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

A STUDY OF STRESS RELAXATION PROCESSES IN SELECTED SEGMENTED POLYURETHANE ELASTOMERS

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A study had been made of the correlation between the chemical structure and the relaxation processes for varied structures of polyurethane elastomers (PUs). In particular, two hard segments were compared, based on the diisocyanates: 4,4'-methylene bis(phenyl isocyanate) (MDI) and 4,4'-dibenzyl diisocyanate (DBDI) giving rise to hard segments with a local intramolecular mobility generating a higher tendency to crystallization and self-association by hydrogen bonding. For the adopted structures, a constant isocyanate index I = 100 has been approached giving thermoplastic polyurethanes. For comparison reasons, similar polymers but achieved as crosslinked PUs (I = 110) were synthesized. The mechanical response of polymers was studied in the context of high deformations, with constant rate of deformation. PUs mechanical response was investigated when the materials were subjected to tensile stress relaxation tests and when subjected to fixed or gradually increasing cyclic deformation. Tensile stress relaxation tests included interrupted tests with step stress relaxation under load by interrupting the increase of strain stress, to observe the relaxation of stress at constant strain over 10 min, before resuming extension. With DBDI as the hard segment, the extent of relaxation was greater than with MDI. When subjected to fixed or gradually increasing cyclic deformation where the specimens were subjected to a continuous pseudo-cyclic straining sequence, such that on the nth cycle it was cycled between a maximum nominal strain $\varepsilon_{\max} = n$ and zero load, all the materials showed substantial deviations from hyperelastic response, indicating the presence of relaxation processes The influence of the hard domain crystallinity in the materials with DBDI was more pronounced, leading to a dramatic increase in stress, showing a more pronounced apparent yield phenomenon.

INTRODUCTION

The role of elastomers within the field of polymer science has been and is one of key importance. Elastomeric materials, and particularly synthetic elastomers, are virtually indispensable with regard to their myriad industrial, medical, and consumer applications. They continue to make up a considerable portion of annual polymer production and sales.[1-4] Those elastomeric materials based on polyurethane and/or polyurethane-urea chemistry have a rich history, both in terms of practical application and research.[5-7]

The present paper is part of a wider study made of numerous block copolyurethane elastomers (PUs), based on several diisocyanates, macrodiols and chain extenders, with the aim of improving the understanding of the relationship between molecular/supramolecular architecture at the nm-scale and macroscopic mechanical properties in such systems.[8-12] A novel diisocyanate (4,4'-dibenzyl diiscyanate (DBDI)) and a triol chain extender (1,1,1-trimethylol propane (TMP))[13] were included as well as more widely-used components, in order to widen the range of structures. A systematic investigation was made on the effects of varying the chemistry of hard and soft segment and chain extender, and the preparation procedures employed, on mechanical response of the PUs. Since their structures could be varied systematically, they were used to probe the sensitivity of elastic and inelastic responses to

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structural detail, more comprehensively than has been possible previously. Structures had been characterized by wide and small angle X-ray scattering SAXS and WAXS as described elsewhere.[7,10,11]

Mechanical responses studied were small strain linear viscoelasticity (by tensile creep and tensile DMA tests) and large strain, constant strain-rate and cyclic strain responses, including interrupted tests. In polymers with diol chain extenders there were tendencies to phase separation, with a characteristic length of ca 20 nm, and, when DBDI was employed with certain chain extenders, to crystallization of the hard phase.[7,10,11]

