



*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 80th anniversary*

IMPROVEMENT OF POLYURETHANE ELASTOMER PRODUCTS PERFORMANCE *VIA* CONTROL OF CHEMICAL STRUCTURE

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The overall objective of the present study was to improve the understanding of the relation between molecular architecture and mechanical properties/ thermal behavior for a large series of polyurethane copolymers, in which there was systematic variation of the four key chemical features: hard segments based on different geometries, soft segments, low molecular mass diols acting as chain extenders and degree of crosslinking [isocyanic index 100% (no crosslinking) or 110% (crosslinking)]. The specific aims were to characterize the materials with respect to the aspects of mechanical response and thermal behaviour of practical interest; and to use microstructural information to assist in the interpretation. A major structural feature which has been explored was the nature of the hard segment (crystallising or not); and the effect of increasing the hard segment percent on the mechanical response. The mechanical and thermal performance of these materials as elastomers was shown to vary greatly depending on the composition. When the diisocyanate of variable geometry 4,4'-dibenzyl diisocyanate (DBDI) was employed as hard segment with ethylene glycol (EG) or 1,4-butanediol (BG) (but not diethylene glycol DEG) as chain extender, there was crystallization of the hard segments, and this caused a large increase in the stress on loading to any given extension. The presence of DBDI as hard segment also led to a significant reduction in relative energy recovery compared to other conventional rigid diisocyanates – a fact of considerable importance for materials such as the polyurethanes with potential as elastomers. These trends were visible irrespective of the choice of soft segment and whether the polymer was crosslinked or not. All of the polymers kept their elasticity modulus very well on heating. Materials characterized by the presence of accumulated DEG-DBDI blocks displayed a higher resistance at temperatures situated around 140 °C.

INTRODUCTION

The block copolyurethanes, consisting of isocyanate hard segments, macrodiol soft segments and chain extenders, represent an extraordinarily versatile family of polymers where a wide variety of physical properties may be achieved via variations in chemical composition and synthesis route.¹⁻³ An important sub-group is the polyurethane elastomers (PUs), where at least one ingredient has a glass transition below room temperature. PUs are all characterized by presence of the urethane link -NH-CO-O- in the macromolecular backbone, and formed by reaction between isocyanates and polyols, but materials

with wide variations in physical properties are possible, by varying the choice of these ingredients.⁴⁻⁶ 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.⁷⁻⁹ The structure is therefore that of a polymer matrix microcomposite.

The present work is part of a wider study of the effects on constitutive response of systematically varying the four key structural variables: hard

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segments based on different conventional isocyanates of rigid geometries and on a novel isocyanate of variable geometry, 4,4'-dibenzyl diisocyanate (DBDI), soft segment [polyethylene adipate (PEA), polytetrahydrofuran (PTHF) or polybutylene adipate (PBA)]; a low molecular mass diol acting as chain extender [ethylene glycol (EG), diethylene glycol (DEG) or butylene glycol (BG)]; degree of crosslinking [isocyanic index 100% (no crosslinking) or 110% (crosslinking)]. Such variations in composition lead to significant changes in the key mechanical properties of the elastomer, such as stiffness, strain recovery and strain energy recovery. Our goal was to generate understanding of the constitutive response in terms of the molecular structure. A specific aim of the work reported here was to bring new contributions towards the investigation of the role of hard segment structure on the mechanical performances and thermal behaviour of such block copolyurethanes.⁵ In particular two hard segments were compared, based on the diisocyanates: 4,4'-

methylene bis(phenyl isocyanate) (MDI) (Fig. 1a) and DBDI (Fig. 1b). As reported^{3,5,6} the MDI molecule introduces the rigid -Ph-CH₂-Ph- moiety in the elastomeric PUs hard segments. In contrast when using DBDI, the specific -Ph-CH₂-CH₂-Ph- moiety introduces a variable geometry into the hard segments due to the possibility of internal rotation of this isocyanate around the -CH₂-CH₂-ethylene bridge. This leads to the appearance of both "syn" and "anti" rotational conformations, which coexist in the DBDI based PUs macromolecules. As a result, in this latter case the PUs macromolecules can adopt a more compact packing which enhances significantly the ability to order in crystalline structures involving predominantly the "anti" form.³ 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 other conventional rigid isocyanates as it is MDI in melt-cast polyurethanes.

