

Optimizing Physical and Chemical Properties of Hard Segment Reinforced Polyurethane Elastomers Via Control of Hydrogen Bonding

C. Prisacariu*, E. Scortanu and V. A. Prisacariu

Abstract—A family of polyurethane elastomers (PUs) was achieved, with analogous structures, but gradually reducing the percents of hydrogen bonding. Materials were compared with similar structures but achieved with 100% hydrogen bonding and with similar materials but where hydrogen bonding was 100% replaced with inert (-CH₃) groups. The effect of hard segment (crystallizing or not) was followed 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)). Polyesteric macrodiols: poly(ethylene adipate) PEA poly(tetramethylene adipate) glycol (PBA) and polyetheric macrodiol polytetrahydrofuran (PTHF) were used. The effect of hydrogen substitution with inert (-CH₃) groups on the PUs stress-strain data was followed. For comparison reasons, a series of deuterated PUs were also synthesized, for which the following preparation procedures were adopted: (a) the substitution of hydrogen bonding with deuterium of D₂O in the case of up to 20 μm thin PUs films; (b) the deuteration by synthesis on employing deuterated chain extenders or deuterated macrodiols. The stress-strain data of uniaxial tension indicated a dramatic decrease of the mechanical properties data and load/unloading cycles when hydrogen bonding of the urethane groups was replaced with inert (-CH₃) groups unable of intermolecular interactions. Similar observations were made for materials where hydrogen was replaced partially (90%, 70% and 20%) with -CH₃ groups. This was in contrast with the observations made on analogous structures but synthesized with deuterated chain extenders where the elastomeric behavior of the materials was observed to improve.

Index Terms— hydrogen bonding, flexible hard segments, polyurethanes, stress-strain data.

I. INTRODUCTION

Polyurethanes (PUs) are extensively hydrogen bonded. Hydrogen bonding in PUs can be readily detected and studied by IR spectroscopy. The hydrogen bonded and free N-H and urethane carbonyl C=O are the peaks of interest [1, 2]. The

effect of hydrogen bonding is frequently used to explain various anomalies or improved properties. However it is difficult to isolate this effect from the effects of physical and chemical structure. Some studies have concluded that molecular mobility is not controlled by hydrogen bonding.

The hydrogen bonding interaction in PUs is illustrated in Figures 1-3.

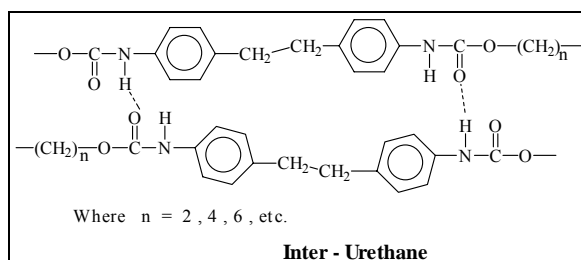


Figure 1. Inter - urethane hydrogen bonding interaction in polyurethanes.

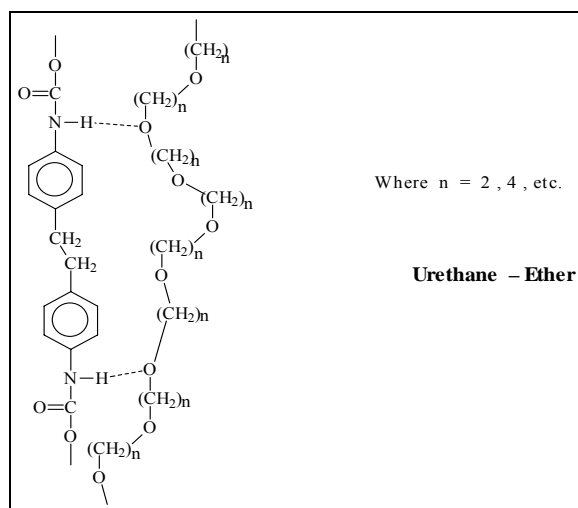


Figure 2. Urethane - ether hydrogen bonding interaction in polyurethanes.

It is believed that a rapid increase in molecular mobility accompanying glass transition allows the hydrogen bonding to dissociate [1, 3]. Therefore the hydrogen bonding does not necessarily enhance mechanical properties, although there is insufficient published data that quantitatively demonstrates the effect of hydrogen bonding on the mechanical properties.

