Polyurethane Materials Using Aliphatic Diisocyanates for Passive Isolation in Buildings Applications

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During the past decade, a lot of effort has been spent to develop strategies to mitigate the damaging effects of earthquakes. This work has been directed at both civil structures and nuclear facilities. Polyurethane elastomers (PEs) based on polyethylene adipate diols and aliphatic diisocyanates can be used as passive isolation bearings in buildings applications. In the present study, polyesterdiol and 1,6-hexamethylene diisocyanate (HDI) have been used in polyurethanes, using glycerine, ethylene or diethylene glycols as chain extenders. Effect of varying the concentrations of diisocyanates and structure of chain extenders on PEs has been discussed with reference to mechanical properties. IR and thermal analysis techniques (TGA) were used for characterization. The results reveal that aliphatic character of diisocyanates lowers the temperature required to achieve the flexibility in the polymer. Based on their mechanical properties, PEs have great potential for applications where wind and earthquake loads resistance, dynamic-to-static stiffness ratio and vertical and lateral load characteristics are required.

Keywords: aliphatic diisocyanates, passive isolation, chain extenders

The protection of nuclear and civil structures from the devastating effects of earthquakes has been the focus of intense research and development throughout the world. Seismic isolation is an effective means for reducing and even eliminating the devastating effects of earthquakes on people, equipment and structures. A seismic isolation device is placed between the ground and the structure. The isolators effectively decouple the structure from the strong earthquake motion.

Polymers can absorb mechanical energy and convert this energy partially into heat through viscous deformation [1].

Polyurethane elastomers (PEs) have a very unique property of shape memory. These (PEs) basically consist of two phases, a frozen phase and a reversible phase [2-6]. Thermally reversible phase maintains a transient shape while fixed structure allows the recovery of the original shape. Shape memory property is governed by glass transition and melting temperature of polymer segments [7]. Polyurethanes are formed by linear polymeric chains of segmented structure.

Physical properties of polyurethanes depend on the raw materials used for their synthesis. The hard segments act as physical crosslinks and, as a consequence, the physical[8], mechanical [9-11] and adhesive [12] properties depend on the degree of phase separation between hard and soft segments and interconnectivity of the hard domains.

Most of conventional PUs are based either on polyester or polyether polyols, 4,4-diphenylmethane diisocyanate (MDI) as an isocyanate component and 1,4-butanediol (BDO) as a chain extender [13].

Development of soft grades of PUs (having hardness about 70-85 Shore A) has been reported among the latest trends that are taking place in the PU market. The main interest of researchers is focused on the polyol components [14].

In this study, shape memory (PEs) based on polyethylene adipate diol (PEA), 1,6-hexamethylene diisocyanate (HDI) and glycerine, ethylene or diethylene glycols as chain extenders were synthesized. The thermo-mechanical properties have been studied to estimate the building isolators properties of synthesized polymers.

Experimental part

Materials

All 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 the content of moisture and, if necessary, dried under a vacuum until the content of water was below 0.03%.

Designation	Mol. Wt.	Melting point °C	Boiling point. °C	Density g/cm^3	Refract. index	Obs.
Ethylene glycol (EG)	62,07	-13	196-198	1,113	1,4310	
diethylene glycol (DEG)	106,12	-10	245	1,118	1,4460	
glycerine	92,9		182	1,261	1.4740	
1,6 hexamethylene diisocyanate (HDI)	168,2		255	1,040	1,4520	
Polyethylene adipate diol (PEA)	2000	50-55	—	1.175	—	C_{OH}=56mg KOH/g

Table 1
MATERIALS USED TO OBTAIN ALIPHATIC POLYURETHANE FOR PASSIVE ISOLATION BEARINGS

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Preparation of polyurethanes

All the polymers were synthesized by bulk polymerization.

The synthesis of PUs was performed in a one 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 1 hour to yield a prepolymer that was mixed in the second step with a 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.

