

Influence of the Synthesis Conditions on the Properties of Thermoplastic Polyurethane Elastomers

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Received 28 July 1999; accepted 22 October 1999

ABSTRACT: Thermoplastic polyurethane elastomers (TPUs) of constant composition were prepared by using the prepolymer method and by changing the reaction conditions (prepolymerization and chain-extension time) to study the influence of these conditions on the final TPU properties. The TPUs were characterized by gel permeation chromatography, differential scanning calorimetry, strain–stress measurements, and contact-angle measurements. To test the adhesion properties of the TPUs, poly(vinyl chloride) strips were bonded to each other by using TPU solutions and the T-peel strength of the adhesive joints was measured. It was found that provided a threshold is crossed, the prepolymerization time markedly influences the final properties of the TPUs (viscosity of solutions, molecular weight, mechanical and adhesive behavior), whereas the chain extension time does not. Therefore, it is possible to prepare TPUs with specific properties by playing with the prepolymerization conditions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1590–1595, 2000

Key words: thermoplastic polyurethane elastomers; synthesis conditions; prepolymerization; chain extension; control of the TPU properties

INTRODUCTION

The widely known importance of thermoplastic polyurethane elastomers (TPUs) in many industrial fields has resulted in a marked increase in the research on this subject.^{1–4} There are studies dealing with different topics from fundamentals of structure^{5–7} to applications in such varied fields as automotive or footwear industry,⁸ biomedical materials,⁹ elastomers,¹⁰ or adhesives.^{11–12}

To understand the behavior and properties of TPUs, it is essential to understand first their structure. In this sense, with the aim of using

TPUs as adhesives, we have already carried out several studies related to the influence of the chemical composition of TPUs onto their structure (phase separation, structure organization) and properties (mechanical, rheologic, and adhesive, among others).^{13–17} However, when we synthesized the TPUs by using the two-step prepolymer method,^{18,19} we never considered the influence of each step (prepolymerization and chain extension) on the TPU properties. As far as we know, such a study has never been done, although it takes on practical importance. Its importance remains in the fact that if both or one of the steps can be proved deciding, then the properties of the TPUs could be controlled and adjusted to any specific application simply by optimizing the corresponding step. Therefore, the aim of this article is to find out the step in the prepolymer method that determines the properties of TPUs. The in-

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Contract grant sponsor: Spanish Dirección General de Enseñanza Superior e Investigación Científica.

Journal of Applied Polymer Science, Vol. 76, 1590–1595 (2000)
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fluence of the prepolymerization and chain extension time is studied at constant TPU composition. The results provide useful information on the preparation of suitable adhesive TPUs.

EXPERIMENTAL

Materials

TPUs were prepared by using MDI (diphenyl methane-4,4'-diisocyanate) as the diisocyanate, poly(ϵ -caprolactone) (molecular weight = 3000 g mol⁻¹) as the macroglycol, and 1,4-butanediol as the chain extender. MDI (98% minimum purity) and 1,4-butanediol (99% minimum purity) were supplied by Aldrich (Dorset, England), and the poly(ϵ -caprolactone) macroglycol by Solvay Interlox (Cheshire, England). Water absorbed in the macroglycol was removed by heating overnight at 70°C under 5 torr reduced pressure. The prepolymer NCO content was obtained by titration with *n*-butylamine (ASTM standard method D 2572-80).

Preparation of Polyurethane Elastomers

TPUs were prepared by using the so-called two-step or prepolymer method. In a first step, prepolymers were obtained by reacting poly(ϵ -caprolactone) and MDI at 1.2 NCO/OH ratio, keeping the temperature always <80°C, for controlled prepolymerization times (t_{pp}). In a second step, each prepolymer was reacted with stoichiometric amounts of the chain extender (remaining NCO/OH = 1) at 80°C for controlled chain extension times (t_{ce}). Two types of experimental assays were achieved:

- Influence of the prepolymerization time: typical t_{pp} = 1, 1.5, and 3 h, with t_{ce} = 12 h
- Influence of the chain extension time: t_{pp} = 3 h and typical t_{ce} = 12, 48, and 72 h.

To test the TPUs properties, 18% weight solutions in 2-butanone were prepared in a laboratory mixer (3 h at 500 rpm). From the solutions, thin films were obtained and used for the TPUs characterization, by slow room temperature evaporation of the solvent.

