

A Study of Toluene Diisocyanate-Based Polyurethanes of Various Isomer Ratios

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Synopsis

Several urethane elastomers based on poly(oxytetramethylene glycol), butanediol 1,4 and various mixtures of 2,4 and 2,6 toluene diisocyanates were prepared. The tensile strength, moduli, glass transition temperatures, flow temperatures and relaxation properties were measured. These properties are discussed with reference to changes in microphase separation.

INTRODUCTION

Toluene diisocyanate (TDI) is still one of the most frequently used diisocyanates in the urethane technology. In most cases the commercial TDI is an 80 : 20% mixture of 2,4 and 2,6 isomers. In the recent years several papers were published concerning the properties of urethane elastomers obtained from either pure 2,4 TDI or from pure 2,6 TDI.¹⁻⁵ However, to the author's knowledge, there have not been published yet data obtained for polyurethanes synthesized from TDI isomer mixtures, covering the whole composition range from pure 2,4 TDI to pure 2,6 TDI. The essential difference between the 2,4 TDI and 2,6 TDI-based urethane elastomers is the asymmetry of the 2,4 TDI unit which creates a disruptive influence within the hard segment structure. That is why the mechanical properties of the polyurethanes synthesized from the commercial TDI and glycol chain extenders are very poor. Sufficiently high mechanical properties can be obtained only if an aromatic diamine chain extender is employed, since the aromatic urea groups produce stronger intermolecular interactions than the urethane ones. The application of aromatic diamine chain extenders involves, however, at least two disadvantages: the reaction rate is very often too fast to be properly controlled and not enough time is available for adequate mixing. In addition, many aromatic diamines are suspected to present health hazards. On the other hand, glycol-extended TDI elastomers exhibit good mechanical properties if pure 2,6 (i.e., the symmetrical isomer) is used in the preparation. This isomer is unfortunately much more expensive than the aforementioned commercial mixture and therefore has little, if any, practical applicability. One might expect, however, an intermediate composition of 2,6 TDI and the commercial TDI to lead to polymers of properties sufficiently high for many applications even if a glycol extender is used.

It is also known⁶ that the main factor determining the properties of urethane elastomers is the so-called microphase separation of flexible and hard segments. Changes in the TDI isomer ratio in the reaction mixture may lead to changes

in the microphase separation of the synthesized elastomers, since the separation is rather sensitive to changes in the molecular structure. Thus, the work on a series of urethane elastomers prepared from different mixtures of TDI isomers may contribute to our knowledge of microphase separation effects in this class of polymers.

EXPERIMENTAL

Materials

The polyurethanes investigated in this work were prepared by a prepolymer method from poly (oxytetramethylene glycol), PTMO, of molecular weight 1000 or 2000 (A. G. Bayer), 2,4 TDI and 2,6 TDI (supplied by Dr. L. Szczepkowski from Organika-Zachem, Bydgoszcz, Poland) and from butanediol-1,4,BDO (BASF). The prepolymer method consisted of drying the polyether diol under reduced pressure (330°K, 1 mmHg, 2 h). Then, the prepolymerization with a mixture of TDI isomers was carried out at 360°K for 30 min. Under vigorous stirring BDO was added to the prepolymers and the reaction mixture was poured into a centrifuge to form film. The reaction was completed in an oven for 24 h at 360°K. The composition ratio of PTMO : TDI : BDO was 1 : 2.5 : 1.5 in all cases. In similar conditions an elastomer based on 4,4' diphenylmethane diisocyanate, MDI, and the above given diols were synthesized as a reference material, since most of the urethane elastomers of commercial importance are produced using this diisocyanate and BDO. The composition ratio of PTMO : MDI : BDO was also as 1 : 2.5 : 1.5.

Measurements

The tensile measurements were done on a tensile tester (VEB Thüringer Industriewerk) for standard dumbbell samples and the tensile strength with tensile modulus at 100% elongation were determined. The same tester was used for stress relaxation measurements that were done on strips (23 × 5 × 1 mm) extended to 20%. The variation of load with time was recorded with accuracy of 0.08 N in the temperature range 300°K–380°K.

Thermomechanical analysis (TMA) was carried out in compression by means of a DuPont analyzer TMA 943 at a heating rate of 10°/min. From TMA measurements, the flow temperatures, T_f , were determined by taking as a flow temperature the temperature corresponding to the point of tangency of the 45° tangent to the curve reflecting the penetration of the rod of the TMA instrument.