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 DERIVATOGRAF 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

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

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

-Hard segment content

PEA, HDI and EG lead to polyurethanes with Shore hardness about 50-90. A which may be classified as soft grade PUs. Their mechanical properties are comparable with those of good quality general purpose rubber materials.

In an attempt to obtain even softer PUs, a series of samples with decreasing hard phase content was synthesized (table 2, formulations 1-4). By increasing the hard segment content, it was possible to prepare a PU with hardness as low as 50 Shore.

The role of chain extenders molecular weight and of the type of OH groups can also be seen in table 2. All these elastomers have similar properties, however, the use of ethylene glycol resulted in an increase of Shore hardness and a slight change in softening and glass transition temperature. A formulation with diethylene glycol yielded a very 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. The C-O-C stretching frequency (1370 cm^{-1}) for ester with the inclusion of polyester in the polymer chain. Similarly the peak for CH_2 stretch appears at 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.

Table 2

HARDNESS OF THE OBTAINED POLYURETHANES

Nr.	Designation samples	Rate Polyester/Diisocyanate/ Chain extenders	Diisocyanate	Chain extenders	Hardness Shore A
1.	PU5	1:2:1	HDI	EG	95
2.	PU6	1:3:2	HDI	EG	50
3.	PU7	1:2:1	HDI	DEG	55
4.	PU8	1:3:2	HDI	DEG	50

