Effect of γ-ray irradiated MWCNTs on electrical conductivity of a PET/graphite composite for a bipolar plate application

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ABSTRACT

The effects of a compounding method and γ-ray treated multiwall carbon nanotubes (MWCNTs) on the electrical conductivity of graphite/PET composites were investigated. We found that dispersion of MWCNTs in the PET phase plays a critical role in determining the electrical conductivity of graphite/PET/MWCNT composites. Dispersion and electrical conductivity were enhanced by a two-step method in which PET and MWCNTs are compounded in advance and the MWCNT/PET mixture is then compounded again with graphite. It was also observed that γ-ray treated MWCNTs provide enhanced conductivity in the graphite/PET/MWCNT composite. The synergetic effect of the two-step mixing method and γ-ray treatment made it possible to increase the conductivity of graphite/PET composites to a great extent with a very small amount of γ-ray irradiated MWCNTs.

Keywords: γ-ray irradiation, MWCNT, graphite composites, bipolar plate

1 INTRODUCTION

Recently, graphite/polymer composites for a bipolar plate have drawn substantial attention, since they can be processed by rapid and low cost processing techniques such as compression and injection molding, thereby reducing the machining cost for the gas flow channel [1]. Since most polymers are intrinsically insulators, large amounts of conductive graphite must be added to the graphite/polymer composites in order to meet the requirements of the bipolar plate. The viscosity of the graphite/polymer composites for the bipolar plate application is consequently very high. Reducing the graphite fraction leads to decreased viscosity of the composites, but at the same time it also decreases the conductivity of the composite. Decreasing the viscosity without reducing the conductivity is favorable and this task can be accomplished by the incorporation of small amounts of conducting fillers with a high aspect ratio, such as carbon fiber (CB) and carbon nanotubes (CNTs).

There have been many studies on the incorporation of anisotropic fillers into graphite/polymer composites [2-5]. Both CF and CNTs increase the conductivity of graphite/polymer composites when incorporated into the composites. However, the increase of conductivity by the addition of CNTs is much higher than that with CF for the same amount of fillers due to the higher aspect ratio of CNTs. It was reported that more than a ten-fold greater amount of CF is needed to achieve the same degree of increase in conductivity compared to the case of using CNTs [4].

Well dispersed structure of CNTs in the polymer matrix is essential to form conducting channels (or bridges) between the graphite particles with a small fraction of CNTs. Aggregated CNTs do not contribute to an increase of conductivity, but instead deteriorate the physical properties of the composite [1].

Many efforts have been devoted to enhancing the dispersion of CNTs by the application of high shear force [6, 7], incorporation of compatibilizers [8, 9], and chemical modification of CNTs [9-14]. Among these approaches, surface treatment of CNTs, (e.g. acid treatment to induce functional groups or graft organic molecules) is known to be the most successful route. Gamma ray (γ-ray) irradiation has been widely used in reaction engineering. Irradiation of γ-rays is a useful tool to induce chemical reactions on the surface of CNTs [15-16]. In a previous study, Kim et al. investigated the effects of γ-ray irradiation on the dispersion of CNTs and the electrical conductivity of a polyamide 6,6/MWCNT nanocomposite. They found that γ-ray irradiation under a dry oxygen atmosphere induces attachment of oxygen functional groups on the surface of the MWCNTs. The γ-ray treated MWCNTs improved the dispersion of MWCNTs and decreased the electrical percolation threshold.

In this study, we investigated the effect of incorporated γ-ray irradiated MWCNTs on the electrical conductivity of graphite/PET composites. We found that a very small amount of γ-ray irradiated MWCNTs increased the conductivity of the composite to a great degree. This paper reports experimental results and the underlying mechanism for the effect of the γ-ray irradiated MWCNTs.

