THE EFFECT OF FUNCTIONALIZED REDUCED GRAPHENE OXIDE ON THE ELECTRICAL CONDUCTIVITY AND THERMAL STABILITY OF EPOXY

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ABSTRACT

In our study, reduced graphene oxide (RGO) was prepared by three typical reduction methods: \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \), solvothermal, and high-temperature methods, and then functionalized by cetylpyridinium chloride (CPC) and sodium dodecyl benzene sulfonate (SDBS). The surface morphology, structural changes of the functionalized reduced graphene oxide (FRGO) were studied by field emission scanning electron microscopy (FESEM) and Raman spectroscopy, respectively. These results illustrated that the FRGO were prepared successfully. Subsequently, pristine and functionalized reduced graphene oxide composite films were fabricated by solution casting method. Thermal stability of composites was measured by thermal gravimetric analysis (TGA). The results indicated that electrical conductivity and thermal stability of composites were closely related to the RGO obtained by different reduced methods. Furthermore, composites added with functionalized graphene showed different electrical conductivity and thermal stability compared with the neat epoxy.
1 INTRODUCTION

Polymer composites have an extensive application over the last decades. Epoxy resins as a member of thermoset polymer are widely used in aerospace, automotive, construction, electronics and adhesive because of its excellent engineering properties such as stiffness, mechanical strength, chemical resistance and easy processing; however, most of these applications require enhanced thermal stability and electrical performance, which can be realized by adding reinforcing fillers. Graphene is recognized as ideal filler to overcome these disadvantages of epoxy owing to its unparalleled thermal, mechanical and electrical properties.

Graphene was discovered in 2004[1] by method of mechanical exfoliation. Afterwards, a series of methods had been developed to fabricate graphene, including liquid-phase exfoliation[2], chemical vapor deposition (CVD)[3], epitaxial growth[4], oxidation-reduction method[5], and so on. Among these methods, oxidation-reduction method can realize low cost and high amount production spontaneously. This method used graphene oxide (GO) as a precursor to prepare reduced graphene oxide (RGO). During the oxidation of graphite, a variety of oxygen-containing functional groups were introduced into the surface and edge of graphite layer, for instance, hydroxyl, epoxide and carboxyl[6]. Until now, plenty of technologies, for example, chemical reagent reduction[7], high temperature reduction[8], microwave reduction[9], electrochemical reduction[6], solvothermal reduction[10] and so on, have been developed to eliminate these oxygen-containing functional groups in order to translate GO into RGO. Now that all these methods can acquire RGO, its reduction degree, electrical conductivity, defect repair degree are closely related to its preparation method[11]. The improvements in electrical and thermal properties by the addition of graphene in epoxy as a polymer matrix have been reported by previous researchers [12-16]. However, it still lacks of comprehensive comparison about the conductivity and thermal stability properties of epoxy/RGO composites filled with RGO fabricated by different methods. Furthermore, uniform dispersion of RGO in polymer matrix has an enormous influence on its properties [17, 18]. Adopting surfactants for surface functionalization of RGO to improve its chemical compatibility with polymer matrix is a common approach to inhabit aggregation of RGO in polymer matrix [18, 19]. Generally, the head group charge, alkyl chain length and presence of benzene rings structure of surfactant are main factors on select surfactant for preparing polymer composites[20]. Cetylpyridinium chloride (CPC) and sodium dodecyl benzene sulfonate (SDBS) representing cations and anions surfactant were selected as surfactants to functionalize RGO in our research. They all have a long alkyl chain and an ionic head, furthermore, SDBS has benzene ring in its structure, and their chemical structures were presented in Figure1.

In this study, three typical reduction methods: N₂H₄·H₂O, solvothermal, and high temperature were selected to prepare RGO. Two types of surfactant: CPC and SDBS were employed to functionalize RGO. Afterward, RGO and functionalized RGO were incorporated into epoxy to fabricate polymer composites and the effect of different RGO on the composites properties including thermal stability and electrical properties were explored.
2 Experimental

2.1 Materials

Natural flake graphite powders (325mesh, 99%) were bought from Qingdao Dasheng Co. Ltd., China. Concentrated sulfuric acid (H$_2$SO$_4$, 98%), hydrochloric acid (HCl, 37%), hydrogen peroxide (H$_2$O$_2$, 30%), potassium permanganate (KMnO$_4$, 99%), and sodium nitrate (NaNO$_3$, 99%) were purchased from Kermel Chemical Reagent Co. Ltd., China. Sodium dodecyl benzene sulfonate (SDBS) and cetylpyridinium chloride (CPC) were obtained from Tianjin Guangfu Fine Chemical Research Institute, China.

