

Mechanical Properties of Crosslinked Polyurethane Elastomers Based on Well-Defined Prepolymers

Piotr Król, Barbara Pilch-Pitera

Department of Polymer Science, Faculty of Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

Received 19 December 2006; accepted 21 February 2007

DOI 10.1002/app.26482

Published online 12 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article presents research findings for selected mechanical properties of polyurethane elastomers. The studied elastomers were synthesized with the prepolymer-based method with the use of controlled molecular weight distribution (MWD) urethane oligomers and with the classical single-stage method. Prepolymers with defined MWDs were obtained with the use of a multistage method, that is, step-by-step polyaddition. To produce elastomers, isocyanate oligomers were then crosslinked with triethanolamine, whereas hydroxyl oligomers were crosslinked with 4,4',4''-triphenylmethane triisocyanate (Desmodur RE). The tensile strength of the obtained elastomers ranged from 1.0 to 7.0 MPa, the ultimate elongation approached 1700%, the Shore A hardness varied from 40 to 93°, and the abrasion resistance index fell within 15–140. The effects of the types of raw materials used, the chemical

structures, the production methods, and the supermolecular structures on the mechanical properties of the obtained polyurethane elastomers were examined. When the obtained findings were generalized, it was concluded that the structural changes in the polyurethanes, which were favorable for intermolecular interactions, improved the tensile strength, hardness, and abrasion resistance of the materials and impaired their ultimate elongation at the same time. More orderly supermolecular structures and, therefore, superior mechanical properties were found for polyurethane elastomers produced with the prepolymer method. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1439–1448, 2008

Key words: elastomers; mechanical properties; polyurethanes

INTRODUCTION

As a follow-up report to our earlier research findings, which have already been published, on the effects of the synthesis method and chemical structure on the phase structure and thermal properties¹ of polyurethane (PU) elastomers obtained with a multistage polyaddition process of diisocyanate and polyols, in this article we concentrate on the effects of a number of structural and process-related factors on selected mechanical properties of produced PUs. The purpose of this research was to provide an explanation for the effects of structural factors, such as the structures and contents of the rigid and flexible segments, their ability to crystallize, phase separation, the number and types of crosslinking covalent bonds and hydrogen bonds, and, in particular, the molecular weight of the urethane prepolymer, on the mechanical properties of PUs. Moreover, we tried to develop a sweeping statement for the observed relations. Special PU elastomers were used for that purpose that had been produced by the extension of prepolymers with well-defined structures and narrow molecular weight distributions (MWDs).

Urethane–isocyanate prepolymers were subjected to chain extension and crosslinking by means of triethanolamine (TEA), whereas 4,4',4''-triphenylmethane triisocyanate was used for urethane–hydroxyl prepolymers. PU elastomers with known block structures were produced in that way.^{2,3} The potential applicability of individual elastomers could be directly defined by the evaluation of their mechanical properties, that is, the measurement of their tensile strength (TS), ultimate elongation, hardness, impact strength, and resistance to abrasion.

The available literature^{4,5} widely discusses the physicommechanical properties and resulting performance properties, that is, the resultant applicability, of PU plastics. However, some general conclusions on the effects of structural factors and, in particular, the molecular weights and chemical structures of chains on the mechanical properties of PUs are much more harder to draw, and those issues have not been completely clarified yet. It also needs to be taken into consideration that the group of the most essential performance properties covers not only static and dynamic mechanical properties but also the thermal stability, chemical (corrosion) resistance, and electrical properties in many cases. Those kinds of properties of PU materials are decided by the structures of the constitutional base units of the polymer chains, by the molecular weights of the linear structures,

Correspondence to: B. Pilch-Pitera (barbpi@prz.edu.pl).

and by the phase structure of the polymer. The effects of the chemical structures and physical properties of the raw materials employed in the production of PUs, especially diisocyanate, polyol, and the type of chain extender, on the mechanical properties of PU elastomers are very complicated. Those properties are usually the results of structural factors and physicochemical interactions, such as the sizes of the hard and soft segments, the degree of their separation (microphase separation), the ability to form crosslinking covalent bonds (allophanate bonds and biuret bonds) and intermolecular hydrogen bonds, the potential for the formation of van der Waals interactions within segments and between segments agglomerated in domains, the size and symmetry (or lack of symmetry) of aromatic ring structures or alicyclic ring structures derived from the isocyanate components used, the degree of splicing of molecular chains, the orientation of segments forced in the elastomer molding process, and the type and content of the crystalline phase.

