Polymer 145 (2018) 80–87

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Coarse-grained molecular-dynamics simulations of nanoparticle diffusion in polymer nanocomposites

I.V. Volgin [a], S.V. Larin [a], A.V. Lyulin [a, b], S.V. Lyulin [a, *]

[a] Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoj Pr. V.O., 31, 199004, Saint Petersburg, Russia
[b] Group Theory of Polymers and Soft Matter, Department of Applied Physics, Technische Universiteit Eindhoven, 5600, MB, Eindhoven, The Netherlands

ARTICLE INFO

Article history:
Received 30 January 2018
Received in revised form
10 April 2018
Accepted 21 April 2018
Available online 23 April 2018

Keywords:
Coarse-graining
Nanoparticle dynamics
Molecular dynamics simulations

ABSTRACT

Molecular-dynamics simulations have emerged as an effective tool to characterize polymer systems. Molecular level effects (even on microsecond time scales) are nowadays well reproduced by atomistically detailed models. Beyond this, further insights into the properties of the polymer system at a mesoscopic level can be gained by resorting to simulations based on appropriate coarse-grained models. However, reducing the number of degrees of freedom during the coarse-graining procedure may have a significant impact on atomistic level effects. A common example is the overall enhancement of the diffusive motion of polymer chains in coarse-grained simulations, which arises from the reduced friction of the coarse-grained beads. In the present work we investigate this well-known effect and study how the diffusive properties of the nanoparticle are affected by the coarse-graining procedure. To this end, we apply iterative Boltzmann inversion to develop two coarse-grained models of a nanocomposite based on the thermoplastic polyimide R-BAPB, containing a single fullerene C_{60} nanoparticle. By changing the size and, correspondingly, the total number of coarse-grained beads in each polymer chain, we can control the effect of chemical detalization on various phenomena. We exploit this idea to study the influence of the degree of detalization of polymer chains on their structural properties as well as on the diffusive properties of the fullerene nanoparticle, whose detalization is kept fixed. Although the structural properties of the coarse-grained systems are in good agreement with those of the fully atomistic system, the nanoparticle diffusion is significantly affected by the local chain structure. In particular, we find that the coarse-graining of the polymer chains on the length scale of the nanoparticle size leads to a full suppression of the subdiffusive regime observed in the fully atomistic system.

1. Introduction

The properties of polymer systems originate from the hierarchy of their different time and length scales. A better understanding of how microscopic mechanisms taking place at the atomistic level give rise to the observed macroscopic effects would open new routes for the rational design of novel materials with advanced properties. Over the past decades, computer simulations have emerged as a powerful tool to solve this fundamental problem. Starting from the simple freely-jointed and bead-spring models [1], we are nowadays able to benefit from the highly detailed simulations on time scales approaching the experimental ones. Indeed, the rapid increase of the computational performance of modern supercomputers allows one to perform computer simulations on the microsecond time scale within «united-atom» [2–5] and even atomistically-detailed models [6–12]. However, even such long-time simulations are not long enough to capture all the macroscopic effects in polymers and in polymer nanocomposites (PNCs), i.e., polymer crystallization, kinetics of nanoparticle aggregation, etc. Moreover, in the framework of atomistically-detailed models, significant computational efforts are still required to understand the properties of well-equilibrated, highly-entangled polymer systems (especially of those with rather complex chemical structures, such as heterocyclic polymers). In view of this, there is a pressing need to develop suitable computational frameworks allowing one to attain sufficiently long times and sufficiently large length scales.

In the above context, recent years have seen a rapid development of multiscale simulation approaches aimed at linking together the different time and length scales, in order to correctly

---

[*] Corresponding author.
E-mail address: s.v.lyulin@gmail.com (S.V. Lyulin).

https://doi.org/10.1016/j.polymer.2018.04.058
0032-3861/© 2018 Published by Elsevier Ltd.

predict the properties of complex polymers [13]. Among the most commonly used and effective tools are various coarse-graining (CG) techniques [14]. These techniques allow one to access much larger time and length scales due to the effective averaging over the microscopic details of the underlying atomistic system. In practice, the averaging process is performed by merging groups of atoms into CG beads. A major challenge in this context consists in attaining a suitable balance between the computational efficiency characteristic of simple polymer models and the high degree of detalization achieved in fully atomistic simulations.

Much effort in this field has been put into the understanding of the influence of the degree of the polymer coarse-graining on the structural, rheological and thermal properties of different bulk polymers, such as polystyrene (PS), polyisoprene (PI), polyethylene (PE), poly(3-hexylthiophene) (P3HT), sulfonated polyetherketone (sPEEK) and even aromatic polyimides [15–24]. Concerning the effects governing structural properties, Harmandaris et al. have studied the influence of the effective-bead mass on the structural properties of PS [20,21]; Tripathy et al. examined the critical level of coarse-graining and the effect of a sequence of CG beads in a polymer chain on structural properties of sPEEK [15]. Ohkuma and Kremer investigated the effect of pressure correction on the structural properties of PI [22]. Pandiyan et al. studied the influence of the degree of coarse-graining on the mechanical properties of aromatic polyimides [16]. The polymer dynamical properties were also addressed in the above studies. A common feature was the observation of an overall enhancement of diffusive transport introduced by the CG procedure. This enhancement was attributed to the much softer CG interaction potentials, resulting in the need of applying a suitable scaling procedure to match the dynamical properties of both the original and the CG systems [25]. In this context, various features have been the object of vivid discussions, notably the dependence of the scaling factor on the chain length [17,21] or on temperature [24]. Particularly strong efforts were devoted to correct reproducing of the dynamics obtained using all-atom (AA) models by increasing the friction of the coarse-grained beads [16].

