

Structure - Property Relationships for Polyisocyanurates with Varied Modulus

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Introduction.

Vibrations in mechanical parts create unwanted noise and cause wear. Viscoelastic materials act as good damping agents due to their ability to absorb vibrational energy. The construction of elastomers with a range of glass transition temperatures, T_g , has been predicted to give the optimum performance when these materials are used as damping coatings[1]. A polyisocyanurate system was employed to achieve controlled variation in the density of cross-links and therefore T_g . Both static and dynamic Nanoindentation have been used in conjunction with Small Angle X-Ray Scattering (SAXS) to investigate how the mechanical properties of these materials are affected by microphase separation.

Experimental Procedure

Polyisocyanurates were prepared via a two-stage reaction pathway [2]. Various lengths of polyether were end-capped by the reaction between methylenediphenyldiisocyanate and poly-propyleneoxide forming a urethane bond. The trimerisation of the isocyanate end groups was then undertaken using a heat activated catalyst, enabling processing of the liquid 'prepolymer' before network formation. Thus a range of materials, with polyether molecular weights varying from 192 to 8200, and hard segment (isocyanurate and excess diisocyanate) content from 15 to 80% have been prepared. The length of polyether chain used and the density of cross-links determined the modulus of the resultant material.

Mechanical Properties - Nanoindentation

Mechanical measurements were made using a Triboscope[®] Nanomechanical test system made by Hysitron Inc. This is an adapted Scanning Probe Microscope with the SPM head (cantilever and detector) replaced with a Hysitron transducer, giving accurate numerical data from precise nanoindents

and *in situ*, high resolution, surface imaging [3,4].

Figure 1 shows indents made in a 425 54% sample from static nanoindentation and figure 2 shows values of reduced modulus obtained from a number of polyether M_w and hard segment contents. A consistent value is obtained after overcoming surface effects by applying higher loads.

The nanoindenter has been fitted with a heating stage to allow a much larger range of dynamic mechanical data to be collected. A set load was applied and the tip oscillated $\pm 5\%$ of this load. Figure 3 shows the results of time - temperature - superposition for 725 40% after performing frequency sweeps of 10 - 110 Hz at temperatures ranging from 15 to 60 °C. The maximum in $\tan \delta$, seen at 35 - 40°C corresponds to the T_g for this material as obtained by Differential Scanning Calorimetry.

Structure Development - Small Angle X-Ray Scattering

SAXS measurements were carried out on Beamlines 8.2 of the SRS, Daresbury Laboratory, Warrington, U.K., details of which have previously been recorded [5]. Static measurements were taken by mounting the polyisocyanurate sample in the X-Ray beam. Time-resolved measurements monitoring the curing of the prepolymer were taken by loading DSC pans fitted with mica windows with prepolymer and trimerisation catalyst. Samples were heated from 25°C to 120 °C at 50 °C minute⁻¹ and held there until no further change was seen. Data were collected in 6 second frames.

Figures 4a and 4b show Lorentz corrected SAXS patterns from a range of 2200 and 4200 M_w polyether segment polyisocyanurates with varying hard segment contents. As indicated by the maximum peak height occurring at lower q , domain spacing increases with hard segment content and

with polyether segment length. The development of phase separation in 2200 M_w polyether segment with increasing amounts of hard segment content can be seen in Figures 5a, 5b and 5c.

Relating Structure to Mechanical Properties

For each prepolymer length, as the hard segment content increases, the modulus increases. However, whilst the d-spacing increases with polyether length, the modulus decreases. Highest modulus polyisocyanurates are not phase separated. The highest tan δ values are seen from phase separated materials with larger polyether length and smaller d-spacings.

References

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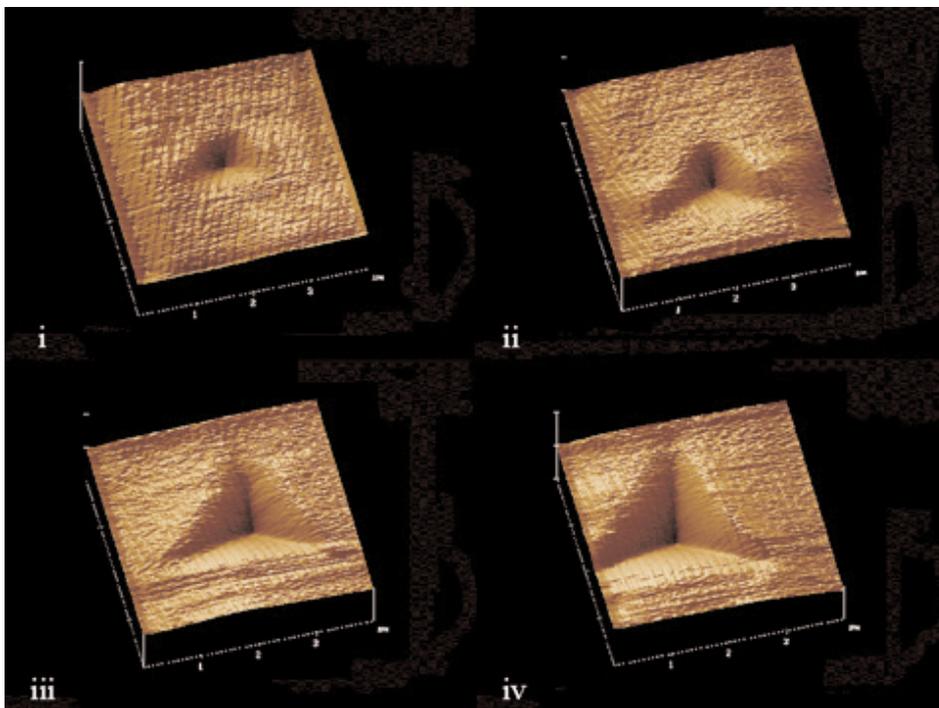


