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A synchrotron SAXS study of structure development in a copoly(isocyanurate-urea) formed by RIM

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Structure development during reaction injection moulding of a copoly(isocyanurate-urea) was studied using time-resolved, synchrotron SAXS. During the rapid copolymerization of liquid reactants, incipient microphase separation was shown to occur at a critical conversion of isocyanate groups and to proceed via the kinetics associated with spinodal decomposition. Microphase separation was halted prematurely by vitrification of the polyisocyanurate phase, thus producing a copoly(isocyanurate-urea) with a non-equilibrium, co-continuous morphology with a size scale of ≈100 Å. Crown copyright © 1996 Published by Elsevier Science Ltd.

(Keywords: structure development; SAXS; reaction injection moulding)

Introduction

Isocyanurate-based polymers are currently of great interest as matrix materials for structural composites formed by reaction injection moulding (SRIM), due to their good thermal and mechanical properties and controllable processing behaviour[1]. Copolyisocyanurate SRIM systems are based on the reaction of polyisocyanates with either hydroxyl- or amine-functionalized polyether prepolymers to form copoly(isocyanurate-urethane)s[1] or copoly(isocyanurate-urea)s[2], respectively. The polyether acts as a carrier for the trimerization catalyst required for isocyanurate formation, and is incorporated into the final copolymer as a rubbery microphase[3] which toughens the intrinsically brittle polyisocyanurate[3,4]. Formation of copoly(isocyanurate-urea)s occurs via a two-stage reaction[4], shown schematically in *Figure 1*. The first stage involves the rapid, almost instantaneous, reaction of the polyamine to form NCO-tipped polyether-urea oligomers. This is followed, after an induction period, by the second-stage trimerization reactions of various NCO-tipped moieties to produce a glassy, highly crosslinked copoly(isocyanurate-urea). Consequently, these systems exhibit low initial viscosity to enable rapid filling of moulds packed with pre-placed reinforcements, followed by rapid development of stiffness and strength *after* the mould is full. Development of morphology in RIM copolymers is a result of competition between polymerization kinetics, chemical gelation, vitrification and microphase separation[5-7]. The morphology of the copoly(isocyanurate-urea) used in this study has been shown[3] via static SAXS and TEM to be isotropic and co-continuous with a size scale of ≈100 Å, indicative of microphase separation via spinodal decomposition. In this paper, the results of synchrotron SAXS studies of real-time structure development during the formation of a copoly(isocyanurate-urea) are presented, and interpretation of the kinetics and mechanism of microphase separation and crosslinking during rapid copolymerization is addressed.

Experimental

The copoly(isocyanurate-urea) used in this study was formed from two liquid reactants: (i) a polyisocyanate, and (ii) an amine-functionalized polyether containing an added organic trimerization catalyst. The polyisocyanate, Isonate™ M143 (ex. Dow Chemical), contains 80% by weight of 4,4′-diphenylmethane diisocyanate (MDI) and 20% of the uretonimine derivative. The isocyanate equivalent weight of M143, as determined by end-group analysis, was 143.8 ± 0.9 g mol^{-1}. The amine-functionalized polyoxypropylene, Jeffamine™ D2000 diamine (ex. Texaco Chemical Co.), has a nominal molar mass of 2000 g mol^{-1} and an equivalent weight of 980 g mol^{-1}, as determined by end-group analysis. The trimerization catalyst DABCO-TMR™ (ex. Air Products), is a quaternary ammonium carboxylate, N-2-hydroxypropyl-trimethyl-ammonium 2-ethylhexanoate. The reactant volume ratio (M143:D2000) used during RIM was 1.67:1, which corresponds to a mass ratio of ≈2:1 and a stoichiometric ratio [NCO]:[NH$_2$] of 14. The level of TMR™ catalyst used was 1.6% relative to the total formulation weight (M143 and D2000).