Experimental Techniques

GPC. Molecular weight values were determined by using a gel permeation chromatography unit

consisting of a Varian 9001 solvent delivery pump, a Varian RI-4 (refractive index) Spectra series UV150 (UV) twin detection system, and a high-mass (up to 10⁶ g mol⁻¹) Polymer Laboratories column set. Standard reference sample was polystyrene. THF solutions (250 μ L) of TPU samples (50 mg in 2 mL) were introduced into the system by using a flow of 0.5 ml min⁻¹ and a pressure of 30 atm.

DSC. DSC analyses were carried out on a Mettler DSC 30 apparatus to determine the glass transition temperature (T_g) and the melting enthalpy (ΔH_m) of TPUs. Aluminum pans containing 5–9 mg of TPU samples were heated at 10°C min⁻¹ from –100 to 100°C under nitrogen atmosphere.

Strain–Stress Measurements. The mechanical properties of the prepolymers were tested on an Adamel–L'Homargy DY-25 device by using 0.6-mm thick and 0.4-mm width dog-bone test samples according to standard procedure.²⁰ Tensile strength and elongation at break were determined (average values of at least three experimental determinations) at 5 cm min⁻¹ pulling-up rate.

Contact-Angle Measurements. Contact-angle measurements were carried out on a Krüss device according to the sessile drop method. Ethylene glycol was chosen as the test liquid. Measurements were achieved at 25°C under an atmosphere saturated with ethylene glycol. Single drops (2 μ L) of ethylene glycol were placed on the surface of the TPU films, and the contact angle at each side of the drop was measured. Although the values obtained were always reproducible, at least three measurements on the same film were obtained with an error less than $\pm 2^\circ$.

T-Peel Test. T-peel tests were carried out between solvent-wiped (2-butanone-soaked cotton pads) poly(vinyl chloride) (PVC) strips. The solvent was allowed to evaporate for at least 30 min and subsequently the PVC strips were brushed over with the adhesive solution and allowed to dry for 30 min. Then the PVC strips were heated at 80°C by using infrared radiation (to soften the adhesive films) and immediately put in contact (3.5 MPa pressure applied for 10 s) to facilitate the TPU chains interlocking. The samples were left for 72 h in a controlled environment [23°C,

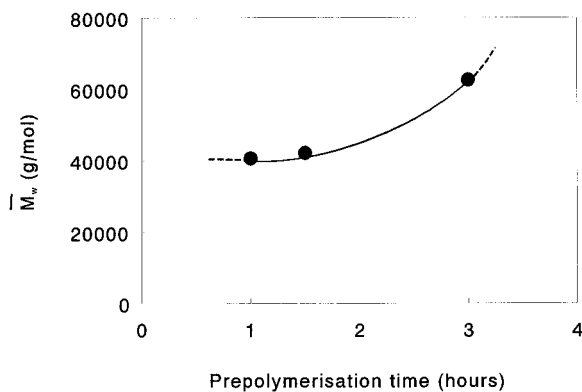


Figure 1 Variation of the TPUs average molecular weight (\bar{M}_w) with the prepolymerization time.

50% relative humidity (RH)] before the T-peel tests were achieved on an Adamel-L'Homargy DY-25 dynamometer. The peel rate was 10 cm min⁻¹ and the values obtained were the average of at least five experimental determinations with a maximum deviation <10%.

RESULTS AND DISCUSSION

The prepolymerization and chain extension steps have been considered separately.

Prepolymerization Step

To study the importance of the prepolymerization step in the TPUs structure, different times of reaction, typically 1, 1.5, and 3 h, were used.

Figure 1 gives the variation of the TPUs average molecular weight (\bar{M}_w) with the prepolymerization time. \bar{M}_w does not change for a prepolymerization time between 1 and 1.5 h, but increases for prepolymerization times higher than 1.5 h, showing that the chain dimensions of the

Table I Glass Transition Temperature (T_g), Melting Enthalpy (ΔH_m), and Contact Angles (ethylene glycol, 25°C) for TPUs Prepared with Different Prepolymerization Times

Prepolymerization Time (h)	T_g (°C)	ΔH_m (J/g)	Contact Angles (degrees)
1	-45	62	64
1.5	-45	59	62
3	-43	63	64

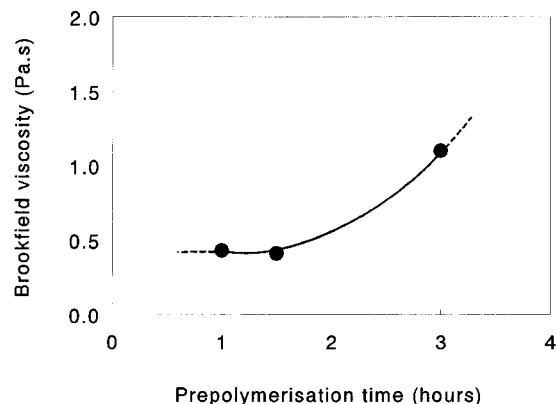


Figure 2 Variation of the Brookfield viscosity for the TPU adhesive solutions with the prepolymerization time.

final polymers depend on the conversion of the reactants in the prepolymerization step after a threshold is crossed. In the same way, the increase in the prepolymerization time also results in an increase in the Brookfield viscosity of the TPU adhesive solutions after a threshold is crossed (1.5 h of prepolymerization), as can be observed in Figure 2.