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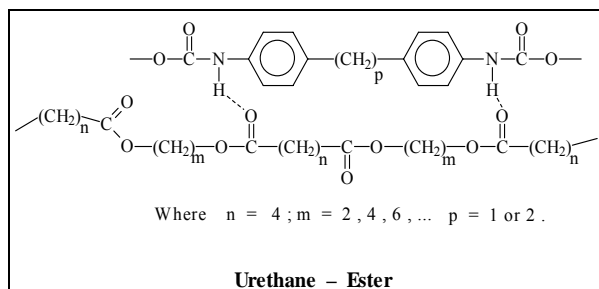


Figure 3. Urethane – ester hydrogen bonding interaction in polyurethanes.

As shown, a clear effect of hydrogen bonding could be observed only if mechanical tests are carried out on polyurethanes of analogous structure with and without hydrogen bonding. Therefore in the present work this problem was addressed by studying a series of PUs with analogous structures, but gradually reducing the percents of hydrogen bonding. The effect of hard segment (crystallizing or not) was followed by inclusion of a diisocyanate (DI) with a large conformational mobility (4,4'-dibenzyl diisocyanate (DBDI)). Polyester macrodiols (MD): poly(ethylene adipate) PEA, poly(tetramethylene adipate) glycol (PBA) and the polyether macrodiol polytetrahydrofuran (PTHF) were used.

The effect of hydrogen substitution with inert (-CH₃) groups on the PUs stress-strain data was followed. The partial (90%, 70% and 20%), or total (100%) hydrogen substitution with inert (-CH₃) groups was carried out using the following synthesis routes: (a) chemical modification of usual PUs by substitution after synthesis, using lithium hydride and methyl chloride; (b) using dichloroformyl based on PEA, PBA or PTHF and chain extenders (CE) diethylene glycol (DEG) or ethylene glycol (EG) reacted with -NN'-dimethyl diaminodiphenyl methane. For comparison reasons, to follow the influence of the hydrogen bonding on the PUs mechanical properties, a series of deuterated PUs were also synthesized, where hydrogen was replaced with deuterium. For this series, the following preparation procedures were adopted: (a) the substitution of hydrogen bonding with deuterium of D₂O in the case of up to 20 μm thin PUs films; (b) the deuteration by synthesis by using deuterated chain extenders; (c) the deuteration by synthesis using deuterated soft segments (PTHF), of molar mass M = 2000±50, (Figure 4).

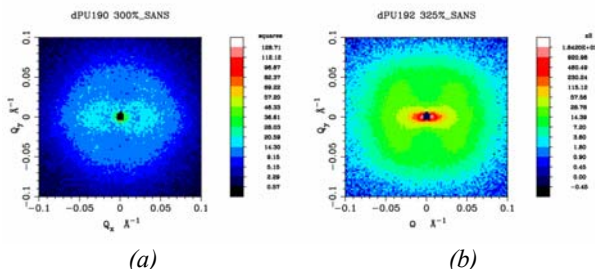


Figure 4. 2D scattering plots from the SANS measurements for 2 deuterated bulk PUs elastomers during extension to 300%: (a) deuterated MDI based PU (MDI:DEG:PTHF); (b) deuterated DBDI based PU (DBDI:DEG:PTHF); by courtesy of Dr D.Bucknall, Virginia Tech. Univ.

In both images of Figure 4, the strain direction of the sample is in the y-axis. The anisotropy of the structures relative to the strain direction was clearly visible in the 2D images in the

deformed samples. The materials strained showed various degrees of anisotropy depending on the structure and especially on the hard segment (crystallizing or not). Materials were compared with similar structures but achieved with 100% hydrogen bonding and with similar materials but where hydrogen bonding was 100% replaced with inert (-CH₃) groups.

