

Combining Advanced Polymerization Methods with Molecular Modeling for the Design of Graphene Dispersing Agents towards Fabrication of Polymer Nanocomposites

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Graphene has attracted increasing attention since its discovery a decade ago because of its extraordinary electronic, thermal, and mechanical properties and the potential of a variety of promising applications. Due to strong π - π stacking interactions, the graphene sheets tend to agglomerate into multilayer graphene structures. Therefore, it is of particular importance to prevent graphene aggregation in order to obtain monolayer graphene, well dispersed in various media towards the fabrication of functional graphene-based nanocomposites for a variety of novel applications. 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.

To this end, a pyrene functionalized PMMA (e.g. py-PMMA-py) was successfully synthesized and characterized in order to be used as dispersing agent for the direct exfoliation of micro-sized graphite sheets in low boiling point organic media and subsequent dispersion in the PMMA polymer matrix. The polymers were prepared via Activator ReGenerated by Electron Transfer (ARGET) ATRP polymerization. A particular pyrene-functionalized ATRP initiator was synthesized first via an esterification reaction and used for the initiation of MMA to produce α -functionalized, py-PMMA-Br. In order to prepare telechelic py/PMMA, the py-PMMA-Br was transformed to py-PMMA-N₃. Subsequently, the synthesis of py-PMMA-py was accomplished via a copper-catalyzed azide-alkyne cycloaddition (click chemistry), between the azide-terminated py-PMMA and an alkyne-functionalized pyrene, specially synthesized for this purpose. A similar synthetic procedure was followed for the synthesis of 3-armed end-functionalized py/PMMA by designing a tri-functional initiator.

Tip sonication of graphite was carried out in CHCl₃ in the presence of the synthesized py/PMMA to obtain stable graphene dispersions. Subsequently, the graphene/PMMA nanohybrids were mixed with PMMA (matrix) to fabricate graphene/PMMA nanocomposites to estimate the reinforcing effect of the dispersed graphene sheets on the nanocomposite mechanical properties. More importantly, the influence of macromolecular architecture was also evaluated.

The capability of pyrene functionalized PMMA to serve as an excellent dispersing agent of graphene was demonstrated through detailed, atomistic-level simulations of model systems carried out exclusively for the purpose of this project. The simulations showed that the pyrene end-functional groups adsorb strongly on the two faces of graphene sheets and, as a result of the intervening polymer mass, graphene sheets are kept separate and well dispersed in the nanocomposite at all conditions studied. Several interesting structures were observed in the 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. More interesting these structures will allow a deeper understanding of the influence of macromolecular architecture on the mechanical properties of the nanocomposites.

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