Table I gives structural parameters determined by DSC as well as the contact angles characteristic of the TPUs surface. The T_g does not depend on the prepolymerization time, which indicates that all the TPUs prepared have the same miscibility (same degree of phase separation) between the hard and soft segments. As changes in the phase separation are related to changes in the hard- to soft-segments ratio in TPUs structure,¹ constant T_g values (for different \bar{M}_w values) can

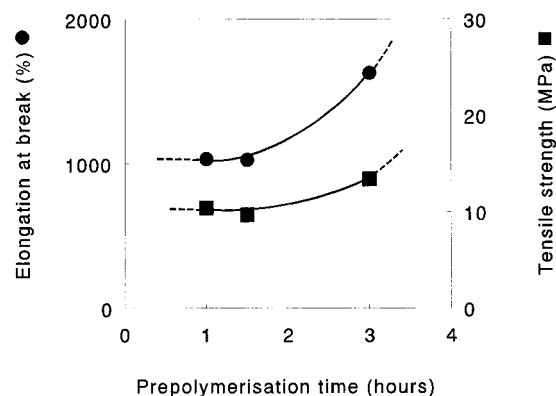


Figure 3 Variation of the elongation at break and the tensile strength of the TPUs with the prepolymerization time.

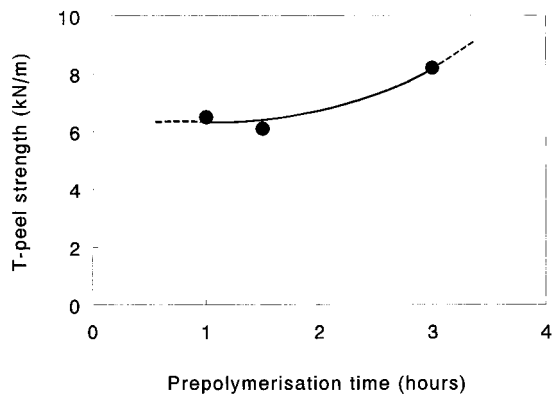


Figure 4 Variation of the T-peel strength of PVC/TPU adhesive joints as a function of the prepolymerization time.

only be explained by a constant amount of hard segments dispersed in the soft segments.

On the other hand, the melting enthalpy (ΔH_m , Table I) does not show any significant change for the TPUs prepared with different prepolymerization times. As ΔH_m of TPUs is related to the organization of the soft segments (i.e., interactions between TPU chains), the almost constant value of the melting enthalpy indicates that the organization of the structure (i.e., crystallinity) does not change. As changes in the interactions between the chains are related to changes in the composition of TPUs,^{14–17} constant ΔH_m values can only be explained by the constant composition of the TPUs prepared, whatever the molecular weight.

Summarizing, both T_g and ΔH_m indicate that the conversion of the reactants in the prepolymerization step does not influence either the phase

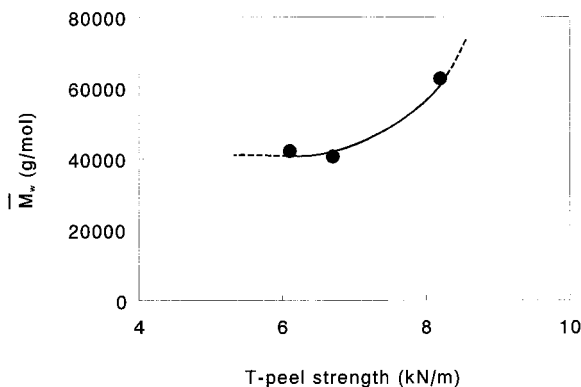


Figure 5 Relationship between the T-peel strength and the average molecular weight (M_w) for the TPUs prepared with different prepolymerization times.

