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Facile synthesis of graphene sheets decorated nanoparticles and flammability of their polymer nanocomposites

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ABSTRACT

Novel and facile method was developed for the synthesis of graphene based flame retardant for acrylonitrile-butadiene-styrene. Graphene has been exfoliated by using ultrasonication in maleate diphosphate as dispersant. The exfoliation media produced high quality less defected graphene layers. The graphene wrapped with maleate diphosphate was decorated with TiO_2 nanoparticles with an average size of 21 nm. Polymer composites of acrylonitrile-butadiene-styrene with maleate diphosphate, graphene wrapped with maleate diphosphate and decorated ones have been synthesized with solvent blending method. The flammability properties of the polymer nanocomposites were significantly reduced. The peak heat release rate (PHRR) and total heat release (THR) of the polymer nanocomposites contains nanoparticles decorated graphene achieved 49% reduction. Also, average mass loss rate was reduced by 50% and emission of carbon dioxide was suppressed by 37%. The rate of burning of nanocomposites was found to be 12 mm/min compared to virgin polymer of 42.5 mm/min achieved 71% reduction. The effect of combining graphene and the materials was investigated. The graphene wrapped with maleate diphosphate and maleate diphosphates itself were characterized using FTIR spectroscopy. The different polymer nanocomposite materials were characterized using thermal gravimetric analysis, UL94 flame chamber and cone calorimeter. The exfoliation of graphene was elucidated by Raman spectroscopy and XRD and the dispersion of graphene sheets in maleate diphosphate and their decorated composites with nanoparticle were characterized using transmission electron microscopy.

1. Introduction

Polymeric materials have various applications due to their unique properties and one of these materials is acrylonitrile-butadiene-styrene (ABS) which has been used extensively [1,2]. However, the high flammability properties of ABS limited their use in some applications. Varieties of flame resistant materials have been used to improve the thermal stability and resistance of polymer composites against fire [3–6]. Nanomaterials with different dimensions have been used extensively including nanocomposites with polymer materials due to their excellent properties [7]. The preparation of polymer nanocomposites of well dispersed nanoscale fillers achieved positive improvement in fire resistance and thermal stability of the nanocomposites [8]. Various nanoscale materials have been used as flame retardant fillers in polymer nanocomposites such as clay nanoplates [9], carbon nanotubes [10], inorganic nanotubes [11], expanded graphite [12,13] and nanoparticles [14,15].

On the other hand graphene (GRP) is 2D carbon nanomaterials of one atom-thick and has attracted a lot of attentions due to their excellent physical and chemical properties which are required for various applications [16–20]. Due to the remarkable properties of graphene, their polymer nanocomposites showed outstanding properties which are required in various applications [21]. Graphene materials have been used alone and in conjunction with other traditional flame retardant as a good flame retardant system to polymer nanocomposites [22–25]. This was due to their ability to form good preventive char barrier on the surface of polymer nanocomposites isolating melting polymer from flame [19,24,27]. Recently, graphene decorated with nanoparticles have been used as promising flame retardant for polymer composites [28]. In our previous studies the flammability properties of ABS nanocomposites with inorganic nanotubes have been investigated and

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synergistic effect of inorganic nanotubes and intumescent flame retardant has also studied [6]. It is important to note that, our research group has long been involved in the study of flame retardancy of various materials [6,29–33]. This is in addition to our expertise in polymer nanocomposites for various applications [7,34–36]. Here, we are reporting for the first time the synthesis of graphene sheets using ultrasonication in maleate diphosphate: (MDP) as dispersant and flame retardant media for exfoliation and production of GRP-MDP composites. GRP-MDP has been used as a promising flame retardant material for ABS reducing the flammability of ABS-GRP-MDP nanocomposites. Also decorated graphene sheets with TiO_2 nanoparticles of an average particle size of 21 nm were prepared and the flammability of their polymer nanocomposites was evaluated. The effect of TiO_2 nanoparticles and graphene has also studied.

2. Experimental section

2.1. Materials

Poly (acrylonitrile-butadiene-styrene) with the trade name Terluran GP-22 was obtained from BASF, Ludwigshafen, Germany. Graphite powder (99.5%) was purchased from Alpha chemika, Mumbai, India. Diethyl maleate was purchased from Merck, Schuchardt OHG 85662 hohenbrun, Germany. Phosphoric acid was obtained from Sigma Aldrich Co., USA. Acetone was purchased from El Nasr Pharmaceutical Chemicals Co., Egypt. TiO_2 nanoparticles with diameter 21 nm were obtained from Sigma Aldrich chemie GMBH, Germany.

