Electrical and Thermal Properties of Poly(*p*-phenylene sulfide) Reduced Graphite Oxide Nanocomposites

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Abstract

Graphite oxide (GO) was produced using the modified Hummer's method. Poly(*p*-phenylene sulfide) (PPS)/reduced graphite oxide (RGO) composites were prepared by *in situ* polymerization method. The electrical conductivity of the PPS/RGO composites was no more than 82 S/m. It was found that as GO content increased in the PPS/RGO composites, the crystallization temperature and electrical conductivity of the composites increased and the percolation threshold value was at 5-8 wt% of GO content.

Key words: Poly(*p*-phenylene sulfide), graphite oxide, conducting polymer nanocomposites, *in-situ* polymerization

1. Introduction

Recently, graphene has been recognized as the most promising of the 2D nanomaterials due to its excellent electrical, thermal, and mechanical properties. Graphene is receiving much interest in the field of high performance polymer nanocomposites [1-5]. In order to produce high performance graphene nanocomposites, however, it is necessary to be able to produce a large amount of graphene, and the issue of graphene dispersibility must be resolved. In order to produce graphene in large amounts and to use it with composite materials, the method of using strong acid treatment and oxidation of graphite to graphite oxide (GO) and thermal or chemical reducing to produce reduced graphite oxide (RGO) has been widely reported [3,4]. GO produced as such exhibits a strong hydrophilic property; the inter-layer gap is broader than that of pristine graphite so that the material can be easily exfoliated through sonication or long-time stirring. It also has excellent dispersibility [6]. However, many oxygen atoms are found on the surface of a functional group, so that the electrical conductivity is usually low, which is a disadvantage when producing conducting composite materials. For the chemical reduction of GO, hydrazine (N₂H₄) is a well-known reducing agent [6,7]. However, a reduction process using hydrazine has disadvantages such as toxic gas generation and attachment of nitrogen atoms to the graphene sheet. Another reduction method is the heat treatment technique. Heating of GO at a temperature over 800 °C removes the oxygen groups, which improves the electrical conductivity [7]. However, heating to a high temperature can cause large energy consumption. *In situ* polymerization at a relatively low temperature may be applied to produce high performance polymer composites that are soluble in polar solvents [2]. GO has excellent dispersibility in polar solvents such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethyl formamide [5]. Therefore, it is expected that the addition of GO to NMP may maintain the dispersibility while reducing the GO *In situ* by heating it to produce conducting polymer composites. Other polymer composites with RGO may be produced by mixing polymer precursors such as polyamic acid for polyimide and GO in solvent and then removing the solvent with heat treatment at a relatively low temperature

[1,8]. In this study, Poly(*p*-phenylene sulfide) (PPS) was chosen in order to produce conducting composite materials through not only *in situ* polymerization but also through a reduction of GO in NMP, with heat treatment to enhance the dispersibility of GO and the properties of the composites. PPS has excellent chemical resistance, flame resistance, heat deflection temperature, and mechanical strength; it is the representative engineering plastic that is commonly used in automobile parts, electric/electronic parts, electric heating parts, chemical devices, etc. [9,10]. Many methods have been reported for PPS polymerization. Among them, the reaction of 1,4-dichlorobenzene and sodium sulfide in NMP at a relatively low temperature (>260°C) and high pressure has been widely used [11–14]. This experiment involves the production of conducting composite materials without additional GO reduction in the preparation of the complex of PPS and GO. In order to reduce GO, either chemical or heat treatment is necessary, as mentioned above. However, it was expected that high performance composite materials with high electrical conductivity could be produced without an additional reduction process by utilizing the step of reacting the materials at high-temperature/high-pressure in the PPS polymerization process.

2. Experimental

2.1. Materials

GO was produced using the modified Hummer's method [15] and was supplied by Nanosolution Co., Ltd (Korea). $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ was supplied by Yakuri (Japan), and NaOH by Showa (Japan). NMP and 1,4-dichlorobenzene (Sigma-Aldrich Corporation, USA) were used without purification.

