Development of Polyurethane Engineering Thermoplastics. II. Structure and Properties

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SYNOPSIS

Rigid, tough thermoplastic polyurethanes were synthesized by a two-step technique. These materials presented a complex structure consisting of a continuous, rigid, amorphous, or semicrystalline matrix with a dispersed soft phase. The influence of soft-segment content upon rigidity modulus, heat-distortion temperature, and fracture behavior has been determined on model amorphous polyurethanes. The influence of crystallinity upon final properties has been studied on two materials: a preparation of ours and a commercial product. Various degrees of crystallinity have been induced in the samples by annealing. Phase structure was characterized by differential scanning calorimetry and wide-angle X-ray scattering. Some of the polyurethane samples assayed in this paper exhibited similar properties to those reported in respect of more conventional engineering thermoplastics, such as ABS or nylon. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In Part I of this work,[1] we considered the possibility of preparing segmented copolyurethanes to be used as engineering thermoplastics. The samples obtained presented a complex phase structure. All cases seemed to consist of a soft phase, dispersed in a continuous, rigid, amorphous, or semicrystalline matrix. Generally, the samples examined by DSC displayed three second-order transitions, as well as endo- and exothermic peaks. The influence of formulation, polymerization conditions, and processing on the final phase structure was investigated, and it was possible to clarify the nature of the three second-order transitions and of the endo- and exothermic peaks. The aim of Part II was to provide a mechanical characterization of these new materials and to correlate their properties with their physical structure.

Although many physicomechanical studies have been done on elastomeric polyurethanes (see, e.g., Refs. 2–14), little has been published on rigid versions,[15-17] especially on those having more than 70% hard-segment content.[18] Some preliminary studies[19] showed that physicomechanical properties are dependent on both the hard-to-soft-segment ratio and crystallinity. Model polyurethanes were thus prepared to determine independently the contribution of these two variables to the final properties of the material.

To determine the influence of the former variable, two series of samples with varying soft-segment content were specially prepared. To examine the influence of the latter variable, some originally amorphous samples were subjected to different annealing treatments, so as to induce them to crystallize to different degrees. The effect of crystallinity was also studied on a commercial polyurethane material.

EXPERIMENTAL

Materials

Model polyurethanes based on 4,4'-diphenylmethane diisocyanate, 1:1 mass ratio of polypropylene oxide diol and polypropylene oxide endcapped with ethylene oxide as polyols, and 4:1 mol ratio of 1,4-butanediol and 1-phenyl-1,2-ethanediol as chain

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extenders were prepared in our laboratory by the prepolymer method, as previously described.[1] This polyurethane, called Type VI in our previous paper,[1] was chosen for the present investigation because its crystallinity turned out to be more easily controllable. Henceforth, a two-sequence code nomenclature, indicating only hard/soft-segment content and the curing temperature used, will be employed to label the different samples.

Two series of samples with a hard-to-soft-segment ratio varying from 95/05 to 75/25, but differing in the "curing temperature" (110 or 250°C), were prepared. Materials cured at 250°C were cooled to room temperature by immersion in cold water and then dried at 100°C under vacuum for 24 h, before being molded, while, after curing at 110°C, the materials were just left to cool naturally to room temperature. The commercial product examined was Isoplast 201 (Upjohn), which is defined as an engineering thermoplastic.[20,21]

Specimen Preparation

All materials were compression-molded into platelets of about 6 mm thickness. The procedures followed were different for the materials prepared in our laboratory and for the commercial product. In the case of the polyurethanes synthesized by us, the air embodied during the violent stirring in the second step of polymerization led to foamy pieces not suitable for direct mechanical characterization. In addition, their low melt viscosity and their tendency to present bubbles made compression molding also rather difficult. The following procedure was finally adopted: A single piece cut from the polymerization product was introduced into a mold preheated at 200°C, gently pressed and kept at this temperature for 15 min under a very low pressure. Subsequently, pressure was increased to 6 MPa, and the mold was then rapidly cooled with running water at 15°C. Isoplast 201 was available in the form of pellets. These were first dried under vacuum at 100°C for 4 h, following the recommendations given by the manufacturer.[20,21] They were then kneaded on a two-roll mill at 190°C and the calendered material was then introduced into the mold, preheated to 230°C, and kept at this temperature for 10 min without any pressure, after which the mold was cooled suddenly with running water and the temperature was continuously monitored with a thermocouple. When the temperature reached 180°C, a pressure of 6 MPa was applied, and cooling continued down to room temperature.