In polymers prepared with the triol TMP as chain extender a crosslinked system was obtained, preventing phase separation. Measurements of the mechanical responses revealed clear evidence for a change in relaxation spectrum with phase separation, showing a bimodal distribution of molecular mobility of the soft segments: a 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.[13] 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 on the flow stress.[16] In the present work the problem of sensitivity of inelasticity to structural detail on the nm scale was addressed by studying the stress relaxation processes for a series of model thermoplastic and crosslinked polyurethane elastomers (PUs). The system of segmented copolyurethanes studied were related to those described previously.[7,10] As before, hard segments were chosen to be generated either from 4,4'-methylene bis(phenyl isocyanate) (MDI) or from the diisocyanate DBDI (Fig. 1). Since TPUs derived from MDI does not crystallize when the polyaddition was performed in the bulk, whereas those derived from DBDI can crystallize. These choices allowed the authors to compare the effects of this important structural variant on the constitutive response.[8]
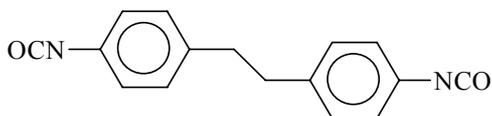

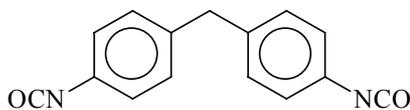Fig. 1 (a)   Fig. 1 (b)

Fig. 1 – Schematic of DBDI and of MDI; a) 4,4'-dibenzyl diisocyanate (DBDI)–*crystallizing;*
b) 4,4'-methylene bis(phenyl isocyanate) – *non-crystallizing.*

RESULTS AND DISCUSSION

As is widely known, PUs elastomers are not perfectly elastic. Thus, when deformation is held constant, the induced stress relaxes gradually. Fig. 2 shows example data, for stress relaxation over 100 hours, for a thermoplastic polyurethane stretched to 300% elongation. It was noticed that the main relaxation process occurs within the first 10 min (70% of the relaxation value after 100 h and that the 24 h was 95% of the relaxation value after 100% h). Over the range shown it was observed a linear dependence of stress on the logarithm of time, as expressed by equation (1).

$$\sigma = \sigma_o - a \log t \qquad (1)$$

where σ_o and a are constants for a given material. This relation was found to hold for all the materials tested.

Values of percentage stress relaxation, 10 minutes after straining to 300% elongation at 3.1×10^{-2} s^{-1}, are collected in Table 1 for several of the thermoplastic PUs studied, together with the initial nominal stress on reaching 300% elongation $\sigma_{300\%}$. Also shown, for comparison, are the values of first and second cycle hysteresis E_{1H}^* and E_{2H}^* and the residual elongation after unloading from 300% elongation. Table 1 presents the initial stress $\sigma_{300\%}$. For comparison, the table also shows the residual elongation and relative hysteresis in first and second cycles of elongation at the same rate E_{1H}^* and E_{2H}^*. The measured values of percent relaxation over 10 minutes at 300% elongation

were found to lie in the range 15-20% in the case of DBDI based PUs, which may be compared with the range 16-24% mentioned by Abouzahr and Wilkes[14] or similar MDI based polyurethane elastomers,[15] and also may be compared with the range of similar PUs but achieved as crosslinked materials, (I=110), 17 – 21%.[7] As may be seen, the range of stress relaxation for the DBDI and MDI based PU does not differ greatly. However, some interesting differences are visible in Table 1.

Comparing the results for PU$_4$ and PU$_5$, it may be seen that there is an increase in stress relaxation when the MDI hard segment is replaced by DBDI, for the same MD/CE combination and urethane group concentration. This is consistent with the increase in residual elongation and hysteresis also shown in Table 1; and it is also consistent with the observations made for similar but crosslinked PUs

as detailed elsewhere.[7] This table also shows some influence of changing the MD resulting in increase in stress relaxation from PTHF to PEA or the CE, from BG to DEG, when DBDI was the hard segment. But, as in the case of crosslinked PUs, these increases do not correlate with increases in residual elongation or hysteresis. Other factors are at work here, including the fact that use of DEG as chain-extender inhibits crystallization of the DBDI.