The conductance G and capacity C were measured by means of a semiautomatic bridge BM 484 Tesla at a frequency $f = 1592$ Hz. The loss factor, $\tan \delta$, was calculated⁷ as $\tan \delta = G/2\pi fC$. The measurements were recorded in the temperature range from 220°K to 320°K. The data obtained were used to determine the glass transition temperature, T_g , that was taken as the temperature corresponding to the maximum of the loss factor, $\tan \delta$, in the dependence of $\tan \delta$ vs. T .

RESULTS AND DISCUSSION

The mechanical properties (tensile strength and modulus) of the investigated urethane elastomers are shown in Figures 1 and 2. A slight curvature can be

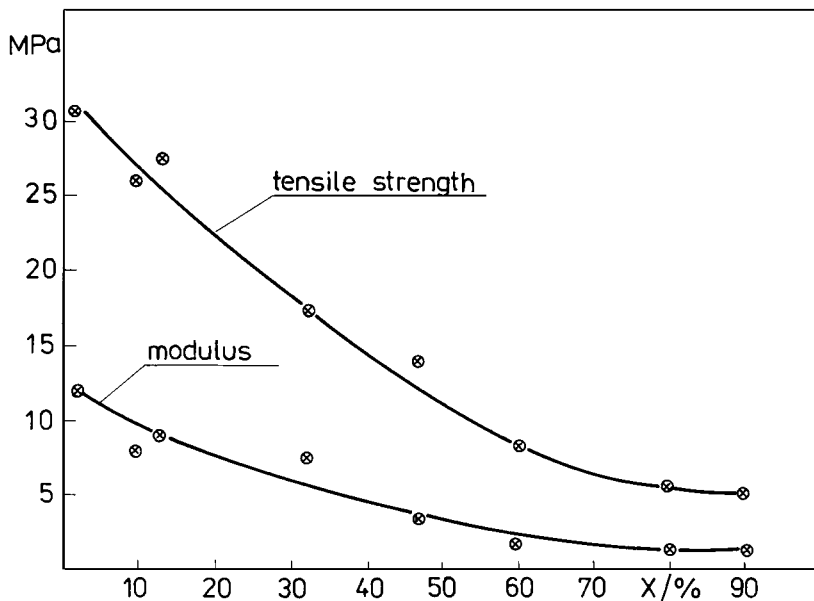


Fig. 1. Mechanical properties of the elastomers from the PTMO 1000/TDI-X/BDO series vs. the weight fraction, X, of the 2,4 TDI isomer in the isomer mixture. For PTMO 1000/MDI/BDO of similar molar composition the tensile strength is 42 MPa and the modulus at 100% elongation is 13 MPa.

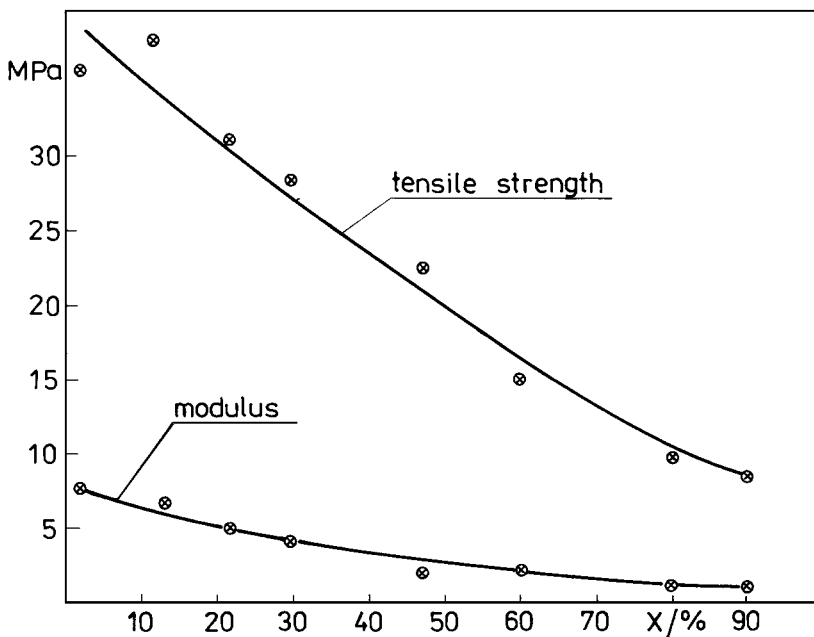


Fig. 2. Mechanical properties of the elastomers from PTMO 2000/TDI-X/BDO series vs. the weight fraction, X, of the 2,4 TDI isomer in the isomer mixture. For PTMO 2000/MDI/BDO of similar molar composition the tensile strength is 43 MPa and the modulus at 100% elongation is 3.7 MPa.

