Graphene/poly(ethylene glycol) nanocomposites as studied by molecular dynamics simulations

Roza-Eleftheria Roussou, Kostas Karatasos *

Laboratory of Physical Chemistry, Department of Chemical Engineering, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

A B S T R A C T

Fully atomistic molecular dynamics simulations were utilized to examine melt dispersions of graphene nanosheets in a poly(ethylene glycol) (PEG) matrix, in a wide temperature range and for two different polymer sizes. The resulted mixtures were characterized by the organization of graphene in oligomeric clusters. No indications for polymer crystallization were noted in the examined time window. Instead, a weak thermal transition was observed upon cooling, at a temperature higher than the nominal glass transition and the melting point of the polymer. This was found to be associated with the formation of a kinetically-arrested graphene network within the polymeric matrix. Close and below the transition region PEG chains in the composites exhibited frozen-in configurations with an enhanced degree of conformations bearing short end-to-end distances, with those of the higher molecular weight characterized by more distorted shapes close to graphene planes. No polymer intercalation between graphene sheets was observed in the examined samples, while only a weak interaction between the two components was noted. Polymer dynamics in the mixtures were slowed down both in local and in global length scales, accompanied by a distinctly different temperature dependence of the pertinent relaxation rates, compared to those in the pristine macromolecular systems.

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1. Introduction

Graphene-based polymer nanocomposites have recently attracted a strong scientific and industrial interest [1–4] towards an effort to fabricate materials with high added value, which combine the advantageous features of the two components. Graphene (GR), being a high aspect ratio filler with enhanced electronic and thermal conductivity [5,6], thermal stability [7–9], gas barrier behavior [10,11] and mechanical properties [7,12,13], appears as a highly promising additive for the improvement of the overall performance of the host polymeric component. In general, the physical properties of such mixed systems were found to depend on several parameters, among others on the characteristics of the dispersion of the GR layers and the nature of the interactions between GR and the polymeric matrix [1,14,15], the amount of wrinkling in the GR [15], the polymer architecture [16,17] and the sample preparation procedure [1,5].

One of the most extensively examined polymers acting as the host matrix for composite materials based on carbon nanofillers [14,18–23], is poly(ethylene oxide) (PEO), due to its high technological importance in areas such as biomedicine [24,25], polymer-based electrolytes [26–28], fuel cells [29] and smart materials (phase switching components) [30,31]. For the production of PEO/graphite-based nanocomposites several protocols have been developed [14,32–34] which

resulted in systems appropriate for a wide range of novel applications [18,21,29,32]. Among them, melt blending appears as a cost-effective and scalable procedure [35–37] which may offer a faster route towards the industrialization of the production and thus the commercialization of such materials. Apart from their technological importance, PEO/graphite-based composites have also been utilized as model systems for a more detailed examination of the microscopic mechanisms which are ultimately responsible for the manifestation of the macroscopic behavior of this class of polymer/filler materials.

Along these lines recent studies have focused on the effects of the presence of the filler (in most cases graphite oxide) on the thermal properties [9,38], the structural characteristics [19,39,40] and the dynamics [23,40] of the polymeric component. In these and other studies it was demonstrated that the presence of the graphite-based filler (reduced GR, or graphite oxide) resulted in a shift to lower temperatures of observables such as the glass transition and the melting point of PEO [21,22,34,40]. In some of these works which focused on the examination of local PEO dynamics [19,23] and the interactions between PEO and the graphite-based filler [22,34,40], a correlation between the conformational changes and the mobility of polymer chains near the polymer/filler interface, and the thermal response of the polymeric phase was conjectured. In other recent studies [41], the degree of physical adsorption of non-conjugated polymers, such as PEO, onto chemically reduced GR was found to depend on the molecular weight of PEO, particularly in the low molecular weight range (between 200 and 1500 g/mol). This is exactly the range within which a steep change of

* Corresponding author.
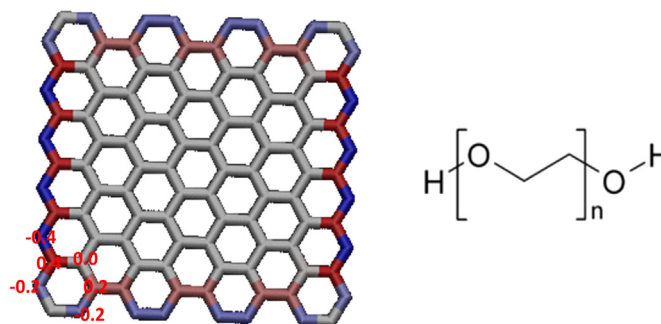E-mail address: karatas@eng.auth.gr (K. Karatasos).

the melting temperature of PEO as a function of molecular weight in the bulk takes place [42,43].

To obtain a more detailed microscopic view on issues related to the spatial arrangement of the two components in the composites, to the conformational features and the dynamics of the polymer in the presence of the filler, to possible effects of polymer molecular weight and of temperature in these characteristics, we have performed fully atomistic molecular dynamics simulations of GR nanosheets dispersed in low molecular weight fragments of PEO, i.e., poly(ethylene glycol) (PEG), in a wide temperature range. We have opted in studying mixtures mimicking the melt-blending procedure without a chemical modification of GR or covalent attachment between the two constituents, in order to describe systems without any potentially destructive effects [44] in the desirable properties of the two components. To better assess the effects of the presence of GR in the behavior of PEG, we have compared our findings to results from analogous simulations of the corresponding pristine polymers. To our knowledge, this is the first attempt of examining multi-GR/multi-PEG chain mixtures in full atomistic detail and in a temperature range spanning 400°.