To relieve possible residual stresses generated during molding, all the platelets were subjected to a postmolding thermal treatment at 120°C for 5 h, followed by 10°C/h cooling to room temperature. All subsequent measurements were performed on pieces or specimens machined from the molded platelets.

Measurements

Thermal properties were determined using a Mettler TA 300 system equipped with a DSC 30 low-temperature unit. Temperature calibration was done with a multiple indium–lead–nickel standard. An indium standard was used for heat-flow calibration. Measurements were taken at a scanning rate of 20°C/min from −100 to 300°C.

Glass transition temperatures were taken at the inflection point of the thermograms, and the melting points were taken at peak temperatures. The heat of fusion was calculated by measuring the area under the endothermic peaks.

Crystallinity was analyzed by wide-angle X-ray scattering (WAXS). Studies were performed on a Philips PW 1050 diffractometer, employing nickel-filtered CuKα radiation, in the reflectance mode. The 2Θ scan rate was 2°/min. For quantitative purposes, data were normalized by background noise. For each type of material, a standard amorphous template was defined as the one that displayed the most diffuse scattering and for which DSC thermograms showed no simultaneous melting. The amorphous index was calculated as the relative area of the amorphous region.[22] The degree of crystallinity reported here is the complement to the amorphous index.

Flexural modulus was measured in three-point bending, at a crosshead speed of 5 mm/min, using an Instron 1121 dynamometer. Bars 127 × 12.7 × 6 mm were used and modulus determined from the slope of the initial straight portion of the stress–strain curve.

Heat-distortion temperature was measured on 127 × 12.7 × 6 mm bars according to ASTM D648-72 specification, under a load giving a maximum fiber stress of 1820 kPa.

Fracture mechanics characterization was performed in three-point bending with a span-to-width ratio of 4, using an Instron 1121 dynamometer, at room temperature, at a constant crosshead speed of 5 mm/min. Specimens were single-edge-notched 63.5 × 12.7 × 6 mm bars. Sharp notches were introduced by scalpel-sliding a razor blade having an on-edge tip radius of 13 μm.

For materials that exhibited brittle behavior, the critical stress intensity factor, K_{Ic}, at fracture ini-

tiation was determined according to ASTM Standard E399-83 for metals.[23] (Variants, such as those introduced by the testing protocol recently developed by the Task Group on Polymers and Composites of the European Structural Integrity Society [ESIS, formerly EGF],[24] would not alter the significance of the data here obtained for the purpose of comparing different materials within a same family.)

Tests were carried out with specimens of varying notch length, a. The value of K was obtained from the slope of the plot $\sigma_c^2 Y^2$ vs. a^{-1}, σ_c being the critical stress for fracture initiation, and Y, a geometrical factor taken from Ref. 23.

For the characterization of fracture resistance in more ductile materials, the J-integral method was adopted. We determined the J-resistance curve, J_R, according to the multispecimen technique covered by ASTM Standard E813-81.[25] (Although the data handling recommended by the ASTM Standard E813-81 has now been questioned and some variations in the testing procedure have been proposed for both metallic[26] and polymeric[27] materials after our measurements were carried out, we believe that the data presented here are still significant for comparing different materials within a same family). Each of several specimens was loaded to a different

deflection, and J was calculated from the input energy U, measured at the final deflection according to the expression

$$J = \frac{2U}{B(W - a)}$$

in which B, W, and a are the specimen thickness, width, and initial notch length, respectively. The crack growth was evidenced by painting the fractured surface with an iodine solution before unloading.[28]

The specimens tested were then fractured completely at a higher speed so as to change the fracture regime and, therefore, the fracture surface morphology. The initial crack length and the amount of crack extension could thus be measured from the surface of the completely broken samples with a microscope.