Further tensile load-unload stress relaxation tests were conducted by interrupting constant strain-rate tests (again 3.1×10^{-2} s^{-1}) with 200s waiting times during loading and reloading, to observe the relaxation of stress at constant strain over 200s, before resuming extension. Sample results are shown in Figs. 3 and 4, where materials based on DBDI and MDI were compared (PU$_9$ and PU$_{12}$).
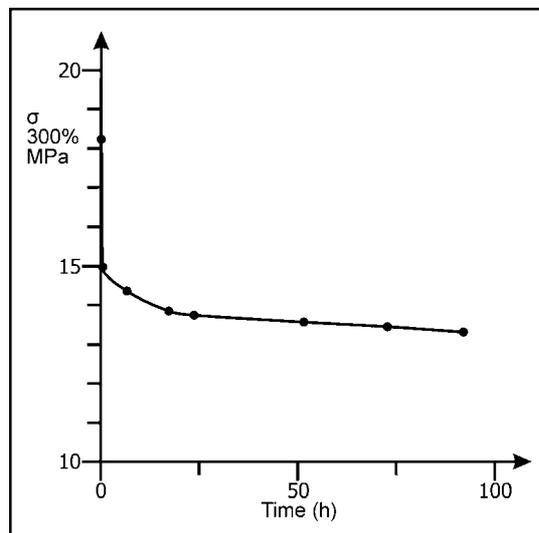

Fig. 2 – Stress relaxation of a PU (DBDI-PEA-BG, I=100) following 300% elongation at nominal strain-rate 3.1×10^{-2} s^{-1}. Time is expressed in hours.

Table 1

Percentage stress relaxation in various PUs, 10 minutes after elongation to 300% at a nominal strain rate 3.1×10^{-2} s^{-1}

PU type	PU structure	$\sigma_{300\%}$ MPa	SR %	E_{1H}^{*} %	E_{2H}^{*} %	ε_r %
PU$_1$	DBDI-PEA-DEG	12.7	20.0	82.6	45.7	20
PU$_2$	DBDI-PTHF-DEG	10.8	19.4	80.8	48.2	760
PU$_3$	DBDI-PEA-BG	17.6	19.0	84.7	68.5	170
PU$_4$	DBDI-PTHF-BG	15.2	16.2	87.3	62.6	250
PU$_5$	MDI-PEA-BG	16.4	15.2	78.2	40.3	40

$\sigma_{300\%}$ - stress at 100% strain; SR – stress relaxation, [%]; E_{1H}*, E_{2H}* - first and second cycle hysteresis; ε_r – residual deformation.
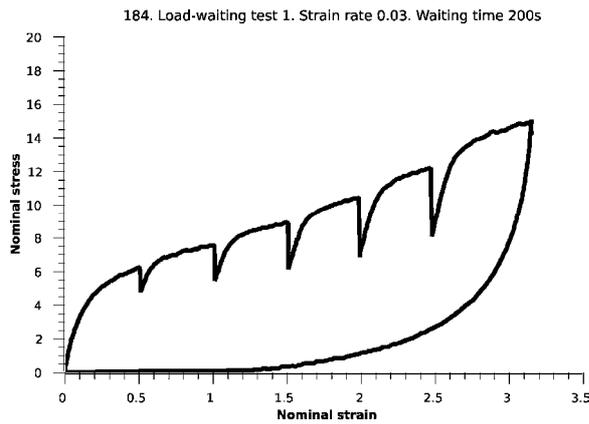
Fig. 3 – Tensile load-unload cycle for PU$_5$ based on the MDI-BG couple: interrupted test during loading with 200s waiting times during loading and reloading; continuous unloading.
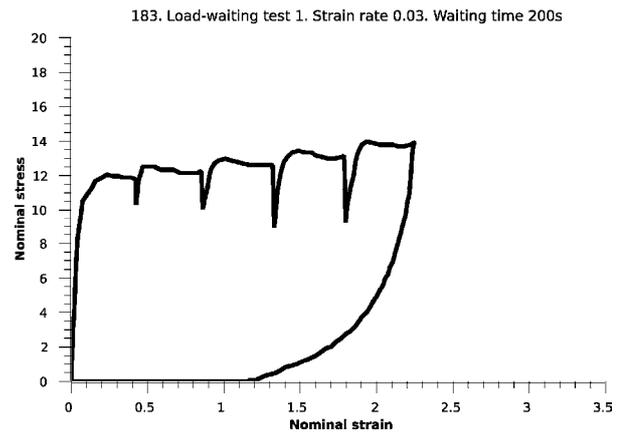

