

Influence of the Prepolymerization on the Properties of Thermoplastic Polyurethane Elastomers. Part II. Relationship between the Prepolymer and Polyurethane Properties

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ABSTRACT: The synthesis of thermoplastic polyurethane elastomers (TPUs) is generally carried out using the prepolymer method. To study the influence that the properties of the prepolymer may have in the final TPUs, four TPUs were prepared by using different NCO/OH ratios. The prepolymers and the macroglycol used in their synthesis were characterized in the first part of this article. TPUs were characterized by using gel permeation chromatography, strain–stress measurements, differential scanning calorimetry, and contact-angle measurements. To test their adhesion properties, the T-peel strength of PVC/TPU/PVC adhesive joints was determined. It was found that the properties of the prepolymers determine the properties of the TPUs when the amount of hard segments (related to the soft-segments size) is small. In contrast, when the amount of hard segments (related to the soft-segments size) is high, it is the chain extension step that determines the TPUs structure and properties. On the other hand, it was observed that a high amount of ever hard or soft segments gives TPUs with similar properties. This behavior is explained by the structure of the prepolymer (related to the degree of polymerization) and the TPUs. Finally, it was found that the adhesive properties of the finished TPUs are comparable to those of blocked prepolymers prepared with low NCO/OH ratio. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1602–1607, 2000

Key Words: thermoplastic polyurethane elastomers; hard and soft segments; prepolymer; degree of polymerization; chain extension; TPUs properties control

INTRODUCTION

Thermoplastic polyurethane elastomers (TPUs), widely used in such many different fields as biomedical materials,^{1–3} elastomers,⁴ or adhe-

sives,^{5–7} are generally prepared by using the prepolymer, or two-step, method. However, even if the TPU morphology has been widely studied, and if it has been established that the raw materials and the preparation procedure determine their structure,^{8–10} the relationship between the prepolymers (synthesized in the first step of the reaction) and the final TPU properties has not been established.

Owing to previous reports on the influence of the prepolymerization step on the final properties

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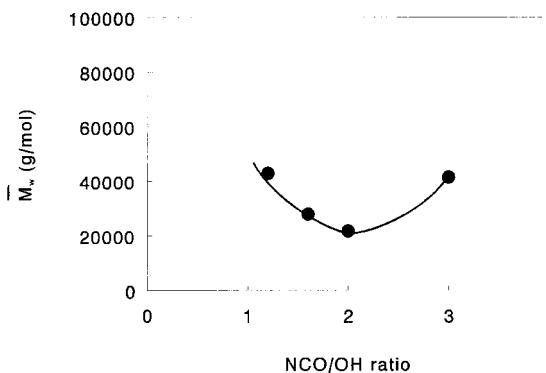


Figure 1 Variation of the average molecular weight (\overline{M}_w) with the NCO/OH.

of TPUs,¹¹ this situation prompted us to undertake a study on the relationships between the prepolymers and the final TPU properties. In the first part of this article,¹² we characterized the structure and properties of the prepolymers, establishing a correlation between the composition, properties, and prepolymer structure. Therefore, the aim of this second part is to find out the relationships between both the prepolymers and TPU structures and properties. To get relevant experimental data, different hard to soft segments ratios were used in the synthesis of TPUs, in accordance with the good correlation of these parameters with the TPUs properties, as stated in a previous work.¹³

EXPERIMENTAL

Preparation of Polyurethane Elastomers

Four TPUs were prepared from previously described raw materials,¹¹ according to the prepolymer (or two-step) method. Prepolymers were obtained by reacting the diphenyl methane-4,4'-diisocyanate (MDI) and the poly(ϵ -caprolactone) at NCO/OH ratios >1 (3/1: PU1; 2/1: PU2; 1.6/1: PU3; 1.2/1: PU4), keeping the reaction temperature always <80°C. After the expected residual NCO contents were reached (titration with *n*-butylamine: ASTM standard method D 2572-80), the prepolymers were reacted with the chain extender (1,4-butanediol) in stoichiometric amounts (NCO/OH = 1), the polymerization being completed in an oven at 80°C for 12 h.

To achieve the characterization of TPUs and to check their adhesive properties, solutions were prepared by mixing 18 wt % TPUs with 2-butanone. The mixture was stirred at 500 rpm for

3 h until a homogeneous liquid was obtained. Thin films were also prepared by slow evaporation of the solvent in PTFE molds.