The J values obtained are then plotted against the Δa measure, giving the J_R curve. Since with ductile materials some crack tip blunting may occur prior to the real crack propagation, to determine the onset of crack extension according to Ref. 25, the J vs. Δa curve is extrapolated to intersect the blunting line, which is assumed to be expressed by
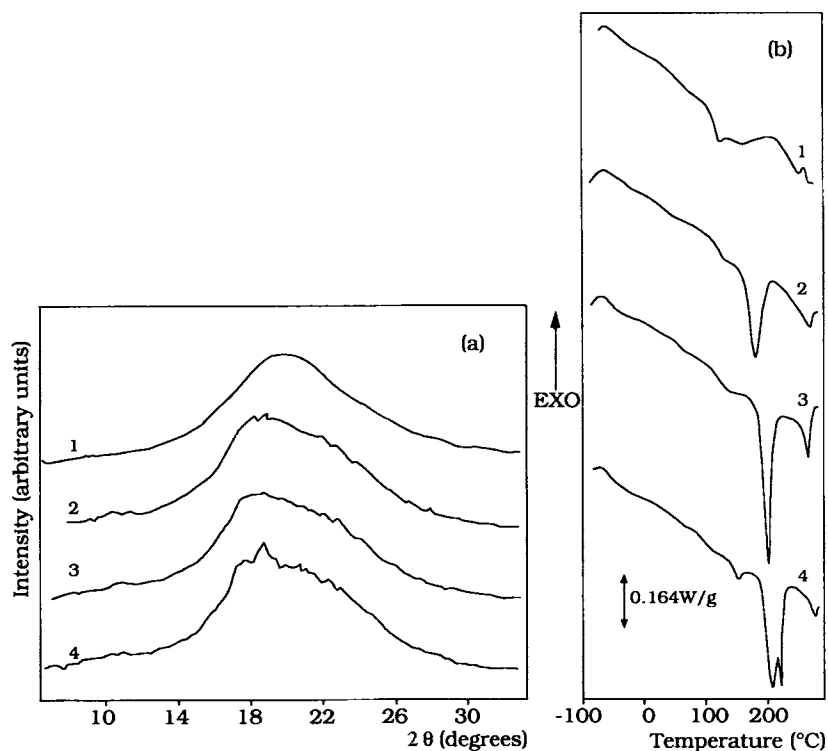

Figure 1   (a) WAXS patterns and (b) DSC thermograms of samples of 80/20:250 polyurethane subjected to different thermal treatments (see Table I).

$$J = 2\sigma_y \Delta a$$

in which σ_y is the tensile yield stress. While the intersection gives the fracture resistance, J_{Ic}, at fracture initiation, the slope dJ/da of the linear region of the J_R curve represents the resistance to crack propagation.

In all the fracture tests performed, the size requirements set by Standards E399-83 and E813-81 for the validity of both K_{Ic} and J_{Ic}, respectively, were always met.

RESULTS AND DISCUSSION

Effect of Crystallinity

Structural Analysis

As we showed in our previous work,[1] crystallinity may be induced in rigid thermoplastic polyurethanes by annealing. Samples of the 80/20:250 polyure-

thane and of Isoplast were annealed for time periods of 12–48 h, at constant temperatures between 150 and 170°C.

Figures 1 and 2 show the relevant WAXS patterns and DSC thermograms, and Table I, the results of their analysis. Figures 1(a) and 2(a) show that WAXS results are rather similar for the two materials; untreated samples (curve 1 in both figures) display a diffuse scattering maximum for 2Θ from 12 to 30°, suggesting an amorphous morphology. Afterward, annealing changes in the diffraction patterns are observed; samples annealed at intermediate temperatures display weak diffraction peaks that become more distinct peaks as annealing temperature increases. The diffraction peaks appear more distinct for Isoplast than for the 80/20:250 polyurethane. Table I shows crystallinity indices calculated from these patterns, and it may be observed that crystallinity increases with annealing temperature.
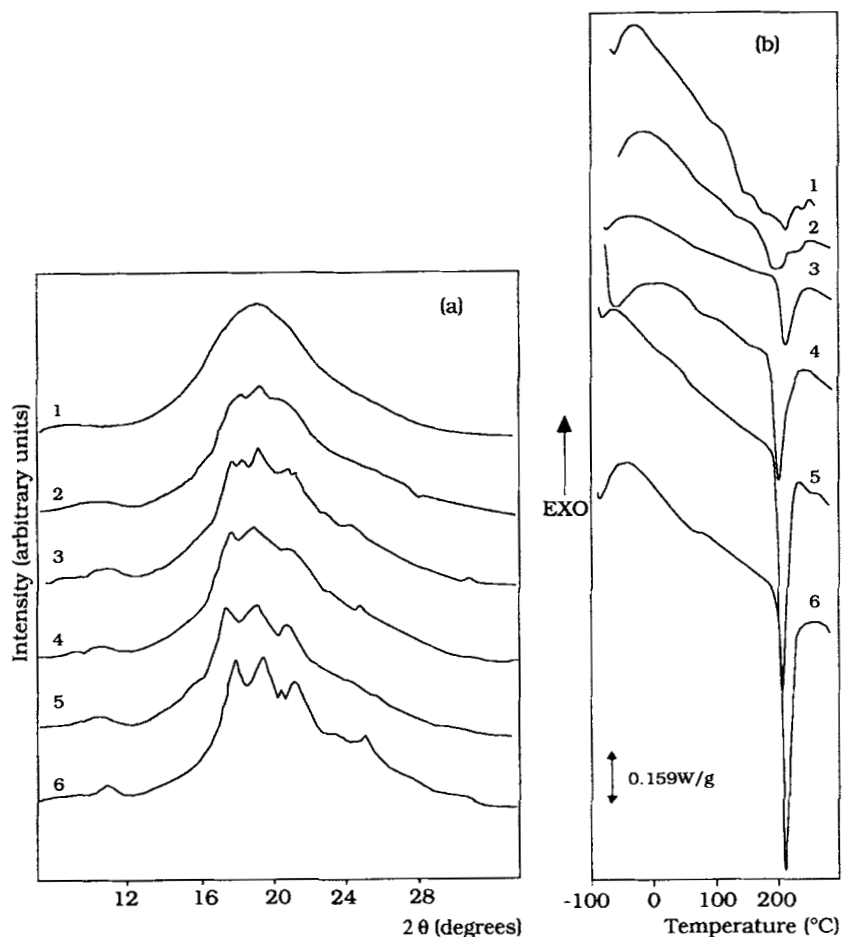

