

Influence of the Prepolymerization on the Properties of Thermoplastic Polyurethane Elastomers. Part I. Prepolymer Characterization

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Received 28 July 1999; accepted 22 October 1999

ABSTRACT: Thermoplastic polyurethane elastomers (TPUs) are generally synthesized by using the two-step, so-called prepolymer, method. To study the influence of the prepolymer on the properties of the final TPUs, four polyurethane prepolymers were prepared from a diisocyanate and a macroglycol by using different NCO/OH ratios. The prepolymers and the macroglycol used in their synthesis were characterized by using gel permeation chromatography, differential scanning calorimetry, and strain-stress measurements. Additionally, to test the adhesion properties of the prepolymers and the macroglycol, adhesive solutions were prepared, and the T-peel strength of plasticized poly(vinyl chloride)/prepolymer solution joints was determined. It was found that the properties of the prepolymers depend on those of the macroglycol used in their synthesis in such a way that the lower the relative amount of macroglycol units in the prepolymer molecules (higher NCO/OH ratio), the closer the properties of the prepolymer and macroglycol. The maximal theoretical degree of polymerization ($DP_{n_{max}}$) determines the relationship between the macroglycol and prepolymer properties. Finally, the possibility of obtaining good adhesives from prepolymers, using low NCO/OH ratio in the synthesis, is evidenced. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1596–1601, 2000

Key words: thermoplastic polyurethane elastomers; polyurethane prepolymer; macroglycol; prepolymerization; maximal theoretical degree of polymerization

INTRODUCTION

The properties of thermoplastic polyurethane elastomers (TPUs) are directly related to their microphase-separated structure,^{1–4} which is due to the incompatibility between the hard or glassy segments and the soft or rubbery segments constituting their molecules.^{5–7} Their particular structure allows TPUs to be used in such different

applications as biomedical materials,^{8–10} elastomers,¹¹ or adhesives.^{12–14}

Extensive studies of TPU morphology have established that the raw materials and the preparation procedure determine their structure.^{15–17} Accordingly, we have shown in previous works^{7,18–20} that the soft-segments molecular weight and nature, the hard-/soft-segments ratio, and the chain extender length have a marked influence on the properties of the TPUs. We have also reported on the importance of the synthesis conditions, indicating the influence of the prepolymerization step on the final properties of the TPUs prepared according to the two-step proce-

Correspondence to: M. S. Sánchez-Adsuar.
Contract grant sponsor: Spanish Dirección General de Enseñanza Superior e Investigación Científica.
Journal of Applied Polymer Science, Vol. 76, 1596–1601 (2000)
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ture.²¹ However, no further information on this subject has been found, even though the main part of the TPUs described in the literature are prepared in this way. Moreover, although the morphology of TPUs has been extensively studied, only a few references can be found regarding the prepolymer.^{22,23} Therefore, we have completed a study about the factors that determine the properties of the TPUs during the prepolymerization, looking for the relationships between the structure and properties of the prepolymer on the one hand and their influence on those of the final TPUs on the other. The aim of the present article is to report the detailed investigation of the prepolymerization step and the characterization of the structure of prepolymers corresponding to different hard-/soft-segments ratios (determining factor of final TPUs properties¹⁸) and to compare the prepolymers to their macroglycol precursor.

EXPERIMENTAL

Materials

The prepolymers were prepared from MDI (diphenyl methane-4,4'-diisocyanate) and a poly(ϵ -caprolactone)-type macroglycol ($\bar{M}_n = 3000 \text{ g mol}^{-1}$) at different NCO/OH ratios (3/1: Pp1, 2/1: Pp2, 1.6/1: Pp3, 1.2/1: Pp4). The MDI (98% minimum purity) was supplied as a solid by Aldrich (Dorset, England) and the poly(ϵ -caprolactone) macroglycol was supplied by Solvay Interlox (Cheshire, England). The water in the macroglycol was removed by heating overnight at 70°C under a vacuum of 5 torr. The NCO content in the prepolymer was obtained by titration with *n*-butylamine (ASTM standard method D 2572-80).

Preparation of Prepolymers

The prepolymers were obtained by reacting the poly(ϵ -caprolactone) and the MDI at a NCO/OH ratio >1 (to obtain isocyanate-terminated prepolymers), keeping the reaction temperature always <80°C. When the expected free NCO content (corresponding to the NCO excess) was reached, the reaction was stopped and the prepolymer blocked by stoichiometric reaction (NCO/OH = 1) with nonylphenol (Aldrich, Tech.). The mixture was kept in an oven at 80°C for 12 h.

