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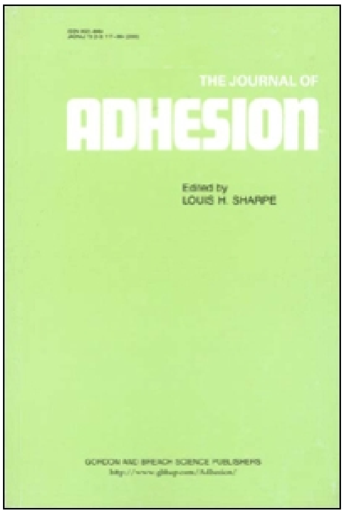

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Characterization of Thermoplastic Polyurethanes Prepared Using Different Macroglycols

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Three polyurethane elastomers (PUs) were prepared using macroglycols of different nature (ε-polycaprolactone, polyadipate of 1,6-hexanediol) and length of the hydrocarbon chain (polyadipate of 1,4-butanediol, polyadipate of 1,6-hexanediol). The PUs were characterized using Gel Permeation Chromatography, Differential Scanning Calorimetry, Wide X-ray angle Diffraction, Dynamic Thermal Mechanical Analysis, stress-controlled rheometry and stress-strain experiments. The surface properties were evaluated from contact angle measurements. The PUs were used as raw materials for solvent-based adhesives, whose adhesion properties were measured from T-peel strength of plasticized poly(vinyl chloride) (PVC)/polyurethane adhesive joints. The use of polyadipate of 1,6-hexanediol produced a polyurethane with high crystallinity (*i.e.* poor rheological and mechanical properties) and enhanced interactions between soft segments. Low adhesion was obtained in joints produced with this polyurethane and a cohesive failure of the adhesive was produced. The decrease in the polyadipate hydrocarbon chain length decreased the degree of crystallinity between polymer chains, therefore, no reduction in rheological and mechanical properties was obtained; a higher joint strength was also obtained. In this study the best performance was obtained with the polyurethane based on ε-polycaprolactone, presumably because of its higher surface energy and reduced crystallinity. The properties of the polyurethanes prepared in this study were more affected by the characteristics of the macroglycol, and the crystallinity of the polyurethane had a more marked effect on the properties than the degree of phase separation.

Keywords: Elastomeric polyurethane; macroglycol; adhesive; rheology; DSC; T-peel strength

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1. INTRODUCTION

The segmented structure of polyurethane elastomers (PUs) is mainly composed of glassy or "hard" segments and rubbery or "soft" segments which have a glass transition temperature (T_g) usually below room temperature [1–3]. The incompatibility between hard and soft segments induces segregation into domains, and the domain structure is well recognized as the key feature which controls the properties of these elastomers [4–7].

Several experimental variables determine the degree of phase separation in PUs. The molecular weight of the reactants, the nature and characteristics of the chain extender (length of chain, branching degree), the hard/soft segment ratio and the polymerization method, among other factors, play a key role in the extent of phase separation in the PUs [8–11].

Polyurethane elastomers are commonly used as solvent-based adhesives in the footwear, furniture and automotive industries, among others [12–14]. Typical PUs for elastomeric adhesives have a relatively reduced number of hard segments, and therefore, their properties are mainly determined by the characteristics and morphology of the soft segments (*i.e.* the nature and dimensions of the macroglycol), the incompatibility between the soft and hard segments, and the heat history of the polyurethane. Although these polyurethane elastomers are commonly used in industry, only a few references have been previously published [14, 18], and to our knowledge no fundamental studies have as yet been carried out. Previous studies performed by our research group [3, 19, 20] showed the influence of the molecular weight of the soft segments, the hard/soft segment ratio, and the nature and length of the chain extender, on the PUs properties. In this study, three macroglycols with different hydrocarbon length and chemical nature have been used to prepare PUs, the properties of which were characterized. Although there is some information in the literature concerning the effect of the macroglycol on the physical [21, 22] and other properties [23] of polyurethanes, there are no conclusive results for elastomeric PUs used as adhesives. The objective of this study is the understanding of the influence of the nature and length of the hydrocarbon chain of different macroglycols on the polyurethane structure and properties, mainly rheological, thermal, mechanical, surface and adhesion properties.

2. EXPERIMENTAL

Materials

Three polyurethanes were prepared using MDI as isocyanate, 1,4-butanediol as chain extender, and three different macroglycols: polyadipate of 1,4-butanediol (M_w = 3000 Daltons), polyadipate of 1,6-hexanediol (M_w = 2800 Daltons), and ε-polycaprolactone (M_w = 3000 Daltons). The polyesters studied are difunctional with hydroxyl end groups. The isocyanate/OH ratio was maintained at about 1.6 in all PUs, *i.e.* the hard segment content in the PUs was quite similar (about 13.5 wt% as shown in Tab. I). The MDI (diphenyl-methane-4,4′-diisocyanate), a mixture of 97 wt% of 4,4′ isomer and 3 wt% of the 2,4′ isomer, was supplied as a solid with high purity by Synthelast S. A. (Elche, Spain). The 1,4-butanediol was supplied by Aldrich (99% purity). The polyadipate of 1,4-butanediol and 1, 6-hexanediol were supplied by Hooker S. A. (Barcelona, Spain), and the ε-polycaprolactone was supplied by Solvay Interox (Cheshire, England). The water in the 1,4-butanediol was removed using molecular sieves (4 Å pore size, supplied by Scharlau.) The water in the macroglycols was removed by heating overnight at 70°C under reduced pressure (about 5 torr). The NCO content of the prepolymer was determined by titration with *n*-butylamine (ASTM D 2572–80).

