

NEW TRENDS IN THE SYNTHESIS AND PROPERTIES OF POLYURETHANE AND POLYURETHANE-UREA ELASTOMERS BASED ON DIBENZYL DIISOCYANATE

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Polyurethanes (PUs) and polyurethane-ureas (PUUs) were prepared by the polyaddition reaction between a macrodiol (MD) like polyester-diol, polyethylene adipate (PEA), or polyether-diol, polytetrahydrofuran (PTHF), a diisocyanate (DI) e.g. 4,4'-dibenzyl diisocyanate (DBDI) or 4,4'-methylene bis (4-phenyl isocyanate) (MDI), and as chain extenders (CE), like ethylene glycol (EG) or an aromatic diamine like 4,4'-dibenzyl diamine (DAB), 4,4'-methylene dianiline (MDA), or a heterocyclic diamine, like 2,5-bis-(4-amino-phenylene)-1,3,4-oxadiazole (DAPO) or 2,6-diaminopyridine (DAPy). The resulting polymers were characterized by means of the IR spectra, inherent viscosity measurements, and wide angle X-ray scattering (WAXS). PUs mechanical properties were investigated. Special consideration was given mainly to the study concerning the PUs energy loss. The study of the relationships between structure and properties reveals the influence of the nature of starting materials, macrodiols, diisocyanates and chain extenders on the mechanical properties of the polymers. The great number of hydrogen bonding that formed between urea and urethane groups of polyurethane-ureas (PUUs) and the presence of oxadiazole or pyridine rings in the polymer chain induced an improved thermal stability in these polymers. PUUs mechanical behavior was discussed by comparison with those of polyurethanes based on DBDI or MDI and chain-extended with EG.

INTRODUCTION

The present work deals with the synthesis and characterization of polyurethanes (PU) based on classical MDI and the relatively new available 4,4'-dibenzyl diisocyanate (DBDI). DBDI has the particularity to possess a variable geometry due to the ethylene bridge connecting the two aromatic rings bearing the NCO groups. The effects of DBDI on polyurethane properties are quite important. As earlier reported,¹⁻⁵ the MDI molecule introduces a rigid moiety (Ph-CH₂-Ph) in the hard segment, while the DBDI specific moiety (Ph-CH₂-CH₂-Ph) induces into the hard segment the possibility of an internal rotation of aromatic rings around the ethylene bridge. This leads to the appearance of both "syn" and "anti" rotational conformations, which coexist in the PU macromolecules based on DBDI. As a result, the macromolecules can adopt a more compact packing arrangement (in the case of the "anti" conformation),

with increasing the tendency of ordering into crystalline domains.⁵⁻⁷ During the mechanical stress relaxation measurements it occurs a change in the geometry of macromolecules. The contorted "syn" forms tend to disappear in the favour to the appearance of the extended linear "anti" DBDI structure. In the present paper polyurethanes (PUs) and polyurethane-ureas (PUUs) chain-extended with diols and with diamines, respectively, were synthesized starting from MDI or DBDI. The study of the influence of both structures on the polymer properties has been followed. We have compared the influence of the type of CE, for example diols like EG or diamines like DAPO and DAPy on the PUs mechanical performance.⁸ All polyurethanes were synthesized by a stepwise polyaddition reaction as shown in Fig. 2. The physical-chemical and mechanical properties of these polymers were then discussed.

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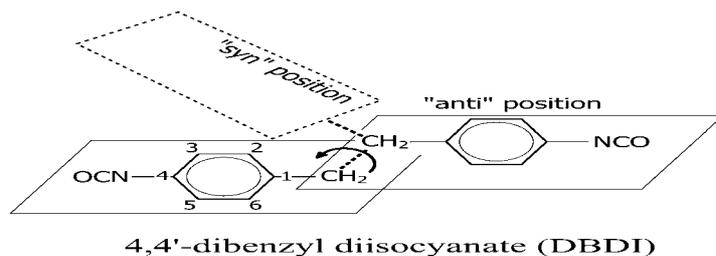


Fig. 1 – Schematic of DBDI „syn” and „anti” rotational conformations.

