

*Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)*

THE THERMAL BEHAVIOUR OF SELECTED CROSSLINKED POLYURETHANES AS REVEALED BY THERMOGRAVIMETRY AND STATIC COMPRESSION TESTS

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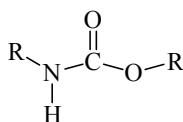
A series of polyurethane elastomers was achieved, with a controlled ordering of copolymer hard segment blocks on the macromolecular chain. They derived from diisocyanates of rigid 4,4'-diphenyl methane diisocyanate (MDI) or variable geometries 4,4'-dibenzyl diisocyanate (DBDI). The range of polymers was designed to reveal the roles of choice of macrodiol (MD) and of diol or diamine chain extender (CE) in determining the thermal performance as an elastomer. The soft segment MD was polytetrahydrofuran (PTHF), or poly(ethylene adipate) (PEA) of molar mass $M=2000\pm 50$. The chain extenders used in the synthesis were ethylene glycol (EG), diethylene glycol (DEG) and 4,4'-methylene bis(2-chloroaniline) (MOCA). Polyurethanes thermal behaviour was investigated by means of thermogravimetry (TGA) and static compression experiments. Variable hard segment percents were chosen for the study of the materials mechanical response in the frame of static compression tests.

INTRODUCTION

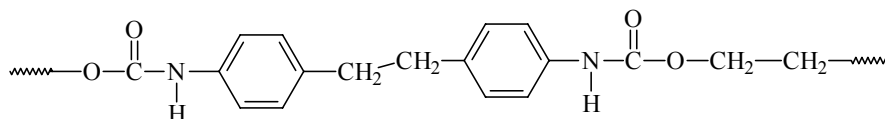
Polyurethane elastomers (PUE) represent a class of products which occupy a special place in the materials properties spectrum. They are defined in terms of their physical property and chemical structure relationship. PUEs are all characterized by presence of the urethane link $-\text{CO}-\text{NH}-\text{O}-$ in the macromolecular backbone, and formed by reaction between isocyanates and polyols, but materials with wide variations in physical properties are possible, by varying the choice of these ingredients. PUEs are characterized by a segmented structure (polymeric blocks) made up of two different polymeric phases: hard and soft segment. Long flexible blocks of chains (1000-2000 nm) are joined to shorter rigid segment

blocks of chains (150 nm). These segmented structures are responsible for the excellent PUEs properties.¹ Segmented PUEs are formed by the reaction of a macrodiol (MD), diisocyanate (DI) and a chain extender (CE), which can be a glycol, diamine or water. The present study is dedicated to PUEs with urethane linkages (Scheme 1) which are based on diol chain extenders. PUEs based on 4,4'-dibenzyl diisocyanate (DBDI) with hard segments of conformational mobility²⁻⁷ were compared to PUEs derived from conventional isocyanates of rigid geometries, mainly 4,4'-diphenyl methane diisocyanate (MDI).^{1,2} PUEs thermal behaviour was investigated by means of thermogravimetry (TGA), and static compression experiments.

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The urethane linkage



The urethane linkage in a polyurethane elastomer

Scheme 1 – Flexible and rigid domains in a polyurethane elastomer.

RESULTS AND DISCUSSION

1. PUEs Thermogravimetry

Thermogravimetric (TGA) experiments were made by a MOM–Budapest instrument type Derivatograph, System: F. Paulik, I. Paulik, L. Erdley, with a heating rate of 12 °C/min till 600 °C, in air. As seen in Figure 1, and in Table 1 also, the presence of the different DTG maxima show that the degradation process is made up by subsequent processes which are different from a PUE to another. The TGA analyses showed that the dibenzyl-based materials start to decompose at higher temperatures (up to 290 °C) as compared to

similar materials derived from conventional commercial diisocyanates with rigid structures, (Figure 1). As observed, the limits of the thermal stability for the three types of PUE were closed as follows: PUE with CE MOCA (290 °C) > PU with CE DEG (280 °C) > commercial Adiprene L 100 (100 – 270 °C). As shown in Figure 2, TGA analyses were also made for a series of intermediates which were synthesized with two identical functional groups situated in different rings: 2,2'-DBDI, 2,4'-DBDI and 4,4'-DBDI.³ For these structures the melting point of the polymer was 312 °C and the initial decomposition temperature of the polymer was 220 °C.