Preparation of Polyurethane Elastomers

The PUs were prepared by using the prepolymer method. The prepolymers were obtained by reacting the MDI and the macroglycol

TABLE I Some characteristics of polyurethane elastomers prepared using different macroglycols

Nomenclature	*Macroglycol*	*Hard segment (wt%)*	*Mn*	*Mw*	*Mw/Mn*
PBD	polyadipate of 1,4-butanediol	13.9	19000	42000	2.2
PHD	polyadipate of 1,6-hexanediol	13.1	20000	78000	3.8
PC	ε-polycaprolactone	13.3	26000	65000	2.5

(isocyanate/macroglycol ratio = 1.6). The reaction temperature was always kept below 80°C. The prepolymers were reacted with the chain extender (1,4-butanediol), and the mixture was allowed to complete the polymerization overnight in an oven at 80°C.

Adhesive solutions were prepared by mixing 18 wt% PU with 2-butanone in a laboratory mixer. The mixture was stirred at 500 rpm for 3 hours until an homogeneous solution was obtained. The characterization of the PUs was carried out using films which were prepared by placing about 100 cm^3 of solution in a mould, allowing the slow evaporation of the solvent (to avoid air bubbles in the films). The nomenclature of the PUs is given in Table I and corresponds to the type of macroglycol used in the synthesis (*i.e.* PBD = polyurethane prepared with polyadipate of 1,4-butanediol).

Experimental Techniques

GPC

Molecular weight distributions were measured in a Gel Permeation Chromatography unit consisting of a solvent delivery pump (Varian 9001), a refractive index detector (Varian RI-4) and an UV detector (Spectra series UV150). Four columns, TSK-HXL 1000–2000–3000–4000, filled with poly(styrene-divinylbenzene) were used, which were able to measure molecular weight up to 10^6 Daltons. The standard reference sample was polystyrene. 250 μl of THF solution of the PU film (50 mg in 2 ml – 0.25% wt/vol) were introduced into the system using a flow of 0.5 ml min^{-1} and a pressure of 80 atm.

FTIR Spectroscopy

IR spectra of the PU films were obtained in transmission mode using a FTIR Nicolet 205 apparatus. PU films (around 100 μm thickness) were prepared by spontaneous evaporation at room temperature of a diluted adhesive solution (1 part of adhesive: 5 parts of 2-butanone). The number of scans per experiment was 60 and the equipment signal/noise ratio measured at 2000 cm^{-1} was 0.04%. More details have been given elsewhere [3].

DSC

DSC experiments were carried out in a Mettler DSC 30 apparatus to determine the glass transition temperature (T_g) and the softening temperature (T_s) of the PUs (*i.e.* the temperature at which the tertiary structure of thermoplastic polyurethane starts to collapse). Aluminum pans containing 5–9 mg of PU films were heated from −100°C to 100°C under nitrogen atmosphere. The crystallization temperature (T_c) and the enthalpy of crystallization (ΔH_c) were obtained by cooling down the PUs from 100°C to −50°C. A heating and cooling rate of 10°C min^{-1} was used. The time necessary for crystallization of PUs was obtained using the procedure proposed by Duswalt [24]: After melting the PU between 35 and 100°C, the temperature was decreased to 25°C and the evolution of heat with time under isothermal conditions was monitored until a crystallization peak appeared.

WAXD

X-ray diffraction patterns of the PUs were obtained in a Seifert JSO-Debyeflex model 2002 apparatus in the range of Bragg's angle $2\theta = 6-60°$. A monochromatic K_α Cu radiation was used. The sample dimensions were 30×30 mm.

Dynamic Mechanical Thermal Analysis (DMTA)

The variation of the viscoelastic properties of the PUs at low temperature was measured in a *Polymer Mk III* DMTA system manufactured by Rheometric Scientific. The measurements were obtained using a bending mode, with a frequency of 1 Hz and an amplitude of 64 μm peak–peak. The dimensions of the samples were 0.7×11×20 mm, the temperature range considered was between −100 and 100°C and the heating rate used was 5°C min^{-1}.

Stress-controlled Rheometer

The rheological properties of the PUs were obtained in a *Bohlin CS-50* rheometer, using a plate–plate geometry (upper plate diameter = 20 mm), a frequency of 1 Hz and a target strain of 0.05 (located in the

Newtonian region by means of a stress sweep at 100°C). The gap between the plates was always 0.6 mm, and fixed at 200°C. The samples were cooled during the experiments. The temperature range considered varies between 200 and 25°C, using a cooling rate of 5°C min^{-1}. The samples used were rounded PU pieces of 20 mm diameter.

