PMMA/GRAPHENE NANOCOMPOSITES: Atomistic simulation to predict graphene fine dispersability in polymer composites with the aid of functional PMMA

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ABSTRACT

A large number of experimental studies in the last decade have demonstrated that the introduction of oxygen-containing functional groups in graphene sheets (GS) can greatly enhance the mechanical properties of their nanocomposites with polar polymers, even at extremely low loadings. Motivated by these reports, we recently presented a novel computational methodology for determining the elastic constants of syndiotactic poly(methyl methacrylate) (sPMMA) at small wt.% loadings of GS using atomistic modeling.[1] To carry out a comparative study of the effect of graphene functionalization on the degree of mechanical reinforcement, we addressed both pure (i.e., unfunctionalized) and functionalized GS bearing epoxy and hydroxyl groups randomly bound on both sides of their surface in the host sPMMA matrix. The calculation of elastic constants (which involves no adjustable parameters) followed the methodology originally proposed by Theodorou and Suter,[2] and was based on the use of the very accurate all-atom DREIDING[3] forcefield.

However, an important finding of our simulations was also that GS (either functionalized or non-functionalized) tend to self-assemble in the PMMA matrix in the form of stacks due to strong π-π stacking, and this lowers the degree of their interactions with the host matrix. Currently, covalent or non-covalent functionalization of graphene is widely used to improve its dispersibility in various media. Among these methods, non-covalent functionalization of graphene through π–π interactions is the preferred non-destructive method, which enables the modification of material properties without inflicting any damage to the crystalline structure of graphene.

In this work, we have used molecular modeling as a design tool for proposing strategies that can help alleviate the problem of graphene stacking in the polar PMMA matrix. The key idea is to leave the GS intact and, instead, to functionalize the PMMA chains with proper end groups, such as pyrene end-functional groups (Figure 1), with a strong tendency to absorb on graphene sheets. The resulting α,ω-poly(methyl methacrylate) (py-PMMA-py) chains are thought of excellent dispersing agents for GS. We thus carried out a detailed simulation study of py-PMMA-py/GS nanocomposites in full atomistic detail with a very efficient Molecular Dynamics (MD) algorithm, which verified the unique capability of α,ω-poly(methyl methacrylate) to prevent GS from coming together to form stacks. The simulations were

carried with the LAMMPS[4] code using the DREIDING force-field in the isothermal-isobaric (*NPT*) statistical ensemble at T=550K and P=1atm. Nanocomposites with several %wt. loadings in GS were tested. The polymer matrix in all cases was composed by 40 py-PMMA-py chains and 60 simple PMMA chains.

The simulations showed that the pyrene end-functional groups adsorb strongly on the two faces of GS and, as a result of the intervening polymer mass, GS are kept separate and well dispersed in the nanocomposite at all conditions studied. Several interesting structures were observed in the MD simulations: a) py-PMMA-py chains adsorbed on the same face of a graphene sheet through their end pyrene groups (a *loop*), b) py-PMMA-py chains adsorbed on the two faces of the same graphene sheet (an *extended loop*), and c) py-PMMA-py chains connected through their two end pyrene groups to two different graphene sheets thereby (a *bridge*). It is these loop and bridge structures that prevent graphene sheets from coming together in the polymer matrix to self-assemble and form stacks. We will present these findings and discuss them in relation to experimental observations. We will also present additional simulation predictions for the strcutural, thermodynamic and conformational proeprties of the simulated systems, and a detailed comparison with the more conventional case (already studied Ref. 1) where functionalized GS are used but the PMMA chains bear no pyrene functional groups.

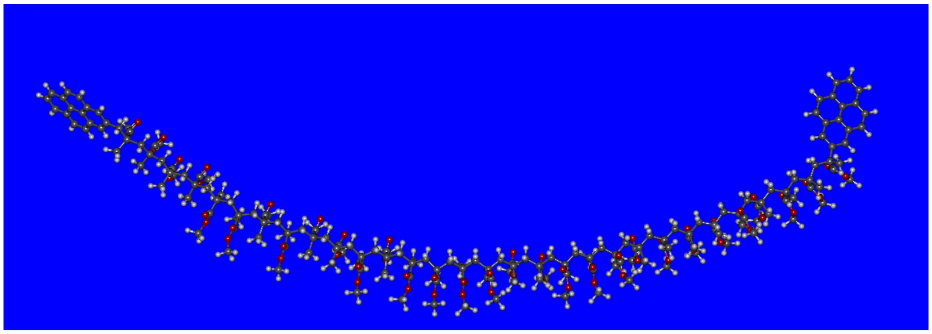

Figure 1. Typical atomistic configuration of a py-PMMA-py chain.

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