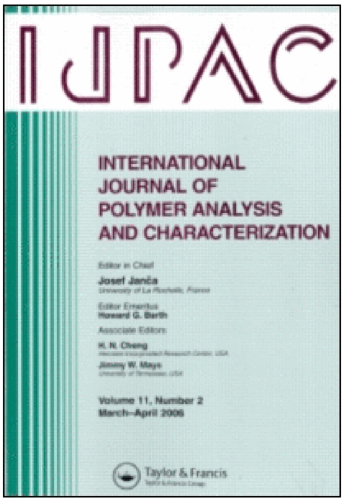

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Hard Segment Inelastic Effects on the Stress–Strain Response of Polyurethane Elastomers Based on Hard Segments of Variable Geometry

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Abstract: A study was made of a family of thermoplastic polyurethane copolymers, in which the nature and number of the hard segment components (crystallizing or not) were varied. Materials were synthesized with ethylene glycol (EG) as chain extender. Changes induced by varying the type and the number of isocyanates and the order of their introduction were followed and the mechanical responses were measured in cyclic tensile tests and stress relaxation in interrupted tests. Polymers based on DBDI hard segments showed lower strain recovery and strain energy recovery on cycling than did the conventional materials with MDI and the materials based on mixtures of isocyanates MDI/DBDI. Such features of the response were attributed to differences in hard phase plastic flow stress; hard domain hydrogen bonding exerted strong influences on the inelasticity of polyurethane elastomers. Stress-strain cycles reflected the resistance to plastic deformation occurring in the hard domains. This was enhanced by more pronounced hydrogen bonding achieved in the more mobile DBDI than in MDI.

Keywords: Diisocyanates; Flexible hard segments; Physical-mechanical properties; Polyurethanes

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INTRODUCTION

Polyurethane (PUs) polymers form a class of materials with unique versatility. They are all characterized by the presence of the urethane link –CO–NH–O– in the macromolecular backbone and are formed by reaction between isocyanates and polyols,[1] but materials with wide variations in physical properties are possible[2] by varying the choice of these ingredients.[3,4] An important subgroup is polyurethane elastomers, where at least one ingredient has a glass transition below room temperature.[5,6] In the segmented copolyurethane elastomers studied in the present work, molecules consist of alternating flexible (soft) and relatively rigid and/or mobile (hard) segments.[7] 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. The structure is therefore that of a polymer matrix microcomposite.[8]

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 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 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.[9–13] A novel diisocyanate, 4,4′-dibenzyl 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 increase the range of structures achievable beyond those normally available.[9,10,12]

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 $–CH_2–CH_2–$ bond in DBDI allows alignment of successive aromatic rings, thus favoring the tendency of crystallization, which involves the DBDI hard phase.[9,10]

As previously shown, in the case of PUs with DBDI that were synthesized with ethylene glycol (EG) as a chain extender, we observed a remarkable tendency of the EG-DBDI segments to crystallize. The origin of these effects was intimately related to the nanoscale structure of the elastomers: the degree of phase segregation and the size and perfection of the hard domains.[13]

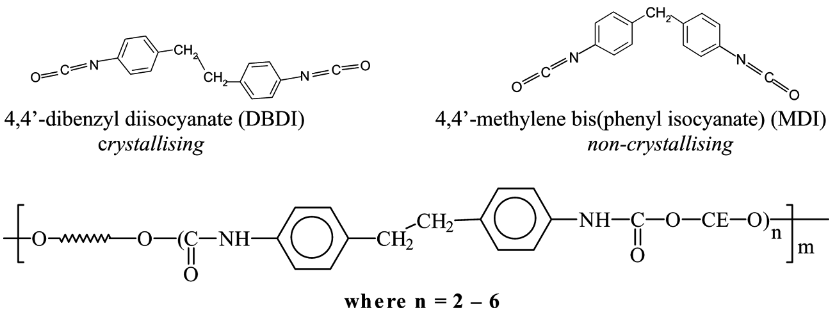

Figure 1. Schematic of isocyanate DBDI, MDI and the structural unit of macromolecular chain.

In polymers with diol chain extenders there were tendencies to phase separation, with a characteristic length of approximately 20 nm, and, when DBDI was employed with certain chain extenders, to crystallization of the hard phase. PU crystallization was inhibited when using the flexible chain extender diethylene glycol (DEG).[9,10]

In polymers prepared with the triol TMP as chain extender a cross-linked system was obtained, preventing phase separation.[12] 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 cross-linked systems a similar effect was observed, with the isocyanate-capped cross-link 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. Shown in Figure 2 is a schematic of the chemical structure for the materials investigated in this article. PUs were prepared with no excess of NCO (isocyanate) groups, giving isocyanic index $I = 100$.