Figure 2   (a) WAXS patterns and (b) DSC thermograms of samples of Isoplast subjected to different thermal treatments (see Table I).

Table I   DSC and WAXS Data for 80/20:250 Polyurethane and Isoplast 201, Annealed at Different Temperatures

Material	Sample	Thermal Treatment	T_m (°C)	ΔH (J/g)	Crystallinity Index (%)
80/20:250	1	Untreated	—	—	0
	2	24 h at 140°C	186	18.1	11
	3	24 h at 160°C	205	22.4	14
	4	24 h at 170°C	210–225	26.6	33
Isoplast	1	Untreated	—	—	0
201	2	48 h at 130°C	180–200	16.2	7
	3	12 h at 150°C	210	18.9	8
	4	24 h at 150°C	190	26.5	11
	5	24 h at 160°C	210	32.4	13
	6	24 h at 170°C	218	39.3	17

DSC thermograms for the two materials are shown in Figures 1(b) and 2(b). For the 80/20:250 polyurethane, the untreated sample [curve 1 in Fig. 1(a)] displays the three transitions discussed previously[1] and named hard (T_h), intermediate (T_i), and soft (T_s), at about −50, 50, and 100°C, respectively. After annealing, the samples display endothermic peaks indicating the presence of crystallinity, and both the peak temperature and the heat of fusion increase with the annealing temperature. As for the amorphous phase of the annealed samples, the three transitions are still observable, and their relative importance does not change so much as crystallinity changes, indicating that the amorphous phase, although quantitatively decreasing with increasing crystallinity, does not appear to change much qualitatively.

As for Isoplast, DSC thermograms [Fig. 2(a)] show for the untreated sample (curve 1) two hard-phase, second-order transitions, T_i and T_h, at about 50 and 100°C, like our polyurethanes, and a less evident soft-phase, second-order transition, T_s, at about −20°C. The annealed samples show an endothermic peak that becomes larger and shifts toward higher temperatures as annealing temperature increases. However, it may be observed that, for the crystalline Isoplast samples, as crystallinity increases, the hard transition, T_h, practically disappears, while the intermediate one, T_i, is still present. In our previous work,[1] the presence of the two transitions, T_i and T_h, was attributed to the existence of a length distribution in the segments of the rigid phase, in agreement with other authors.[29] Accordingly, it seems from the DSC results that the crystallinity in Isoplast develops at the expense of the segments that give rise to T_h, indicating a qualitative structural change in the hard amorphous phase as crystallinity increases.

Mechanical Properties

The mechanical properties of the samples of the series with varying degrees of crystallinity were related to the crystallinity index: Flexural modulus, E, and heat-distortion temperature, HDT, as a function of crystallinity index are shown in Figures 3 and 4 for the 80/20:250 polyurethane and Isoplast, respectively. As expected, in the case of 80/20:250, both E and HDT slightly increase as the crystallinity index increases. For Isoplast, however, a decreasing trend between flexural modulus and crystallinity index was found. This unexpected result may be explained in terms of the structural changes accounted for above, which take place as crystallinity develops. As crystallinity increases, the part of the amorphous phase with higher transition temperature becomes less, and the overall rigidity at room temperature decreases, at least for the crystallinity levels examined.