The phase structures of PUs are critically affected by the segmented structures,^{6,7} which are specific for PU elastomers. The most critical contributions come from the structures of rigid and flexible segments and from the interactions between those segments that are decisive for the supermolecular structures within the hard phases and soft phases, which are formed spontaneously in the PU product molding processes.⁸ The presence of flexible segments, with negative glass-transition temperatures, imparts the performance of the elastomer to the polymer, whereas the presence of rigid segments, with high melting points, contributes to its good mechanical strength. The lower the glass-transition temperature is and the higher the melting point is, the wider the span is in which PU offers the most desirable performance of an elastomer.

Whether the phases can crystallize or not is determined by the regularity of the chain structures,¹⁰ the symmetry of the segments formed,^{11,12} the nature of the phase-separation phenomena, and the thermal conditions of the plastic formation process. The possible presence of a crystalline phase (e.g., in the form of spherulites)¹³ further improves the TS, tearing strength, hardness, and abrasion resistance.

Improved flexibility, on the other hand, is favored by reduced intermolecular interactions. In contrast to the mechanical strength, which is strongly dependent on the structure of the rigid segments, the flexibility is predominantly affected by soft segments. For that reason, the lower energy of the intermolecular interactions, which is typical for poly(ether urethane)s, makes them much more flexible than poly(ester urethane)s.¹⁴

The quality of PU as an elastomer material is decided chiefly by the negative glass-transition

temperature of its soft segments and also by its mechanical properties—the TS (usually 0.2–40 MPa), ultimate elongation (50–1500%), Shore A hardness (10–95°), and flexibility—as well as good abrasion resistance and impact resistance.^{15–22}

EXPERIMENTAL

Raw materials and reagents

Toluene diisocyanate (TDI) was a commercial product. It was a mixture of 2,4-TDI and 2,6-TDI isomers in a ratio of 80% to 20% from Aldrich (Buchs, Switzerland).

Poly(oxyethylene glycol)s (POGs) with number-average molecular weights (M_n 's) of 200, 300, 400, 600, and 1000 g/mol (Aldrich) were used. The glycols were dried *in vacuo* in N_2 at 110°C over 2 h.

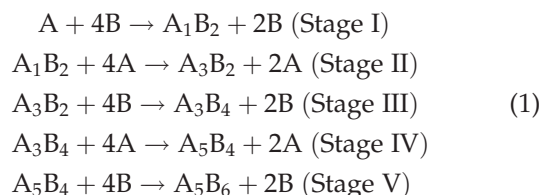
Polycaprolactone diols (PCDs) with M_n values of 530 and 1250 were acquired from Aldrich (Buchs, Switzerland).

TEA (pure) was obtained from POCh (Gliwice, Poland).

Desmodur RE (D-RE; 4,4',4''-triphenylmethane triisocyanate) was obtained from Bayer A.G. (Leverkusen, Germany).

Synthesis of the urethane prepolymers with controlled MWDs

The prepolymer materials used in the synthesis of the PU elastomers were obtained with the step-growth polyaddition process with the use of a considerable excess of one of monomers according to the following model:^{1–3}



where A is the polyol component (polyol or urethanediol) and B is the isocyanate component (diisocyanate or urethane-isocyanate oligomer).

The reactions were carried out in bulk in a glass reactor under nitrogen. Benzoyl chloride was used (0.3 wt % with respect to TDI) as a viscosity-control agent; moreover, its use made it possible to expand the stability period of the synthesized prepolymers (A_nB_{n+1}), and hence the prepolymers could be employed as parent substances in subsequent reactions. The polyaddition process was always initiated by a reaction that proceeded with a considerable excess of the diisocyanate (B). A calculated amount of the hydroxyl-terminated or isocyanate-terminated oligomer prepared at an earlier stage was introduced