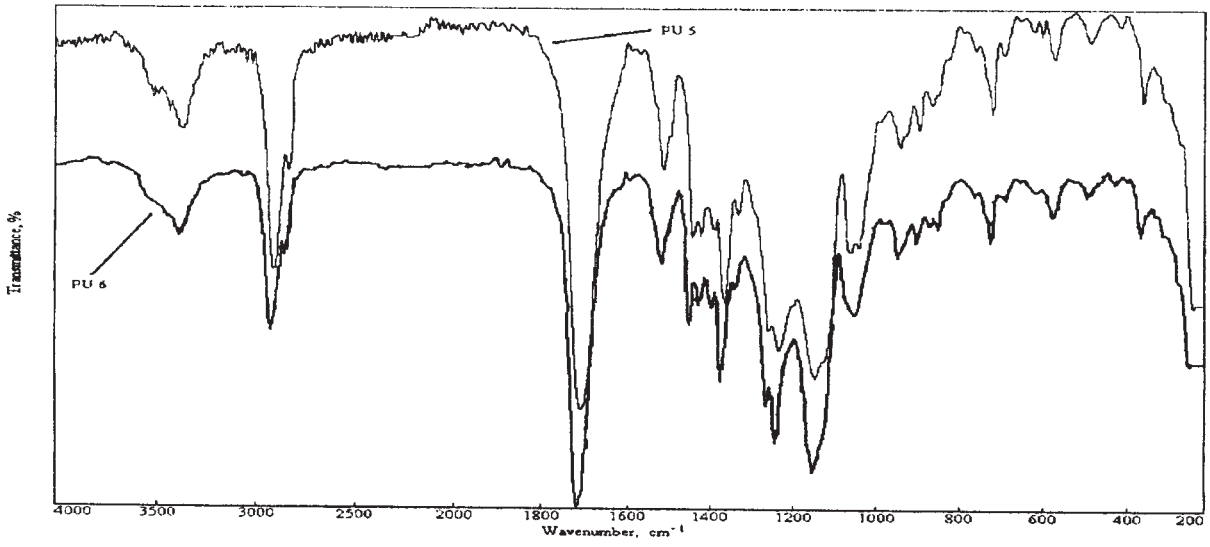

Fig. 1. IR spectra of polyurethane samples synthesized with EG

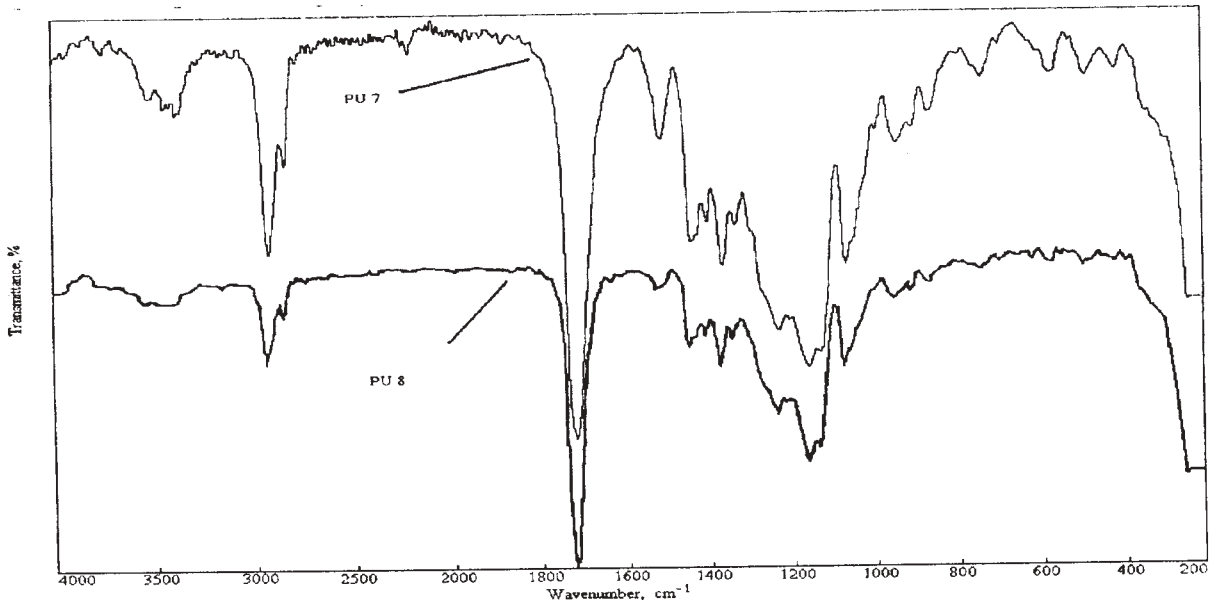

Fig. 2. IR spectra of polyurethane samples synthesized with DEG

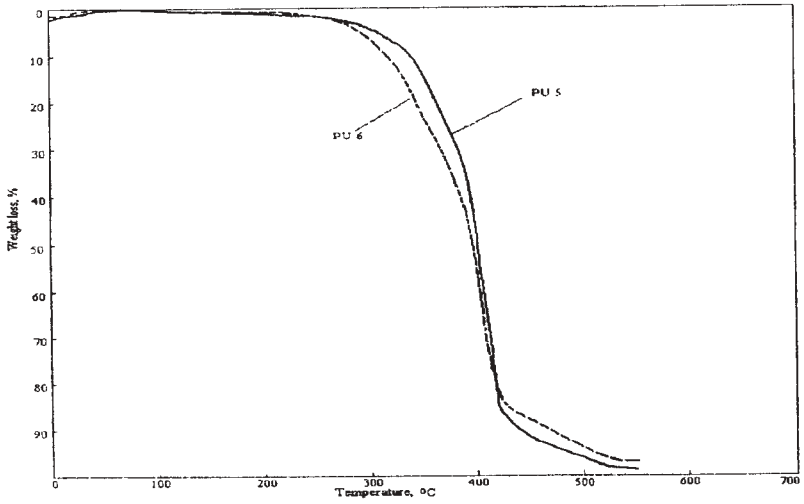