Strain-Stress Measurements

The mechanical properties of the PUs were obtained in an *Adamel-L'Homargy* DY-32 test instrument, using dog-bone test samples of 0.6 mm thickness and 0.4 mm width (in the centre of the test sample) and following the procedure stated in Ref. [25]. The pulling rate used was 10 cm min^{-1}. The tensile strength and the elongation at break were measured. The values obtained were the average of at least three experimental determinations.

Contact Angle Measurements

Contact angle measurements were carried out in a *Ramé-Hart* 100 system by using the sessile drop method. Ethylene glycol was chosen as the test liquid. The samples used were prepared by placing a thin film (0.2 mm thick) of adhesive solution on a polyethylene piece (dimensions = 30×20 mm) and allowing the solvent to evaporate slowly. Measurements were obtained at 25°C under an ethylene glycol saturated atmosphere. Single drops (2 μL) of ethylene glycol were placed on the surface of the PU films, and the contact angle at each side of the drop was measured (they were very similar). Although the values obtained were always reproducible, at least three measurements on the same film were obtained with an error less than ± 2 degrees.

T-peel Test

T-peel tests were carried out between solvent-wiped plasticized polyvinyl chloride (PVC) samples. Table II shows the formulation of PVC used in this study. The PVC was wiped by rubbing the surface

TABLE II Composition of polyvinyl chloride (PVC)

Component	*wt%*
Polyvinyl chloride	57.1
Di-octyl phthalate	36.5
Epoxidized soya oil	1.9
Calcium carbonate	2.3
Stabilizer	1.7
Titanium dioxide	0.5

with a cotton swab saturated with 2-butanone, allowing the evaporation of the solvent for at least 30 minutes before applying the adhesive solution. Subsequently, 100 mg of adhesive solution was applied to each PVC strip to be joined, and left to dry for 30 minutes. A solid adhesive film was formed by evaporating the solvent and these dried films were suddenly heated to 80°C using infrared radiation in order to facilitate the interlocking of the PU chains on the two PVC strips. The strips were immediately placed in contact and a pressure of 0.8 MPa was applied for 10 seconds to achieve a suitable joint. The joints were kept at 23°C and 50% relative humidity for 72 hours before the T-peel test was carried out in an *Adamel-L'Homargy* DY-32 test instrument. The peel rate was $100\,\mathrm{cm\,min^{-1}}$ and the values obtained were the average of at least five experimental determinations with an error smaller than 10%.

3. RESULTS AND DISCUSSION

Table I shows no significant differences in the hard segment content of the three PUs (13.1–13.9 wt%), based on the stoichiometry of the reaction. ^{1}H NMR spectra (not shown here) confirm such stoichiometry. The chemical composition of the PUs is quite similar and only one IR spectrum is given in Figure 1 as representative example. The IR spectrum shows typical bands corresponding to the hard segment, N—H(1536, $3350\,\mathrm{cm^{-1}}$), C=O($1731\,\mathrm{cm^{-1}}$), C—O—C(1080, $1222\,cm^{-1}$) groups, and to C—H groups (2863, $2938\,\mathrm{cm^{-1}}$).

The average molecular weights and the polydispersity index (M_w/M_n) of the PUs are included in Table I. Average molecular weights are within the usual values for thermoplastic polyurethanes [26]. As expected, M_w values are higher than M_n ones, and the highest M_n

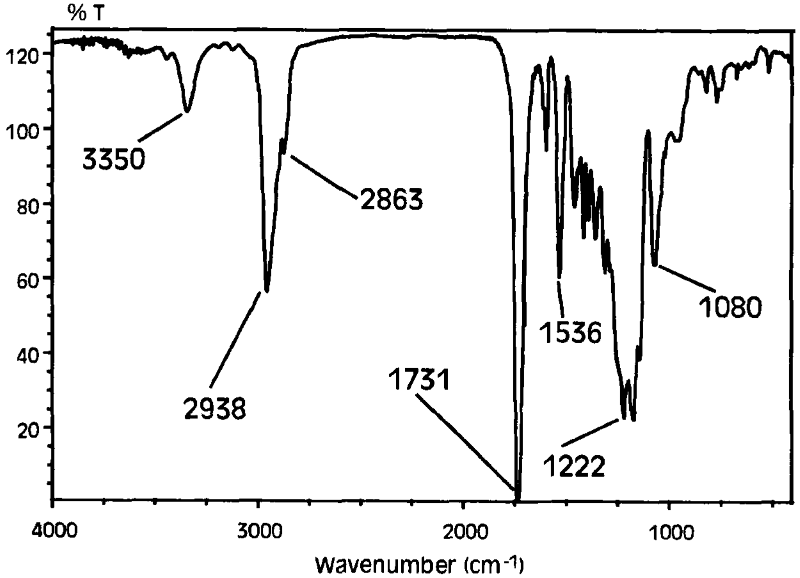

FIGURE 1 IR spectrum of PBD polyurethane.

corresponds to PC; the other two PUs show about the same M_n values. The trend in M_w and M_n values indicates a greater length of the soft segments in the PC polyurethane. Furthermore, the M_w/M_n ratio is somewhat higher than 2.

