

Recent Perspectives Into The Study of Copolyurethane Elastomers With Varying Hard and Soft Segments

C. Prisacariu, E. Scortanu, B. Agapie and F. Piana

Abstract – The present work is a part of a wide study of the effects on structure, mechanical and thermal response of copolyurethane elastomers by varying the key structural variables: hard segment, soft segment, and crosslinking in polyurethane elastomers. The effects of varying hard segment were studied in the context of a variety of combinations of chain extender, macrodiol and their proportions. Two hard segments were considered, based on the model diisocyanate 4,4'-methylene bis(phenyl isocyanate (MDI) and on the flexible diisocyanate 4,4'-dibenzyl diisocyanate, (DBDI). The mechanical performance of these materials as elastomers was shown to vary greatly depending on the composition. Due to the greater flexibility of DBDI allowing a higher tendency to self-associate by hydrogen bonding, the polymers with DBDI hard segments, showed higher stiffness and strength than the conventional MDI based polymers, but with lower strain recovery and strain energy recovery on cycling—a primary consideration for elastomers. Materials with mixed MDI and DBDI hard segments were found to give the optimum combination of high input strain energy, but minimum residual strain, compared to equivalent materials based on MDI or DBDI alone.

Index Terms — segmented polyurethane elastomers, flexible hard segments, cycling tensile tests, structural studies.

I. INTRODUCTION

POLYURETHANE polymers form a class of material that are characterized by presence of the urethane link —CO—NH—O— in the macromolecular backbone, and formed by reaction between a isocyanates and polyols, but materials with wide variations in physical properties are possible, by varying the choice of these ingredients [1].

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In the segmented copolyurethane elastomers studied in the present work, molecules consist of alternating flexible (soft) and relatively rigid (hard) segments. Phase segregation occurs during and following polymerization, to produce an elastomeric matrix of the soft segments, containing rigid inclusions (of size scale 10-100 nm) formed by association of the hard segments

A series of segmented thermoplastic polyurethanes (TPUs) based on 4,4'-dibenzyl diisocyanate monomer (Figure 1) were obtained. This monomer belong to a large category of diaromatic compounds with a variable geometry which induces significant effects in the macromolecular chains, especially those in connection to the rearranging capacity of the molecular fragments and thus to the increase in the degree of crystallinity [1-6]. The present paper deals with the study of physical, mechanical and chemical aspects of TPUs block copolymers derived from the diisocyanates 4,4'-dibenzyl diisocyanate (DBDI) [1-7], 4,4'-methylene bis(phenyl isocyanate (MDI), or combinations of those.

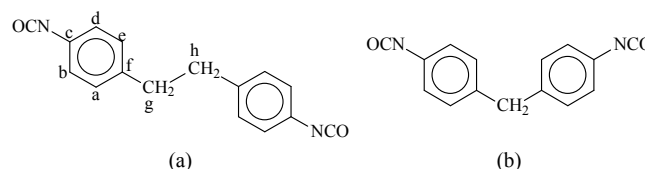


Fig. 1. Schematic of 4,4'-dibenzyl diisocyanate (DBDI) (a) and of 4,4'-methylene bis(phenyl isocyanate) (MDI) (b).

An investigation was made of the effects of varying hard segment chemistry on the mechanical response of melt-cast polyurethane elastomers. Rotation around the central —CH₂—CH₂— bridge in DBDI allows alignment of aromatic rings and hence crystallization within the hard phase, which is not available with MDI in melt-cast polyurethanes.

