Preparation of highly conductive reduced graphite oxide/poly(styrene-co-butyl acrylate) composites via miniemulsion polymerization

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ABSTRACT

Polymer/reduced graphite oxide (rGO) composite nanoparticles with a high electrical conductivity were synthesized using the miniemulsion polymerization technique. The rGO was modified with a reactive surfactant, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), to facilitate monomer intercalation into the rGO nanogalleries. The AMPS-modified rGO was emulsified in the presence of styrene (St) and butyl acrylate (BA) monomers, and the stable miniemulsion was polymerized to form poly(St-co-BA)/rGO composite latex nanoparticles. The transition in the composite nanoparticles from an electrical insulator to an electrical conductor occurred at an rGO content of 10 wt% (relative to the monolayer content), yielding an electrical conductivity of 0.49 S/cm. The electrical conductivity of the composite nanoparticles reached 2.22 S/cm at 20 wt% rGO, yielding a much better conductivity than other polymer composites prepared using a GO filler. Importantly, the miniemulsion polymerization method for fabricating poly(St-co-BA)/rGO composite nanoparticles is easy, green, low-cost, and scalable, providing a universal route to the rational design and engineering of highly conductive polymer composites.

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1. Introduction

Polymer-based materials with a high electrical conductivity are highly desirable in practical applications, such as electronic devices, sensors, and electromagnetic shielding [1—7]. Because most polymers are insulating, a variety of materials may be used as a conducting filler, such as metal nanoparticles [8], metal nanowires [9], and metal oxide particles [10]. Among these conducting fillers, graphite, which is naturally abundant, has been used in recent decades to prepare conducting polymer composites [11—13]. The introduction of graphite into polymer matrices has led to remarkable improvements in the electrical, thermal, and mechanical properties of the composites relative to the pure polymer materials. Polymer/graphite composites with a high electrical conductivity have been the subject of recent studies, with a focus on optimizing the dispersibility of graphite nanosheets or flake graphite in polymer matrices.

Pristine graphite nanosheets (i.e., flake graphite) are difficult to disperse in polymer matrices because the absence of reactive groups on the graphene layer surfaces prevents organic molecules or polymers from stably solvating the surface [14,15]. Graphene has a low affinity for hydrophilic or hydrophobic molecules, and the inter-layer spacing prevents polymers from intercalating into its galleries. Thus, pristine graphite is usually functionalized prior to use in the synthesis of polymer composites. Oxidizing graphite yields functionalized exfoliated graphite sheets. Graphite oxide (GO) may be obtained using the Hummers and Offeman method, in which graphite is oxidized in the presence of strong concentrated sulfuric acid and a strong oxidizing agent, such as potassium permanganate [16,17]. The oxidation chemistry introduces a variety of oxygen-containing groups, including hydroxyl, epoxy, carbonyl, and carboxyl groups, at different sites on the graphite surface. The presence of these functional groups renders the surface strongly hydrophilic, thereby facilitating the dispersion of GO in aqueous and polymeric media. As a result, composites comprising uniformly dispersed GO in a polymer matrix may be obtained.

Despite the availability of this method, the utility of GO in polymer composites remains limited. Polymer/GO composites display a low electrical conductivity because the electrical

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conductivity of the GO is poor [17–19]. The low conductivity of GO may result from damage to the structural integrity and conduction mechanism of the graphite, which inevitably occurs during the graphite oxidation process. Additionally, hydrophobic monomers or polymers, such as polystyrene (PS) or poly(methyl methacrylate) (PMMA) cannot easily intercalate into the hydrophilic GO layers to stabilize the dispersion of the GO in the polymer media [14,20,21]. To address these problems of a low electrical conductivity in GO and incompatibility between GO and hydrophobic polymers, we reduced the GO prior to fabricating polymer composites. The reduced GO (rGO) has a graphene-like sheet structure in which the oxygen-containing groups are removed and the conjugated structure is recovered [22–24]. rGO is usually considered to be a chemically derived graphite [22–24], although a few oxygen-containing groups may remain present. rGO displays a superior electrical conductivity and relatively hydrophobic properties compared to GO, thereby improving the compatibility with hydrophobic polymers, such as PS or PMMA. rGO is an attractive electrically conductive filler for polymer matrices, and it can be used to prepare highly conductive composite materials.

Several methods have been established for fabricating polymer/graphite composites, including mechanical mixing [25], melt mixing [26], and in-situ controlled radical polymerization [27]. Among these techniques, miniemulsion polymerization is a useful method for preparing nanoscale latex particles, including the graphite filler [2,14,15]. Miniemulsion polymerization offers several advantages over other dispersion polymerization methods, such as the preparation of nano-sized latex particles with finely controlled shapes. The miniemulsion process involves dispersing the oil phase containing the monomer and filler in an aqueous phase using a surfactant to stabilize the emulsion. The stabilized monomer/filler droplets directly polymerize to form composite particles through an emulsion polymerization step. The method can polymerize hydrophobic monomers with low solubility in water [28,29]. The advantages of miniemulsion polymerization make it attractive to synthesize the composites.