As for the HDT, a slight decrease is observed for crystallinities up to about 12%, after which an increase takes place. These results are also in agreement with this picture. HDT indicates the temperature at which a certain deformation is reached under a fixed load while temperature increases linearly. Thus, at low degrees of crystallinity, we observe only the result of the diminishing of part of the amorphous rigid phase with higher transition temperature; at higher levels of crystallinity, the amount of crystalline phase becomes sufficient to limit the deformation of the specimen up to higher temperatures.

Results of fracture mechanics tests are shown in Figures 5 and 6 for 80/20:250 and Isoplast, respectively. The 80/20:250 polyurethane showed ductile behavior at least for crystallinities up to about 14%; therefore, we should use the J-integral method for
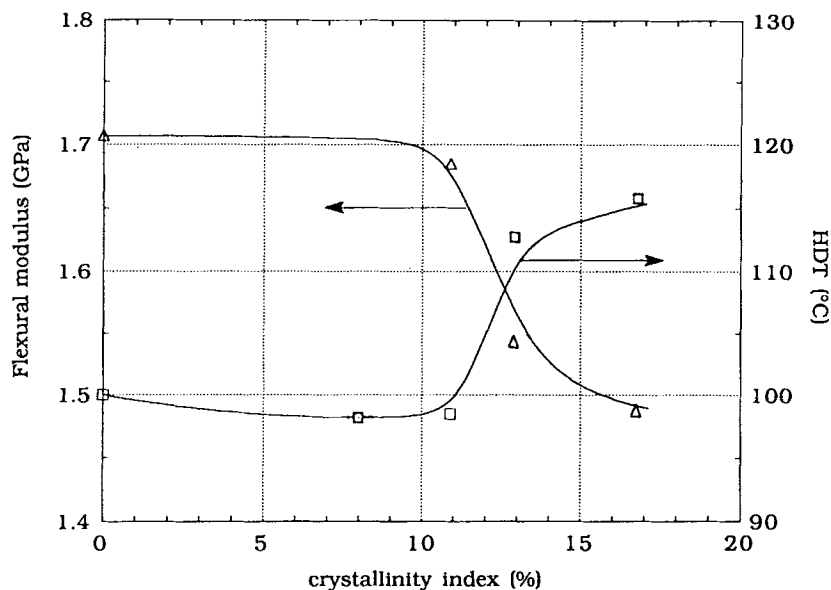
Figure 3 Flexural modulus, E, and heat-distortion temperature, HDT, vs. crystallinity index for 80/20:250 polyurethanes.

the characterization of its fracture resistance. The sample with 33% crystallinity was too brittle to be mechanically tested. Figure 5 shows the trend of J_{Ic} and dJ/da with the crystallinity index. Both resistance to fracture initiation, J_{Ic}, and resistance to crack propagation, dJ/da, decrease with increase in the crystallinity index, with a marked drop around a crystallinity index of 10%. For Isoplast, only the amorphous sample exhibited ductile behavior, giving

a J_{Ic} value close to 6 kJ/m^2; semicrystalline Isoplast samples all exhibited brittle behavior. Hence, K_{Ic} was used to measure the material toughness except for the amorphous sample for which it was deduced from the measured value of J_{Ic} through the relationship as $K_{Ic} = J_{Ic}(E/1 - \nu^2)^{0.5}$, in which E is the elastic modulus, and ν, the Poisson coefficient (taken as 0.33). The variation of K_{Ic} with crystallinity (Fig. 6) shows a drop of 200% in mater-
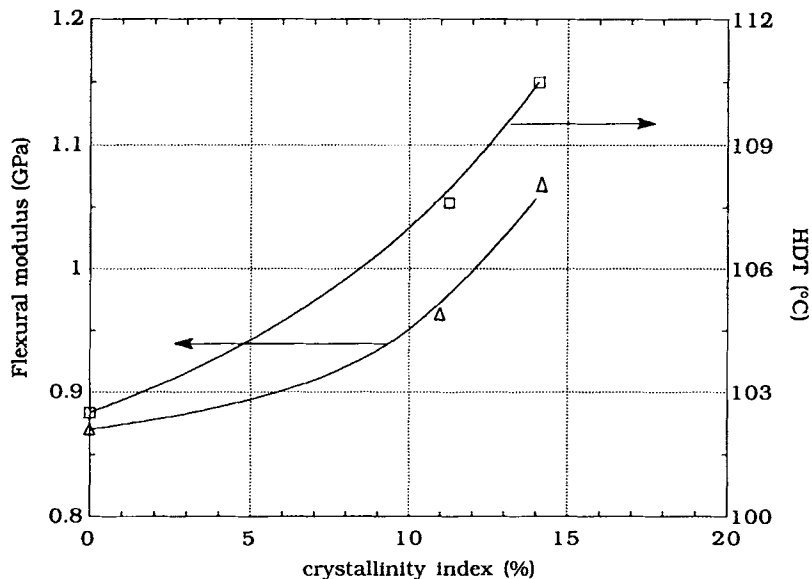

