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Self-Assembly and Nanomechanical Properties of Block Ionomer Complexes

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Block ionomer complexes exhibit many attractive properties in solid state and in solution. Much attention, in recent times, is focused on block ionomer complexes based on block copolymers containing ionic and non-ionic chains blocks ("block ionomers") with oppositely charged molecules such as polyions, surfactants or metal ions. Recently, we reported the preparation of a class of new block ionomer complexes, namely SSEBS-c-PCL, based on sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS) and tertiary amine terminated poly(e-caprolactone), i.e., 3-dimethylamino propylamine-terminated poly(e-caprolactone) (APCL). The formation of these complexes is a result of the protonation from the sulfonic acid groups to the tertiary amine end group. The resultant block ionomer complexes have been successfully used as a template to prepare tough nanostructured epoxy thermosets. However, to-date, little work has been done on the phase structure and properties of these novel block ionomer complexes.

In the present work, we report a detailed study of the self-assembly, phase behavior and nanomechanical properties of these new block ionomer complexes. Small-angle X-ray scattering study revealed that SSEBS-c-PCL displays less ordered micro-phase structure compared to SSEBS. Quantitative mapping of mechanical properties at the nanoscale was achieved using peak force mode atomic force microscopy. Fig 1 shows the elastic modulus maps of SEBS, SSEBS and SSEBS-c-PCL as well as the corresponding histograms of elastic modulus. It is found that the block ionomer complex possesses higher average elastic modulus after complexation with crystallizable APCL. The moduli for both hard and soft phases increase and the phase with the higher modulus assignable to the hard SPS component shows much more pronounced changes after complexation, confirming that APCL interacts mainly with the SPS blocks. This provides an understanding of the composition and nanomechanical properties of these new block ionomer complexes and an alternative insight into the micro-phase structures of these chemically and mechanically heterogeneous materials at the nanoscale.

Figure 1. Elastic modulus maps of (a) SEBS, (b) SSEBS and (c) SSEBS-c-PCL and the corresponding elastic modulus histograms.


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