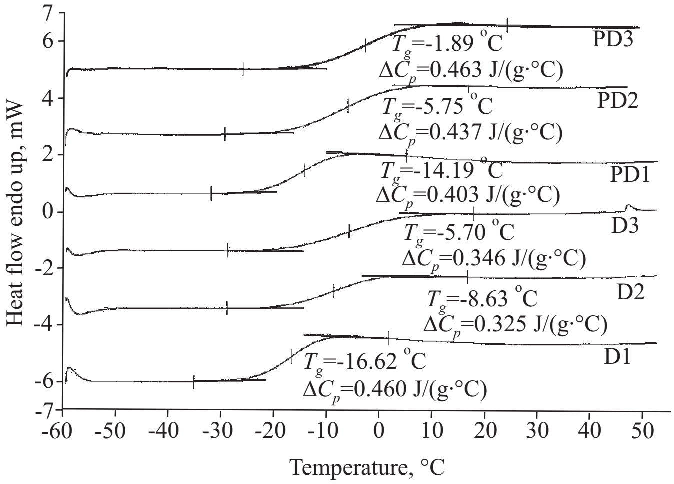

Fig. 4. DSC scans of cross-linked PEURs

The DSC scan of the propane diol based PEURs (samples D1—D3) exhibits a T_g from -16.6 °C to -5.7 °C, depending on HS content. The T_g value is higher than that T_g of the pure soft segment oligomer, indicating that there is some mixing of HSs in the soft segment phase [22, 23] has occured. The DSC scan of pentane diol based PEURs (samples PD1—PD3) exhibits a T_g from -14.19 °C to -1.89 °C.

The T_g for cross-linked poly(esterurethane) with higher HS content is higher because of an increase in cross-link density resulting in a stronger interaction between the molecules in the hard domains.

The transition at higher temperatures corresponds probably, to the disruption of the ordered segments [24]. A continuum of ordered segment morphologies exists between the completely amorphous and perfectly crystalline states. This is referred to as the order-disorder transition [25]. The increase in the glass transition temperature caused by an increase in the HS content corresponds with the modulus results.

Stress-strain behavior

Stress-strain, modulus and elongation are important parameters for PEUR characterization and are dependent on structural differences, cross-linking density and intermolecular interactions between their respective HS.

Higher HS contents results in higher modulus and lower elongations. This may be due to an increase in the content of polar groups, cross-linking density and cohesive energy density. Polar groups, which have a high cohesive force participate in intermolecular hydrogen bonding and restrict the rotation of polymer segments, thus generating hardness.

The stress-strain curves representing the various chain extender/diisocyanate ratios, but with a common OH/NCO ratio, are grouped in Figs. 5 and 6. A change in tensile properties depending on the cross-linking of HS can be observed.

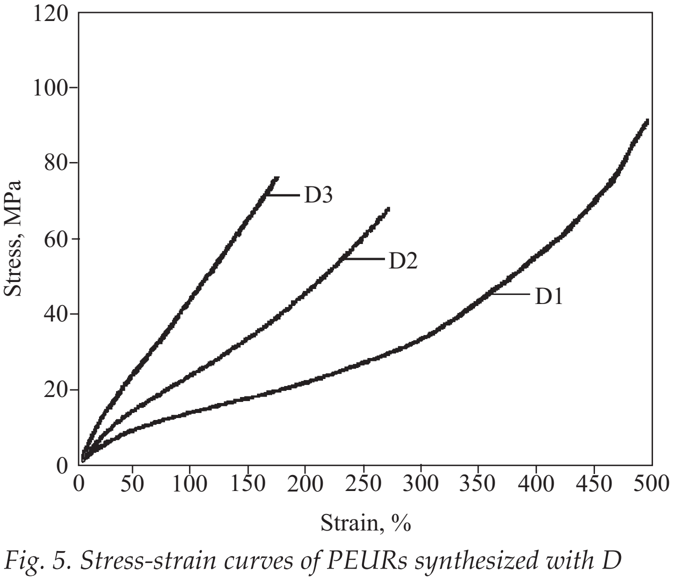

Fig. 5. Stress-strain curves of PEURs synthesized with D

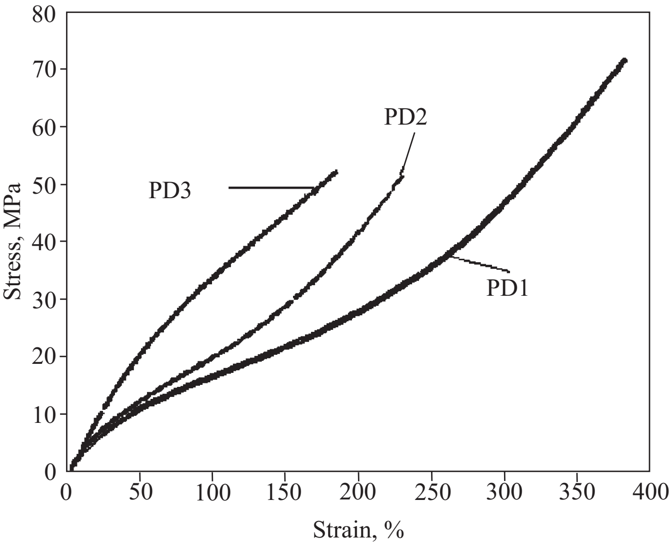

Fig. 6. Stress-strain curves of PEURs synthesized with PD

Young's modulus of propane diol based PEURs follows the sequence 18 < 42 < 90 MPa while the order for pentane diol based PEURs 22 < 27 < 57 MPa corresponding to the increase in cross-linked HS content from 1/2/1 to 1/4/3 molar ratio.

