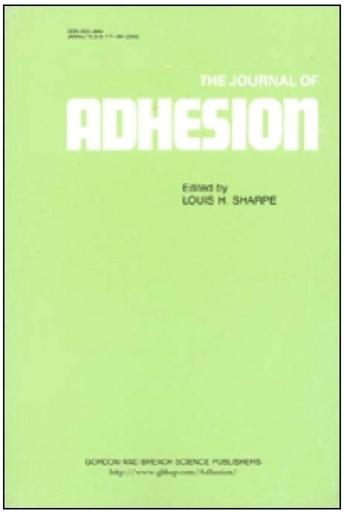

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Properties of Polyurethane Elastomers with Different Hard/Soft Segment Ratio*

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Three polyurethane elastomers (PU) containing different hard/soft (h/s) segment ratios were prepared. The PUs were characterized using Gel Permeation Chromatography (GPC), DSC, Wide Angle X-ray Diffraction (WAXD), Dynamic Mechanical Thermal Analysis (DMTA), and Stress-controlled rheometry. 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 tests of solvent-wiped polyvinyl chloride (PVC)/polyurethane adhesive joints. The increase in the amount of h/s segment ratio affected the structure and morphology of the PUs, reducing the degree of phase separation and the extent of the secondary interactions between polymer chains. The h/s segment ratio determined the thermal, mechanical, rheological and adhesion properties of the PUs.

Keywords: Elastomeric polyurethane; hard/soft segment ratio; phase separation; polyurethane adhesive; DMTA; rheology; T-peel strength

1. INTRODUCTION

Thermoplastic polyurethane elastomers (PUs) are commonly used as raw materials to prepare solvent-based adhesives, which are generally used as contact adhesives in the automotive, footwear and furniture

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industries [1–3]. Chemically, these PUs are prepared by reacting an isocyanate, a macroglycol and a chain extender (generally a short diol).

The structure of PUs consists of block copolymers of the $(AB)_n$ type, containing soft and hard segments [4]. The hard segments are formed by reacting the isocyanate with the chain extender (*i.e.*, 1,4 butanediol), and are rigid and polar. On the other hand, the soft segments consist of long polymeric chains of the macroglycol (polyether or polyester type), and are flexible and non-polar. The differences in polarity between hard and soft segments contribute to produce phase separation in the PU structure [5–13] and the unique properties of polyurethanes are caused by the phase segregation of hard domains. The hard domains are created by the hard segments interacting each other, are responsible for the rigidity of the PU and present a relatively high melting temperature. On the other hand, the soft domains are created by interaction of the soft segments, give flexibility and elastomeric properties to the PU, and present a relatively low softening temperature. The segregation in PUs is allowed to occur in the melt and the hard phase allowed to cool to a glass or to crystallize. The hard segments then act as pseudo-crosslinks to increase the modulus of the polymer.

Typical PUs for adhesive manufacturing have a relatively reduced number of hard segments, and their properties are mainly determined by the soft segments. Therefore, the PUs will be mainly elastic in the range of temperature between the glass transition temperature (T_g) – generally located about −60°C – and the softening temperature of the elastomeric domains (60–100°C) [14].

The domain morphology of segmented PUs has been extensively studied to understand the molecular basis of the polymer properties [15], but only a few studies dealing with PUs prepared from raw materials, and with their application as adhesives, have been carried out [16–20]. On the other hand, it is known that several experimental variables affect the segmented structure and properties of PUs, such as the hard/soft segment ratio (*i.e.*, the equivalents of isocyanate-chain extender in respect to the macroglycol in the reaction), the nature and structure of the raw materials (mainly the macroglycol and the chain extender), and the preparation procedure (synthesis procedure, temperature, reaction time, etc.), among other [12, 21–23]. Probably, the hard/soft (h/s) segment ratio is the experimental variable more noticeably affecting the PUs properties.

Previous studies regarding the influence of the h/s segment ratio on the properties of linear segmented polyurethane elastomers have shown its influence on the molecular weight and on the rheological, thermal and mechanical properties of two series of polyester-based urethanes [23]. On the other hand, the effect of the h/s segment ratio on the morphology and microphase separation of ester-based polyurethanes has also been studied [24–26], showing that a higher amount of hard segments leads to a smaller degree of phase separation. Therefore, the aim of this study is the characterization and the study of the thermal, mechanical, rheological, surface and adhesion properties of three PUs with different h/s segment ratio by combining several experimental techniques, and to contribute to the sparse literature in thermoplastic (or elastomeric) PUs related to their adhesive properties.

