

Effects of Filler Characteristics and Processing Conditions on the Electrical, Morphological and Rheological Properties of PE and PP with Conductive Filler Composites

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Abstract: The electrical, morphological and rheological properties of melt and dry mixed composites of polyethylene (PE)/graphite (Gr), polypropylene (PP)/Gr and PP/nickel-coated carbon fiber (NCCF) were investigated as a function of filler type, filler content and processing temperature. The electrical conductivities of dry mixed PP/NCCF composites were increased with decreasing processing temperature. For the melt mixed PP/NCCF composites, the electrical conductivities were higher than those of the melt mixed PE/Gr and PP/Gr composites, which was attributed to the effect of the higher NCCF aspect ratio in allowing the composites to form a more conductive network in the polymer matrix than the graphite does. From the results of morphological studies, the fillers in the dry mixed PP/NCCF composites were more randomly dispersed compared to those in the melt mixed PP/NCCF composites. The increased electrical conductivities of the dry mixed composites were attributed to the more random dispersion of NCCF compared to that of the melt mixed PP/NCCF composites. The complex viscosities of the PP/Gr composites were higher than those of the PP/NCCF composites, which was attributed to the larger diameter of the graphite particles than that of the NCCF. Furthermore, the fiber orientation in the 'along the flow' direction during melt mixing was attributed to the decreased complex viscosities of the melt mixed PP/NCCF composites compared those of the melt mixed PP/Gr composites.

Keywords: polymer composites, conductive filler, electrical conductivity, morphology, rheology.

Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a very promising power source for residential and mobile applications with its attractive features such as high power density, relatively low operating temperature, convenient fuel supply and long lifetime, etc.^{1,2} Currently, challenges for PEMFC technology include reducing the cost and weight of the fuel cell stack.

One of the key components is bipolar plate which is the electrode plate that separates currents to individual cells in a stack.³ The bipolar plate requirements include low-cost materials and processing, light weight, thin thickness (<3 mm), sufficient mechanical integrity, high surface area and volume electro-conductivity higher than 100 S/cm, low permeability (boundary between fuel and oxidant) and corrosion resistance (in the moist atmosphere of the cell).^{4,5} Metal is also a good material for a bipolar plate, it offers the attributes of good electrical conductivity, low cost, excellent

mechanical properties, and ease of fabricate. Metal is, however, unable to resist corrosion in fuel cells.⁶⁻⁹

A less-expensive and lighter-weight alternative to graphite and steel could come from polymer/carbon composites. These conductive blends could be a promising solution, as their thermal and chemical stability is matched by good mechanical strength and dimensional stability values. Additional advantages could be gained if thermoplastic resins can be used, as this would enable the use of high-productivity, conventional molding processes, such as injection molding or compression-injection molding.¹⁰⁻²³ Furthermore, the use of thermoplastic resins would provide recyclability and improved chemical stability. According to previous studies, it is clear that achieving 100 S/cm level of resistivity with thermoplastic composite is a challenging task.²⁴

The electrical conductivity-temperature dependence of polymer/conductive filler composites were well documented in the literatures.²⁵⁻²⁸ In regard to the bipolar plate material selection, care should be taken in selecting a polymer matrix. Glass transition or solid-liquid transition of matrix should be far above the operating temperature of the fuel cell

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(80~100 °C) in order to avoid the conductivity loss. Fluidity of polymer is also a key factor in polymer selection for good processability even at high content of conductive fillers.²⁴

In this study, electrical, mechanical and rheological properties of the polymer/conductive filler composites were investigated with the type of mixing processes such as dry mixing and melt mixing, and filler type such as graphite and nickel-coated carbon fiber (NCCF). The polymers used in this study as a matrix are polyethylene (PE) and polypropylene (PP) which can be used in the bipolar plate for PEMFC.

Experimental

Materials. Polyethylene (PE) and polypropylene (PP) were used as matrix phases for the polymer/conductive filler composites. All the polymers were obtained from commercial sources. Grade names, properties, melt flow indices, and suppliers are given in Table I. The materials were dried in a drying oven at 120 °C for 24 h before use. Thermal properties of polymers were measured using a DSC (Perkin-Elmer, Model DSC 7). Both PE and PP used in this study present good chemical and thermal resistances. Graphite and nickel-coated carbon fiber (NCCF) were used as conductive fillers for the polymer/conductive filler composites. Densities of the graphite and NCCF used in this study were 2.23 and 0.75 g/cm³, respectively. All conductive fillers were obtained from commercial sources, and characteristics of graphite and nickel-coated carbon fiber are given in Table II. Also, scanning electron micrographs of graphite and NCCF are shown in Figure 1.