Table 1

Thermogravimetric data of PUE-Adiprene L 100, PU with CE DEG and PUE with CE MOCA

PU	T ₀ ^a (°C)	T ₅ ^a (°C)	T ₁₀ ^a (°C)	MaxDTG ₁ ^b	MaxDTG ₂ ^b
PUE-Adiprene L 100	270	305	325	405	–
PU with CE DEG	280	315	320	334	430
PUE with CE MOCA	290	322	337	366	415

- a) T₀, T₅, and T₁₀ represent the start of degradation, respectively, the temperatures of 5% and 10% weight loss. T(°C) are expressed as Celsius degrees. (Chimia generala, C. D. Nenitescu, Editura didactica si pedagogica, Bucuresti, 1972)
- b) MaxDTG represents the peak(s) of DTG curves corresponding on the inflexion points of TG curves as determined by TGA. Experimental Methods in Polymer Chemistry, Physical Principles and Applications, Jan F. Rabek; A Wiley-Interscience Publication, John Wiley & Sons, New York, 1980.

2. MECHANICAL TESTS. PUEs STATIC COMPRESSION

The interaction between the chemical structure and compression properties in casting PUEs and the influence of the specimen shape on the Young Modulus (E) was followed. PUE specimen shape factor (θ) was expressed as the ratio between the PUE specimen charged area and the sum of the free areas of the specimen. The dependence $E = f$

(θ) was discussed. At room temperatures the values of the PUE Young Moduli at a 20% compression (E₂₀) were comparable between the DBDI-based polymers and different conventional polyurethanes derived from MDI or other classical DI. At higher temperatures (up to destruction compression at 80 °C) the DBDI-based PUEs displayed a better elastomeric compression behavior, which was revealed by higher E₂₀ values in comparison to the classical PUE moduli.

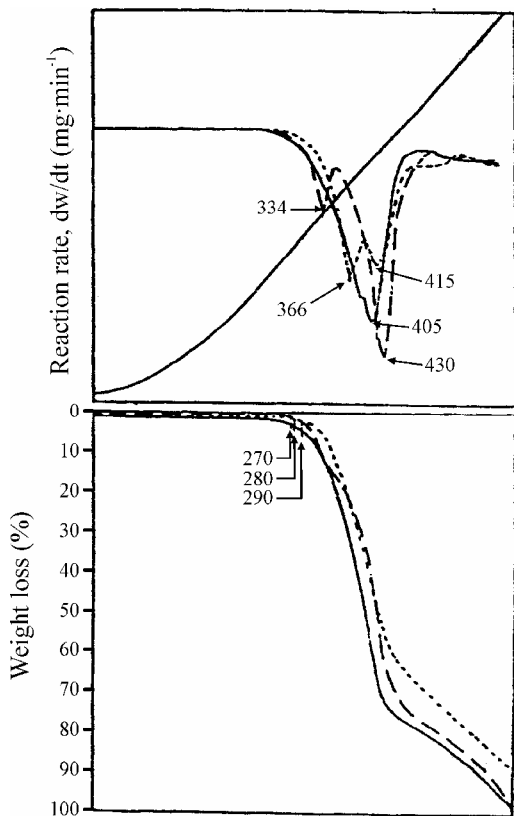


Fig. 1 – TGA and DTG curves for 3 PUEs:
 (—) commercial PUE-Adiprene L 100;
 (---) casted dibenzyl-based PUE derived from polyester MD (DBDI: PEA₂₀₀₀-DEG, I=110); (····) casted dibenzyl-based PUE with poly-ether MD and 4,4'-methylene bis(2-chloro-aniline) (MOCA): (DBDI: PTHF₁₀₀₀-MOCA).