II. EXPERIMENTAL

A. Materials

20 μm thin PUs films (MD:DI:CE / 1:3.03:2.02) were casted via the prepolymer route. The cast melt was poured between teflon plates at 110 °C. The films were suspended in 250 ml volume glass ampoules which contained 5 ml D₂O on the bottom. To achieve the PU sample dehydration, the inferior part of the glass ampoule was cooled for 24 hours with solid CO₂, vacuumed to 0.1 mm Hg and sealed under vacuum. For deuteration, the ampoules were kept at room temperature and alternatively at 60 °C for 24 hrs. PUs films were then dried in closed precincts containing P₂O₅. The pressure of water vapors varied between the values of 0.0004 mm Hg (-80 °C) and 149.3 mm Hg (60 °C) (the corresponding values for D₂O were about equivalent).

For PUs sheets of thicker 2 mm a similar procedure was carried out. To speed up the isotope exchange it was applied a cyclic hydrating-dehydrating procedure in closed systems where the PUs specimens were fixed on the upper part of the system. Heating-cooling cycles were repeated 17 times during 34 days after which the degree of deuteration was followed by IR spectra.

The polyaddition procedures to obtain polyurethanes where hydrogen was replaced with inert (-CH₃) groups were described elsewhere [4].

B. Mechanical tests

The polymers in the form of films prepared as described above, were subjected to uniaxial tensile tests at constant nominal strain-rate. In addition, to investigate mechanical hysteresis, cyclic tensile tests were carried out, cycling between a fixed strain limit and zero load, with the same magnitude of strain-rate for loading and unloading. Test specimens were cut from films using dimensions given in ASTM D1708, i.e. a dumbbell – shaped specimen with a length 53 mm between shoulders, a gauge length of 20 mm (on which the strain was measured), a width of 5.8 mm, and a thickness of 0.3 up to 2 mm. The stress-strain data on these specimens presented here were obtained using an Instron 4204 Testing Machine or Schopper MZ Gip Testing Machine, at room temperature (T≈25 °C). Strain was measured manually from the movement of fiducial marks or obtained from grip displacement, after using video images of the gauge length to correct for non-uniform strain outside the gauge length.

III. RESULTS AND DISCUSSION

A. Deuterated materials. Hydrogen substitution with deuterium.

On employing the IR measurements the degree of isotope exchange was estimated by the decrease of the ν_{NH} stretching vibration and concomitantly the increase of ν_{ND} corresponding to the step by step appearance of the ND

groups as a result of the hydrogen replacement by deuterium. Quantitative IR measurements confirmed a 65% deuteration degree but only for up to 0.2 mm thin PUs films. The position of the urethane hydrogen replacement was strongly influenced by the adopted polyaddition procedure. While in the case of direct deuteration by isotope exchange using D₂O, the hydrogen replacement with deuterium occurred preferentially at the joint points between hard segments and polyesters, by using a deuterated glycol, chain extender (DEG or EG) during the PUs synthesis, the exchange of hydrogen with deuterium proceeded especially within the middle of the hard segment urethane groups.

The percent of hydrogen bonding was investigated by means of NMR studies. PUs cast melt sheets were turned into films obtained by dissolving them in DMF followed by evaporation from solution.

In the case of thicker films, the direct replacement of hydrogen with deuterium by using D₂O failed. This was due to the difficulty of D₂O molecules to penetrate thicker PUs macromolecular networks. However, concomitantly with the experiments achieved on thicker sheets immersed in D₂O, similar experiments were done on similar PU films but immersed in H₂O. The stress – strain data of the two series of polymers were achieved. They were compared with the data obtained for similar structures but achieved as 0.2 mm thin films where it obtained a 65% exchange of hydrogen with deuterium by direct exchange, using D₂O. It observed that while the samples immersed in H₂O presented significant hydrolytic degradation, the properties of the series of films immersed in D₂O were not altered. Not any degradation effects were evidenced. Apparently unexpectedly, for the similar samples subjected to the same treatment with H₂O, the mechanical properties decreased appreciably as a result of the appearance of a significant hydrolytic degradation, (Figure 5). That has suggested that D₂O does not penetrate a thicker macromolecular network because of the higher D₂O molecule volume than that of normal H₂O. Shown in Figure 5 are example stress-strain curves of a material with the structure (PBA:DBDI:DEG).