noted in these relationships although a linear relationship might be expected for such copolymers of varying isomer composition. It is likely that the curvature is one more reflection of the microphase separated structure existing in these polymers. The linear relationships seem to be typical of homogenous systems. From Figures 1 and 2 it is also seen that polymers get stiffer and stronger if the contribution of the symmetric isomer in the TDI isomer mixture used in the preparation is increased. Such a trend is not, in fact, unexpected. The hard domains that act as multifunctional crosslinking volume elements seem to be the main factor in determining the ultimate properties of the polymers. Partly, they determine the deformation behavior as well. The stability of the domains is certainly greater if they are composed of linear hard segments than of bent ones. Stronger interactions between the hard segments should favor the microphase separation of the soft and hard segments and the changes in the mechanical properties of the systems should be a reflection of the changes in the perfection of the separation.

Quite commonly, the information on the perfection of the separation is extracted from the glass transition temperatures, T_g . The glass transitions for two series of elastomers, one prepared from PTMO of MW 1000 and the other from PTMO of MW 2000, are collected in Figure 3. In both cases the glass transition temperature drops if the fraction of 2,6 TDI isomer in the isomer mixture is increased, which is equivalent to saying that the perfection of the microphase separation is improved. Also, the glass transition in the series PTMO 1000/TDI-X/BDO is always about 10 to 25° higher than in the series PTMO 2000/TDI-X/BDO. This means that the soft and hard segments are better separated in the series with longer soft blocks, which is in line with all predictions concerning the microphase separation in block copolymers.⁸ However, one should note a remarkable difference in shape of the T_g vs. X (i.e., vs.

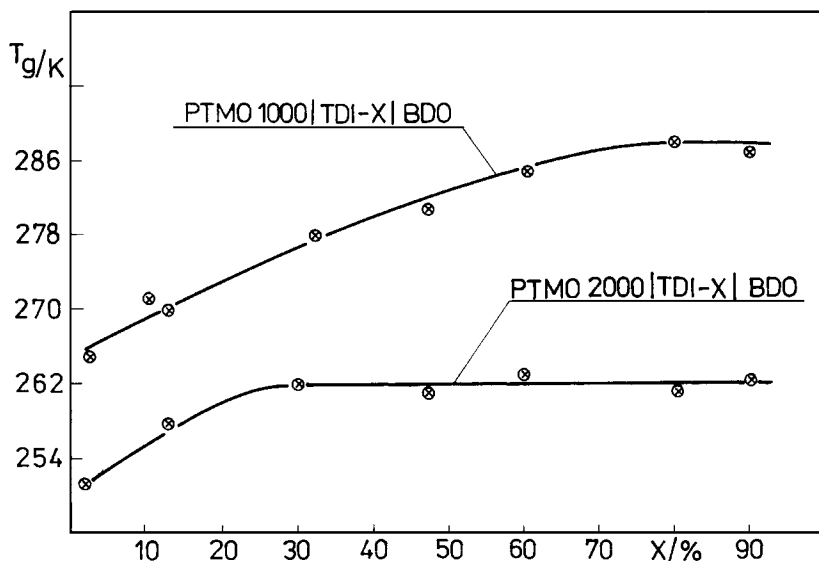


Fig. 3. Glass transition temperatures, T_g , of the soft phase in the investigated systems vs. the weight fraction X , of the 2,4 TDI isomer in the isomer mixture.

the fraction of 2,4 TDI in the TDI isomer mixture). As seen, T_g is quite insensitive for PTMO 2000-based elastomers in the range of X from 100% down to about 30%, while below this limit it quickly drops down. For the PTMO 1000-based series, T_g drops down nearly constantly in the whole composition range of X from 100% to 0%.

