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Graphene Oxide-terminated Partially Fluorinated Poly(arylene ether sulfone)

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Graphene oxide-terminated partially fluorinated poly(arylene ether sulfone) (GO-PAES) was synthesized via step growth polymerization with graphene oxide. A small amount of graphene oxide was incorporated into the polymer matrix to enhance the properties of the polymer/GO composites. The chemical structures of the synthesized copolymers containing graphene oxide were confirmed by ^{1}H NMR and FT-IR spectra. The thermal properties of GO-PAES analyzed by TGA and DSC were significantly improved due to the thermal stability of graphene oxide.

Recently, graphene has attracted a lot of scientific interest due to its outstanding properties.[1–5] Chemically fabricated graphene sheets, such as graphene oxide (GO) and reduced graphene oxide (rGO), offer a wide range of possibilities for the synthesis of graphene-based functional materials for various applications.[6] Carbonaceous materials, such as carbon blacks and carbon nanotubes (CNTs), are common fillers for reinforcing the thermal, electronic, and mechanical properties of the polymer matrix. CNT has been considered one of the most powerful filler materials. However, it is relatively cost-inefficient and has limitations in processing and dispersions. Graphene-based fillers are expected to be promising alternatives to CNT due to easy access to mass-production in a cheap way. The homogeneous distribution of graphene via chemical bonding with the polymer matrix is an important factor to achieve optimal properties of the composites with the minimum content of graphene fillers.[7] So far, graphene/polymer composites have been commonly prepared by solution mixing,[8] melt blending,[9] and in situ polymerization.[10] In this work, we report a direct route to synthesize graphene oxide/polymer composites with high thermal stability via in situ polymerization of aromatic nucleophilic substitution.

Graphite (Bay-carbon, sp-1), H_2SO_4, $KMnO_4$, $NaNO_3$ (Aldrich), 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA) (Aldrich Co.), bis(4-fluorophenyl) sulfone (DFDPS) (Aldrich Co.), potassium carbonate (K_2CO_3), dimethyl acetamide (DMAc) (Kanto Chem Co.), and benzene (Kanto Chem Co.) were used without any further purification.

First, 0.5 g of graphite and 0.5 g of $NaNO_3$ were placed in a 2-neck flask with an ice bath, and 23 mL of H_2SO_4 was added to the mixture with stirring. Next, 3 g of $KMnO_4$ was slowly added to the mixture to prevent abrupt reaction. The solution was stirred at 35 °C for 2 h, and 40 mL of aqueous solution was slowly added and stirred for 1 h while the reaction temperature was kept at 90 °C. Then, 100 mL of deionized water was added, and the solution was cooled to room temperature. Finally, washing of prepared graphite oxide was conducted through the following procedure. 1) The reaction solution was mixed with 200 mL of deionized water to precipitate graphite oxide. 2) Filtration was performed using a glass fiber membrane, followed by rinsing with 1 wt % HCl and deionized water. 3) Centrifugation of the graphene oxide solution was done several times at 4000 rpm for 10 min until the pH of the supernatant became nearly neutral.[11]

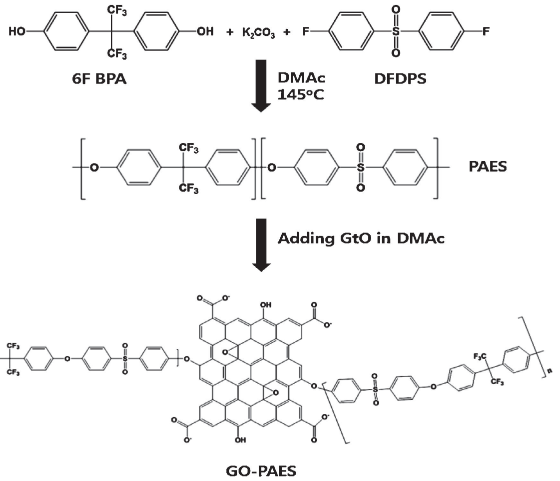

Figure 1. Reaction scheme for the synthesis of GO-PAES.