Experimental Techniques

The experimental techniques used to characterize TPUs were gel permeation chromatography (GPC), differential scanning calorimetry (DSC), strain-stress, and contact angle measurements. To test their adhesion properties, T-peel tests were carried out between solvent-wiped (2-butanone-soaked cotton pads) poly(vinyl chloride) (PVC) strips. More details are given elsewhere.¹¹

RESULTS AND DISCUSSION

Analysis of the Experimental Data

Figures 1 and 2 show the variation of the average molecular weight (\overline{M}_w) and the polydispersity index ($\overline{M}_w/\overline{M}_n$), respectively, with the NCO/OH ratio. \overline{M}_w values are maximal for both the lowest (1.2/1) and the highest (3/1) NCO/OH ratio, passing through a minimum for an intermediate NCO/OH (2/1) ratio. The same tendency is found for ($\overline{M}_w/\overline{M}_n$) values. Therefore, TPUs synthesized with the highest and the lowest NCO/OH ratios resemble each other, which indicates that they should have similar molecular structures.

Figure 3 shows the variation of the glass transition temperature (T_g) with the NCO/OH ratio. The T_g of the TPUs is almost constant for the TPUs synthesized with NCO/OH ratios between 1.2/1 and 2/1, but it steadily decreases for the maximal NCO/OH ratio (3/1). This indicates that the TPUs prepared with the highest hard seg-

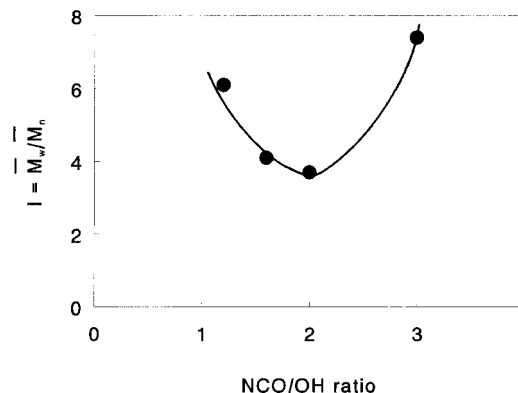


Figure 2 Variation of the polydispersity index ($\overline{M}_w/\overline{M}_n$) with the NCO/OH ratio.

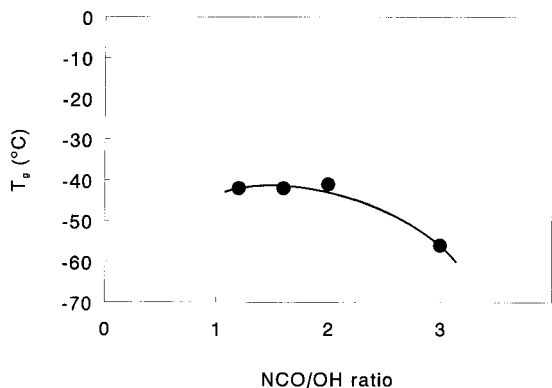


Figure 3 Variation of the glass transition temperature (T_g) as a function of the NCO/OH ratio.

ments content have less miscibility between the hard and soft segments (a higher degree of phase separation) than the rest of the series. This is due to the fact that when the amount of hard segments is maximal, they have a tendency to interact with each other. Thus, they are less dispersed in the soft segments, which, in turn, are less hindered, allowing the degree of phase separation in the TPU structure to be higher.

Therefore, the TPU synthesized with the highest NCO/OH ratio shows the highest phase separation, whereas NCO/OH ratios between 1.2/1 and 2/1 give TPUs with almost the same phase separation. This fact is quite surprising considering the results obtained in a previous work,¹³ in which it was found that a high amount of soft segments (considered between 1.2/1 and 2/1) gives a high phase separation in the structure of TPUs synthesized from a macroglycol with a molecular weight of 2500 g mol⁻¹. Our hypothesis is that the explanation of this apparent contradiction can be found in the molecular weight of the macroglycol used in the synthesis (3000 g mol⁻¹ for the present TPUs), as stated in a previous work.¹⁴ An increase in the molecular weight of the macroglycol gives longer soft segments, and hence, the relative amount of hard segments dispersed among them becomes smaller. If the soft segments are long enough, the phase separation does not depend on the NCO/OH ratio (i.e., on the hard to soft segments ratio), as long as the hard-segments amount (NCO/OH ratio) is high enough to allow them to interact with each other, to be less dispersed in the soft segments, and to increase the phase separation due to a decrease of the soft segments hindrance.

