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Promoting dispersion of graphene nanoplatelets in polyethylene and chlorinated polyethylene by Friedel–Crafts reaction

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ABSTRACT

Graphene nanoplatelets (GNPs) are the stacks of multi-layered graphene sheets which can be incorporated with different polymers in order to gain outstanding performance in mechanical, thermal, electrical, optical and barrier properties. However, the strong van der Waals interactions between graphene sheets make GNPs tend to agglomerate in polymer matrix, resulting in the concentration of stresses. In this paper, GNPs were compounded with high density polyethylene (HDPE) and chlorinated polyethylene (CPE) in the presence of a Lewis acid catalyst ($AlCl_3$). The macrocarbocations in polymer chains, initiated by Friedel–Crafts reaction, formed strong interaction with delocalized conjugated π electrons of graphene sheets, which benefited to unfolding the aggregations of GNPs and improving its dispersion in the composites.

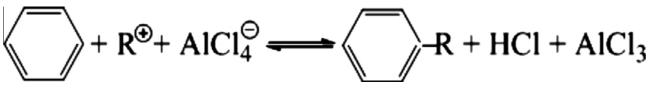
1. Introduction

Graphene nanoplatelets (GNPs) are the stacks of multi-layered graphene sheets which attracted tremendous attention in recent years. GNPs have been incorporated with different polymers in order to gain the outstanding performance in mechanical, thermal, electrical, optical and barrier properties [1,2]. However, the strong van der Waals interactions between graphene sheets make GNPs tend to agglomerate in polymer matrix, resulting in the concentration of stresses. The major challenge for fabrication of GNPs-based nanocomposites is, indeed, the dispersion of GNPs in polymer [3–5]. Therefore, many efforts have been made to solve the agglomeration of GNPs in polymer matrix, including the covalent functionalization and the non-covalent functionalization [6–9].

Graphene consists of a monolayer of sp^2-hybridized carbon atoms arranged in a two-dimensional lattice [1,2]. The assembly of six membered carbocyclic rings of graphene has similar structure to the benzene ring of aromatic compounds. Also, graphene has abundant radial delocalized conjugated π–π electrons. Thus, a new solution of promoting the dispersion of GNPs in polymer matrix may be found by grafting polyolefin to the carbocyclic rings of graphene through Friedel–Crafts reaction in the presence of a Lewis acid catalyst.

Friedel–Crafts alkylation reaction is one of the most effective methods to build C–C bonds with aromatic compounds [10]. The halogenated compound or unsaturated compound can form carbocations in the presence of Lewis acid (for example, aluminum chloride), as shown in Eq. (1). The carbocation can serve as an electrophile to hit negative groups, which makes the conjunction of C–C bonds possible by electrophilic substitution, as shown in Eq. (2). The benzene ring of aromatic compounds is susceptible to electrophilic attack easily because of its exposed π electrons [11]. Therefore, the alkylation of aromatic compounds can be achieved by Friedel–Crafts reaction.

$$AlCl_3 + RCl \rightleftharpoons AlCl_4^{\ominus} + R^{\oplus} \tag{1}$$



(2)

In our preliminary study [12–17], a Lewis acid catalyst, $AlCl_3$, was adopted to initiate the Friedel–Crafts alkylation reaction between polystyrene (PS) and polyolefin elastomer (POE). The result of experiments confirmed that PS had chemically bonded to POE chains and the formation of PS-*graft*-POE copolymer improved the compatibility of PS/POE blends.

In this work, a Lewis acid catalyst ($AlCl_3$) is added to the HDPE/GNPs and CPE/GNPs composites in order to initiate the Friedel–Crafts reaction. The morphology of the GNPs-based nanocomposites is evaluated and the effect of Friedel–Crafts reaction in promoting dispersion of GNPs in polymer matrix is illustrated.

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2. Experimental parts

2.1. Materials

High-density polyethylene (HDPE, code 5000S, MFR = 0.9 g/10 min) was purchased from Yangzi Petrochemical Co., Ltd., Nanjing, China. Chlorinated polyethylene (CPE, code 135A, chlorine content = 36.21%) was obtained from Feihe Chemical Co., Ltd., Zibo China. Anhydrous aluminum chloride ($AlCl_3$, analysis grade) was purchased from Shuanglin Reagent Co., Ltd., Hangzhou, China.

Graphene nanoplatelets (GNPs, code KNG-150) were obtained from Xiamen Knano Graphene Technology Co., Ltd., Xiamen, China. The graphene nanoplatelets are stacks of multi-layered graphene sheets having platelet morphology (as shown in Fig. 1). The carbon content is greater than 99.5%, and the density is about 2.25 g/cm^3.

2.2. Preparation of HDPE/GNPs and CPE/GNPs composites

HDPE/GNPs (100/1, mass ratio, the same hereinafter), HDPE/GNPs/$AlCl_3$ (100/1/0.8), CPE/GNPs (100/1) and CPE/GNPs/$AlCl_3$ (100/1/0.8) composites were prepared via a twin-screw mini-extruder (MiniLab, Germany) at 180 °C with the screw rotation speed of 100 rpm, and changes in torque with blend time were recorded.

2.3. Characterization

The samples frozen by the liquid nitrogen were sliced using a microtome and then examined with a JEM-1200EX transmission electron microscope (TEM, JEOL, Japan) at an accelerating voltage of 120 kV.