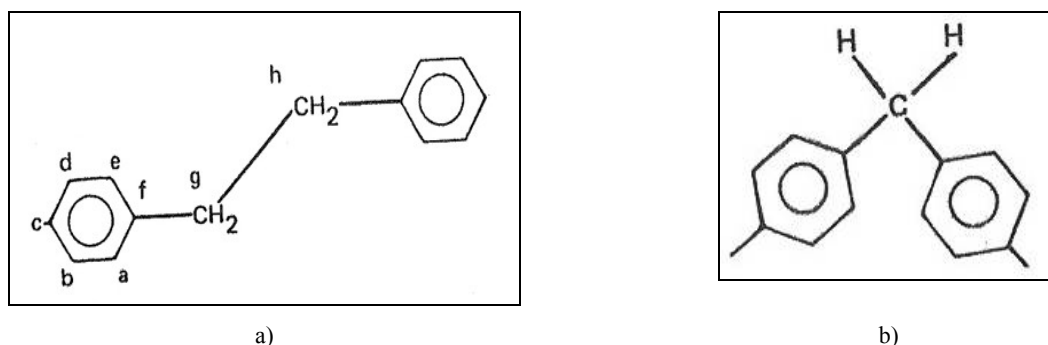


Fig. 1 – a) Schematic of DBDI (4,4'-dibenzyl diisocyanate). b) Schematic of MDI (4,4'-methylene bis(phenylisocyanate)).

RESULTS AND DISCUSSION

Mechanical test results

Our approach was to carry out several different types of well-defined mechanical tests, with a wide range of PUs of known and systematically-varied composition, prepared under well-defined conditions. Several features of behaviour have been investigated. First cycle tensile load-unload response was studied at room temperature for PUs elastomers with differing hard segments (MDI or DBDI) to capture the effect of varying the hard segment, (Fig. 2a and 2b). Large differences between hysteresis seen with the two different hard segments based on MDI and DBDI were found which was explicable in terms of the different plastic flow resistances of different hard segments,

and especially the hard domain crystallisation of DBDI/PTHF/EG polymers.^{5,8}

The hysteresis loop varied between the polymers with DBDI and those with MDI.^{10,11} Polymers with MDI hard segments gave lower stresses and least hysteresis, whereas polymers with DBDI hard segments gave higher stresses and most hysteresis.

The most extreme difference between the effects of MDI and DBDI hard segments was observed in the case of PUs where the chain extender–diisocyanate couple was EG-DBDI, where the hard segments were observed to crystallize, irrespective of the selected macrodiol (PEA, PTHF or PBA). In the first deformation steps the materials with hard segments based on DBDI displayed a higher strength, followed by values of strain which required smaller stress

increments. This observation was correlated to the appearance of better structured EG hard segment domains, in the case of the EG-DBDI couple, determined by their tendency to self-associate in hard crystalline zones.⁹ In contrast, PUs based on the MDI-EG couple, where the crystallinity was practically absent, exhibited proportionality between the increase of nominal stress and stretching degree. A second study aimed to investigate how aspects of the mechanical responses of selected PUs vary with the variation of the hard segment percent. The influence of the increasing the hard segment percent from 20% to 100%, on the mechanical properties was followed. The study of the stress-strain response included tensile tests, and load-unload cycles to a nominal strain of 3, at constant rate of extension, with measurement of hysteresis and strain recovery, (Fig. 3a).

Increasing the hard segment percent led systematically to increases in the input strain energy elongation. With increasing the hard segment percent polymers based on DBDI hard segments, displayed higher stiffness and strength than the conventional MDI-based PUs. Both features of the response were attributed to differences in hard phase plastic flow stress, resulting from crystallinity in the DBDI phase. With increasing the hard segment percent from 20% to 100%, lower strain recovery and strain energy recovery on cycling were observed in the case of PUs derived from dibenzyl structures. Inelasticity (residual strain, hysteresis) increased with increasing the hard-phase percent and was greater for DBDI hard segment than for MDI. Young modulus values increased proportionally with increasing the isocyanate content and were higher in the case of materials with DBDI.