GO-terminated PAES was synthesized via step growth polymerization of graphene oxide as shown in Figure 1. First, 6F-BPA (6.9263 g, 20.0 mmol) was mixed with K_2CO_3 (3.455 g, 25 mmol) dissolved in a mixture of 50 mL of DMAc and 20 mL of benzene. The mixture was then placed in a 250 mL, 2-neck flask equipped with a Dean–Stark trap in nitrogen atmosphere. The reaction mixture was heated to 145 °C and maintained for 6 h. Benzene was refluxed into the Dean–Stark trap. Second, DFDPS (5.2128 g, 20.0 mmol) dissolved in DMAc (50 mL) was added to the prepared solution, and the reaction mixture was stirred for 8 h. Graphite oxide (GtO) dispersed in 10 mL of DMAc was added to samples of the mixture solution at time interval of 5, 1, and 0 h, and samples were named as GO-PAES2, GO-PAES3, and GO-PAES4, respectively.[12] The thermal properties and chemical structures of the mixtures were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and ^{1}H NMR spectroscopy.

Graphene oxide-terminated partially fluorinated poly(arylene ether sulfone) (GO-PAES) was synthesized via aromatic nucleophilic substitution reaction. The 6F-BPA monomer was reacted with DFDPS in DMAc. GtO dispersed in DMAc was added to the mixture solution to make GO-PAES as shown in Figure 1.

The chemical structures of PAES were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of PAES showed four doublet peaks at 7.92 (d), 7.41 (c), 7.08 (a), and 7.02 (b)

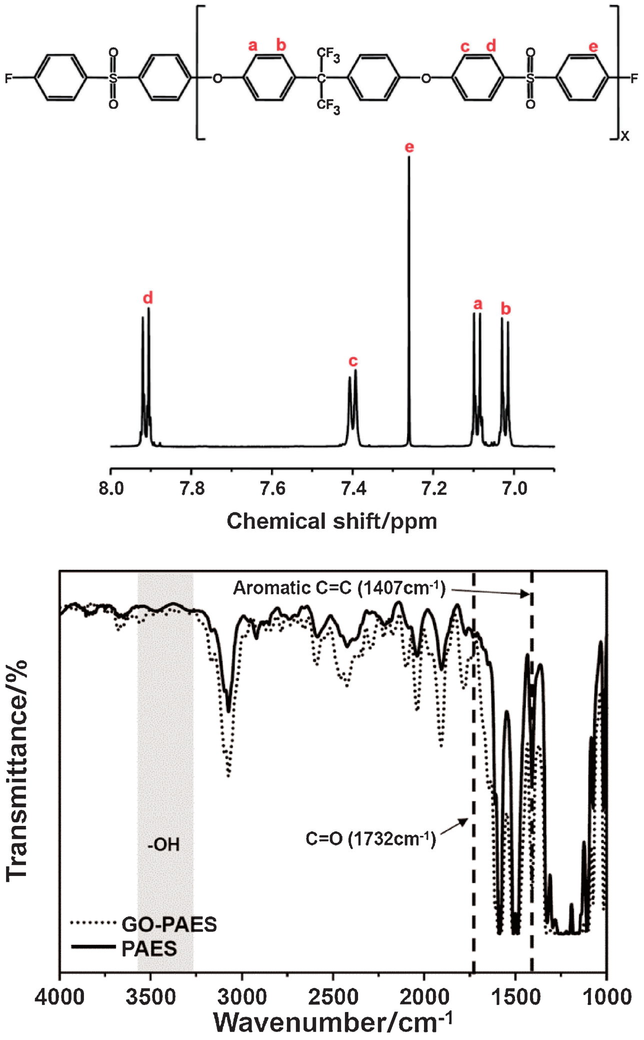

Figure 2. ^{1}H NMR and FT-IR analysis of the partially fluorinated poly(arylene ether sulfone) and GO-PAES.

ppm and one single peak at 7.25 (e) ppm as seen in Figure 2. These kinds of peaks were specific spectra for PAES, which indicates that the synthesis of PAES was successfully carried out.[13] The FT-IR spectrum of GO-PAES shows hydroxy group (–OH) and ketone (C=O) moiety peaks at 3400–3600 and 1732 cm^{-1} corresponding to functional groups of graphene oxide, respectively.[14,15]