TABLE I
Specifications for the Obtained PUs^a

Polyol ^b	Prepolymer method			One-step method		Type of chain extender
	Prepolymer sample	PD of the prepolymer ^c	PU sample	Molar ratio of the raw materials (A : B) ^d	PU sample	
POG 200	I-200	1.31	PU-I-200(2)	1 : 2	PU-I-200(1)	TEA
	II-200	1.36	PU-II-200(2)	3 : 2	PU-II-200(1)	D-RE
	III-200	1.43	PU-III-200(2)	3 : 4	PU-III-200(1)	TEA
	IV-200	1.50	PU-IV-200(2)	5 : 4	PU-IV-200(1)	D-RE
	V-200	1.29	PU-V-200(2)	5 : 6	PU-V-200(1)	TEA
POG 300	I-300	1.12	PU-I-300(2)	1 : 2	PU-I-300(1)	TEA
	II-300	1.19	PU-II-300(2)	3 : 2	PU-II-300(1)	D-RE
	III-300	1.21	PU-III-300(2)	3 : 4	PU-III-300(1)	TEA
	IV-300	1.25	PU-IV-300(2)	5 : 4	PU-IV-300(1)	D-RE
	V-300	1.53	PU-V-300(2)	5 : 6	PU-V-300(1)	TEA
POG 400	I-400	1.24	PU-I-400(2)	1 : 2	PU-I-400(1)	TEA
	II-400	1.60	PU-II-400(2)	3 : 2	PU-II-400(1)	D-RE
	III-400	1.67	PU-III-400(2)	3 : 4	PU-III-400(1)	TEA
	IV-400	1.30	PU-IV-400(2)	5 : 4	PU-IV-400(1)	D-RE
	V-400	1.39	PU-V-400(2)	5 : 6	PU-V-400(1)	TEA
POG 600	I-600	1.21	PU-I-600(2)	1 : 2	PU-I-600(1)	TEA
	II-600	1.66	PU-II-600(2)	3 : 2	PU-II-600(1)	D-RE
	III-600	1.64	PU-III-600(2)	3 : 4	PU-III-600(1)	TEA
	IV-600	1.50	PU-IV-600(2)	5 : 4	PU-IV-600(1)	D-RE
	V-600	1.23	PU-V-600(2)	5 : 6	PU-V-600(1)	TEA
POG 1000	I-1000	1.37	PU-I-1000(2)	1 : 2	PU-I-1000(1)	TEA
	II-1000	1.35	PU-II-1000(2)	3 : 2	PU-II-1000(1)	D-RE
	III-1000	1.35	PU-III-1000(2)	3 : 4	PU-III-1000(1)	TEA
	IV-1000	1.44	PU-IV-1000(2)	5 : 4	PU-IV-1000(1)	D-RE
	V-1000	2.37	PU-V-1000(2)	5 : 6	PU-V-1000(1)	TEA
PCD 530	I-530	1.22	PU-I-530(2)	1 : 2	PU-I-530(1)	TEA
	II-530	1.83	PU-II-530(2)	3 : 2	PU-II-530(1)	D-RE
	III-530	1.61	PU-III-530(2)	3 : 4	PU-III-530(1)	TEA
	IV-530	1.26	PU-IV-530(2)	5 : 4	PU-IV-530(1)	D-RE
	V-530	1.12	PU-V-530(2)	5 : 6	PU-V-530(1)	TEA
PCD 1250	I-1250	1.73	PU-I-1250(2)	1 : 2	PU-I-1250(1)	TEA
	II-1250	1.26	PU-II-1250(2)	3 : 2	PU-II-1250(1)	D-RE
	III-1250	1.51	PU-III-1250(2)	3 : 4	PU-III-1250(1)	TEA
	IV-1250	1.11	PU-IV-1250(2)	5 : 4	PU-IV-1250(1)	D-RE
	V-1250	1.17	PU-V-1250(2)	5 : 6	PU-V-1250(1)	TEA

^a The data were taken from refs. 1 and 3.

^b The numbers are the M_n values.

^c Polydispersity degree (PD) = M_w/M_n .

^d A is the polyol component, and B is the isocyanate component.

procedure.²³ The sample holder travel speed was 500 mm/min, and the measurements were taken over the distance of 25 mm. The measurements were controlled with LaborPoint 10.01 software. What was recorded was the tensile force versus the sample tensile strain. That relation was computer-processed and presented in charts as a function of the tensile stress versus the sample elongation.

The TS_b (MPa) values were calculated with the following formula:

$$TS_b = \frac{F_b}{d \cdot b} \quad (2)$$

where F_b is the force recorded at rupture (N), b is the width of the measurement distance (mm), and d is the thickness of the measurement distance (mm).

The elongation at break [E_b (%)] was calculated with the following relation:

$$E_b = \frac{L_b - L_0}{L_0} \cdot 100 \% \quad (3)$$

where L_b is the measurement distance at rupture (mm) and L_0 is the initial measurement distance (mm).

Hardness

A Shore hardness tester from Zorn (Stendel, Germany) was employed in accordance with the standard.²⁴ The Shore A hardness (°) was read directly from the instrument after 15 s.

Impact resistance

The impact resistance of the PU samples was found with the use of the standard Charpy method²⁵ and a pendulum machine from Ohst (Potsdam, Germany). The test pieces with no notch had the shape of small beams with the following dimensions: length = 50 ± 1 mm, width = $6 \pm 0,2$ mm, and thickness = 4 ± 0.0 mm. The supports were arranged at a distance of 40 mm, and the striking energy was 1.0 J.

