Modelling the viscoelasticity of polymer-based nanocomposites guided by principles of non-equilibrium thermodynamics

By appropriately adding nanoparticles to a polymer matrix can lead to materials with dramatically improved properties, especially under conditions of good dispersion. From a rheological point of view, polymer nanocomposites are typically considered to be soft colloidal dispersions, with an intrinsically disordered structure that greatly affects their viscoelastic or mechanical properties. Despite that the rheological properties of nanocomposites in the melt can be predicted or explained via entanglement network simulations based on multi-scale simulation strategies, large-scale macroscopic calculations of their processing flows require reliable constitutive (viscoelastic) equations which are currently missing.

In the present research activity, the Generalized Bracket framework has been extended to handle mixed systems consisting of two phases: a polymer matrix and a dispersed phase of spherical nanoparticles. The proposed work is, to the best of our knowledge, one of the very first efforts undertaken world-wide to describe the mechanical-rheological response of these materials through thermodynamically admissible, closed-form constitutive expressions. For the polymer component, we have used the general viscoelastic model for homopolymer melts, of which the structural variable is the conformation tensor C, accounting for several complex phenomena and interactions proposed recently by Stephanou et al. (Ref. 1). To account for the nanoparticles, we employ the orientation tensor a which attains a constant trace. This continuum model can describe in a unified and self-consistent way the microstructure, phase behavior, and rheology in both the linear and non-linear regimes of polymer nanocomposites. The dynamic equations are developed for nanoparticles with an arbitrary shape but then they are specified to the case of spherical ones (Ref. 2). Restrictions on the parameters of the model are provided by analyzing its thermodynamic admissibility. A key ingredient of the model is the expression for the Helmholtz free energy A of the polymer nanocomposite. At equilibrium, this reduces to the form introduced by Mackay et al. to explain the phase behavior of polystyrene melts filled with silica nanoparticles (Ref. 3). Beyond equilibrium, A contains additional terms that account for the coupling between microstructure and flow. In the absence of chain elasticity, the proposed evolution equations capture known models for the hydrodynamics of a Newtonian suspension of particles (Ref. 2). A thorough comparison against several sets of experimental and simulation data demonstrates the unique capability of the model to accurately describe chain conformation and swelling in polymer melt nanocomposites, and to reliably fit measured rheological data for their shear and complex viscosity over large ranges of volume fractions and deformation rates (Refs. 2, 3). We also address the issue of flow effects on the phase behavior of polymer nanocomposite melts (Ref. 3). For this purpose, we calculate the spinodal curve, by computing values for the nanoparticle radius as a function of the polymer radius-of-gyration for which the second derivative of the generalized free energy of the system with respect to the volume fraction becomes zero. Under equilibrium conditions, we recover the phase diagram predicted by Mackay et al. Overall, our model predicts that flow enhances miscibility, since the corresponding miscibility window opens up for non-zero shear rate values. To the best of our knowledge, this is the first theoretical study which addresses this problem and produces results in accord with experimental findings, especially for the phase behavior. These theoretical results provide new insights into understanding the interrelation of nanostructure, phase behavior (miscibility) and rheology.
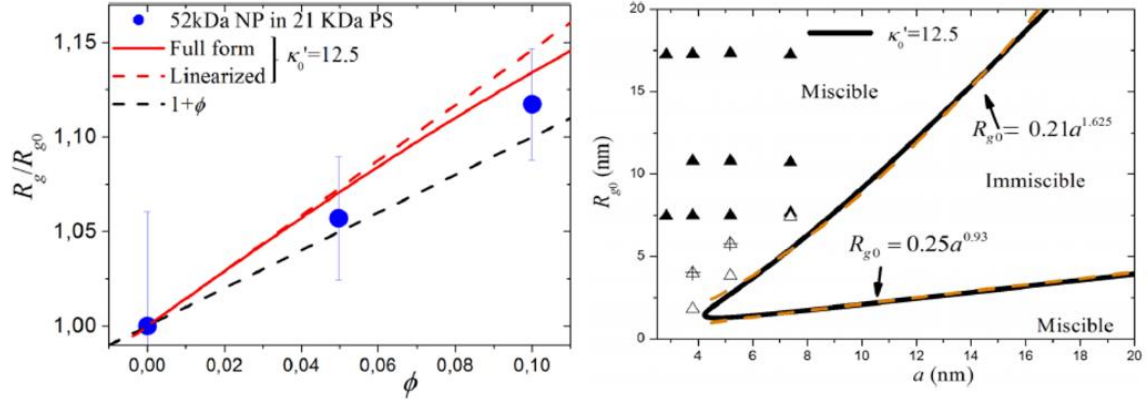
Fig. 1: Predictions at equilibrium: variation of the polymer radius-of-gyration with NP volume fraction and comparison with experimental data (left) and the phase behavior of polymer nanocomposites and comparison with experimental data (right)
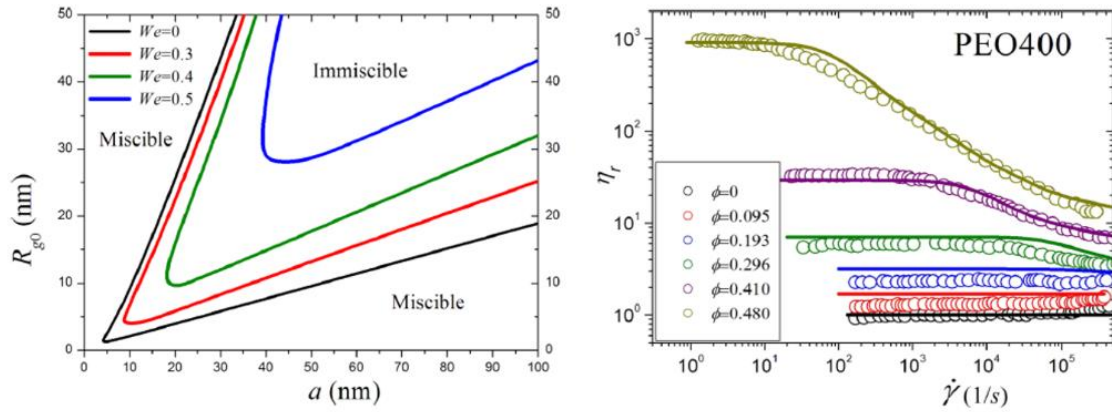

Fig. 2: Predictions under flow for the phase behaviour under simple shear flow (left) and the relative viscosity of a PNC as a function of the imposed shear rate (for several volume fractions of nanoparticles) and comparison with the experimental data (right)

References

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