



# Effect of the hydrogen bonding on the inelasticity of thermoplastic polyurethane elastomers

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## ABSTRACT

The effect of hydrogen bonding on the cycling tensile responses of thermoplastic polyurethane elastomers (TPUs) was followed. Hydrogen substitution was carried out by replacing the usual fully hydrogenated forms of the diol chain extender diethylene glycol (DEGh) or of the macrodiol polytetrahydrofuran (PTHFh) with their fully deuterated analogues DEGd and PTHFd. The TPUs segmental orientation was followed by means of infrared dichroic measurements. The hard segment (crystallizing or not) was varied by inclusion of a conventional rigid diisocyanate, 4,4'-diphenyl methane diisocyanate (MDI) and of an isocyanate with a large conformational mobility 4,4'-dibenzyl diisocyanate (DBDI). Inelastic effects were most pronounced when the hard segment crystallized. Irrespective of the isotopic forms of the chain extender and macrodiol used in the material synthesis, the residual strain and hysteresis energy dissipation were highest for hard segments of DBDI than of MDI. While the TPUs derived from DEGd were more resilient than the similar polymers obtained with the DEGh, there were no significant differences between the resilience of the TPUs achieved with the PTHFh and PTHFd. A quantitative correlation was found between the magnitude of the Mullins effect and the fractional energy dissipation by hysteresis under cyclic straining, giving a common relation that was approached by all the materials studied. The results provide new perspectives into the physical origin of inelastic effects in reinforced elastomers.

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## 1. Introduction

As widely known, polyurethanes are extensively hydrogen bonded. As shown by others and by ourselves [1–6] although the effect of hydrogen bonding is frequently used to explain the variation of the polyurethanes properties, it is difficult to separate this effect from those involving the physical and chemical structure.

To assess the influence of hydrogen bonding on the mechanical behaviour of segmented polyurethane elastomers (TPUs), in our previous studies, a series of materials was achieved by us, with analogous structures, but varying the percent of hydrogen bonding, which was done by decreasing gradually the hydrogen percentage from 80% to 8% hydrogen [6]. This resulted in a decrease of the stresses measured in tensile tests and of the molecular weight values expressed as the inherent viscosity. The hard segment (crystallizing or not) was varied by inclusion of a

conventional rigid diisocyanate, 4,4'-diphenyl methane diisocyanate (MDI) and of an isocyanate with a large conformational mobility 4,4'-dibenzyl diisocyanate (DBDI). Rotation around the central  $-\text{CH}_2-\text{CH}_2-$  bond in DBDI allows alignment of successive aromatic rings thus favouring the tendency of crystallization which involves the DBDI hard phase [7–11]. Thus, whilst the MDI hard segments are intrinsically kinked in shape, reducing conformational mobility and thereby hindering close packing and achievement of hydrogen bonding, the DBDI hard segments can adopt a linear conformation facilitating packing and inter-chain hydrogen bonding [7–11].

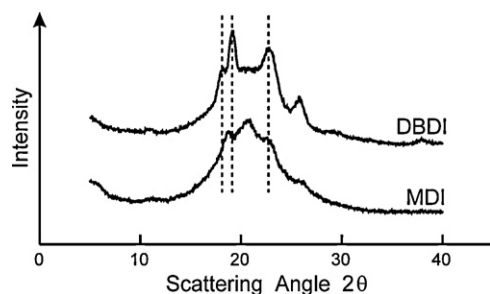
As detailed elsewhere, in the case of TPUs with DBDI which were synthesized with ethylene glycol (EG) as a chain extender, we observed a remarkable tendency of the EG-DBDI segments to crystallize (Fig. 1). The origin of these effects was intimately related to the nano-scale structure of the elastomers: the degree of phase segregation and the size and perfection of the hard domains [8].

As previously shown by others and by us [6], a clear effect of hydrogen bonding can be observed only if mechanical tests are carried out on polyurethanes of analogous structure with and without hydrogen bonding. In the light of these observations, in our earlier works, we also investigated a series of materials with similar structures, but achieved with or *without* hydrogen bonding,

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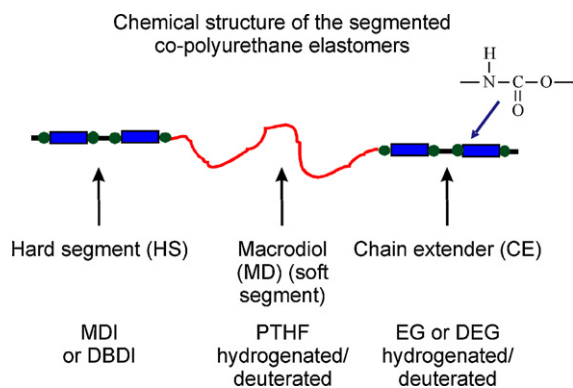
**Fig. 1.** Wide-angle X-ray diffractograms from two TPUs with similar structures based on ethylene glycol (EG) resulting in hard segments of MDI (non-crystallizing) and DBDI (crystallizing).

where hydrogen was totally substituted with inert ( $-\text{CH}_3$ ) groups. The stress–strain data and cyclic tensile responses indicated a dramatic softening and weakening when the hydrogen of the urethane groups was replaced by inert ( $-\text{CH}_3$ ) groups which are unable of intermolecular interactions [6].