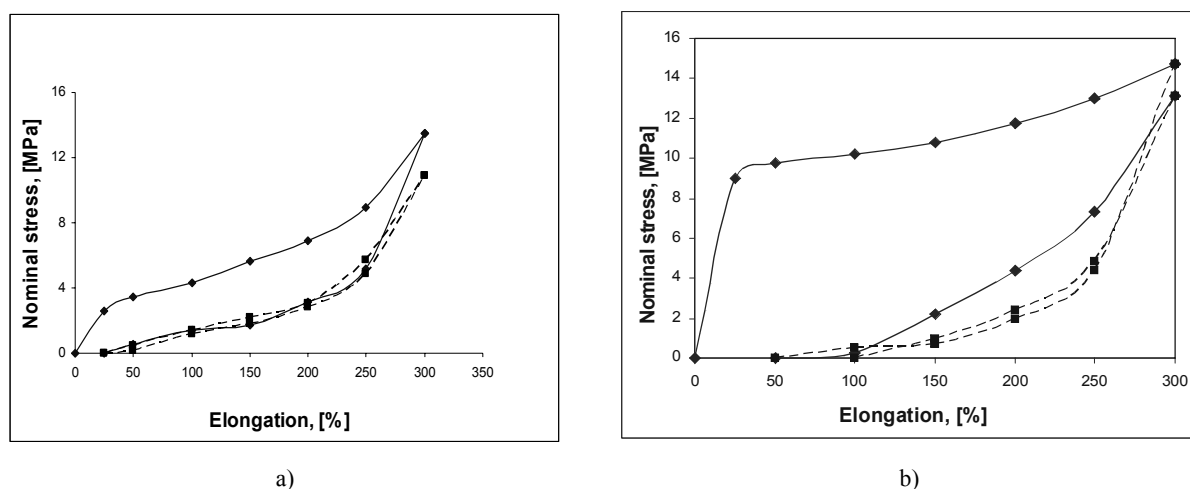


Fig. 2 – a) Tensile load/unload cycles for a thermoplastic material based on MDI: (EG-PTHF-MDI, I=100), at strain rate 0.03 s^{-1} . b) Same but for a thermoplastic material based on DBDI: (EG-PTHF-DBDI, I=100), at strain rate 0.03 s^{-1} .

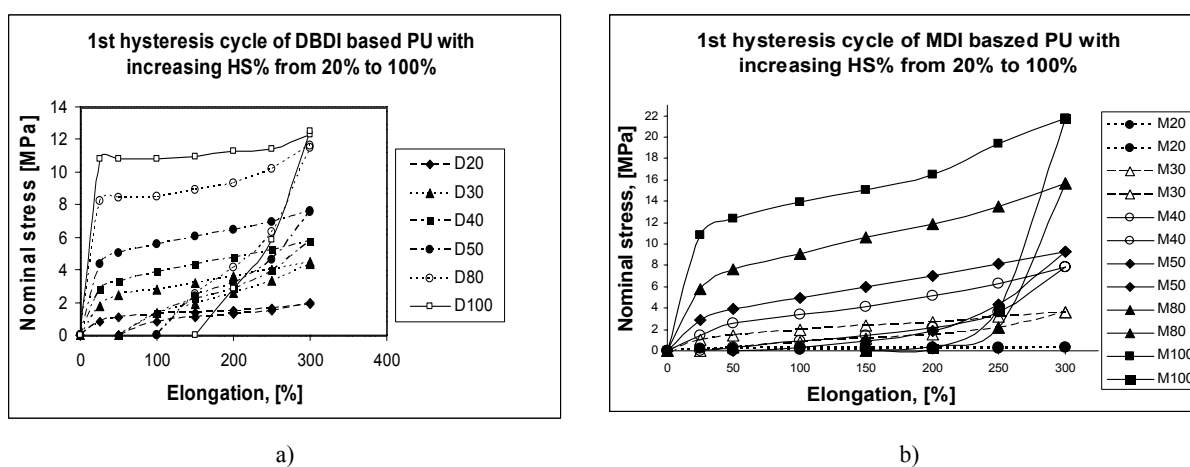


Fig. 3 – a) Tensile load/unload cycles for a thermoplastic material based on DBDI: (EG-PTHF-DBDI, I=100), at strain rate 0.03 s^{-1} , with increasing the hard segment percent from 20% to 100%. b) Tensile load/unload cycles for a thermoplastic material based on MDI: (EG-PTHF-MDI, I=100), at strain rate 0.03 s^{-1} , with increasing the hard segment percent from 20% to 100%.