2 EXPERIMENTAL

Materials: Synthetic graphite powder used in this study has a density of 2.25 g/cm^3, and an average particle size of 21 μm. It was supplied by Hankook Tire Corporation. Commercially available multi-walled carbon nanotubes (Nanocyl^{TM} NC7000, thin MWCNT, 90% of carbon purity, average diameter: 9.5nm, average length: 1.5μm), synthesized by catalytic carbon vapor deposition, were used in this work. Polyethyleneterephtalate (PET) (SKYPET-BB8055, density: 1.40 g/cm^3, intrinsic viscosity: 0.8 cm^3/dg) was used as a binder polymer. Low viscosity of the composite is crucial for rapid and low cost production, as mentioned earlier. PET with a normal level of molecular weight has very low viscosity allowing flow even by gravitational force alone. Therefore, PET is a very good candidate for a binder polymer of the graphite/polymer composites.

Preparation of surface-treated MWCNTs by γ-ray irradiation: MWCNT powder was directly irradiated with ^{60}Co γ-ray (1.17, 1.33 MeV per an atom) under a dry O_2 atmosphere to induce oxygen-containing functional groups on the surface of the MWCNTs, with a γ-ray irradiation dose of 30 kGy for 2 h. The irradiation process was performed using high-level γ-ray irradiation equipment at the Korea Atomic Energy Research Institute.

Preparation of the graphite/PET/MWCNT composites and measurement of the electrical conductivity: The conducting composites were prepared by melt mixing. Prior to compounding, PET pellets were grinded by a lab grinding mill and particles less than 0.1 mm were separated by a standard mesh. PET and graphite powder were first dry-blended in a plastic bag and melt compounded in an internal batch mixer (model: Haake PolyLab QC-3000) at 120 rpm and 275^{o}C for 10 min. The graphite/PET/MWCNT composites were prepared by two different methods. In the first method, a dry blend of graphite powder, PET powder, and MWCNT is assembled in a batch mixer and compounded (Hereinafter, this is denoted as the one-step method). In the second method, PET and MWCNTs are melt-compounded in advance and the PET/MWCNT mixture is grinded to a fine powder. The PET/MWCNT mixture is then dry-blended with graphite powder and melt compounded again. (This method is hereinafter denoted as the two-step method). The composites were compression molded to discs with 25 mm diameter and 1 mm thickness. The electrical conductivities of the composites in the plane direction were determined by using the four-point probe method (CMT-SR 1000N, Advanced Instrument Technology).

3 RESULTS AND DISCUSSION

Fig. 1 shows the electrical conductivities of the graphite/PET and graphite/PET/MWCNT composites as a function of graphite content. The conductivities of the graphite/PET composites increase with graphite content up to 90 wt.% of graphite (equivalent to 14.3 vol. % of PET), as shown in Fig. 1. Lee et. al. reported that the conductivity increases with the graphite content, showing a maximum value at a certain graphite content, and decreases with further increase of graphite content [4]. The decrease of the conductivity was attributed to the insufficient amount of binder failing to wet the entire surface of graphite, and the cavities that are consequently formed act as an insulator. The decrease of conductivity at a high concentration of graphite was not observed in this study. Thus, there is room for further increase of the conductivity by increasing the graphite content.

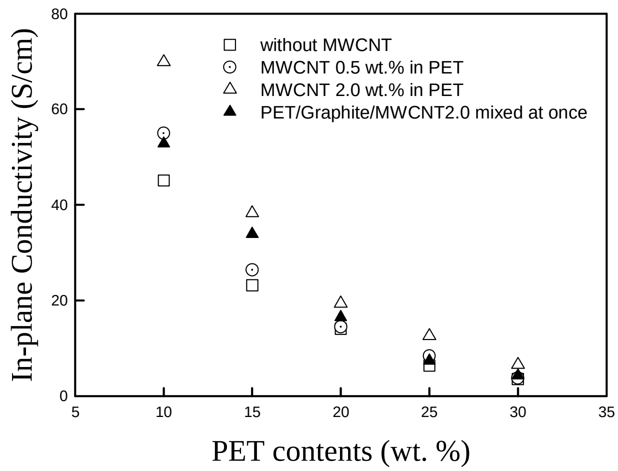

Figure 1: Electrical conductivities of graphite/PET and graphite/PET/MWCNT composites. The standard uncertainty is less than 20 %.