Figure 2a shows the DSC graphs corresponding to the heating of the three PUs. The graphs show one T_g located at low temperature and the softening process (*i.e.* the decrease of interactions within the soft segments) at higher temperature. These transitions are affected by the nature of the macroglycol used in the PUs synthesis, in agreement with previous work [2]. On the other hand, Figure 2b shows the crystallization process of the PUs. Table III contains different parameters of the PUs obtained from DSC curves. Although the softening process is quite similar in all PUs, independent of the macroglycol used in their manufacture, there are differences between the PUs: the increase in the hydrocarbon length of the polyadipate implies a more positive T_g, *e.g.* a higher restriction on the movement of polymer chains and the crystallization peak of PU is displaced to higher temperature; furthermore, an increase in crystallization enthalpy and faster

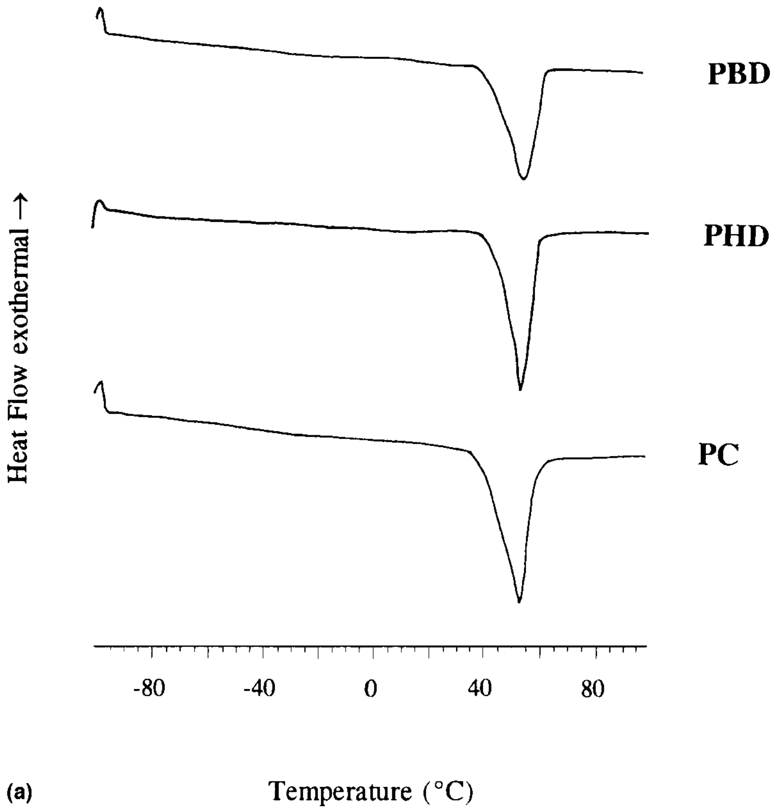

FIGURE 2 a) DSC diagrams obtained by heating the PUs; b) DSC diagrams showing the crystallization process of the PUs.

crystallization rate (indirectly estimated from the time necessary to produce the crystallization of PU) are obtained. Therefore, due to the length of the hydrocarbon chains in the PHD polyurethane, low segment–segment interactions can be produced, but crystallization may be allowed due to the higher ability of the soft segments to conform into the crystal matrix. The ε-polycaprolactone presents a more negative T_g value than the PUs prepared using polyadipates, and the crystallization is produced at lower temperature, involving a lower enthalpy and slower crystallization rate than the PUs obtained using a polyadipate. Therefore, PC is the PU with lower degree of interactions between polymer chains. However, because the percentages of hard

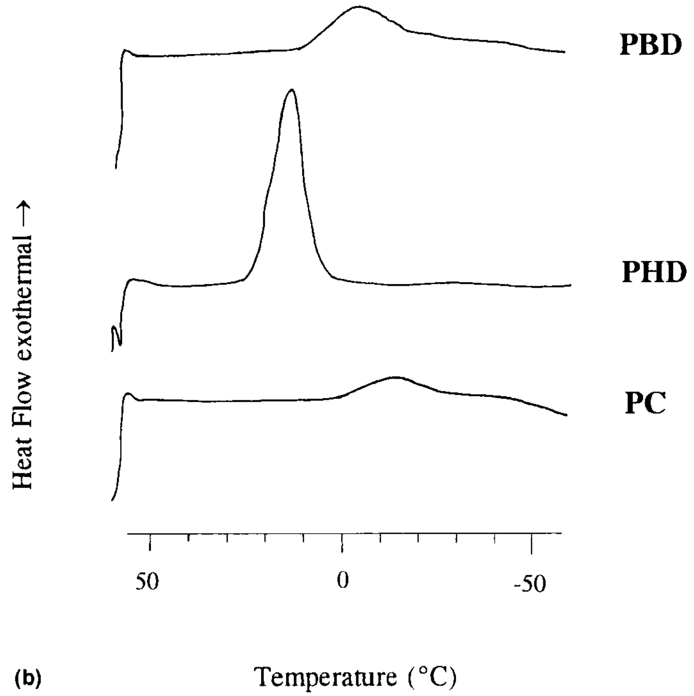

FIGURE 2 (Continued).

