

Polyurethane Elastomeric Bearing Materials for Passive Isolation of Railway

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Developed in last decade, the shape memory polymers have been gaining widespread attention for new product innovation. They are lightweight, have high strain/shape recovery ability, easy to process and required properties can be tailored for variety of different applications. Polyurethane elastomers (PUs) based on polyether diols and aliphatic diisocyanates can be used as passive isolation bearings in railway applications. In the present study poly(1,4-butane) diols (Terathane) and 1,6-hexamethylene diisocyanate (HDI) have been used in polyurethanes, using glycerin, 1,4-butane diol or 1,6 hexane diol as chain extenders. Effect of varying the concentrations of diisocyanates and structure and amount of chain extenders on polyurethane elastomers has been discussed with reference to mechanical properties. IR and thermal analysis techniques (TGA) were used for characterization.

Keywords: polyurethane elastomers, chain extenders, mechanical properties, railway isolation

Urban land availability for building new structures is becoming more restrictive, thereby accelerating the trend for the new construction and other noise and vibration-sensitive structures above, or in close proximity to, existing railway lines, major roads and other "noisy" infrastructure.

The acoustic vibration isolation of a building requires the structure to be supported on a comprehensive system of isolating bearing pads designed to perform under specific operating criteria.

Trains running in underground railway tunnels generate ground-borne vibration that can propagate through the ground and into buildings. Typical vibration levels lie in the range from 0.1 to 1.0 mm/s and peak in the frequency range from 40 to 80 Hz. Although these levels are unlikely to cause even light damage to buildings, they can cause unacceptable levels of internal noise and vibration.

Bearings are commonly used in the rail industry to prevent damage resulting from high impact loads on the rail support system. These rubber pads are subjected to high compressive loads and are exposed to direct sunlight.

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].

Although most of published literature [2-11] interpret the temperature spread in a dynamic-mechanical analysis as the damping capacity, this interpretation has received some criticism and the application of the integration of the area under the linear loss modulus function of temperature curves has been suggested as a quantitative measurement of the damping capacity of the material by many authors [7-11], supported by the fact that the loss modulus E'' is directly proportional to the heat dissipated per cycle of dynamic deformation.

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

Specific interactions among non-miscible dissimilar components tend to increase damping as it contributes to increase the cohesiveness and the connectivity between phases separated components, while the intermolecular cross-linking density increases the cohesiveness of each phase and its influence on the damping depends on the morphology of the resultant system. Hence, 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. In all materials studied it has been proved to be essential to track their morphology, and in heterogeneous polymeric system it has been noted that finer dispersed phase meant higher damping, as an expected result of the increase in damping by the interface of the immiscible system.

In this study, polyurethane elastomers based on poly(1,4-butane)diols (Terathane1400), 1,6-hexamethylene diisocyanate (HDI) and glycerin, 1,4-butane diol or 1,6-hexane diol as chain extenders were synthesized. The thermo-mechanical properties have been studied to estimate the railway isolators properties of synthesized polymers.

Experimental part

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 de-moistured under vacuum at 120°C for about 2 h prior to use.

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Table 1
MATERIALS USED TO OBTAIN ALIPHATIC 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	—	
1,6 hexane diol (HD)	118,1	38	250	—		
glycerin	92,9		182	1,261	1.4740	
1,6 hexamethylene diisocyanate (HDI)	168,2		255	1,040	1,4520	
Poli(1,4-butanediol) Terathane 1400	1400	33-36				