Fig. 3. TG curves of polyurethanes with EG

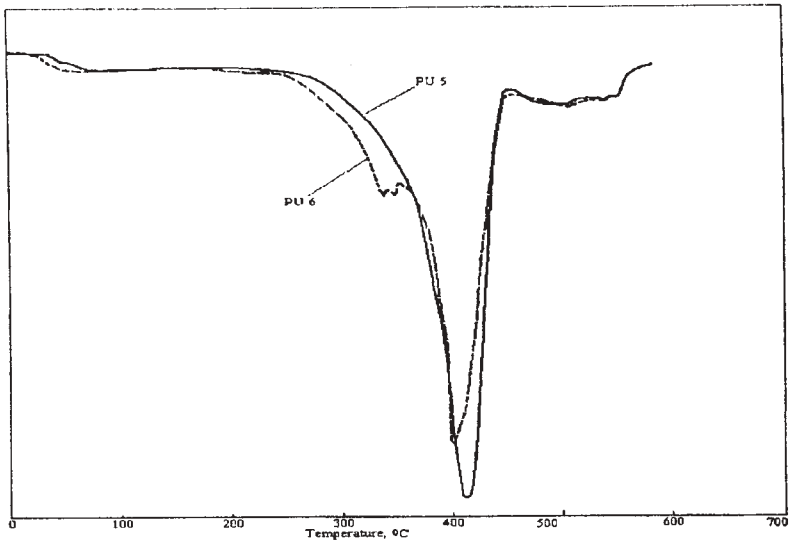

Fig. 4. DTG curves for polyurethanes with EG

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 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