RESULTS AND DISCUSSION

1. Polymer synthesis

Generally, polymers with urethane linkages were based on three-component systems consisting of: (1) a diisocyanate (DI) generating hard segment (HS) (MDI or DBDI); (2) a macrodiol (MD) (PEA or PTHF); (3) a small molecule diol like EG, or diamines as CE. In all cases the molar ratio of DI:CE:MD was of 2:1:1. The hard segment mass fractions were in the region of 21-27% (Table 1)

and isocyanic index $I = 100$. DI and MD were vigorously mixed under vacuum at 100°C , to give an NCO end-capped prepolymer. This was then mixed with the CE at 90°C , and cast into closed sheet moulds for curing at 110°C for 24 hours. Polymer sheets with thickness in the range 0.3-0.6 mm were obtained. The sheets were stored at room temperature for at least two weeks before testing. PUs and PUUs were labeled PU_{1-4} and PUU_{1-6} , respectively, according to their combination of DI, MD and CE, as indicated below (Table 1).

Table 1

Characteristics of PUs with diol or diamine chain extension

PU _i	Composition	Molar ratio	Hard segment content		η_{inh} dL/g
			(%)	NHCOO mol/kg polymer	
PU ₁	PEA - DBDI - EG	1 - 2- 1	22.79	1.544	0.776
PU ₂	PEA - MDI - EG	1 - 2- 1	21.19	1.560	1.155
PU ₃	PTHF - DBDI - EG	1 - 2- 1	22.79	1.544	0.621
PU ₄	PTHF - MDI - EG	1 - 2- 1	21.19	1.560	1.002
PUU ₁	PEA-DBDI-DAPO	1 - 2- 1	27.02	1.384	0.623
PUU ₂	PEA-MDI-DAPO	1 - 2- 1	26.30	1.398	0.881
PUU ₃	PTHF-DBDI-DAP	1 - 2- 1	24.93	1.501	0.453
PUU ₄	PEA-MDI-DAPy	1 - 2- 1	23.13	1.458	0.382
PUU ₅	PTHF-DBDI-DAB	1 - 2- 1	27.03	1.459	0.942
PUU ₆	PTHF-MDI-MDA	1 - 2- 1	25.03	1.482	0.991

PUUs were synthesized in a similar manner by a modified two step polyaddition reaction. In the first step a NCO end-capped prepolymer was obtained in melt from a MD and a DI as for PU, followed in the second step of the chain extension of diluted prepolymer by using a dissolved diamine in DMF (Table 1). During the synthesis, some reaction mixture became hazy (PUU₁ and PUU₅) due to the tendency of dibenzyl structure to crystallize, emphasized by the stiffness of aromatic diamine DAPO also (PUU₁). Polymer films were cast from genuine solutions by removing the solvent at $60\text{-}80^{\circ}\text{C}$ for 24 h. Translucent elastoplastic films were obtained.