Due to the rapid rate of the copolymerization, a micro-RIM machine was required to meter and mix the reactants and to inject the reactant mixture into a specially-constructed mould, designed for use as a cell in the optical bench assembly of a beamline[6,7]. The temperature-controlled cell comprised two outer steel

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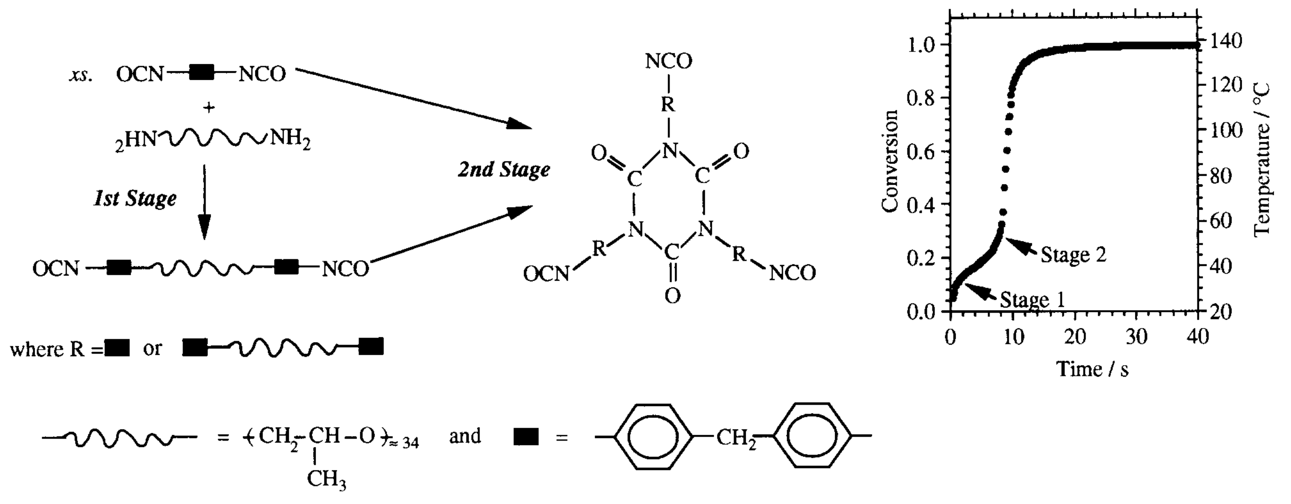

Figure 1 Schematic representation of the two-stage reaction to form a copoly(isocyanurate–urea), showing the almost instantaneous end-capping reaction between the polyisocyanate and the polyether diamine (first stage) and the slower isocyanate trimerization (second stage). These two stages are clearly visible in the conversion *versus* time plot calculated from adiabatic temperature rise experiments[4]

plates fitted with thermocouples and had countersunk holes of 4 mm diameter covered with polyimide (Kapton^{TM}) windows. The mould cavity ($\approx$75 × 20 × 2 mm) in the cell was created by using a U-shaped PTFE insert between the outer plates. Four 250 W cartridge heaters were inserted into the steel plates and the cell temperature was controlled using a microcomputer equipped with Strawberry Tree Workbench^{TM} software and ACM2-12-8 data acquisition hardware. A copper tube with Swagelock^{TM} fittings was used to feed the reaction mixture from the RIM machine nozzle to the SAXS cell mould. SAXS measurements were made on beamline 8.2 of the synchrotron radiation source (SRS) at the CLRC Daresbury laboratory. The camera was equipped with a multiwire quadrant detector, which has an opening angle of 70°, an active length of 0.2 m, and can handle count rates up to approximately 250 000 counts s^{-1}. For the calibration of the sample to detector distance, the scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used. Parallel-plate ionization counters were positioned before and after the SAXS cell to record the incident and transmitted intensities. The SAXS patterns were recorded every 0.5 s, and the experimental data obtained were corrected for background scattering (subtraction of the scattering from the empty cell and camera), for sample thickness and transmission, and for the positional alinearity of the detector. Isothermal copolymerizations were carried out at different cell temperatures, i.e. 70, 90, 110 and 135°C. The capacity of the mould cavity was $\approx$3 cm^3, and the output of the RIM machine was such that the time taken for the reactant mixture to cover the cell windows was $\approx$0.05 s.