2. Description of the models and simulation methodology

Two models of PEG/GR mixtures and two systems containing only polymer chains with molecular weights corresponding to those in the composite systems, were simulated in temperatures varying between 300 K–700 K. In the PEG/GR models the volume fraction of GR was kept constant to approximately 22%. We have chosen to study systems with a rather high loading in GR, in order to consider composites with a high degree of reinforcement of the polymer's properties [45,46]. In such systems we can also anticipate more pronounced effects, related to the increased amount of polymer/GR contacts, in the conformational characteristics and the dynamic properties of the polymeric component while also improving the statistical reliability of the analysis associated with the behavior of polymer chains close to graphene. We have examined two different sizes of PEG chains with one about double than the other, namely 855 g/mol (19 monomers) and 1736 g/mol (39 monomers), both lying below the entanglement limit [47], mixed with the same number of GR nanosheets bearing lateral dimensions comparable to the average size of the polymeric constituents, i.e., 15 Å × 15 Å. Details of the examined systems are provided in Table 1.

Forcefield parameters for the linear polymers of the mixtures were taken from the AMBER forcefield [48] which has been shown to be appropriate for the description of fully atomistic models of PEO in different thermodynamic environments [49–51]. Validation of the used parameter set for the pristine PEG models was provided via comparison to available pressure-volume-temperature (PVT) data (see Section 3.1), the characteristic ratio of the chains (see Section 3.2) and the solubility parameters of the polymer (see Section A in supplementary material). Bonded and non-bonded interactions for GR were also modeled using the AMBER forcefield parameters for generic aromatic carbon atoms, on account of recent fully atomistic molecular dynamics simulations which examined properties of pristine GR [52–54] and complexes of GR with other polymeric components [17,55–57]. No special constraints were imposed to keep the GR flakes perfectly planar. Fig. 1 provides a

Table 1
Details on the composition of the examined systems.

Systems' notation	Number of polymer chains	Number of GR sheets	Volume fraction of GR at 300 K (v/v %)
20peo39	20	0	0
20peo39g	20	20	22.1
40peo19	40	0	0
40peo19g	40	20	22.3

Fig. 1. (Left) A graphical representation of a GR nanosheet used in the model mixtures. The carbon atoms are represented as rods. Partial charges in |e| assigned to the edge carbons are also displayed, following Ref. [60]. (Right) A PEG monomer as used in the present study.

graphical representation of a GR sheet together with a repeat unit of ethylene glycol as used in our study.

The construction of the initial configurations both for the systems with the pristine polymers and those with the GR inclusions, was performed by utilizing the open-source package Packmol [58], in boxes corresponding to densities expected for room temperature conditions. The polymer chain models were taken from our previous work [51] by appropriately adjusting the molecular weight per chain, while the GR nanosheets were constructed by the aid of the VMD package [59]. Ensuing the construction of the initial configurations, the systems were subjected to energy minimization in order to reduce possible close contacts. Those models were taken as initial inputs for an annealing procedure comprised by combined isobaric-isothermal (NPT) MD simulations and further steepest descent and conjugate gradient energy minimization cycles at each temperature.

Starting from a temperature of 300 K and increasing it by steps of 50 K until a temperature of 700 K was reached, each model was equilibrated as described above for several tens of ns depending on the temperature and the system under examination. For all systems the collection of data was performed during the cooling procedure from 700 K down to 300 K, also with 50 K steps. The last frame at each temperature served as the initial configuration for the equilibration procedure targeting the immediately lower temperature. Again, at each temperature during the cooling process, energy minimization as well as several tens of ns of NPT MD runs were performed prior to the commencement of the production trajectories, so that characteristic energetic, static and thermodynamic properties of the systems (total energy, specific volume, average size of the polymer molecules and spatial arrangement of the two components in mixtures) were stabilized within the duration of the equilibration period; at the end of this procedure polymer chains have diffused at distances several times longer than their average size (as the latter is expressed by their radius of gyration).

In the MD productions runs a timestep of 1 fs was used in conjunction with a velocity Verlet algorithm, with a saving frequency of 1 ps. Pressure was kept at 1 bar by means of the Nose-Hoover Langevin piston method [61] (using a piston period of 0.1 ps and a decay time of 0.05 ps) while temperature was controlled with the Langevin algorithm (using a damping coefficient of 3 ps^{-1}). For the computation of electrostatic interactions the particle mesh Ewald (PME) scheme was employed [62]. All simulations were performed with NAMD 2.9 [63] using periodic boundary conditions and with a cutoff of the Van der Waals interactions at 12 Å (a switching function was also employed at the last 2 Å to avoid discontinuities in the potential and the forces). Fig. 2 shows an example of the result of the equilibration procedure followed, for the composite systems.

After equilibration, there was a departure of the graphene geometry from a perfectly-flat plane. Our calculations showed that the degree of shrinkage in the lateral dimensions of the graphene sheets remained