2. EXPERIMENTAL

Materials

Three polyurethanes were prepared from MDI as isocyanate, 1,4-butanediol as chain extender and the polyadipate of 1,4-butanediol ($M_w = 2440$ Daltons) as macroglycol; different NCO/OH ratios (1.2, 1.6, 2.0) were used. The MDI (diphenylmethane-4,4'-diisocyanate) – a mixture of 97 wt% of the 4, 4' isomer and 3 wt% of the 2,4' isomer-, was supplied as a high-purity solid by Synthelast S. A. (Elche, Spain). The 1,4-butanediol was supplied by Aldrich (99 % purity), and the polyadipate of 1,4-butanediol was supplied by Hooker S. A. (Barcelona, Spain). The water in the 1,4-butanediol was removed using molecular sieves (4 Å pore size, supplied by Scharlau). 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 Polyurethane Elastomers

The PUs were prepared by using the prepolymer method. The prepolymers were obtained by reacting the macroglycol and the MDI, different NCO/OH ratios being used (Tab. I). The reaction temperature was always kept below 80°C. The prepolymers were reacted with the chain extender (1,4-butanediol) – the amount of chain extender was estimated by considering the amount (in equivalents) of unreacted NCO groups in the prepolymer – and the mixture was allowed to complete the polymerization in a oven at 80°C for 12 hours.

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 suspension 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 and allowing the slow evaporation of the solvent (to avoid air bubbles in the films). The nomenclature of the PU samples consists in the capital letters PU followed by the NCO/OH ratio (MDI to macroglycol equivalents) between brackets (Tab. I).

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 a UV detector, Spectra series UV150. Four columns, TSK-HXL 1000-2000-3000-4000, filled with poly(styrene-divinylbenzene) were used. The standard reference sample was polystyrene. 250 μl of THF solution of the PU film (50 mg in 2 ml, *i.e.*, 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 the 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 (1:5) adhesive solution (in 2-bu-

TABLE I Some properties of polyurethane elastomers

Nomenclature	*NCO/OH ratio in the prepolymer*	*Hard segment (wt%)*	M_n	M_w	M_w/M_n
PU (1.2)	1.2	11.5	28400	87700	3.1
PU (1.6)	1.6	15.7	22700	64300	2.8
PU (2.0)	2.0	19.5	16600	42000	2.5

tanone) placed on a KBr window. 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 [27].

DSC DSC experiments were carried out in a Mettler DSC 30 apparatus to determine the T_g and the melting temperature (T_m) of the PUs. Aluminum pans containing 5–9 mg of the films were heated from −100°C to 100°C under nitrogen atmosphere to determine the glass transition temperature and the melting properties of PUs. After that, the PUs were cooled down to −50°C to obtain the crystallization temperature (T_c). A heating rate of 10°C min^{-1} was always used.

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

Dynamic Mechanical Thermal Analyzer (DMTA) The viscoelastic properties of the PUs as a function of temperature were measured in a *Polymer Mk III* DMTA system manufactured by Rheometric Scientific. The measurements were obtained in bending mode, using a frequency of 1 Hz and an amplitude of 64 μm peak-peak. The dimensions of the samples were 0.7 × 11 × 20 mm and the range of temperature used was between −100°C and 100°C; the heating rate 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 temperature range considered varied between 200 and 25°C, a cooling rate of 5°C min^{-1} being used. The gap between the plates was always 0.6 mm, and fixed at 200°C. The samples used were round PUs pieces of 20 mm diameter.

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 a saturated ethylene glycol 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 on solvent-wiped plasticized PVC/polyurethane adhesive joints. Table II shows the formulation of PVC used in this study. The wiping of PVC was carried out by rubbing the surface with a piece of cotton dipped in 2-butanone, allowing the evaporation of the solvent for, at least, 30 minutes. Subsequently, 100 mg of adhesive solution was applied to each PVC strip to be joined, and left to dry for 30 minutes. By evaporation, a solid adhesive film was formed, which was 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 immediately 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 0.1 m 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 the differences in the hard segment content of the PUs, 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 according to the FTIR spectra given in Figure 1. The FTIR spectra show typical bands corresponding to the

TABLE II Formulation of polyvinyl chloride (PVC)

Ingredient	*Percentage* (*wt* %)
Polyvinyl chloride	57.1
Di-octyl ftalate	36.5
Epoxylated soya oil	1.9
Calcium carbonate	2.3
Barium-cadmium stabilizer	1.7
Titanium dioxide	0.5

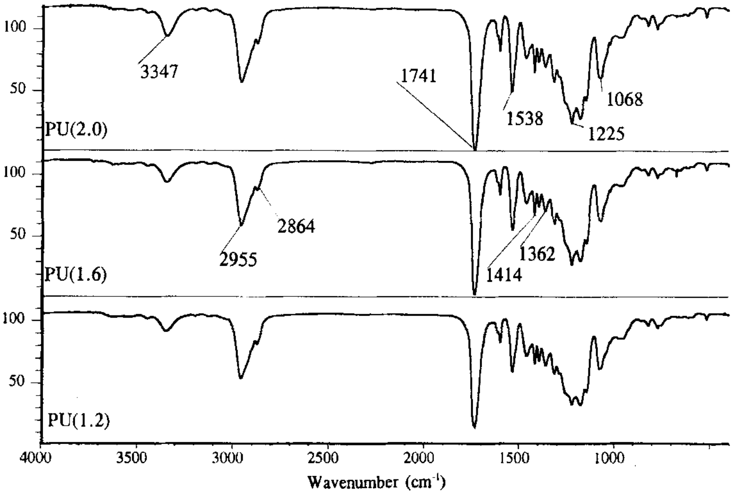


FIGURE 1 FTIR spectra of PUs.

hard segments - N—H (1538, 3347 cm^{-1}), C=O (1741 cm^{-1}), C—O—C (1068, 1225 cm^{-1}) groups - and to soft segments - C—H (1362, 1414, 2864, 2955 cm^{-1}) groups. There are no qualitative differences between the FTIR spectra of the three PUs, although the ratio of the intensities of the bands at 2955 (due to hard + soft segments) and 3347 cm^{-1} (only due to hard segments) decreases as the h/s segment ratio increases.