Shear tests

Exposure of rubber to vibration and shock causes shear. Shear is in effect a combination of tensile and compressive forces acting at right angles to one another. These tests also serve to verify the ability of the isolation bearings to withstand numerous cycles of shear displacements.

The behavior of PEURs elastomer bearings under compressive as well as cyclic horizontal loading conditions is presented in this work. The hysteretic behavior of the cross-linked poly(esterurethane) bearings was studied for different loading amplitudes and repeated cycles. A series of shear tests was performed to determine the effective horizontal stiffness and equivalent viscous damping for varying shear strains.

The change in energy and shear modulus was caused by the breakdown of intermolecular bonds. The addition of chemical cross-links to physical cross-links formed a coherent network. The relaxation of the elastic network is often assumed to be limited to the relaxation of chain segments between covalent cross-links. If this network is then subjected to an external load the response is viscoelastic.

A higher amount of energy can be dissipated during shearing by viscoelastic effects and strain induced crystallization. These studies confirm, that the shear modulus of cross-linked PEURs increases with increasing cross-link density.

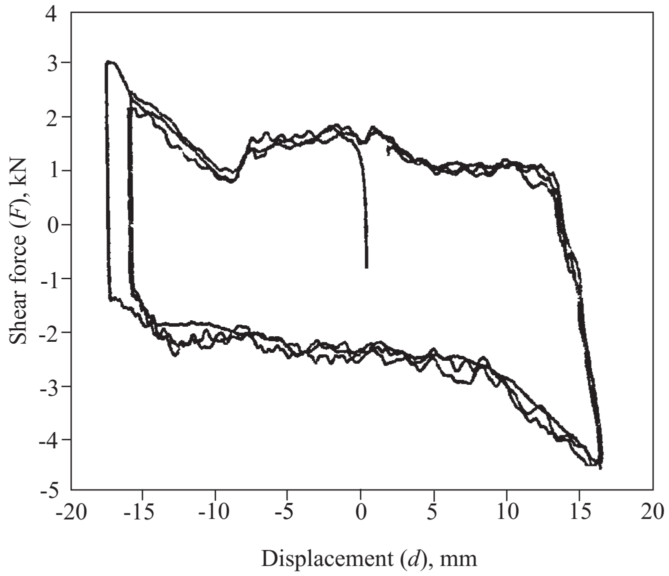

Fig. 7. Load-deflection behavior of PEUR bearing D1 in quasi-static test (amplitude = 5 kN)

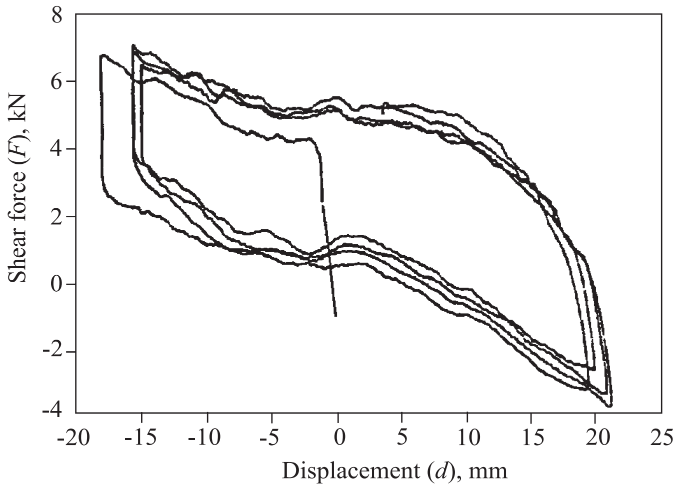

Fig. 8. Load-deflection behavior of PEUR bearing PD1 in quasi-static test (amplitude = 5 kN)

Permanent deformation is an important parameter since it is directly related to the hysteresis phenomenon. The sample is deformed cyclically. It is known that fundamental mechanical characteristics of viscoelastic materials are influenced by temperature, frequency, and share strain [26].

Figures 7—10 show test PEUR bearings D1 and PD1 under combined vertical and horizontal loading. The damping of the bearing has to be kept low but sufficient enough for displacements to be maintained within acceptable limits.