Preparation of polyurethanes

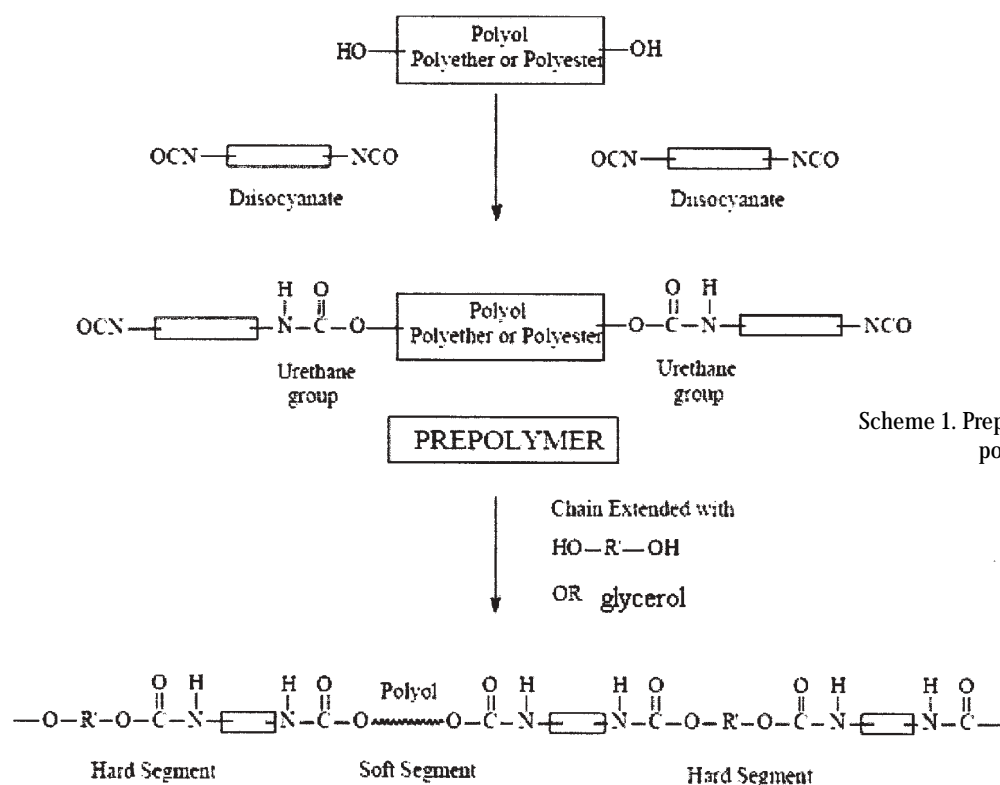
All the linear polyurethane systems presented in the following paragraph are synthesized according to the prepolymer method. Polyurethane elastomers are produced on an industrial scale by means of this technique. In this process, isocyanate-terminated pre-polymers are obtained by reaction of difunctional, hydroxy-terminated oligoethers with an excess of a low molecular weight diisocyanate. Low molecular weight diols are added as called chain extenders to a further couple of these prepolymers. Linear, phase segregated polyurethane-block copolymers are obtained in this way. Each polymer chain contains segments of high polarity composed of urethane bonds that are linked through chain-extender molecules. As a consequence of their high intermolecular interaction, they form the so called hard segments. They represent the hard-segment forming phase that is embedded in an amorphous elastic matrix. This amorphous matrix, with its low glass transition temperature lying far below the normal operating temperature, forms the so called soft

segment. In the case of polyurethanes with shape-memory effects, this segment serves as a switching segment. For this purpose it is modified in such way that the thermal transition is located in a temperature range relevant for the respective application.

Practically, the synthesis of PUs was performed in a one litre 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 hour to yield a prepolymer that was mixed in the second step with chain extenders at 90°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 polyurethane sheets thus prepared were used for the determination of mechanical and physical properties and for the resistance study.

IR spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique.



Scheme 1. Prepolymer method for the synthesis of polyurethane elastomers

Table 2
HARDNESS OF THE POLYURETHANES OBTAINED

Nr.	Designation samples	Rate Polyether/Diisocyanate/ Chain extenders	Diisocyanate	Chain extenders	Hardness Shore A
1.	PU11	1:2:1	HDI	BD	53
2.	PU12	1:2:1	HDI	HD	65
3.	PU15	1:3:2	HDI	BD	76
4.	PU16	1:3:2	HDI	HD	73

Hardness was measured on Instron Shore Durometer using scale-A.

Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films at room temperature on a TIRA test 2161 apparatus from Germany. Measurements were run at an extension rate of 10 mm/min, at 25°C.

Thermogravimetric analyses were performed on a DERIVATOGRAPH Q-1500 D apparatus (Hungary) in a temperature range from 0-700°C. The heating rate was 12°C/min in air atmosphere and sample size was 50 mg.

Results and discussion

Any alterations in the polyol and prepolymer ratio (-NCO/-OH) cause substantial morphological changes in the

resins' chains, leading to modifications in the material mechanical properties, such as flexibility and rupture stress. The degree to which the polymer chains cross-link is controlled by the isocyanate group (-NCO-) existing in the pre-polymer and by the hydroxyl group existing in the chain extenders.