2.2. Polymerization

$\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ (0.2 mol), NMP (100 mL), DI-water (1.2 mol), and NaOH (0.006 mol) were added to a round flask and heated in a silicon oil bath at 190°C for the dehydration reaction. After the dehydration, 1,4-dichlorobenzene and NMP were mixed with water-free Na_2S solution; the resulting solution was put inside a Parr reactor. The reactor was filled with nitrogen. Afterwards, the temperature was increased and pressure was applied to initiate the reaction. The temperature was raised to 265°C within 1 h; temperature was then maintained for 5 h for polymerization. After 5 h, the reactor was cooled. Once the temperature dropped to room temperature, the polymerized compound was filtered and washed with water, methyl alcohol, and hot DI-water. Afterwards, the compound was dried for over 15 h in a vacuum oven at 100°C. The molecular weight (M_w) of pure PPS was about 6000 (g/mol). In order to produce PPS/RGO composites, GO was first mixed with $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ and then dehydration was conducted. In this experiment, the weight ratio of GO to PPS was varied during the polymerization.

2.3. Characterization

The intrinsic viscosities of pure PPS were obtained using a Brookfield viscometer with a thermosel system and a S18 spindle (DV-II+Pro, Brookfield Co., UK). Sample was dissolved in

Fig. 1. FT-IR spectra of graphite oxide produced by modified Hummer's method.

1-chloronaphthalene in order to prepare 4 wt% polymer solutions at 210°C. The intrinsic viscosities were calculated using the Solomon-Ciuta relation, as follows:

$$[\eta] = \frac{\eta_{sp}/C}{1 + k\eta_{sp}}$$

where k is 0.302 for PPS as a material property, C is the concentration of polymer in 1-chloronaphthalene, $[\eta]$ is the intrinsic viscosity, and η_{sp} is the specific viscosity. The viscosity-average molecular weight was calculated using the Mark-Houwink-Sakurada equation, as follows:

$$[\eta] = KM_v^a$$

where K and a are 8.91×10^{-5} and 0.747 for PPS, respectively.

The surface functional groups of GO were measured by Fourier transform infrared spectroscopy (IS 10, Sincro, Japan). The KBr disks were prepared by mixing KBr and the sample powder homogeneously. Fig. 1 shows that the functional groups of GO were carboxylic acid, ketone, and so on. Thermal analysis was conducted using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA). For DSC (Q20, TA Instrument, USA) analysis, the increment of temperature rise of the nitrogen was set at 10°C/min; temperature was kept at 350°C for 10 min, and was then dropped at the speed of 10°C/min to 40°C. TGA (Q50, TA Instrument, USA) was conducted until the temperature of 900°C was reached, at a speed of 10°C/min in nitrogen. An scanning electron microscope (SEM) image was obtained using a Hitachi S-4700 field emission SEM. Electrical conductivity was measured using a 4-point probe employing the FPP-RS8 of DASOL ENG.

3. Results and Discussion

Fig. 2 shows the DSC thermograms of pure PPS and PPS/RGO nanocomposites. First, it was seen that there are two melting temperatures in the heating process; this might be due to the unstable and small crystals of PPS fabricated using GO. Also,

Fig. 2. Differential scanning calorimeter thermograms of pure PPS and PPS/RGO nanocomposites in (a) the first heating, (b) the first cooling at a rate of 10°C/min. PPS: poly (*p*-phenylene sulfide), RGO: reduced graphite oxide.

it was observed that the melting temperature dropped with increasing GO content; this may be caused by interference of the polymerization of PPS on the high molecular weight polymers due to the addition of GO. When Na_2S reacts with the epoxy group of GO, the ratio of the *p*-DCB monomer to the Na_2S may change. This may decrease the degree of polymerization of PPS. Therefore, the higher the GO content, the higher the PPS content will be expected to be, with low molecular weight. It is confirmed that the crystallization temperature (T_c) of the PPS/RGO nanocomposite material is affected in the cooling process after melting. The T_c increases as the GO content increases because GO in a nanocomposite material acts as a nucleating agent. Therefore, as the GO content increases, T_c increases as well. Note that the difference between melting and crystallization temperatures decreases (Table 1) as the GO content increases.