Figure 4 shows the variation of the melting

enthalpy (ΔH_m) with the NCO/OH. Agreeing with the tendencies shown by T_g , the melting enthalpy remains constant for the TPUs synthesized with a NCO/OH ratio between 1.2/1 and 2/1, but decreases markedly when the NCO/OH ratio is maximal (3/1). As the enthalpy value is related to the organization of the soft segments (i.e., interactions between TPU chains), it can be stated that the TPU synthesized with the highest NCO/OH ratio has a less organized structure (i.e., less crystallinity) than the rest of the series. The fact that the NCO/OH ratio does not have a remarkable influence on ΔH_m until it reaches its maximal value (3/1) can be explained with the same arguments used for the phase separation. We assume that the size of the soft segments is high enough to allow them to establish organized interactions in such a way that variations in the soft segments ratio do not influence the interactions between chains. For the highest NCO/OH ratio (3/1), a high amount of hard segments is created in the chain extension, the crystallization of which is difficult. In fact, unless the corresponding TPU (PU1) has been annealed (slow crystallization), its structure is scarcely crystalline,¹⁶ which explains its low ΔH_m value.¹⁵

Summarizing, a NCO/OH ratio superior to 2 gives TPUs with high phase separation and low crystallinity, due to the high amount of hard segments in the TPU structure.

The mechanical properties of the TPUs were determined by using a strain-stress test.¹⁶ Figure 5 gives the variation of the tensile strength, on the one hand, and the elongation at break, on the other, with the NCO/OH ratio. It can be noted that the TPUs structure becomes weak and rigid when a middle NCO/OH ratio (1.6/1 and 2/1) is

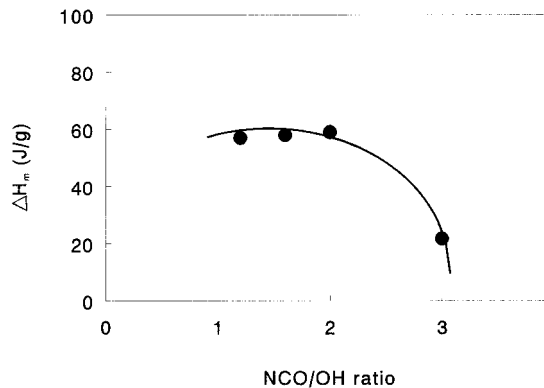


Figure 4 Variation of the melting enthalpy (ΔH_m) with the NCO/OH.

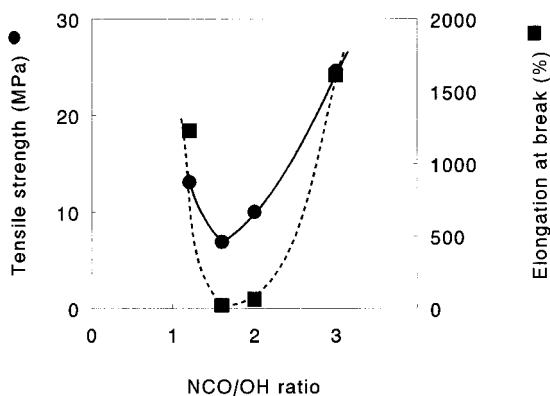


Figure 5 Variation of the elongation at break and the tensile strength with the NCO/OH ratio.

used in their synthesis, whereas the minimal and, even more, the maximal NCO/OH ratios (1.2/1 and 3/1, respectively) give TPUs with strong and flexible structures. These results are in agreement with those obtained for the molecular weight (Fig. 1), showing that a TPU with high molecular weight will have good mechanical properties.

Contact-angle measurements were achieved to analyze the influence that the NCO/OH ratio may have in the surface properties of TPUs. The contact angle values obtained for the four TPUs (Table I) do not show any significant difference, considering the experimental error ($\pm 2^\circ$). Therefore, it can be stated that the surface properties of the TPUs are not influenced by the NCO/OH ratio used in their synthesis, agreeing with previous results.¹³

The adhesion properties of the TPUs were determined in PVC/TPU adhesive/PVC joints (Fig. 6). For the four TPUs, the locus of failure after the T-peel test was adhesive at the PVC/TPU interface. The NCO/OH ratio affects the joint strength in such a way that the TPUs that show the lowest joint strength are those synthesized with a middle NCO/OH ratio. Both the maximal (3/1) and