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

- Type of OH groups (primary or secondary) of the chain extenders diol and its structure and molecular weight
- Hard segment content

Polyether, HDI and BD lead to polyurethanes with Shore hardness about 50-80. That may be classified as soft grade PUs. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

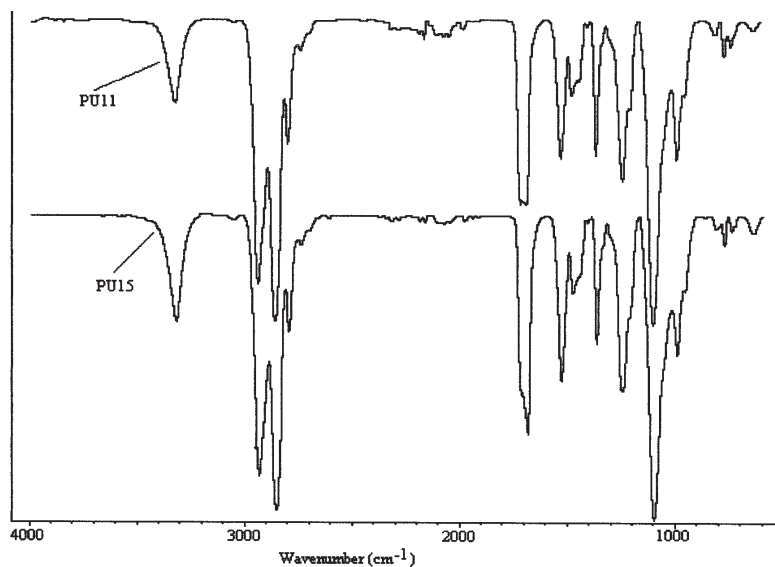


Fig. 1. IR spectra of polyurethane samples synthesized with BD

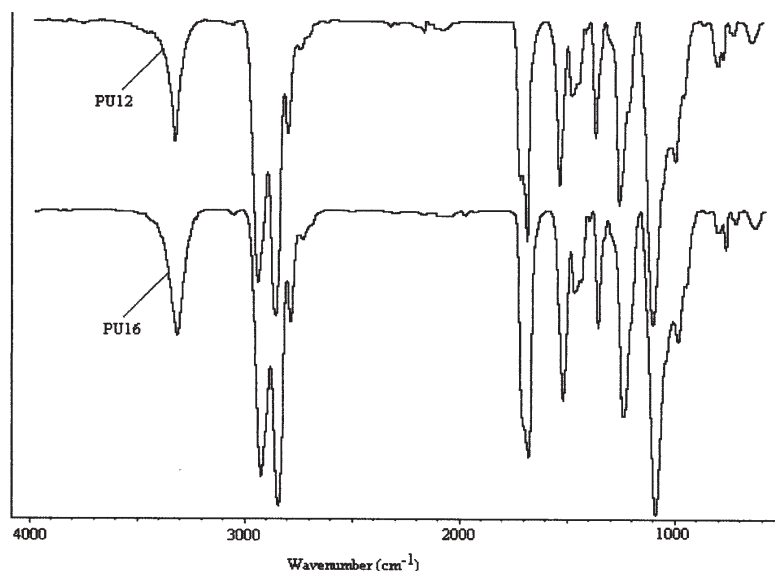


Fig. 2. IR spectra of polyurethane samples synthesized with HD

The role of chain extenders molecular weight 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 1,6 hexamethylene 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 yielded a soft PU product with hardness 50-55 Shore A, good elongation and relatively high softening temperature.

IR Spectroscopy

IR spectra of the polymers were used to confirm the formation of PU.

Formation of the polymer was confirmed by the disappearance of the isocyanate stretching band at 2200-2300 cm^{-1} . Appearance of new sharp peak for N-H stretch and for NHCOO (urethane) at 1740 cm^{-1} verifies the formation of polyurethane. Similarly the peak for CH_2 stretch appears to 1470 cm^{-1} . Participation in hydrogen bonding decreases the frequency of the NH vibration and increases its intensity, making this absorption useful in the study of hydrogen-bond effects. The peak is located at about 2980-2990 cm^{-1} in the spectra (figs. 1,2), which is characteristic of hydrogen-bonded NH groups.

Thermogravimetric analysis

Representative thermogravimetric (TG, DTG) curves for various copolymers have been reproduced in figures 3-6. However details of degradation temperatures have been elaborated in table 3.