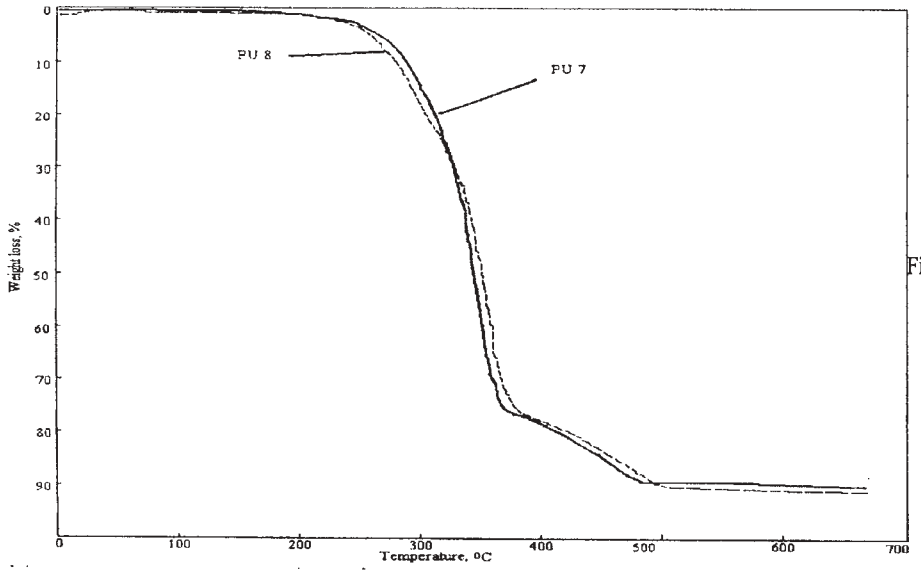

Fig. 5. TG curves of polyurethane with DEG

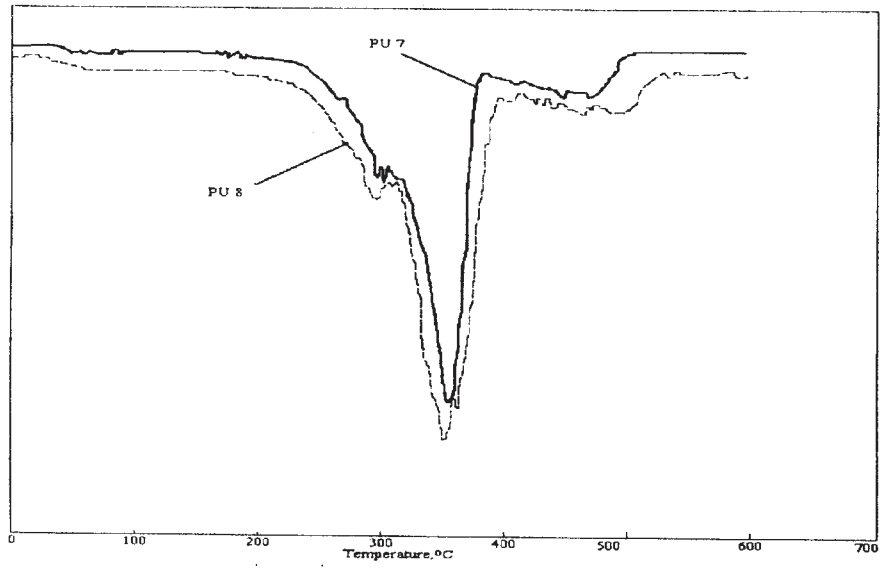

Fig.6. DTG curves for polyurethanes with DEG

Table 3
THERMOGRAMIMETRIC DATA FOR THE ALIPHATIC POLYURETHANES

Sample code	Weight losses (%) and decomposition temperature ranges			
	Global	Step I	Step II	Step III
PU5	98	12(100-350)	78(350-470)	8(470-550)
PU6	98	11 (120-380)	80(380-450)	9(450-530)
PU7	90	9,6(115-300)	70(300-380)	10,4(380-480)
PU8	92	10(100-280)	69(280-380)	16(380-500)

the decomposition step with the horizontal zero-line of the TG curve [15,16].

The physical crosslinks are important to providing dimensional stability and to stop 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. The crystalline polyester domain acts as an additional physical crosslink site below the melting temperature.

Generally, analyzed polyurethanes decomposed in three steps and the temperature which the weight losses were maximum is 300-450°C and increase of flexible chain lead to relative stability, because the posibility of order the molecular chain is high, folowing a 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 400°C for polyurethane with EG and 350°C for polyurethane with DEG

The increase of the temperature maximum 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.