Figure 4 Flexural modulus, E, and heat-distortion temperature, HDT, vs. crystallinity index for Isoplast 201.
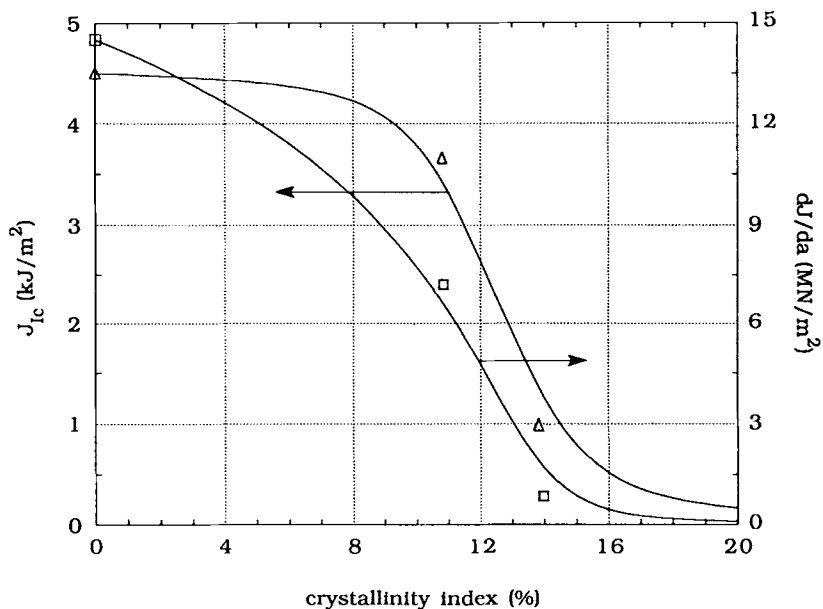
Figure 5   Fracture behavior of 80/20:250 polyurethane: J_{Ic} and dJ/da vs. crystallinity index.

ial fracture toughness for a crystallinity index above 6%.

Finally, comparison between the two materials shows in any case that the more amorphous the material the better its fracture toughness. However, our polyurethane has a greater potential for toughness over a larger range of the crystallinity index, i.e., up to at least 14%.

Effect of Hard-to-Soft-Segment Ratio

Structural Analysis

The effect of soft-segment content on mechanical properties was studied on two series of polyurethanes, prepared with curing temperatures of 110 and 250°C. DSC thermograms of these materials are shown in Figure 7(a) and (b). Materials 95/5:
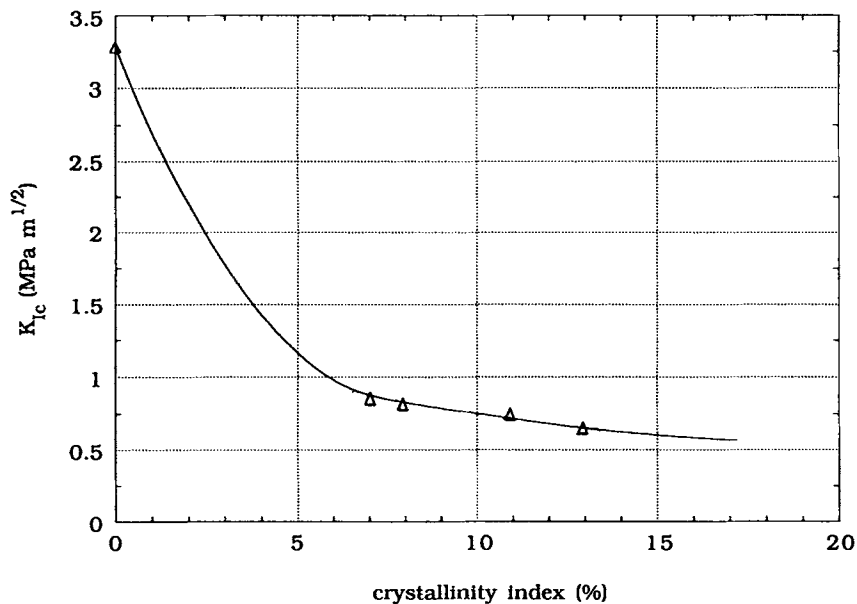

