

# New Developments in Thermoplastic Elastomers: The Hard Segment Inelastic Effects OnThe Mechanical Performance of Polyurethane Elastomers

Cristina. Prisacariu, Elena Scortanu, and Paul C. Buckley

**Abstract**— A study was made of a family of polyurethane copolymers, in which the chemical components were: a hard segment (giving, on phase separation, hard nano-scale reinforcing particles); a soft segment (giving, on phase separation, an elastomeric matrix), and a diol chain extender. The chemical compositions of all three components were varied systematically and independently, and their mechanical responses were measured in cyclic tensile tests at room temperature, up to stretches in the range 5-6. Particular attention was paid to characterizing the inelastic features – hysteresis, and stress relaxation in interrupted tests – and their variations between the materials. The same materials were also studied by wide-angle X-ray scattering (WAXS), to determine levels of crystallinity. Results showed that hysteresis was increased by increasing hard phase crystallinity. This was the case for polyurethanes based on the novel diisocyanate 4,4'-dibenzyl diisocyanate (DBDI). The extent of stress relaxation in interrupted tests was found to increase with hysteresis and hence with hard segment crystallinity, reflecting the higher flow stress of the reinforcing hard domains. Polymers based on DBDI hard segments, displayed higher stiffness and strength than did the conventional materials. Both features of the response were attributed to differences in hard phase plastic flow stress, resulting from crystallinity in the DBDI phase.

**Index Terms**—flexible hard segments, physical –mechanical properties, polyurethanes. .

## I. INTRODUCTION

A study has been made of inelastic effects in the deformation of thermoplastic copolyurethane elastomers, where there is potential for formation of a two-phase

Manuscript received October 9, 2007. This work was supported in part by an ongoing NATO Collaborative Linkage Grant, 2005 – 2008, Project nr: PDD(CBP.EAP.CLG 981805/ 22.07.2005).

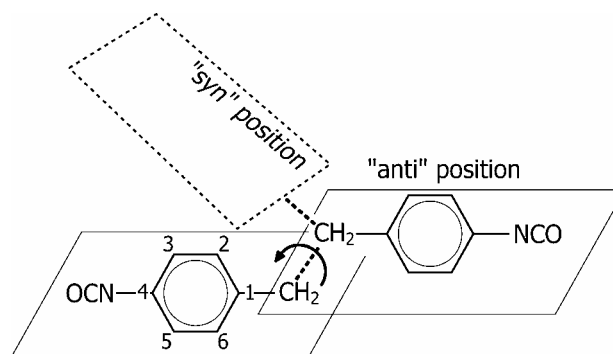
F.A. Author (presenting author), C. Prisacariu is with the Institute of Macromolecular Chemistry Petru Poni, Iasi, Romania, (phone: 40-232-217454; fax: 40-232-211299; e-mail: [crispris@icmpp.ro](mailto:crispris@icmpp.ro)).

S. B. Author, E. Scortanu is with the Institute of Macromolecular Chemistry Petru Poni, Iasi, Romania, (phone: 40-232-217454; fax: 40-232-211299; e-mail: [nutiscor@icmpp.ro](mailto:nutiscor@icmpp.ro)).

T. C. Author, C. P. Buckley, is with The Department of Engineering Science, University of Oxford, OX1 3 PJ, Oxford, UK; e-mail: [paul.buckley@eng.ox.ac.uk](mailto:paul.buckley@eng.ox.ac.uk)

microstructure (hard reinforcing particles embedded in an elastomeric matrix), but where the *nature* of the hard phase and the *degree* of phase separation can be controlled via the chemical structure and preparation conditions.

Numerous block copolyurethanes (PUs) were investigated, based on several diisocyanates, macrodiols and chain extenders, with the aim of improving understanding of the relationship between molecular/supramolecular architecture at the nm-scale and macroscopic mechanical properties in such systems. A novel diisocyanate, DBDI, (Figure 1) and a triol chain extender (1,1,1-trimethylol propane (TMP)) were included as well as more widely-used components, in order to widen the range of structures achievable beyond those normally available.



4,4'-dibenzyl diisocyanate (DBDI)

Figure 1. Schematic of isocyanate DBDI. Ref: [1].

It has been shown already that these chemical changes, and variation of thermal history, lead to varying degrees of phase segregation and crystallization in the hard segment, particularly when using DBDI which displays a variable geometry due to which there result PUs with increased degrees of crystallinity. Rotation around the central -CH<sub>2</sub>-CH<sub>2</sub>- bond in DBDI allows alignment of successive aromatic rings thus favoring the tendency of crystallization which involves the DBDI hard phase [1-5].

