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Morphological and mechanical properties of graphene-reinforced PMMA nanocomposites using a multiscale analysis

F. Lin[a], C. Yang[a,b], Q.H. Zeng[a,b], Y. Xiang[a,b,*]

[a] School of Computing, Engineering and Mathematics, Western Sydney University, Locked Bag 1797, Penrith, NSW 2751, Australia
[b] Centre for Infrastructure Engineering, Western Sydney University, Locked Bag 1797, Penrith, NSW 2751, Australia

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ABSTRACT

In this study, a multiscale simulation analysis combining mesoscale dissipative particle dynamics (DPD) method and continuum mechanics based finite element method (FEM) is adopted to study the morphological and mechanical properties of graphene-reinforced poly(methyl methacrylate) (PMMA) nanocomposites. Specifically, DPD simulations are performed for PMMA nanocomposite systems with graphene of different surface chemistries (i.e., GN, FGN and PMMA@FGN) and different process routines. It is found that the covalently functionalised PMMA@FGN/PMMA system can achieve a better dispersion than that of untreated GN/PMMA system, which is attributed to the intercalated coating molecules between graphene nanofillers. However, increasing shear rate during processing may not result in a better nanofiller dispersion or orientation as expected. The DPD microstructures of nanocomposite systems are subsequently mapped onto a 3D finite element representative volume element (RVE). The mechanical properties obtained from FEM match reasonably well with those from experiments in literature, which further demonstrated the effectiveness of the proposed multiscale approach.

1. Introduction

Graphene has exceptional thermal, mechanical and electrical properties. It has been envisioned as a key ingredient for many futuristic applications since its discovery more than a decade ago [1]. One promising application is graphene-reinforced polymer nanocomposites in which a small amount of graphene or its derivatives is incorporated into a polymer matrix. It has been confirmed through experimental and numerical studies that the material properties of such nanocomposites can be greatly improved [2–5]. However, such improvements depend largely on the morphologies of the resulting nanocomposites which are further attributed to the nature of individual components (e.g., filler, polymer matrix), their interaction strength, and manufacturing techniques [6–8].

Experimental efforts were recently made to produce a uniform dispersion of graphene nanofillers in polymer matrix through the change of graphene surface chemistry and its interaction with the polymer matrix. This was usually achieved through hydrogen bonding or covalent functionalisation. The effect of hydrogen bonding between graphene derivatives and poly(methyl methacrylate) (PMMA) matrix was recently studied. It was found that the interface tends to be stiffened and strengthened owing to improved interfacial interactions via hydrogen bonds [9,10]. The presence of oxidative debris in the as-made graphene oxide (GO) could benefit to the formation of PMMA nanocomposites due to a good dispersion and strong interfacial interaction between GO and polymer matrix [11]. Putz et al. [12] demonstrated that GO-reinforced PMMA nanocomposites may have different morphologies, modulus and strength, which can be attributed to the hydrogen bonding ability of intercalating species within GO.

Covalent functionalisation is also a promising method to form a strong interaction between graphene nanofillers and polymer matrix. For example, the latex and in-situ polymerisation technique can be used to attain a better dispersion of graphene in polymer matrix and desired material properties of polymer nanocomposites. The emulsion and mini-emulsion techniques were also used to graft PMMA chains onto GO surface [13–15]. Jiang et al. [16] developed one-step covalent functionalisation and simultaneous reduction of GO with hydroxyethyl acrylate, resulting in a functionalised graphene with double bonds. Covalent functionalisation of graphene surface has also been reported for PVC nanocomposites [17] and PMMA nanocomposite films [18].