The hysteresis loops obtained from these tests are analyzed to compute such parameters as effective horizontal stiffness (S_{eff}) and equivalent viscous damping (E_{vd}). S_{eff} is based on the values of peak force (*F*) and peak displacement (*d*):

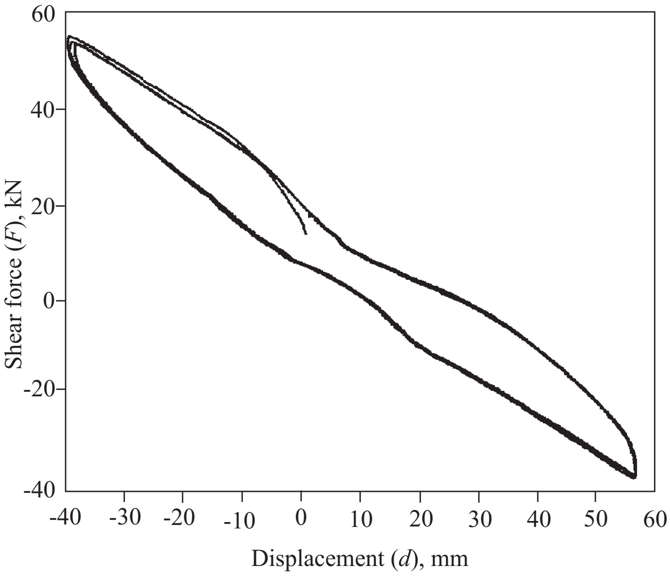

Fig. 9. Load-deflection behavior of PEUR bearing D1 in quasi-static test (amplitude = 50 kN)

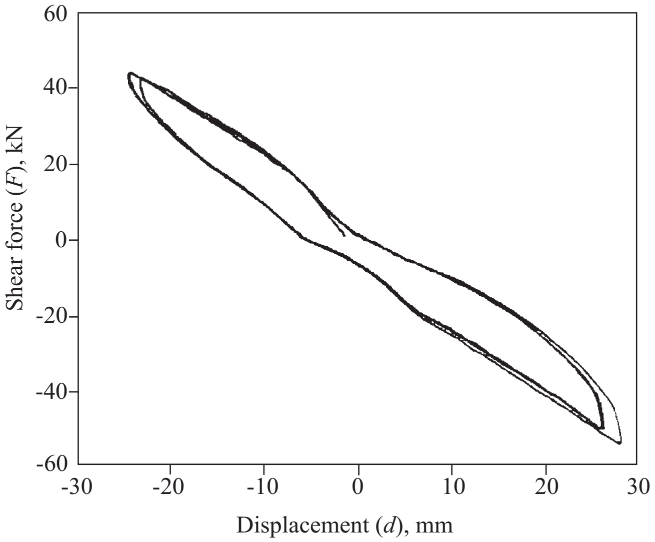

Fig. 10. Load-deflection behavior of PEUR bearing PD1 in quasi-static test (amplitude = 50 kN)

$$S_{eff} = \frac{F_{\max} - F_{\min}}{d_{\max} - d_{\min}} \tag{1}$$

The area within the hysteresis loop represents the energy dissipated by the bearing.

E_{vd} value exhibited by the bearing is calculated from the expression [27]:

$$E_{vd} = \frac{W_d}{4\pi W_S} \tag{2}$$

where: W_d — *dissipated energy (area of the hysteresis loop),* W_S — *elastic strain energy equal to 1/2* $S_{eff}\, d^2_{max}$.

To observe the effect of the number of cycles on the behavior of laminated rubber bearings, the tests were performed for 5 cycles of sinusoidal waveform with constant amplitude of ±5 kN (Figs. 7 and 8) or ±50 kN (Figs. 9 and

10). Five cycles of horizontal load were applied at each amplitude level. S_{eff} at 5 kN shear strain has the value of 198 kN/m which decreased to 123 kN/m at 50 kN shear strain. The computed design value of horizontal stiffness is 95 kN/m.

The equivalent viscous damping, obtained from the area of hysteresis loops for different shear strains, shows a downward trend with an increase in shear strain. Namely, with the increase of shear strain from 5 kN to 50 kN, the damping decreases from 5.5 % to 3.5 %. It is observed from the Figures 7 and 9 that area of loop decreases with the increase in loading from 5 to 50 kN.

The results of shear tests conducted for repeated cycles show that no degradation of stiffness observed during the continuous cycles. The described isolation system shows stable hysteretic behavior.

CONCLUSIONS

Glicerine and 1,3-propane diol or 1,5-pentane diol have been formed to be suitable chain extenders for elastomeric poly(esterurethane)s synthesized from poly(ethylene adipate) diol and MDI.

Depending on the formulation parameters, the resulting products exhibited hardness in the range of 50—80 Shore A, making them potential materials classified as soft grade polyurethanes.

Thermal stability of the poly(etherurethane)s depends on the components used for formulation. The two-stage decomposition was associated with HS soft segments degradation respectively. A higher content of HS and the presence of glycerin linkages increased the polyurethane thermal stability.

Longer chain lengths between cross-links result in larger elongation at break and lower mechanical modulus. The cross-linking process increases the domain rigidity of the urethane, but decreases the soft segment crystallinity. These factors enhance the tensile strength of the materials.

The PEUR bearings perform well under repeated cycles of loading. They exhibit stable hysteretic behavior without any significant degradation stiffness degradation and are effective for based-isolated structures.

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