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Reinforced local heterogeneities in interfacial tension distribution in polymer blends by incorporating carbon nanotubes



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ABSTRACT

The modification of interface using nanoparticles in emulsions and immiscible polymer blends introduces elaborate methods to develop functional materials. In this study, we perform dissipative particle dynamics simulations to evaluate the distribution of interfacial tension over a polymer-polymer interface in the presence of carbon nanotubes (CNTs). The localization and interfacial self-assembly of CNTs is discussed in connection with their aspect ratio (AR) and entropic contributions. The distribution of interfacial tension is demonstrated in terms of the distribution of pressure differences across the interface. The results show large variations in the local pressure differences in the vicinity of CNTs. These variations are more pronounced when low AR CNTs are incorporated into the blends. It is argued that the self-assembly of large AR CNTs at the interface severely restricts their domain of influence while random dispersions of low AR CNTs can effectively dominate the entire interface of the dispersed phase. These new findings can help explain the shape irregularities observed in the particle-covered droplets.

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1. Introduction

The incorporation of nanoparticles in immiscible polymer blends is an attractive field for research due to its key role in the fabrication of cost-effective functional polymer materials. In case of the selective localization of nanoparticles at the interface, they can become confined to fluid-fluid interfaces and stabilize the morphology through a coalescence suppression mechanism [1,2]. In such systems, often interfacial crystallization takes place at higher volume fractions [3]. This phenomena could lead to an emulsion with unique material properties and offer an important route to new soft materials. Stabilizing emulsions using nanoparticles is an alluring approach towards development of highfunctioning materials in the food, cosmetics, and medical industries.

The localization of particles at the interface of emulsions has been an intriguing topic for modelling and simulation, since, in particular, it is not only controlled by the thermodynamics but also

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by the kinetics as well as the aspect ratio of the nanoparticles [4-9]. For colloidal particles, Aland et al. [10] developed a Navier-Stokes-Cahn-Hilliard model for the macroscopic two-phase fluid system combined with a surface phase-field-crystal model for the microscopic colloidal particles along the interface. Later, this model was improved further based on the conservations of mass and thermodynamic consistency to avoid spurious velocities at larger spatial and temporal resolutions [11]. In a numerical investigation of the role of surfactants and nanoparticles interfacial localization in emulsions, Frijters et al. [12] incorporated the lattice Boltzmann method and quantified the effects of such additives on interfacial tension. Moreover, the deformation and breakup of droplets with nanoparticle covered surfaces were studied in shear flows. The results demonstrated a heterogeneous distribution of nanoparticles over the interface with preferred clustering in more stable regions when subjected to flow. However, the authors do not take into account the local heterogeneities of the interfacial tension and fail to capture irregular shapes of particle-covered droplets observed in experiments [13]. Other significant aspects which influence the localization of nanoparticles have also been treated theoretically. For instance, Krasovitski and Marmur developed a model which explained the diffusion and localization of nanoparticles within a blend in terms of their aspect ratio [7]. The founding ideas of this







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model further led to an interpretation of the so-called slim-fast mechanism which could describe important features of experimental observations [6]. Despite all these efforts, many aspects still remain unexplored including the local distribution of stresses over the polymer-polymer interface with or without nanoparticles.

There are only few studies which consider the spatial distribution of the tension at an interface in some special systems. The works of Baus and Lovett on the tension profiles of the planar liquid-vapor and vapor-liquid-wall interfaces are two instances [14,15]. In their study, the authors used density functional arguments and showed that the van der Waals theory can describe interfacial tension distribution. This methodology, however, has never been applied to interfaces with more complex geometries probably due to its calculation inefficiency. Also, the development of local oscillations in the interfacial tension upon the addition of nanoparticles to the interface has never been considered before in this framework. From an experimental viewpoint, it becomes even more challenging to measure anisotropic interfacial tensions. In recent studies, Danov et al. [16,17] showed the possibility of using capillary meniscus dynamometry to effectively estimate isotropic and anisotropic surface tensions of bubbles and droplets adhering to solid surfaces. They illustrated their method to be successful for soybean-oil droplets adherent to hydrophilic and hydrophobic substrates [16]. As it is also stated by the authors, this approach needs further improvements and testing to be applicable to viscoelastic polymers. To characterize the interfacial properties of polysaccharide and poly(amino acid) nanomembranes, Ferri et al. [18] used a modified pendant drop test. In this way, the authors were able to establish a theoretical framework for data interpretation of anisotropic tension distributions on droplets and bubbles. In such studies the nature of the developed interfacial distributions reciprocates a certain dependency with the shape of the droplet rather than any nano inclusions ever being considered. Recently, the direct calculation of anisotropic surface stresses of a particlecovered droplet was investigated in the pendant drop technique using a customized fast Eulerian-Lagrangian simulation method [19]. In these simulations, the pendant drop was covered by colloidal particles with purely repulsive particle-particle interactions. It was observed that the surface stress changed from homogeneous to heterogeneous when the droplet form was altered from stable to unstable. This simulation study is expected to increase our understanding of the pendant drop technique when applied to particle-covered droplets. Such efforts are necessary to help devise superior techniques to correctly measure anisotropic interfacial tensions. However, this simulation framework does not allow the particles to freely relocate within the blend and reach a thermodynamic equilibrium. In their work, the formation of thinner and thicker parts in the pendant droplet due to the gravity re-arranges the particles at the interface and develops a local interfacial tension anisotropy at the neck of the pendant droplet. This phenomenon is in its nature different from our observations here where the sole presence of the CNTs disturbs the interfacial tension distribution.