II. EXPERIMENTAL

The materials were synthesized in the Romanian laboratory. They were all three-component systems combined in stoichiometric proportions, and consisting of: (1) a diisocyanate (DI) generating hard segment (HS) (MDI or DBDI); (2) three soft segment macrodiols (MD) – polyethylene adipate (PEA), polybutylene adipate (PBA) and polytetrahydrofuran (PTHF), and (3) three small molecule diols as chain extenders (CE) - anhydrous ethylene glycol (EG), 1,4-butanediol (BG) and diethylene glycol

(DEG) as shown in Figure 2. The MDs were all of molar mass $M_w = 2000 \pm 50 \text{ g mol}^{-1}$. The three components were always mixed in the proportions HS:CE:MD = 4:3:1, giving hard segment mass fractions in the region of 35%, and isocyanic index $I = 100$. The synthesis procedure followed was the pre-polymer route described previously by Prisacariu et al. (2005). The HS and MD components were reacted together with vigorous mixing under vacuum at 100°C , to give prepolymer terminated by HS. This was then thoroughly mixed with the CE at 90°C , and cast into closed sheet moulds for curing at 110°C for 24 hours. The final result was polymer with M_w in the range $60\text{-}120 \text{ kg mol}^{-1}$, in the form of sheets with thickness in the range $0.3\text{-}0.6 \text{ mm}$. The sheets were stored at room temperature for at least one month before testing. For TPU with mixtures of DI (MDI/DBDI), the synthesis was performed as previously reported elsewhere [5].

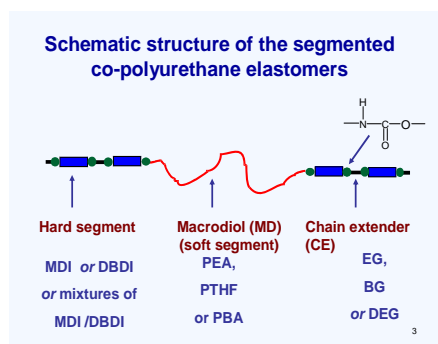


Fig. 2. Chemical structures of the TPUs prepared and studied in this work.

III. RESULTS AND DISCUSSION

A. Structural studies

In polymers there were tendencies to phase separation, with a characteristic length of ca 20 nm, and, when DBDI was employed with certain chain extenders (EG or BG), to crystallization of the hard phase. In all cases the more mobile DBDI structure lead to HS with a higher tendency to self associate evidenced by higher melting points and crystallization tendency which is visible even when such structures are included in the polyurethane soft segment matrix. The X-ray diffraction patterns of Figure 3a show that crystallizability of DBDI based PU largely remains even after of inclusion of soft segments. The crystallinity is however absent in the model TPU obtained with MDI materials, Figure 3b.

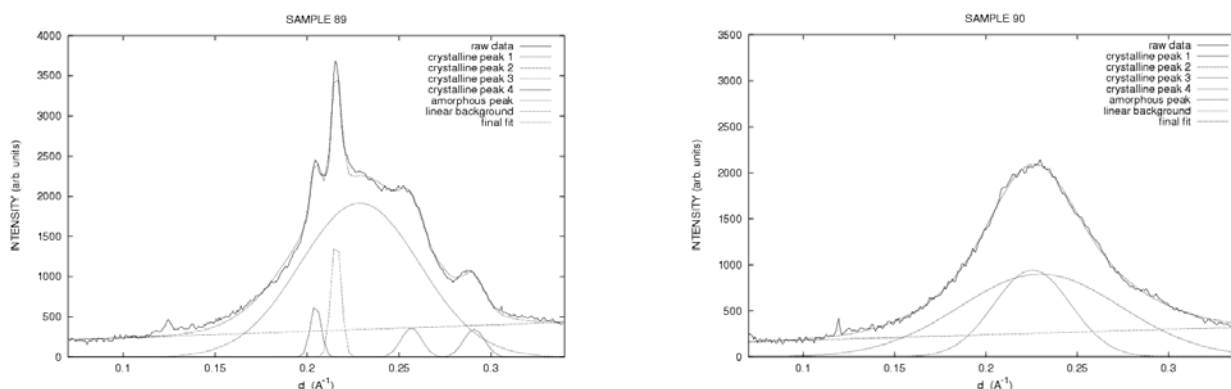


Fig. 3. WAXS profiles: (a) Hard segments = DBDI $\chi=0.14$; (b) Hard segments = MDI $\chi=0$.