In spite of the considerable attention paid to the development of CG polymer models, the computational design of high-performance specific materials for modern industry calls for the study of more complex systems, namely, polymer nanocomposites. Nowadays, PNC filled with carbon nanoparticles (nanotubes, graphene or fullerene) are becoming widely employed in various industrial applications. Among different polymers heterocyclic ones (for example: polythiophenes, polybenzimidazole, aromatic polyimides etc.) represent a promising class of materials which may be utilized as binders for advanced PNC for solar cell applications, fuel cell membranes and optoelectronics [26,27]. Properties of such systems are largely controlled by the complex microstructure, which is typically formed during the nanoparticle diffusion. Due to the rapid development of the modern industry significant efforts are made to understand better PNC properties from the standpoint of the complexity of polymer chemical structure or nanoparticle induced effects. Considerable understanding may be achieved while employing computer simulations to study such systems, especially within the coarse-grained simulations. Nevertheless, the impact of the underlying coarse-grained models on the relevancy of the simulation results are nowadays less understood, thus limiting their application.

The properties of PNC are controlled not only by the chemical structure of their components (polymer matrix and filler nanoparticles), but also by the specific polymer-filler nanoparticle interactions [28–35]. This imparts additional complexity into the problem, especially when suitable CG models are to be developed. Moreover, since the polymer-nanoparticle interactions and the associated dynamics control the rheology and multi-scale mechanics of the PNC, among the key problems is understanding the variation of dynamical properties of the filler nanoparticles during the coarse-graining procedure. Though there exist numerous works on structure and dynamics of bead-spring nanocomposites with varied polymer-nanoparticle interactions [28–35], there are no studies considering nanoparticle diffusion in polymers within chemically specific CG models of different detalization.

When simulating nanoparticle diffusion, it should be taken into account that the nanoparticle dynamics is a rather complicated process characterized by different diffusion regimes, i.e. ballistic, subdiffusive and normal diffusive. In general, the characteristics of these three regimes (including typical crossover times) depend on the relaxational properties of the embedding polymer matrix. Moreover, since nanoparticle diffusion has been shown to be scale-dependent [36,37], the characteristics of the nanoparticle motion in a polymer matrix depend on the ratio between the size of the filler particle and the most relevant length scales of the polymer system.

Within the range of length scales associated with the subdiffusive regime of the nanoparticle, the chemical heterogeneity of polymer chains plays the most important role, since this heterogeneity is responsible for the local viscosity felt by the nanoparticle. However, in any coarse-grained simulations, the level of detail of the chemical structure is always reduced in comparison with all-atom models. Establishing how the degree of coarse-graining of the polymer affects the diffusive properties of the nanoparticles in PNC on various length scales of diffusion is crucial to develop suitable coarse-grained PNC models. The answer to this question will provide the information about the critical length scale and the necessary degree of coarse-graining which is needed to preserve the local effects.

In this paper we address the above problem by studying the diffusion of the nanoparticle in the framework of two PNC models differing in their degree of coarse-graining. In both models, the nanoparticle is modeled as a single coarse-grained bead. We use these CG models to simulate the diffusion of a single fullerene C_{60} in the melt of R-BAPB high-performance thermoplastic crystallizable polyimide based on 1,3-bis-(3,3′,4,4′-dicarboxyphenoxy)benzene (dianhydride R) and 4,4′-bis-(4-aminophenoxy) biphenyl (diamine BAPB), This polymer system has a high industrial impact, and has already been the object of previous studies by ourselves [6–10,38].

The complex chemical structure of the R-BAPB polyimide makes it a promising object to be used while investigating the role of the local chain structure and its coarse-graining on the nanoparticle diffusion. To minimize the number of parameters which may contribute to the nanoparticle diffusion, a simple nanoparticle should be utilized as a model diffusive object. Due to its spherical symmetry, small sizes and electrical neutrality, fullerene C_{60} seems to be the most reasonable candidate among other carbon nanoparticles, being typically used in modern nanocomposites.

In the present study we focus our attention on the structural and dynamical properties of the PNC, and compare CG simulation results with those obtained previously in the framework of fully-atomistic molecular-dynamics (MD) simulations of the same system [38].

The paper is organized as follows. In Section 2 we describe the simulation models and the details of the applied coarse-graining procedure. In Section 3 we discuss the results for the structural properties of the polymer and for the diffusive properties of both the polymer chains and the nanoparticle. In this context, special attention is paid to the nanoparticle diffusion in the framework of two different CG models. Finally, the general conclusions are summarized in Section 4.