Figure 6   Fracture behavior of Isoplast 201: K_{Ic} vs. crystallinity index.
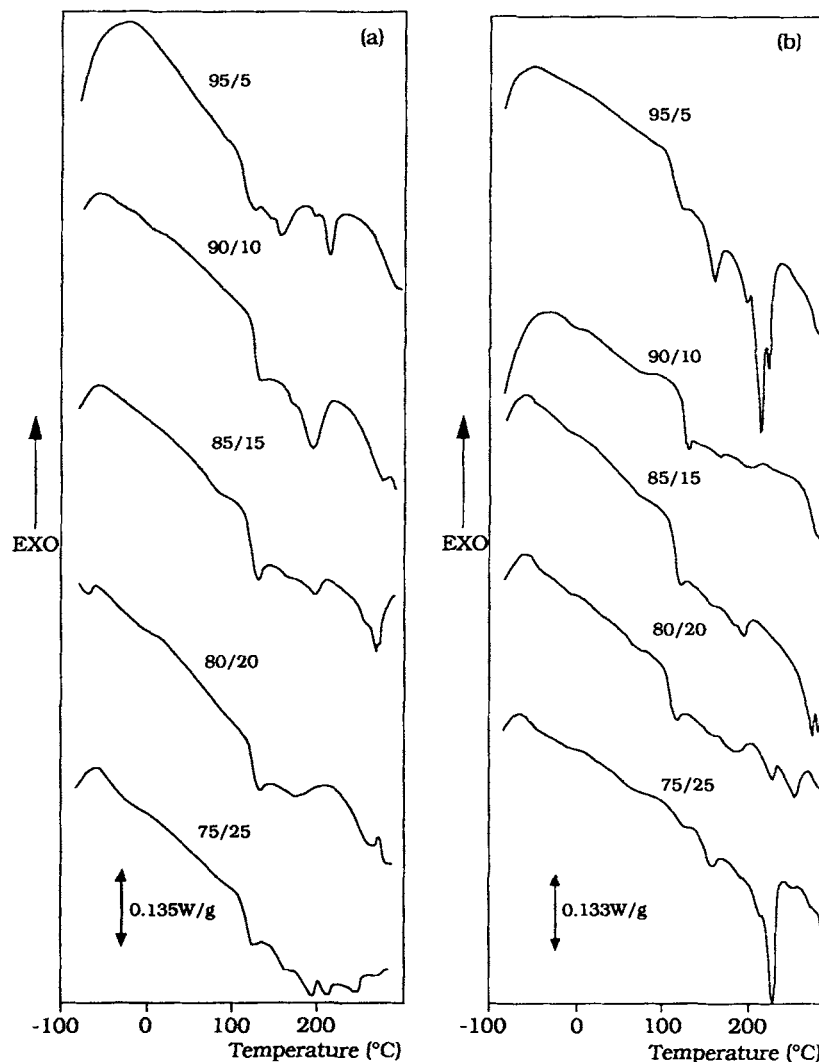
Figure 7 DSC thermograms of polyurethanes having different hard/soft-segment ratios (a) cured at 110°C and (b) cured at 250°C.

110 and 75/25:110 display high endothermic peaks. All other materials appear fairly amorphous. The usual three second-order transitions, T_h, T_i, and T_s, are present, and their relative intensity depends on the hard/soft-segment ratio and on the presence of crystallinity.

Mechanical Properties

Although the samples obtained from the polymerization procedure having a soft-segment content of more than 20% did not present any noticeable anomaly after being compression-molded, they exhibited some tendency to delamination, and some samples also showed some macroscopic phase separation. Heterogeneities in bulk-polymerized poly-

urethanes had previously been reported.[18,30] This fact made test specimen preparation difficult. Subsequent mechanical testing, especially fracture measurements, was therefore not possible on all the materials with different hard/soft-segment ratios prepared.