Raman spectroscopic observation was applied with a Raman spectrometer (Jobin Yvon, France) equipped with 514.5 nm Ar$^+$ laser in an ambient atmosphere and at room temperature.

Scanning electron microscopy (SEM) was used to analyze the char residues by S-4800 microscopy (TSM-5510, Japan) under an accelerating voltage of 3 kV. Samples used for the char analysis were $30 \times 6 \times 3$ mm^3 in size and were placed in a muffle furnace at 400 °C for 5 min.

3. Results and discussions

TEM images of HDPE/GNPs and HDPE/GNPs/$AlCl_3$ composites are shown in Fig. 2. GNPs particles could be found to disperse heterogeneously in HDPE matrix with large and dense stacking structure, as shown in Fig. 2a. The laminated structure of GNPs could hardly be seen due to the strong interaction between graphene platelets. The high resolution TEM image shown in Fig. 2b suggests that the typical GNPs aggregate appear leaf-like orientation, with the length of 4–5 μm and the width of 0.5–1 μm. However, the morphology of HDPE/GNPs composites shows a dramatic change after adding $AlCl_3$, as shown in Fig. 2c and d. The compact aggregates of GNPs have been unfolded partly and the multilayer structure of GNPs could be observed. The phase size of GNPs decreases into 1–1.5 μm and the leaf-like orientation weakens.

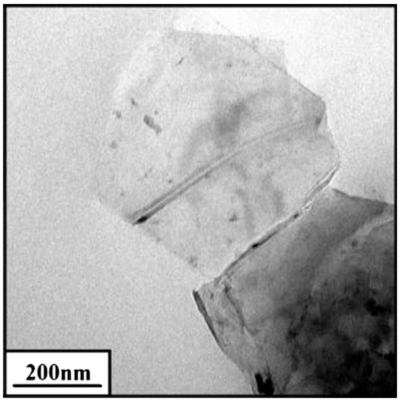

Fig. 1. TEM images of GNPs.

In CPE/GNPs composites, GNPs presents an obvious change in their aggregation state as shown in Fig. 3. The leaf-like orientation of GNPs has disappeared and, instead, the unordered dispersion of GNPs has been seen in CPE matrix. A few GNPs aggregate severely into the blocks (Fig. 3a), while most of GNPs disperse in the size of 0.2–0.5 μm (Fig. 3b). The addition of $AlCl_3$, interestingly, has more benefit in improving the phase dispersion of GNPs in CPE matrix than in HDPE matrix. The distinct reduction in the domain size of GNPs aggregates is observed in Fig. 3c and d. The severe aggregation of GNPs in matrix has disappeared, which reveals that the dispersive states of GNPs in matrix become more ideal.

There is intimate relationship between the dispersive states of graphene and mechanical properties in graphene-based polymer composites. The better dispersion of graphene sheets in polymer matrix may improve mechanical properties of composites. The tensile strength and elastic modulus achieves some increase when $AlCl_3$ is added into HDPE/GNPs and CPE/GNPs composites, as shown in Table 1.

The change of torque with processing time of HDPE/GNPs and CPE/GNPs composites during melt blending are depicted in Fig. 4. Torque values give the idea about the nature of flow, which is proportional to the viscosity of materials during processing. The influence of GNPs on the torque of melts is not obvious due to the poor interaction between GNPs and the matrix. When $AlCl_3$ is added into the composite, however, the torques of composites increase significantly, especially in CPE/GNPs composite. In our point of view, the addition of $AlCl_3$ improves the interaction between GNPs and polymer matrix, thus restricts the movement of polymer chains and increases the viscosity of melt.

Raman spectroscopy is applied to obtain the information of interfacial interaction between polymer matrix and GNPs, as shown in Fig. 5. The spectra of GNPs displays two characteristic peaks, the first at 1350 cm^{-1} (D band) derived from defects/disordered graphite structure, the second at 1583 cm^{-1} (G band) associated with vibration of sp^2-hybridized and highly oriented graphite structure [18]. It is expected to graft polymer chains to the carbocyclic rings of GNPs via Friedel–Crafts alkylation reaction in the presence of $AlCl_3$. However, there is no obvious red-shift or blue-shift in the Raman spectra of PE/GNPs (Fig. 5a) and CPE/GNPs (Fig. 5b) composites after adding $AlCl_3$, which reveals that no polymer chains have been grafted to the carbocyclic rings of GNPs.

Graphene is the assembly of six membered carbocyclic rings and has the similar structure to benzene, but there are no protons on the carbocyclic rings of graphene. Therefore, it is impossible that the polyolefin substitutes a proton to *in situ* generate the PE-*graft*-GNPs or CPE-*graft*-GNPs.

Analyzing the Raman spectra, the G band peak of GNPs is downshifted by 6 cm^{-1} when GNPs are blended with HDPE and 7 cm^{-1} when GNP is blended with CPE. The aggregation of GNPs in polymer matrix compresses the monocrystal of graphite, and the in-plane tangential stretching mode of carbon–carbon bonds is restricted. But after adding $AlCl_3$, the G band peaks are up-shifted by 2 cm^{-1} and 6 cm^{-1}, respectively.

As discussed above, it seems that $AlCl_3$ has no effects on the original structure of GNPs in HDPE/GNPs and CPE/GNPs composites. There are no clear chemical reaction occurring between polymer chains and graphene sheets. No polymer chains have been grafted to the surface of GNPs, and also no graphene sheets have been wrapped with polymer chains. The dispersion of HDPE/GNPs and