Shown in Figures 4 and 5 are example IR spectra for two materials with analogous structures where only the type of the DI differs.

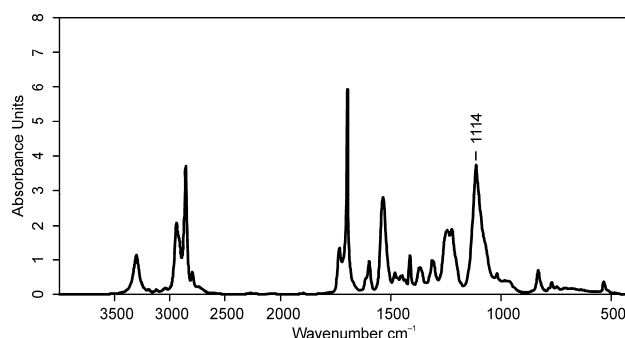


Fig. 4. IR spectrum of a DBDI/PTHF based TPU extended with DEG (non-crystallizing HS)

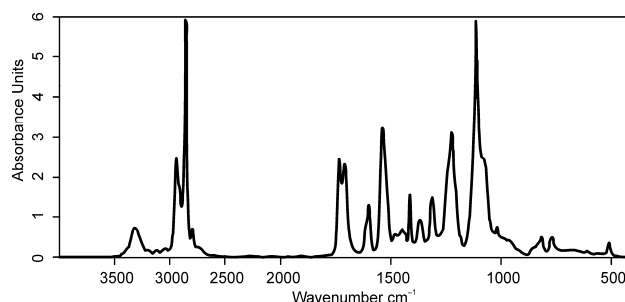


Fig. 5. IR spectrum of a MDI/PTHF based TPU extended with DEG (non-crystallizing HS)

TABLE I.
ASSIGNMENTS OF THE ABSORPTION BANDS IN IR SPECTRA OF THE TPU DESCRIBED IN FIGURES 3 AND 4.

DBDI:PTHF:DEG	MDI:PTHF:DEG	Attribution
2940s	2941m	vC-H asym
2741w		vC-H sym
2272w		vC-d asym
1733m	1733s	vC=O asym
1697s	1709s	vC=O sym
1245m		δ C-H
1224m	1223s	vC-N sym
1114s	1117vs	vC-N

The decrease in intensity of the signals 1733 cm^{-1} , can be attributed to a stronger interaction $\text{C}=\text{O} \cdots \text{H}-\text{C}$ with DBDI than with MDI but it also observes a shift due to an elongation of the C—O bond. A small shift in the right direction is observed in another peak: vC=O sym. Comparing the samples, the C=O moiety in the materials with DBDI has less freedom of movement. Similarly, with regard to the vC—N peaks, no shift and intensity stronger

were observed in the MDI based material. A possible explanation for this behaviour is that in the DBDI based TPUs the higher mobility due to two CH₂ between the phenyl groups consent a better arrangement of the chains to form more and more stable C—H---X—C interactions. This is consistent with our previous observations revealed by IR dichroic studies and DSC experiments.

The degree of crystallinity of the DBDI based PUs was sensitive to the choice of chain extender. EG lead to distinct diffraction peaks, whereas DEG gave amorphous DBDI based polymers. The crystallinity index (χ) was higher for PUs with DBDI and PEA or PCD, extended with EG at lower SAXS peak areas; EG lead to distinct diffraction peaks. Inelasticity was greater for DBDI hard segments than for MDI. Polymers with DBDI but extended with DEG were amorphous ($\chi = 0$) [5,6]. There was evidence of the appearance of more or less complete phase separation associated with the formation of discrete crystalline hard domains.

All the MDI-based polymers showed no, or only slight, crystallinity, whereas those with DBDI had degrees of crystallinity up to 16% as revealed by the crystallinity index (χ). The only polymers that had significant crystallinity were those based on DBDI. This is consistent with previous reports of comparisons between melt-processed polyurethanes based on these two DI and other CE like BG [2, 7]. The presence of DBDI does not always lead to crystallinity: it depends on the choice of chain extender. The DBDI-based polymers with DEG as chain extender can be seen to have no detectable crystallinity [2, 5, and 7]. The central —O— atom present in DEG introduces kinks into the DBDI hard segment and disrupts the chain packing that could otherwise be achieved.