Figure 1: Images obtained after indentation with loads of (i) 50, (ii) 100, (iii) 150 and (iv) 200 μN .

Variation of Reduced Modulus with Indent Depth

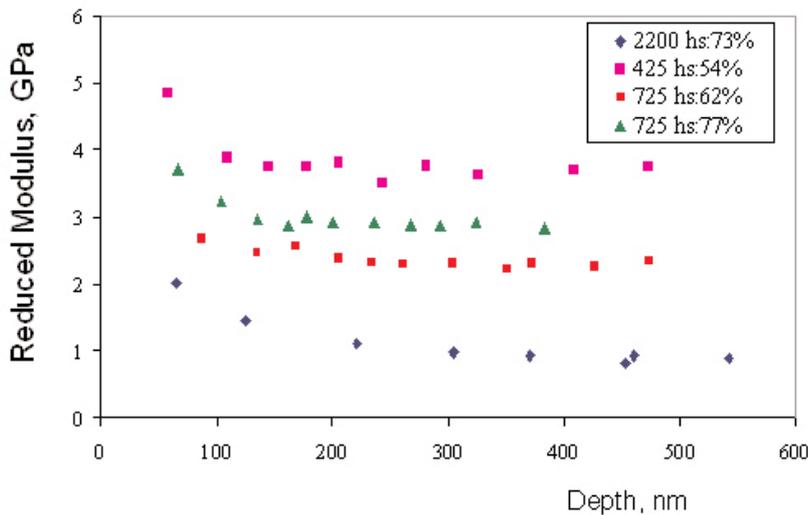


Figure 2: The variation in obtained modulus with indent load for 4 polyisocyanurates with varying polyether segment length and hard segment content.

Time - Temperature - Supposition 725 40%

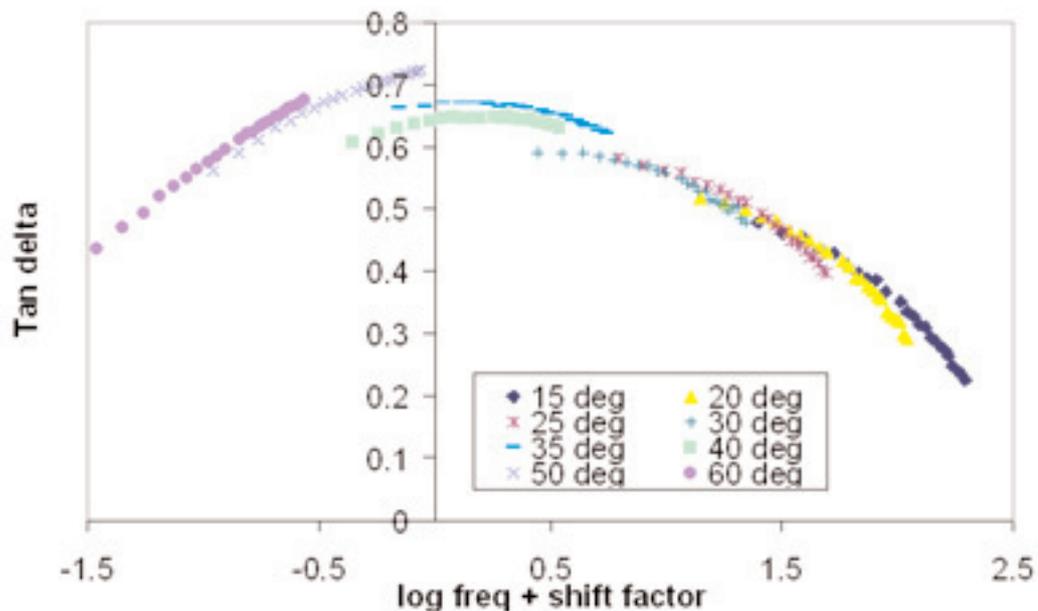


Figure 3: Time-Temperature-Superposition according to the WLF equation for sample 725 M_w polyether with 40% hard segment content