The open-air TGA was used to study some linear polyether 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 [17,18].

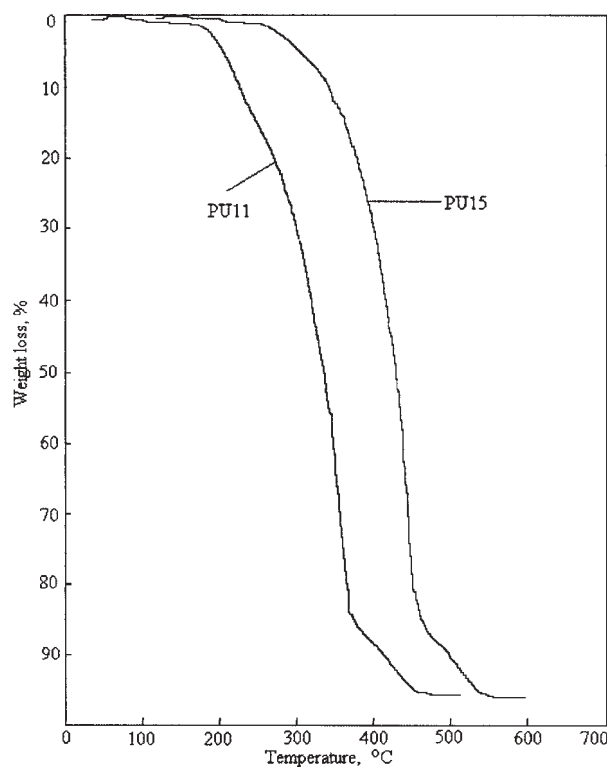


Fig. 3. TG curves of polyurethanes with BD

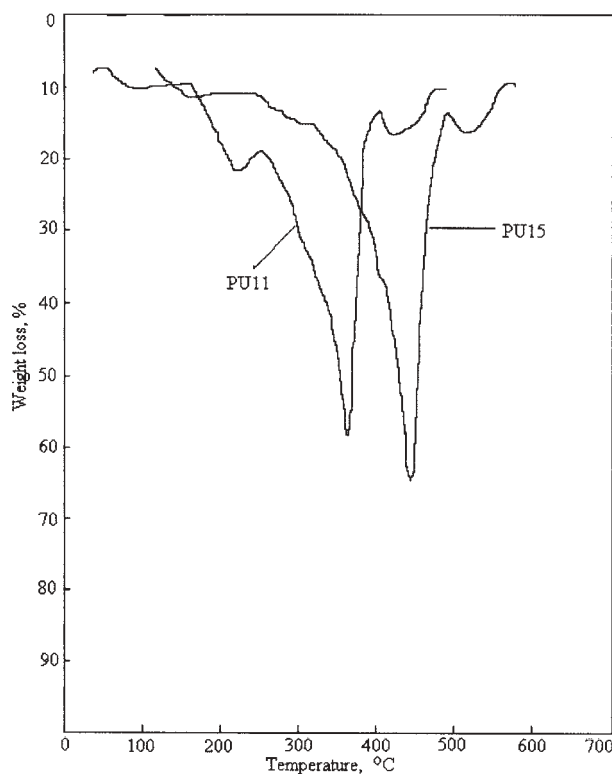


Fig. 4. DTG curves for polyurethanes with BD

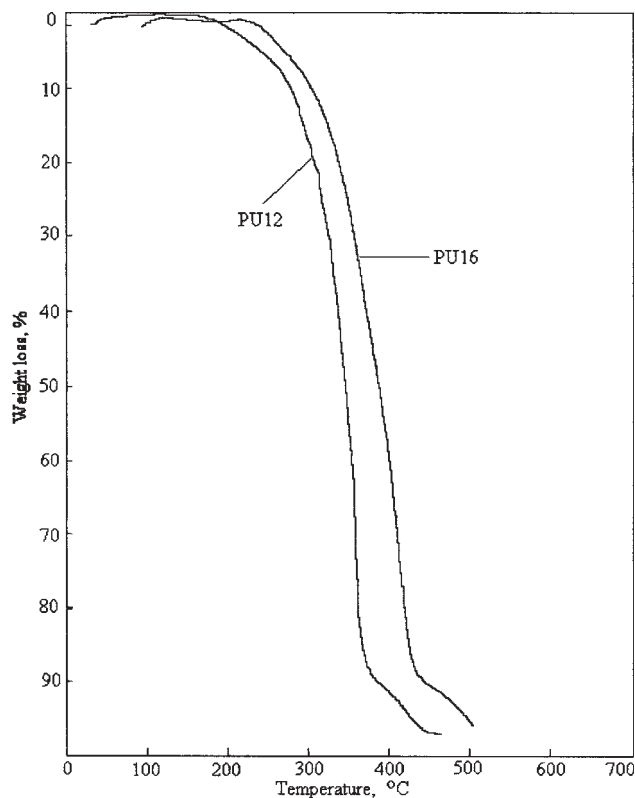


Fig. 5. TG curves of polyurethane with HD

The MDI based system can also have more complete microphase separation. The physical crosslinks 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 crosslink sites is similar to that of microdomain physical crosslinks, except that the former is irreversible.

Generally, polyurethanes analyzed decomposed in three steps and the temperature for which the weight losses were maximum is 220-450°C. The increase of

Table 3
THERMOGRAVIMETRIC DATA FOR THE ALIPHATIC POLYURETHANES

Sample code	Weight losses (%) and decomposition temperature ranges			
	Global	Step I	Step II	Step III
