

Kinetics and thermodynamics of polymer grafted nanoparticle composites

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In this work, model binary and ternary polymer nanocomposites (PNCs) of poly(methyl methacrylate) grafted silica nanoparticles (PMMA-NP), poly(styrene-*ran*-acrylonitrile) (SAN), and PMMA homopolymers are examined to probe thermodynamic and kinetic parameters underlying phase behavior and nanoparticle assembly. Using complimentary techniques, the addition of PMMA to the binary PMMA-NP/SAN composite is observed to increase the miscibility in off-critical compositions of the ternary blend. This compatibilization is attributed to interfacial segregation of PMMA and supported by polymer reference interaction site model theory calculations and molecular dynamics simulations. Knowing the phase diagram, the interplay between phase separation and wetting is then studied by quenching the binary PNC films into the two-phase region. The PNC morphology exhibits symmetric wetting layers of PMMA-NPs at the surface and substrate, separated by “pillars” of PMMA-NPs that span the thickness. This composite morphology enhances the film modulus and hardness, as measured by nanoindentation, as well as the films thermal stability. The growth of this PMMA-NP surface excess increases rapidly with time and reaches a plateau that is dependent on quench depth. The diffusion coefficients of PMMA-NPs are measured and compared with prevailing models. Overall, these results highlight the complex parameter space in PNCs and provide new insights and control over both the bulk and surface morphologies of PNCs.