TABLE III Parameters obtained from DSC curves

Polyurethane	$T_g (°C)$	$T_s (°C)$	$T_c (°C)$	$\Delta H_c (J/g)$	$t_c (min.)$
PBD	−35.8	51.8	−3.0	20.2	7.3
PHD	−31.8	51.2	14.4	50.5	0.6
PC	−37.4	51.6	−13.6	8.7	24.4

and soft segments are similar in the three PUs, the differences in the glass transition and crystallization processes cannot be associated with a different degree of phase separation but to interactions within the soft segments which contribute to produce crystallinity and are intrinsically associated with the characteristics of the macroglycol.

The crystallinity of the PUs related to the characteristics of the macroglycol can be obtained from X-ray diffraction patterns. Figure 3 shows as a typical example the X-ray diffraction pattern of PC. This diffractogram shows two peaks at 2θ values of 21 and 24 degrees which

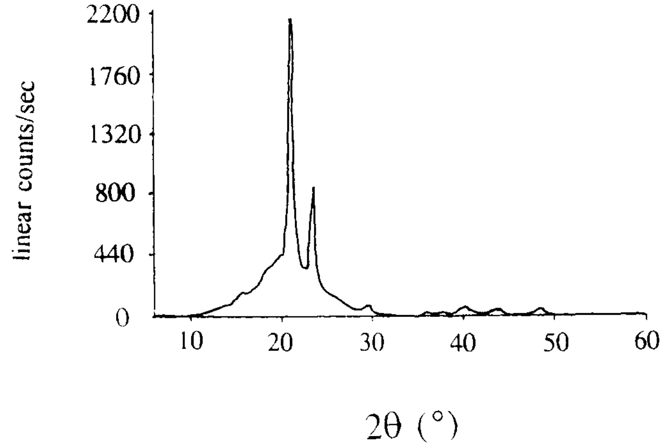

FIGURE 3 X-ray diffractogram of PC polyurethane.

corresponds to the (110) and (020) diffractions of a polyester urethane [16, 27], respectively. The intensities of these peaks are related to the crystallinity of the polyurethane elastomers. In Figure 4, the relative intensity of the (110) diffraction peak, I_{110}, is plotted as a function of the crystallization enthalpy of the PUs. There is a linear relationship between the crystallinity and the degree of interactions within soft segments, indicating that PHD is the most crystalline polymer and at the same time the polyurethane with higher degree of interaction between chains. PC is the less crystalline and the polyurethane with the smaller degree of interaction between chains. Furthermore, it is interesting that the most crystalline PU also has the highest T_g value (which is associated with the amorphous regions of the PUs), Figure 5.

The rheological properties of the PUs also support the evidence obtained from DSC and WAXD. Figure 6 shows the experimental results obtained from DMTA. The variation of the storage modulus (E′) as a function of the temperature (Fig. 6a) shows the glass transition process at low temperature by means of the knee in the curve; no important variation in storage modulus is obtained below the glass transition temperature and the increase in temperature produced a decrease in modulus until the softening of the PU occurs (at about 50°C); it can be easily distinguished because of the significant decrease in storage modulus. Before and after the glass transition

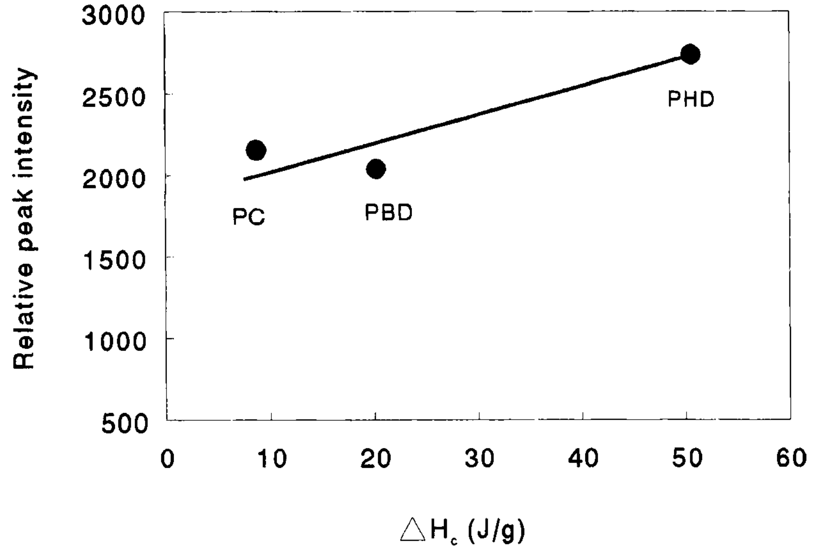

FIGURE 4 Variation of the relative peak intensity of (110) diffraction as a function of the crystallization enthalpy of the PUs.