Fig. 3 shows the TGA analysis, revealing the thermal stability of PPS, GO, and PPS/RGO composite materials. Comparing the temperature (T_{10}) with a 10 wt% decrease and the temperature (T_{20}) with a 20 wt% decrease, it can be seen that the thermal stability decreases as the GO content increases (Table 2). This, as seen in the DSC results, appears to be because as GO increases, the polymerization of PPS is restricted and GO is not well reduced during the PPS polymerization, thus decreasing the

Table 1. DSC thermograms of PPS/RGO nanocomposites

GO content (wt%)	T_m (°C)	T_c (°C)	ΔT (°C)
0	286.6	224.0	62.6
5	(272) 283.3	248.6	34.7
8	(268) 280.3	252.1	28.2
10	(269) 280.0	254.2	25.8

DSC: differential scanning calorimeter, PPS: Poly(*p*-phenylene sulfide), RGO: reduced graphite oxide.

Fig. 3. Thermogravimetric analyzer curves of pure PPS, GO, and PPS/RGO nanocomposites. PPS: poly (*p*-phenylene sulfide), RGO: reduced graphite oxide.

Table 2. TGA results of PPS/RGO nanocomposites

Sample	Decomposition temperature (°C)		Char yield at 800°C (%)
	T_{10}	T_{20}	
GO	76.9	213.3	54.1
Pure PPS	539.4	560.9	47.5
5 wt% GO	529.4	553.4	46.7
8 wt% GO	481.5	535.8	45.1
10 wt% GO	477.3	534.3	30.3

TGA: thermogravimetric analyzer, PPS: Poly(*p*-phenylene sulfide), RGO: reduced graphite oxide.

thermal stability. If GO is efficiently reduced in the polymerization reaction, the thermal stability should increase with the increase of the GO content. The graphite nanoplatelets produced in the direct exfoliation method have relatively fewer functional groups than do the oxidized GO, so that there is less weight loss incurred by the functional groups. In the case of the PPS/graphite composite material produced as such, the thermal stability increased along with the increase of the amount of graphite [16].

Fig. 4 provides an FE-SEM image of the PPS/RGO composites obtained from pure PPS to 20 wt% of GO composite. The FE-SEM image shows that the GO in the PPS substrate is well dispersed and that the graphene network has become much more

Fig. 4. Scanning electron microscope images of pure PPS, and PPS/GO nanocomposites: (a) pure PPS, (b) 5 wt% GO, (c) 10 wt% GO, (d) 20 wt% GO. PPS: poly (p-phenylene sulfide), RGO: reduced graphite oxide.

Table 3. Electrical conductivities of pure PPS, GO, and PPS/RGO nanocomposites

Sample	Electrical conductivity (S/m)	Shape
Pure PPS	3×10^{-15}	Film
GO	26	Pellet
R-GO ^a	800	Pellet
5 wt% GO	1×10^{-7}	Pellet
8 wt% GO	1.9	Pellet
10 wt% GO	2.9	Pellet
20 wt% GO	82	Pellet

PPS: Poly(p-phenylene sulfide), RGO: reduced graphite oxide.

^aHeated at 300°C for 6 h.

dense above 10 wt% of GO. The dispersed structure of the GO affects the electrical conductivity and the thermal properties of the PPS/RGO composites.

Table 3 shows the electrical conductivity values of the PPS/RGO nanocomposite material with different GO contents. The electrical conductivity of GO appears to be higher than the reported conductivity of GO [8]; however, with heat treatment at 300°C, the conductivity drops 10 times. Such different results appear to be caused by the different degree of oxidation during the acid treatment for GO production. For the case of PPS composite materials, it appears that the percolation threshold of GO is between 5–8 wt%. Compared to the value of 5 wt% GO composites, the electrical conductivity of 20 wt% GO composites is improved over 10^8 times.

4. Conclusions

It was found that GO is better dispersed and reduced by heat during *in situ* polymerization of PPS with GO. As the amount of GO in PPS increased, the crystallization temperature of the polymer composites increased while the thermal stability decreased. The electrical conductivity of 20 wt% GO/PPS com-

posite material was improved over 10^8 times with respect to that of 5 wt% of GO composites; percolation threshold appeared at 5–8 wt%. It is expected that the effective exfoliation of GO and control of the mixture ratio of the monomer and GO can enhance the conductivity of PPS composite materials with excellent thermal stability.

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