Graphite oxide/poly(methyl methacrylate) nanocomposites prepared by a novel method utilizing macroazoinitiator

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ABSTRACT

Graphite oxide (GO)/poly(methyl methacrylate) (PMMA) nanocomposites were prepared by a novel method utilizing macroazoinitiator (MAI). The MAI, which has a poly(ethylene oxide) (PEO) segment, was intercalated between the lamellae of GO to induce the inter-gallery polymerization of methyl methacrylate (MMA) and exfoliate the GO. The morphological, conductivity, thermal, mechanical and rheological properties of these nanocomposites were examined and compared with those of intercalated nanocomposites prepared by polymerization with the normal radical initiator, 2,2′-azobisisobutyronitrile. The improvement in conductivity by GO was more evident in exfoliated nanocomposites compared to that of intercalated nanocomposites. For example, a conductivity of 1.78×10^{-7} S/cm was attained in the exfoliated nanocomposite prepared with 2.5 parts GO per 100 parts MMA, which was about 50-fold higher than that of the intercalated nanocomposite. The thermal, mechanical and rheological properties also indicate that thin GO with a high aspect ratio is finely dispersed and effectively reinforced the PMMA matrix in both exfoliated and intercalated nanocomposites.

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1. Introduction

Nanocomposites composed of polymer matrices with reinforcements of less than 100 nm in size have attracted considerable attention as advanced materials because many physical properties of matrix polymers, such as their mechanical, electrical, barrier, and flame-retarding properties can be substantially enhanced with small amounts of reinforcements compared to conventional composites [1,2]. Because these unique properties of polymer nanocomposites come from their peculiar phase morphologies of intercalation or exfoliation, which maximize interfacial contact between the matrix polymer and reinforcements, the fillers with high surface-to-volume ratio, for example, layered silicates such as montmorillonite, that are composed of stacks of parallel lamellae with a 1 nm thickness and a high aspect ratio are most commonly utilized [3].

Graphite oxide (GO), which is prepared by the oxidation of graphite, has a layered structure composed of parallel pseudo two-dimensional lamellaes. Each layer consists of randomly distributed unoxidized aromatic regions and six-member aliphatic regions attached with polar groups, such as hydroxyl, epoxide, ether, and carboxylate groups, as a result of oxidation [4–6]. GO is quite similar to montmorillonite in that it can have intercalated or exfoliated structures in the polymer matrix to create a nanocomposite

[7–9]. In addition, GO can impart electric conductivity to polymers [10], and GO can be used as host material for the synthesis of conducting polymer intercalated nanocomposites [11–14].

Because exfoliated nanocomposites usually provide the best property enhancements due to a large interfacial area and homogeneous dispersion, many efforts have been devoted to design methods that improve the delamination of silicate layers in the polymer matrix. Polymerization in the galleries between the silicate layers can promote exfoliation because the growing polymer chain can push apart and eventually delaminate the silicate layers. Therefore, the initiator, or co-monomer, located in the gallery, which induces inter-gallery polymerization, can be utilized for exfoliation [15,16].

The polar functional groups attached to carbon sheets make GO hydrophilic [5,6]. Therefore, the dispersion of GO in the hydrophobic polymer matrix requires a large favorable enthalpic contribution to overcome this discrepancy in polarity, as well as the entropy loss required for the chain to diffuse into the gallery. Therefore, hydrophobic modification of GO [17,18], block or graft copolymers containing a block that is miscible with the matrix polymer and another block that is compatible with GO can be utilized for the favorable enthalpic contribution.

Because GO has a larger interlayer spacing (I_c) compared to graphite, as well as polar functional groups, hydrophilic polymers such as poly(ethylene oxide), poly(vinyl alcohol), poly(diallyldimethylammoniumchloride), poly(furfuryl alcohol) can be easily inserted into the gallery of GO to make intercalated nanocomposites [19–23].

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Since poly(ethylene oxide) (PEO) can be easily intercalated at the GO gallery [19,20], the macroazoinitiator (MAI) containing a PEO segment, as shown in the following chemical structure, can also be intercalated easily in the GO gallery. Therefore, it is anticipated that intercalated MAI can be utilized to prepare exfoliated nanocomposites by inducing inter-gallery radical polymerization of vinyl monomers, and the polymerized PEO-vinyl monomer multi-block copolymer will have an affinity to GO due to the presence of PEO block.
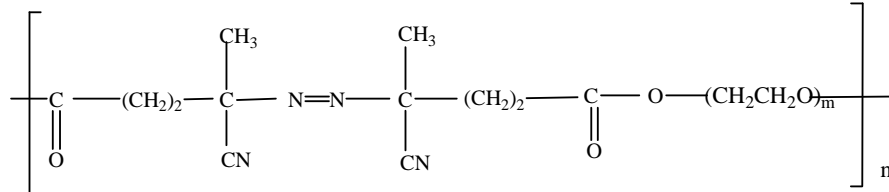
In the present study, we prepared exfoliated GO/poly(methyl methacrylate) (PMMA) nanocomposites with an MAI intercalated in the gallery of GO. The morphological, conductivity, thermal, and mechanical properties of these nanocomposites were examined and compared to those of nanocomposites prepared by normal radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as an initiator.

