

Mechanical Reinforcement in Architecturally Engineered All-polymer Nanocomposites

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The addition of nanoparticles is known to dramatically enhance the mechanical properties of polymeric materials. Crucial to the mechanical response of a polymer nanocomposite is the dispersion state of the nanoparticles (NPs); controlling the spatial distribution of NPs is necessary to optimize the properties of polymer nanocomposites. To this end, theoretical¹ and experimental² works are instructive about how entropic and enthalpic interactions between polymer-tethered nanoparticles and a polymer host can be used to control the dispersion state of NPs. Here, in order to take advantage of these developments, we utilized glassy, stiff/rigid, high- T_g nanostructured polymer particles as additives to a low- M_w poly(ethylene oxide), PEO, to prepare all-polymer nanocomposites with well-defined, controlled morphologies. The NPs were high-functionality mikto-arm star copolymers comprising polystyrene (PS) and poly(methyl methacrylate) (PMMA) arms, (PS)_n(PMMA)_n. We show that by varying their characteristics, namely the M_w of the PS and PMMA arms, nanocomposites with controlled/on-demand morphologies and tunable rheological properties could be obtained: from liquid-like behavior when the NPs were homogeneously dispersed in polymeric liquid host, to solid-like behavior when the high- T_g NPs formed a highly interconnected network. The final morphology is the result of two competing interactions: (i) inter-molecular attractions between the PS, which promote aggregation, as they are immiscible with the oligomeric PEO, and (ii) the favorable enthalpic interactions of the PMMA arm with the oligomeric PEO host that promote particle dispersion.

Acknowledgments.

This research has been co-financed by the European Union and Greek national funds through the Operational Program Competitiveness and innovation, under the call RESEARCH – CREATE –INNOVATE (project code: T1ΕΔΚ-02576, MIS5033805)



¹Borukhov, I. & Leibler, L. Enthalpic stabilization of brush-coated particles in a polymer melt. *Macromolecules* **35**, 5171–5182 (2002).

²Kumar, S. K., Jouault, N., Benicewicz, B. & Neely, T. Nanocomposites with polymer grafted nanoparticles. *Macromolecules* **46**, 3199–3214 (2013).