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Reduced silanized graphene oxide/epoxy-polyurethane composites with enhanced thermal and mechanical properties

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ABSTRACT

This paper describes the synthesis of reduced silanized graphene oxide/epoxy-polyurethane (EPUAs/R-Si-GEO) composites with enhanced thermal and mechanical properties. Graphene oxide (GEO), prepared from natural graphite flakes, was modified with methacryloxypropyltrimethoxysilane to prepare silanized GEO (Si-GEO), and was then reduced by $NaHSO_3$ to prepare R-Si-GEO (partially reduced Si-GEO). EPAc/R-Si-GEO (R-Si-GEO/epoxy acrylate copolymers) was synthesized via an in situ polymerization of R-Si-GEO and epoxy acrylic monomers. EPUAs/R-Si-GEO was obtained by curing reaction between EPAc/R-Si-GEO and an isocyanate curing agent. Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) were used to characterize the surface and crystal structure of the modified graphene and EPUAs/R-Si-GEO. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize their morphology. Thermal gravimetric analysis (TGA), tensile strength, elongation at break, and cross-linking density measurements showed that the thermal stability and mechanical properties of EPUAs/R-Si-GEO were greatly enhanced by the addition of R-Si-GEO.

1. Introduction

Over the past few decades, graphene/polymer composites have attracted considerable interest in both academia and industry due to their extraordinary physico-chemical properties [1–6]. Notably, these composite materials are featured by enhanced tensile strength, excellent thermal stability, electrical conductivity, flexibility, and transparency as compared to composites made of conventional nanofillers, such as Na-montmorillonite, layered hydrotalcite, CNT, CNF, etc. [7–9]. However, productions of graphene/polymer composites are limited by the poor distribution of pristine graphene in most polymers, where dispersity of graphene in the composite is one of the key factors that determines the physico-chemical properties of composites [10,11]. In order to solve this issue, various methods have been used to modify the surface properties of graphene in order to improve their compatibility and distribution in polymers. The physico-chemical properties of graphene/polymer composites and interfacial bonding among the component materials are greatly improved when graphene is evenly distributed within a polymer matrix [12–16]. Among the existing methods developed to improve the solubility and compatibility of graphene [17–21], oxidization and exfoliation of graphite to produce graphene oxide (GEO) are very promising. While GEO sheets bear hydroxyl, epoxide, diol, ketone, and carboxyl groups on their surfaces [22–25], and can be well-dispersed in polar solvents, therefore being compatible with hydrophilic polymers [26–31], it is still incompatible with most lipophilic polymers. Compatibility with lipophilic polymers is required in a variety of chemical engineering applications, particularly for the productions of most graphene/polymer composites [1,7]. Therefore, further modifications to GEO are required for the production of high performance graphene/polymer composites.

Polyurethane acrylate (PUA) is a material characterized by excellent flexibility, high resilience, and durability. PUA has been applied in a wide range of industrial applications including coatings, adhesives, fibers, foams, and elastomers [32–35]. Despite the advantages of PUA, it is limited by its poor resistance to high temperatures and low strength. Thus, PUA is restricted in applications that require these conditions. In order to overcome these limitations, we hypothesized that a combination of graphene

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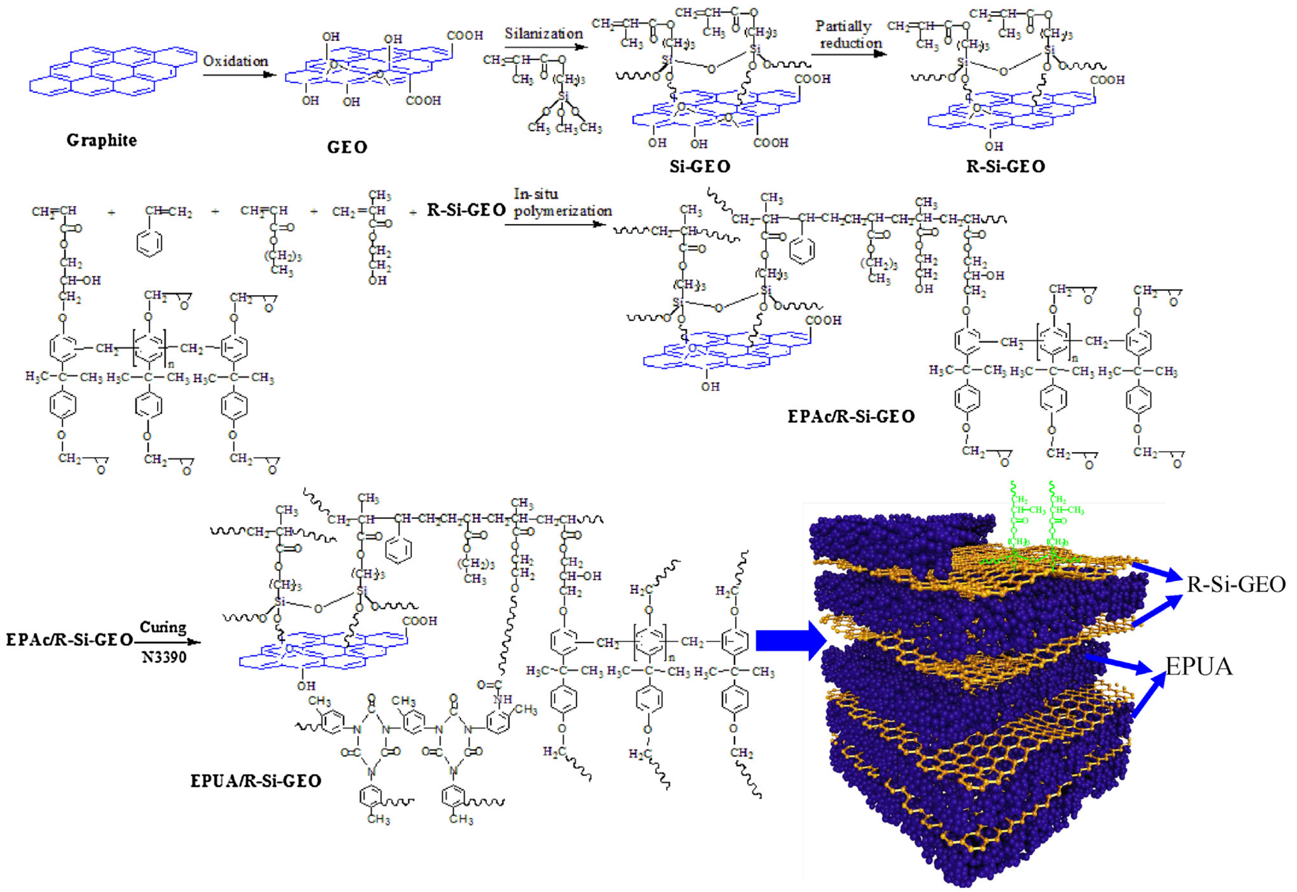