In Fig. 1, 0.5 wt. % in PET represents the amount of MWCNTs in the PET phase. Thus, the composition of MWCNTs based on entire composite weight is much smaller. For example, 2 wt.% in PET implies 0.2 wt.% in graphite/PET(9/1), 0.4 wt.% in graphite/PET(8/2), and so on. It is observed that the addition of such a small amount of MWCNTs into the graphite/PET composites dramatically increases the conductivity of the composites. As far as we know, there has been no report of a comparatively large increase of conductivity with the addition of such a small amount of MWCNTs. Most studies have reported that MWCNTs become effective when used in quantities above 1.0 wt. % of the total weight of the composite. It is noteworthy that the increase of conductivity by the incorporation of MWCNTs is pronounced at higher graphite content. It is also notable that one-step mixing and two-step mixing lead to different results. The conductivity of the graphite/PET/MWCNT composites prepared by the two-step method is significantly higher than that of the composites prepared by the one-step method. These two experimental results can be explained as follows.

The affinity of MWCNTs with graphite is expected to be higher than that with PET, since both MWCNTs and graphite are carbon allotropes. Therefore, MWCNTs tend to be located near graphite particles, as schematically demonstrated in Fig. 2. When the graphite content is lower, the distance between graphite particles is longer and the formation of conducting channels by the MWCNTs between graphite particles becomes difficult, leading to lower conductivity. However, as the graphite particles come

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into closer proximity by an increase of graphite content, more conducting channels are formed, as depicted in Fig. 2b. Thus, the increase of conductivity by the addition of MWCNTs is pronounced at high graphite content. The same principle can be applied to interpret the finding of different conductivities between the one-step and two step methods. When graphite, PET, and MWCNTs are compounded simultaneously (one-step method), agglomerates composed of MWCNTs and graphite particles have greater likelihood of forming since their affinity is higher than those with PET. However, when PET and MWCNTs are compounded in advance prior to being compounded with graphite (two-step method), there is less likelihood of forming agglomerates composed of MWCNTs and graphite. Therefore, the two-step method provides better dispersion of MWCNTs and more conducting channels.

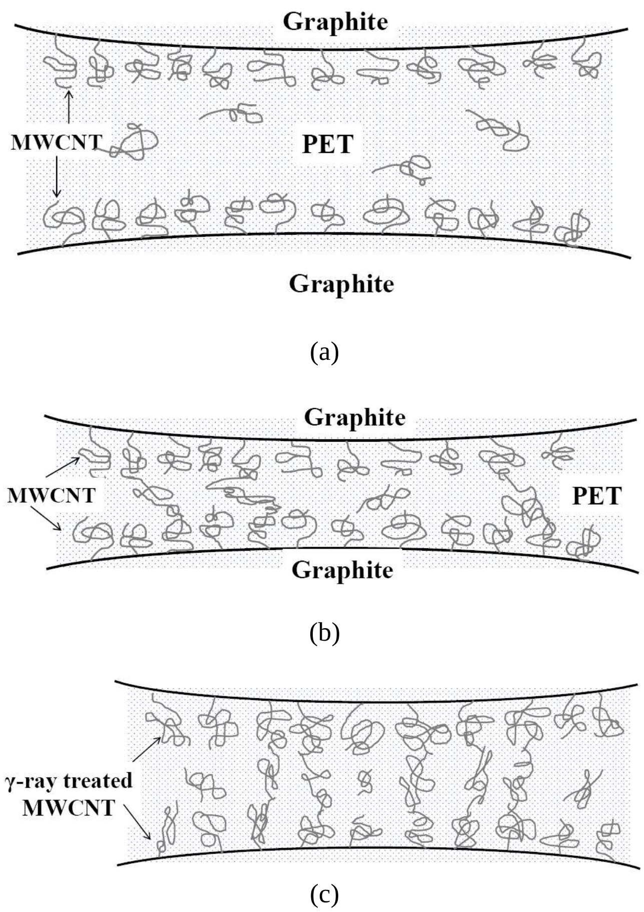

Figure 2: Schematics of dispersion state of graphite/PET/MWCNT composites. (a) at lower graphite content, (b) at higher graphite content, (c) γ-ray treated MWCNT