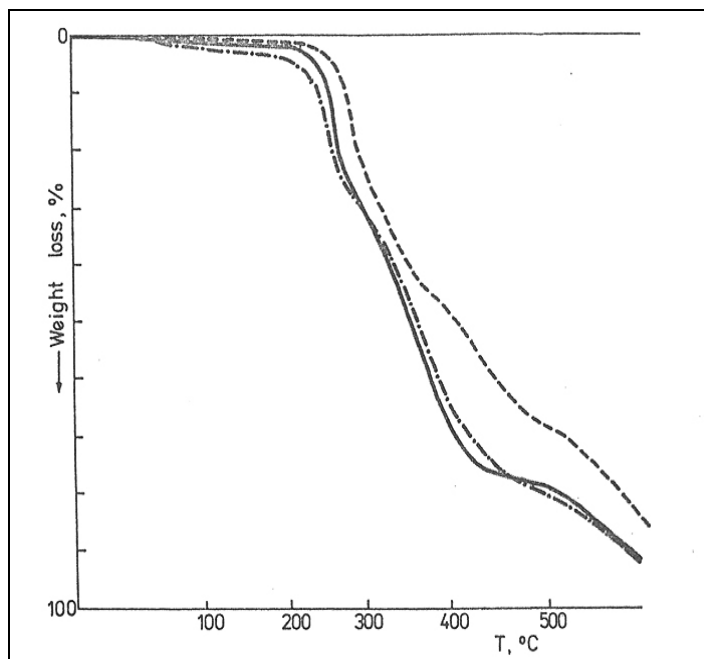


Fig. 2 – TGA curves for PUEs based CE ethylene glycol (EG), and DBDI isomers, 2,2'-DBDI (—), 2,4-DBDI (- - -) and 4,4'-DBDI (- · -).

Shown in Table 2 is the influence of the PUE hard segment concentration on the residual elongation (ϵ_r) and Young Modulus at a 20% polymer compression (E_{20}) on employing two different chain extenders, i.e. EG and DEG and the macrodiol PEA. The differences between the thermal behaviour of these materials could be explained in terms of the chain extender–diisocyanate couple: the couple EG-DBDI where the hard segments were observed to crystallize as compared to the diisocyanate couple DEG-DBDI where the hard segment do not crystallize.^{2,3} As seen in Table 2, in general all the studied DBDI-based polyurethanes showed a good compression behavior which was revealed by small values of the compression sets (2-3%).

When the materials were tested to compression under extreme conditions (313 MPa) and $t^0=80$ °C (the CD case in Table 2), there were observed higher compression set data. The best compression behavior was found for a DBDI-based material with DEG 50, i.e. where a hard segment

percentage (50 wt %) was adopted, when it obtained a smaller compression set $\epsilon_r = 6.2\%$ as compared to other commercial PUEs like Continental and Vulkollan 30,¹ where ϵ_r ranged between higher values from 12.5% (PUE type Continental) to 25 ÷ 37.5% (PUE type Vulkollan 25) and 9.1 (PUE type Vulkollan 30). It should be mentioned that the better mechanical behaviour of the DBDI-based PUEs under CD conditions could be obtained by consolidating the macromolecular network achieved by adding small quantities (1%) of trifunctional agents (TMP). With regard to the Young Modulus dependence on the PUE structure, the following general remarks could be made: (a) the nature of the CE influenced the E_{20} values in the following order DEG < EG < BG < MOCA. The DBDI based materials derived from chain extender MOCA displayed higher E_{20} Modulus values even at 80 °C; (b) the nature of the soft segment (MD) influenced the E_{20} Modulus variation degree with increasing the temperature.

Table 2

Influence of the hard segment concentration on the residual deformation (ϵ_r) and Young Modulus at a 20% compression (E_{20}) and variable temperatures, for a series of DBDI-based PUEs obtained with DEG and macrodiol PEA; (CM) - compression under medium conditions; (CD) - distruction compression.

CE type DEG hard segment percentage (wt %)	T°	Immediate ϵ_r , [%]	ϵ_r after 30 min, [%]	ϵ_r after 24 hrs, [%]	E_{20} [MPa]	
DEG 32	CM	20	3.73	2.74	2.24	31.2
		50	2.73	2.48	2.48	21.2
		80	-	-	-	-
DEG 40	CD	20	28.36	12.69	11.2	
		50	12.03	6.02	6.02	
		20	5.29	2.52	2.52	22.8
DEG 47	CM	50	6.28	4.52	4.52	20.0
		80	6.00	5.00	5.0	13.7
		20	5.96	3.23	2.73	47.6
DEG 50	CM	80	3.74	3.49	3.49	29.6
		20	12.5	1.56	1.56	
		CD	50	-	-	-
DEG 50	CD	80	19.69	18.11	18.9	
		20	20.5	2.75	2.50	38.1
		CM	50	7.58	6.6	6.36
DEG 60	CM	80	4.34	4.10	3.80	30.0
		20	5.10	3.06	2.04	
		CD	50	9.84	8.20	8.00
DEG 60	CD	80	11.43	9.52	9.52	
		20	3.10	2.26	1.75	29.1
		CM	50	4.25	3.75	3.75
DEG 27	CM	80	5.00	4.75	4.75	24.3
		20	5.10	3.06	2.04	
		CD	50	9.84	8.20	8.00
DEG 27	CD	80	11.43	9.52	9.52	
		20	2.49	0.50	0.5	15.9
		50	2.48	2.23	1.99	15.2

