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Effect of Cu-doped graphene on the flammability and thermal properties of epoxy composites

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ABSTRACT

Cu-doped graphene (graphenit-Cu) was successfully prepared through chemical reduction method, and its surface morphology, crystalline structure and Cu content in graphenit-Cu were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), inductive couple plasma (ICP) and electrochemical cyclic voltammetry, respectively. Graphenit-ox/epoxy systems and graphenit-Cu/epoxy systems were prepared, and the contents of graphenit-ox and graphenit-Cu were kept as 1 and 3 wt%, respectively. The effect of graphenit-ox or graphenit-Cu on the flame retardancy, combustion properties, thermal degradation and thermomechanical properties of epoxy resin was investigated systematically by limiting oxygen index (LOI), cone calorimeter (Cone), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Compared to graphenit-ox, the addition of graphenit-Cu reduced the heat release rate (HRR), total smoke production (TSP) and smoke production rate (SPR), and improved LOI values of epoxy composites. Moreover, the addition of graphenit-ox also had little flame retardant effect on epoxy composite. The possible synergistic effect between graphene and Cu was confirmed in the flame retardant epoxy composites. TGA and DMA results also indicated the considerable effect on the thermal degradation and thermomechanical properties of epoxy composites with the addition of graphenit-Cu. The results supplied an effective solution for developing excellent flame retardant epoxy composites.

1. Introduction

Epoxy resin (EP) has been widely utilized in a variety of fields, such as electronic/electrical insulation, laminates and composites, adhesives, and coatings, due to its outstanding properties such as high thermal stability, great versatility, good mechanical properties, strong adhesion, low shrinkage, chemical resistance and as an excellent solvent [1–4]. However, the high flammability of epoxy resin has hindered its application in some fields, especially in electronic/electrical insulation, laminates and composites. Thus, the research on flame retardant epoxy resin is increasingly attracting more attention [5–8]. There are two methods to improve the flame retardant properties of epoxy resin. In the first method, some flame retardants are physically added into epoxy resin [9–11]; and in the other method, some intrinsic flame retardant elements like P [3,12], Si [13], N [14] are grafted into the macromolecular chains through chemical reactions. An efficient and versatile method to prepare flame retardant epoxy composites is the physical addition method, but it is difficult to disperse the flame retardant homogeneously into epoxy resin. Alternatively, an intrinsic flame retardant epoxy resin provides better mechanical properties; however, their preparation process is more complicated.

During the past decade, one of the promising solutions to improve the flame retardant properties of epoxy resin is to incorporate nanoparticles as filler into epoxy resin [15]. Likewise, different kinds of nanomaterials, such as montmorillonite (MMT) [16], sepiolite [17], carbon nanotube (CNT) [6], or layered double

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hydroxide (LDH) [18] have been introduced into epoxy resin. These nanofillers have already showed interesting results on the flame retardant properties of epoxy composites. Recently, we have reported that functionalized LDH-based epoxy nanocomposites reached V-0 rating in the UL-94 vertical burning test with low loading functionalized LDH [18–20]. The introduction of these nanoparticles reduced the heat release rate (HRR) and simultaneously improved the mechanical properties of epoxy composites.

Since its discovery in 2004, graphene has attracted much attention due to its Young's modulus, fracture strength, specific surface, electron mobility and thermal conductivity [21–23]. These remarkable properties made graphene and its derivatives to be applicable in the field of batteries, sensors, electronic devices and hydrogen storage. Also graphene based nanofillers were utilized to improve the performance of polymers [24,25]. Due to its high thermal resistance, graphene behaved as an effective barrier which slowed down the heat/mass transfer during the combustion of polymer [22]. Based on this, further research was directed towards graphene and its derivatives as flame retardants to enhance the flame retardant behavior of polymeric materials [26–28]. The results indicated that the addition of graphene and its derivatives improved the flame retardant properties of polymeric materials [26–28]. However, the effect of Cu-doped graphene on the flame retardant properties of polymers is virtually not reported.

This paper describes the complete characterization of successfully synthesized Cu-doped graphene (graphenit-Cu) by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Inductive couple plasma (ICP) and electrochemical cyclic voltammetry. Further, we report the preparation and characterization of graphenit-ox and graphenit-Cu based Epoxy composites; and their significant effect on the flame retardant properties, combustion properties, thermal degradation and thermomechanical properties of epoxy resin, are systematically studied using limiting oxygen index (LOI), cone calorimeter (Cone), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) techniques.

