

Notes to the Editor

Thermoplastic polyurethane elastomers based on aliphatic diisocyanates: thermal transitions

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INTRODUCTION

It is now generally accepted that thermoplastic polyurethane elastomers of commercial interest which are derived from a polymeric diol, bis(4-isocyanatophenyl)methane (MDI) and 1,4-butanediol exist at equilibrium as two phase systems¹. The continuous, elastomeric soft phase consists of segments derived mainly from the polymeric diol in which are dispersed a proportion of the hard phase segments in the form of domains, these being derived from the MDI and butanediol.

As the proportion of hard phase segments is increased from zero the glass transition temperature (T_g) of the elastomer, attributable to the soft phase, initially rises rapidly and then more or less levels off². The increase in T_g compared with that of the pure polymeric diol, which is noted at lower hard segment contents, is due in part to decreased mobility of the soft segments because of their attachment to stiffer groups. Penetration of isolated hard segment units into the soft segment phase also contributes to the effect on T_g . The fact that increasing the hard segment content beyond a certain limit results in only minimal further increases in T_g indicates a limited solubility of hard segments in the soft segment phase or an increased tendency for hard segments to remain in the hard segment domains because of the increased ability for the hard segment phase to form more ordered domains simply by virtue of the greater concentration of hard segments.

A similar set of circumstances is reported for elastomers in which 2,6-tolylene diisocyanate (2,6-TDI) replaces MDI². In this case there is a greater tendency for penetration of the soft segment phase by the hard phase

so that the T_g of the soft segment phase is raised to a higher value before the maximum value is reached. On the other hand with 2,4-tolylene diisocyanate (2,4-TDI) no maximum is reached within the limits of hard segment concentration studied². This does not necessarily imply that the product is homogeneous but the evidence is that any phase separation is minimal.

Factors influencing the MDI-based hard segments to exist as a separate phase are (a) their tendency to crystallize (b) the ease of access, i.e. low steric hindrance, of urethane groups in a hydrogen bonding process and (c) the inherent insolubility in the soft phase segments. In the case of the 2,6-TDI-based materials all three factors probably contribute but to a lesser extent whereas with 2,4-TDI-based elastomers (a) will be absent (b) reduced and (c) probably similar to that obtained with 2,6-TDI-based elastomers. The main factor contributing to the differences between MDI and 2,6-TDI on the one hand and 2,4-TDI on the other is probably the unsymmetrical nature of the latter.

From the above it might be predicted that unsymmetrical diisocyanates would give rise to elastomers with little or no phase separation and that the use of symmetrical diisocyanates would result in substantial phase separation. This postulate was tested on the elastomers described below.

EXPERIMENTAL

Prepolymers were made by reacting poly(ethylene adipate) of \bar{M}_n 2000 with the diisocyanates below in the molar ratio 1:4. The prepolymers were then mixed with a slight excess of 1,4-butanediol whilst raising the temperature to 180°C. The products

were converted to films by solvent casting from dimethylformamide. The diisocyanates used were (A) an 80:20 molar mixture of 2,4- and 2,6-tolylene diisocyanates (TDI), (B) hexamethylene 1,6-diisocyanate (HDI), (C) bis(4-isocyanatocyclohexyl)methane (H₁₂MDI) and (D) 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI).

Samples of the films, some 3 years old, were examined in a Du Pont 990 Thermal Analyzer equipped with a differential scanning calorimeter attachment, over the range from -100° to 200°C at the rate of 20°C/min. The samples were then quenched in liquid nitrogen and returned to room temperature. These samples were re-examined under the conditions specified above after storage at room temperature for 12–13 days. Results obtained during both runs in the thermal analyser are outlined in Table 1. A typical analysis of an MDI-based elastomer of similar constitution is included.

RESULTS AND DISCUSSION

TDI-based elastomer

The high T_g compared with that of the MDI-based elastomer indicates a considerably higher penetration of the soft segments by hard segments (i.e. higher solubility) than is obtained in the MDI-based equivalent.