Test solutions were prepared by mixing 18 wt % prepolymer with 2-butanone. The mixture was stirred for 3 h until a homogeneous solution was

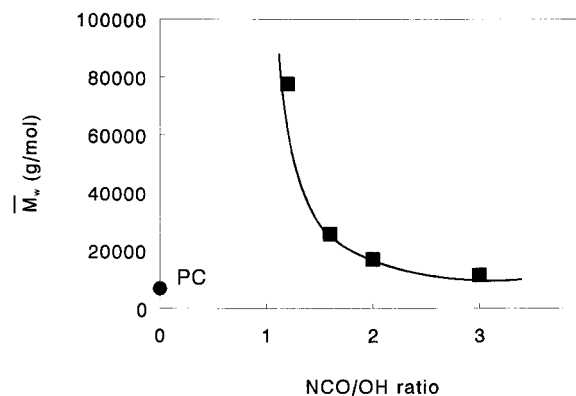


Figure 1 Variation of the average molecular weight (\bar{M}_w) as a function of the NCO/OH ratio (\bar{M}_w value for PC is shown at NCO/OH = 0).

obtained. The characterization of the prepolymers was carried out by using films prepared by evaporating the solvent in a PTFE mold. The evaporation was achieved slowly to avoid air bubbles in the films.

Experimental Techniques

The experimental techniques used to characterize the prepolymers and the macroglycol precursor were gel permeation chromatography (GPC, to determine the molecular weight and the polydispersity index), differential scanning calorimetry [DSC, to determine the glass transition temperature (T_g) and the melting enthalpy (ΔH_m)] and strain-stress measurements (to determine the mechanical properties). Additionally, to test the adhesion properties of the prepolymers and the macroglycol, T-peel tests were carried out between solvent-wiped (2-butanone-soaked cotton pads) poly(vinyl chloride) (PVC) strips. More details are given elsewhere.²¹

RESULTS AND DISCUSSION

Analysis of the Experimental Data

Figure 1 shows the variation of the average molecular weight (\bar{M}_w) of the four prepolymers as a function of the NCO/OH ratio, with reference to the molecular weight of the poly(ϵ -caprolactone) (PC) used in their synthesis. Prepolymer \bar{M}_w values observe a decreasing tendency as the NCO/OH ratio increases, becoming closer and closer to the PC \bar{M}_w . The same tendency is found in the variation of the polydispersity index (\bar{M}_w/\bar{M}_n) as a function of the NCO/OH ratio (Fig.

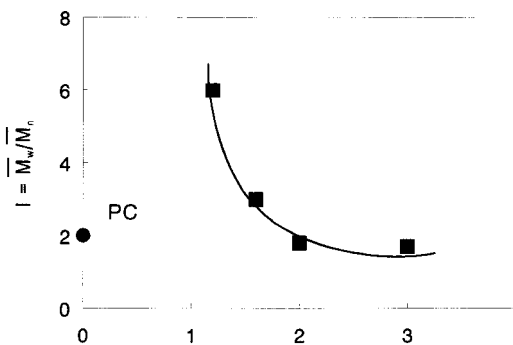


Figure 2 Variation of the polydispersity index ($\overline{M}_w/\overline{M}_n$) as a function of the NCO/OH ratio (\overline{M}_w value for PC is shown at NCO/OH = 0).

2), indicating that the prepolymers synthesized with the higher NCO/OH ratio have almost the same polydispersity as PC.

Figure 3 shows the variation of the glass transition temperature (T_g) with the NCO/OH ratio. It is remarkable that PC does not get any T_g , which means that its structure should be mainly crystalline. The T_g values of the prepolymers become less negative as the NCO/OH ratio increases, indicating a decrease in the amount of amorphous phase in the structure of the prepolymers, and therefore, an increase in their crystallinity. At a NCO/OH ratio equal to 3/1, the crystallinity of the prepolymer is close to that of PC. It is worth noting that as the hard segments have not been already created, the concept of phase separation (which can be related to T_g , as shown by Chen et al.⁶) cannot be applied to the prepolymer.