The average molecular weight values 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 [28]. As expected, M_w values are higher than M_n ones, and there is a decrease in molecular weight as the hard segment content of the PUs increases (Fig. 2), because the molecular weight of the macroglycol is higher than that of the chain extender and MDI. The M_w/M_n ratio is somewhat higher than 2 and increases as the soft segment content in the PUs increases, indicating that the molecular weight distribution becomes wider due to a relatively lower polymerization rate in the PU manufacture when the amount of macroglycol increases (reduced amount of isocyanate).

Figure 3a shows some DSC graphs of the three PUs. The graphs show one T_g value located at low temperature (which corresponds to the beginning of the movement of soft segment chains), as well as the

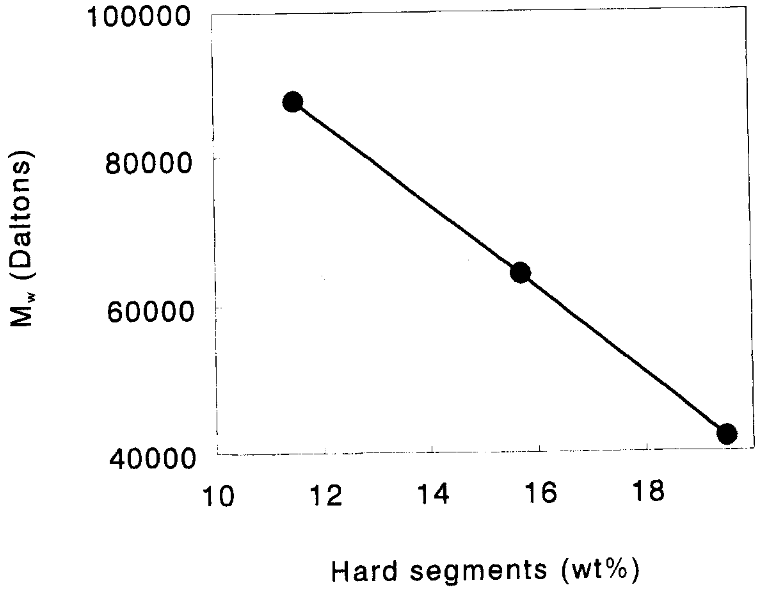


FIGURE 2 Relationship between M_w and hard segment content in PUs.

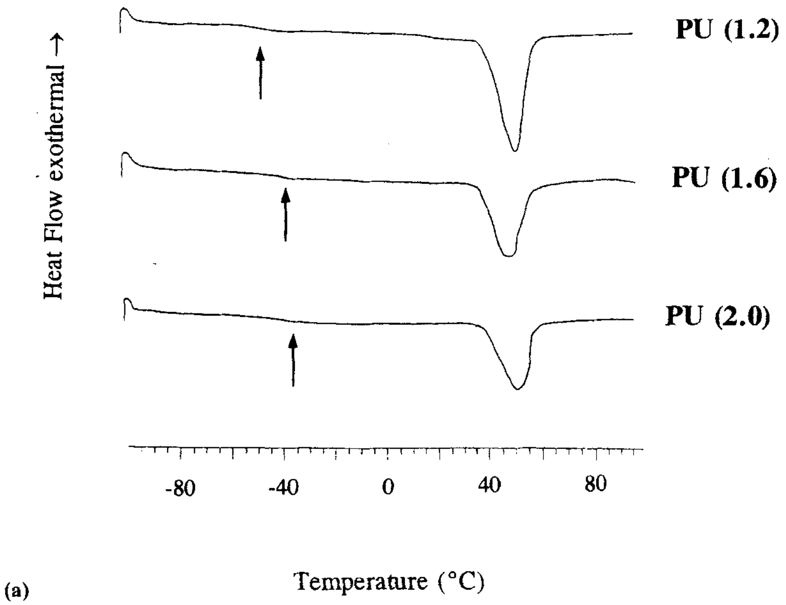


FIGURE 3 a) DSC plots of PUs; b) Crystallization process in the PUs.