We have no proof that the endotherm noted at 43°C can be attributed to a melting phenomenon of the soft segment phase. However endotherms in similar elastomers which occurred at temperatures below the melting point of the pure polymeric diol have been attributed to melting of the soft segments in derived elastomers³. Thus, the endotherm at 43°C noted in the sample aged for some 3 years may indicate that a relatively pure soft segment phase can separate under certain circumstances which cannot be specified from the present study. The absence of

Table 1 Thermal transitions

Diisocyanate	Hard segments (wt %)	First heating cycle				Second heating cycle	
		T_g^b ($^{\circ}\text{C}$)		Endotherms ($^{\circ}\text{C}$)		T_g^b ($^{\circ}\text{C}$)	
TDI	32	-16	43 (Very small)	-21	None		
HDI	32	-42	42 (Sharp, medium strength) 156 (Sharp, strong)	-46 (Very sharp)	32 (Medium strength) 156 (Sharp, strong)		
H ₁₂ MDI	40	-39	52 (Small) 80 (Small) 130 (Sharp, strong)	-43 (Sharp)	66 (Broad) 132 (Sharp, strong)		
IPDI	36	-32 to -35	51 (Broad, very strong)	-37	38 (Strong)		
MDI ^a	39	~-31	~205 (Sharp, strong)	~-31	~205 (Sharp, strong)		

^aThe elastomer based on MDI was prepared by injection moulding, not solvent casting.

^b T_g as indicated by the onset of the transition

an endotherm above 100°C, though it cannot be taken as proof of the absence of a separate hard segment phase, indicates that if such a phase exists the binding forces are weak.

HDI- and H₁₂MDI-based elastomers

The much lower T_g found in these elastomers compared with the MDI based equivalent point to more complete phase separation than in the latter. Both provide evidence of the existence of a separate hard segment phase in the endotherms noted above 100°C. The presence of a separate soft segment phase is further indicated in the HDI-based material by the endotherm noted below 100°C. As with the TDI-based elastomer an endotherm below 100°C appeared in the H₁₂MDI-based sample only in the sample aged for 3 years.

We offer no explanation of the endotherm noted below 100°C in the latter elastomer but above the melting point of the soft segment (~54°C).

IDPI-based elastomer

Judged by its T_g the IPDI-based elastomer appears to show better phase separation than the MDI-based equivalent. There is evidence for the existence of a relatively pure soft segment phase in the endotherm noted below 100°C. As with the TDI-based elastomer, the absence of an endotherm above 100°C is not proof of the absence of a hard segment phase but again indicates weak binding forces if a hard segment phase exists.

The results obtained in this study indicate a much stronger tendency for aliphatic diisocyanate-based urethane

thermoplastic elastomers to exist in two phases than do aromatic diisocyanate-based equivalents. Surprisingly this occurs even when an unsymmetrical aliphatic diisocyanate is used and therefore in the absence of the driving force in phase separation involving the tendency of the hard segments to form crystallites. We conclude that the main driving force leading to improved phase separation in the aliphatic diisocyanate based materials is connected with the greater strength of hydrogen bonds formed from aliphatic diisocyanate derived urethane groups and/or the different polarities. The greater flexibility of segments derived from aliphatic diisocyanates may also contribute to the effect in that they are less liable to be trapped in the soft segment and held there by ester/urethane hydrogen bonds.

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Effect of photodegradation on the rate of spherulitic growth of poly(ethylene glycol adipate)

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INTRODUCTION

The effect of degradation on the rate of crystallization of polymers has received little attention. Polymer degradation generally results in one or several of the following main effects: crosslinking, main chain scission and side chain scission sometimes accompanied by unsaturation formation¹.

The present study concerns the rate of growth of spherulites in poly(ethylene glycol adipate) (PEGA) irradiated at room temperature in air, either pure or in the presence of benzophenone, with u.v. light of wavelength 253.7 nm. Crosslinks are formed in the polymer in both cases.

The rate of crystallization of the undegraded polymer has been thor-

oughly investigated by numerous authors owing to the large size of the formed spherulites, their easily observable growth rate and their interesting morphology²⁻⁴. Three major structures of spherulites have been identified between 15° and 50°C by polarizing optical microscopy, X-ray diffraction and calorimetry, but their regime of crystallization has not been determined.

EXPERIMENTAL

The polymer was prepared by condensation of adipic acid and ethylene gly-