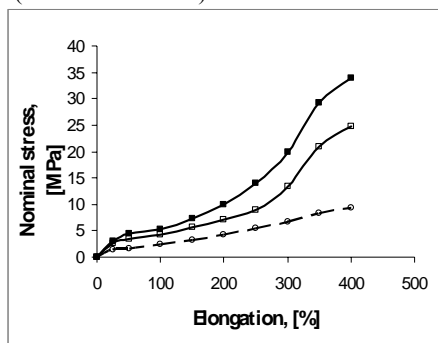


Figure 5. Stress-strain curves of uniaxial extension:
(■) – 20 μm thin PU film deuterated by direct exchange of hydrogen with deuterium; (□) – 2 mm thick PU immersed in D₂O; (○) – 2 mm thick PU immersed in H₂O.

To enable the replacement of hydrogen with deuterium in the case of thicker PUs, the authors proceeded to the deuteration by synthesis. This was achieved by using a deuterated chain extender DO-CH₂-CH₂-O-CH₂CH₂-OD (*DEG d*) (isotopic purity 90%) instead of DEG. *DEG d* was obtained from a

mixture of D₂O:DEG (25:6 vol) by fractionated distillation after 24 hrs of isotopic exchange at 60 °C. Quantitative measurements confirmed a 66.7% deuteration degree. The stress-strain data of uniaxial static tension (Table 1) and the hysteresis curves at a 300% level of extension showed that for the PUs derived from deuterated chain extenders it obtained better elastomeric mechanical properties.

Table 1. Tensile properties of a polyetheric DBDI based PU derived from the macrodiol PTHF and normal / deuterated DEG

The Tensile Property	Normal DEG	Deuterated DEG
100% Tensile Stress, [MPa]	3.85	5.74
300% Tensile Stress, [MPa]	7.67	10.6
Tensile Strength, [MPa]	41.2	56.3
Residual Elongation, [%]	50.0	22.0
Hardness, Shore A	90	94
Strain Energy 300%, [MPa·cm]	14.7	17.2
300% Permanent Hysteresis,	45.5	45.22

B. Hydrogen substitution with inert (-CH₃) groups

In a second stage of the study, a series of PUs were achieved where the hydrogen bonding was replaced partially with -CH₃ groups, (Figure 6), by decreasing gradually the percent of hydrogen bonding (90%, 70% and 20%). The materials were compared with similar structures but where hydrogen was replaced 100% with inert (-CH₃) groups.

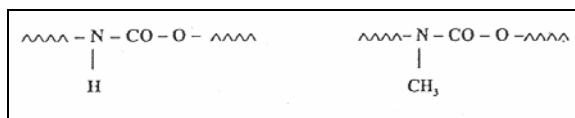


Figure 6. Hydrogen substitution with inert (-CH₃) groups.

Decreasing gradually the percent of hydrogen resulted in the decrease of the molecular weight expressed as the inherent viscosity, as shown in Table 2.

Table 2. Inherent viscosity as a function of the percent of hydrogen bonding for selected PUs

PUs Structure	Inherent Viscosity, [dl/g]		% H
	Initial 100% H	modified	
DEG:PEA:DBDI	0.78	0.67	77
EG:PEA:DBDI	0.62	0.52	20
EG:PEA:MDI	1.15	0.23	92

As seen in Tables 3 and 4, and in Figure 7, the materials stress-strain behaviour differed depending on the PU structure and % hydrogen bonding. The common feature for the materials labeled in Tables 2- 4 was that the stress-strain data values decreased dramatically and proportionally with diminishing the % H bonding and molecular weight.

As long as these two processes could not be separated, to assess what is the main process that determines the decrease of the mechanical data, we proceeded to the total replacement of hydrogen with inert CH₃ groups.

Table 3. Nominal stress at a 300% strain as a function of percent of hydrogen bonding for the same series of PUs structures as in Table 2.

PUs Structure	Nominal Stress at 300% strain, [MPa]		% H
	Initial 100% H	modified	
DEG:PEA:DBDI	7.7	2.76	77
EG:PEA:DBDI	20.9	16.9	20
EG:PEA:MDI	13.5	-	92

Table 4. Tensile strength as a function of percent of hydrogen bonding for the same series of PUs structures as in Table 2.