The above-described difference in the behavior might be rationalized by referring to the works of Seymour and Cooper.^{9,10} These authors studied the deformation behavior of a series of elastomers of different hard segment content and found that a basic change in morphology occurred over a rather small composition range. According to the authors, above a certain hard segment content (about 25%) it is impossible, due to spatial limitations, to have separate, discrete hard segment domains. Instead, an interlocking hard domain structure is formed. In the case of the PTMO 1000 series studied in our work, the weight fraction of the hard segments is 36%, while for PTMO 2000-based elastomers the fraction is 22%. Thus, the interlocking morphology seems to be developed in the elastomers from the PTMO 1000 series, while the independent hard domains may be expected to exist in the PTMO 2000 series. If so, one may conclude that the T_g of the soft phase are more sensitive to changes in the chemical composition and presumably to changes in the perfection of the separation when the interlocking morphology is developed.

There is, however, one more possible explanation of the differences discussed. As is known,⁸ the microphase separation takes place if the length of the blocks exceeds a certain value. From the work of Senich and McKnight³ one can conclude that the elastomers based on PTMO 1000 and 2,4 TDI are, because of the relatively short blocks, on the verge of microphase separation. If so, even small changes in the chemical composition may lead to distinct changes in the degree of separation. In the case of PTMO 2000-based elastomers the microphase separation is well established and the degree of separation is sensitive to changes in the chemical composition only in the composition range where the amount of the crystallizable (i.e., more favorable for separation), hard segment built from 2,6 TDI and BDO units is predominant. Unfortunately, the results obtained in this work do not allow a distinction as to which of the two explanations is correct.

In Figure 4 the flow temperatures of the investigated elastomers are collected. The flow temperatures reflect the thermal stability of the hard domain structure and, as is seen from Figure 4, they are always higher for elastomers based on PTMO 2000. Apparently, the solubilization of the soft segment within the hard domains is smaller in this case than in the case of the PTMO 1000 series, which is in line with the conclusion derived from T_g on poorer separation in the latter elastomers and is also in line with the findings of Bonart et al.¹¹ that the nature of the soft segments affects the flow temperature of hard domains. One should also note that the flow temperatures drop slightly down if the content of 2,6 TDI in the isomer mixture is increased (in the composition range of 2,4 TDI above about 25%). The 2,4 TDI/BDO hard segments form glassy, amorphous domains,³ thus the flow temperature can be interpreted as the glass temperature of these domains. The fact that the glass temperature drops down in the aforementioned composition range can be due either to increased solubilization of the soft segments in the hard domains or to changes in the relative ratio of 2,6 TDI/BDO to 2,4 TDI/BDO segments within these domains. Assuming the

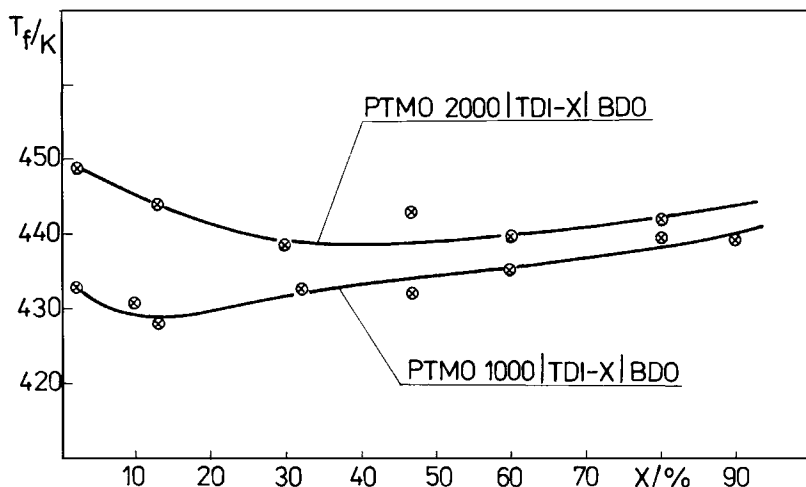


Fig. 4. Flow temperatures, T_f , vs. the weight fraction, X , of the 2,4 TDI isomer in the isomer mixture for the indicated elastomers.