2.2 Fabrication and surface functionalization of reduced graphene oxide

2.2.1 Preparation of functionalized graphene oxide and reduced with chemical reagent

GO was prepared by Hummers method according to reference[21]. 100mg GO and equal amount of surfactant was added into water, then the mixture was sonicated at 150W for 1h to form a homogeneous brown GO/surfactant aqueous suspension. The aqueous suspension was then heated up to 90°C and 3μl of hydrazine hydrate was added, 2h later the brown suspension turned into black color, FRGO was filtrated through the polypropylene membranes (0.5μm pore size), afterwards washed with deionized water several times and dried in a vacuum oven at 60 °C for 24 h[7]. The reduction of graphene oxide by chemical reagent of hydrazine hydrate without surfactant was named as CRGO. We denoted the functionalized CRGO by SDBS and CPC as SDBS-CRGO, CPC-CRGO, respectively.

2.2.2 Preparation of reduced graphene oxide by high temperature and functionalization with surfactant.

100mg graphene oxide powder was transferred to a quartz boat, and then placed quarter boat into the edge of a long quartz tube. Before heating, argon was introduced flush the sample. Afterward the powder was heated to 1000 ℃ in a short time with quick annealing oven, when GO was heated to high temperature in a short time, it expanded; the product was labelled as HRGO. It should be noted that there is strong electrostatic repulsion among HRGO. Equal amount of HRGO and surfactant were added into water, when the mixture was sonicated at 150W for 1h, the solid was separated by filtration,
washed and vacuum dried in a vacuum oven at 60 °C overnight. We called the functionalized HRGO by SDBS and CPC as SDBS-HRGO and CPC-HRGO, respectively.

2.2.3 Preparation of functionalized graphene oxide and reduced by solvothermal method

100 mg of surfactant, SDBS and CPC were added into 200mL of 0.5 mg/mL GO aqueous and sonication for 1 h, respectively. Then the functionalized GO suspension was transferred into Teflon-lined autoclave and heated at 180 °C for 6 h. Thereafter, the SDBS-RGO and CPC-RGO were obtained according to above process.

2.3 Processing of epoxy composites

Epoxy composites with RGO/FRGO were fabricated as following procedure. 35mg functionalized RGO/FRGO was added into bottle with 35 mL DMF and sonicated about 60 min until the RGO/FRGO was dissolved completely into DMF, the solution was added into 5.6 g epoxy resin, the mixture was adequately blend by mechanical stirring with 2000 rpm for 10 min, afterward, the solvent in the mixture was evaporated in a vacuum oven at 60°C for 72 h. Then 1.4 g hardener (weight ratio epoxy resin and hardener was 5:1) was added to the mixture and stirred until formed uniform mixture. The mixture was shaped into standard specimen by silicon mold for measurement. Finally, the samples was annealed at 60°C to eliminate the residual stress.

2.4 Characterization

The surface morphology of RGO/FRGO was studied by field emission scanning electron microscopy (FESEM, S4800, Hitachi, Japan). Raman spectroscopy (Thermo Fisher Scientific, Germany) was used to investigate the structural changes in the RGO upon functionalized using a 532 nm laser at room temperature in the range of 500-3000 cm⁻¹. Thermal stability of composites was measured by thermal gravimetric analysis (TGA) experiments using TA instruments (Q600, USA). Sample around 10mg were placed in a alumina pan and heated from 25°C to 700°C at a heating rate of 10°C/min in an nitrogen atmosphere with a flow rate of 100 ml/min. Take account of insulation of epoxy. Electrical conductivity of epoxy composites was reflected by measured electrical conductivity of reduced graphene oxide. The electrochemical impedance spectroscopy (EIS) was used to teste electrical properties of RGO. The EIS was measured with the sandwich-like symmetrical dummy cells comprising two identical electrodes (10 x 10 mm²) with electrolyte under open-circuit voltage condition were performed using a CorrTest CS350 electrochemical workstation (Wuhan, China) at frequency range from 0.1 Hz to 1 MHz.