PUs Structure	Tensile Strength, [MPa]		% H
	Initial 100% H	modified	
DEG:PEA:DBDI	61.6	9.1	77
EG:PEA:DBDI	50.3	36.1	20
EG:PEA:MDI	61.5	3.1	92

Five families of PUs were prepared: A,B,C,D,E where hard segment molar compositions were as follows (%H/%-CH₃ groups): (A) 100/0; (B) 90/10; (C) 70/30; (D) 20/80; (E) 0/100. The MD was PTHF or PEA of molar mass 2000±50 and the CE was EG. The molar proportion used in the syntheses were: MD:DI:CE = 4:1:2.64.

As seen in Figure 7, inelasticity increased dramatically with decreasing the percent of hydrogen bonding, and this resulted in a constant degree of elongation at break, and an increase of the residual elongation showing a pronounced tendency of polymer plasticization, mostly in the case of polymer (E)-0/100 achieved with no hydrogen bonding.

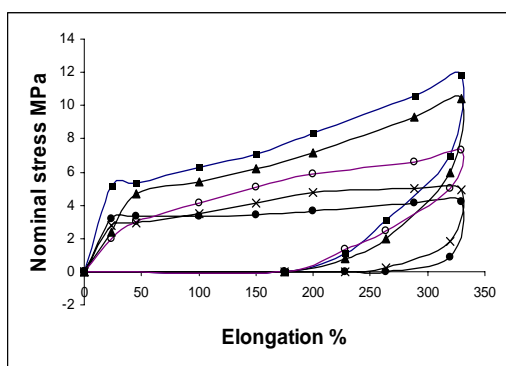


Figure 7. Tensile load/unload cycles for a material (EG-PEA-DBDI, I=110), at strain rate 0.03 s⁻¹ where hydrogen was substituted gradually with inert (-CH₃) groups: (%H / %CH₃ groups): (■)-(A) 100/0; (▲)-(B) 90/10; (○)-(C) 70/30; (x)-(D) 20/80; (●) (E)-0/100.

Inelasticity (residual strain, hysteresis) increased when hydrogen was substituted with inert (-CH₃) groups. Inelastic effects were even more pronounced when hard segment crystallized.

Table 5. Stress-strain data of a PU (PEA:EG:DBDI) with / without hydrogen bonding, (%H/%-CH₃ groups): 100/0; 0/100% obtained by the prepolymer technique

PU Synthesis route	Inherent viscosity [dl/g]	Hardness, [Sh ⁰ A]	Stress at 300% strain, [MPa]
with hydrogen bonding	1.18	89	14.6
without hydrogen bonding	0.37	72	3.8
PU Synthesis route	Tensile strength, [MPa]	Elongation at break, [%]	Residual elongation, [%]
with hydrogen bonding	66.7	550	20
without hydrogen bonding	7.4	780	220

IV. CONCLUSION

Deuterated thin PUs films were obtained by means of the direct hydrogen exchange using heavy water (D₂O). A significant isotope exchange of up to 65% at 60 °C was achieved. For thicker PU sheets, the deuteration by synthesis was approached by using deuterated diol chain extenders. The stress-strain data of uniaxial static tension showed that for the PUs derived from deuterated chain extenders it obtained better elastomeric mechanical properties. The stress-strain data of uniaxial tension indicated a dramatic decrease of the mechanical properties data and load/unloading cycles when hydrogen bonding of the urethane groups was replaced with inert (-CH₃) groups unable of intermolecular interactions. Similar observations were made for materials where hydrogen was replaced partially (90%, 70% and 20%) with -CH₃ groups. This was in contrast with the observations made on analogous structures but synthesized with deuterated chain extenders where the elastomeric behaviour of the materials was observed to improve. The PU inelasticity increased with the hydrogen substitution with inert (-CH₃) groups leading to a constant degree of elongation at break, as well as an increase of the residual elongation which resulted in a pronounced tendency of polymer plasticization.

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REFERENCES

1. Z. S. Petrovic, J. Ferguson, "Polyurethane Elastomers", in *Prog. Polym. Sci.*, 16, (1991) 695-836
2. G. M. Estes, R. W. Seymour, S. L. Cooper, "Infrared studies of segmented polyurethane elastomers. II. Infrared Dichroism", in *Macromolecules* 4, (1971), pp. 452-457 (1971).
3. 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.
4. C. Prisacariu, E. Scortanu, "Structural studies and the correlation with the stress-strain response in polyurethanes"- in the press, in *Encyclopedia of Analytical Chemistry*, (2010).