Results and discussion

Interdomain spacing and degree of microphase separation. *Figure 2* shows plots of Lorentz-corrected intensity, $I(q)q^2$, *versus* scattering vector, q, for selected times after mixing (20–70 s) at a cell temperature of 90°C. After approximately 20 s of reaction, a maximum in the scattering profile occurs which remains essentially constant at a scattering vector of $q^* \approx 0.065\,\text{Å}^{-1}$, but increases in intensity as the second stage of the copolymerization proceeds and the microphase-separated structure develops. The interdomain spacing (d) of this structure was calculated from the scattering maxima using Bragg's law ($d = 2\pi/q^*$) to give a value of $d \approx 97$ Å, which agrees well with post-moulding values of d determined via static SAXS and TEM measurements on this system[3].

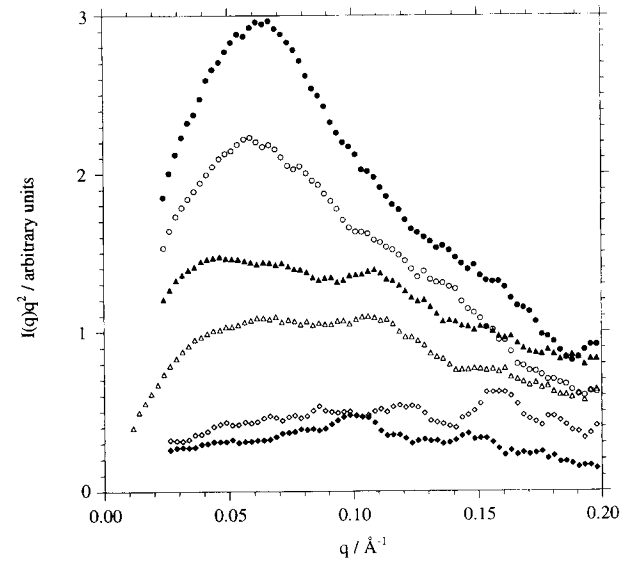

Figure 2 Lorentz-corrected intensity, $I(q)q^2$, *versus* scattering vector, q, at increasing times after mixing at a cell temperature of 90°C. Each curve comprises 0.5 s of data collection

The growth in scattered intensity during the copolymerization can be related to the degree of microphase separation via the relative invariant, Q'. Values of Q' were calculated via Simpson's rule integration of the $I(q)q^2$ *versus* q curves between the experimental limits of the first and last reliable data points, *viz.*, $q = 0.01$ and 0.18 Å, respectively. Plots of Q' *versus* time for the four cell temperatures are shown in *Figure 3*, and each shows three distinct regions in the microphase separation process. Initially there is an induction period showing negligible growth, followed by a period of rapid structure development as microphase separation occurs. At longer times, Q' reaches a plateau as growth retards and eventually stops. The induction times (determined by

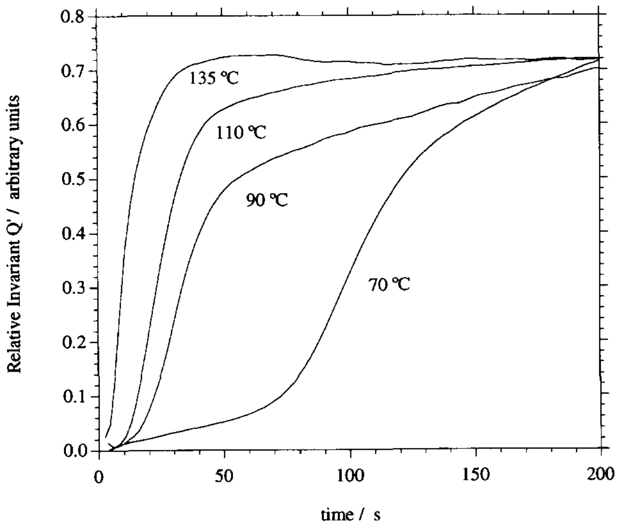

Figure 3 The SAXS relative invariant, Q', as a function of time at four cell temperatures (70, 90, 110 and 135°C)