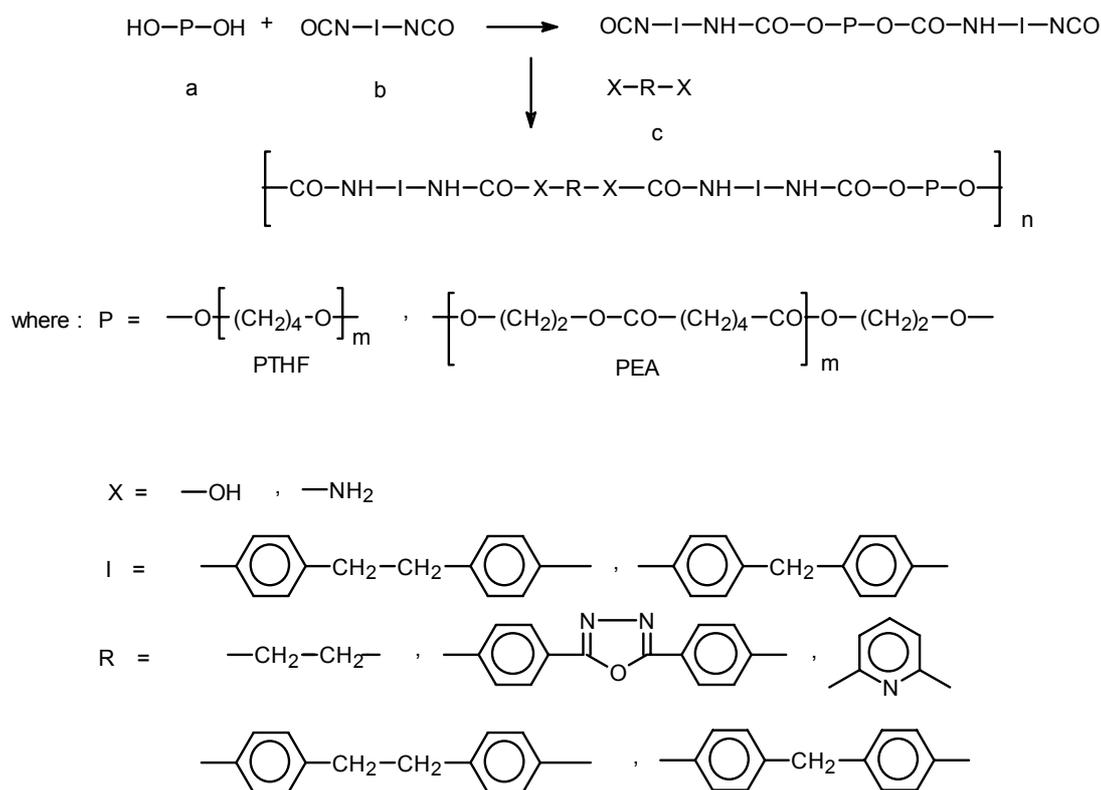
2. Polymer characterization

All the polymers were characterized by means of the IR spectra that contain IR absorption bands

attributed to urethane or urea groups at $3330\text{-}3300\text{ cm}^{-1}$ (NH), $1690, 1660\text{ cm}^{-1}$ (C=O). In the case of PUUs the characteristic bands of 1,3,4-oxadiazole ring were observed at $750, 825, 875\text{ cm}^{-1}$ (PUU_{1,2}) or of pyridine ring at 790 cm^{-1} (PUU_{3,4}). Polyurethanes PU₁₋₄ have shown higher inherent viscosities than that of the polymers obtained by diamine chain extension. The PUs inherent viscosities (η_{inh}) have ranged between 0.776 – 1.155 whereas the η_{inh} of PUUs ranged between 0.623 to 0.991 dL/g as shown in Table 1. Heterocyclic polyurethanes presented smaller values of viscosity probably due to the tendency of crystallization and separation of the product from the solution before the end of synthesis. The lower reactivity of amino groups of DAPy can be considered as well. The films of polyurethane-ureas PUU_{1,2} and PUU₅ have an appearance rather hazy than transparent, as comparing to those of

polymers based on pyridine (PUU_{3,4}) or, only on the diphenyl-methane structure (PUU₆). As previously discussed,² the x-ray diffractograms depend on the chemical structure of polymers. The crystallinity of PUs based on EG was previously discussed in detail and crystallinity degree values were found between 14-25%.^{2,11,12} Of all the polymers presented in Table 1, the dibenzyl-based

PU₁, PEA:DBDI:EG (1:2:1) and PU₃, PTHF:DBDI:EG (1:2:1) have clearly displayed the highest degree of crystallinity as shown in Fig. 8. On the other hand, as previously mentioned,⁸ the crystallinity degrees of PUUs containing DBDI differ only with 1-3% of those of PUUs based on MDI.



Molar ratio : a = 1 ; b = 2 ; c = 1

Fig. 2 – PU synthesis from MD and diisocyanates MDI or DBDI and chain extended with diol or aromatic diamines.

