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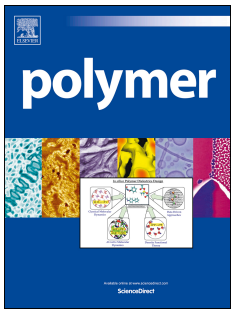

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Unveiling the Impact of Nanoparticle Size Dispersity on the Behavior of Polymer Nanocomposites

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Abstract

Polymer nanocomposites (PNCs), a class of polymer materials incorporating nano-sized particles (NPs), have tremendous potential in industrial formulations and technological applications, such as protective coatings and food packaging. In this work, we perform Molecular Dynamics simulations to unveil the impact of NP size dispersity on a variety of properties that characterize the response of PNCs at the nano and macro scales. In particular, at the nano scale, we investigate the space distribution of small and large polydisperse NPs and their ability to diffuse through a dense isotropic distribution of unentangled polymer chains. We find very interesting scaling laws relating the average size and polydispersity index of NPs with their diffusion coefficients, generally underestimated by existing theoretical models. These theories are here adapted to include the effect of NP size dispersity and their predictions, confirming the relevance of incorporating such contributions, are validated against our simulation results. We also analyze the diffusivity of the polymer chains as a function of the interparticle distance for a spectrum of NP diameters and confirmed the existence of a single master curve as recently observed experimentally (S. Gam *et al.*, Soft Matter, **2012**, *8*, 6512). To assess the effect of NP size dispersity on the macroscopic response of our model PNC, we evaluate two key transport properties, shear viscosity and thermal conductivity, which are found to display an intriguing universal behavior when plotted against the polymer/NP specific interface area and the inverse of the NP's mass, respectively.

Keywords: Polymer nanocomposites, Nanoparticles, Polydispersity, Molecular Dynamics

1. Introduction

Polymer nanocomposites (PNCs) are materials composed of a polymer matrix incorporating particles with at least one dimension in the nanometer scale [1]. The presence of such nanofillers can dramatically alter the local dynamics and morphology of the polymer chains as well as the macroscopic response of the polymer, including its mechanical, thermal, and rheological properties. If rationally formulated, PNCs can have a high impact on a number of key industrial applications, including, but not limited to, coatings, paints, electronics, food packaging, and personal care [2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. The origin of such remarkable properties as compared to a pristine polymer is usually ascribed to the delicate balance between enthalpic and entropic forces established at the nanoscale between host and guest. More specifically, the small size of the nanoparticles (NPs) provides larger surface to volume ratios as compared to traditional composites. As a consequence, the interface between NPs and polymer increases and a larger number of chains can interact with the NPs. Additionally, the NP/polymer relative size controls the relaxation of the polymer chains across several time scales and influences their response to external stimuli. Equally noticeable is the possibility to improve the performance of a polymer by adding only a little amount of NPs (generally around 5 wt. %), so that the overall weight of the material, a crucial parameter for many industrial applications, and its cost do not increase significantly. This twofold positive effect, enhancing the material properties by keeping its weight to satisfactory levels, cannot be achieved by employing conventional microfillers.

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