Regarding the melting enthalpy (ΔH_m), Figure 4 shows that it increases as the NCO/OH ratio increases, coming close to the value found for PC

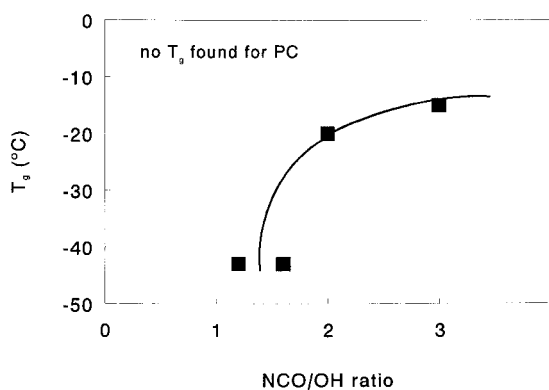


Figure 3 Variation of the glass transition temperature (T_g) with the NCO/OH ratio (T_g value for PC is shown at NCO/OH = 0).

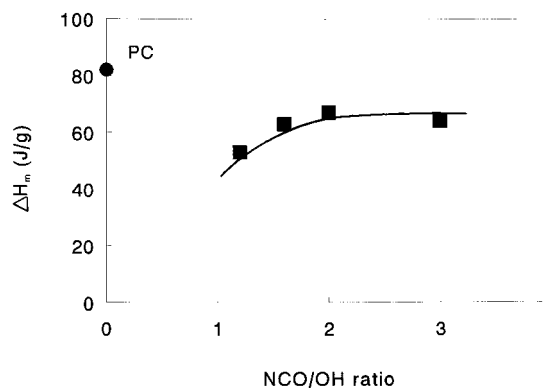


Figure 4 Variation of the melting enthalpy (ΔH_m) with the NCO/OH ratio (ΔH_m value for PC is shown at NCO/OH = 0).

(the highest of the series). As the enthalpy value is related to the interactions between the prepolymer chains, it can be stated that a prepolymer synthesized with a high NCO/OH ratio has much interaction between the chains in its structure, which is in agreement with the increase in crystallinity (as stated from T_g values), and indicates the likeness with PC.

The mechanical properties of the prepolymers and PC were determined by using a strain–stress test.²⁴ The tensile strength and the elongation at break values presented in Table I, and the variation of both parameters with the NCO/OH ratio (Fig. 5), indicated that the prepolymer structure becomes weaker as the NCO/OH ratio increases, showing at the highest ratios the same behavior as PC. This tendency is due to the increase in the number of crystalline interactions between the chains in the prepolymer structure (according to the variation of the ΔH_m values) and to the decrease of the prepolymeric chain length (Fig. 1) as the NCO/OH ratio increases, agreeing with the principles stated by Flory.²⁵

Table I Tensile Strength and Elongation at Break for the Poly(ϵ -caprolactone) Macroglycol and the Prepolymers

Sample	Tensile Strength (MPa)	Elongation at Break (%)
PC	0	0
Pp1	0	0
Pp2	0	0
Pp3	1	20
Pp4	20	1800

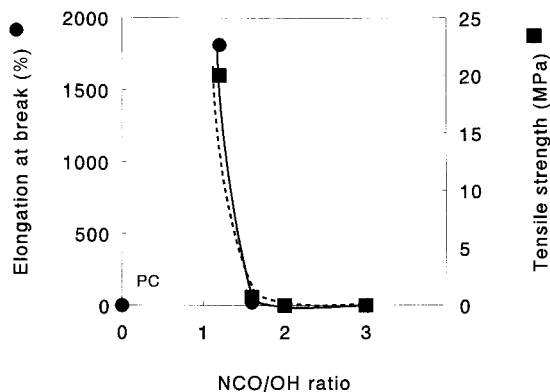


Figure 5 Variation of the elongation at break and the tensile strength with the NCO/OH ratio (the values for PC are shown at NCO/OH = 0).

The results obtained from the mechanical tests are in agreement with the conclusions stated from T_g and ΔH_m values and from \overline{M}_w and the polydispersity index, which indicates that the lower amount of PC units in their structure (higher NCO/OH ratio), the closer the prepolymer properties to PC ones (smaller molecular weight and polydispersity index, higher crystallinity, weaker structure).