To investigate the graphene-filler effects on the thermal properties, the original PAES, GO-PAES2, -3, and -4 were analyzed by DSC and TGA. Figure 3a shows the DSC thermograms of the original PAES, GO-PAES2, -3, and -4. As expected, the T_g of the GO-PAES proportionally increases with the reaction time of graphene oxide except in the case of GO-PAES4. The relatively low T_g of GO-PAES4 is probably because of the formation of a lower molecular weight copolymer caused by the impurity effect of excessive graphene oxide during the polymerization reaction. Figure 3b shows the TGA curves of the original PAES, GO-PAES2, -3, and -4, demonstrating the improved thermal stability of GO-containing PAES. As shown in Figure 3c, the temperature where 5 wt% of loss in weight occurred increases with the increase in the amount of graphene

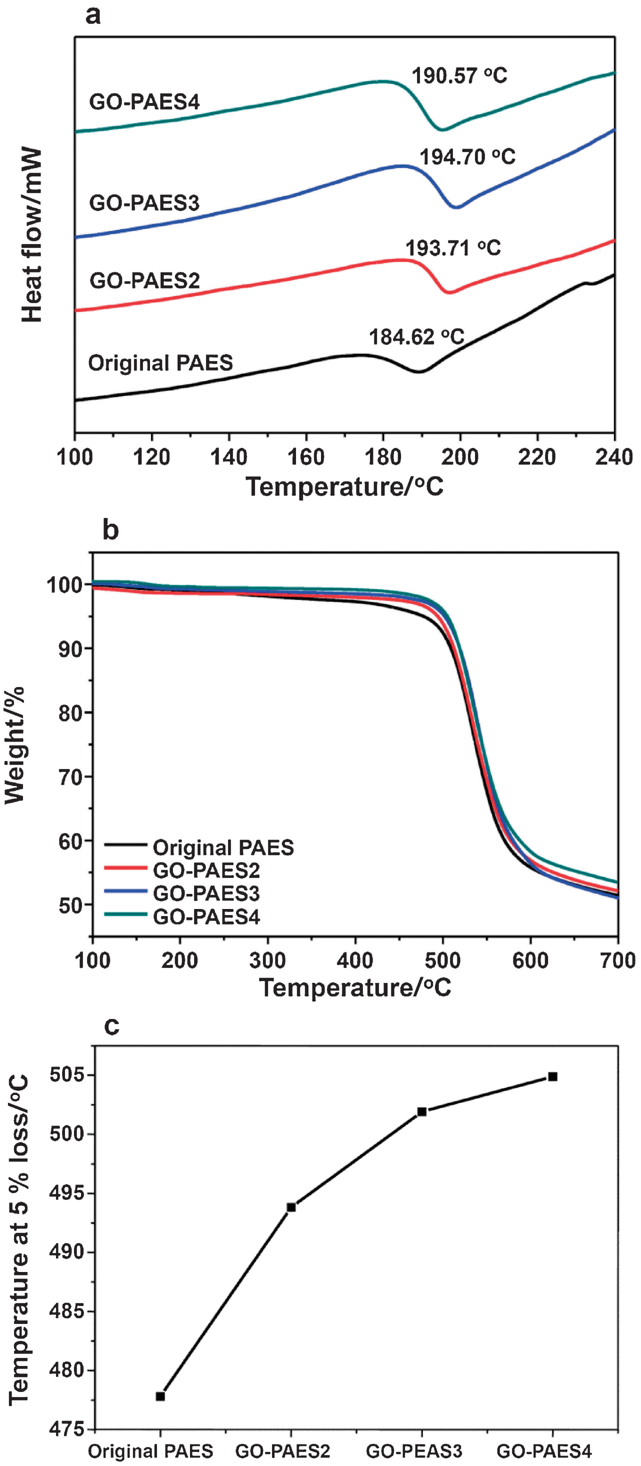

Figure 3. The thermal properties of original PAES, GO-PAES 2, -3, and -4: (a) DSC analysis, (b) TGA analysis, and (c) the temperature at 5% of loss in weight.

oxide. This implies that the thermal properties of GO-PAES were significantly improved by the addition of graphene oxide with high thermal stability.

In summary, graphene oxide-terminated partially fluorinated poly(arylene ether sulfone) copolymers were prepared via aromatic nucleophilic substitution reaction. The chemical structures of the synthesized copolymers were confirmed by ^{1}H NMR. The thermal properties of the graphene oxide-terminated polymers analyzed by TGA and DSC were considerably improved. The GO-PAES we fabricated in this study has potential for application in proton exchange membrane fuel cells with improved properties.

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