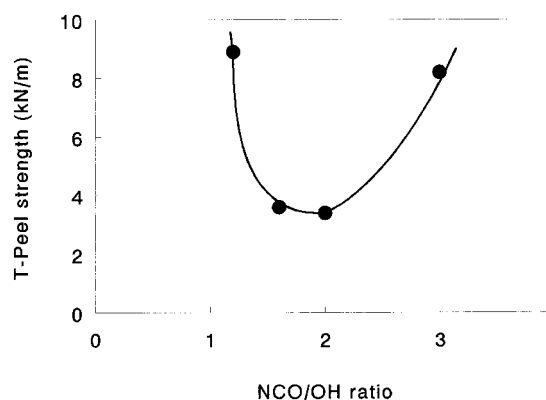


Figure 6 Variation of the T-peel strength of PVC/TPU adhesive/PVC joints as a function of the NCO/OH ratio.

minimal (1.2/1) NCO/OH ratio give the highest joint strength, because of the high polarity of the chains (high concentration of hard and soft segments, respectively) and their ability to interact with each other and the PVC strips. It should also be considered that the maximal and minimal NCO/OH ratios give TPUs with stronger mechanical properties (Fig. 5) and hence, it proves that the joint strength is also influenced by the mechanical properties of the TPUs.

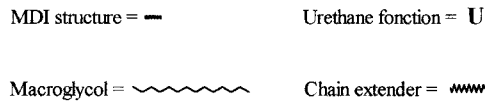
Prepolymer and TPUs Structure

From the results discussed above, it can be stated that the TPUs synthesized with the maximal and minimal NCO/OH ratio have almost the same properties. We assume that this similarity can be explained by the structure of the prepolymers¹² and the TPUs (Fig. 7).

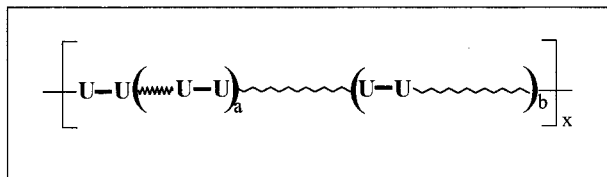
For the prepolymers, we proposed that their degree of polymerization (\overline{DP}_n) can account for their particular properties through the influence that it exerts on the prepolymer structure. Thus, a prepolymer prepared with a low NCO/OH ratio (1.2/1) has a high \overline{DP}_n , which gives a structure characterized by a high molecular weight and polydispersity index and by the presence of many pairs of urethane groups (U—U) in the chain (high b value, Fig. 7).¹² Moreover, as its free NCO content is low, this prepolymer will have a low degree of chain extension in the second step of the synthesis reaction, giving a final TPU with a structure close to its own structure. Regarding the TPU synthesized with the maximal NCO/OH ratio, as the free NCO content of the prepolymer is high, it will have a high degree of chain exten-

TABLE I Contact Angle Values (ethylene glycol, 25°C) for the TPUs

| Polyurethane | NCO/OH Ratio | Contact Angle (degrees) |
|--------------|--------------|-------------------------|
| PU1 | 3/1 | 61 |
| PU2 | 2/1 | 60 |
| PU3 | 1.6/1 | 64 |
| PU4 | 1.2/1 | 63 |



TPUs structure:



- * "a" increases with the NCO/OH ratio used in the synthesis
- * "b" increases when the NCO/OH ratio used in the synthesis decreases

Figure 7 TPUs structure.

sion in the second step of the synthesis reaction, giving a structure characterized by a high molecular weight and polydispersity index and by the presence of many hard segments (high value of *a* and *x*, Fig. 7), regardless of the small size of its prepolymer.¹² Therefore, the high amount of soft segments in the TPUs prepared with the smallest NCO/OH ratio (1.2/1), as well as the high amount of hard segments in the highest NCO/OH ratio TPUs (3/1), gives to the corresponding polymers (PU1 and PU4) structures with different polarities (which explains the different phase separa-

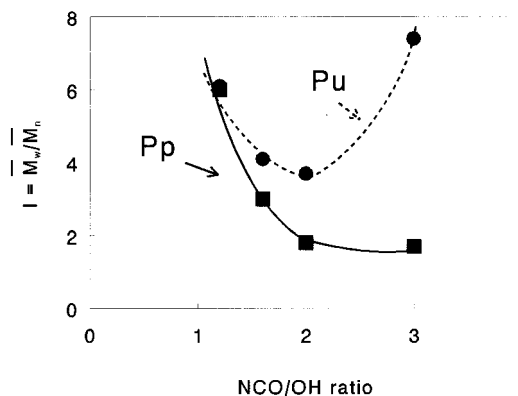


Figure 8 Variation of the polydispersity index (M_w/M_n) with the NCO/OH ratio for both TPU and prepolymer.