3. Mechanical behaviour

3.1. PUs and PUUs Stress-strain data

Mechanical tests including the stress–strain data and the load-unload cycles at constant rate of

extension, with measurement of hysteresis and strain recovery have been approached for two subsets of PU_i based on DBDI and MDI according to the structures detailed in Table 1. The results of the stress-strain measurements are given in Table 2.

Table 2

Mechanical properties of PUs and PUUs elastomers: the behaviour on tensile tests, strain and recovered energy during the first and the second loading-unloading at 300% strain

PU _i	Modulus [MPa]		Strength Stress [MPa]	Elongation at break [%]	Residual elongation [%]	E _{1C} [MPa]	E _{1R} * [%]	E _{2C} * [%]	E _{2R} * [%]
	100%	300%							
PU ₁	11.6	18.8	31.7	425	145	41.8	38.5	12.8	14.7
PU ₂	8.4	17.4	37.3	625	75	21.7	62.7	33.3	33.0
PU ₃	7.8	10.6	22.3	450	55	31.1	41.7	12.5	16.4

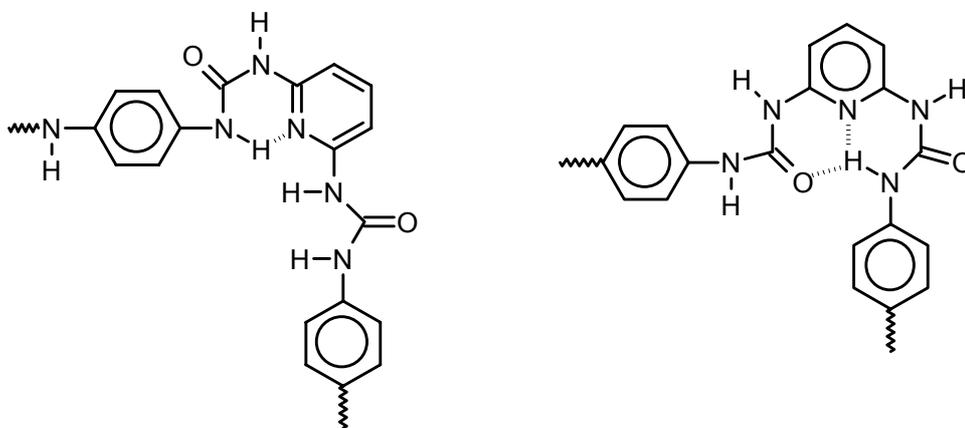
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Table 2 (continued)

PU ₄	6.7	14.7	20.3	550	80	21.8	61.9	37.5	37.3
PUU ₁	1.4	-	1.8	250	39	-	-	-	-
PUU ₂	1.9	3.4	15.7	800	216	13.62	35.1	66.8	30.5
PUU ₃	2.0	3.0	5.7	700	72	11.79	47.1	65.8	38.3
PUU ₄	1.52	2.8	5.3	750	23	10.22	32.8	73.1	38.9
PUU ₅	6.0	9.7	19.9	750	272	32.07	31.1	50.5	24.7
PUU ₆	6.3	11.4	33.5	600	50	36.48	41.6	61.5	39.5

The highest 100% Modulus values were found in the case of PU₁ with EG as a chain extender. This fact can be explained by an increased phase separation between soft and hard segments. In contrast, the smallest 100% Moduli were found as corresponding to the PUU_{1,2} and PUU_{3,4} in the synthesis of which DAPO or DAPy was used. This is due to the smaller interaction between hard segments in the case of polymers based on DAPO or DAPy, respectively. Similar conclusions could be drawn for the 300% Modulus. In the case of PUU_{1,2} and PUU_{3,4} based on DAPO (or DAPy), the values of the 300% Moduli ranged between 0 – 3.4 MPa, whereas higher Moduli were observed for the polyurethanes based on DAB and MDA: 9.7 MPa to 11.4 MPa. The best 300% Modulus (18.8 MPa) was obtained in the case of PU₁ that contains the ratio PEA:DBDI:EG of 1:2:1.