Structural studies

A. WAXS Measurements

The remarkable PUs properties are mainly due to their special tendency to form discrete regions in which the hard segments made up by diisocyanate and chain extender tend to self associate in separate microdomains. Materials were characterised by SAXS and WAXS,^{3,5,12} enabling differences in mechanical response to be related systematically to variations in supermolecular structure. It was found that, for zero crystallinity, hysteresis and permanent set reduced with higher degrees of phase segregation, or with reducing crystallinity. PUs obtained by the reaction between DBDI and EG or BG were polymers with a high tendency of crystallization, irrespectively of the adopted macrodiol (PEA, PBA or PTHF). This behaviour was evidenced by the self separation of a crystalline polymer from its solution in time. However, a similar phenomenon did not occur in the case of a BG-MDI system. Fig. 4a displays typical Wide Angle X-ray scattering curves for materials with MDI and DBDI and a corresponding homopolyurethane based on DBDI made up only by hard segments. Phase separation, crystallization and orientation phenomena in the present materials were also studied by means of DSC and IR dichroism from which results are reported elsewhere.^{5,7,13}

As seen in Fig. 4a and 4b, as compared to curve 4.c of the MDI-based material, for the DBDI-based material and its corresponding homopolyurethane [BG-DBDI]_n the crystallization did not disappear with the inclusion of the hard segments in the block copolyurethane elastomeric matrix, indicating the appearance of more or less phase separations associated with the formation of

crystalline hard domains. The presence of these structures induced a special mechanical behaviour in the obtained elastomers. Due to the disordered orientation of these domains in the polymer matrix the materials appear initially isotropic on the macroscale but when subjecting the polymer to stretching, these micro domains tend to orient in parallel, maintaining in some extent their anisotropy even after removing the stress. As a result some enhanced residual elongation was evident, being substantially confirmed by using a polarizing optical microscope.¹² Note that after annealing the elastomer at 110°C for 60 minutes, the crystallinity of materials with DBDI decreased significantly.

B. DMA Results

The tests started at -140 °C and the complex modulus (E^*), storage modulus (E'), loss modulus (E'') and the loss factor ($\tan \delta$) were measured as a function of temperature at a heating rate of 1 K/min. The instrument was operated with controlled sinusoidal force with a frequency of 1 s⁻¹. Depending on the type of synthesis and PU structure, significant differences of the Storage Modulus (E'), and consequently differences in softening were found. The glass transition temperature depended on the mobility of the macromolecular chain. Materials derived from the DBDI type of diisocyanate proved a higher tendency to crystallize. The DMA measurements have shown that the Storage Modulus (E') in the temperature range above the glass transition region was the highest for the DBDI material of the type EG-DBDI-PEA (Fig. 5a). This was because of the higher content of DBDI based hard segments with a coplanar packing.

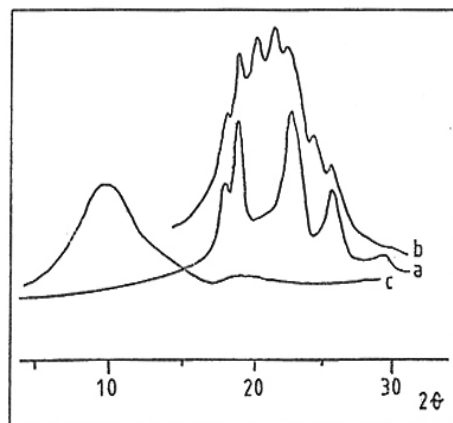


Fig. 4 – WAXD of PUs with BG-MDI and BG-DBDI hard segments: (a) homopolyurethane -[BG-DBDI]_n - model; (b) PU with structure DBDI:PEA:BG = 3:1:1.727; I=110; (c) – same as above but for a MDI based PU with the same structure.