Fig. 1. The synthesis route for EPUAs/R-Si-GEO composites.

and EPUA in a composite may produce materials with enhanced physico-chemical properties, especially thermal and mechanical properties.

In this work, graphene/epoxy-polyurethane composites were generated by evenly dispersing surface modified graphene sheets in the composites, where the general procedure of synthesis is illustrated in Fig. 1. Briefly, GEO was prepared using the Hummers method [36], and was modified with a coupling agent, methacryloxypropyltrimethoxysilane (MPS), to produce Si-GEO. The Si-GEO was then partially reduced by $NaHSO_3$ to form R-Si-GEO. EPAc/R-Si-GEO were prepared via an in situ polymerization reaction between R-Si-GEO, acrylic monomers, and epoxy acrylate resin (EA) which was prepared by a partial ring-opening reaction between novolac epoxy resin (EP) and acrylic acid (AA). EPUAs/R-Si-GEO composites were obtained by curing reaction between the as-prepared EPAc/R-Si-GEO and the isocyanate curing agent. FTIR, XPS, XRD, SEM, and TEM were employed to characterize the structural changes of the silane-modified graphene and the EPUA/R-Si-GEO composites. Thermal properties of the composites, e.g. thermal stability (T_g), were investigated using TGA and differential scanning calorimetry (DSC). Several mechanical and chemical properties of the EPUAs/R-Si-GEO composites, e.g. tensile strength, elongation at break, shore hardness, cross-linking density, and water resistance, were also studied. The characterizations indicate that the EPUAs/R-Si-GEO composites were successfully prepared by forming covalent bonds between the component materials. Moreover, the EPUAs/R-Si-GEO composites showed a great enhancement of thermal and mechanical properties as compared to PU without graphene.

2. Experimental

2.1. Materials and methods

Natural graphite flakes were purchased from Nanjing High Technology Nano Material Co., Ltd. MPS was purchased from Diamond Chemical Material Co. Ltd. The isocyanate curing agent used in this work was Desmodur®N3390 (NCO weight 19.6%, equivalent weight ~216 g/mol) and was supplied by Bayer Material Science. Bisphenol-A type novolac epoxy resin (EP) CYDBN240 with epoxide number of 0.57 was supplied by Yueyang Chemical Factory, PRC. All chemicals used in this work were of analytical grade, including $NaNO_3$, $KMnO_4$, H_2SO_4 (98 wt%), HCl (36 wt%), DMF, H_2O_2 aqueous solution (30 wt%), styrene (ST), butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), azobisisobutyronitrile (AIBN), and tetramethylammonium bromide (TMAB). FTIR spectra of pure graphite, GO, GEO, Si-GEO, and R-Si-GEO were performed over the range of 4000–400 cm^{-1} using a spectrophotometer (Bruker Vector 33, Bruker Biospin Corp.). The thermal decomposition of graphite, GEO, Si-GEO, R-Si-GEO, and EPUAs/R-Si-GEO were determined by TGA (STA449C, NETZSCH). Samples were heated from 35 °C to 800 °C at a rate of 10 °C/min within a nitrogen atmosphere. The surface chemical compositions of GEO, Si-GEO, and R-Si-GEO were determined by XPS (Vario EL III Elemental Analyzer, Elementar). The binding energies used the C_{1s} peak (285 eV) as an internal standard to account for charging effects. The crystallographic structures of graphite, GO, GEO, Si-GEO, and R-Si-GEO were characterized with XRD (D8 ADVANCE-TXS, Bruker AXS). The morphologies of graphite, GO, GEO, Si-GEO, and R-Si-GEO were observed with TEM (Hitachi