The adhesion properties of the prepolymers were determined by T-peel testing of PVC/prepolymer/PVC adhesive joints (Fig. 6). The

NCO/OH ratio affects the adhesive strength as well as its locus of failure in such a way that the prepolymers that present the lowest adhesive strength (and a 100% cohesive failure in the adhesive) are those synthesized with the highest NCO/OH ratio (2/1, 3/1). As the NCO/OH ratio decreases, the joint strength increases and the locus of failure becomes 100% adhesive in adhesive/PVC interfaces. Considering that an increase in the NCO/OH ratio gives prepolymers with weaker mechanical properties (Table I and Fig. 5), it can be concluded that the joint strength and the locus of failure are strongly influenced by the mechanical properties of the prepolymers and PC. Finally, it is worth to noting the outstanding adhesive properties of Pp4 (NCO/OH = 1.2, T-peel strength about 8 kN/m), which is quite surprising for an unfinished polymer.

Interpretation: Structure of Prepolymers

From the above data, one of the most remarkable statements is that the prepolymers become more alike to PC when they have been synthesized with a high NCO/OH ratio (i.e., when the relative amount of PC units in their molecules is low). This fact, even though surprising at first sight, can be explained by taking into account the prepolymer structure, in agreement with relevant assumptions.²²

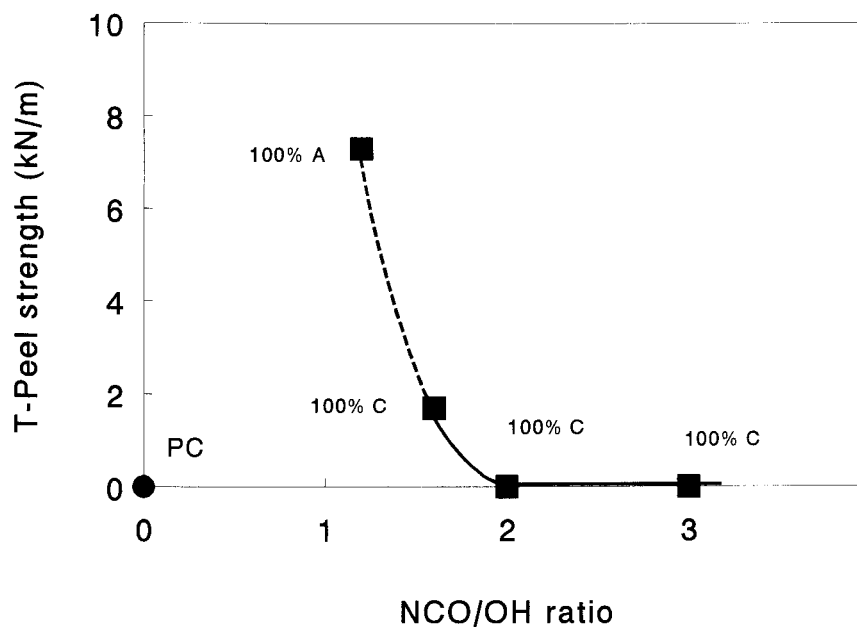


Figure 6 Variation of the T-peel strength of PVC/prepolymer joints as a function of the NCO/OH ratio. Locus of failure: C = cohesive failure in the adhesive; A = adhesive failure in the interface PVC/adhesive.

by the presence of many urethane groups in the chain (bonded to each other [U—U]), which justifies the difference between the properties of this prepolymer and PC. In more detail, as the U—U groups have a high polarity, they will easily create interactions between the different prepolymer chains (so-called virtual crosslinking^{26–28}) that are amorphous unless the prepolymer is annealed.²⁹ Then, Pp4 (NCO/OH = 1.2) will have a more amorphous structure which justifies the decrease in its melting enthalpy and its more negative T_g .

Summarizing, $\overline{DP}_{n_{\max}}$ justifies not only the fact that the prepolymers synthesized with a higher NCO/OH ratio have properties nearer to the PC ones, but also explains why these prepolymers have a smaller molecular weight and worse mechanical properties. It also explains the fact that a prepolymer synthesized with an NCO/OH = 1.2 has such outstanding adhesive properties just because this prepolymer already has the size and structure of a macromolecule.

CONCLUSIONS

The properties of the prepolymers depend on those of the macroglycol used in their synthesis in such a way that the lower the relative amount of macroglycol units in the prepolymer molecules (higher NCO/OH ratio), the closer the properties of the prepolymer and macroglycol. The maximal theoretical degree of polymerization ($\overline{DP}_{n_{\max}}$) determines the relationship between the macroglycol and prepolymer properties. It is possible to obtain an efficient adhesive from a prepolymer by using a low NCO/OH ratio in the synthesis.

Financial support from Spanish Dirección General de Enseñanza Superior e Investigación Científica is gratefully acknowledged.

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