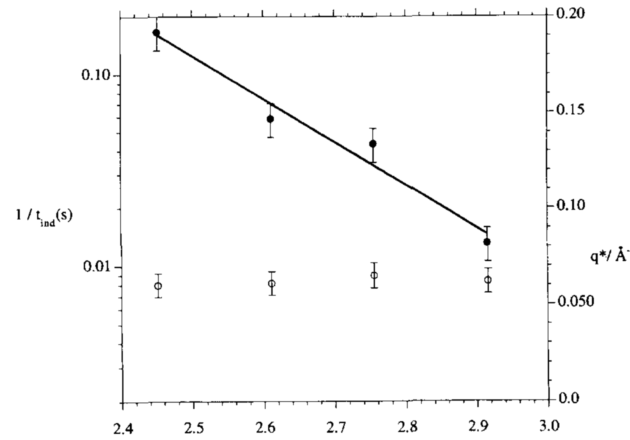

Figure 4 Arrhenius plot of induction time *versus* temperature (filled symbols). (In addition, the temperature dependence of the peak intensity position, q^*, is indicated by the open symbols)

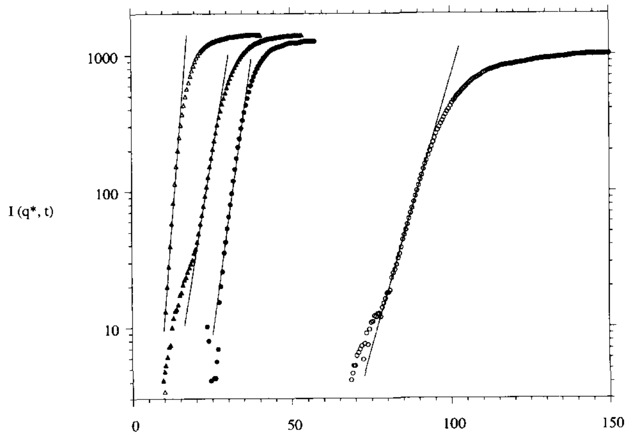

Figure 5 Peak intensity *versus* time for the cell temperatures 70, 90, 110 and 135°C. The solid lines are exponential fits (after Cahn and Hilliard[11])

drawing tangents to the first two regions of the experimental curves) were observed to decrease with increasing temperature, from ≈76 s at 70°C to ≈6 s at 135°C, following an Arrhenius rate dependence as shown in *Figure 4*. Thus, assuming that the copolymerization kinetics of the copoly(isocyanurate–urea) system also exhibit an Arrhenius temperature dependence, then the onset of the microphase separation transition (MST) could be assumed to occur at the same level of isocyanate conversion at all four cell temperatures. *Figure 4* also shows q^* to be independent of temperature. This is not unexpected as the material is effectively a block copolymer, and molecular connectivity between the polyether and polyisocyanurate phases restricts the interdomain spacing to values in the range, $2 \leqslant \{q^* R_g\} \leqslant 3$, as predicted by Leibler[8], where R_g is the radius of gyration of a combined hard block (polyisocyanurate) and soft block (polyoxypropylene, POP) segment. The value of R_g for the copoly(isocyanurate–urea) is not known. However, measurements of R_g using SANS have been carried out[9] on a polyurethane block copolymer formed using a POP prepolymer of similar molar mass ($2000\,\text{g}\,\text{mol}^{-1}$). For the POP chains, the radius of gyration $(R_g)_{\text{pop}}$ was measured as 13.5 Å in the disordered (relaxed) state, and 16 Å in the ordered (stretched) state. Using these values for the copoly(isocyanurate–urea), for which the volume fraction of POP, ϕ_{pop}, is 0.43 and R_g is approximated by $\{(R_g)_{\text{pop}}/\phi_{\text{pop}}\}$, gives values of $\{q^* R_g\}$ in the range 2.0–2.4. These values are typical of a block copolymer. Thus, values of d calculated using $(R_g)_{\text{pop}} = 16$ Å lie in the range $74 \leqslant d \leqslant 115$ Å and are in reasonable agreement with our experimental value of 97 Å.