As shown elsewhere, all materials with PTHF showed much higher intensity in SAXS. TePUs with PTHF displayed higher phase segregation as revealed by higher values of the Q scattering invariant. Such TPUs have fewer H bonding: only 40% of the carbonyl in polyether urethanes are hydrogen bonded than polyester urethanes (PEA, PBA) with same hard segment content. PEA and PBA have a greater affinity for the DI through hydrogen bonding to their ester groups and hence are more miscible with the DI and phase segregation is expected to be less pronounced.

B. Mechanical tests results. Cycling tensile tests

The materials were cycled between an extension of 3, and zero loads, for 3 cycles. As shown elsewhere, the TPUs based on DBDI hard segments, displayed higher stiffness and strength than the analogous conventional MDI based materials.

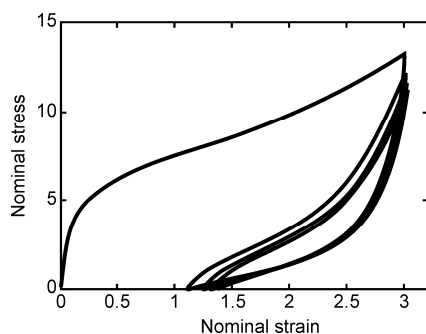


Fig 6. Example curves of nominal stress versus nominal strain for three cycles of a MDI based TPU (MDI:EG:PBA) between zero stress and a nominal strain of 3.

Example curves of nominal stress versus nominal strain are shown in Figures 6 and 7 for materials based on the macrodiol PTHF and diisocyanates MDI (not crystallizing), or DBDI (crystallizing). Polymers based on DBDI hard segments, display higher stiffness and strength than the conventional MDI-based materials.

Significant higher Young Modulus value were found for the materials achieved with the couples DBDI/BG and DBDI/EG.

Some examples are shown in Figure 8 for six materials all of them extended with EG, three of which were obtained with DBDI (open symbols) and the other three were achieved with MDI (filled symbols). Tensile modulus is plotted versus degree of crystallinity deduced from WAXS as detailed elsewhere. Lines are only to guide the eye: they link materials differing only in diisocyanate. The E moduli $E = d\sigma / d\varepsilon$ at $\varepsilon = 0.01$, were determined as detailed elsewhere by fitting a quadratic function to the stress-strain curve over the range 0.005-0.015 and differentiating analytically [5]. As seen in Figure 8, the tensile modulus (E) increased significantly with degree of hard phase crystallinity.

The highest Young Modulus values were observed in the case of the TPUs based on hard segments (crystallizing) based on DBDI and extended with EG or BG (up to 185-190 MPa), followed by lower E values for the materials achieved with DBDI and extended with DEG (not crystallizing) (approximately 138 MPa), as compared to significantly smaller E values for the MDI based polymers non crystallizing regardless the type CE used in the material synthesis (85 MPa).

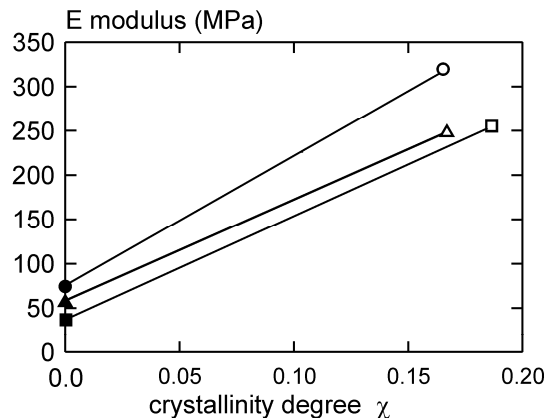


Fig.8: Tensile modulus versus degree of crystallinity deduced from WAXS. Filled symbols – MDI-based polymers; open symbols – DBDI-based polymers