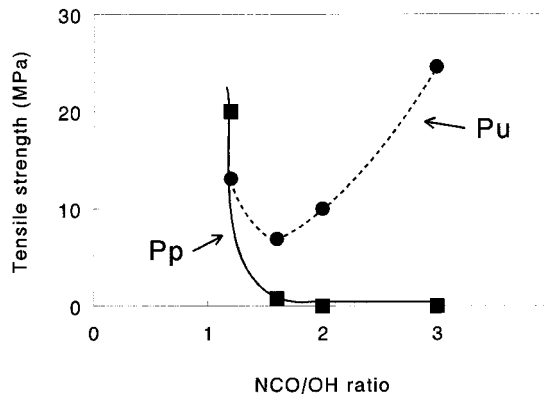


Figure 9 Variation of the tensile strength with the NCO/OH ratio for both TPU and prepolymer.

tion and organization), but with similar size long chains, resulting in quite close overall properties. TPUs synthesized with middle NCO/OH ratios (PU2, PU3) have neither such a large chain extension in the second step or a high \overline{DP}_n in the prepolymerization step.¹² Hence, their molecular weight and polydispersity index are lower than those of PU1 and PU4, resulting in worse mechanical and adhesive properties.

Therefore, it can be stated that the properties of TPUs are determined by those of their prepolymers when they have a high amount of soft segments in their structure (low NCO/OH ratio), because their structure has been built up in the first step of the reaction, which agrees with previous results.¹¹ In contrast, when the concentration of hard segments is high, the second step of the synthesis does determine the TPUs properties. This is illustrated in Figures 8–10, where some

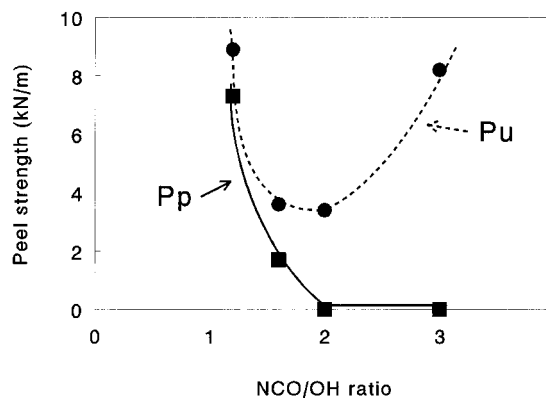


Figure 10 Variation of the T-peel strength of PVC/TPU adhesive/PVC joints as a function of the NCO/OH ratio for both TPU and prepolymer.

properties of the prepolymer (polydispersity index, tensile strength, and T-peel strength, respectively) are compared to those of the final TPU. When the NCO/OH ratio is low, the properties of the prepolymer and the TPU are quite alike, but at the highest NCO/OH ratio, the properties of the TPU are much better than the prepolymer ones, due to the change produced in the structure in the second step of the reaction. TPUs prepared with an intermediate NCO/OH ratio just have a moderated improvement of their properties (related to the prepolymer ones), due to a smaller chain extension in the TPUs structure compared to PU1 and PU4.

It is important to note that the high concentration of hard segments is always related to the soft segment size in such a way that a longer soft segment will dilute the concentration of hard segments. So, the same NCO/OH ratio can be high or low if the molecular weight of the macroglycol used in the synthesis is low or high, respectively.

CONCLUSIONS

The properties of the prepolymers determine the properties of the TPUs when the amount of hard segments (related to the soft segments size) is small. In contrast, when the amount of hard segments (related to the soft segments size) is high, the chain extension step actually determines the TPUs structure and properties.

The high molecular weight of the macroglycol used in the TPUs synthesis controls the phase separation and the organization (i.e., crystallinity) of the polymer structure until the amount of hard segments (related to the soft segments size) is high enough to overtake its influence.

A high amount of both hard and soft segments gives TPUs with similar properties, due to their similar-sized long-chain structures.

At low NCO/OH ratio, the adhesive properties of the final TPUs are comparable to those of the corresponding blocked prepolymers.

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