Dispersion of MWCNTs can be enhanced by introducing functional groups on the surface of the MWCNTs [9-12, 16]. Figure 3 shows the electrical conductivities of graphite/PET/γ-ray irradiated MWCNT composites. The conductivity of the graphite/PET (9/1) composite was increased more than two-fold by the addition of 0.2 wt. % of γ-ray irradiated MWCNTs in entire composite weight. This large increase of the conductivity is also attributed to the enhanced dispersion of γ-ray irradiated MWCNTs and formation of more conducting channels. Since the MWCNTs are strongly hydrophobic and PET is hydrophilic, inducing hydrophilic functional groups on the MWCNT surface increases the affinity between these two materials. A previous study by Kim et al. showed that oxygen atoms were attached on the surface of MWCNTs by γ-ray treatment in a dry O_2 atmosphere, and the γ-ray treated MWCNTs improved the affinity with hydrophilic polymers such as polyamide 6,6 [16]. The γ-ray irradiated MWCNTs used in the present work were prepared by the same method as described in their study. Thus, it is expected that the γ-ray treated MWCNTs are well dispersed in the PET phase, leading to increased electrical conductivity.

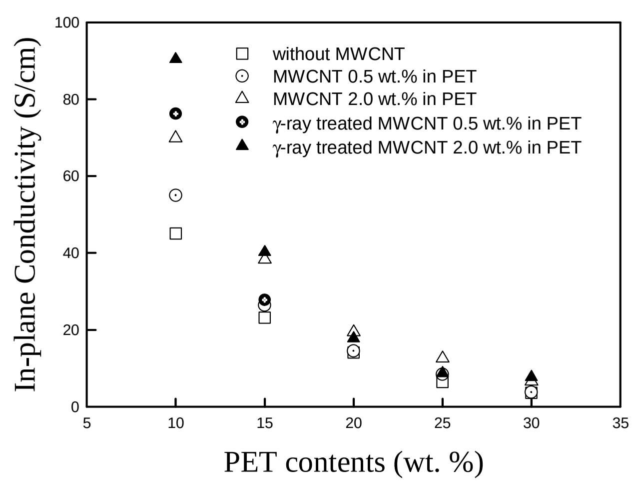

Figure 3: Electrical conductivities of graphite/PET/MWCNTs and graphite/PET/ γ-ray irradiated MWCNT composites. The standard uncertainty is less than 20 %.

There have been many studies on the surface modification of MWCNTs by various methods [9-12, 16], and the modified MWCNTs have been used as conductive fillers. However, there have been few research papers documenting the use of modified MWCNTs to increase the conductivity of graphite/polymer composites. Furthermore, the γ-ray irradiation in the present work is carried out by a direct method without any solvent. In the present work, the synergetic effect of the two-step mixing method and γ-ray treatment increased the conductivity of graphite/PET/γ-ray irradiated MWCNT composites to a great extent with a very small amount of MWCNTs, which has not been accomplished in previous works. The cost of MWCNTs is still very expensive compared to graphite. In this regard, the present study helps the research community take a step forward toward the commercialization of polymer electrolyte membrane fuel cell.

In this study, we proposed an approach to substantially increase the conductivity of graphite/PET composites by the incorporation of irradiated MWCNTs. Experimental evidence for the underlying mechanism and investigation of mechanical and rheological properties will be addressed in future studies.

4 CONCLUSION

It was found that the proposed two-step method and the addition of γ-ray irradiated MWCNTs are effective ways of increasing the conductivity of graphite/PET composites. The increase of conductivity is attributed to enhanced dispersion of the MWCNTs in the PET phase by the improved the compounding technique and increased affinity between the MWCNTs and PET via modification of the MWCNTs.

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