The impact resistance [a_n (kJ/m²)] was calculated with the following formula:

$$a_n = \frac{A_n}{b \cdot d} \cdot 10^3 \quad (4)$$

where A_n is the breaking energy required to break a test sample (J), b is the width of the test sample (mm), and d is the thickness of the test sample (mm).

Abrasion resistance

The abrasion resistance of test samples was measured with a Schopper-Schlobach instrument with an APGi circulating roller from Heckert, and the procedure complied with the standard PN-ISO.²⁶

The test pieces in the form of a roll (16 ± 0.2 in diameter and 2 mm high) were cut with the use of a cylindrical rotary tool installed on the instrument. The pieces were then glued to rubber discs, which made the footing elements for the former. The test pieces were circulated during the test. Because of considerable weight losses for some pieces, their tests were stopped half-way (20 m), and the findings were multiplied by 2 to make them comparable to the other findings. Standard rubber from Stomil Rub-

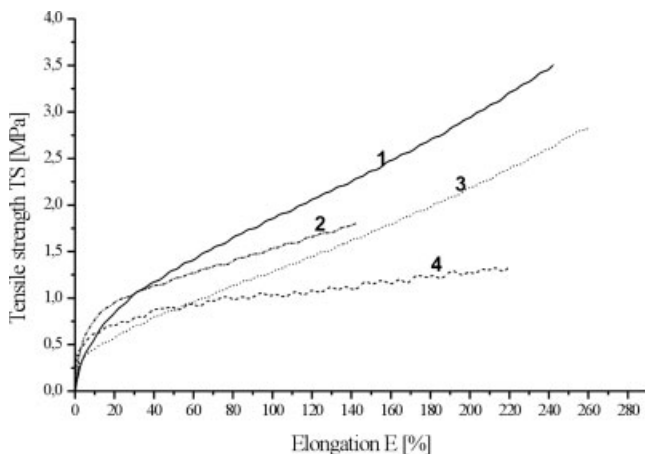


Figure 1 Tensile strength (TS) versus the elongation (E) for the obtained PUs: (1) PU-II-300(2), (2) PU-II-300(1), (3) PU-IV-300(2), and (4) PU-IV-300(1).

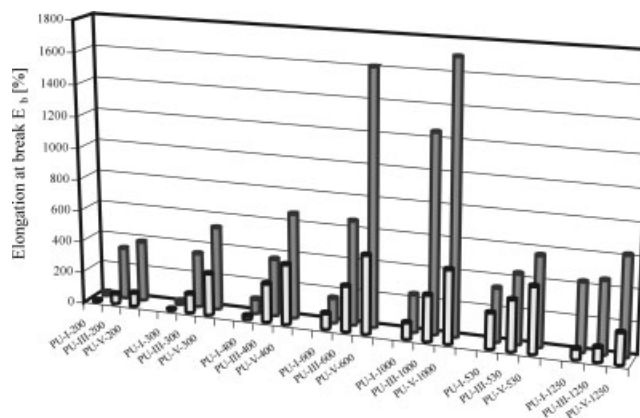


Figure 2 E_b of PU cured with TEA: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

ber Processing Plant S.A. (Sanok, Poland) was used as the reference material.²⁷

The abrasion resistance index (ARI) was calculated with the following relation:

$$ARI = \frac{V_s}{V_t} \cdot 100 \% \quad (5)$$

where V_s is the loss of volume of the standard rubber (mm³) and V_t is the loss of volume of the test sample (mm³).

The density figures for the test pieces, which were necessary for calculations, were found by the method described in the standard PN-ISO,²⁸ section A (the test pieces were weighed in air and then in CH₃OH as the immersion liquid).

The density of PU (g/cm³) was calculated with this equation:

$$\rho = \frac{g_1}{g_1 - g_2} \cdot \rho_1 \quad (6)$$

where g_1 is the mass of the test sample in air (g), g_2 is the mass of the test sample in CH₃OH (g), and ρ_1 is the density of CH₃OH ($\rho_1 = 0.7920$ g/cm³).

The findings for the mechanical properties are presented later in Figures 1–10.

RESULTS AND DISCUSSION

The values measured for the TS versus the elongation, the hardness, the abrasion resistance, which is important for every elastomer (static performance), and the impact resistance (dynamic performance) were analyzed from the viewpoint of the effects exhibited by the PU synthesis method, by the values of the average molecular weights for polyols inserted into the PU chains, and by the types of urethane prepolymer crosslinking agents used.