2.2. Synthesis of maleate diphosphate

The maleate diphosphate (MDP) was prepared based on previous report [31]. In synthesis details, in a round bottom flask 1 mol of diethyl maleate was mixed with 2 mol of phosphoric acid then, refluxed for 4 h at 120 °C. The colorless liquid obtained was filtered and cooled at room temperature then used for graphene exfoliation step.

2.3. Synthesis of graphene sheets (GRP)

The graphene sheets have been exfoliated from commercial graphite using ultrasonication with the aid of MDP viscous as dispersant and supporting flame retardant media. For synthesis in a glass vial containing 20 ml of MDP 40 mg of graphite was added, then ultrasonication using ultrasonic with probe (ultrasonic processor equipped with a standard probe, Branson digital sonifier 450, Frequency: 20 kHz) with the output power set at 70% for one hour produced black dispersion. Afterwards, the black dispersion centrifuged at 3000 rpm for 30 min (Laboratory centrifuge Model 800) to get GRP-MDP dispersion.

2.4. Synthesis of graphene-TiO_2 nanoparticles composites (GRP-MDP-TiO_2NP)

In a glass vial containing graphene dispersion (GRP-MDP), add two different weight percent of TiO_2 nanoparticles (1 and 5 wt.%) based on MDP weight as tabulated in Table 1. Afterwards, ultrasonication process was performed at the same sonication conditions as in exfoliation step except power output was at 50% for 5 min.

Table 1
Composition of ABS and their nanocomposites.

Sample code	ABS (wt.%)	MDP (wt.%)	GRP (wt.%)	TiO_2NP (wt.%)
ABS	100	0	0	0
ABS-MDP	70	30	0	0
ABS-GRP-MDP	70	29.8	0.2	0
ABS-GRP-MDP-TiO_2NP-1%	70	28.8	0.2	1
ABS-GRP-MDP-TiO_2NP-5%	70	24.8	0.2	5

2.5. Synthesis of ABS-MDP, ABS-GRP-MDP and ABS-GRP–MDP-TiO_2 NP nanocomposites

In ABS solution in acetone quantized amount of MDP was mixed and then mechanically stirred for 3 h forming 30wt.% composite of ABS-MDP based on total mass of the composite (Table 1) In ABS solution GRP-MDP was mixed under the same stirring conditions produced ABS-GRP-MDP nanocomposite (Table 1) Using the same trend ABS-GRP- MDP-TiO_2 nanocomposites were prepared as tabulated in Table 1 (TiO_2 NP was 1 and 5 wt.% based on MDP weight) after mixing of GRP-MDP-TiO_2NP with ABS solution, the dispersion was stirred under same stirring conditions. After that, the solvent was evaporated and samples were molded at 180 °C for 10 min.

2.6. Characterization

FTIR spectroscopy analysis was carried out using a Nicolet 380 spectrophotometer, (Thermo Scientific), over the spectral range 4000-400 cm^{-1} with resolution of 4 cm^{-1}. The TGA analysis was implemented using the TGA 50 (TA Shimudzu, Inc.) at temperature range from room temperature to 750 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. TEM images were taken with a JEOL (JEM-1400) microscope with an accelerating voltage of 100 kV. The evaluation of the flammability properties of different samples were performed by UL94 flame chamber using horizontal test according to international standard IEC 60695-11-10 [37]. Furthermore the blank and nanocomposites samples were also evaluated using a Fire Testing Technology cone calorimeter according to ISO 5660-1 [38]. The samples were irradiated in a horizontal position at 35 kW/m^2 and then the samples were ignited using a spark igniter. The fire parameters considered were: peak heat release rate (PHRR), average effective heat of combustion (AEHC), total heat release (THR) and average mass loss rate (AMLR). This in addition to time to ignition (t_{ign}) and average emission of carbon monoxide and carbon dioxide.

3. Results and discussion

3.1. Structural and morphological characterization of exfoliated graphene

The exfoliated GRP sheets in MDP were characterized using microscopic and spectroscopic techniques which support in confirmation of synthesized GRP sheets. During the GRP sheets exfoliation MDP molecules help in the exfoliation process by wrapping the exfoliated layers of GRP and suspend them in their solution. The MDP interact with GRP through π-π interactions as the MDP molecule contain π bond and the exfoliation process schematically depicted in Fig. 1. This facile exfoliation process gave rise to a very high quality GRP layers as the viscous nature and structure of MDP play an important role in the exfoliation of GRP. This produced less defected sheets structure and good conversion yield of GRP from graphite which was found to be 40%. GRP exfoliation process was implemented through harsh cavitation