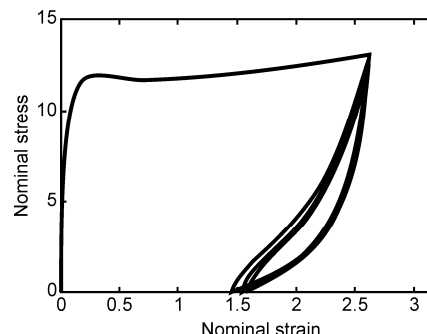


Fig7. Same as Fig.6 but for DBDI based TPU with a similar structure(DBDI:EG:PBA.)

C. Optimizing the TPUs tensile cycling properties.

Materials derived from mixtures of diisocyanates

In a further stage of our study three families of TPUs materials based on mixtures of the two diisocyanates MDI and DBDI were prepared: A, B, C, where HS molar compositions were as follows (%MDI/%DBDI): A 100/0; B 0/100; C 50/50. The soft segment macrodiol PTHF or PEA of molar mass 2000 ± 50 , and the chain extender was EG. In the case of family C, equal molar quantities of MDI and DBDI were pre-mixed before the combination with MD, followed by chain extension. Further details of the synthesis are given elsewhere [5]. The molar proportions used in the syntheses were: DII:MD:EG = 4:1:3.

In particular, polymer B with DBDI hard segments, showed higher stiffness and strength than the conventional MDI-based polymer A, but with lower strain recovery and strain energy recovery on cycling—a primary consideration for elastomers. Shown in Figure 9 is the residual strain depicted as a function of the nominal strain for the three polymers A, B and C.

Such features of the response were attributed to differences in hard phase plastic flow stress, resulting from crystallinity in the DBDI phase [2, 3, 5], that is absent in MDI. Polymer C (with randomly mixed MDI/DBDI hard phase), however, showed advantages of increased strength and stiffness, plus *increased* strain recovery, compared to polymer A, thus offering improvements in all these properties.

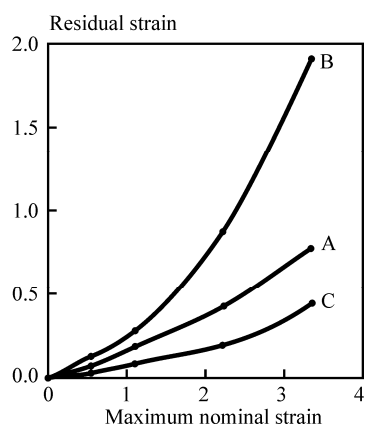


Fig.9. Comparison of materials with macrodiols PBA- residual strain from one load/unload cycle (nominal strain 0.0042/s).

IV. CONCLUSION

An investigation was made of how aspects of the constitutive responses of segmented polyurethane elastomers vary with composition: the hard segment, soft segment and chain extender were varied. Hard segments were generated from 4,4'-methylene bis(phenyl isocyanate)

(MDI), or from 4,4'-dibenzyl diisocyanate (DBDI). A series of mechanical tests was designed to compare inelasticity of polymers under cycling to fixed extension. Results were related to microstructural changes, on the basis of evidence from x-ray scattering (WAXS). Inelastic effects were most pronounced when the hard segment crystallized. The dominant results from these tests were the differences between polymers based on the two hard segments DBDI and MDI. Hard domain hydrogen bonding and crystallinity exert strong influences on inelasticity of TPU elastomers. The presence of DBDI hard segments instead of MDI led to increases in the Young Modulus and residual strain under cyclic loading. This revealed that the observed effects of varying hard segment could all be explained by the hard domains having a higher flow stress in the presence of DBDI relative to MDI, associated with increased hydrogen bonding in DBDI-based polymers, which is enhanced in some by hard segment crystallinity. Materials with mixed MDI and DBDI hard segments were found to give the optimum combination of high input strain energy, but minimum residual strain, compared to equivalent materials based on MDI or DBDI alone.

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