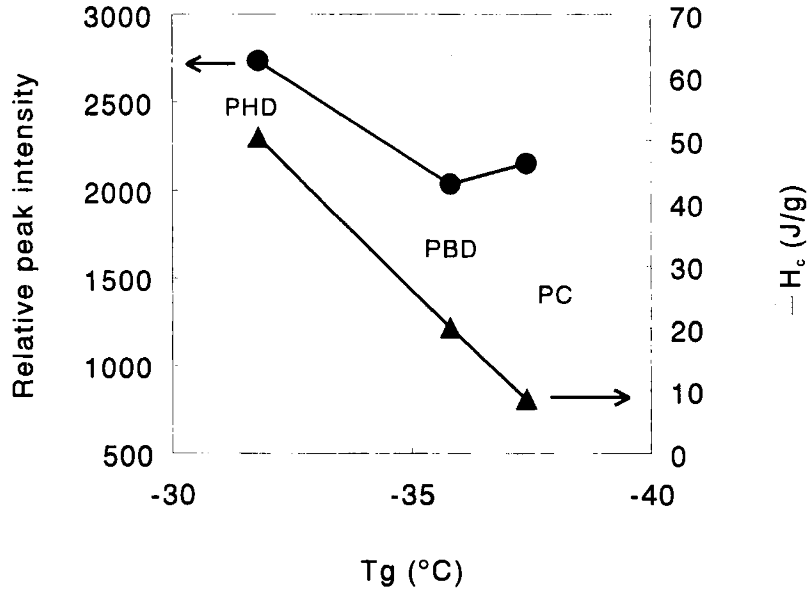

FIGURE 5 Variation of the relative peak intensity of (110) diffraction and the crystallization enthalpy as a function of the glass transition temperature of the PUs.

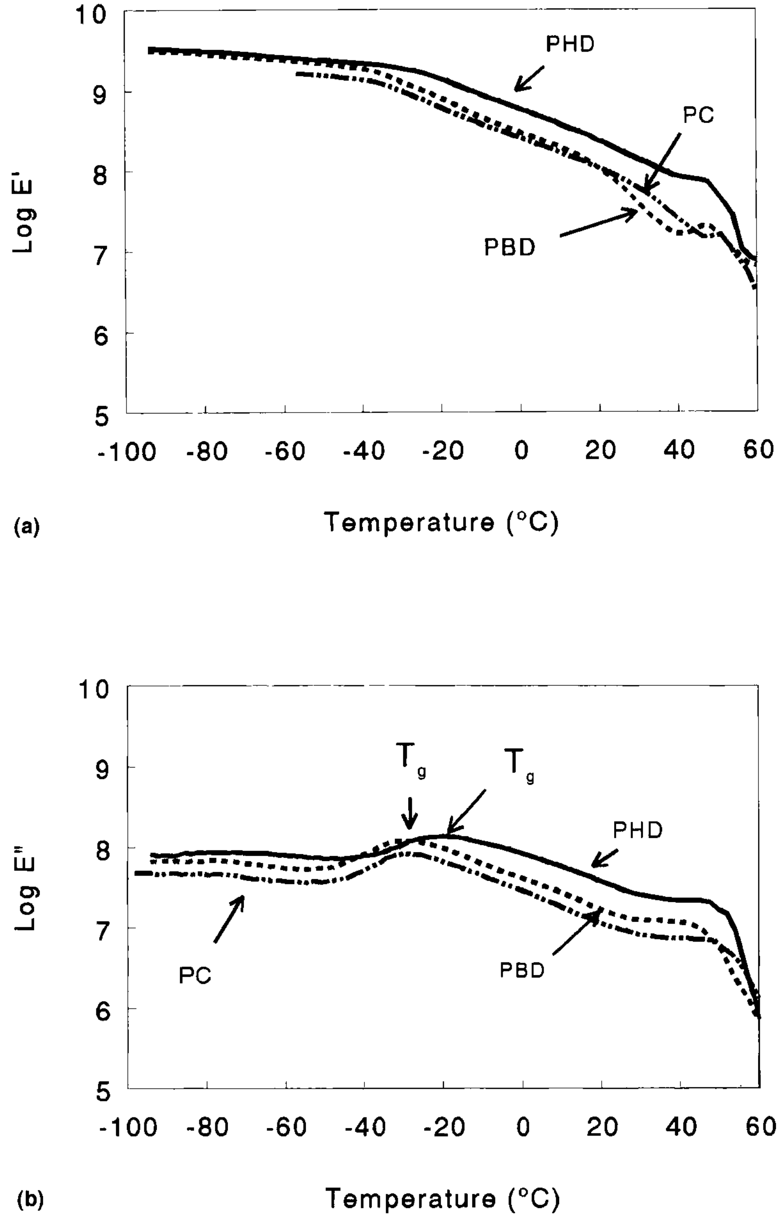

FIGURE 6 Variation of: a) Storage modulus (E′), and b) Loss modulus (E″), as a function of the temperature in the PUs. Frequency = 1 Hz. Amplitude = 64 μm peak–peak.

process, the storage modulus in PHD is higher than in PC and PBD, indicating the higher number of interactions within the soft segments in PHD. Similar trends are obtained for the variation of the loss modulus (E″) with temperature (Fig. 6b) but the T_g value is more clearly marked (the maximum in the curve). A similar evolution of T_g is obtained from DSC and DMTA experiments: the most positive T_g corresponds to PHD and the lowest one to PC. These evolutions indicate the stronger interactions within the soft segments of the PUs prepared using polyadipate of 1,6-hexanediol, which exhibits improved crystallinity and enhanced viscoelastic properties (high storage and loss moduli).

