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Preparation of amino-functionalized graphene oxide by Hoffman rearrangement and its performances on polyacrylate coating latex

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ABSTRACT

Amino-functionalized graphene oxide (NGO) was prepared by Hoffman rearrangement where carboxyl group was replaced directly by amino group instead of using long-chain containing amino group. The chemical structure of NGO was studied by FT-IR, UV–vis, Raman, XPS and TGA. NGO was incorporated into polyacrylate latex (PA) by blending to prepare PA/NGO composite. The dispersibility of NGO in PA latex was significantly influenced by pH values. When the pH value was higher than 6, NGO uniformly dispersed in PA. The mechanical properties of the PA/NGO film were relayed on the pH. The break strength of the film was increased from ~2 MPa to ~5 MPa but the elongation at break decreased from 475% to 258% compared with those of PA film. The glass transition temperature (T_g) of PA/NGO film increased by 3.48 °C. For the sake of comparison, the mechanical properties and T_g of a similar composite but with bare graphene oxide (PA/GO) are presented.

1. Introduction

Owing to its fantastic electrical, optical, thermal, and mechanical properties, graphene, an atomically thin sheet composed of two dimensional p-conjugated sp^2 carbons, has attracted a great attention in recent years [1–3]. Graphene has been applied in various fields such as electronic [4] and energy devices [5,6], catalysts [7,8], sensors [9], high performance fibers [10] and composites [11]. Polymer-graphene nanocomposites are very promising because the combination of graphene and polymer substantially improves the properties of the nanocomposites [12]. For example, polymethyl methacrylate/graphene nanocomposite shows better flame-retardant property than bare polymethyl methacrylate [13], and polylactic acid/graphene composites prepared by masterbatch-based melt blending has improved thermal degradation and combustion properties as compared with the bare polymer [14]. Lots of studies has focused on the dispersion of graphene because of the easily re-aggregation due to the intrinsic van der Waals forces. That makes dispersion difficult and reduces the interfacial area between the graphene and the polymer matrix [15,16].The solubility of graphene or graphene oxide in solvents is enhanced by the incorporation of organic chains such as phenyl isocyanate [17], octadecylamine [18] and 2-amino-4,6-didodecylamino-1,3,5-triazine [19], because they have a good compatibility with the polymer matrix and solvents.

Waterborne polyacrylate latex has been widely used in coatings [20], leather finishing [21], biomaterials [22], and pressure sensitive adhesives [23] because of their attractive properties such as weather fastness, aging resistance and inoxidizability. Nevertheless, its thermal and mechanical properties need to be improved for higher performance in applications. One of most common methods is to modify the polyacrylate with nanomaterials. An immense amount of reports suggests that the incorporation of nanomaterials, such as SiO_2 [24], ZnO [25] and TiO_2 [26], into the polymer matrix could enhance the properties of the polymer, including the improvement of photoelectricity, photocatalysis, thermal behavior [27], etc. Graphene has also been incorporated into polyacrylate matrix by solvent blending, melt blending, in situ polymerization, and latex blending [28–30].Jiang [31] et al. reported on the introduction of graphene oxide in poly methyl methacrylate via melt blending after it was successfully grafted with double bonds by hydroxyethyl acrylate. For molding, solvent blending or melt blending would lead to great performances, but that is not suitable for waterborne polyacrylate, especially for polyacrylate latex.

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Latex blending and in situ latex polymerization are frequently used for the preparation of polyacrylate latex/graphene composites which had been reviewed in detail by Elodie et al. [32]. D. Spasevska et al. bonded reduced graphene oxide (rGO) with polyacrylate by polyurethane prepolymer [33] or hexamethylene diisocyanate [34] in semicontinuous emulsion polymerization or emulsion mixing, respectively. The bonding was established through spontaneous NCO reaction with OH functionalities present on the rGO platelet's surface and through OH functionalities present on the polymer nanoparticle's surface. Amélie Noël et al. prepared a cellular microstructure by blending nanosize multilayered graphene with different sizes of polyacrylate latex without high temperature curing or additional hot-pressing and studied the percolation behavior [35,36]. The composite could demonstrate highly conductive behavior by percolation approach of filler architecture.

The composite of polyacrylate latex and graphene can also be prepared with the help of functionalization which facilitates the uniform insertion of graphene. Functional groups such as amino are necessary for waterborne polymer systems equally. Graphene oxide (GO), as the precursor of graphene, facilitates the functionalization via solution reactions by the oxygen-containing groups, such as —OH, —COOH and epoxy. Polyacrylate latex can be viewed as the dispersion of polyacrylate in aqueous solutions with the help of emulsifier. Both graphene and graphene grafted with organic chains cannot disperse in water. Nevertheless, graphene oxide with carboxyl group or amino group can change the dispersion in water and, further, latex easily. These groups help graphene to disperse in aqueous solution and to interact with the side chains of polyacrylate. Thus, the compatibility between graphene and polyacrylate will be promoted. Amino group is a pH-sensitive and hydrophilic group which is promising and practical in aqueous solution or latex. A few reports about the combination of amino-functionalized graphene oxide (NGO) and polyacrylate have been published.

