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Poly(meth)acrylate nanocomposite membranes containing *in situ* exfoliated graphene platelets: Synthesis, characterization and gas barrier properties

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ABSTRACT

Here we report a novel method for the preparation of polymer nanocomposites containing *in situ* exfoliated graphene nanoplatelets. First, graphite particles were modified by sodium and ethylenediamine (en), yielding first-stage graphite intercalation compounds (GICs) containing $[Na(en)]^+$ complex between carbon sheets. After subsequent ion-exchange reaction of the intercalated complex with quaternary ammonium salt bearing methacrylamide group, GICs possessing polymerizable double bond were obtained. It was found that the extent of $[Na(en)]^+$ complex intercalation as well as the ion-exchange reaction was significantly dependent on the type of the graphite used (natural vs. synthetic). GICs derived from natural graphite were further employed in the synthesis of polymer nanocomposites. Using NMR and TEM it was confirmed that the methacrylamide group in GICs participated successfully in the process of copolymerization with 2-hydroxyethyl methacrylate and 2-ethylhexyl acrylate, resulting in the *in situ* GICs exfoliation. The prepared nanocomposite membranes were further characterized using X-ray diffraction, DSC and TGA. Gas permeability measurements on the polymer composites were also carried out, confirming that the initial GIC was present in an exfoliated form.

1. Introduction

Graphite is distinguished by its unique multilayered structure, consisting of mutually parallel two-dimensional carbon sheets bonded by weak van der Waals interactions. This bond arrangement allows intercalation of anions or cations *via* oxidation or reduction reactions without disrupting the layered topology of graphite, resulting in a formation of graphite intercalation compounds (GICs) [1–5]. In a GIC not every layer is necessarily occupied by guests; in so-called first-stage compounds, graphene layer and intercalate layer alternate, whereas in high-stage compounds, intercalate layer randomly separates stacks of graphite multilayers [6]. Obviously, a large variety of possibilities exists between these two extreme cases.

In recent years, GICs prepared with the use of low molecular weight quaternary ammonium salts as graphite delaminating agents have been intensively studied by many authors [1,2,7,8]. Several GICs were employed as intermediates for the preparation of exfoliated single or few layered graphene flakes. Zhou et al. obtained high-quality graphene nanoplatelets by mild sonication of graphite intercalated by tetraethylammonium salt [3]. Li et al. inserted tetrabutylammonium hydroxide into previously modified

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thermally expanded graphite, and then sonicated the product in a solution of a surfactant in DMF, yielding a homogenous suspension of graphene monolayers [9]. Process of GICs exfoliation is generally irreversible, and leads to a spongy, low-density and high-surface-area carbon material. The resulting materials exhibit, besides others, excellent electrical [10,11] and thermal conductivity [12,13], high thermal stability [10,11], or gas sorption properties convenient for example as gas sensors [14] or membranes for gases separation [15–17].

The application of GICs for fabrication of graphene/polymer nanocomposites presents an alternative route to mainstream methods utilizing graphene oxide (GO) or its reduced analog (RGO), beneficially avoiding large formation of oxidative defects in the graphene structure. Generally, there are many synthetic ways leading to preparation of graphene-containing polymer nanocomposites using GICs [18]. The first approach involving direct intercalation of polymer chain between graphene sheets is, however, limited to oligomers or low molecular weight polymers [19]. Thermal shock treatment of GICs followed by ultrasonication was applied for preparation of semi-interpenetrating network of epoxy resin and unsaturated polyester containing graphite nanosheets [20]. An *in situ* exfoliation of GICs by melt blending [21–24] or in polymer solution [25,26] were also mentioned. An *in situ* polymerization is another way of nanocomposite preparation, which has been proved to be more efficient overcoming common drawbacks of the above mentioned methods such as too high polymer viscosity, the necessity of a solvent usage, low GICs exfoliation degree, etc. During the *in situ* polymerization, a monomer is first introduced into GIC galleries, and subsequently (co)polymerized. The GICs expansion took place only when the reactivity of monomer is high enough, for example in the case of vinyl monomers (isoprene, styrene, 1,3-butadiene) in the presence of donor-type GICs (e.g. KC_{24}) [27]. Xu et al. performed the *in situ* polymerization of methyl methacrylate (MMA) in the presence of graphite nanoplatelets with the assistance of sonication and heating, which helped MMA and growing polymer chains to penetrate into the pores of graphite enabling its exfoliation [28]. These examples demonstrate that an initiator or a monomer located in the GIC galleries induce inter-gallery polymerization and subsequently might promote delamination of graphene layers.

