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Multifunctional hybrid films prepared by aqueous stabilization of graphene sheets viaing cellulose nanofibers and exfoliated montmorillonite system

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ABSTRACT

In this paper, reduction of graphene oxide (RGO) nanosheets were stably dispersed in water directly in the presence of montmorillonite (MMT) nanoplatelets and cellulose nanofibers (CNFs). This could be attributed to the steric hindrance of CNFs and the repulsion between different charges which exist in RGO nanosheets, MMT nanoplatelets and CNFs. Taking advantage of these stable hybrids, the films with unique microstructure have been fabricated successfully via vacuum filtration. For the highly oriented layer structures, the films have been given excellent fire resistance, high thermal stability and good flexibility. Meanwhile, because of the excellent electrical property of RGO nanosheets and the dielectric property of MMT nanoplatelets, there are lots of micro-capacitors in the film which has unique microstructure, and these micro-capacitors can impart the film high dielectric constant and relatively low dielectric loss.

1. Introduction

Nanocomposite technology is an effective approach to significantly improve the fire resistance, thermal properties, electric properties as well as mechanical properties. Recently, graphene, a single of graphite which has a layer of carbon atoms packed into a honeycomb crystal, shows unusual electronic characteristics, thermal conductivity, specific surface area and very excellent mechanical strength [1–3] and has got a lot of attention. Previous reports have revealed that graphene was used as a multifunctional reinforcer in electrodes, dielectric materials, supercapacitors and so on [4–8]. However, the application of graphene sheets in reinforcing polymers is usually challenged by their propensity to aggregate. Nowadays, though there have been many preparation methods of graphene sheet, the most promising method is the chemical reduction of exfoliated graphite oxide with hydrazine or other reducing agents, and the graphite oxides are always produced by Hummers' method [1,9,10]. For the carboxyl groups, hydroxyl groups, and other hydrophilic oxygen groups in the sheet edge of graphene, the graphene oxides can be dispersed in the many solvents to form stable suspensions easily, and graphene sheets after being reduced by chemical agents also have lots hydroxyl groups and give the possibility to overcome the dispersion problem by chemical modification [11,12], though the sheets would aggregate together resulting from the π-stocking interactions of RGO sheets. While, for the chemical modification, it can not only improve the dispersion but also give graphene nanosheets some other performances which may affect RGO sheets' performances, and at the same time it's very hard to

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react with the groups in the graphene oxides and reduction graphene oxides at the nanoscale, so it is not applicable for industrialized production. To retain the properties of RGO sheets, finding a simple system to keep graphene sheets dispersing stably is very necessary. Zhang [13] finds that the existence of montmorillonite (MMT) nanoplatelets can help RGO sheets dispersing in the water. While there is a limitation for the content of MMT nanoplatelets, if we want more RGO nanosheets, we need to add more MMT nanoplatelets, and the high MMT content would result in rapid deterioration of the nanocomposites' mechanical properties. So we need to find a new system to disperse the RGO.

Same as nanofillers, cellulose nanofibers (CNFs) with high aspect ratios, have shown the excellent mechanical performance and the Young's modulus and the tensile strengths can be evaluated as 140 GPa and 2–4 GPa by theories respectively [14–18]. For the CNFs prepared by TEMPO-mediated system, almost all of the C6-primary hydroxyl groups exposed on the crystalline cellulose microfibrils are converted to sodium C6-carboxylate groups, so the surfaces of the CNFs are negatively charged and they repel one another to disperse well in water. As we know RGO with the residual hydroxyl groups on surface are also negatively charged, thus when CNFs and RGO coexist, the negative charges on each surface would repel each other too [8]. Meanwhile, CNFs have great length to diameter ratios and steric hindrances, so they are difficult to enter into the space of RGO sheets. In order to overcome this problem, we are inspired by the effect of MMT nanoplatelets to disperse the RGO nanosheets, and introduce the MMT to disperse the RGO nanosheets and use CNFs to keep all the nanosheets stable. At the same time, MMT as common fire retardant have been used in many biological materials [19–21] and all of them have shown excellent flame retardant property.

In this paper, we prepare the nanocomposite films of RGO/MMT/CNFs by the stable hybrid via vacuum filtration. For the unique structure of these films, the RGO nanosheets and MMT nanoplatelets in the film form numerous micro-capacitors [22,23], which give the film excellent dielectric content and low dielectric loss. Furthermore, in contrast to the pure CNFs film, the incorporation of RGO nanosheets and MMT nanoplatelets results in the nanocomposite films with superior thermostability, flame retardancy and flexibility.

2. Experimental details

2.1. Materials

Graphite flake (<300 mesh), sulfuric acid (98%), TEMPO, sodium bromide, hydrogen peroxide (36 wt%), dried softwood breached kraft pulp, sodium hypochlorite solution, sodium montmorillonite (Na^{+}MMT). All the chemicals are used without further purification.

2.2. Preparation RGO

GO nanosheets dispersion were prepared by the modified Hummers Tung's method which used by Gao [1,8]. Briefly, the aqueous suspension of GO was obtained by dispersing 0.2 g GO in 200 ml DI water with ultrasound for an hour. Then the suspension was reduced with 1 ml hydrazine hydrate at 95 °C for 1 min by using microwave reactor. A black turbid liquid was obtained, and RGO was washed by DI water three times. Finally, wet RGO precipitation was obtained by filtering and the solid content of RGO was calculated before using.

2.3. Preparation of cellulose nanofibers dispersion

CNFs was prepared by the method of Tsuguyuki [16]. First, dried wood pulp (15 g) were suspended in 3 L water by stirring for 10 h. Subsequently, adding 0.5 g TEMPO and 5 g sodium bromide with vigorous stirring until all of the chemicals were dissolved. Then 100 g NaClO solution was added into the suspension slowly to keep the pH at 10.00, and at this time the reaction was started. When all of the NaClO was added, 0.5 M NaOH was added slowly to keep the pH at 10 for 10 h. Then, the oxidized cellulose were washed by water three times and 200 ml 1% oxidized cellulose suspension was sonicated for 15 min by an ultrasonic generator (SCIENTZ-II D, NINGBO Scientz biotechnology Co., Ltd., China) with an output power of 300 W. Finally, the nanocellulose fibers dispersions were centrifuged at 10,000 rpm for 15 min to get the transparent suspension and stored at 4 °C before using.

2.4. Preparation of RGO/MMT/CNFs hybrids in water

Firstly, MMT dispersions were prepared before mixing. Briefly, the MMT dispersions were obtained by dissolving 2 g Na^{+}-MMT in 98 g water. After vigorously stirring for 1 h at room temperature, the suspensions were sonicated by sonic washer at room temperature for another 1 h. The exfoliated MMT nanoplatelets dispersion was then collected by centrifuging at 10,000 rpm for 15 min to remove the unexfoliated MMT. And, the solid contents of MMT dispersion were calculated before using. Then, desired amounts of the MMT nanoplatelets suspension and RGO nanosheets were added to 30 ml CNFs suspension and the hybrids were named as RGO/MMT/CNFs with different weight ratios of MMT and RGO such as RGO(10%)/MMT (50%)/CNFs. The MMT concentrations in the composite suspensions were 10%, 20%, 30%, 40%, 50% and the RGO concentrations