Mechanism of microphase separation. Depending upon the route that the copolymerizing mixture follows through phase space, two distinct mechanisms of phase separation are observed, namely, nucleation and growth, and spinodal decomposition[10–13]. Nucleation and growth, which leads to a continuous phase-dispersed phase morphology, is not well-defined in terms of a kinetics scattering theory. Nevertheless, the scattered intensity at a fixed angle has been shown[14] to increase with the square of time for well-characterized nucleation and growth systems. However, in contrast to data reported[6] on RIM polyurethane elastomers, plots of the peak intensity $I(q^*, t)$ *versus* t^2 for all four cell temperatures did not exhibit clear, distinct linear regions, indicating that structure development in the poly(isocyanurate–urea) is not via nucleation and growth. Two previous studies[7,10] of structure development during RIM copolymerizations have shown that spinodal decomposition is the dominant mechanism of microphase separation. In these rapidly reacting systems, spinodal decomposition leads to the formation of non-equilibrium, co-continuous morphologies comprising two interconnecting networks. In order to determine whether the mechanism of microphase separation in the copoly(isocyanurate–urea) system was spinodal decomposition, the logarithm of the peak intensity $I(q^*, t)$ was plotted as a function of time, as shown in *Figure 5*. At all four cell temperatures, there is a good fit of the data to an exponential increase in intensity with time, which is indicative of spinodal decomposition, as predicted by the linearized theory of Cahn and Hilliard[11]. After the linear region, all four curves turn over to give plateau values of peak intensity as the rate of microphase separation slows, and is arrested, due to vitrification of the polyisocyanurate phase. As the copolymerization progresses, this phase attains a composition with a T_g equal to that of the surrounding copolymerizing medium and therefore vitrifies, and 'freezes' the co-continuous morphology at that point. Thus, the copoly(isocyanurate–urea) produced exhibits a non-equilibrium morphology which may be modified by subsequent annealing[3].

Summary and conclusions

Structure development during the formation of a copoly(isocyanurate–urea) was studied using time-resolved, synchrotron SAXS. A micro-RIM machine was used to meter and mix the two reactants, and to inject the reactant mixture into a mould cell positioned in the optical bench assembly of the beamline. As the copolymerization progressed, a maximum in the scattering profile developed at $q^* \approx 0.065\,\text{Å}^{-1}$ and increased in intensity as the microphase-separated structure developed. The interdomain spacing (d) of this structure was calculated from the scattering maxima to give a value of $d \approx 97\,\text{Å}$ that was shown to be independent of temperature. The induction times for the onset of microphase separation decreased with increasing temperature following an Arrhenius rate dependence, indicating that the MST occurs at the same degree of isocyanate conversion, independent of temperature. At all four cell temperatures, there was a good fit of the scattering data to an exponential increase in intensity with time, indicative of spinodal decomposition as predicted by the linearized theory of Cahn and Hilliard[11]. Microphase separation was arrested prematurely by vitrification of the polyisocyanurate phase, and produced a copoly(isocyanurate–urea) with a non-equilibrium, co-continuous morphology. The results presented lead to the somewhat surprising conclusion that a complex copolymerization, producing ultimately a microphase-separated polymer network, shows the dynamics of a simple liquid–liquid phase separation. Though beyond the scope of this report, the data may be fitted to a time-dependent Ginzburg–Landau model[15], as described in other studies on structure development in block copolymers[7,16]. A fuller analysis of microphase separation kinetics will be reported, along with copolymerization kinetics, in a future publication.

Acknowledgements

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