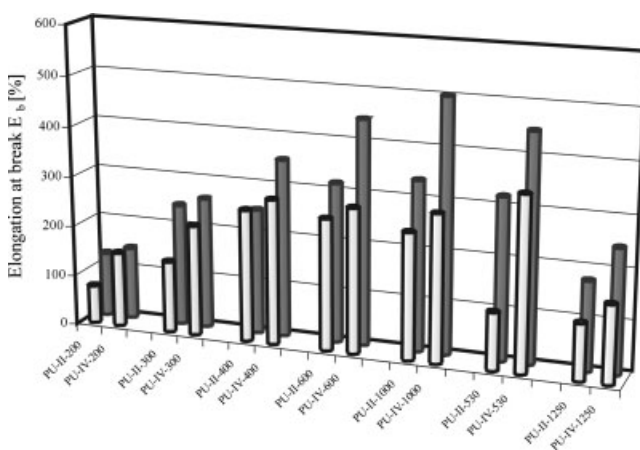


Figure 3 E_b of PU cured with D-RE: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

Strength tests

The values for TS or TS_b and E_b were assumed to be the comparative criteria for the strength performance of the studied PU materials. The stress curves (TS) versus the elongation were recorded during our study (Fig. 1). The majority of the profiles obtained in our tests corresponded to those specific for elastomers.

Figures 2–5 illustrate the values of E_b and TS_b as measured for all the synthesized PUs. The findings have been arranged in series: the length of the linear urethane segment increases, or the molecular weight of the polyol component increases. For comparison, strength parameters for PUs obtained by the single-stage method and by the chain step-growth method can be found in the same diagrams. Figures 2 and 4 present the data for PUs crosslinked with TEA, whereas Figures 3 and 5 present crosslinking with D-RE.

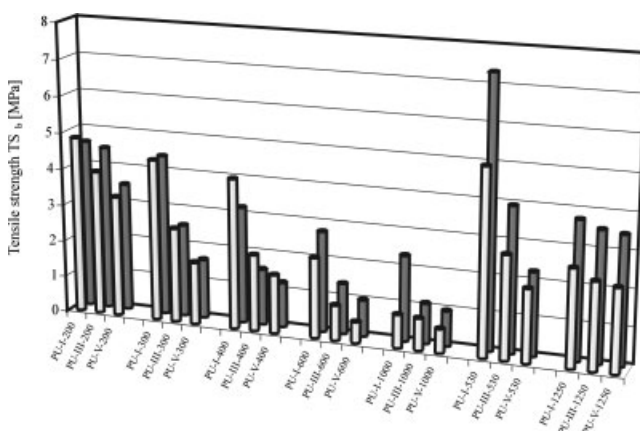


Figure 4 TS_b of PU cured with TEA: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

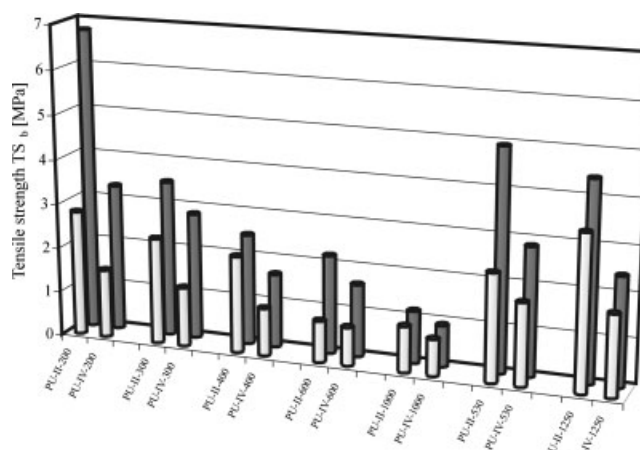


Figure 5 TS_b of PU cured with D-RE: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

When the data within each series are analyzed, increasing E_b and decreasing TS_b values can be observed for the growing urethane chain lengths. Higher molecular weights of oligourethanes increase the polydispersity in those compounds,^{2,3} and this results from the inferior order within the domains of the flexible segments¹ as well as the lower and lower stiffness of the chains. Those effects explain the deterioration of the studied mechanical properties, as observed in individual series of samples. In the case of PUs synthesized from PCD with a molecular weight of 1250 g/mol [PU-I-1250(1), PU-I-1250(2), PU-III-1250(1), PU-III-1250(2), PU-V-1250(1), and PU-V-1250(2)], the drop in TS with an increasing molecular weight of the oligourethane is not so clear, and this can be caused by an improvement in the intermolecular interactions due to the lower cross-linking density.