As previously shown, in the case of PUs with DBDI which were synthesized with ethylene glycol (EG) as a chain extender, we observed a remarkable tendency of the EG-DBDI segments to crystallize. As shown, the origin of these effects was intimately related to the nano-scale structure of the elastomers: the degree of phase segregation and the size and perfection of the hard domains [5]

In polymers with diol chain extenders there were tendencies to phase separation, with a characteristic length of ca 20nm, and, when DBDI was employed with certain chain extenders, to crystallization of the hard phase. PUs crystallization was inhibited when using the flexible chain extender DEG [2].

In polymers prepared with the triol TMP as chain extender a crosslinked system was obtained, preventing phase separation [4]. Measurements of the mechanical responses revealed clear evidence for phase segregation causing a bimodal distribution of molecular mobility of the soft segments: a more mobile fraction remote from the hard phase and a constrained fraction at junctions with the hard phase. Moreover the relative mobilities of the constrained fractions could be seen to reflect those of the corresponding hard segments (DBDI being more flexible than the more usual MDI) to which they were joined. Even in the crosslinked systems a similar effect was observed, with the isocyanate-capped crosslink junctions playing the role of a hard phase.

In the present study such PUs based on the diol chain extender EG and DBDI were compared to polymers derived from the conventional rigid isocyanate 4,4'-diphenylmethane diisocyanate (MDI) alone; and to PUs based on mixtures of the rigid MDI and flexible diisocyanate DBDI.

PUs were prepared with no excess of NCO groups, giving isocyanic index  $I = 100$ . The changes in crystallinity occurring in PUs based on mixtures of isocyanates (DI) were followed as compared to those observed in PUs based on MDI and/or DBDI alone. Wide angle X-Ray scattering (WAXS) were employed to follow the changes that were brought about by changing the type and the number of isocyanates (one or two DI), and the order of their introduction in the material synthesis.

## II. EXPERIMENTAL.

### II.1. MATERIALS

A. PUs derived from a single diisocyanate ( $PU_D$  with DBDI, and  $PU_M$  with MDI) (Table 1), were obtained as follows: 100g (0.05 mol of macrodiol polyethylene adipate (PEA) was dehydrated under mixing at 110° C and vacuum (< 1mm Hg) for 2 hours. 52.8g (0.2 mol) of DBDI for the  $PU_D$  type or respectively 50g (0.2 mol) of 4,4'-methylene bis (phenyl isocyanate) MDI in the case of  $PU_M$  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 isocyanic NCO groups in mixture with the excess of isocyanate. Next 9.295 g (0.150 mol) of chain extender were added at once under rapid stirring. The mixing was continued for maximum 30-40 seconds. The "pot life" of the mixture was between 3 and 10 minutes depending on the PU structure. For the cure process the closed mouldings 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 PU oligomer with NCO final groups, were demoulded.

B. Copolyurethane elastomers from two diisocyanates randomly distributed ( $PU_{C1}$ ), were synthesized starting from PEA as seen in table 1.

C. Copolyurethane elastomers from two diisocyanates with selective diisocyanate distribution ( $PU_{C2}$  and  $PU_{C3}$ ) were obtained by a prepolymer synthesis in two steps and were also synthesized starting from PEA as seen in Table 1. The general procedure was described elsewhere [1,3].

Table 1. Composition of the family of PUs

Recipe	PU structure
$PU_{C1(91)}$	EG-PEA-(DBDI-MDI)
$PU_{C2(92)}$	EG-(PEA-DBDI)-MDI
$PU_{C3(93)}$	EG-(PEA-MDI)-DBDI
$PU_{D(94)}$	EG-PEA-DBDI
$PU_{M(95)}$	EG-PEA-MDI

### II.2 TEST METHODS

Wide-angle X-ray scattering patterns were collected using an URD 63 diffractometer (FPM-Seifert, Germany), which was equipped with a scintillation detector. Ni-filtered  $Cu K\alpha$  radiation of wavelength 1.5418 Å was used, and the machine was operated in transmission mode. The counting time and the angular increment in data collection were 5 s and 0.05° (2 $\theta$ ), respectively.