Changes induced by varying the type and the number of isocyanates and the order of their introduction were followed, and the mechanical responses were measured in uniaxial tensile tests and 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.

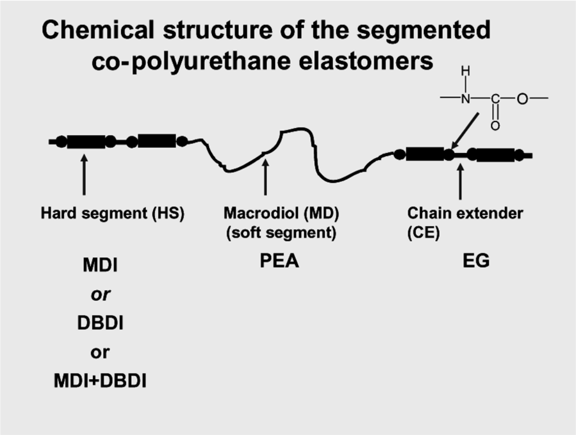

Figure 2. Chemical structure of the segmented PUs.

EXPERIMENTAL SECTION

Materials

PUs derived from a single diisocyanate (PU_D with DBDI and PU_M with MDI) (Table I) were obtained as follows: 100 g (0.05 mol) of macrodiol polyethylene adipate (PEA) was dehydrated under mixing at 110°C and vacuum (<1 mm Hg) for 2 h. Then 52.8 g (0.2 mol) of DBDI for the PU_D type or respectively 50 g (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

Table I. Structure and molar composition of the family of PUs

Recipe	PU structure
PU_{C1}	EG-PEA-(DBDI-MDI) 3 1 2 2
PU_{C2}	EG-(PEA-DBDI)-MDI 3 1 2 2
PU_{C3}	EG-(PEA-MDI)-DBDI 3 1 2 2
PU_D	EG-PEA-DBDI 3 1 4
PU_M	EG-PEA-MDI 3 1 4

restored. After 30 min of mixing under vacuum at 100°C the temperature was reduced to 90°C and vacuum was removed. A prepolymer was obtained with final isocyanic NCO groups in the mixture with the excess of isocyanate. Next, 9.295 g (0.150 mol) of chain extender was added at once under rapid stirring. The mixing was continued for a maximum of 30–40 s. The "pot life" of the mixture was between 3 and 10 min depending on the PU structure. For the cure process the closed moldings were maintained after casting at 110°C for 24 h. After an additional time of 24 h at room temperature, the polymeric sheets representing an active PU oligomer with NCO final groups were de-molded.

Copolyurethane elastomers from two diisocyanates randomly distributed (PU_{C1}) were synthesized starting from PEA, as seen in Table I.

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 I. The general procedure was described elsewhere.[9,10]

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 $\pm 3 \times 10^{-2}\,s^{-1}$. This was chosen for consistency with previous studies of the same materials.[10] As shown, this was close to the regime of extension rate where adiabatic heating may become significant in the testing of elastomers, but this was believed to be negligible in the present tests, which were treated as being isothermal.

MECHANICAL TEST RESULTS

PU Tensile Load/Unload Cycles

The materials were cycled between an extension of 3 and zero load, for three cycles.

Consider the first cycle for material PU_M, shown below, in Figure 3. It defined three zones, A, B, and C, in the stress–strain diagram. In the

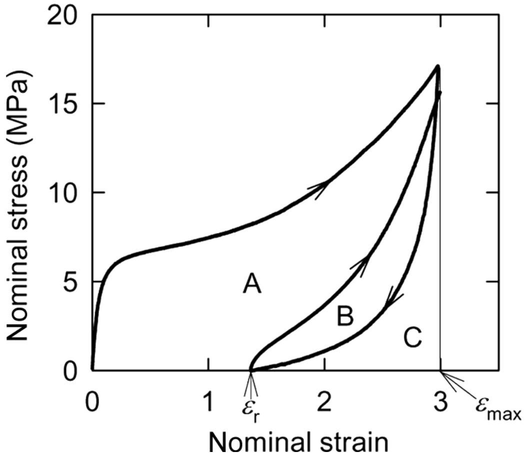

Figure 3. Loading-unloading-reloading cycle for material PU_M, with definitions of zones A, B, C of the diagram, maximum nominal strain $\varepsilon_{\max}$ and residual nominal strain ε_r.