Finally, an interesting field of research in emulsions is the droplet deformation and relaxation where the droplets are filled with nanoparticles such as carbon nanotubes (CNTs) [4,20]. Following Taylor, the deformation process is generally modelled in terms of the capillary number and viscosity ratio of the two phases [21,22]. The capillary number is the ratio of the deforming forces (viscous forces) to the shape-preserving forces. The latter is generally defined in terms of the interfacial tension. The present study contributes to the models developed for such systems by providing valuable insights into the effects of nanoparticle inclusions. This is crucial since the available rheological models typically ignore the role of nanoparticles in the emerging interfacial

heterogeneities as well as increasing the average interfacial behavior [23–25]. On the other hand, recent empirical investigations on the deformation and breakup of nanoparticle-filled/-covered polymer droplets has posed serious questions regarding the mechanisms involved in the formation of irregular shapes during deformations [4,13,26]. The numerical investigations on such effects in droplet deformation and breakup are also scarce. The works of Usta et al. [27] and Frijters et al. [12] are two valuable examples of using the lattice Boltzmann method to demonstrate the role of nanoparticle inclusions on the droplet deformation phenomena in a systematic manner, however, without considering the local heterogeneities in the interfacial tension.

Therefore, we aim to provide insights to the emerging heterogeneities in interfacial tension distribution when CNTs are added into immiscible polymer blends. To do this, we use the wellcredited dissipative particle dynamics (DPD) simulation method and study the equilibrium morphology of the blends [28,29]. Two CNT types with different aspect ratios are used to find out their differences in localization as well as in interfacial tension distribution. We discuss the results in term of the classic thermodynamics arguments and underline the involved mechanisms. The effect of the blend ratio is also manifested by decreasing the volume of the dispersed phase in the blends. Finally, some future outlooks and perspectives are briefly addressed. This study sheds light on the emerging interfacial heterogeneities by incorporating CNTs in polymer blends. These heterogeneities become significant in the development of stable surface shapes of the dispersed phase in quiescent and dynamic conditions. This work is expected to enable the design of functional emulsions and polymeric materials in a more elaborate way.

2. Simulation details

We use DPD to simulate the blends. DPD is a coarse-grained method developed by Hoogerbrugge and Koelman [30] in which several atoms are lumped into the so-called beads [28,31]. The time evolution of beads is dictated by three central pairwise forces: the conservative force F_{ij}^C , the dissipative force F_{ij}^D , and the random force F_{ij}^R . For any pair of *i* and *j* beads within the force cutoff radius r_c , these forces are defined by

$$F_{ij}^{\mathsf{C}} = a_{ij}\omega^{\mathsf{C}}(r_{ij})\widehat{r}_{ij},\tag{1}$$

$$F_{ij}^{D} = -\xi_{ij}\omega^{D}(r_{ij})r_{ij}[(\nu_{i}-\nu_{j})\cdot\hat{r}_{ij}]\hat{r}_{ij}, \qquad (2)$$

$$F_{ij}^{R} = \sigma_{ij}\omega^{R}(r_{ij})r_{ij}\zeta_{ij}\hat{r}_{ij}.$$
(3)

Here, r_{ij} is the distance between the beads with the corresponding unit vector of \hat{r}_{ij} which points from bead *j* to bead *i*. v_i and v_j are the velocity vectors of beads *i* and *j*, respectively. The model parameters used in DPD are a_{ij} , ξ_{ij} , σ_{ij} , and ζ_{ij} which indicate the maximum repulsion coefficient, the friction coefficient, the noise amplitude, and a Gaussian random number, respectively. $\omega^C(r_{ij})$, $\omega^D(r_{ij})$, and $\omega^R(r_{ij})$ are the conservative, dissipative and random weight functions, respectively, which are defined as

$$\omega^{D}(r_{ij}) = \left[\omega^{C}(r_{ij})\right]^{2} = \left[\omega^{R}(r_{ij})\right]^{2} = \left(1 - \frac{r_{ij}}{r_{c}}\right)^{2}.$$
 (4)

In its basics, DPD is similar to molecular dynamics. However, its coarse-grained approach and the softer interaction potentials that it uses make it an efficient mesoscopic method to study the Download English Version:

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