PU11	96	5(100-210)	81(210-380)	10(380-520)
PU15	97	6 (120-320)	84(320-470)	7(470-600)
PU12	97	8(115-270)	82(270-375)	7(375-480)
PU16	95	6(100-340)	85(340-460)	4(460-500)

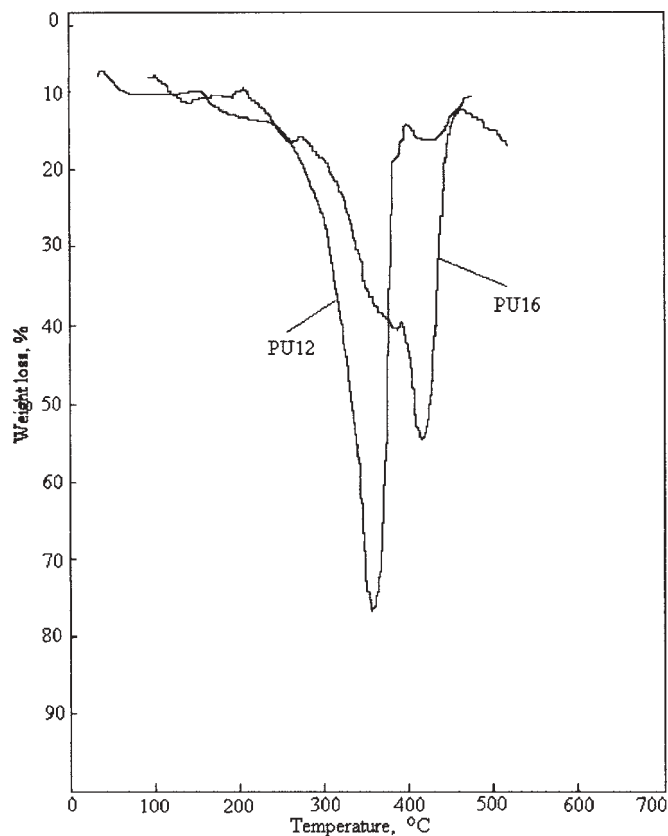


Fig. 6. DTG curves for polyurethanes with HD

flexible chain leads to relative stability, because the possibility of molecular chain order to be high, after an accentuated decomposition.

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 a rate of the reagents 1/2/1 and 450°C for polyurethane with a rate of the reagents 1/3/2.

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.

Mechanical properties

The mechanical behavior 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,

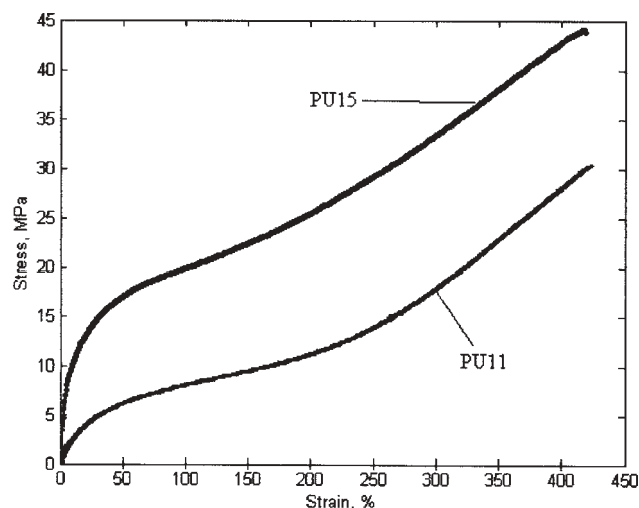


Fig. 7. Stress-strain curves of polyurethane prepared with BD

as well as variation of chain extenders structure, leading to modifications of stress-strain, modulus and elongation [19].