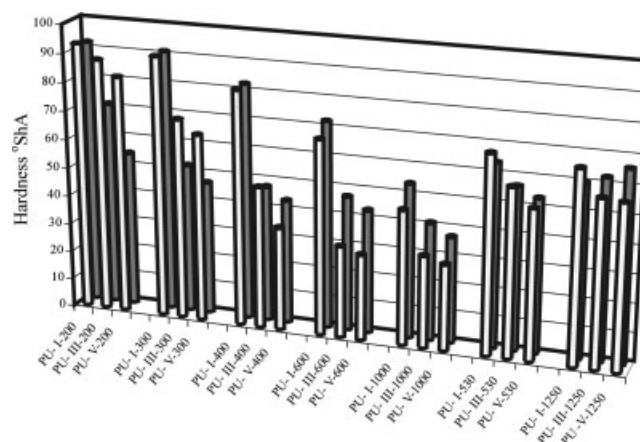


Figure 6 Hardness of PU cured with TEA: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

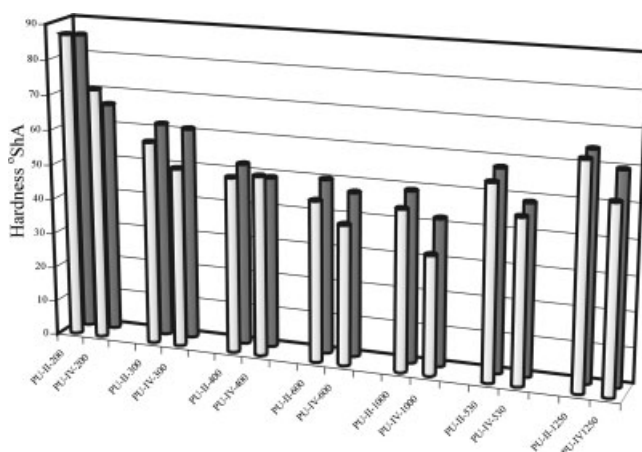


Figure 7 Hardness of PU cured with D-RE: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

When the molecular weight of a polyol increases, the number of urethane groups in the polyol chain is reduced at the same time, and hence the number of rigid segments is lower;²⁹ consequently, the possible number of intermolecular hydrogen bonds goes down in which —NH— and C=O groups are active. All those factors account for the decline in TS_b and increase in E_b observed in such cases. Although the increasing M_n value of the polyol component boosts the trend to create hydrogen bonds between the group —NH— and the ether group oxygen atom, such hydrogen bonds are too weak^{30–33} to compensate for the simultaneous drop in other interactions.

PU obtained from PCD generally offer TS superior to that of their counterparts derived from POG, and their ultimate elongation is lower. That can be explained by the presence in poly(ester urethane)s of additional hydrogen bonds between the group

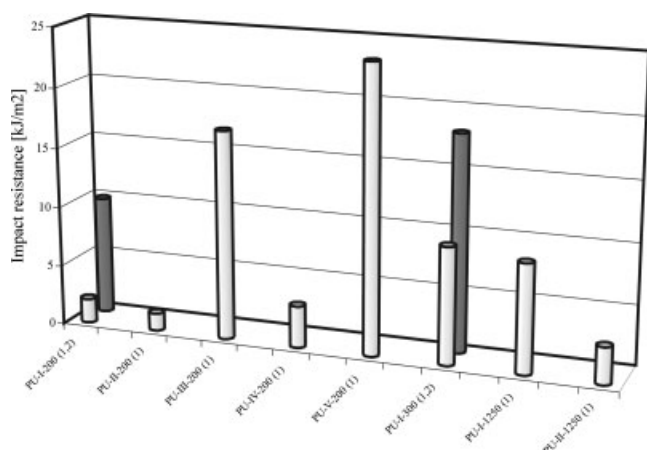


Figure 8 Impact resistance of PUs (□) obtained with the one-step method and (■) obtained with the prepolymer method.

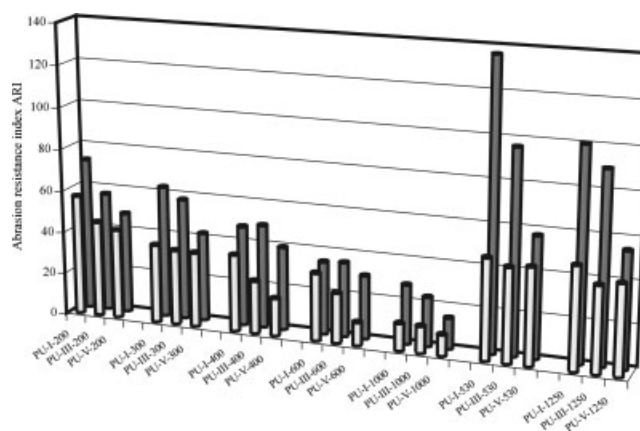


Figure 9 ARI of PU cured with TEA: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

—NH— and the carbonyl group oxygen atom within the ester group.