latter case, one can apply the well known Fox formula¹² for the glass transition of a mixture of compatible polymers (blocks)

$$1/T_g = w_{2,4}/T_{g2,4} + w_{2,6}/T_{g2,6} \quad (1)$$

where T_g is the glass transition temperature of the hard domains (in our case), $w_{2,4}$ and $w_{2,6}$ are the weight fractions of the 2,4 TDI/BDO and 2,6 TDI/BDO hard segments, respectively, within the domains. $T_{g2,4}$ and $T_{g2,6}$ are the glass transition temperatures of respective hard segments. Since $w_{2,4} + w_{2,6} = 1$, the above equation can be transformed into

$$1/T_g = 1/T_{g2,4} + [1/T_{g2,6} - 1/T_{g2,4}]w_{2,6} \quad (2)$$

If eq. (2) is applied to the flow temperatures of Figure 4, a relationship as in Figure 5 is obtained. As is seen, $1/T_f$ can be approximated in the discussed composition range by straight lines, as is predicted by the Fox formula. It may suggest that in the composition range in question there are no essential changes in the solubilization of the soft segments in the hard domains. Analyzing the data in Figure 5, one has to take into account that the calculations based on eq. (2) are approximate. The weight fractions of the hard segments in the hard domains are not known precisely, since a part of the hard segment material is dissolved in the soft segment matrix. Thus, the glass transition of the 2,6 TDI/BDO hard segment calculated from the tangent of eq. (2) (426°K from the data for PTMO 1000 series and 438°K from the data for PTMO 2000 series) should not be taken too seriously, not only because of the depression caused by the solubilization effect. However, it should be noted that the glass transition of the hard segments are very close to the glass transition of 2,4 TDI/BDO segments (442°K from PTMO 1000 series and 444°K from PTMO 2000 series) which is in agreement with the findings of Senich and McKnight.³ The glass

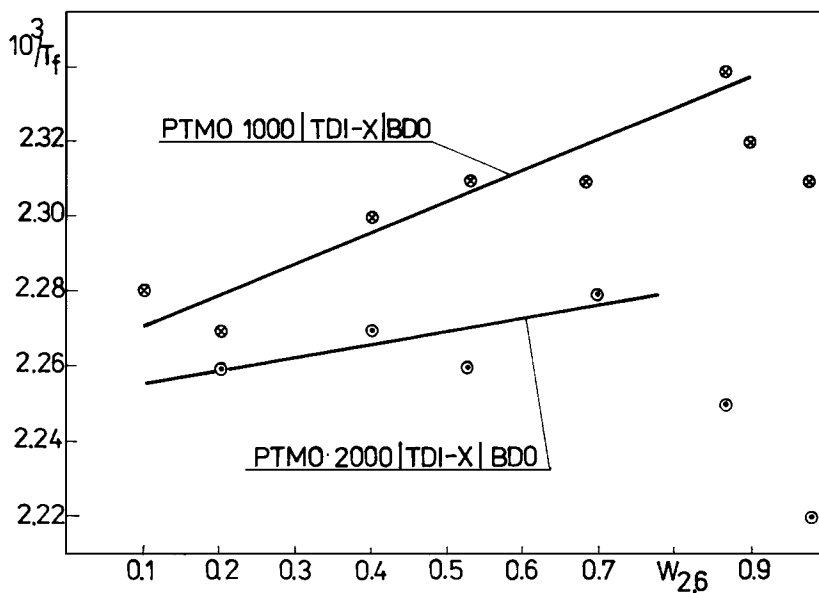


Fig. 5. Experimental data presented as required by eq. (2).

transition of the 2,4 TDI/BDO hard domains can be found directly from PTMO/2,4 TDI/BDO elastomers. The direct determination of T_g for the domains of 2,6 TDI/BDO from the synthesized elastomers is not possible since in the composition range where the content of 2,4 TDI is small the hard domains turn from glassy to crystalline.³ The flow temperature in this composition range should be identified rather with the melting temperature than with the glass temperature and the deviation from linearity in Figure 5 may be explained by the crystallization phenomena.

The changes in the perfection of microphase separation should also affect the viscoelastic response of these materials. Figure 6 shows the decay of stress with time over a range of temperatures together with the so-called master curve. The data presented are typical for the whole PTMO 1000 series. However, one should note that the shifting procedure does not produce a smooth master curve, as is normally obtained for many polymers, including some segmented polyurethanes.¹³ The time-temperature superposition principle does not hold in the case of our systems, as can be also judged from the values of C_1 and C_2 constants of the WLF equation (for the data presented in Figure 6 $C_1 = 21$ and $C_2 = 116$, while the "universal" constants are 17 and 52, respectively). Eisenberg et al.¹⁴ report a similar behavior with the master curve of increased breadth for the ionomers with cluster ion structure. The hard domains in the investigated polyurethanes may play an equivalent role in the relaxation mechanism as the ion cluster in the ionomers. The shifting procedure fails completely for the elastomers from the PTMO 2000 series. While for the PTMO 1000-based polymers the stress drops down with increased temperature, the PTMO 2000 based elastomers exhibit this only in a small temperature range. In a broader temperature range one observes an increase of stress with an increase of temperature. Apparently, strain-induced crystallization contributes to this behavior