Mechanical tests: the sheet materials were cut into rectangular strips of dimensions 6 mm × 0.3-0.6 mm, and tested in tension at ambient temperature and humidity (50% RH) using an Instron model 4204 testing machine, with 50 mm between the grips. Extension was measured using an Instron "elastomer" extensometer, with a gauge length of 20 mm. All the tests reported here were conducted at a nominal extension-rate of  $\pm 3 \times 10^{-2} s^{-1}$ .

The data were processed to quantify specific inelastic features in the mechanical responses of the materials: unrecovered strain, hysteretic energy dissipation, and stress relaxation.

### III. MECHANICAL TESTS RESULTS

A series of mechanical tests was designed to compare inelasticity of materials under cycling to increasing extension. Each specimen was subject to a continuous pseudo-cyclic straining sequence, such that on the  $n$ th cycle it was cycled between a maximum nominal strain  $\epsilon_{max} = n$  and zero load. A typical curve of nominal stress versus nominal strain for an MDI-based material is shown in Figure 2. It shows a clear example of the Mullins effect [5] whereby, on each cycle, the material appears softer on reloading than during loading, until the previous maximum extension is reached, when the curve rejoins the previous curve. The results were compared with corresponding data for DBDI-based materials, as shown in Figure 3. It observed that: (a) the sign of stress changes and is different between loading and unloading of PU; this is consistent with a two phase microstructure where there are two contributions to the stress: an elastic component and a viscous component [2]. The sign of the viscous stress changes sign on reversal of straining, and therefore relaxation of this stress during unloading produces an increase in net stress.

(b) the magnitude of the mechanical stress relaxation is higher in the case of PUs with DBDI as compared to those

with MDI; this is again consistent with the larger contribution of hard phase stress [2,5] in the case of the DBDI based PUs; Note that the magnitude of stress relaxation increases with strain during loading. This indicates that the stress contribution from the hard phase is increasing with strain, i.e. the strain-stiffening is not only from the soft (rubberlike) matrix. This is consistent with the arguments used on our earlier works [2,5], that the flow process needs to be considered as intrinsically anisotropic: with deformation the relaxing units tend to align with the direction of straining.

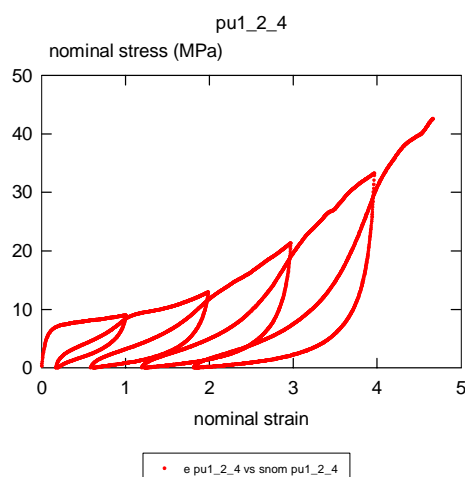


Figure 2. Stress-strain curve for a MDI-based material  $PU_M$ , during continuous cycling between increasing extension and zero load.. Ref: [5].

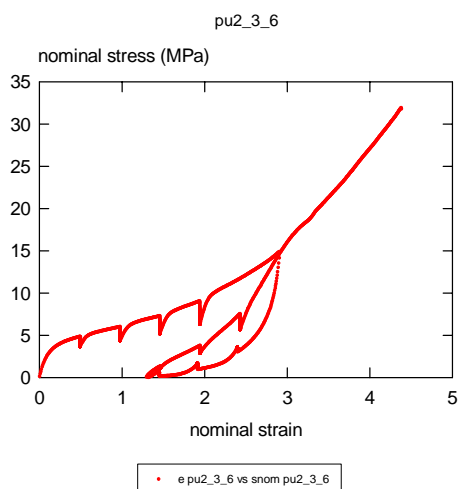


Figure 3. As in Figure 2 but for a polymer with DBDI

In general for the same type of diisocyanate the value of the strain energy input of the first loading to a 300% level of elongation, increases with the enhance of the hard segment content and with the increase of the PU toughness respectively. This is due to the stronger consolidation of the macromolecular network determined by the enhance of the number of hydrogen bonding.

Due to the DBDI crystallization, in the case of cyclic loading – unloading experiments PUs with dibenzyl structures have lower values of the strain input energies and recoverd energies respectively,.