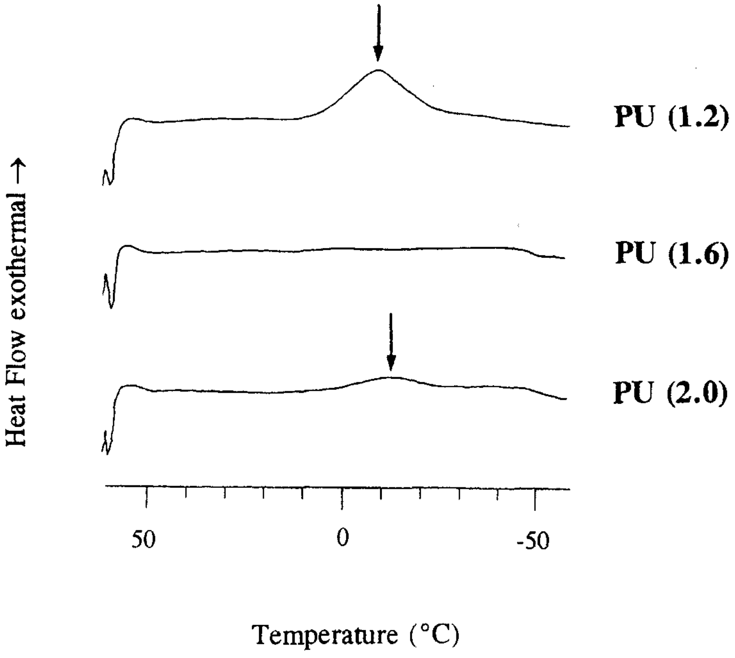
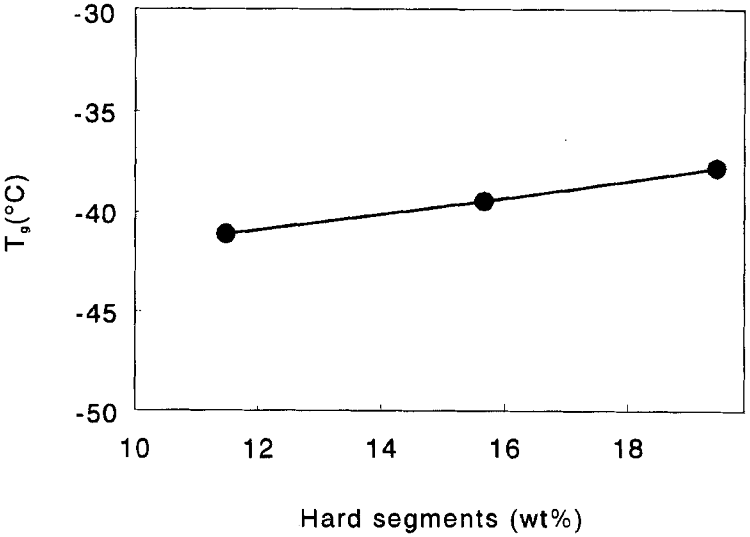


FIGURE 3 (Continued).

melting process (located at higher temperature). These transitions are affected by the h/s segment ratio in the PUs. The glass transition temperature (T_g) increases (becomes less negative) with increasing hard segment content in the PU (Fig. 4a). This indicates that the polyurethane prepared with a higher h/s segment ratio has more miscibility between the hard and soft segments. The more of the hard segments dispersed into the soft segments, the more restricted the movement of the soft segment [4], *i.e.* the increase in h/s segment ratio reduces the extent of the phase separation in the PU elastomers. According to Figure 3a, the melting process is always produced between 40 and 60°C but the melting enthalpy decreases as the h/s segment ratio increases (Fig. 4b), due to a reduction in the strength of the secondary interaction between polymer chains (mainly between the soft segments), which is in agreement with a reduction in the degree of phase separation. On the other hand, Figure 3b shows the crystallization curves of the PUs determined using DSC. The crystallization of the PUs is



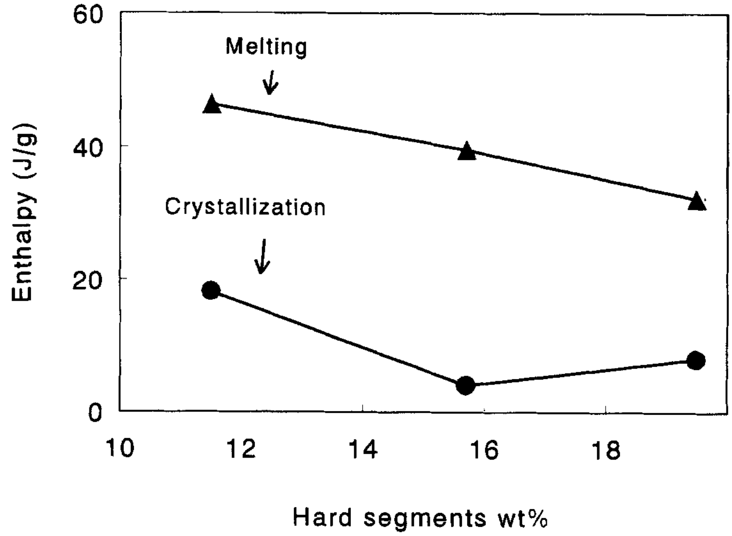


FIGURE 4 a) Variation of glass transition temperature (T_g) with the hard segment content in PUs; b) Variation of melting and crystallization enthalpies with the hard segment content in PUs.

produced at about −10°C and the crystallization enthalpy (Fig. 4b) decreases as the h/s segment ratio in the PUs increases. Therefore, the increase in the h/s segment ratio reduces the interaction between the polymer chains in the soft segments, producing a reduced degree of phase separation in the PUs (*i.e.*, a decrease in melting and crystallization enthalpy, and an increase in T_g).