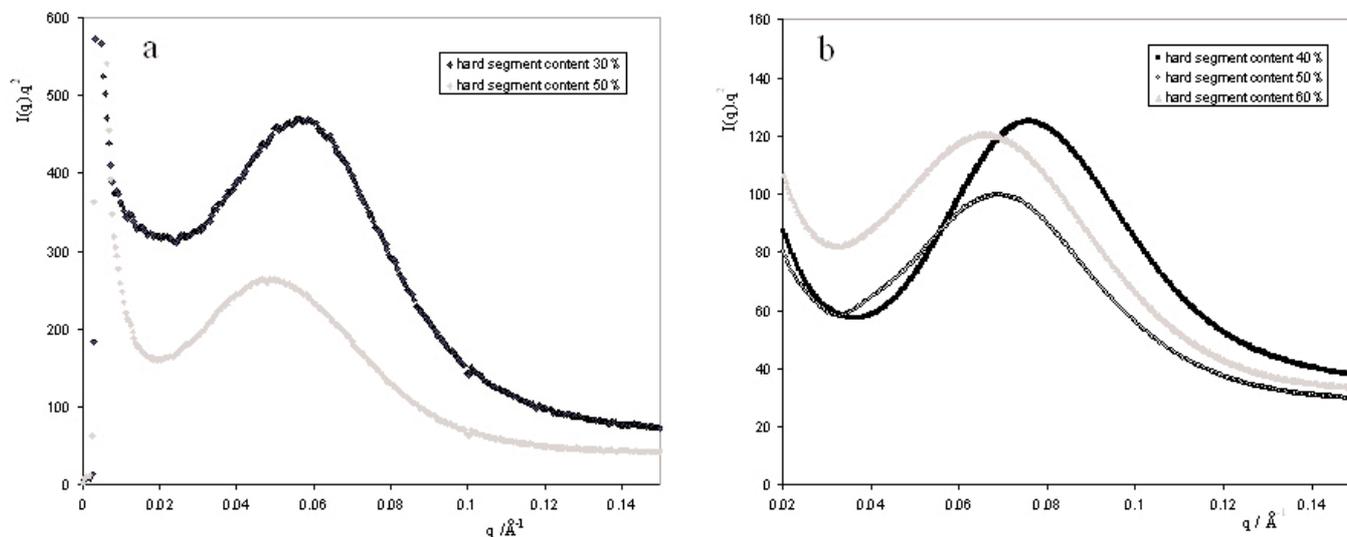


Figure 4: Lorentz corrected SAXS patterns for 2 different prepolymer lengths with varying amounts of hard segment content - a) 2200 M_w prepolymer, d-spacing for 40% - 81 \AA , 50% - 90 \AA , 60% - 97 \AA and b) 4400 M_w prepolymer, d-spacing for 30% - 108 \AA and 50% - 128 \AA

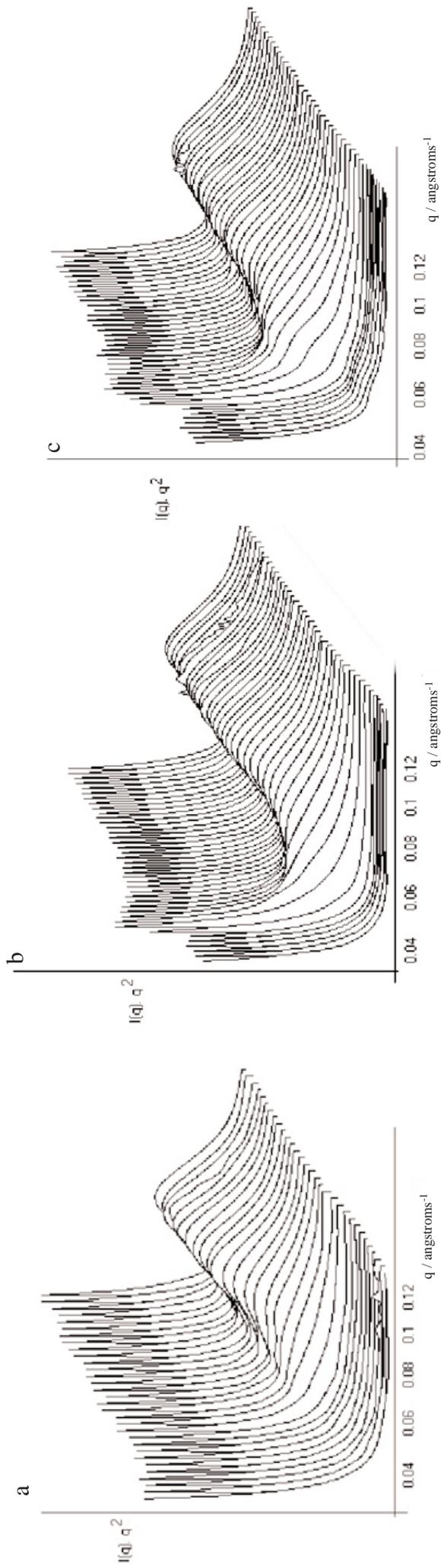


Figure 5: Lorentz corrected SAXS patterns showing the development of phase separation in 2200 M_w polyether segment with a) 40%, b) 50% and c) 60% hard segment content.