2. Experimental

2.1. Materials

Natural graphite (HC-598) with an average particle size of 11 μm was purchased from Hyundai Coma Co., Ltd. MAI (VPE-0201) was purchased from Wako Pure Chemical. It is the condensation polymer of 4,4'-azobis(4-cyanopentanoic acid) (ACPA) and poly(ethylene glycol) (molecular weight 2000) [24]. It has a molecular weight of about 22,000 and an azo group content of 0.45 mmol/g. MAI, methyl methacrylate (MMA, Aldrich), AIBN (Aldrich), acetonitrile (Aldrich), methanol (Aldrich), concentrated H_2SO_4 (96%, DC Chemical Co., Ltd.), $KMnO_4$ (Duksan Pure Chemical), H_2O_2 (30%, DC Chemical Co., Ltd.), and hydrochloric acid (35%, Daejung Chemicals & Metals Co., Ltd.) were used as received.

2.2. Preparation of GO

GO was prepared by oxidation with $KMnO_4/H_2SO_4$ [10]. In a typical experiment, $KMnO_4$ (15 g) was added slowly to a cooled 500 mL round-bottomed flask that contained conc. H_2SO_4 (110 mL) and graphite powder (10 g) with care that the reaction mixture be maintained below 20 °C, and the reaction mixture was stirred for 30 min at 30 °C. After slowly feeding distilled water (230 mL) into the reactor with care that the reaction mixture to be kept below 90 °C, the mixture was allowed to stir for another 30 min at 90 °C. To stop the oxidation reaction, additional distilled water (250 mL) and 30% H_2O_2 (20 mL), which reduced the excess $KMnO_4$, were fed sequentially into the reactor. The oxidized product, GO, was filtered, washed with 5% HCl aqueous solution several times and then with distilled water until neutralization, and dried in a vacuum oven at 50 °C for 24 h. Elemental analysis showed that the composition of GO was $C_{1.00}O_{0.23}H_{0.13}$.

2.3. Preparation of GO/PMMA nanocomposite

The GO intercalated with MAI (MAI/GO) was prepared using an acetonitrile/methanol mixture (1/1 by volume) as the solvent. After dissolving 0.10 g of MAI into 100 mL of the solvent, 0.50 g

of GO was put into the solution and ultrasonic irradiation was applied for 30 min. Solid state MAI/GO was obtained by evaporation of the solvent at 25 °C under vacuum conditions.

The recipes for the preparation of GO/PMMA nanocomposites are shown in Table 1. In the case of Series A, bulk radical polymerization of MMA was carried out in the presence of GO with AIBN as an initiator under N_2 atmospheric conditions at 65 °C for 2 h while stirring with a magnetic bar. For the preparation of Series B, MAI/GO was swelled in a reactor with a 100-fold volume of water and then MMA was fed into the reactor while being stirred by a magnetic bar at room temperature. This heterogeneous system was heated to 65 °C to cause polymerization under N_2 atmospheric conditions for 5 h, and this was further polymerized for 1 h at 65 °C after feeding additional initiator, AIBN dissolved in MMA. The prepared GO/PMMA nanocomposites were crushed into powder and dried at 65 °C under vacuum conditions for 24 h to remove low molecular weight components.

2.4. Measurements

X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku, RAD-3C) using Cu K_α radiation (λ = 1.54 Å) as the X-ray source. The diffraction angle was scanned from 2° at a rate of 1.2°/min.

The morphology of nanocomposites was examined with a transmission electron microscope (TEM, Hitachi H-8100). Thin sections were cut perpendicularly to the nanocomposite fiber, which was extruded by a melt indexer at 240 °C. The acceleration voltage of TEM was 200 kV.

The direct current conductivity at room temperature across the 1 mm thick film, which was compression molded at 190 °C and a pressure of 22 MPa, was measured with a picoamperometer (Keithley 237) utilizing round-shaped silver electrodes measuring 0.28 cm^2 attached at both surfaces of the specimen. Silver paste was used to ensure good contact between the specimen surface and the electrode.

Table 1
Recipe for the preparation of GO/PMMA nanocomposites and polymerization yield.

Sample	Feed (by weight)				Concentration of azo group in feed (mmol/ 100 g-MMA)	Polymerization yield (%)
	MMA	AIBN	GO	MAI/GO		
Series A						
A-0	100	0.300	–	–	1.83	87.3
A-8	100	0.300	0.833	–	1.83	82.4
A-25	100	0.300	2.500	–	1.83	87.7
A-42	100	0.300	4.167	–	1.83	88.2
A-67	100	0.300	6.667	–	1.83	87.2
Series B						
B-8	100	0.288	–	0.167/0.833	1.83	86.6
B-17	100	0.275	–	0.333/1.667	1.83	84.5
B-25	100	0.263	–	0.500/2.500	1.83	80.7
B-33	100	0.251	–	0.667/3.333	1.83	86.4
B-42	100	0.239	–	0.833/4.167	1.83	85.6
B-50	100	0.226	–	1.000/5.000	1.83	87.4
B-67	100	0.202	–	1.333/6.667	1.83	84.7