present study, we denoted by E_1 the energy density expended on first loading to a nominal strain of 3, thus, from Figure 3:

$$E_1 = E_A + E_B + E_C \tag{1}$$

So that the relative first cycle hysteresis energy dissipation (E_{1H}) was defined by

$$E_{1H} = (E_1 - E_C)/E_1 \tag{2}$$

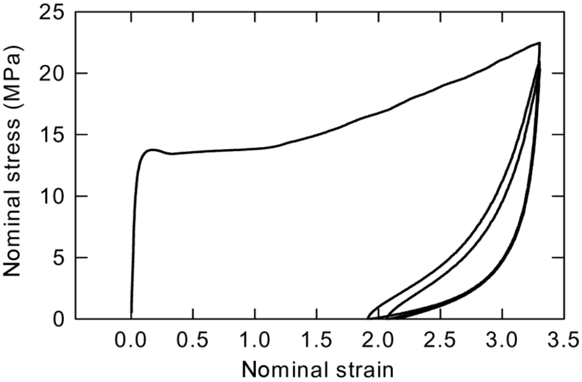

Figure 4. Cycling to fixed extension: tensile load–unload cycles for material PU_D.

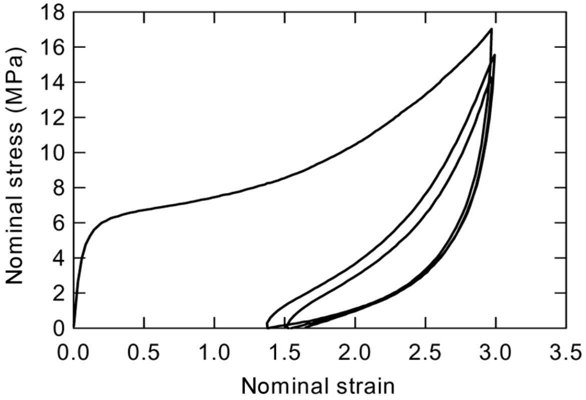

Figure 5. Cycling to fixed extension: tensile load–unload cycles for material PU_M.

in which E_1 is the area beneath the first load path and E_B is the area encompassed between a following hysteresis loop.

To calculate the hysteresis number, the first hysteresis loop after the first load path was considered. Shown in Figures 4–6 and Figure 7 (below) is the variation of the hysteresis loop and of the hysteresis number with increasing the nominal strain. Three materials were compared, based on the single diisocyanates MDI (PU_M) and DBDI (PU_D) and mixtures of MDI + DBDI (PU_{C1}). The nominal strain was increased from 0 to 300% levels of elongation.

Notable features were pronounced hysteresis and unrecovered strain. Due to the DBDI crystallization,[10] PU with DBDI had lower values of

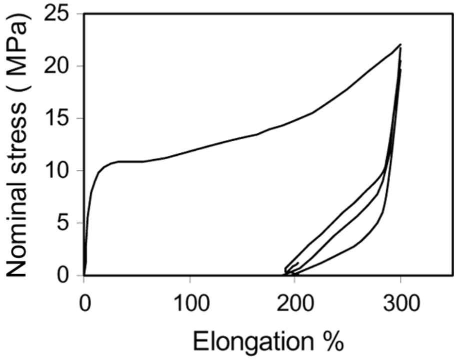

Figure 6. Cycling to fixed extension: tensile load–unload cycles for material PU_{C1} based on mixtures of MDI/DBDI.

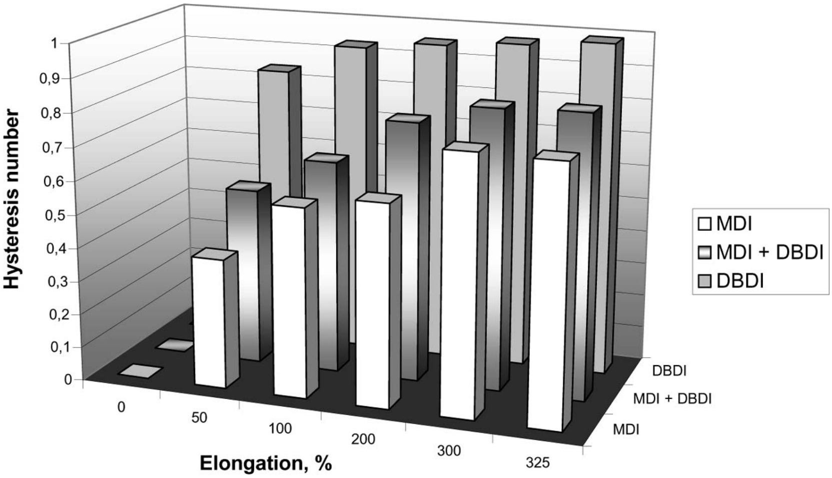

Figure 7. Variation of hysteresis number with increasing the elongation percent from 0 to 325%, for materials PU_D (DBDI) and PU_M (MDI).

strain recovery and strain energy recovery on cycling (hysteresis), which was due to the flow stress characteristic to the hard phase, regarding the percentage of the strain energy input that can be recovered.