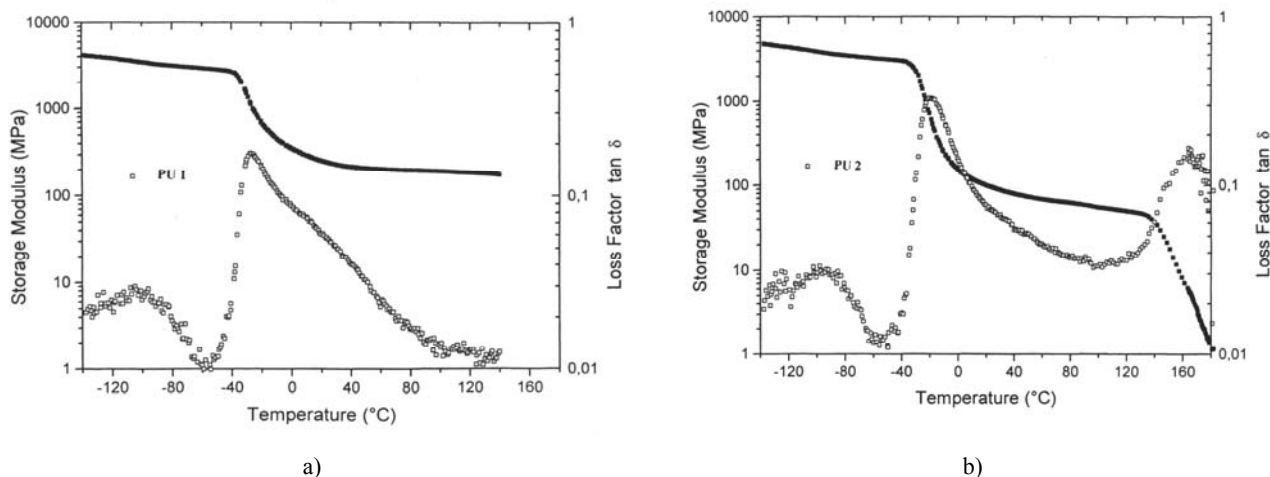


Fig. 5 – a) Storage modulus and Loss Factor as a function of temperature for a crosslinked PU based on DBDI with the structure EG:PEA:DBDI (3:1:1.727), $I=110$. b) Storage modulus and Loss Factor as a function of temperature for a crosslinked PU based on MDI with the structure EG:PEA:MDI (3:1:1.727), $I=110$.

The glass transition temperatures in the maximum of the loss factor at $f=1 \text{ s}^{-1}$ were: for PU1 (with DBDI): $T_G = -24 \text{ }^\circ\text{C}$. $\text{Tan } \delta = 0.198$; for PU 2 (with MDI, Figure 9) $T_G = -16 \text{ }^\circ\text{C}$, with $\text{Tan } \delta = 0.418$. For the series of elastomers the glass transition temperatures as defined by the maximum of the loss factor at $f=1\text{Hz}$ was found to range from $-11 \text{ }^\circ\text{C}$ to $-27 \text{ }^\circ\text{C}$, the lowest T_G value corresponding to materials with DBDI of the type (EG-PEA-DBDI), which displayed a variable geometry.

Thermomechanical experiments

Thermomechanical analyses were performed with the aid of a home made thermal creep testing machine of own design and construction⁵ which follows the course of elongation under constant load of a pre-tensioned sample so to start from a constant initial 50% strain level. The variation of polymer elongation under the constant characteristic initial 50% strain load was followed on employing a constant temperature increase increment of about $1 \text{ }^\circ\text{C}/\text{min}$. and the PUs thermomechanical ($\epsilon - t$) curves were compared. In Table 1 there are depicted some examples of $\epsilon - t$ curves for some DBDI based PUs. As seen in Table 1, the following criteria were used: (a) σ_{50} – the stress corresponding to a 50% strain level; (b) T_R – the temperature of polymer rupture; (c) E – elongation at break; R-residual elongation; (e) T_{100} – the temperature for which the sample reached a 100% level of elongation. A comparison between different crosslinked and

thermoplastic PUs was made. The thermomechanical curves corresponding to different PUs with DBDI, of variable crystallinity, degree of crosslinking, and variable molar mass were performed.

The best thermal behavior was found for thermoplastic DBDI based materials with PTHF and DEG (curve 1), and for two similar but achieved as crosslinked ($I=110$) materials where the molar mass of the macrodiol PTHF was lower: PTHF₁₀₀₀ and PTHF₁₅₄₆, (curves 6 and 9 in Table 1). Changing the chain extender type leads to significant changes as it observed the case of the material with BG (curve 5), which displayed a poor thermal behaviour with $T_R = 76 \text{ }^\circ\text{C}$. A similar situation was found in the case of crosslinked PUs based on the chain extender EG (and with lower values of the isocyanic index (I) (curve 4), PU with $I = 105$). The difference in the thermal behaviour of these materials was due to the chain extender–diisocyanate couple EG-DBDI or BG-DBDI, where the hard segments were observed to crystallize.⁵⁻⁹ In such materials, the stiffness, hysteresis, residual elongation and stress relaxation were all increased relative to the corresponding MDI based materials. A constant hard segment percentage (40 wt %) was adopted for all materials. The polymers characterized by the presence of accumulated DEG-DBDI blocks displayed a highest resistance at temperatures situated around $140 \text{ }^\circ\text{C}$.