Composite Preparations. Three combinations of polymer/conductive filler composites were prepared such as PE/graphite, PP/graphite and PP/NCCF. Dry mixed composites of PE/graphite, PP/graphite and PP/NCCF were manufactured by simply mixing of the materials with a mixer at 3,000 rpm for 5 min at room temperature, then, compression molded

Table I. Characteristics of Polyethylene and Polypropylene Used in this Study

Polymer	MFI ^a (g/10 min)	T _m (K) ^b	Density (g/cm ³) ^c	Grade Name
Polyethylene ^d	0.9	413.0	0.96	Y910A
Polypropylene ^e	11.0	443.0	0.91	HJ500

^aMelt flow index by ASTM D1238. Data from supplier. ^bMeasured in our laboratory by DSC. ^cData from supplier. ^{d,e}Supplied from Samsung Total Petrochemicals.

Table II. Characteristics of Graphite and Nickel-coated Carbon Fiber Used in this Study

Conductive Fillers	Diameter ^a	Length ^b	Grade Name	Comments
Graphite ^c	280 μm	-	HCN-598	Purity +98%
NCCF ^d	10 μm	120~130 μm	E-FILL 2901	CF/Nickel (wt%) 11.73/88.27

^aData from supplier. ^bMeasured in our laboratory by SEM. ^cSupplied from Hyundai Coma Industry Co. ^dSupplied from Sulzer Metco Inc.

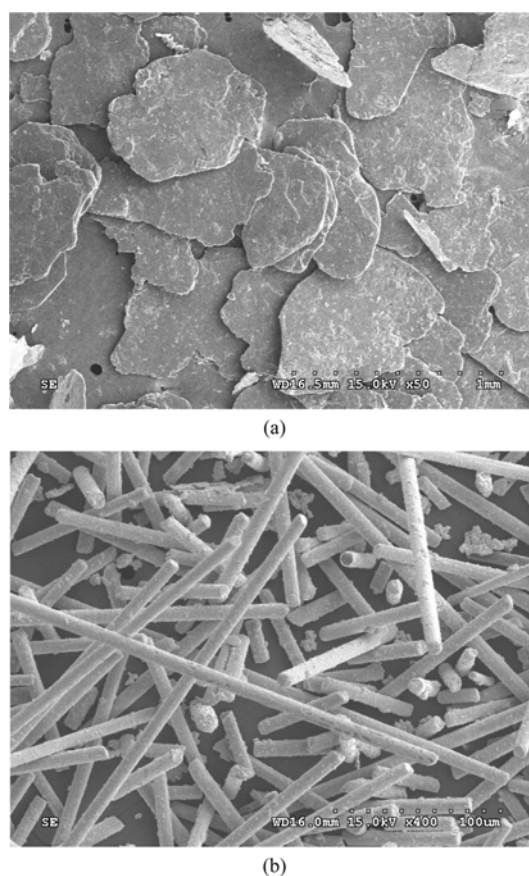


Figure 1. Scanning electron micrographs of conductive fillers used in this study: (a) graphite and (b) nickel-coated carbon fiber.

using press (Carver, model 3925) at 450 kg_f/cm² for 30 min. The temperatures 1, 2 and 3 of the press were 140, 150 and 160 °C for PE, and 170, 180 and 190 °C for PP, respectively. Melt mixed composites of PE/graphite, PP/graphite and PP/NCCF were prepared by mixing of the materials with a co-rotating twin screw extruder (Bau technology, model L40/D11). The temperature of feeding and die zones was 240 °C. For compression zone, the temperature was 250 °C. The screw speed of the extruder was 50 rpm for PE/graphite. For PP/graphite and PP/NCCF composites, the screw speed was 80 rpm.