Using our DMTA system it was not possible to follow the evolution of storage and loss moduli after softening of the PUs occurs. Therefore, a plate–plate stress-controlled rheometer was used, and the results obtained for the variation of the storage modulus (G′) with temperature above room temperature is included in Figure 7. According to this figure, the storage modulus of PHD is noticeably reduced after the softening process and the increase in temperature produces a more marked loss of mechanical properties in this

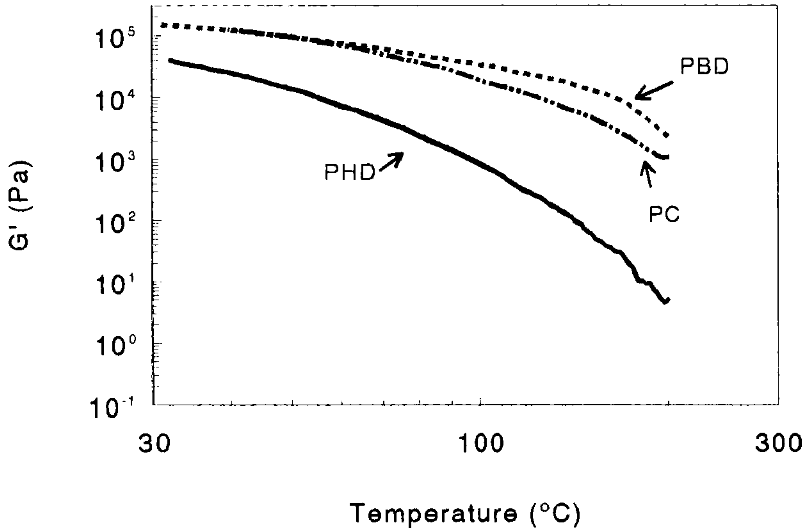

FIGURE 7 Variation of storage modulus (G′) as a function of the temperature in the PUs. Frequency = 1 Hz. Target Strain = 0.05.

polyurethane. Since the softening process produces a decrease of secondary interactions between the polymer chains (which are more important in PHD due to the long length of the hydrocarbon chains), the loss of rheological properties in PHD can be explained considering its high crystallinity which is responsible for its high rigidity and lower resistance to external stresses of the polyurethane. Furthermore, the curves corresponding to the storage and loss modulus do cross at a temperature below 30°C, confirming the crystalline nature of the PHD. The decrease in storage modulus as the temperature increases is less pronounced in PBD and PC because of the weaker interactions between polymer chains and their lower crystallinity, and the curves of the storage and loss modulus cross at 125 and 60°C, respectively; these data cofirm the weaker interactions in PC (the crossing is produced at lower temperature) with respect to the PBD polyurethane.

The mechanical properties of the PUs confirm the above statement. According to Figure 8, the tensile strength and elongation at break in PHD are too low, due to the high crystallinity in this polyurethane. The lower the crystallinity, the higher the tensile strength and the

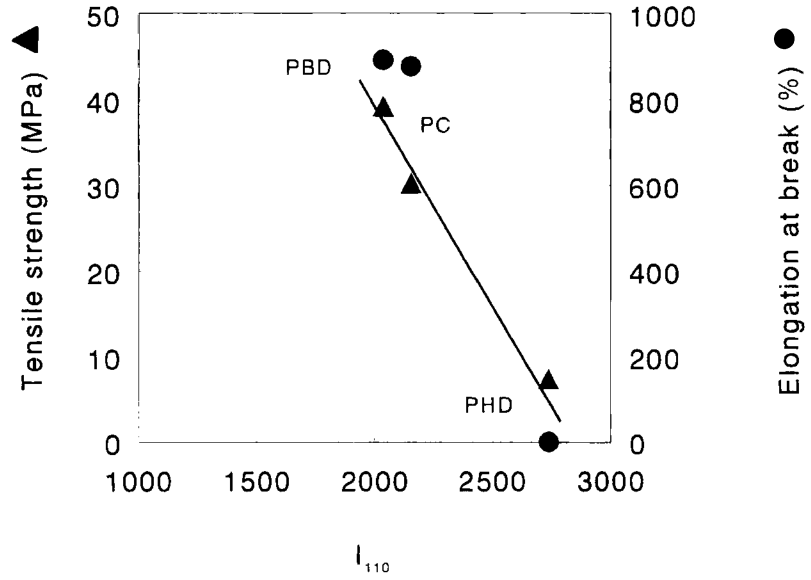

FIGURE 8 Variation of the tensile strength and elongation at break as a function of the relative peak intensity of (110) diffraction in the PUs.

elongation at break of the PU. Due to the stronger interactions between polymer chains in PHD, the application of a stress produces a quick rupture of the crystallites due to the rigid nature of this polyurethane [28]. Therefore, the best performance in terms of mechanical and rheological properties corresponds to the polyurethanes prepared using a polyadipate of a short hydrocarbon chain length or an ε-polycaprolactone, because they produce less crystalline and more flexible polyurethane polymers.