If the amount of 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/diisocyanate ratios, but with a common OH/NCO ratio, are grouped in figures 7,8. This figure, in essence, shows the change in tensile properties with crosslink density.

Increasing the amounts of chain extenders in the polyurethane 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 hard segments. As a result, with increasing weight percentage of chain extenders, the reinforcement from hydrogen bonding was enhanced and the cohesive energy density also increased.

The results of physico-mechanical measurements are presented in table 4, evidencing that an increase of 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 than with the OH/NCO ratio. This effect is understandable since the former ratio has a more drastic effect on crosslink density. With increasing relative chains of the difunctional curing agent, and consequently a decrease in crosslink 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.

The results of physico-mechanical measurements are presented in table 4, evidencing an increase of the tensile

Table 4
TENSILE PROPERTIES OF POLYURETHANES OBTAINED WITH ALIPHATIC DIISOCYANATES

Sample code	E ₁ MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PU11	4.5	25	28	430	29	429	29.4
PU15	12	16	49	481	49.7	477	194
PU12	9.3	15	14	130	15.5	135	183
PU16	9	19.7	35.7	283	35.7	282.9	94.6

E₁ - 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

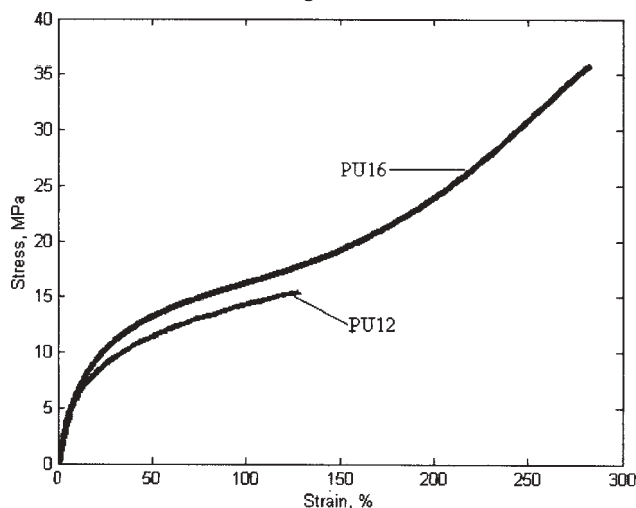


Fig. 8. Stress-strain curves of polyurethane prepared with HD

strength from 28 to 50 MPa, for a rate of reagents 1/2/1 at 1/3/2.

This fact, can be explained by the formation of hydrogen bonds (NH...O=C<) with a much higher frequency in the case of 1/3/2 rate [20].

With increasing concentration of the hard segments in the formulations of polyurethane elastomers, the tensile strength and modulus increased. Because the crystalline regions play a similar role to crosslinks in improving mechanical properties, the tensile properties of crystallizable material are superior to non-crystallizable material. The influence of molecular weight on the ultimate tensile properties of the hard segment is larger than that of the previously studied factors, especially at low molecular weight. It is clear that, the content of the hard segment increases, and the crosslinking density increase. Varying the chain extenders molecular weight affects the tensile properties of the polyurethanes and the crosslinked materials.

In segment polyurethanes, the mechanical properties were generally accredited to the result of a pseudo-crosslinking effect resulting from the hard-segment aggregation. The hard-segment domain generally exhibits a different degree of order or semicrystalline structure, which was considered to be able to reinforce the hard segment domain and, in the case of these polyurethanes, added a crosslinking effect of the glycerin.

This present study may provide possibilities of enhancing the mechanical properties of the polyurethane material.

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).

The mechanical resistance, increasing values of stress with strain and modulus of elasticity, was favored by increasing NCO/OH ratio and decreasing length of chain extender.

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 crosslinks 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. The use of all aliphatic diisocyanate structures enables light and color stable PU elastomers to be obtained.

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