CD – distructive compression at 313 MPa and $t^\circ = 80^\circ\text{C}$; CM – medium compression at $t^\circ = 20 \div 80^\circ\text{C}$.

Table 3

Influence of the nature of MD on ϵ_r and E_{20} for a series of PUEs based on macrodiol PTHF, at variable temperatures and two shape factor values: ($\vartheta = 0.25$) for PUE compression under medium conditions (CM) and ($\vartheta = 0.35$) for distruction compression (CD)

CE type BG hard segment percentage (wt %)	T°	Immediate ϵ_r , [%]	ϵ_r after 30 min, [%]	ϵ_r after 24 hrs, [%]	E_{20} [MPa]	
BG 32	CM	20	4.3	2.5	2.5	44.0
		50	4.3	3.8	3.8	42.0
		80	1.8	1.8	1.8	34.8
BG 37	CM	20	4.8	3.3	2.8	35.2
		50	1.8	1.8	1.8	33.7
		80	3.8	3.8	3.3	37.8
BG 37	CD	20	33.3	21	17.5	
		50	28.8	28	28	
		80	36.8	35.2	35.2	
CE type BG and DEG hard segment percentage (wt %)	T°	Immediate ϵ_r , [%]	ϵ_r after 30 min, [%]	ϵ_r after 24 hrs, [%]	E_{20} [MPa]	
BG 40	CM	20	4.3	2.0	2.0	44.8
		50	1.5	1.5	1.5	42.9
		80	3.25	0.5	0.5	41.1
	CD	20	25.4	17.2	14	
		50	29.1	28.2	28.2	
		80	42.0	42.0	42.0	

DEG 40	CM	20	4.3	2.5	2.5	31.6
		50	6.1	5.4	5.4	32.1
		80	2.3	0.3	0.3	13.0
	CD	20	19.6	15.2	12.5	
		50	13.3	10.8	10.8	
		80	16.7	13.3	13.3	
DEG 47	CM	20	4.3	2.5	2.5	35.0
		50	3.5	2.3	2.3	35.8
		80	1.8	1.6	1.6	10.5
	CD	20	18.0	14.0	10.0	
		50	15.8	12.5	12.5	
		80	17.0	15.3	15.3	

CD: destructive compression at 313 MPa and $t^\circ = 80^\circ\text{C}$; CM: medium compression at $t^\circ = 20 \div 80^\circ\text{C}$.

In Table 3 there are depicted the compression data achieved for a series of materials employed with the macrodiol PTHF. Two chain extenders were used, 1,4-butanediol (BG) and diethylene glycol (DEG). The hard segment percent was varied from 32% to 40% in the case of PUEs with BG, and from 40% to 47% in the case of the polymers achieved with DEG. The highest modulus was observed for a DBDI based polymer derived from BG 40 wt%.³ There is direct proportionality between the modulus and the hard segment weight percent. The enhance of the hard segment percent determined an increase of the Young Modulus values. As expected the Young Modulus data decreased with increasing the temperature.

EXPERIMENTAL PART

Materials synthesis

The following general procedure was undertaken: 100g (0.05 mol of macrodiol polyethylene adipate (PEA) or polytetrahydrofuran (PTHF) respectively was dehydrated under mixing at 110°C and vacuum ($< 1\text{mm Hg}$) for 2 hours. 52.8g (0.2 mol) of DBDI for the PUE_D type or respectively, 50g (0.2 mol) of MDI in the case of PUE_M type of elastomer, was added at once under intense mixing to the anhydrous macrodiol, and vacuum was restored. After 30 minutes of mixing under vacuum at 100°C the temperature was reduced to 90°C and vacuum was removed. It obtained a prepolymer with final NCO groups in mixture with the excess of isocyanate. Then 8.18g (0.1318 mol) ethylene glycol (EG) were added at once under rapid stirring. For a series of PUEs, EG was replaced with diethylene glycol (DEG). The mixing was continued for maximum 30-40 seconds. The "pot life" of the mixture was between 3 and 10 minutes depending on the PUE structure. During this time the liquid mixture was cast onto closed teflonated moldings pre-heated at 90°C so as to avoid the interface of air humidity during the cure process. In the cast of open molding the presence of air usually leads to some perturbing uncontrolled and inhomogeneous enhancement of the mechanical properties. For the cure process the closed moldings were maintained after casting at