As seen in Figure 4 , the recovered energy value is always smaller in the case of the PUs based on the flexible DBDI than in the case of conventional materials with MDI[2,3]; this is due to the flow stress characteristic to the hard phase,

regarding the percent of the strain energy input that can be recovered.

We have found trends in the cyclic stress-strain response, including a systematic variation in the degree of Mullins effect shown, with varying chemical structure [4,5]. It appears the origin of these effects is intimately related to the nano-scale structure of the elastomers: presumably the degree of phase segregation and the size and perfection of the hard domains.

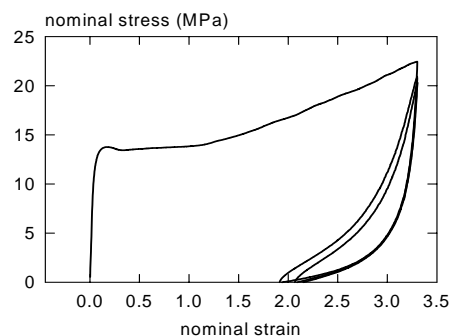


Figure 4. Tensile load –unload cycles for a DBDI based PU. Ref: [3].

A unifying feature of the cyclic stress-strain response of the different categories of reinforced elastomers mentioned above was that the pattern of behaviour was similar in all cases[2,5].

PUs stress-strain data were compared. Significant differences were found between PUs, revealing differences in the mechanical contribution of the hard phase, since the matrix was formed from the same macrodiol (PEA) and same chain extender (CE), in each case ethylene glycol (EG). As seen in Figures 5 and 6 the 300% tensile stress modulus was significantly higher in the case of copolyurethanes  $PU_{C1}$  (91) obtained by a single step prepolymer synthesis which used a melt mixture of the two isocyanates (M+D), when the two different diisocyanates were inserted more or less randomly into the prepolymer.

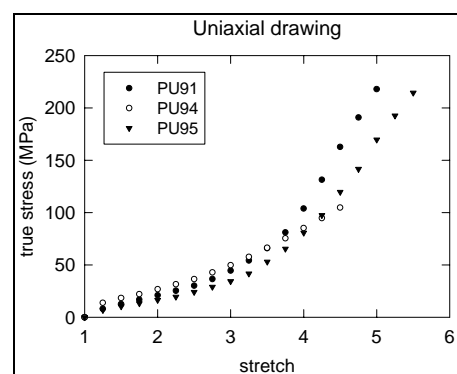


Figure 5. Stress-strain data of PU elastomers  $PU_{C1}$ (91),  $PU_{C2}$  (92) and  $PU_{C3}$  (93), obtained using mixtures of isocyanates

The lowest tensile strength value was found in the case of PUs derived from a single diisocyanate  $PU_D$  (94) with DBDI). Similar conclusions could be drawn with regard to the strain energy input (at 300% elongation) and strain energy recovery (on unloading from 300% elongation).

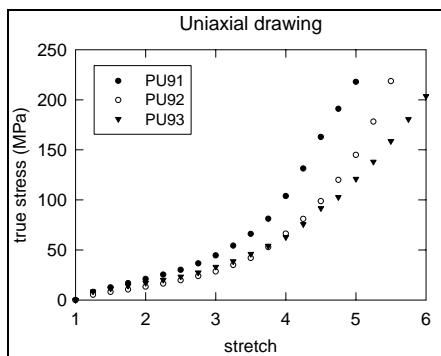


Figure 6. Stress-strain data of  $PU_D$  (94) – based on only DBDI, and  $PU_M$  (95) – based on only MDI, as compared to  $PU_{C1}$  material single step prepolymer synthesis which uses a melt mixture of the two isocyanates (M+D).

The most extreme difference between the effects of MDI and DBDI hard segments was observed in the case of PUs based on a single diisocyanate, where the chain extender–diisocyanate couple was EG-DBDI, where the hard segments were observed to crystallize. In the first deformation steps the materials with hard segments based on DBDI ( $PU_D$ ) displayed a higher strength, followed by values of strain which required smaller stress increments. This observation was correlated to the appearance of better structured hard segment domains, in the case of the EG-DBDI couple, determined by their tendency to self-associate in hard crystalline zones. In contrast,  $PU_M$  based on the MDI-EG couple, where the crystallinity was practically absent, exhibited proportionality between the increase of nominal stress and stretching degree. Copolyurethanes  $PU_{C2}$  (92) and  $PU_{C3}$  (93) derived from mixtures of DBDI and MDI, generally exhibited an intermediary behaviour. The presence of the flexible DBDI hard segments instead of other conventional rigid isocyanates led systematically to increases in: the input strain energy to a given elongation, hysteresis and residual strain under cyclic loading, and stress relaxation. They were found to be greatly enhanced by hard-phase crystallinity.