As seen in Figures 4–6, the observed dominant feature was a hysteresis loop with a width that varied between the three polymers. Polymer PU_M with MDI hard segments gave the lowest stresses and least hysteresis, whereas polymer PU_D with DBDI hard segments gave the highest stresses and more hysteresis. Polymer PU_{C1} with mixed MDI/DBDI hard segments occupied an intermediate position. This is reflected in Figure 7 by a more pronounced increase of the hysteresis number with increasing the level of extension in the case of the material derived from PU_D with DBDI than with the material PU_M based on MDI alone and with the material PU_{C1} based on mixtures of the two diisocyanates.

The hysteresis number values ranged between 0.56 and 0.75 (for the PU_M type polymer) and between 0.93 and 0.99 (for the PU_D type material), while in the case of material achieved with mixtures of diisocyanates the values were intermediary, 0.63–0.84, as shown in Figure 7. The differences between MDI and DBDI were attributed to the greater flexibility of DBDI allowing a higher tendency to self-associate by hydrogen bonding.[9,10]

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. Similarly, increasing the time interval between the end of one unloading cycle and the start of the next, from a few seconds to several hours (up to 24 h), had no sensible effect on the measured recoverable strain energy. This was in contrast to the input energy, which was clearly dependent on both the previous strain history and the relaxation time between loading cycles. PU hysteresis was not influenced significantly by variation of strain rate. However, for all three materials, the strain energy input increased with increasing strain amplitude. As seen in Figures 4–6, the energy dissipation data were highest for materials with hard segments of DBDI, which was due to the stronger consolidation of the macromolecular network determined by the enhancement of the number of hydrogen bonding.[9,10]

Interrupted Tests

Further interrupted tests with 100 s waiting times during loading and unloading were made. The interesting points to emerge from the interrupted tests concerned the magnitude and sign of stress relaxation during the 100 s interruptions between loading and unloading. Shown in Figure 8 is the load/unload cycle on the material PU_D, based on the single DBDI. It observed that:

(a) The sign of stress changed and was different between loading and unloading of the material; this was consistent with a two-phase

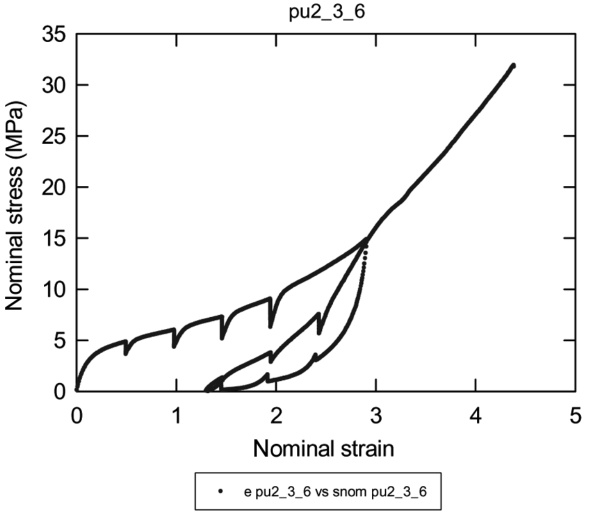

Figure 8. Interrupted test with 100 s waiting time during loading and unloading of PU_D net stress.

microstructure where there are two contributions to the stress: an elastic component and a viscous component.[10] The sign of the viscous stress changed on reversal of straining, and therefore relaxation of this stress during unloading produced an increase in the net stress.

(b) The magnitude of the mechanical stress relaxation was higher in the case of PUs with DBDI than with MDI; this was again consistent with the larger contribution of hard phase stress[10] in the case of the DBDI-based PUs.

Note that the magnitude of stress relaxation increased with strain during loading. This indicated that the stress contribution from the hard phase was increasing with strain, i.e., the strain stiffening was not only from the soft (rubberlike) matrix. This was consistent with the arguments used on our earlier works[10,13] that the flow process needs to be considered as intrinsically anisotropic: with deformation, the relaxing units tend to align with the direction of straining.