As shown by the DSC analyses presented earlier,¹ this results from the increasing capacity for crystallization within the flexible segments with higher M_n values^{34,35} in PU composed of POG 1000 [$W_{c,s} = 2.14\%$ for PU-II-1000(2)] and PCD 1250 [$W_{c,s} = 34.67\%$ for PU-III-1250(2), $W_{c,s} = 0.31\%$ for PU-IV-1250(2), and $W_{c,s} = 35.09\%$ for PU-V-1250(2)]; this also contributes to the relative decline in the ultimate elongation of these samples. A TS increase was not, however, observed.

PU subjected to crosslinking with TEA (Figs. 2 and 4) usually have lower TS and higher ultimate elongation parameters than PUs crosslinked with D-RE (Figs. 3 and 5). As shown earlier,¹ the latter suffer from inferior separation of the soft phase and increased crystallinity in the hard phase at the same

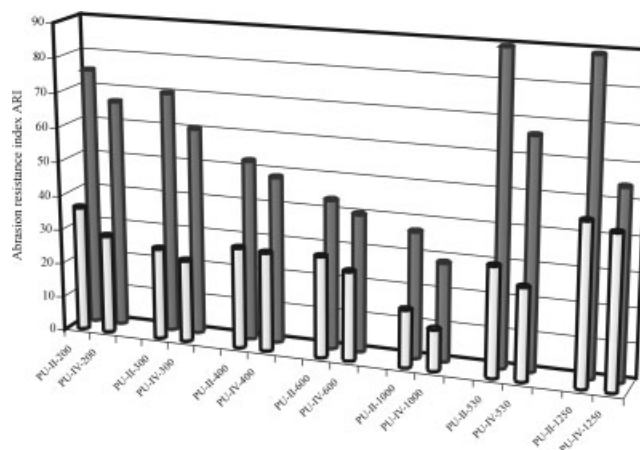


Figure 10 ARI of PU cured with D-RE: (□) PU obtained with the one-step method and (■) PU obtained with the prepolymer method.

time in comparison with PUs that contain rigid blocks derived from TEA. A more orderly arrangement within the hard phase, which is composed of symmetrically spaced aromatic rings, can also lead to higher TS and lower ultimate elongation values for PUs crosslinked with the use of D-RE.

PUs obtained with the prepolymer method are usually characterized by higher TS and ultimate elongation values than their equivalents produced with the single-stage method (Figs. 1–5). That should be explained on the basis of the earlier analysis of the phase structure¹ by the higher content of the hard phase, which is mechanically tough. The superior spatial order within the hard phase in PUs available from the prepolymer method is particularly visible in those polymers produced by the oligomer chain-expansion operation, which was repeated a few times. Moreover, an inferior spatial arrangement within the hard phase in samples PU-I-200(2), PU-I-300(2), PU-I-400(2), and PU-III-400(2), obtained by one or two prepolymer chain-expansion processes, versus their single-stage counterparts explains their observed lower TS values.³⁰

Hardness

Figure 6 presents the hardness test findings for PUs hardened with TEA, whereas Figure 7 presents the hardness test findings for those hardened with D-RE.

The hardness decreases with the increasing length of the linear urethane chain within each PU series tested. That is connected to the lower stiffness of the chains and lower intermolecular forces due to sparser crosslinking.

However, the hardness increases in a number of PUs: PU-I-1250(2), PU-III-1250(2), and PU-V-1250(2). This can result in an increasing tendency of crystallization of the soft phase with higher M_n values of the polyols.

The hardness of PUs generally declines with the increasing molecular weight of the polyol, just like the TS, because the higher the content is of the flexible segment, the lower the stiffness of the total structure becomes, and the effects from intermolecular forces grow weaker.

PCD-derived PUs offer higher hardness specifications than their POG-derived analogues with comparable M_n values, and this probably results from the higher energy of the interactions between the urethane group and the ester group with respect to analogous interactions with the ether group oxygen atom in POG.

Within PUs synthesized from polyesters, the hardness of the samples prepared with the use of PCD with $M_n = 1250$ g/mol is higher than that of their analogues containing segments derived from PCD

with $M_n = 530$ g/mol. That is also connected to the higher potential of polyester flexible segments to crystallize when their M_n grows higher, and this is advantageous for the stiffness of the whole structure.

A lower hardness is observed for PUs hardened with TEA (Fig. 6) than that for their counterparts hardened with D-RE (Fig. 7). This, like the TS, should be explained by the presence of symmetrically substituted aromatic rings that could crystallize more easily.