The highest strength stress values, ranging between 31.7 MPa to 37.3 MPa, were found in the case of PUs with EG chain extension, and of a polyurethane-urea, PUU₆ based on MDI and MDA (33.5 MPa). The PUUs with aromatic diamine chain extension, PUU_{5,6} have displayed better mechanical properties due to the stronger hydrogen bonds between the hard segments. The relative smaller values of the mechanical properties of heterocyclic PUUs based on DAPO can be explained by the increase of distances between urea and urethane groups on the macromolecular chain. In the case of PUUs containing DAPy some intramolecular hydrogen bonds could appear diminishing in this way the intermolecular interactions⁹ (Fig. 3).

Fig. 3 – Intramolecular hydrogen bonds attributed to PUUs with pyridine rings.⁹

As a general conclusion the higher values of the stress-strain data correspond to PUs with diol chain extension based on EG and diisocyanates DBDI (PU₁) and MDI (PU₂). The investigation of the elongation at break has revealed that as compared to PU₁ – PU₄ with diol chain extension, PUU₂ to PUU₆ with diamine as CE display higher values of the elongation at break ranging between 600% to 800%, the highest value corresponding to PUU₂ PEA:MDI:DAPO (1:2:1).

3.2. Hysteresis behaviour and the energy loss

Of particular interest was the investigation of polymer strain energy input (E_C) and of the strain energy recovery (E_R) on unloading. Polyurethanes were tested by a series of cyclic tensile tests, at a constant nominal strain-rate of $3.1 \times 10^{-2} \text{ s}^{-1}$, cycling between 300% elongation and zero load. The initial input strain energy density (E_{1C}) was computed as the area under the first cycle loading

curve of nominal stress versus nominal strain up to the elongation limit of 300%. In the same way was calculated the strain energy density (E_{2C}) for the second load cycle. Similarly, recovered energy densities (E_{1R}) and (E_{2R}) were computed as the areas under the *unloading* curves for first and second cycles respectively.^{11,12} In the present paper, E_{2C} , E_{1R} and E_{2R} are expressed as fractions of the initial input energy density E_{1C} , and denoted as such by an asterisk. In Table 2 there are presented the strain energy values both in the case of PUUs based diamine chain extenders and for PUs derived from EG. The PU strain energy values ranged between 13.62 MPa to 41.8 MPa for the strain energy input of the first loading (E_{1C}) and between 12.5%–66.8% in the case of the strain energy input of the second loading (E_{2C}^*).

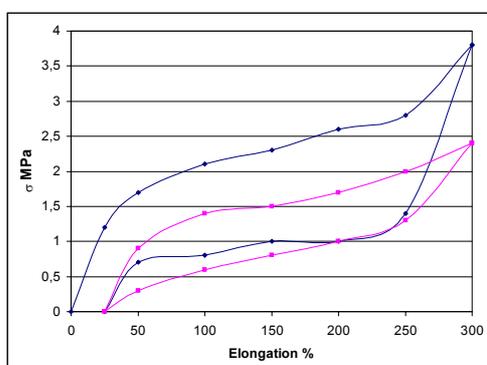


Fig. 4 – Hysteresis behaviour of the DAPO based polyurethane-urea elastomer: PUU₂.

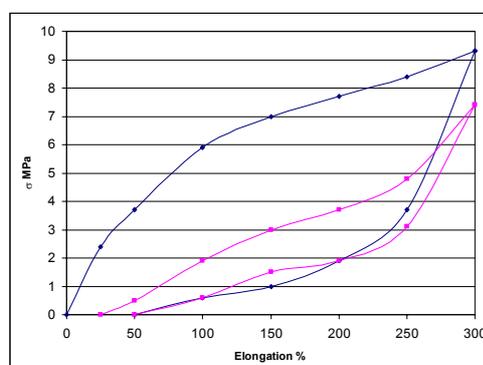


Fig. 5 – Hysteresis behaviour of the dibenzyl-based polyurethane-urea elastomer: PUU₅.