Electrical Conductivity. Measurements of volume electrical conductivity were carried out on compression molded polymer/conductive filler composite discs of 30 mm in diameter and 3 mm in thickness. The composite discs were

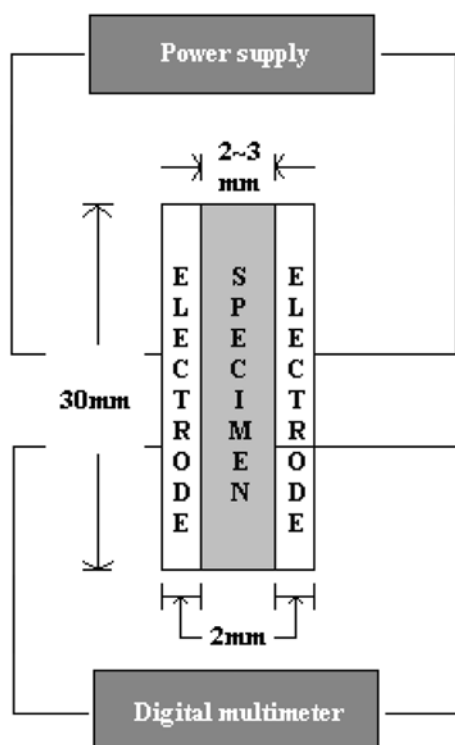


Figure 2. Schematic diagram of a measurement unit of electric conductivity.

pressed in the space between two highly conductive gold-coated disc electrodes of 30 mm in diameter as shown in Figure 2. Pressure was 45.4 kg that was typical pressure condition experienced in a fuel cell stack.²⁵ To reduce the contact resistance between electrodes and test sample, silver paste was coated uniformly to both surfaces of disc test sample. Both electrodes were connected to a power supply (Zahner messTechnik, Model IM6ex potentiostat) and a digital multimeter (Keithley, Model 2000 multimeter). The volume conductivity, γ_v is defined by eq. (1), where A is the effective area of the measuring electrode, t is average thickness of the specimen and G_v is measured volume conductance in siemens.

$$\gamma_v = \frac{t}{A} G_v \quad (1)$$

Morphology. The morphology of the cross section of polymer/conductive filler composite was analyzed by scanning electron microscopy (SEM, Hitachi, model S-4300SE) at 15.0 kV accelerating voltage after platinum deposition. The fractured surface of the composites was prepared by cryogenic fracturing.

Rheology. Dynamic measurements were carried out by advanced rheometric expansion system (ARES, Rheometric) with oscillatory shear at 6% strain in the parallel-plate having diameter of 25 mm. samples were pressed on compression molded discs of 25 mm in diameter and 2 mm in

thickness The frequency sweeps from 0.1 to 100 rad/s were carried out at 250 °C.

Results and Discussion

Electrical Conductivity. Figure 3 shows electrical conductivities of polyethylene/graphite (PE/Gr) composites prepared by both dry and melt mixed methods. From the results of Figure 3, it is observed that the electrical conductivities of dry mixed PE/Gr composites are found to be about 3.6~7.1 S/cm with filler content and press temperature. For melt mixing, the electrical conductivities of the PE/Gr composites are found to increase from 2.4×10^{-4} to 8.0×10^{-2} S/cm with filler content. From the results of Figure 3, it is observed that the filler content does not seem to affect the electrical conductivities of dry mixed PE/Gr composites. For melt mixed PE/Gr composites, however, the filler content seems to affect appreciably the electric conductivities of the composites. Also, the values of electrical conductivity

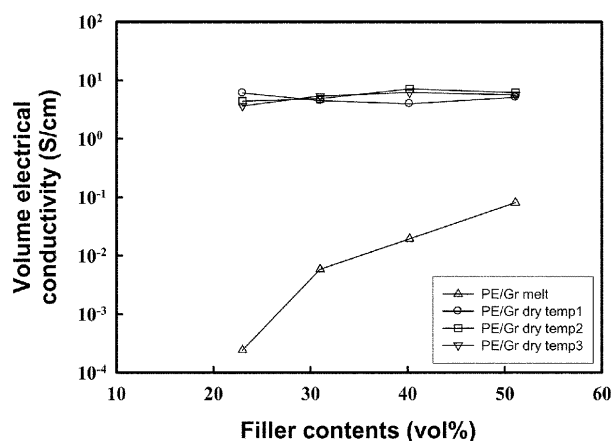


Figure 3. Electric conductivity of polyethylene/graphite (PE/Gr) composites with filler content. Temperatures 1, 2 and 3 are 140, 150 and 160 °C for PE, respectively.