3. Results and Discussion

3.1 Morphology analysis

Field emission scanning electron microscopy (FESEM) was employed to illustrate the morphology of different RGO. SEM images of CRGO, HRGO, TRGO and functionalized RGO were presented in Figure 2. It is obvious that morphology of RGO fabricated by different methods have a big difference, as can be seen in Figure 2, all the RGO are composed of layered structures with corrugation, which is part of the intrinsic nature of graphene in order to come to be thermodynamically stable via bending [21]. When CRGO, HRGO and TRGO were functionalized by SDBS and CPC, agglomeration of
RGO was prevented in different degrees, CPC-CRGO, CPC-HRGO and CPC-TRGO all formed spread appearance with large area (Figure 2(c), (f), (i)); SDBS-CRGO, SDBS-HRGO and SDBS-TRGO also have unfold morphology (Figure 2(b), (e), (h)) compared with their control group (Figure 2(a), (d), (g)) while expansion extent is inferior to CPC-CRGO, CPC-HRGO and CPC-TRGO, respectively.

Figure 2: SEM morphology of CRGO, HRGO, TRGO and their functionalized RGO.

3.2 Functionalization of RGO

3.2.1 Raman Spectroscopy Analysis

Raman spectroscopy was introduced to evaluate the defect density of various RGO. There are two characteristic peaks at about 1352cm\(^{-1}\) and 1580cm\(^{-1}\) which were called “D band” and “G band”, respectively. D band is affected by defects and impurities of RGO; G band is related to well-ordered graphite lattice. The intensity ratio between D band and G band (I\(_D\)/I\(_G\)) generally is used to evaluate the density of surface defects. From the Raman spectra in Figure 3, it is obvious that HRGO have a least surface defect density compared with CRGO and TRGO, its I\(_D\)/I\(_G\) is lower than 1 while I\(_D\)/I\(_G\) of other
RGO is higher than 1, this is due to high temperature can remove the oxygen-containing groups as soon as possible at 1000℃. $I_D/I_G$ of CRGO and TRGO exceed 1 and also CRGO has a greater $I_D/I_G$ than that TRGO. It maybe that solvothermal is a moderate reaction while the hydrazine hydrate is strong reductant which triggers a dramatic chemical reaction.

![Raman spectra of various RGO.](image)

The Raman spectra indicated that simultaneous reduction and functionalization of graphene oxide using surfactant (SDBS and CPC) will increase the defect density of RGO in different degree depending on the reduction method, and the presence of CPC in the reduction can cause greater damage onto the surface of RGO than SDBS. When the graphene oxide was firstly reduced, and then functionalized, its defect density will decrease, because surfactant wraps around the surface of RGO, its defects not easy to be detected.

### 3.3 Dispersion of RGO and functionalized RGO in composites

Light optical microscope (LOM) is an effective tool to characterize distribution of filler in polymer. Figure 4 presented existential state of several of RGO in epoxy matrix. It is obvious that CRGO, HRGO and TRGO agglomerated in matrix, especially CRGO and TRGO (Figure 4 (a), (d), (g)). On the whole, HRGO and functionalized HRGO have relatively homogeneous distribution in epoxy matrix (Figure 4 (d), (e), (f)). When the RGO was functionalize by SDBS and CPC, Their dispersion
in epoxy changed significantly, even though SDBS-CRGO and SDBS-TRGO still exist in agglomeration particles in epoxy, the particles size is relatively small (Figure 4 (b), (h)). CPC-CRGO and CPC-TRGO in polymer become more even-distributed (Figure 4 (c), (i)) compared with matched group (Figure 4 (a) and (g)). The results indicated that SDBS and CPC functionalize RGO can improve its dispersion in polymer effectively. The functionalization of CPC is more suitable for RGO.

Figure 4: Comparison of light optical microscope (LOM) images of the different composites.