The variation of the storage modulus (E′) and the loss modulus (E″) as a function of the temperature is given in Figure 5. After the glass transition process, the moduli steadily decrease as the temperature increases, until the softening of the PU occurs (about 40°C). The increase in hard segment content produces a reduction in moduli (before and after the glass transition process) because of the reduced interactions between the soft segments in the PU. T_g values decrease as the hard segment content in the PUs increases (it can be more clearly noticed in Fig. 5b), due to a reduced resistance to the movement of the soft segments under bending. This trend, which is opposite to that obtained with DSC measurements, can be ascribed to the influence of the viscoelastic deformation on the morphology of the

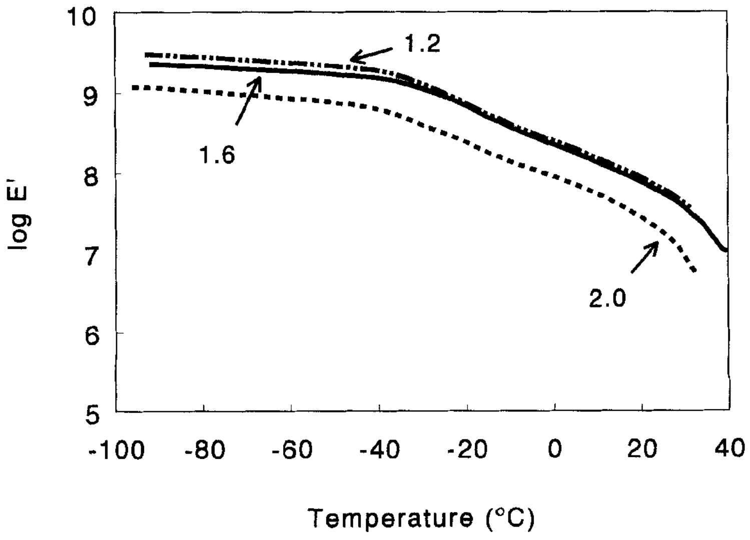
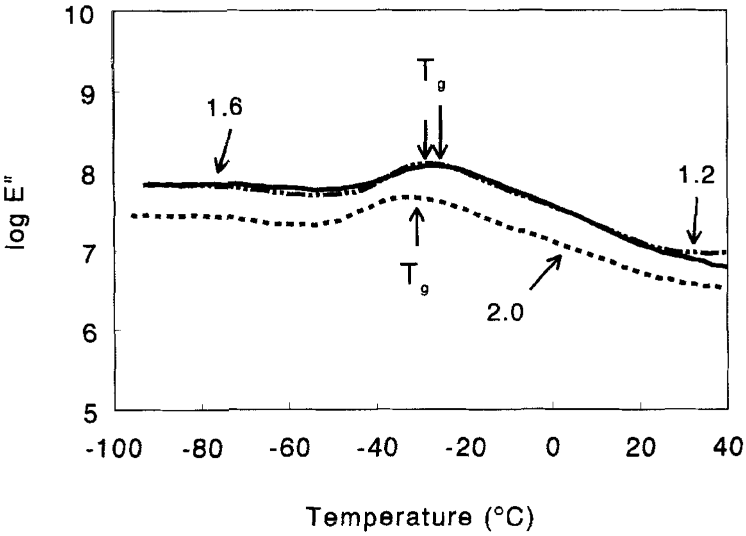


FIGURE 5 Variation of : a) Storage modulus (E′) and b) Loss modulus (E″), as a function of temperature in the PUs. Frequency = 1 Hz. Amplitude = 64 μm peak-peak.



(b)

FIGURE 5 (Continued).

PUs. The differences in T_g values determined from DSC and DMTA have been previously found in other polymers [4].

The stress-controlled rheometer experiments in the PUs provide the experimental results given in Figure 6. The experiments were carried out from room temperature up to 200°C (DMTA experiments are limited to temperatures below the melting point of the PUs). The trends followed by the moduli as a function of the hard segment content are similar to those obtained with DMTA (Fig. 5). The increase in the h/s segment ratio facilitated the reduction in moduli (mainly in storage modulus, Fig. 6a) indicating a smaller degree of interaction between hard and soft segments in PU(2.0), *i.e.* a reduced degree of phase separation. At low temperatures (below 70°C) the storage modulus (G′) is higher than the loss modulus (G″) in the three PUs, but the increase in temperature produces a crossing of the curves and at high temperature the viscous properties dominate over the elastic ones. Figure 7 shows the temperature at which the G′ and G″ moduli are similar (crossing temperature) as a function of the hard segment content in the PUs. The crossing temperature is displaced to lower temperatures in PU(2.0) due to a lesser degree of