Reactive surfactants, such as 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) have been successfully used to stabilize rGO–polymer emulsions toward the synthesis of highly electrically conductive polymer/rGO composites. The use of the AMPS surfactant as an rGO modifier plays a major role for exfoliating and dispersing rGO in the composites [2,28,29]. Etmini group used AMPS as a GO modifier in the synthesis of exfoliated polymer/GO composites by emulsion polymerization [2]. They reported that AMPS can increase the interlayer spacing between the modified graphene layers in GO and that AMPS facilitates the insertion of monomers into graphene layers. The sulfate and amido groups of AMPS form hydrogen bonds with polar groups, such as hydroxyl and carboxylic groups, on a GO surface [30,31]. Thus, AMPS can easily intercalate into GO particles. AMPS is expected to form hydrogen bonds with the rGO surfaces in polymer/rGO composites due to the presence of residual oxygen-containing groups on the rGO surfaces as a result of the incomplete reduction of GO. Modifying rGO with AMPS is anticipated to promote the synthesis of polymer/rGO composites using the miniemulsion polymerization method.

Here, we report an efficient method for synthesizing poly(styrene-butyl acrylate)/rGO (poly(St-co-BA)/rGO) composites with a high electrical conductivity using the miniemulsion polymerization technique. In our experiment, rGO was used in place of GO as a highly conductive filler and was modified with the reactive surfactant AMPS to promote the intercalation of water-insoluble monomers (St and BA) into the layered rGO. To the best of our knowledge, this is the first report of the use of AMPS-modified rGO as a conductive filler in the miniemulsion polymerization of St and BA monomers for the preparation of highly conductive composites.

2. Experimental section

2.1. Materials

Styrene (St) (99%) and butyl acrylate (BA, 99%) were purchased from Tokyo Chemical Industry (TCI) and were used as received. Sodium dodecyl sulfonate (SDS) (85%, Samchun Chemical) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (99%, Aldrich) were used as received. Potassium persulfate (KPS) (99%) was obtained from Samchun Chemical and was purified by recrystallization from methanol. Potassium permanganate ($KMnO_4$) (99%), sodium nitrate ($NaNO_3$) (99%), sulfuric acid (H_2SO_4) (98%), and hydrogen peroxide (H_2O_2) (30%) were purchased from Samchun Chemical and were used to oxidize the pristine graphite. Deionized (DI) water was prepared using a Millipore Milli-Q water purification system. GO was synthesized from natural graphite (SP-1, Bay Carbon, MI) using the Hummers method with modification, as described in the literature [32]. Hydrazine monohydrate ($N_2H_2 \cdot H_2O$) was obtained from Sigma–Aldrich to synthesize rGO.

2.2. Preparation of AMPS-treated rGO

GO was prepared by modifying the natural graphite according to the method of Hummers and Offeman [32]. A colloidal suspension of GO (100 mg) in purified water (100 mL) in a 250 mL round-bottom flask was prepared by sonication for 3 h. Hydrazine hydrate (1.0 mL, 32.1 mmol) was subsequently added to the suspension, and the solution was heated in an oil bath at 100 °C for 12 h. During this heating period the rGO gradually precipitated out as a black solid. After cooling to room temperature, the rGO powder was filtered through a fritted glass filter with a medium pore size and washed with copious water and methanol. The resulting black product, rGO, was dried under vacuum conditions of approximately 10^{-3} Torr for 24 h at room temperature. The rGO was treated with various AMPS formulations, as shown in Table 1 rGO was introduced into a 1 L flask containing DI water. The mixtures were stirred at room temperature for 30 min at 1000 rpm and then were sonicated for a further 30 min to achieve complete dispersion of the rGO nanosheets in water. The AMPS was added to the mixture to a concentration of 80 wt% relative to the rGO. The mixture was then stirred for a further 24 h at 800 rpm at room temperature. The AMPS-treated rGO was filtered and dried through a fritted glass filter.

2.3. Synthesis of poly(St-co-BA)/rGO composites by miniemulsion polymerization

AMPS-treated rGO (modified with 80 wt% AMPS relative to the rGO) was added to the monomer mixture of St and BA, and the mixture was stirred for 1 h to allow effective solvation of the rGO

Table 1
Quantities of reagents and monomers used in the miniemulsion polymerization reactions.

	St (g)	BA (g)	rGO (g)	AMPS (g)	SDS (g)	KPS (g)	Water (g)
2wt% rGO	9	1	0.2	0.16	0.2	0.15	300
5wt% rGO	9	1	0.5	0.4	0.2	0.15	300
10wt% rGO	9	1	1	0.8	0.2	0.15	300
15wt% rGO	18	2	3	2.4	0.4	0.3	500
20wt% rGO	18	2	4	3.2	0.4	0.3	500
30wt% rGO	36	4	12	9.6	0.8	0.6	500