In general, PUs produced with the prepolymer method offer hardness superior to that of PUs produced with the single-stage process, yet there are some exceptions to this rule. The observed increase in the hardness results from a more orderly arrangement of the supermolecular structures in PUs obtained with the prepolymer method.¹ The lower hardness for samples PU-I-V-200(2), PU-III-300(2), PU-V-300(2), PU-IV-400(2), PU-I-530(2), PU-III-530(2), and PU-I-1250(2) can be explained by the inferior arrangement within their rigid segments or by the macroscopic inhomogeneity emerging in the molding stage.

Impact resistance

The impact resistance findings are presented in Figure 8. The lowest resistance can be observed for PUs obtained with the single-stage method from low-molecular-weight polyols ($M_n = 200$ or 300 g/mol).

The impact resistance values for PUs in this study range from 1.91 kJ/m² for PU-I-200(1) to 23.81 kJ/m² for PU-V-200(2), with the values for polymers synthesized with the prepolymer method being much higher. For PUs obtained with the single-stage procedure, their impact strength improves when the content of the polyol component is higher. Moreover, the samples hardened with the use of D-RE have lower impact resistance specifications than those after hardening with TEA. Apparently, the presence of aromatic stiffening structures is disadvantageous for the impact strength. On the other hand, the impact resistance is improved at a lower density of crosslinking.

Only two PU samples, obtained from long-chain polyols (PCD 1250) with the single-stage method, could be broken when 1.0 J of energy was applied. Most PU samples were flexible enough, and no impact strength could be measured under the adopted conditions.

Attention should be paid to the samples obtained with the single-stage method from the PU-(I-V)-200(1) and PU-I-1250(1) series. Despite a high Shore A hardness (93–67°), they turned out to be relatively brittle. The reasons were their high content of rigid segments, lower phase separation, and also most

likely numerous defects occurring in their crystalline structures.

PUs PU-I-200(2), PU-II-200(2), PU-III-200(2), PU-III-200(1), PU-V-200(1), PU-I-300(2), PU-I-400(2), and PU-I-600(2) offer pretty high levels of both the Shore A hardness (92–70°) and impact strength (over 10 kJ/m²). On this basis, they make relatively good elastomers with potential structural applications.

Abrasion resistance

The findings for ARI have been organized into groups and are presented in Figures 9 and 10. As for the TS and impact resistance, the abrasion resistance of given samples is determined by the structures of the raw materials, by the type of the formed phase structure, and by the resultant intermolecular interactions.

The reduction of ARI for increasing M_n of the polyol used results from the qualitative and quantitative changes in the nature of the hydrogen bonds created within the flexible and rigid segments, as discussed earlier.

A significant influence of the crystallinity of the soft phase on the abrasion of PU obtained from POG 1000 and PCD 1250 was not observed.

That can be explained by the fact that the crystalline phase formed by flexible segments can melt relatively easily or become amorphous under the measurement conditions. Even small stresses resulting from contact with abrasive cloth at temperatures up to 70°C can cause partial melting of a sample during the test.⁸

The growth in the crosslinking density improves the abrasion resistance, except for samples PU-I-400(2) and PU-I-600(2). In those two cases, the drop in the hydrogen interactions between chains due to higher distances between them can prevail. The observed and distinctly superior abrasion resistance of PUs obtained with the prepolymer method results certainly from the more orderly structures, as discussed earlier.

CONCLUSIONS

The samples used in the tests had precisely defined chemical structures because of the synthesis methods adopted and known phase structures that had been established in earlier studies. That made it possible to employ simple determinations to evaluate the effects of the chemical structures and phase structures on the mechanical properties of the PU elastomers.

The studies made it possible to draw a number of general conclusions, which are important from cognitive and practical point of views, about the effects on the mechanical properties of PU elastomers by

structural factors such as the structures and contents of rigid and flexible segments, their ability to crystallize, phase separation, and the number and types of crosslinking covalent bonds and hydrogen bonds.

In particular, the TS, hardness, and abrasion resistance of synthesized PUs usually increase when polyols with lower and lower M_n values are used and when the orderly arrangement improves within both hard and soft domains. That should be explained by increasing intermolecular interactions within the polymer structures. On the contrary, if those interactions are weakened anyway, the test piece elongation increases, and the impact strength drops. Our investigations have revealed that PUs obtained with the prepolymer method offer generally more favorable physicomaterial properties than their analogues synthesized with the single-stage process. On the basis of these properties, the studied PUs can be classified as elastomers of a wide application spectrum.

The findings available at this stage of the study are predominantly qualitative, but they can create a basis for quantitative relations to be established in further research programs,³⁶ which can be obtained only from empirical models developed by experimental planning methods, whereas the effects of structural factors are precisely defined for a fixed PU elastomer production method.

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