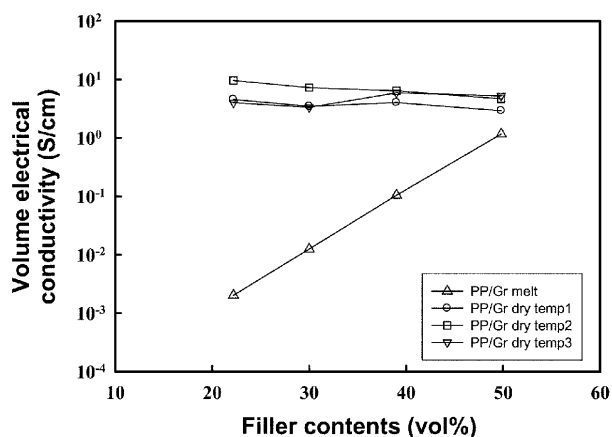


Figure 4. Electric conductivity of polypropylene/graphite (PP/Gr) composites with filler content. Temperatures 1, 2 and 3 are 170, 180 and 190 °C for PP, respectively.

ties of the dry mixed PE/Gr composites show higher than those of the melt mixed PE/Gr composites.

Figure 4 shows the electrical conductivities of melt and dry mixed PP/Gr composites. From Figure 4, it is shown that the electrical conductivities of the dry mixed PP/Gr composites are found to be about 2.9~9.6 S/cm with filler content and press temperature. For melt mixed PP/Gr composites, the electrical conductivities of the PP/Gr composites are found to increase from 2.0×10^{-3} to 1.1 S/cm with filler contents. From the results of Figure 4, it is suggested that the filler content does not seem to affect the electrical conductivities of dry mixed PP/Gr composites. For melt mixed PP/Gr composites, however, the filler content seems to affect appreciably the electrical conductivities of the composites. Also, the values of electrical conductivities of dry mixed PP/Gr composites show higher than those of the melt mixed PP/Gr composites, which is similar behavior of the PE/Gr composites shown in Figure 3.

Figure 5 shows the electrical conductivities of melt and dry mixed PP/NCCF composites. From Figure 5, it is shown that the electrical conductivities of dry mixed PP/NCCF composites are found to be about 1.1~15.2 S/cm with filler content and press temperature. The electrical conductivities of dry mixed PP/NCCF composites seem to increase slightly with the filler content when the press temperatures are 180 and 190 °C. At 170 °C, the electrical conductivities of dry mixed PP/NCCF composites do not seem to change with the filler content. From Figure 5, it is also observed that the electrical conductivities of the dry mixed PP/NCCF composites show higher than those of the melt mixed PP/NCCF composites, which is similar behavior of the PE/Gr and PP/Gr composites shown in Figures 3 and 4, respectively. For melt mixed PP/NCCF composites from Figure 5, the electrical conductivities of the composites are found to increase from 6.4×10^{-2} to 4.9 S/cm with filler contents.

From the results of Figures 3-5, it seems that the electrical

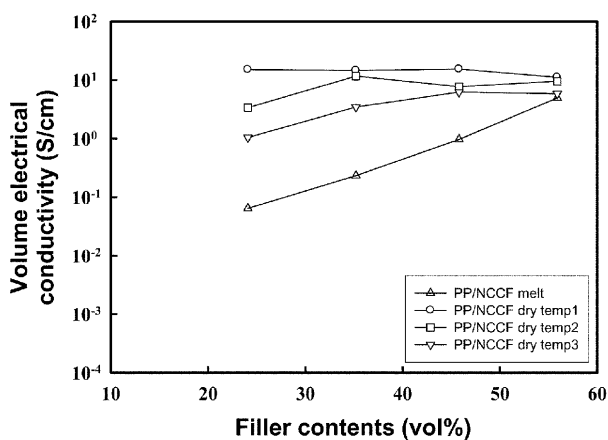
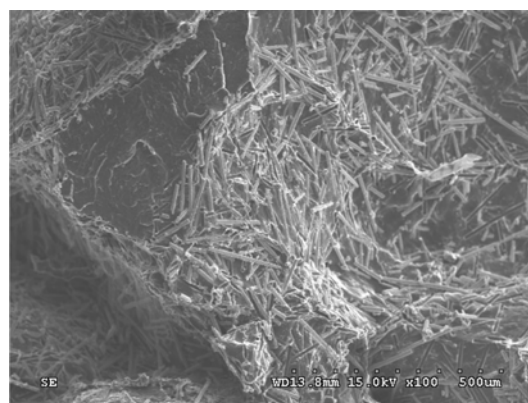