In the present work, we prepared amino-functionalized GO by Hoffman rearrangement to make sure that the amino group grafted on GO directly. For waterborne latex, short and pH sensitive groups such as amino incorporated on graphene help the incorporation of graphene function within latex system well. Amino group can be introduced by diamines, triamines and silane coupling agents which possess an amino group. It is easy to make the graphene oxide crosslinked, because diamines, triamines and silane coupling agents have more than 2 functional groups which all can react with graphene oxide. Therefore, the Hoffman rearrangement was used in our study. The effect of pH on polyacrylate/NGO film was studied by mechanical properties and zeta potential. For the sake of comparison and in order to clarify the role of amino-functionalized GO in the reinforcement of the host polyacrylate, we prepared for investigation both bare polyacrylate samples and polyacrylate/GO composite. The effect of NGO prepared by Hoffman rearrangement on polyacrylate/NGO composite has not been yet reported.

2. Materials and methods

2.1. Materials

Natural graphite flakes with an average particle size of 325 mesh and a purity of >99% was purchased from Qingdao Guangyao Graphite Co. Ltd. (China). Sulfuric acid (98%), potassium permanganate ($KMnO_4$), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, 37%), methyl methacrylate (MMA), n-butyl acrylate (BA), acrylic acid (AA), sodium dodecyl sulfate (SDS), polyethylene glycol-400 (PEG-400, molecular weight 380–430 g/mol), ammonia water (25–28%, aq.), ammonium persulfate (APS) thionyl chloride ($SOCl_2$), N,N-dimethyl formamide (DMF), triethylamine (TEA), sodium hydroxide (NaOH) and bromine (Br_2) were purchased from Sinopharm Chemical Reagent Co., Ltd. $K_2S_2O_8$ was further purified by recrystallization from methanol. DMF and $SOCl_2$ were purified by low pressure distillation before use. All other chemicals were used without further treatment. PVDF membrane was received from Shanghai Yaxin Purification Device Factory. Deionized water was used throughout the experiment.

2.2. Preparation of GO and NGO

Graphite oxide was prepared by a modified Hummers' method [37] from graphite flakes. The preparation of exfoliated GO is described as follows: $K_2S_2O_8$ (2.5 g) was reacted with P_2O_5 (2.5 g) and concentrated sulfuric acid (7.5 mL) in the 100 mL three-neck flask at 25 °C. Natural flake graphite (5 g) was gradually added and stirred uniformly after the flask was heated to 80 °C. After the solution was stirred for 10 h and cooled to room temperature, 500 mL of deionized water was added to the solution. The mixture was filtered through a PVDF filter membrane with a pore size of 0.22 μm and washed out with deionized water until the pH reached 7. The pre-oxidation product was dried in vacuum and mixed with 200 mL of concentrated sulfuric acid in a 2000 mL flask at 0-3 °C for 30 min, and then, $KMnO_4$ (26 g) was put into the flask. The solution was heated to 35 ± 3 °C and maintained for 2 h. Then, 400 mL of deionized water was slowly added while keeping the temperature around 96-100 °C for 0.5 h. With mechanical stirring, 700 mL of deionized water was added and H_2O_2 (30%) was dripped into the suspension until the slurry turned golden yellow. The suspension was washed out with 5% HCl and deionized water until the pH reached 7. The graphene oxide (GO) was obtained by sonication for 30 min and freeze-dried.

The preparation of NGO is presented in Scheme 1. First, GO (1.0 g) was treated with $SOCl_2$ (60 mL) under ultrasonic treatment for 2 h and then refluxed in the presence of DMF (3 mL) at 70 °C for 24 h under N_2 flux. After evaporation of volatile fractions at low pressure, DMF (120 mL), TEA (10.1 g) and $NH_3\ H_2O$ (5.0 g) were added to the residue at 0 °C for 1 h. The mixture was filtered through a PVDF filter membrane and washed with ammonia for several times. The filter cake was added into H_2O (50 g), NaOH (5.76 g) and Br_2 (4.32 g) while stirring for 15 min at 0 °C. Then, the reaction mixture was stirred vigorously at 85 °C for 3 h and 90 °C for 1 h and filtered over PTFE membrane. The product was washed out with deionized water several times and freeze-dried, providing a black powder functionalized by amino.

2.3. Preparation of polyacrylate/NGO composite latex

The synthesis process of polyacrylate latex was as follows: 2.5 g of emulsifier (comprising 2.0 g of SDS and 0.5 g of PEG-400), 142 g of deionized water, and 1/3 mixture monomers of MMA, BA and AA (comprising 9.7 g of MMA, 19.3 g of BA and 1.7 g of AA) were placed in a 500 mL four-necked flask with a mechanical stirrer, a thermometer, and a condenser. The flask was placed in a water bath of 50 °C for 10 min, and then heated to 75 °C and kept for 30 min. The residual mixture monomers (62 g) and 60 g of APS solution (1.6%) were dropwise added into the flask in 2 h. After 2 h, the emulsion was cooled naturally.

The polyacrylate/NGO composite latex was prepared by a magnetic stirring 0.1 wt% NGO in relation to polymer into polyacrylate latex at different pH, and marked as PA/NGO. The precipitate caused by adding of NGO in the composite latex should be removed before film preparation and characterization. Samples of latex with the same amount of GO (PA/GO) were prepared for comparison.