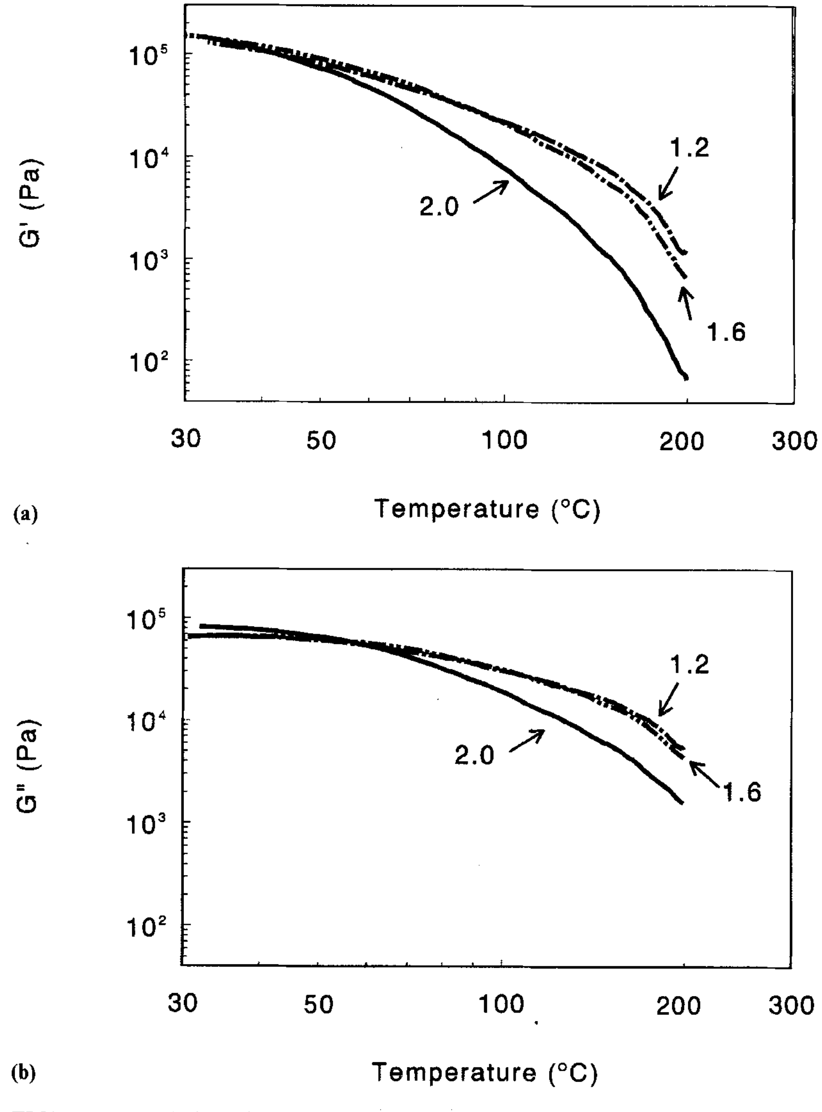


FIGURE 6 Variation of : a) Storage modulus (G′), and b) Loss modulus (G″), as a function of temperature in the PUs. Frequency = 1 Hz. Target strain = 0.05.

phase separation and to a smaller degree of interaction between hard and soft segments.

Previous studies [16, 17] stated that the crystallinity of PU elastomers is provided by the soft segments and that it may be obtained

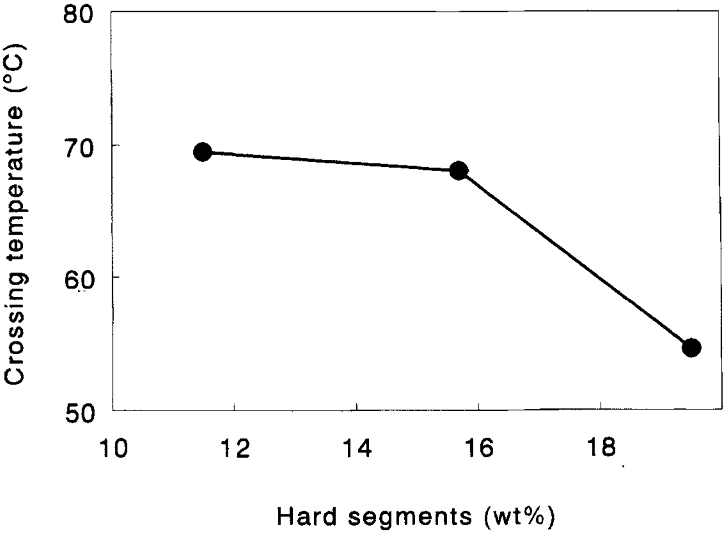


FIGURE 7 Variation of the crossing temperature of storage and loss moduli as a function of the hard segment content in the PUs.

using WAXD. Figure 8 shows, as a typical example, the WAXD pattern of PU(1.2). All diffractograms of the PUs show two peaks at 21° and 24° which correspond to the (110) and (020) diffractions in a polyadipate [16]. The intensity of those peaks is related to the crystallinity of the PUs and the results obtained are given in Figure 9. There is a decrease in crystallinity when the h/s segment ratio increases, the highest variation being produced for amounts of hard segments below 15 wt%. According to Figure 10, there is a relationship between the crystallinity, the melting enthalpy (Fig. 10a) and the T_g value obtained from DSC measurements of the PUs (Fig. 10b). The higher the crystallinity, the higher the melting enthalpy and the lower the T_g, *i.e.* the crystallinity is associated with the degree of phase separation and the interactions between polyurethane chains in the PUs.

The surface properties of PUs were obtained from contact angle measurements. According to Figure 11, the contact angle values are not affected by the h/s segment ratio of the PUs and are close to 58°. Thus, the morphology (*i.e.*, phase separation) and the structure of the polyurethanes do not influence their surface properties.