Table 1

Thermomechanical properties of some DBDI-based polyurethanes

Chain Extender	% I	STRUCTURE			$\sigma_{50\%}$ MPa	Thermomechanical curves								T_R [°C]	E [%]	R [%]	t_{100} [°C]
		Macrodiol	Diisocyanate	Index		[°C]											
						20°	40°	60°	80°	100°	120°	14°					
DEG	40	PTHF	DBDI	100	4.14									153	826	145	132
DEG+TMP	40	PTHF	DBDI	100 crosslink	4.48									116	205	35.5	98
DEG	40	PTHF ₁₀₀₀	DBDI	110	3.88									70	152	0	40
DEG	40	PTHF ₆₅₀	DBDI	105	6.83									60	574	6	30
BG	40	PTHF ₁₀₀₀	DBDI	110	6.64									76	510	80	26
DEG	40	PTHF ₂₀₀₀	DBDI	110	5.34									114	210	6	111
DEG	40	PTHF ₁₀₀₀ (2000+650)	DBDI	110	3.45									79	233	10	42
DEG	40	PBA	DBDI	110	6.18									112	999	319	26
DEG	40	PTHF ₁₅₄₆	DBDI	110	3.78									129	267	10	122

EXPERIMENTAL PART

Materials

Crosslinked PUs were obtained as follows: 100g (0.05 mol) of macrodiol polyethylene adipate (PEA), polytetrahydrofuran (PTHF) or polybutylene adipate (PBA) was dehydrated under mixing at 110 °C and vacuum (< 1mm Hg) for 2 hours. 52.8g (0.2 mol) of DBDI or respectively 50g (0.2 mol) of 4,4'-methylene bis (phenyl isocyanate) MDI in the case of the MDI 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 was obtained a prepolymer with final isocyanic NCO groups in mixture with the excess of isocyanate. Next 9.295 g (0.15 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 moldings 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.

Thermoplastic PUs were obtained similarly as above, except that the materials were prepared with no excess of NCO groups, giving isocyanic index $I = 100$ as detailed elsewhere.^{9,12} To study the effect of increasing the hard segment percent on the mechanical response for the materials of the type EG-PTHF-DBDI, the composition of polyurethane was changed from sample to sample to provide different hard segment ratios ranging between 20% and 100%.

Tests Methods

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 $\pm 3 \times 10^{-2} \text{ s}^{-1}$. The data were processed to quantify specific inelastic features in the mechanical responses of the materials: stress-strain data, and hysteretic energy dissipation.

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 α 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 θ), respectively.

Dynamic Mechanical Analysis (DMA) measurements were carried out with the Gabo Qualimeter Eplexor 150 N. Samples were tested in tensile mode with a starting distance between the clamps of 45 mm. The cross section area of the specimen was 5 mm x 1-2 mm. The samples were placed in the temperature chamber and cooled down to the starting temperature of -140 °C. The cooling conditions were: room temperature to -60 °C cooling rate of 10 K/min, -60 °C to -120 °C 3.5 K/min and -120 °C to -140 °C 2 K/min.

Thermomechanical measurements were performed on a home-made instrument as previously reported.⁵ The variation of polymer elongation under the constant characteristic initial 50% strain load was followed on employing a constant temperature increase increment of about 1 °C/min.

CONCLUSIONS

A range of novel segmented copolyurethane elastomers was synthesized, in which the hard

segments were derived from isocyanates of rigid geometries of from the more flexible DBDI. The effects of varying hard segment were studied in the context of a variety of combinations of chain extender, macrodiol and their proportions. The mechanical and thermal performance of these materials as elastomers was shown to vary greatly depending on the composition. We found trends in the cyclic stress-strain response, with varying chemical structure. This revealed that the origin of these effects is intimately related to the nano-scale structure of the elastomers: the degree of phase segregation and the size and perfection of the hard domains. Materials were studied by wide-angle X-ray scattering (WAXS), to determine levels of crystallinity. The inelasticity (residual strain, hysteresis) increased with hard-phase crystallinity and was greater for DBDI hard segments than for other conventional rigid diisocyanates. Dynamical mechanical analysis (DMA) was approached to study the structural modifications in the materials structure, at variable temperature ranging from $-120\text{ }^{\circ}\text{C}$ to $+160\text{ }^{\circ}\text{C}$. The temperature range above the glass transition region was the highest for the DBDI based materials based on the chain extender ethylene glycol (EG). This was due to the stronger tendency of the DBDI-EG couple to self associate in a coplanar packing. 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. As shown in thermomechanical experiments, the polymers characterized by the presence of accumulated DEG-DBDI blocks

displayed a highest resistance at temperatures situated around $140\text{ }^{\circ}\text{C}$.

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