



Effect of polyethylene glycol-grafted graphene on the non-isothermal crystallization kinetics of poly(ethylene oxide) and poly(ethylene oxide):lithium perchlorate electrolyte systems



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ABSTRACT

Graphene nanoplatelets were chemically modified by polyethylene glycol (PEG), via an amidation reaction. Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray analysis (EDX) and thermo-gravimetric analysis (TGA) revealed the successful accomplishment of reaction. Functionalized graphene (FGnP) were incorporated into poly(ethylene oxide) (PEO) and solid polymer electrolytes (SPE) based on PEO and lithium perchlorate salt (LiClO_4). The non-isothermal crystallization kinetics of samples were studied using differential scanning calorimetry (DSC). Modified Avrami and combined Avrami-Ozawa equations were used to analyze the non-isothermal crystallization. The Avrami exponent values showed that FGnP did not change the nucleation mechanism and crystal growth in neither PEO nor PEO: LiClO_4 . However, the half-time of crystallization increased by addition of FGnP in both PEO and PEO: LiClO_4 systems. A more considerable effect of FGnP on the crystallization behavior of SPE/FGnP electrolytes was found in comparison to PEO/FGnP nanocomposites, which can be related to the FGnP induced dissociation of lithium salt.

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1. Introduction

Synthesis and preparation of new materials with new or improved properties is one of the main objectives of materials chemistry. Polymer-based nanocomposites displaying a considerable enhancement of different properties even at very low loading of nanoparticles, have been widely investigated in recent years [1]. In this context, using different nanoparticles such as nanosilica [2,3], nanoclays [4,5], metallic nanoparticles [6,7] and carbonaceous nanomaterials [8–10] to improve the physical, mechanical, thermal or electrical properties of polymers have been reported in the literature. Graphene, a two-dimensional lattice of carbon atoms, has received much attention recently in the scientific community because of its extraordinary properties including excellent strength and high thermal and electrical conductivity [11–13]. The maximum improvement in the final properties of graphene/polymer nanocomposites will be obtained when strong interfacial interactions exist between graphene surface and polymer chains to achieve a well-dispersed structure of graphene in the matrix. However, pristine graphene usually shows weak

interactions with most polymers. In order to compatibilize graphene with polymer matrices and increase the interfacial interactions, chemical modification is required [14]. Different modification methods have been reported to create proper functional groups on the surface of graphene nanoplatelets. Oxygen containing groups is the most common product of functionalization and in many cases is the commencement of further modifications for displaying other groups such as amine, hydroxyl or isocyanates by forming amide and carbamate ester bonds [15–17].

Poly(ethylene oxide) (PEO) is a semi-crystalline hydrophilic polymer with wide range of applications. One of the important applications of PEO is being the host polymer in solid polymer electrolytes (SPEs) due to its flexible backbone, very low glass transition temperature, electrochemical stability and ability to form complexes with alkali metal salts. SPEs, as a potential material to be used in Li batteries and other electrochemical devices, can provide high specific energy, high specific power and several advantageous over liquid or gel-like electrolytes such as flexibility, non-flammability and non-toxicity [18–20]. As demonstrated by many researchers [18,21–23], ion transport which is the main function of SPE, occurs only in the amorphous phase and by segmental motion of polymer backbone. Accordingly, the ionic conduction would be reflected from factors such as crystallinity,

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spherulitic morphology, size and thickness of spherulites [24]. Since the presence of graphene may substantially influence the crystalline structure of polymer matrices, it is crucial to consider the crystallization behavior of PEO and explore the effect of graphene nanoplatelets. Although in the most composite systems it was found that fillers act as nucleating agent to accelerate the crystallization, incorporation of fillers into the poly(ethylene oxide) matrix leads to a different crystallization behavior. Adhikari and Lozano used DSC to investigate the crystallization behavior of PEO/carbon nanofiber systems under non-isothermal conditions and showed that all carbon nanofiber loadings retard the crystallization of PEO [25]. The effect of two-dimensional silver nanoplatelets on the non-isothermal crystallization of PEO has been discussed by Rahmansyah et al. [26,27]. They found that the overall crystallization rate of nanocomposites was slower than that of neat PEO and the radius of spherulites was greater. Furthermore, analyzing the nucleation activity revealed that nanoplatelets act as anti-nucleating agent to hinder nucleation. Jin et al. investigated the effect of carbon nanotubes on the crystallization behavior of PEO [28]. They observed that by carbon nanotube incorporation, the degree of crystallinity was reduced and the spherical growth rate was restricted. Isothermal crystallization behavior of PEO nanocomposites with single walled carbon nanotube and lithium dodecyl sulfate stabilizer studied by Chatterjee et al. [29]. It was indicated that the crystallization process of polymer chains in the presence of lithium based surfactant and nanotubes slowed down and thinner crystal lamellae were formed. Some interesting results were also reported in the nanocomposite polymer electrolytes with ceramic nanofillers [30,31], cerium oxide nanoparticles [32], organoclay [33] and functionalized carbon nanotube [34] which showed that the addition of nanoparticles into polymer electrolyte caused a further reduction in the crystallinity of PEO.