110°C for 24 hours. After an additional time of 24 hours at room temperature, the polymeric sheets representing an active PUE oligomer with NCO final groups were demoulded. Similarly, a series of polyetherurethanes based on DBDI and by using 4,4'-methylene-bis(2-chloroaniline) (MOCA) as chain extender were synthesized and tested.³ The mechanical properties were measured only after staying at ambient conditions for at least two weeks. This time was necessary to finish the postcure process³ in the case of PUE sheets of 0.3 to 2 mm thick when the whole amount of NCO excess group was consumed in principal through the reaction with the air humidity, leading to new urea group linkages.

It was shown^{2,5} that PUEs with excellent mechanical properties were obtained when in the elastomer synthesis was adopted a technique which uses a small excess of DI relative to the total amount of the hydroxyl partners e.g. MD and CE. This DI excess has to compensate the little secondary NCO group consumption produced by the some allophanate group formation, which perturbs the desired stoichiometrical balance between the OH and NCO group concentration necessary to achieve polymers with high molecular weights.

In concordance with this technique a prepolymer obtained from the reaction between 1 mol of MD, e.g. polyethylene adipate (PEA) or polytetrahydrofuran (PTHF) and 2.64 to 4 moles of DI, was reacted with a low molecular diol as a CE taken in a quantity calculated so that in the product should remain theoretically an excess of unreacted NCO groups corresponding to an index $I = 110$ when $I = ([\text{NCO}] 100) / ([\text{OH}]_{\text{MD}} + [\text{OH}]_{\text{CE}})$ where $[\text{NCO}] =$ equivalents of NCO groups from DI; $[\text{OH}]_{\text{MD}} =$ equivalents of OH groups from MD; $[\text{OH}]_{\text{CE}} =$ equivalents of OH groups from CE.

Thermogravimetry

Thermogravimetric (TGA) experiments were made in air by a MOM-Budapest instrument type Derivatograph, System: F. Paulik, I. Paulik, L. Erdley, with a heating rate of $12^\circ\text{C}/\text{min}$ till 600°C . In all the cases the quantity of polymer used was 50 mg polymer.

Mechanical tests

PUEs were subjected to compression tests at constant nominal strain-rate and temperatures ranging from 20°C to 80°C . The data were obtained using a Schopper MZ Gip Testing Machine, and a home-made hydraulic press which was reported elsewhere.³ Test specimens for compression experiments were prepared as previously reported.³

CONCLUSIONS

In the present study, our approach has been to study the structure–property relationship for a wide range of polyurethanes of known and systematically-varied composition, prepared under well-defined conditions. The range of structures achieved was widened, by inclusion of the diisocyanate DBDI with an unusually large conformational mobility. Two diol chain extenders (CE) were employed: ethylene glycol (EG) and diethylene glycol (DEG). Variable hard segment percents were used. Several types of well-defined static compression tests were made: the stress-strain data were determined at constant and variable temperatures (20 °C – 90 °C), on providing variable values of compression ranging between 5% - 40%. The influence of CE and Shape Factor (θ) on the compression set and Young modulus was followed. For $\theta = 0.25$ at room temperature, Young modulus values were comparable for the DBDI and MDI based materials, (10 ÷ 70 MPa). The compression set values varied between 0% ÷ 24 %, depending on the adopted type of CE (EG or DEG) and nature of the hard segment. In the case of compression tests made at high temperatures (80 °C), there were observed higher Young modulus data for the

materials with DBDI up to 45 MPa as compared to 34.3 MPa for materials based on isocyanates of rigid geometries. The mechanical properties of such materials were greatly enhanced by hard-phase crystallinity. The particular DBDI based hard block components which display flexibility specifically affect modulus and hardness, and also determine the upper use temperature by their special ability to remain associated at elevated temperatures.

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