Composites Science and Technology 154 (2018) 85–91

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Excellent electrically conductive PE/rGO nanocomposites: *In situ* polymerization using rGO-Supported MAO cocatalysts

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ARTICLE INFO

Article history:
Received 28 June 2017
Received in revised form
7 November 2017
Accepted 14 November 2017
Available online 21 November 2017

Keywords:
Electrical conductivity
In situ polymerization
rGO
Percolation threshold

ABSTRACT

Superior electrically conductive PE nanocomposites were prepared with reduced graphene oxide(rGO)-supported MAO cocatalyst via *in situ* ethylene polymerization. The electrical conductivity of the composites was very high at 1.2 S/m. This value is the highest among reported rGO-filled composites. The cocatalyst system was prepared by modifying with alkoxysilane compound to prevent restacking of the GO plane in the reduction process and solvothermal reduction of GO. The effect of cocatalysts on the properties of nanocomposites and distribution of nanosheets in the polymer matrix was investigated in detail. The mechanical properties and thermal stability of PE/rGO nanocomposites were significantly increased via the addition of a small amount of rGO. These properties resulted from the restacked rGO layers exfoliated *in situ* by the ethylene insertion between the intercalated layers.

1. Introduction

Polyolefin nanocomposites are widely used in the plastic industry for many applications. Many studies have reported the benefits of adding nanofillers to polyolefin to reinforce their thermal and mechanical properties [1–5].

Polymer nanocomposites are three-phase systems (the polymer matrix, nanofiller and interfacial region). The interactions are affected by the surface structure of the nanofiller and the adhesion strength between the nanofillers and polymer. The adhesion strength at the interfacial region is sufficiently strong and the elastic deformation and stresses are transmitted from the polymer to the nanofillers [6–9].

Graphene has remarkable thermal, mechanical, and electronic transport properties. Although graphene is considered an excellent filler in the polymer industry, the aggregation and insufficient exfoliation of graphene sheets prevents its superior properties from being exploited in polymer nanocomposites [10–12]. Therefore, graphene oxide (GO) is preferred over graphene as a polymer reinforcement because the functional groups the edge of on the GO increase the interactions between the GO and polymer matrix. GO has abundant functional groups on its surface and thus has attracted significant attention for applications in nanocomposites. However, GO is electrically insulating and thermally unstable; therefore, to restore its electrical and thermal properties, its reduction is necessary [1]. In order to facilitate the industrial fabrication and application of graphene based polymer composites, the direct use of reduced GO (rGO) as fillers to prepare polymer nanocomposites is preferred.

Solution blending, melt mixing, and *in-situ* polymerization have been used to produce these polymer/rGO composites [13–16]. *In situ* polymerization allows the preparation of uniform polymer nanocomposites with strong interactions between the nanofillers and polymer; consequently, significant research into the property enhancement of polymer nanocomposites via *in situ* polymerization has been carried out [3–5,16–18].

Although *in situ* polymerization is a very attractive technique for well dispersed GO and graphene composites, there are several reports available regarding polyolefin/GO composites. Dong et al. reported the functionalization of the GO surface by Ziegler-Natta catalyst for the preparation of conductive isotactic polypropylene [19]. Mülhaupt et al. [20] successfully prepared ultra-high molecular weight polyethylene with an immobilized Cr catalyst on the surface of GO with methylaluminoxane (MAO). For the functionalization of the surface of GO with metallocene catalysts amine groups were introduced to the surface for ethylene polymerization

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https://doi.org/10.1016/j.compscitech.2017.11.012

[21]. Alexandre et al. performed ethylene polymerization with MAO-activated graphite-supported metallocene which was synthesized using a polymerization-filling technique, with graphite distributed evenly inside the nanocomposite [22]. Graphene was treated with zirconocene to achieve the corresponding graphene/Cp_2ZrCl_2 catalyst via π–π stacking electronic interactions for the polymerization of ethylene [23,24]. There have not yet been reports of electrically conductive PE using zirconocene activated rGO-supported MAO cocatalysts, which presents the opportunity of an even distribution of rGO in a polyolefin matrix.

In this work, the preparation of electrically conductive PE/rGO nanocomposites with rGO-supported MAO cocatalysts via *in situ* polymerization is described. The functionalized rGO was synthesized via the treatment of (3-aminopropyl)triethoxysilane (rGO/APTES) to prevent restacking of GO plane in the reduction process and they was reduced using the solvothermal method at N,N-dimethyl formamide (DMF). This was used as a template to form rGO-supported MAO cocatalysts. The polymerization was conducted in a high-pressure reactor using bis(n-butylcyclopentadienyl) zirconium(IV) dichloride ($(n\text{-BuCp})_2ZrCl_2$) as the catalyst.

The structure of the functionalized rGO was investigated by FT-IR and XRD. The mechanical, thermal and electrical properties of the obtained PE/rGO nanocomposites were examined. The morphology and dispersion of rGO sheets were inspected by SEM and optical microscopy. The aim of this study is to broaden the applications of PE by not only transforming an insulator to a conductive PE but also producing PE with excellent thermal stability and mechanical properties.