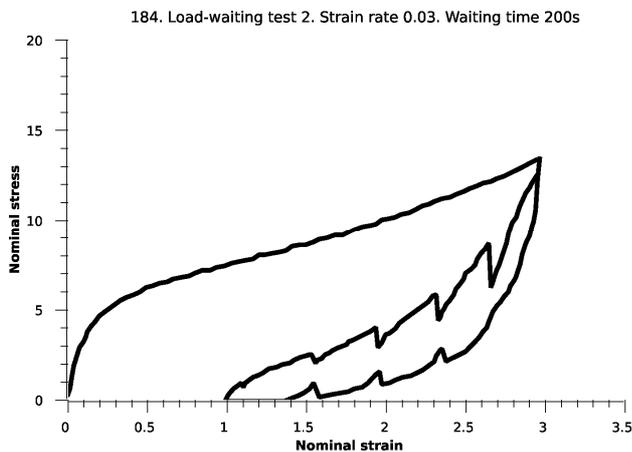Fig. 4 – Same but for a material PU$_3$ with DBDI-BG.

Fig. 5 – Tensile load-unload cycle for the PU$_5$ based on the MDI-BG couple: continuous test during first loading; interrupted test during unloading and second reloading with 200s waiting times during loading and reloading.
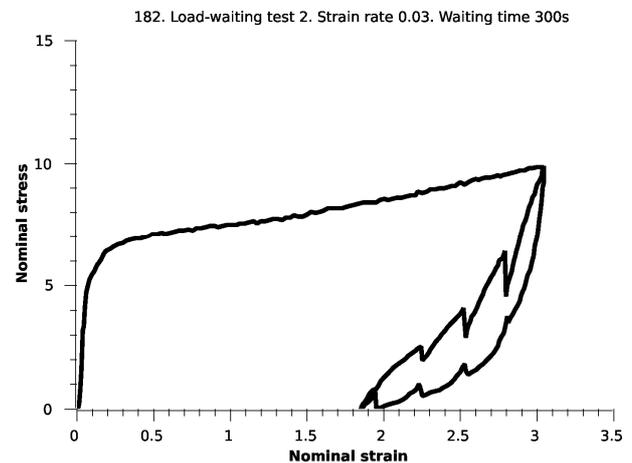

Fig. 6 – Same but for the material PU$_3$ with DBDI.

A common pattern of behaviour for the MDI and DBDI materials could be seen. When straining was resumed after stress relaxation for 200s, the stress rised rapidly before continuing a steady increase with strain, resuming approximately the original curve. But as seen, for the material based on DBDI there were observed higher E modulus and higher stiffness; also lower strain recovery and strain energy recovery and higher residual strain. Further tensile stress relaxation tests were conducted on the series of thermoplastic PUs labeled in Table 1, by interrupting constant strain-rate tests (again 3.1×10^{-2} s^{-1}) at intervals of 25% elongation, both in the loading and unloading cycles to observe the relaxation of stress at

constant strain over 10 minutes, before resuming extension. A common pattern of behavior could be seen. When straining was resumed after stress relaxation for 10 minutes, the stress rose rapidly before continuing a steady increase with strain, resuming approximately the original curve. The fact that the stress-strain curves for continuous straining lay slightly below the corresponding envelope curves for the interrupted tests, was believed to reflect a small degree of adiabatic heating in the continuous tests. The nominal strain-rate employed (3.1×10^{-2} s^{-1}) was at the upper end of the range where isothermal conditions are likely to apply in the testing of an elastomer. Any adiabatic heating is likely to be absent in

interrupted tests, where sufficient time was available for heat to dissipate. Again, with DBDI as the hard segment, the extent of relaxation is greater than with MDI.