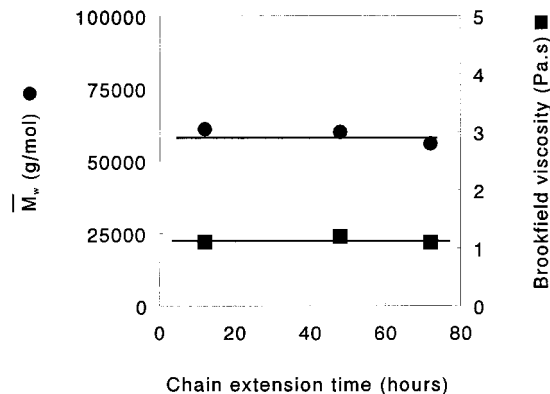


Figure 6 Variation of the TPUs average molecular weight (M_w) and Brookfield viscosity with the chain extension time.

separation or the organization (crystallinity) of the TPU structure provided the composition of the polymers does not change.

Agreeing with the bulk properties (T_g and ΔH_m), the surface properties of the TPUs do not depend on the prepolymerization time. Table I shows that the contact-angle value (ethylene glycol, 25°C) is constant, within an uncertainty domain of 2°. Once again, our interpretation is that the surface properties of the TPUs does not change because their composition remains constant.

The mechanical properties of the TPUs were determined by a strain–stress test. Figure 3 shows the variation of the ultimate (at break) elongation and tensile strength with the prepolymerization time. Both parameters follow the same tendency, keeping almost constant for a prepolymerization time between 1 and 1.5 h, but increasing for prepolymerization times higher

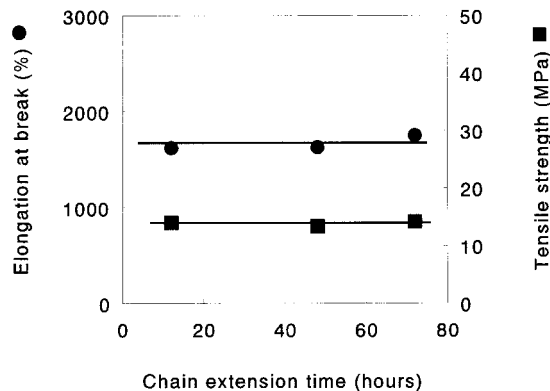


Figure 7 Variation of the elongation at break and the tensile strength of the TPUs with the chain extension time.

than 1.5 h. This result, which indicates an improvement in the mechanical properties of the TPUs, is in agreement with the increase in the molecular weight of the TPUs (Fig. 1) and the viscosity of the TPU solutions (Fig. 2). Therefore, the improvement in the mechanical properties of the TPUs can be directly related to the increase in the size of the prepolymer chains.

Regarding the adhesive properties of the TPUs, they were determined by the T-peel test of PVC-TPU adhesive joints. Figure 4 shows that the T-peel strength only increases for prepolymerization times higher than 1.5 h. This result indicates an improvement in the adhesive properties of the TPUs after a threshold is crossed, agreeing with the results obtained for the mechanical properties (Fig. 3). A relationship between the peel strength and the average molecular weight (M_w) is found (Fig. 5) in such a way that the higher the M_w , the higher the peeling strength, agreeing with the influence of the prepolymer structure on the application properties of the final TPUs.

Chain Extension

Three different times (12, 48, and 72 h) were considered in the chain-extension step to study its influence on the final TPU structure. The prepolymerization time was always 3 h.

TPU average molecular weight and viscosity of the adhesive solutions (Fig. 6), the mechanical (ultimate elongation, at break, and tensile strength; Fig. 7), adhesive (Fig. 8), and surface (Table II) properties do not change with the chain-extension time. These results indicate that the time involved in the chain extension process

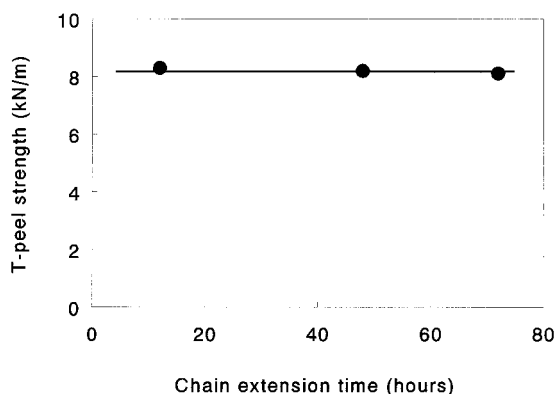


Figure 8 Variation of the T-peel strength of PVC/TPU adhesive joints as a function of the chain extension time.