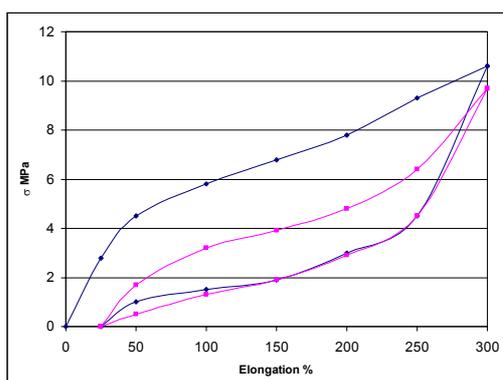


Fig. 6 – Hysteresis behaviour of the MDI-based polyurethane-urea elastomer: PUU₆.

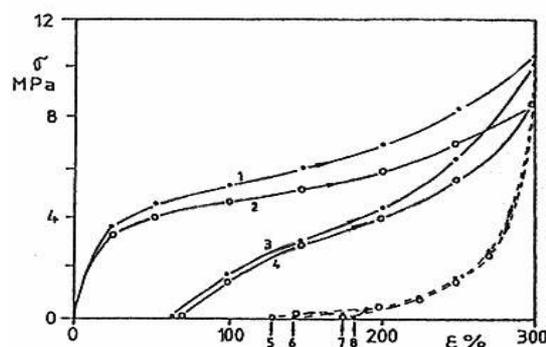


Fig. 7 – Hysteresis behaviour of a DBDI-based polyurethane elastomer based on diol EG and PTHF: PU₃ (PTHF:DBDI:EG) (1:2:1) as compared to a polyurethane elastomer based on diol EG and poly(tetramethylene adipate) glycol (PBA) (PBA:DBDI:EG) (1:2:1).

3.2.2. Hysteresis behaviour of polyurethane elastomers extended with diols (PUs)

In Fig. 7, curve 1 and 2 as well as curve 3 and 4 illustrate the first and second loading curves to a

3.2.1. Hysteresis behaviour of polyurethane-urea elastomers (PUUs)

In the case of PUU₁ that contains DAPO – DBDI structures and PEA as MD, the values of the strain energies could not be determined because the polymer could not be stretched to the level of 300% elongation. PUU₂ derived from DAPO presented significantly smaller values of strain energy input, strain energy recovery and strain recovery on unloading. In the case of PUU₅ that contains DBDI and DAB as compared to the PUU₂, higher strain energy input and energy recovery values ($E_{1C} = 32.07$ Mpa and $E_{2R}^* = 50.46\%$) were found (Table 2). Illustrative hysteresis curves for PUU₂, PUU₅ and PUU₆ are given in Figs. 4, 5 and 6.

300% level of elongation for PU₃ (EG and PTHF as diol and macrodiol) and for a diol based PU derived from another macrodiol, PBA.¹¹ In comparison to polyurethane–urea elastomers (PUUs),

PUs extended with diols have presented comparable input strain energies, with higher (E_C) values, (41.8 MPa), observed in the case of PU₁ (PEA/DBDI/EG). The mechanical performance by means of cycling tests of dibenzyl-based PU elastomers chain extended with diol as compared to other classical MDI-based PUs has been previously studied in detail.¹² The stiffness, hysteresis and residual elongation were increased in the case of PUs containing DBDI-EG couple relative to the corresponding MDI based PU. These differences between DBDI and MDI were attributed to the greater flexibility of DBDI allowing a higher tendency to self-associate by hydrogen bonding.^{2,11,12}

4. Structural studies

Structural studies on polyurethane elastomers with diol chain extension were reported in detail elsewhere^{2,11,12} where PU stress relaxation was discussed also. As shown, X-ray diffraction patterns displayed significant tendency to crystallise