#### IV. WAXS MEASUREMENTS

Figure 6 shows wide-angle X-ray scattering (WAXS) patterns of the PU series from Table 1 (as PU 91 to 95). As seen, the various materials display different degrees of crystallinity, as revealed by the presence of sharp diffraction peaks.  $PU_{C1}$  (PU 91) barely shows any evidence of crystalline reflections, and must be considered as almost but not completely amorphous.  $PU_{C2}$  (PU 92),  $PU_{C3}$  (PU 93), and  $PU_M$  (PU 95) exhibit slightly higher crystallinities than  $PU_{C1}$ , which is still less than 20%. The sample  $PU_D$  (PU 94) based on DBDI alone is the most crystalline sample and displays a crystallinity of 50%.

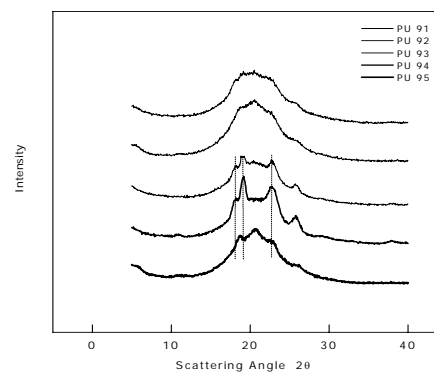


Figure 6. Wide-angle X-ray diffractograms from materials listed in Table 1

#### V. CONCLUSION

A study has been made of inelastic effects in the deformation of copolyurethane elastomers, where there is potential for formation of a two-phase microstructure (hard reinforcing particles embedded in an elastomeric matrix), but where the nature of the hard phase and the degree of phase separation can be controlled via the chemical structure. In polymers with diol chain extenders there were tendencies to phase separation, with a characteristic length of ca 20nm, and, when DBDI was employed with certain chain extenders, to crystallization of the hard phase. In large deformation cyclic experiments at room temperature, the degree of hysteresis and stress relaxation were found to be greatly enhanced by hard-phase crystallinity, through its effect of increasing the flow stress. Hard segments in PU elastomers based on DBDI and EG crystallise readily, but crystallinity is strongly reduced when the hard segment is a mixture of DBDI and MDI. With mixed hard segments, degree of crystallinity is dictated by the diisocyanate introduced first. Materials with mixed MDI and DBDI hard segments were found to give the optimum stress-strain data as compared to equivalent materials based on MDI ( $PU_M$ ) or DBDI ( $PU_D$ ) alone. The stress-strain data of similar but crosslinked postcured PUs obtained with and isocyanic index  $I = 110$  were found to be somewhat higher than those corresponding to PUs when no excess of isocyanate was used.

#### ACKNOWLEDGMENT

The authors are grateful to NATO for support via a CLg grant.

#### REFERENCES

- [1] C. Prisacariu, R.H.Olley, A. Caraculacu, D.C.Bassett and C. Martin, "The effect of hard segment in copolyurethane elastomers obtained by using simultaneously two types of Diisocyanates", in *Polymer* 44, (2003) pp. 5407-5421.
- [2] C. Prisacariu, C.P. Buckley C.P., A. Caraculacu, „Mechanical response of dibenzyl-based polyurethanes with diol chain extension" in *Polymer* 46, (2005), pp. 3884-3894,
- [3] C. Prisacariu, E. Scortanu, "Crystallization and Properties of Novel Polyurethanes Based on the Chain Extender Ethylene Glycol and Aromatic Diisocyanates of Variable Flexibility", in *Macromol. Symp.*, (2007), 254, 153-159.
- [4] C.P. Buckley, C. Prisacariu, A. Caraculacu, „ Novel triol-crosslinked polyurethanes and their thermorheological characterization as shape-memory materials", in *Polymer* 48, (2007), pp.1388-1396.
- [5] Buckley C.P, Prisacariu C., Caraculacu, A., Martin C.M. – "Inelasticity of hard-phase reinforced elastomers: A study of copolyurethanes with varying hard and soft segments", in *Constitutive Models for Rubber IV*, Edited by P.-E. Austrell / L. Hari. ISBN 0415383463. 2005, pp.465-470.