In the present work we have investigated the effect of hydrogen bonding on the TPUs elasticity/inelasticity, by studying the cycling tensile responses of a family of TPUs with similar usual hydrogenated or deuterated structures.

With regard to the selection of the chemical structures (Fig. 2), an important consideration has been given by us, to aspects regarding the hydrogen bonding in glycols. In the TPUs macromolecular synthesis, the glycols represent important raw materials. The glycols display a high tendency to self-associate but in this case it is possible to appear more or less intramolecular hydrogen bonding as well, depending on the molecular structure facilities. The intramolecular hydrogen bonding in diols has a longer life time existence [12,13]. Therefore, as shown in Fig. 2, in this work two low molecular weight diol chain extenders were considered: ethylene glycol (EG), and diethylene glycol (DEG). These were selected by us for comparison reasons so as include two chain extenders that promote crystallinity with DBDI (EG), and DEG that has been shown previously to inhibit crystallinity in DBDI [11]. This is because when DEG is used as chain extender with DBDI, the central  $-\text{O}-$  atom introduces kinks into the DBDI hard segment and disrupts the chain packing that could otherwise be achieved [10,14].

In the case of the deuterated polymers, hydrogen substitution was carried out by replacing the usual fully hydrogenated (DEGh) or the macrodiol polytetrahydrofuran (PTHFh) with their deuterated analogous DEGd or PTHFd. The hard segment (crystallizing or not), was varied by inclusion of the rigid diisocyanate MDI and of the diisocyanate with a large conformational mobility DBDI.



**Fig. 2.** Composition of the materials used in this study.

**Table 1**

Compositions of the family of hydrogenated and deuterated polyurethane elastomers, TPU1–TPU10 prepared and studied in this work.

		PTHFh	PTHFd
MDI	EGh	TPU1	TPu7
DBDI	EGh	TPU2	TPu8
DBDI	DEGh	TPU3	TPU9
MDI	DEGh	TPU4	TPU10
DBDI	DEGd	TPu5	–
MDI	DEGd	TPu6	–

To detail, as shown in Table 1, the following MDI or DBDI based TPUs with similar structures was synthesized by us: (a) two subsets consisting of two materials each, achieved by using usual chain extenders (EGh or DEGh, respectively) and the usual macrodiol (PTHFh); (b) a subset of two materials obtained with the deuterated chain extender (DEGd) and macrodiol PTHFh; (c) two subsets of consisting of two materials each, obtained with EGh or DEGh and the macrodiol PTHFd. The two PTHF isotopic forms were of the same molar mass ( $2000 \text{ g mol}^{-1}$ ).

The cyclic tensile behaviour was studied for the series of polymers. Results are reported here for whole set of 10 model TPU materials.

A series of experiments on the TPUs segmental orientation was achieved by us means of IR dichroic measurements. The segmental orientation of the normal and deuterated materials chain extended with DEGh and DEGd has been followed.

## 2. Experimental methods

### 2.1. Materials

The family of TPUs was synthesized for this work in the authors' Romanian laboratory. As outlined above, they were three-component systems combined in stoichiometric proportions, and consisting of: (1) a diisocyanate (DI) – either MDI or DBDI; (2) a soft segment macrodiol (MD) – PTHF of molar mass  $M_w = 2000 \pm 50 \text{ g mol}^{-1}$ ; and (3) a small molecule diol as chain extender (CE) – anhydrous EG or DEG. Hard segment volume fraction were held constant at approximately 35%. The three components were mixed in the molar proportions DI:MD:CE = 4:1:3, giving isocyanic index  $I = 100$ . Synthesis was carried out by the pre-polymer route described previously by Prisacariu et al. [8,14]. The DI and MD components were reacted together with vigorous mixing under vacuum at  $100^\circ\text{C}$ , to give prepolymer consisting of MD terminated at each end by DI. This was then thoroughly mixed with the CE at  $90^\circ\text{C}$ , and cast into closed sheet moulds for curing at  $110^\circ\text{C}$  over 24 h. The final result was polymer with  $M_w$  in the range  $60\text{--}110 \text{ kg mol}^{-1}$ , in the form of sheets with thickness in the range  $0.3\text{--}0.6 \text{ mm}$ . The materials were labelled TPU1–TPU10, according to their combination of DI, MD and CE, as indicated in Table 1. It should be noted that the stoichiometric proportions used in these polymers ( $I = 100$ ) means that are truly thermoplastic. They do not have the potential for further reaction with ambient humidity to produce chain lengthening and allophanate cross-linking, seen in similar polymers but with excess isocyanate groups (e.g.  $I = 110$ ) [15].

The materials based on the deuterated MD or deuterated CE were also obtained in the Romanian laboratory. The polymers achieved with DEGd were obtained as described elsewhere [6,8]. DEGd (isotopic purity 90%) was used instead of DEGh. DEGd was obtained from a mixture of  $\text{D}_2\text{O}:\text{DEG}$  (25:6, v/v) by fractionated distillation after 24 h of isotopic exchange at  $60^\circ\text{C}$ . Quantitative measurements confirmed an approximately 67% deuteration degree [6].

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