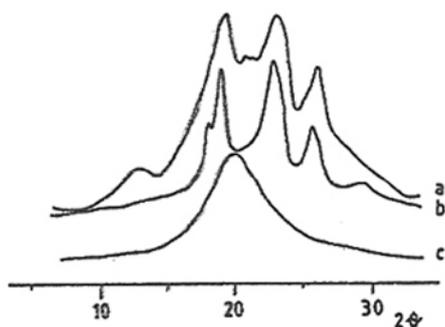


Fig. 8 – Correlation between the WAXS diffractograms of PU₁ (PEA:DBDI:EG) at two different EG/PEA molar ratios as compared to the homopolyurethane polymer model: **a** – polyurethane containing only hard segments of the type EG-DBDI; **b** – PU₁ (PEA:DBDI:EG) with molar ratio EG/PEA = 3; **c** – the same as for **b** but for molar ratio EG/PEA = 2.27.

The investigation of the phase separation in polyurethane-ureas was detailed previously.⁸ In Table 3 the crystallinity degrees of different PUUs PUU₁ - PUU₆ are presented. The X-ray diffractograms depend on the chemical structure of polymers, but the general aspect is rather alike to those of amorphous polymers. PUUs elastomers studied in this paper presented small peaks caused by hard-hard segment interactions, despite of the crystallinity tendency of the dibenzyl radicals leading, for example in the case of simplest polyureas⁵ (that not contain blocks of polyester or polyethers), to crystallinity degrees of up to 67%.⁵ Thus, the crystallinity degrees of PUU_{1,2}

for the PU materials based on DBDI hard segments. There was evidence of the appearance of phase separation associated with the formation of discrete crystalline hard domains. In Figure 8 there are depicted the X-ray diffractograms of some PUs with two different molar ratios in comparison to a polymer model made up only by hard segments (EG-DBDI). As seen, the typical WAXS curve of PU₁ (PEA:DBDI:EG) (curve **b**) is very similar to those of the polymer (curve **a**), and the peaks areas are proportional to the PU hard segment content. If reducing the number of hard segments and consequently the molar ratio from EG/PEA = 3 (curve **b**) to EG/PEA = 2.27 (curve **c**) the shape of the diffractogram changes. There appears crystalline structures of other types¹¹ within the soft segments are involved also. The similarity of curves **a** and **b** confirms the conclusion that the PU hard segments associates preferentially between themselves and the interactions with the soft segments are lower leading to a pronounced phase separation.

were of 11.11% and 8.33%, respectively, and were somehow higher than those of PUU_{5,6} (7.44 and 6.12%, respectively). On the other hand, PUUs containing pyridine are amorphous due to their peculiar structures made by intramolecular hydrogen bonds (Fig. 3).⁹ Smaller crystallinity degrees can be explained by the larger distances between urethane and urea groups belonging to the same repeating units (on the same macromolecular chain) than in the case of PUs chain extended with EG. As comparing to PUs with diols chain extension, PUUs presented a reduced phase separation.

Table 3

Crystallinity of polyurethane-ureas

PU _i	Composition	Molar ratio	Crystallinity (%)
PUU ₁	PEA - DBDI - DAPO	1 - 2 - 1	11.11
PUU ₂	PEA - MDI - DAPO	1 - 2 - 1	8.33

(continues)

Table 3 (continued)

PUU ₃	PTHF-DBDI-DAPy	1 - 2 - 1	Amorphous
PUU ₄	PEA-MDI-DAPy	1 - 2 - 1	Amorphous
PUU ₅	PTHF-DBDI-DAB	1 - 2 - 1	7.44
PUU ₆	PTHF-MDI-MDA	1 - 2 - 1	6.12