Therefore, although the degree of phase separation determines the properties of PUs, in this study there is also an influence of the degree of crystallinity. The crystallinity of the PUs in this study is determined by the nature and characteristics of the macroglycol used in their manufacture. The short length of the hydrocarbon chain in the polyadipate facilitates the formation of a few but sufficient interactions within the soft segments to provide adequate elastic properties. The same applies to the ε-polycaprolactone which introduces inherent chemical heterogeneities in the backbone of the polyurethane chains avoiding the formation of a high degree of crystallinity. In PHD, an important degree of orientation between the polymer chains is produced, facilitating the crystallization and the creation of stronger interactions between the polymer chains. This high degree of orientation of polyurethane chains is responsible for the poor rheological and mechanical properties of PHD.

The surface properties of the PUs were assessed from contact angle measurements (Tab. IV). Similar contact angles were obtained for PBD and PHD, and the value corresponding to PC was somewhat lower. Due to the differences in the chemical nature of the macroglycol, the contact angle measured on the polyurethane obtained using ε-polycaprolactone is smaller.

The adhesion properties of the PUs were obtained by testing PVC/polyurethane adhesive joints (Fig. 9). The nature of the macroglycol affects the joint strength and locus of failure of the joints. The lowest

TABLE IV Contact angles (ethylene glycol, 25°C) measured on the PUs

Polyurethane	*Contact angle (degrees)*
PBD	59
PHD	60
PC	52

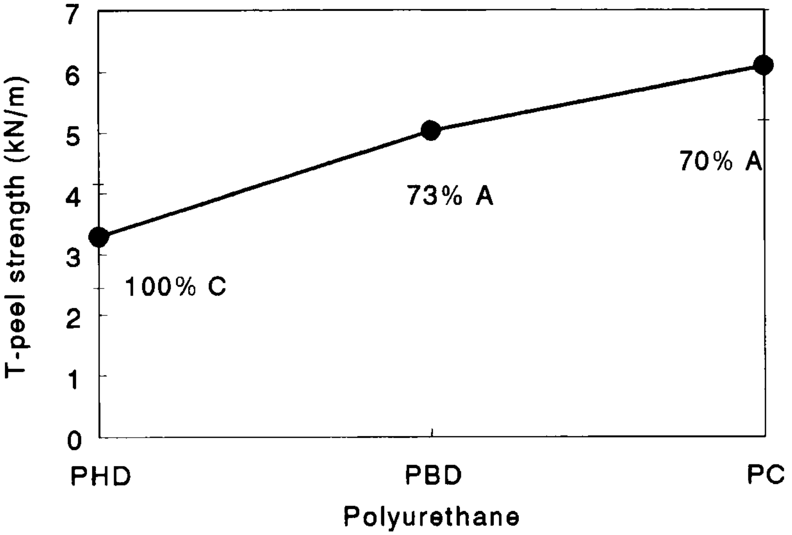

FIGURE 9 Variation of the T-peel strength of PVC/PU adhesive joints with respect to the kind of macroglycol used in the PU synthesis. Locus of failure: C = cohesive failure in the adhesive; A = adhesional failure. Number before the symbol indicates the estimated percentage of each kind of failure.

joint strength is obtained using the PHD adhesive and 100% cohesive failure in the adhesive is produced. The high crystallinity and rigidity of PHD facilitate the concentration of stresses in the adhesive bulk and the joint strength corresponds to the cohesive strength of the polyurethane. In the joints produced with PBD, a higher joint strength is obtained and the locus of failure is mainly adhesional (27% cohesive failure in the adhesive), due to the lower crystallinity, lower M_n and better rheological and mechanical properties of that polyurethane. Finally, the highest joint strength is obtained for the joints prepared with the PC adhesive (an adhesional failure is mainly produced), probably caused by the improved surface and rheological properties of this polyurethane. These results show that a relationship exists between the morphology (or structure), intrinsic properties of the polyurethane adhesives and the adhesion properties. In this study, the characteristics of the macroglycol determine the morphology of the PUs and this morphology affects the adhesive properties more than their degree of phase separation.

4. CONCLUSIONS

The nature and characteristics of the macroglycol determines the properties of PU adhesives. Because the manufacturing procedures were similar, the hard-to-soft segment ratio (related to the degree of phase separation) is similar in all PUs. The use of the polyadipate of 1,6-hexanediol produces a polyurethane with high crystallinity and strong interactions between soft segments. As a consequence, reduced rheological and mechanical properties are produced, and low adhesion is obtained because the failure of the joints is located in the adhesive bulk. The decrease in the length of the hydrocarbon chain in the polyadipate (*i.e.* PBD adhesive) reduces the degree of crystallinity between polymer chains and, therefore, no reduction in rheological, mechanical and adhesion properties are produced. The PU prepared using ε-polycaprolactone produces the best performance as an adhesive, because of the high surface energy and adequate crystallinity. The properties of the PUs prepared in this study are affected by the characteristics of the macroglycol.

Acknowledgements

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