2. Experimental

2.1. Materials

Epoxy resin (L20) was purchased from Faserverbundwerkstoffe® Composite Technology, Germany and 4,4′-Diaminodiphenyl sulfone (DDS) was purchased from TCI Chemicals. Slightly oxidized graphene nanoplatelets (graphenit-ox) were supplied by Nanoinnova Technologies S. L. (Madrid, Spain), and Cu-doped graphene (graphenit-Cu) were prepared through chemical reduction method by Nanoinnova Technologies S. L. (Madrid, Spain).

2.2. Preparation of graphene based epoxy composites

A fixed weight fraction (1 and 3 wt%) of graphenit-ox and graphenit-Cu was added into epoxy resin to prepare epoxy composites. To obtain a favorable dispersion of graphenit-ox and graphenit-Cu into epoxy resin, a three-roll mill from EXAKT® 80E (Advanced Technologies GmbH, Germany) was used. In order to achieve better incorporation as well as dispersion of graphenit-ox or graphenit-Cu into epoxy resin, the whole suspension was milled two times for about 15 min. During the first time of mill, the gap between the feed roll and the apron roll was set to 90 and 20 μm, respectively and for the second time, it was adjusted to 60 and 20 μm, respectively. Then, the suspension in a beaker was heated to 125 °C in an oil bath. DDS was added slowly to the suspension and stirred for 15 min until DDS was totally dissolved. Subsequently, the suspension was placed into a vacuum oven at 110 °C for 10 min to drive off the bubbles and immediately poured into pre-heated (160 °C) silicon-rubber moulds and the curing procedure was set as follows: 160 °C for 2 h, 180 °C for 2 h and 200 °C for 1 h. Following the same procedure, epoxy resin, epoxy composites with 1 wt% and 3 wt% of graphenit-ox (1% and 3% graphenit-ox-epoxy), and epoxy composites with 1 wt% and 3 wt% of graphenit-Cu (1% and 3% graphenit-Cu-epoxy) were prepared.

2.3. Measurements

2.3.1. Limiting oxygen index test

LOI test was carried out with an oxygen index model instrument (Fire Testing Technology, UK), and sheet dimensions of the samples were 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97.

2.3.2. Cone calorimeter test

The combustion behaviors of epoxy composites were investigated by a cone calorimeter (Fire Testing Technology, UK) according to the procedures in ISO 5660-1. Specimens with sheet dimensions of 100 mm × 100 mm × 3 mm were placed on aluminum foil and irradiated horizontally at a heat flux of 50 kW/m^2. Each sample was tested for three times.

2.3.3. Thermogravimetric analysis

Thermal stability of sample was studied on a Q50 Thermogravimetric Analyzer (TA Instruments, USA). The heating rate was set to 10 °C/min, and about 10 mg of the sample was tested under nitrogen with a flow rate of 90 mL/min from room temperature to 700 °C. The temperature of the instrument was reproducible to within ±1 °C, and the mass was reproducible to within ±0.1%.

2.3.4. Dynamic mechanical analysis

Thermomechanical properties of epoxy composites were examined by a Dynamic Mechanical Analyzer Q800 (TA Instruments, USA). The dimensions of sample were 35 mm × 10 mm × 2 mm. The samples were tested in a single cantilever clamp with a frequency of 1 Hz and an amplitude range of 15 μm at the heating rate of 3 °C/min from room temperature to 280 °C.

2.3.5. Scanning electron microscopy

Surface morphology and particle size of graphenit-Cu was characterized using a TM-1000 Tabletop Hitachi microscope. The sample was coated with a conductive gold layer and pasted on carbon conductive belt before SEM observation.

Morphologies of epoxy composites with 3% graphenit-ox and epoxy composites with 3% graphenit-Cu were acquired with focused ion beam-field emission gun scanning electron microscope (FIB-FEGSEM) dual-beam microscope (Helios Nano Lab 600i, FEI). All the samples were coated with a conductive gold layer and pasted on carbon conductive belt before FIB-FEGSEM observation.

2.3.6. X-ray diffractometer (XRD)

Crystallography of graphenit-Cu was investigated by a XPERT-PRO X-ray diffractometer. The Cu K_α (λ = 1.5406 Å) radiation source was operated at 45 kV and 40 mA with a scan speed of 2° min^{-1}.

2.3.7. Electrochemical cyclic voltammetry

Electrochemical cyclic voltammetry of graphenit-Cu was carried out in a three-electrode cell. Glassy carbon, Pt wire and Ag/AgCl in 3 M KCl (BASi) were used as working electrode, counter electrode and reference electrode respectively. All electrodes were introduced in a standard three-electrode cell containing 0.1 mol/L KOH (Scharlau) solution as electrolyte. Graphenit-Cu ink was prepared in milli-Q water with 15 wt% Nafion and the concentration of Graphenit-Cu was 5 mg mL^{-1}. 25 μL of the above ink was pippetted