Dissipative particle dynamics (DPD) was considered as an effective way to understand dynamic and rheological behaviours of complex fluids [19–23]. It has been used to investigate the dispersion, aggregation and morphology of various nanofillers in polymer matrix, such as carbon nanotubes [24–26], aluminosilicate nanotubes [27], and clay nanoparticles [28,29]. In addition, some studies were also

* Corresponding author at: School of Computing, Engineering and Mathematics, Western Sydney University, Locked Bag 1797, Penrith, NSW 2751, Australia
E-mail address: Y.Xiang@westernsydney.edu.au (Y. Xiang).

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conducted to evaluate the effects of some key material and processing parameters (e.g., aspect ratio, rigidity, concentration, diameters of fillers, chain length of polymer, shear flow and rate) on morphologies of such filler-polymer nanocomposites [30,31]. Yet, little work has been done to use the DPD simulation for modelling graphene reinforced polymer nanocomposites. Min et al. [32] performed a DPD simulation to examine the self-assembly of surfactant molecules onto graphene nanosheet in aqueous solution. Ju et al. [33] investigated the structure of graphene/PMMA with different graphene volume fractions using DPD. It was found that for a higher volume fraction of graphene in the polymer system, better graphene functionalisation was required to achieve good dispersion.

Numerical methods such as finite element method (FEM) have been widely used to simulate the mechanical behaviours of multi-phase heterogeneous materials [34,35]. For composites reinforced with nanoparticles, however the size of interfacial zones may be similar to the particle sizes and the elastic properties of the composites are strongly affected by the interfacial zone size [36]. Therefore, it is essential to include the interface as a separate phase in the FEM model. Wang et al. [37] treated the interphase as a two-layer model. Peng et al. [38] developed a computational model in which the effects of filler clustering are captured through overlapping effective interfaces.

In this work, the morphological and mechanical properties of graphene-reinforced PMMA nanocomposites are investigated via developing a multiscale approach, which combines DPD simulation and FE analysis. Specifically, the mesoscale DPD simulation is used to generate the morphology of graphene-PMMA nanocomposites and then representative volume elements (RVEs) for the FE analysis through a morphological and structural mapping. The DPD method can overcome the spatial and temporal limitation of molecular dynamics (MD) simulation and yet still consider the surface chemistry details of functionalised graphene. The DPD method also allows a wrinkled surface and crumpled morphology of graphene. In addition, the Couette shear flows with different shear rates are implemented in the DPD simulations to investigate the dependence of the morphology on shearing conditions. The resultant morphologies of nanocomposite systems from the DPD simulations are spatially mapped onto RVEs using an in-house extension FELIX (Finite Element Local Information X-rays) and a finite element analysis software package – Abaqus. The filler-matrix interfaces are preserved during the mapping process through assigning different interphase region in the RVEs. Upon a validation from experimental results available in literature, the tensile and shear moduli of the nanocomposites are obtained from a series of FE analyses.

2. Multiscale simulation method

2.1. DPD formulation

The DPD theory was initially developed by Hoogerbrugge and Koelman [23], and Groot and Warren [19]. In a DPD simulation, a set of atoms with identical or similar volumes are represented by a type of bead (or particle). The interaction $\boldsymbol{f}_i$ between a pair of beads is governed by the Newton's equation of motion, which can be summed up by a soft repulsion conservative force $\boldsymbol{F}_{ij}^C$, a dissipative or drag force $\boldsymbol{F}_{ij}^D$, and a random force $\boldsymbol{F}_{ij}^R$,

$$\boldsymbol{f}_i = \sum_{j\neq i} (\boldsymbol{F}_{ij}^C + \boldsymbol{F}_{ij}^D + \boldsymbol{F}_{ij}^R) \tag{1}$$

where the conservative force is given by

$$\boldsymbol{F}_{ij}^C = \begin{cases} a_{ij}(1-|\boldsymbol{r}_{ij}|/R_c)\hat{\boldsymbol{r}}_{ij} & (|\boldsymbol{r}_{ij}| < R_c) \\ 0 & (|\boldsymbol{r}_{ij}| \geqslant R_c) \end{cases} \tag{2}$$