This study is motivated by current researches on the development of polymer electrolyte systems performance using nanomaterials. Graphene oxide (GO) and other functionalized GOs, containing many functional groups which disrupts the hexagonal lattice of carbon atoms. As a consequence, they show insulating properties, make them susceptible to be used in solid polymer electrolytes to improve the ionic conductivity and mechanical properties [35,36]. It is of crucial interest to understand how functionalized GO could influence crystallization structure and crystallization kinetics of PEO in PEO based SPEs.

In this work, carboxylic acid groups on the oxidized graphene surface were employed to react with the hydroxyl groups of Poly(ethylene glycol) (PEG) in the presence of a carbodiimide condensing agent. PEO:LiClO₄ electrolytes containing functionalized graphene nanoplatelets (FGnP) were fabricated via solution blending method. The non-isothermal crystallization behavior of samples were investigated using differential scanning calorimetry (DSC). For a better discernment, PEO/FGnP nanocomposites were also prepared and investigated. The overall crystallization kinetics with varying FGnP loadings analyzed using modified Avrami and combined Avrami-Ozawa approaches. In other words, we aimed to understand the roles of added lithium salt and graphene nanoplatelets on the crystallization behavior of PEO.

2. Experimental

2.1. Materials

PEO with a molecular weight, $M_w = 900,000$ g/mol was purchased from Scientific Polymer Products, Inc. (Ontario, NY). Graphene nanoplatelets (xGnP-C750) with a thickness of 1–5 nm and lateral dimensions of $<2 \mu\text{m}$ were supplied from XG Sciences. Acetonitrile as the solvent and N,N-dicyclohexylcarbodiimide (DCC) as the condensing agent were provided by Merck. LiClO₄ (battery grade, dry, 99.9% trace metals basis) and PEG with a molar mass of 400 g/mol were obtained from Sigma-Aldrich. LiClO₄ was dried in vacuum oven at 40 °C for 48 h prior to use.

2.2. Preparation of PEG grafted graphene

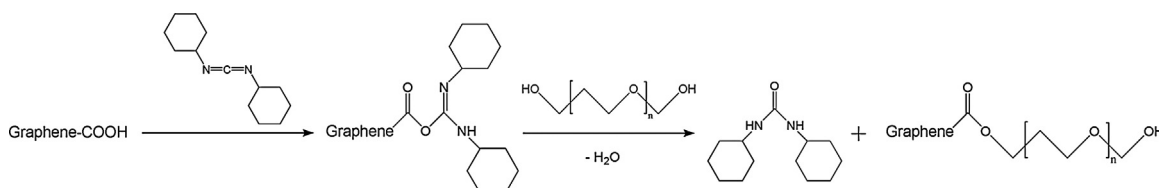
Graphene nanoplatelets (GnP) was firstly mixed with a 1:1 v/v mixture of H₂SO₄ (8 M) and HNO₃ (8 M) and then sonicated in an ultrasonic bath at 60 °C for 2 h to prepare carboxylated graphene (GnP-COOH). The product was repeatedly washed with deionized water by decantation and centrifugation. The solid residue was finally dried under vacuum at 60 °C for 24 h.

In the second stage, GnP-COOH was reacted with PEG400 through a carbodiimide-activated esterification reaction according to literature with slight modification [37]. For this purpose, 0.5 gr GnP-COOH, 2 gr PEG400 and 0.05 gr of dried DCC were added to 40 ml anhydrous tetrahydrofuran (THF) under N₂ atmosphere and sonicated for 30 min. The reaction mixture was heated up to 60 °C and subjected to vigorous stirring under reflux and N₂ atmosphere for 48 h. After completion of the reaction, the suspension was filtered through a 0.45 μm PTFE membrane and washed with THF, absolute ethanol and deionized water to remove the unreacted PEG thoroughly. Final product was obtained after drying under vacuum at 60 °C for 24 h. The preparation procedure of PEG grafted graphene (FGnP) is illustrated in Scheme 1.

2.3. Preparation of PEO/functionalized graphene nanocomposites and electrolytes

PEO and graphene nanoplatelets dried in vacuum before sample preparation. FGnP was dispersed in acetonitrile (1 mg/ml) by magnetic stirring overnight and then by bath sonicating for 3 h. PEO (5 gr) was dissolved in 100 ml acetonitrile at 50 °C and stirred 6 h to ensure complete dissolution of the polymer. Graphene dispersion was gradually added to this solution and stirred for another 24 h. Finally, this homogeneous solution was cast onto glass petri dishes and dried at room temperature. The nanocomposite films were further dried at 40 °C under vacuum for 72 h to remove the residual solvent completely. The prepared nanocomposites labeled as PEO/FGnP, containing 0.1, 0.5, 1 and 3 wt.% of FGnP.

Nanocomposite polymer electrolytes prepared with the same procedure for polymer nanocomposites except that LiClO₄ was dissolved into the polymer solution 1 h before the addition of graphene dispersion. The molar ratio of ethylene oxide units (EO) to that of lithium cations (Li⁺) was kept equal to 8 ([EO]:[Li⁺] = 8).



Scheme 1. Preparation of functionalized graphene from carboxylated graphene.

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