Stress–Strain Diagrams of Uniaxial Tension

PU stress–strain data were compared between the polymers achieved with single diisocyanates and mixtures of diisocyanates. Significant differences were found between materials, 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 Figure 9, comparing the stress–strain data between the three materials achieved with mixtures of isocyanates, PU_{C1}, PU_{C2}, and PU_{C3}, the tensile strength was the highest in the case of copolyurethane PU_{C1} obtained by a single-step prepolymer synthesis that used a melt mixture of the two isocyanates (M + D), when the two different diisocyanates were inserted more or less randomly into the prepolymer. A better balance of elastomeric mechanical properties was observed in the case of materials with mixtures of MDI and DBDI achieved by single-step prepolymer synthesis that uses a melt mixture of the two isocyanates. All materials with mixed MDI and DBDI hard segments were found to give better combination of high input strain energy, but smaller residual strain, than equivalent materials based on MDI or DBDI alone.

The highest tensile strength value was observed in the case of the material derived from DBDI alone, PU_D (Figure 10). Similar conclusions could be drawn with regard to the strain energy input (at 300% elongation) and strain energy recovery (on unloading from 300% elongation). In the first deformation steps, the material PU_D displayed a

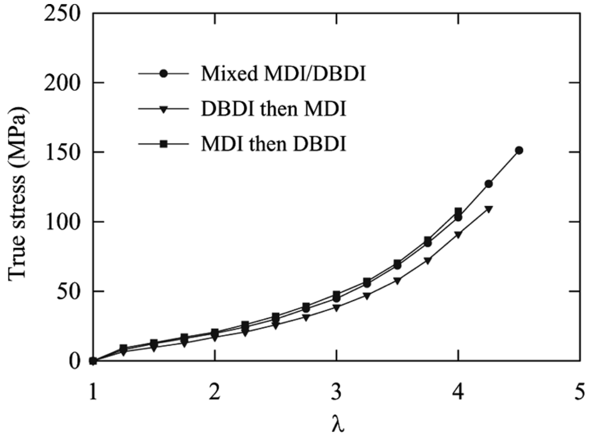

Figure 9. Stress-strain data of PU elastomers PU_{C1}, PU_{C2}, PU_{C3}, obtained using mixtures of isocyanates.

higher strength, followed by values of strain that 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.[9]

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.

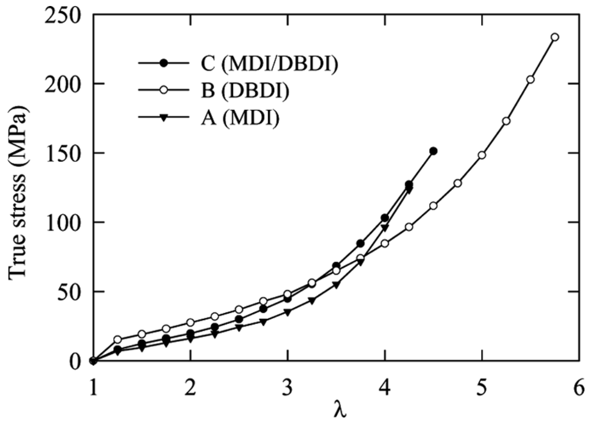

Figure 10. Stress-strain curves of elastomers PU_D, PU_M, and PU_{C1}.

CONCLUSION

A study was performed of how aspects of the mechanical responses of polyurethane elastomers vary with composition by changing the nature of the hard segment based on flexible or rigid diisocyanates or combinations of these. Due to hard-segment crystallization, inelastic effects were more pronounced in the case of polymers based on DBDI. A better balance of elastomeric mechanical properties was observed in the case of materials with mixtures of MDI and DBDI achieved by single-step prepolymer synthesis that uses a melt mixture of the two isocyanates.

The hysteresis number increased with increasing strain amplitude. The residual strain and energy dissipation were higher for materials with hard segments of DBDI than for those of MDI. The highest hysteresis number values were found in the case of materials with DBDI. These differences between MDI and DBDI were attributed to the greater flexibility of DBDI allowing a higher tendency to self-associate by hydrogen bonding. Hard domain hydrogen bonding and crystallinity exert strong influences on inelasticity of PU elastomers. The hard domains do not act simply as rigid cross-links for the soft domains. Stress-strain cycles reflect the resistance to plastic deformation occurring in the hard domains. This is enhanced by more pronounced hydrogen bonding achieved in the more mobile DBDI than in MDI, and especially so when the DBDI hard domains crystallize.

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