the dissipative force can be expressed as

$$\boldsymbol{F}_{ij}^D = -\gamma w^D(|\boldsymbol{r}_{ij}|)(\hat{\boldsymbol{r}}_{ij}\cdot\boldsymbol{v}_{ij})\hat{\boldsymbol{r}}_{ij} \tag{3}$$

and the random force is given by

$$\boldsymbol{F}_{ij}^R = \sigma w^R(|\boldsymbol{r}_{ij}|)\theta_{ij}\hat{\boldsymbol{r}}_{ij} \tag{4}$$

where a_{ij} is the maximum repulsion between particle i and particle j, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, $\hat{\boldsymbol{r}}_{ij} = \boldsymbol{r}_{ij}/|\boldsymbol{r}_{ij}|$. R_c is the cutoff radius for the force summation. $\boldsymbol{r}$ represents position vector and $\boldsymbol{v}$ represents velocity vector of the corresponding particles, respectively. w^D and w^R are the $\boldsymbol{r}$ dependent weight functions which vanish for $|\boldsymbol{r}_{ij}| > R_c$. θ_{ij} is the randomly fluctuating variable with Gaussian statistics, γ is the amplitude of the dissipative force and σ is the noise level.

To fulfill the Gibbs-Boltzmann distribution, the weight functions as well as the amplitudes have the following relationships:

$$w^D(r) = [w^R(r)]^2 \tag{5}$$

$$\sigma^2 = 2\gamma k_B T \tag{6}$$

where k_B is the Boltzmann constant, and T is the absolute temperature.

2.2. Coarse-grained models of graphene and PMMA

The DPD simulations were performed on BIOVIA Materials Studio 2016 [39], A coarse-grained model of PMMA chain with 30 monomers is presented in Fig. 1, in which each bead stands for a single methyl methacrylate monomer. The volume of such PMMA chain was estimated using the Connolly surface to be 2744 Å^3, with the volume of each monomer being 92 Å^3. According to Flory-Huggins theory [40], each microscopic lattice should have approximately the same volume. The coarse-grained model of the pristine graphene was built as shown in Fig. 2. The volume occupied by graphene in terms of Connolly surface is 22,908 Å^3, and each graphene bead is comprised of six aromatic carbon hexagonal with sp^2 orbital hybridisation, with a volume of 95.5 Å^3.

2.3. DPD parameterisation

2.3.1. Parameters for repulsive interactions

To maintain the hydrodynamic characteristics of a system, the compressibility of the system should be similar to that of water according to Groot and Warren [19]. A water molecule has a volume of 30 Å^3. To match the size of a graphene or polymer bead, a coarse-grained water bead should represent three water molecules with a total volume of 90 Å^3. The system should satisfy [21]

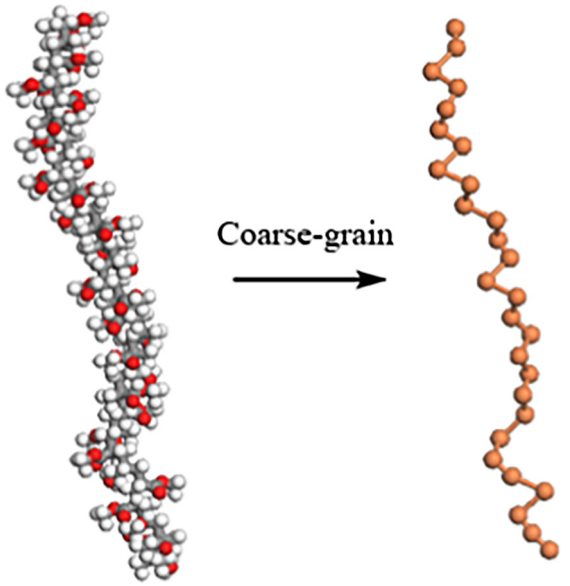

Fig. 1. Coarse-grained model of a PMMA chain.