Table II Glass Transition Temperature (T_g), Melting Enthalpy (ΔH_m), and Contact Angles (ethylene glycol, 25°C) for TPUs Prepared with Different Chain-Extension Times

Chain-Extension Time (h)	T_g (°C)	ΔH_m (J/g)	Contact Angles (degrees)
12	-43	63	64
48	-43	61	66
72	-40	63	66

does not affect the TPU properties, opposite to the results obtained in the prepolymerization step.

Regarding the T_g and the melting enthalpy (Table 2), they do not vary with the chain-extension time. Therefore, there is no change either in the degree of phase separation or in the structure organization (crystallinity). This behavior is due not only to the constant composition but also to the small degree of chain extension in the final TPUs (at 1.2 NCO/OH ratio, the free NCO at the end of the prepolymerization step is very small).

CONCLUSIONS

The prepolymerization time has a marked influence in the properties of the TPUs studied after a threshold in the reactants conversion is crossed, giving polymers with higher molecular weight and solutions viscosity, as well as better mechanical and adhesive properties.

The chain extension does not influence the size and properties of the TPUs studied, indicating that the prepolymerization (first step of the reaction) is indeed responsible for the final properties of these TPUs.

The phase separation, structure organization, and surface properties of the studied TPUs are not affected either by the prepolymerization or by the chain-extension time due to the constant composition of the polymers, a parameter that mainly affects the structure and surface properties of the TPUs.

As the properties of the studied TPUs are given by the prepolymerization, this is the step of the reaction that should be carefully controlled to obtain TPUs with the suitable properties.

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

REFERENCES

1. Chen, W.; Frisch, K. C.; Wong, S. in *Advances in Urethane Science and Technology*, Vol. 11; Frisch, K. C.; Klempner, D., Eds., Technomic: Lancaster, 1992; Chapter 3.
2. Kovacevic, V.; Smit, I.; Hace, D.; Sucasca, M.; Mundry, I.; Bravar, M. *Int J Adhes Adhesives* 1993, 13, 126.
3. Agrawal, R. K.; Drzal, L. T. *J Adhes Sci Technol* 1995, 9, 1381.
4. Dreyfuss, P.; Larive, D. E. *J Adhes* 1989, 27, 105.
5. Shilov, V. V.; Blinznyuk, V. N.; Lipatov, S. Y. *J Mater Sci* 1987, 22, 1563.
6. Miller, J. A.; Wang, C. B. *Org Coat Appl Polym Sci* 1982, 124, 47.
7. Camargo, R. E.; Makosco, C. W.; Tirrel, M.; Wellinghoff, S. T., in *ACS Symposium Series 270, Reaction Injection Moulding*; American Chemical Society: Washington DC, 1985; Papers 6, 7, 27, 111.
8. Dollhausen, M. in *Polyurethane Handbook*; Oertel, G., Ed.; Hanser: Munich, 1985; Chapter 11.
9. Tyler, B. J.; Ratner, B. D.; Castner, D. G.; Briggs, D. *J Biomed Mater Res* 1992, 26, 273.
10. Frontini, P. M.; Rink, M.; Pavan, A. *J Appl Polym Sci* 1993, 48, 2003.
11. Schollenberger, C. S. in *Handbook of Adhesives*; Skeits, I., Ed.; Van Nostrand-Reinhold: New York, 1990; Chapter 20.
12. Woods, G. *The ICI Polyurethanes Book*; ICI Polyurethanes and John Wiley: New York, 1990.
13. Sánchez-Adsuar, M. S.; Pastor-Blas, M. M.; Torregrosa-Maciá, R.; Martín-Martínez, J. M. *Int J of Adhes Adhesives* 1994, 14, 193.
14. Sánchez-Adsuar, M. S.; Pastor-Blas, M. M.; Villenave, J.-J.; Martín-Martínez, J. M. *Int J Adhes Adhesives* 1997, 17, 155.
15. Sánchez-Adsuar, M. S.; Martín-Martínez, J. M. *J Adhes Sci Tech* 1997, 11, 1077.
16. Sánchez-Adsuar, M. S.; Pastor-Blas, M. M.; Martín-Martínez, J. M. *J Adhes* 1998, 67, 327.
17. Sánchez-Adsuar, M. S.; Martín-Martínez, J. M. *J Adhes* 1998, 68, 143.
18. Hepburn, C. *Polyurethane Elastomers*; Elsevier Science: London, 1992.
19. Farrissey, W. J., in *Reaction Polymers*; Gum, W. F.; Riese, W.; Ulrich, H., Eds., Hanser Publishers: Munich, 1992; pp 260–268.
20. NF T51–034, French Normative, December 1981.