2. Experimental

2.1. Materials

Expanded graphite (Timcal Graphite & Carbon, Switzerland, <100 μm, 99.9%), sulfuric acid (H_2SO_4, Duksan Chemical Co., H_2SO_4, ≥95%), hydrochloric acid (HCl, Duksan Chemical Co., HCl, 37%), hydrogen peroxide (H_2O_2, Duksan Chemical Co., H_2O_2, 28%), sodium nitrate (Daejung Co.), potassium permanganate (Sigma Aldrich, US, >99.0%), (3-aminopropyl)triethoxysilane (Sigma Aldrich, US, 99%), triethylaluminium (TEA, Tosoh Akzo, Japan), MAO (MMAO-3A; Al content = 5.9 wt%; Akzo Nobel), (n-BuCp)$_2$ZrCl$_2$ (Strem Chem. Co., 98%), methyl alcohol (CH_3OH, Duksan Chemical Co,. CH_3OH, 99.8%) and dimethyl formamide (DMF, Duksan Chemical Co., 99.9%), were used without further purification. Toluene and hexane were distilled from sodium/benzophenone under nitrogen atmosphere before use.

2.2. Synthesis of GO and rGO-supported cocatalysts

GO was prepared from the expanded graphite using Hummers' method as described in previous reports [25,26]. GO (1 g) was dispersed in DMF (300 mL) via ultrasonication for 7 h, and subsequently, APTES (20 mmol) was slowly added. After stirring for 12 h at 60 °C, the mixture was filtered and repeatedly washed with DMF to remove any unreacted APTES. The obtained GO/APTES was reduced using the solvothermal method as described below. The suspension of GO/APTES (1 g) in DMF (300 mL) was heated to 150 °C, subsequently refluxed for 24 h, and filtered. The powder was dried at 200 °C for 48 h under vacuum and it is hereafter referred to as rGO/APTES (See Supporting Information).

GO, GO/APTES, or rGO/APTES (1 g) were dispersed in toluene (100 mL) via ultrasonication for 7 h. Subsequently, MAO (15 mL) was added to the suspensions at 60 °C, and the reactions were completed after stirring for 12 h. The reaction mixtures were washed several times with toluene to remove the unreacted MAO. The resultant cocatalysts containing GO, GO/APTES, and rGO/APTES are named as Cocat-A, Cocat-B, and Cocat-C, respectively (See Scheme S1).

2.3. In situ polymerization

In situ ethylene polymerization was carried out in an 800-mL stainless steel high pressure reactor with a magnetic stirring bar. The reactor was purged with nitrogen at least five times and the required amount of polymerization medium (n-hexane) was added to the reactor. Subsequently, 0.1 mmol of triethylaluminium (TEA) was placed into the medium as an oxygen scavenger. After that, a suspension of rGO-supported MAO cocatalysts and catalyst ($(n\text{-BuCp})_2ZrCl_2$) which had been ultrasonicated for 20 min was injected into the reactor followed by pressurizing with ethylene (4 atm). The polymerization was conducted at 40 °C for 1 h and terminated by the addition of 10% HCl-MeOH solution after venting the gas. The suspension was poured into 500 mL of methyl alcohol to precipitate the polymers. Further, the polymers were dried under vacuum at 60 °C and weighed. The resultant PE/rGO nanocomposites prepared from Cocat-A/B/C are denoted as Cat-A PE, Cat-B PE and Cat-C PE, respectively.

2.4. Characterizations

The detailed characteristic analysis is presented in the Supporting Information.

3. Results and discussion

3.1. Characterization of rGO-supported MAO cocatalysts

The chemical structures of GO, GO/APTES and rGO/APTES were analyzed using FT-IR and XRD. As shown in Fig. 1, FT-IR was used to determine not only the structures of GO, GO/APTES and rGO/APTES but also to identify the covalent bonds between the components.

The representative peaks of GO were observed, such as hydroxyl stretching (-OH, around 3400 cm^{-1}), carboxyl stretching (C=O, 1720 cm^{-1}), sp^2-hybrided carbon (C=C, 1638 cm^{-1}), and epoxide vibrations (C-O-C, 1320 cm^{-1} and C-O, 1054 cm^{-1}) [27,28].

The functionalization of GO with APTES led to the disappearance of the C=O stretch at 1738 cm^{-1}, and the hydroxyl group (-OH) of

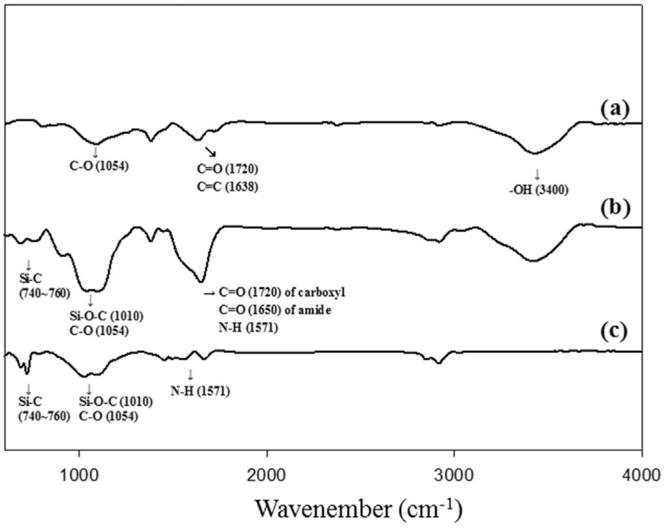

Fig. 1. FT-IR spectra of (a) GO, (b) GO/APTES, and (c) rGO/APTES.