3.4 Thermal stability of composites

The TGA of curves of neat epoxy and its composites were presented in Figure 5. It consists two-stage process, the first stage of weight loss occurred between 25-350 °C is because of evaporation of residual organic solvent and breaking down of uncured epoxy in composites, the second stage of weight loss corresponding to the thermal decomposition of epoxy network[22]. From Figure5 (d), the TGA results reveal that CRGO, HRGO and TRGO can enhance the thermal decomposition temperature of composite in different degree compared to neat epoxy. The
decomposition temperature of composites epoxy/CRGO is greater than epoxy/HRGO composites, and epoxy/TRGO has a lowest decomposition temperature (Figure 5 (d)). This finding suggests that the presence of RGO enhanced the thermal stability of epoxy resin network because of its high thermal resistance and thermal conductivity, in addition to the oxygenic groups not be eliminate in the reduction participate curing reaction, leading to higher crosslinking density, covalent bond network formed between filler and polymer can result in the enhancement of polymer thermal stability and increase composite decomposition temperature [23, 24]. However, RGO with a high specific surface area easy to form agglomerates within the epoxy network which reduced the dispersion of and interfacial adhesion between the fillers and the epoxy, the thermal stability was affected by these agglomerates. Even through HRGO has the best dispersibility in epoxy, the oxygen-containing groups on graphene oxide were removed nearly at 1000°C, the thermal stability enhancement of epoxy/HRGO mainly depend on dispersion of HRGO in epoxy. CRGO/TRGO which reduced by hydrazine hydrate/solvothermal method still have a lot of oxygen-containing groups on its surface or edge, these oxygen-containing groups can form a network with epoxy composites and improve composites decomposition temperature. The dispersion of CRGO in epoxy is inferior to HRGO but superior to TRGO. Take into consideration dispersion and covalent bond network formed between filler and polymer, the decomposition temperature of epoxy/CRGO composites is greater than that epoxy/HRGO composite, and epoxy/TRGO has a lowest decomposition temperature.

Two surfactants used in this experiment both can functionalize RGO successfully and suppress aggregation of RGO in the epoxy so that increase composites thermal stability. The decomposition temperature of epoxy/SDBS-CRGO and epoxy/SDBS-TRGO composites is higher than epoxy/CPC-CRGO and epoxy/CPC-TRGO composites and epoxy with RGO apparently from Figure 5(a) and (c). The composite decomposition temperature various depends on many factors, such as dispersion of filler in polymer matrix, intermolecular attraction and steric effect[23, 24], etc. SDBS and CPC all can ameliorate the dispersion state of RGO in epoxy matrix so that the decomposition temperature of composites was enhanced. Furthermore, SDBS has a rigid benzene ring structure, synergetic effect of dispersion and benzene ring structure can result in a higher thermal stability enhancement of epoxy/SDBS-CRGO and epoxy/SDBS-TRGO[23, 24] than that epoxy/CPC-CRGO and epoxy/CPC-TRGO.
Figure 5: Comparison of thermogravimetric analysis (TGA) images of the different composites. (The graph on the right is a partial enlarged view of the left)
3.5 Electrical conductivity

We tested the volume resistivity of composites directly using a megger, the resistivity of composites is about $10^{15} \Omega \cdot m$, due to its high resistivity, it is not easy to distinguish the different fillers. So we measured the electrical conductivity of different fillers by electrochemical impedance spectroscopy (EIS).

<table>
<thead>
<tr>
<th>Electrical conductivity [S m$^{-1}$]</th>
<th>CRGO</th>
<th>TRGO</th>
<th>HRGO</th>
<th>SDBS-HRGO</th>
<th>CPC-HRGO</th>
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<tr>
<td>$x \times 10^{-2}$</td>
<td>4.7</td>
<td>1.2</td>
<td>5.8</td>
<td>15.7</td>
<td>2.1</td>
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Table 1: Electrical conductivity data of different RGO.

From Table 1, we found that the high-temperature reduction has higher electrical conductivity than that of wet chemical treatment (hydrazine hydrate reduction and solvothermal reduction) because it has the lowest defect density.

In order to explore the functionalization process on the electrical conductivity of RGO, electrical conductivity of SDBS-HRGO and CPC-HRGO were explored; the results indicated that electrical conductivity of SDBS-HRGO increased while CPC-HRGO has a lower electrical conductivity compared with HRGO.

4. CONCLUSION

Raman spectra of RGO that fabricated three methods indicated the HRGO has the lowest defect density, its $I_D/I_G$ less than 1 while $I_D/I_G$ of CRGO and TRGO greater than 1. The results indicated that composites incorporated RGO which fabricated by three different methods all can improve the composites thermal stability and epoxy/CRGO has the highest thermal stability among three composites (epoxy/CRGO, epoxy/HRGO and epoxy/TRGO). The decomposition temperature of epoxy/CRGO composites is greater than that epoxy/HRGO composite, and epoxy/TRGO has a lowest decomposition temperature. Using surfactants to functionalized RGO and fabrication composites, the epoxy/SDBS-CRGO and epoxy/SDBS-TRGO have a highest thermal stability compare with the control group. Electrical conductivity and thermal stability of composites were closely related to the RGO obtained by different reduced methods and SDBS could improve the electrical conductivity of epoxy composites.

5. ACKNOWLEDGEMENT

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