In Figure 8, flexural modulus is plotted against soft-segment content, for both series of materials. Data points for both series overlap, with the sole exception of the extremes values of the series cured at 110°C. As expected, the modulus decreases continuously as soft-segment content increases. The discrepancy found for the extreme values is probably due to the presence of crystalline structures, which were observed to enhance the flexural modulus of this type of polyurethane (see Fig. 3). Values of the
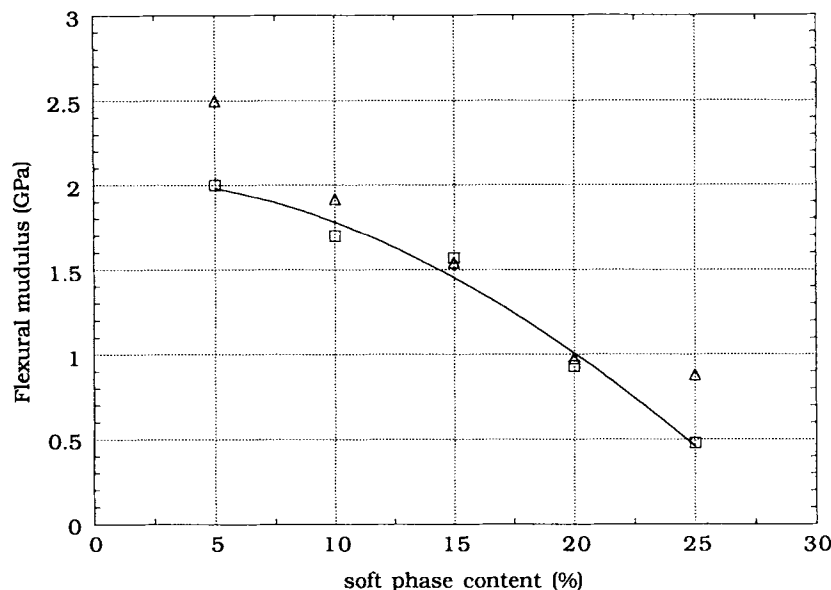
Figure 8 Flexural modulus, E, vs. soft-segment content for the two series of polyurethanes prepared: ($\triangle$) curing temperature 110°C; ($\square$) curing temperature 250°C.

energy for fracture initiation, J_{Ic}, measured on samples with different soft-segment content of both series of materials cured at 110 and 250°C, are reported in Table II. The materials with 90/10 and 80/20 hard/soft ratios for both curing temperatures showed the highest fracture toughness, with good overall mechanical properties. For unknown reasons, the 85/15 hard/soft-segment samples always exhibited a poor fracture resistance.

From the present results, it seems that a soft-segment content of less than 10% is not effective for toughening rigid thermoplastic polyurethanes, whereas materials containing more than 20% lack in mechanical properties, probably because of some substantial degree of macrophase separation.

Table II   Energy-to-Fracture-Initiation, J_{Ic}, for Polyurethane Series Cured at 110°C and 250°C, with Varying Hard/Soft Ratios

Curing Temperature (°C)	Hard/Soft	J_{Ic} (kJ/m²)
250	90/10	6.2
	80/20	5.8
110	95/5	0.1
	90/10	6.0
	85/15	2.5
	80/20	5.0
	75/25	0.1

CONCLUSIONS

Two series of polyurethanes with varying hard/soft-segment ratios, cured at 110 and 250°C, were prepared. High melting point, low melt viscosity, and entrapped bubbles made compression-molding rather difficult. This notwithstanding, we were able to mold fairly amorphous thick platelets suitable for mechanical testing for most of the materials prepared.

For these two series, the best overall mechanical properties were found for materials with 90/10 and 80/20 hard/soft ratios. One of the polyurethanes prepared by us (80/20:250) and a commercial material (Isoplast 201) could be obtained with varying degrees of crystallinity by subjecting amorphous samples to suitable thermal treatments. For both materials, the best fracture resistance was observed in the amorphous state. The 80/20:250 polyurethane appears ductile and tough up to crystallinity indices of about 15%, whereas with Isoplast 201, a great loss in fracture toughness is already observed for a crystallinity index of 6%.

Depending on soft-segment content, molding conditions, and thermal treatments, it was possible to obtain polyurethanes with mechanical and physical properties similar to those reported for conventional thermoplastics, such as ABS[28] and rubber-modified polyamide.[31] Further research should aim to improve polymerization and molding conditions in order to prevent undesirable macrophase separation.

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