Experimental report

10/09/2019

Proposal: **9-11-1935** **Council:** 4/2019

Title: Concentration fluctuations in blends of branched and linear polymers to improve the understanding of phase separation

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Bisphenol A diglycidyl ether, hexamethylenediamine, detuerated poly(ether sulfone)

Instrument	Requested days	Allocated days	From	To
D33	1	1	31/07/2019	01/08/2019

Abstract:

Blends of branched thermosetting and linear thermoplastic polymers are widely used as structural materials in the aerospace industry. The mechanical properties of these materials are largely determined by the extent of phase separation within the blends during cross-linking of the thermoset. However, current methods to predict this process are lacking. As concentration fluctuations form the basis for phase separation, and are therefore a strong indicator of its occurrence, we have created a Monte Carlo model that is capable of predicting concentration fluctuations for blends with various temperatures, compositions and amounts of branched structures. However, to be able to use the model with confidence for industrially-relevant polymer blends, it must first be validated against experimental data for a model system, which neutron scattering is uniquely capable of providing.

Concentration fluctuations in blends of branched and linear polymers to improve the understanding of phase separation

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We measured the scattering from a blend of bisphenol A diglycidyl ether (DGEBA) epoxy with hexamethylenediamine curative as the branched component, and deuterated linear poly(ether sulfone) thermoplastic as the linear component. It is known that the thermoplastic phase separates from the epoxy/amine mixture as the latter cures, but little is known about the physico-chemical behaviour of the blend at low extent of cure prior to phase separation. In part, this is due to the difficulty of studying the blend whilst it is curing, and, in particular, distinguishing equilibrium from non-equilibrium phenomena.

Our choice of amine results in a model system as the epoxy cures to full extent in a stoichiometric mixture at room temperature without unwanted side reactions, a common occurrence with many other choices of amine curatives. This enables us to control the extent of cross-linking via the stoichiometry by limiting the amount of amine available in the system. As a consequence, our measurements are of a system that has equilibriated chemically, at varying extents of reaction, and does not undergo any further reactions at the temperatures of the small angle scattering measurements. We chose epoxy/amine stoichiometries of 10:1, 20:1, 40:1 and 80:1, with a corresponding decrease in epoxy conversion of 20%, 10%, 5% and 2.5%, respectively. Microscopy, thermal analysis and rheology studies all indicated that these mixtures are miscible so we expected that the scattering would follow random phase approximation like behaviour, enabling us to extract a temperature dependent interaction parameter from the low q behaviour.

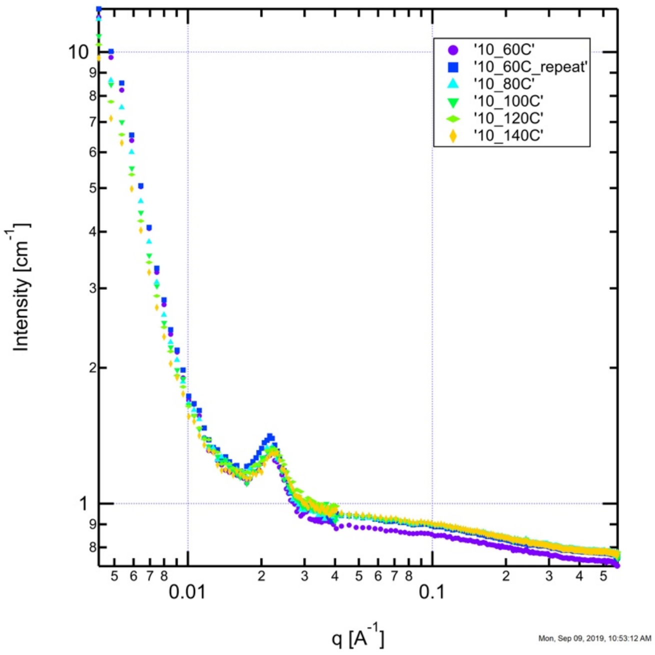

Figure 1: intensity vs q for the 10:1 epoxy:amine mixture at a range of temperatures, as indicated by the caption. The '10_60C_repeat' data was measured after cooling the sample back to 60C following the highest temperature measurement to ensure that the peak is an equilibrium feature.

As can be seen in figure 1, there is a weak but distinct peak at $q{\sim}2.5 \times 10^{-2}\ \text{Å}^{-1}$, which was unexpected. This peak exists in all stoichiometries, although it disappears for lowest extent of reaction (the 80:1) sample at the highest temperature of 140C. The peak is recovered upon cooling to 60C, indicating that whatever is causing it is an equilibrium feature. At lower q, the scattering intensity reduces with increasing temperature in all samples, which is line with the expectations of a miscible blend that phase separates upon cooling, with an inconclusive indication of turnover at the lowest q which requires further verification. Such a turnover could be a consequence of a plateau at the lowest q, as would be expected for RPA like behaviour, or that we are observing the higher q side of another peak. Our initial speculation is that the peak at $q{\sim}2.5 \times 10^{-2}\ \text{Å}^{-1}$ corresponds to some equilibrium microphase separated structures within a matrix, which itself behaves as a traditional miscible blend. Figure 2 shows that the inverse of the intensity vs q^2 at low q may be described by a linear relationship, consistent with the RPA description of a miscible blend.

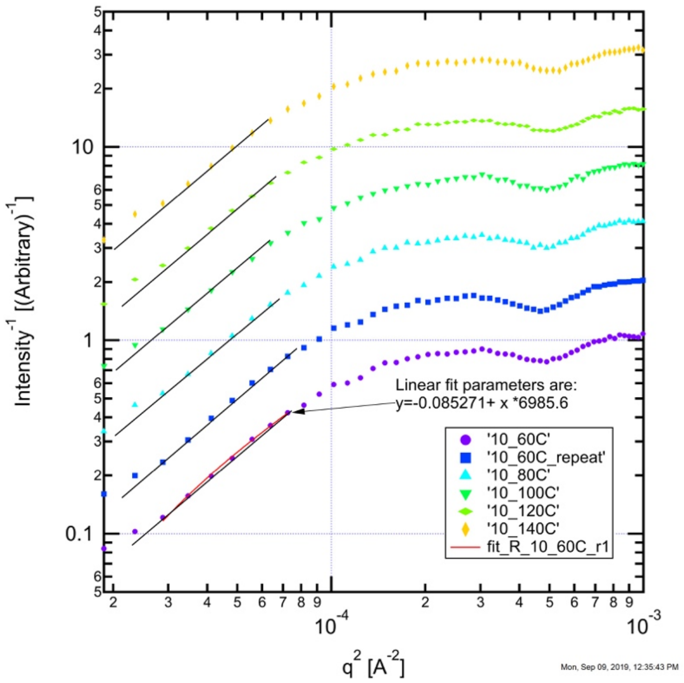

Figure 2: Zimm plot indicating a possible low q linear regime.