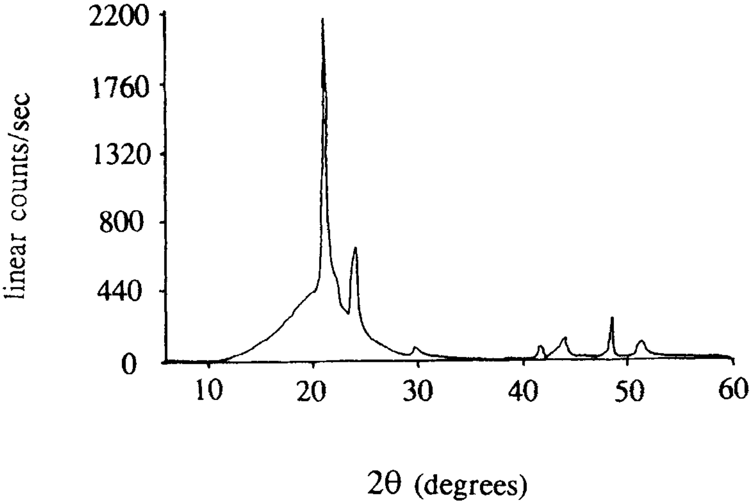


FIGURE 8 X-ray diffractogram of PU(1.2).

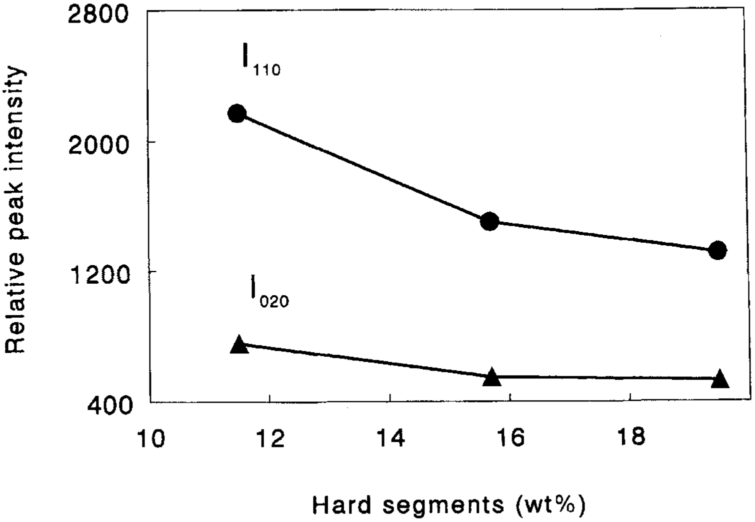


FIGURE 9 Variation of the relative peak intensities of (110) and (020) diffractions with the hard segment content in the PUs.