EXPERIMENTAL PART

Synthesis of polymers

Thermoplastic PUs 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 DBDI type or respectively 50g (0.2 mol) of 4,4'- methylene bis (phenyl isocyanate) MDI in the case of 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. This gave a prepolymer with final isocyanic NCO groups in a mixture with the excess of isocyanate. Next 9.295 g (0.1086 mol) ethylene glycol (EG) 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 moulds were maintained closed 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.

Crosslinked PUs were obtained similarly as above, except that the materials were prepared with excess of NCO groups, giving isocyanic index I = 110 as detailed elsewhere.[7,10]

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. Furthermore, to reveal the time-dependent contribution to stress, some tensile stress relaxation tests were conducted: these included both single strain-step experiments – shown in Figs. 5 and 6 – and interrupted constant strain-rate experiments. 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 nonuniform strain outside the gauge length. True stress was deduced from nominal stress by assuming incompressibility.

CONCLUSIONS

The primary concern of this paper was the question of how the choice of hard segment composition in thermoplastic PU elastomers affects their mechanical response, especially when the relatively rigid MDI segment is replaced by the relatively more flexible, and crystallisable, DBDI segment. Other parameters being equal, replacement of MDI by DBDI was seen to lead to a higher stress relaxation. Changing the macrodiol, resulted in increase in stress relaxation from PTHF to PEA, or the chain extender, when DBDI was the hard segment. But, as in the case of crosslinked PUs, these increases did not correlate with increases in residual elongation or hysteresis. These experiments reveal clearly that inelastic features in the constitutive response of polyurethane elastomers are sensitive to microstructural detail on length scales of order nm. One prominent result is the strong influence that hard-domain crystallinity exerts on inelasticity of the elastomers.

REFERENCES

1. J. H. Saunders and K.C. Frisch, "Chemistry and Technology, Part I and II", 1962, Interscience Publishers., New York, 1962
2. C. Hepburn. "Polyurethane elastomers" 1982, London: Applied Science, 1982
3. Z.S. Petrovic. "Polyurethanes, Handbook of Polymer Synthesis", 2004, second edition, H.R. Kricheldorf, O. Nuyken, and G. Swift (Eds.) CRC Press, 2004
4. D.M. Crawford, R.G. Bass and T. W. Haas, *Termochimica Acta,* **1998**, *323*, 53.
5. C. E. Wilkes and C. S. Yusek, *J. Macromol. Sci., Phys.* **1973**, *B7*, 157.
6. J. Diani, B. Fayolle and P. Gilormini, *Eur. Polym. J.,* **2009**, *45*, 601.
7. C. Prisacariu, C.P. Buckley and A. Caraculacu, *Polymer,* **2005**, *46*, 3884.
8. C. P. Buckley and D.C. Jones, *Polymer*, **1995**, *36*, 3301.
9. C. Prisacariu, A. Caraculacu, E. Scortanu and G. E. Hitruc, *Rev. Roum. Chim.,* **2007**, *52*, 415.
10. C. Prisacariu, R. H. Olley, A. Caraculacu, D.C. Bassett and C. Martin, *Polymer,* **2003**, *44*, 5407.
11. C. Prisacariu and E. Scortanu**,** *Macromol. Symp.*, **2007**, *254*, 153.
12. C. P. Buckley, G. Saccomandi and R. V. Ogden (Eds.), "Mecanics and Thermomecanics of Rubberlike Solids", Vienna: Springer Verlag, 2004, p. 1.
13. C. P. Buckley, C. Prisacariu and A. Caraculacu, *Polymer,* **2007**, *48*, 1388.
14. S. Abouzahr, G. L. Wilkes and Z. Ophir, *Polymer,* **1982**, *23*, 1077.
15. J. N. Gorce, J. W. Hellgeth and T. C. Ward, *Polym. Eng. Sci*., **1993**, *33*, 181170.
16. C.P. Buckley, C. Prisacariu, A. Caraculacu and C.M. Martin, in "Constitutive Models for Rubber IV", P.-E. Austrell, L. Hari (Eds.), Ed. Taylor and Francis, 2005, p. 465.