EXPERIMENTAL PART

1. Materials

Polyethylene adipate (PEA) from Bayer and polytetrahydrofuran (PTHF) from BASF with the molecular weight $M=2000 \pm 50$, both of them with OH final groups, were commercial products. Commercial diisocyanates: 4,4'-methylene-bis(phenyl-isocyanate) (MDI) (Aldrich) and 4,4'-dibenzyl diisocyanate (DBDI) (Savinesti, Romania) were purified before use by distillation at 0.1 mm Hg (MDI) or by recrystallization from dry cyclohexane (DBDI). Commercial ethylene glycol, as well as, aromatic diamines: 4,4'-methylene dianiline (MDA) from Fluka and 4,4' diamino-dibenzyl (DAB) from Savinesti, Romania, were used as received (MDA) or after recrystallization from water (DAB). 2,5-Bis-(4-amino-phenylene)-1,3,4-oxadiazole (DAPO) was prepared by a known method¹⁰ and purified by recrystallization from alcohol. 2,6-Diamino pyridine (DAPy) from Merck (reagent grade) was purified by distillation in vacuum before use. Dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), were commercial products and were purified by keeping on drying agents and distillation before use.

2. Synthesis of polyurethane (PUs) and polyurethane-urea elastomers (PUUs)

Polyurethanes were synthesized by a general method described elsewhere.^{1,2} They were prepared by a two-step polyaddition reaction. In the first step a prepolymer was synthesized in the melt from a macrodiol and a diisocyanate followed by a reaction with a chain extender to build up the hard segments. All the polymers presented a diisocyanate index $I = 100$, e.g., an equimolar ratio of NCO and X groups as shown in Table 1 as well as in Fig. 1. PUs with diol CE were obtained in melt without any solvent. First step of PUU synthesis occurs similar to those of PU synthesis, but in order to maintain the homogeneity of reaction mixture, the chain extension step of NCO end-capped prepolymer consisted of a solution polyaddition reaction between the diluted prepolymer with DMF and a diamine solution.⁸

3. Measurements

The IR spectra of the polymers were recorded with a Specord M80 instrument by using thin films cast from NMP solution on KBr pellets. Inherent viscosities of 0.5% polymer solutions in NMP or DMF at 20°C were performed with an Ubbelohde viscometer. Wide angle X-ray diffraction patterns were performed on polymer films by using Nickel filtered Cu $K\alpha_1$ on DRON-2.0 unit (25 kV, 20 mA). 300% tensile stress and the strength stress determination were made in accordance with standard procedures from the stress-strain curve data of simple uniaxial tension at room temperature. The polymers shown in Table 1 in the form of films prepared as described above, were subjected to uniaxial tensile tests at constant nominal strain-rate. In addition, to investigate mechanical hysteresis, cyclic tensile tests were carried out, cycling

between a fixed strain limit and zero load, with the same magnitude of strain-rate for loading and unloading.

CONCLUSIONS

A series of polyurethanes and polyurethane-ureas was synthesized based on DBDI or MDI, and a diol or diamine as chain extenders. Macrodiol spacers were PEA or PTHF. Of all the polymers studied the dibenzyl-based PUs with PEA extended with EG have clearly displayed the highest degree of crystallinity but remain in all cases significant lower than that of corresponding polymers not containing soft segment spacers. The crystallinity degrees of polyurethane-ureas containing dibenzyl structures has differed only with 1-3% from the crystallinity of polymers based on MDI. Dibenzyl-based polyurethanes chain extended with diol have shown higher inherent viscosities than the dibenzyl-based polyurethanes with diamine chain extension. The mechanical behavior of all the elastomers was investigated. The mechanical properties of polyurethane-ureas chain extended with DAPO (PUU_{1,2}) were weaker than those of polyurethane-ureas chain-extended with aromatic diamines DAB or MDA (PUU_{5,6}) due to the weaker hydrogen bonds between the larger and stiffer hard segments. Comparing successive load-unload cycles, it was found that irreversible changes to the stress-strain response were confined essentially to the first loading cycle. In subsequent cycles the load-unload stress-strain curves remained almost unchanged. In comparison to polyurethane-urea elastomers, polyurethanes extended with diols presented comparable input strain energies, with higher values observed in the case of polymers derived from DBDI, PEA and EG as a chain extender.

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