In our previous work, we have synthesized GICs intercalated by a quaternary ammonium salt bearing polymerizable double bond, and by its subsequent free radical copolymerization with *n*-butyl methacrylate we have obtained polymer composite containing graphite/graphene structures [29]. However, the process of the intercalate *in situ* exfoliation in the composite proceeded to a certain extent only, probably due to more hydrophobic nature of the polymer matrix when compared to the modified GICs.

The current study is therefore focused on (i) optimization of reaction conditions for the synthesis of various GICs possessing polymerizable methacrylamide group (using three different types of graphite as a starting material), (ii) preparation of polymer composite membranes by free radical copolymerization of 2-hydroxyethyl methacrylate and 2-ethylhexyl acrylate in the presence of GICs, and (iii) characterization of the prepared membranes using XRD, NMR and electron microscopy. Gas permeability measurements were carried out to determine the influence of the various filler types on gas transport properties of the related nanocomposites. Thermal stability of the prepared nanocomposites, which is also an important indicator for the membranes applicability, was evaluated by DSC and TGA.

2. Materials and methods

2.1. Materials

Natural graphite (NG; PMM11 Very fine crystalline graphite powder, Koh-i-noor Grafit, Ltd., Czech Republic), synthetic graphite (SG; Synthetic graphite Grade 8028B, Graphite Týn, Ltd., Czech Republic) and TIMREX synthetic graphite (TG; TIMREX® KS75, Songhan Plastic Technology Co., Ltd., China) were used as received. All chemicals were purchased from Sigma-Aldrich Ltd. and used as received. *N*-[3-(dimethylamino)propyl] methacrylamide (DMAPMA), 2-hydroxyethyl methacrylate (HEMA) and 2-ethylhexyl acrylate (2-EHA) were distilled prior to use.

2.2. Synthesis

Monomeric quaternary salt (MQS). MQS was prepared by the reaction of DMAPMA with *n*-hexadecyl iodide [29]. The G1 and G2 intercalates were synthesized using a slightly modified procedure described therein.

G1 intercalates. Natural graphite (500 mg) and freshly cut sodium (100 mg) were dispersed in freshly distilled ethylenediamine (en; 60 mL). The reaction proceeded overnight in nitrogen atmosphere under stirring at 60 °C. Subsequently, en (20 mL) was added to dissolve unreacted sodium, and the reaction mixture was stirred at room temperature for additional 4 h. The black solid was then separated from the supernatant solution by centrifugation, dried under vacuum to a constant weight and designated as NG1. *Yield:* 750 mg. Intercalates of the synthetic graphite and the TIMREX graphite (SG1 and TG1, respectively) were prepared analogically.

G2 intercalates. First, reaction conditions for the G2 synthesis were optimized for NG1 as a starting material by the following procedure. The prepared NG1 intercalate was dispersed in a solution of MQS in DMF (2 mL). The mixture was bubbled with nitrogen and sealed. The ion-exchange reaction was carried out under stirring at 25 °C. Related moieties of starting materials and reaction periods are summarized in Table 1. The product was then separated by centrifugation, washed three times with acetone and methanol to remove salts and unreacted monomer, and dried under vacuum to a constant weight. The extent of the ion-exchange process in dependence on reaction conditions was then carefully assessed using XRD method. Subsequently, the SG2 and TG2 intercalates were synthesized under conditions that have been evaluated as optimal.

2-EHA/HEMA polymer composites. In a typical procedure, NG2_A (22.0 mg, 1.0 wt.%), 2-EHA (0.8 g, 4.3 mmol), HEMA (1.31 g, 10.1 mmol) and acetone (6.3 mL) were placed into an ampoule. After addition of AIBN (35 mg, 213 μmol) the mixture was