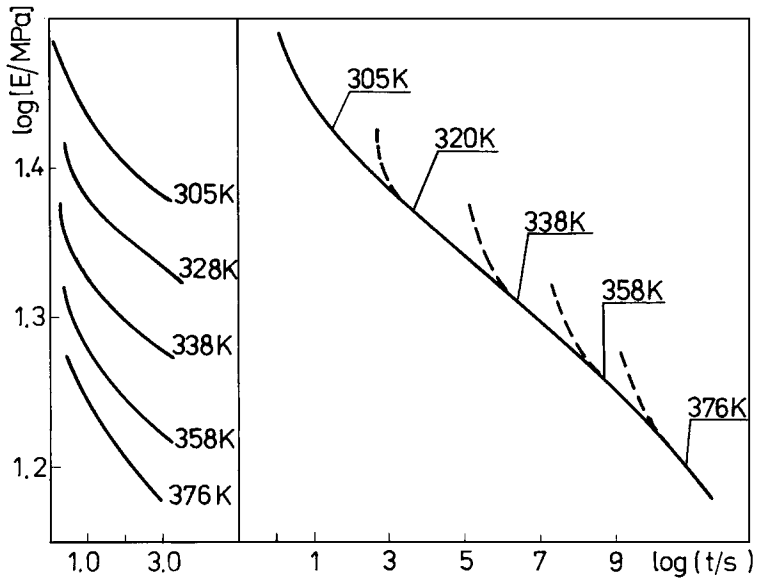


Fig. 6. Stress relaxation master curves at 32°C (305°K) from experimentally measured modulus-time curves at the indicated temperatures for PTMO 1000/TDI-13/BDO elastomer.

and the construction of even the pseudomaster curve, as in Figure 6, is not possible. To summarize the relaxation properties of the whole series of the PTMO 1000/TDI-X/BDO elastomers, the reduced master curves have been

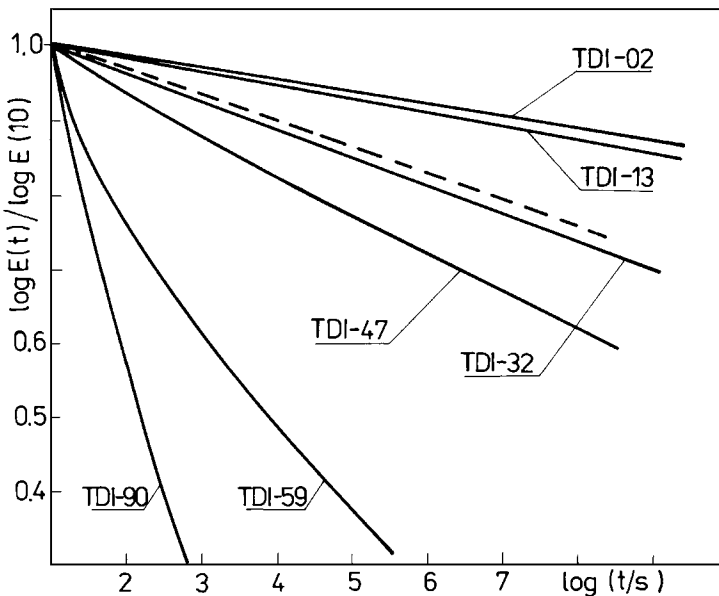


Fig. 7. Reduced master curves for the investigated systems. The "branchings" seen in Figure 6 are omitted. The dotted line refers to the system PTMO 1000/MDI/BDO.

collected in Figure 7. As seen, the decay of stress is very rapid for the polymers of high contribution of the unsymmetric isomer (2,4 TDI) in the isomer mixture used for prepolymerization. When the amount of symmetric isomer (2,6 TDI) in the mixture becomes predominant, the relaxation behavior approaches that obtained for polyurethanes synthesized from MDI, BDO, and PTMO 1000 of similar molar composition. For the elastomers synthesized from almost pure 2,6 TDI the decay of stress is even smaller than for PTMO 1000/MDI/BDO system.

Future work with these materials, with stress on crystallinity effects in the soft segment phase, should provide more information on the structure-property relations in these systems.

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