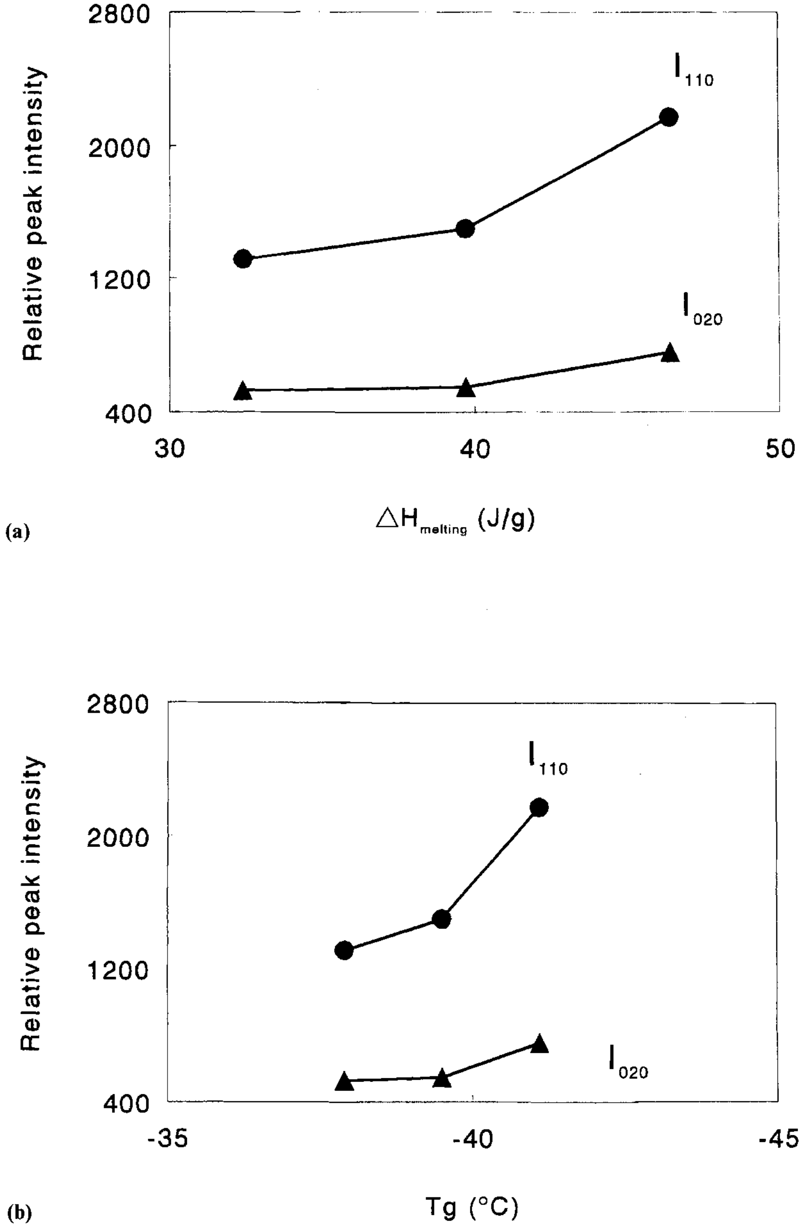


FIGURE 10 a) Variation of the relative peak intensities of (110) and (020) diffractions with the glass transition temperature of the PUs; b) Variation of the relative peak intensities of (110) and (020) diffractions with the melting enthalpy of the PUs.

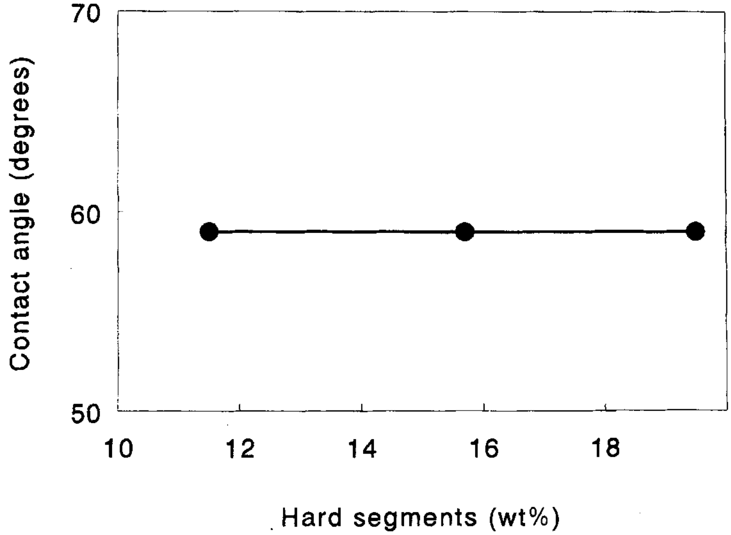


FIGURE 11 Contact angle measurements (ethylene glycol, 25°C) on PUs as a function of their hard segment content.

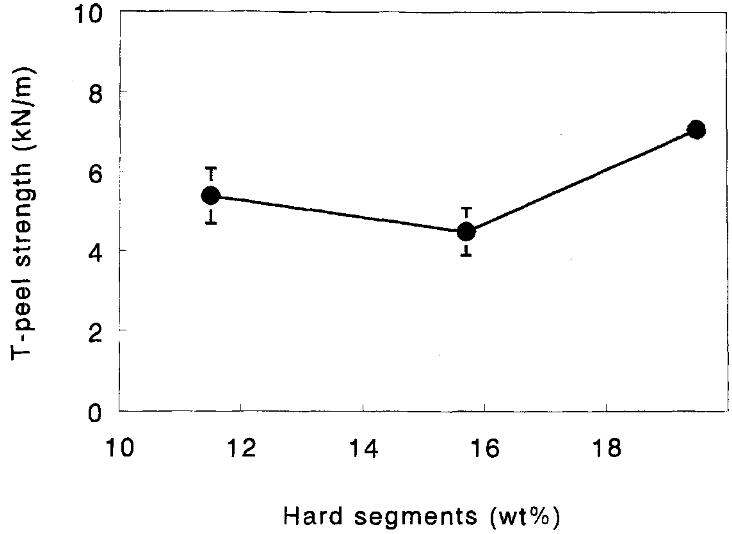


FIGURE 12 Variation of the T-peel strength of solvent-wiped PVC/PU adhesive joints as a function of the hard segment content in the PUs.

T-peel strength values of solvent-wiped PVC/PU adhesive joints are included in Figure 12. In general, an adhesion failure was obtained (assessed by visual inspection of the failed surfaces) and there is an increase in peel strength in the joint prepared using the PU with higher hard segment content. The enhanced interaction at the PVC/PU(2.0) interface is not mainly caused by the surface properties of the polyurethane, but they are influenced by the PU properties (*i.e.*, degree of phase separation and polarity) and thus higher interaction between the hard segments and PVC substrate is produced. This experimental finding has also been previously described in the literature [19, 20]. Thus, Agrawal and Drzal [19] stated that the introduction of phase-separated material in the glass-polyurethane interphase in elastomeric systems had little effect on the adhesion, while Dreyfuss and Larive [20] found that an increase of the polarity of a polyurethane produces enhanced adhesion to glass surfaces.

4. CONCLUSIONS

The h/s segment ratio determines the thermal, mechanical, rheological, surface and adhesion properties of elastomeric PUs. The increase in the amount of hard segments in the PU reduces the extent of phase separation, the degree of secondary interactions between polyurethane chains, and the crystallinity of the PU. On the other hand, the adhesion to PVC is enhanced in joints prepared with PUs having a relatively high hard segment content.

Acknowledgements

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