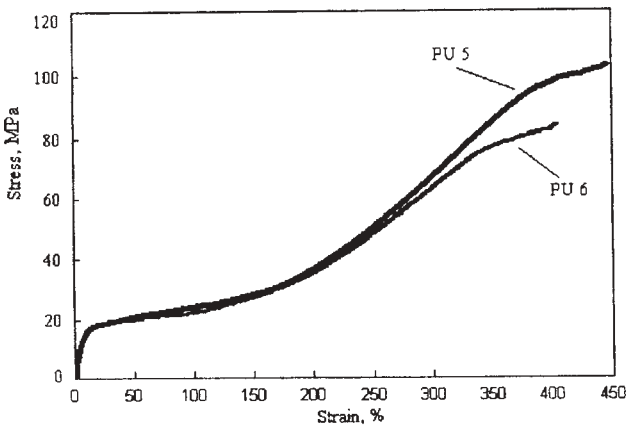

Fig.7. Stress-strain curves of polyuretane prepared with EG

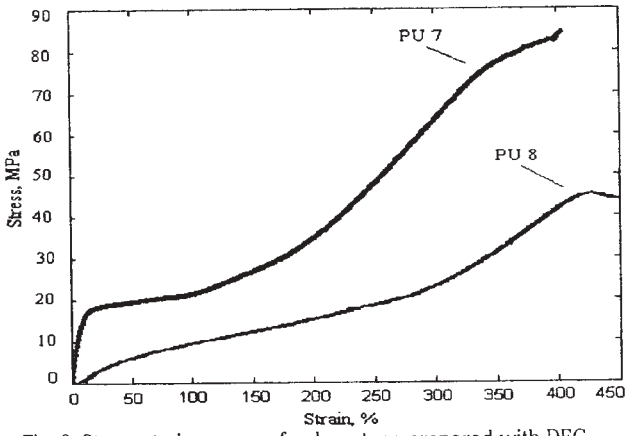

Fig. 8. Stress-strain curves of polyuretane prepared with DEG

Table 4

TENSILE PROPERTIES OF POLYURETHANES OBTAINED WITH ALIPHATIC DIISOCYANATES

Sample code	E_1 MPa	L1 %	FR MPa	AR %	FM MPa	AM %	E MPa
PU5	16,5	15,68	99,9	444	101,8	443	28,9
PU6	7,8	20,7	53,4	370	53,4	369,5	72,6
PU7	18	36,3	82,2	404,4	84,1	404,1	71,7
PU8	6,8	53,1	42,7	431,2	44,9	397,3	15,8

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

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 [17].

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. These figures, in essence, show the change in tensile properties with crosslink density.

The stress-elongation curves measured at constant crosshead speed and temperature were typically nonlinear, and represented the time-dependent viscoelastic properties of these elastomers.

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 a decrease of the tensile strength from 99 to 53 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 1/2/1 rate, may be explained by the transplanar structure formed [18].

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 increases. 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 glycerine.

This present study may provide possibilities of enhancing the mechanical property 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 PEs exhibited hardness about 50-90 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.

Polyurethane elastomers based on an aliphatic diisocyanate and a polyester macroglycol can provide the necessary tensile properties for a satisfactory seismic izolation material.

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 glycerine linkages increased the polyurethane thermal stability. The use of all aliphatic diisocyanate structures enables light and colour stable PU elastomers to be obtained.

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References

1. NASHIF, A.D., JONES,D.I., HENDERSON, J.P., 1985, Vibration Damping (New York: Wiley)
2. JEONG, H.M., KIM, B.K., CHOI, Y.J., Polymer, **41**,2000, p. 1849
3. F LI., Y CHEN., ZHU.,W., ZHANG, X., M XU., Polymer, **39**, 1998, p. 6929
4. HAYASHI.,S., Int Prog Urethanes, **6**, 1993, p. 90
5. KIM, B.K., SHIN, Y.J., CHO, S.M., JEONG, H.M., J Polym Sci Part B, Polym Phys; **38**, 2000, p. 2652
6. JEONG, H.M., LEE, J.B.,Y.LEE,S., KIM, B.K., J Mater Sci, **35**, 2000, p. 279
7. JEONG, H.M., AHN, B.K., KIM, B.K., Polym Int, **49**, 2000, p. 1714
8.YANG, C.Z. , GRASEL, T.G. , BELL, J.L.,COOPER, S.L. , J. Polym. Sc, **29,** 1991, p. 581
9. LU, X., HOU, M. , GAO, X.,CHEN, S., Polymer, **35,**1993, p. 2511
10.LAI, Y.C. , QUINN, E.T., VALINT, P.L., Polym Prep., **33**, 1992, p. 1058
11. SUN, H., Polym Prep., **33**, 1992, p. 556
12.HEPBURN, C., Polyurethane elastomers 2nd ed. Amsterdam, Elsevier Science Publishers Ltd (1991)
13. NISHI, T., WANG, T.T. , Macromolec; **8**, 1975, p. 909
14. AHN, T.O., OH, M.H., YOO, K.S., JEONG, H.M., Polym Int, **36**, 1995, 1995, p. 239
15. NAKAMURA, K., HATAKEYAMA,T., HATAKEYAMA., H., Polym. Adv. Technol., **3,** 1511992
16. HATAKEYAMA, H., IZUTA,Y.,KOBASHIGAWA,K.,HIROSE,S., HATAKEYAMA.,I., Macromol. Symp., **130**, 1998, p. 127
17. OPREA., S., Mat., Plast., **42**, nr. 1, 2005, p.6
18. OPREA, S., VLAD, S., STANCIU, A., Polymer **42,** 2001, p. 7257

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