Figure 5. Electric conductivity of polypropylene/nickel-coated carbon fiber (PP/NCCF) composites with filler content. Temperatures 1, 2 and 3 are 170, 180 and 190 °C for PP, respectively.

conductivities of dry mixed PP/NCCF composites were affected by the different press temperature, but the electrical conductivities of dry mixed PE/Gr and PP/Gr composites were not changed with the press temperature. This is probably due to the different particle size between graphite and nickel-coated carbon fiber in the preparation of the composites. In the case of PP/NCCF composites, as the temperature is getting higher, polymers sink into space among fillers locally and break down current pathways. For the graphite filled composites such as PE/Gr and PP/Gr, however, the diameter of graphite particles (about 300 to 500 μm) is much larger than nickel-coated carbon fibers (about 10 μm), therefore, polymer penetration into the space among fillers is also much difficult. As the results, it is suggested that the graphite filled composites such as PE/Gr and PP/Gr are not affected by the press temperature because of the large diameter of graphite particles.

From Figures 3-5, especially in melt mixed composites, the electrical conductivities of PP/NCCF composites show higher than that of the PE/Gr and PP/Gr composites. This is maybe explained by the higher aspect ratio of NCCF compared the graphite used in the preparation of the composites.



(a)



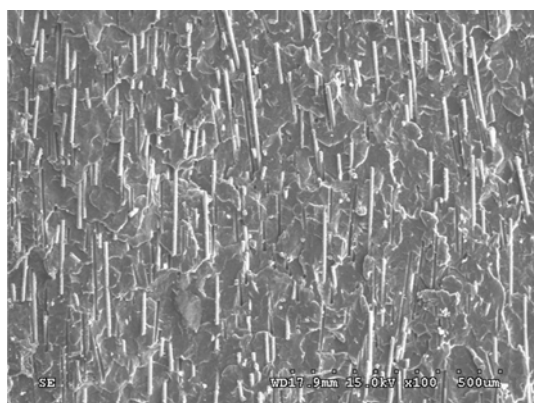
(b)

Figure 6. Scanning electron micrographs of dry mixed PP/NCCF (24 vol%) composites: (a) 100 magnification and (b) 400 magnification. Press temperature is 170 °C.

From the above results, it is suggested that the higher aspect ratio of NCCF can make it more conductive network in polymer matrix than that of the graphite.

Morphology. The cryogenically fractured cross-sectional surfaces of the polymer/conductive filler composites were observed using scanning electron microscopy (SEM). The dry and melt mixed PP/NCCF composites having filler content of 24 vol% are compared in Figures 6 and 7, respectively. From Figures 6 and 7, a difference in filler dispersion between dry mixing and melt mixing is clearly shown in these micrographs.

From Figure 6, it is seen that the fillers in the dry mixed PP/NCCF composites are randomly dispersed with various directions in PP matrix and the degree of connectivity among the fillers appears high. The dense connection of the fillers after dry mixing may form improved current pathway than the melt mixed PP/NCCF composites which will be seen in Figure 7, therefore, the results show a wide disparity in electrical conductivity of the composites with dry and melt mixing. For the melt mixed PP/NCCF composites shown in Figure 7, it is seen that the fillers are oriented to ‘along the flow’ direction, therefore, the degree of connectivity



(a)



(b)

Figure 7. Scanning electron micrographs of melt mixed PP/NCCF (24 vol%) composites: (a) 100 magnification and (b) 400 magnification.

among the fillers appears low. The NCCF may receive damage during melt mixing with PP. Therefore, from the results of morphological studies of Figure 7(b), it seems that the length of NCCFs of the PP/NCCF melt composite is appeared to be shortened compared that of the dry mixed PP/NCCF composite which is shown in Figure 6(b). From the results of Figures 6 and 7, it is suggested that the increased values of electrical conductivities of the dry mixed composites are maybe due to the more randomly dispersed NCCF compared that of the melt mixed PP/NCCF composites.

Rheology. Figure 8 shows the complex viscosities of melt mixed PE/Gr composites with graphite content. As shown in Figure 8, the complex viscosities of the composites are increased with the graphite content. Figure 9 shows the complex viscosities of melt mixed PP/Gr and PP/NCCF composites. From Figure 9, it is shown that the complex viscosities of the composites increase with the filler content. From Figure

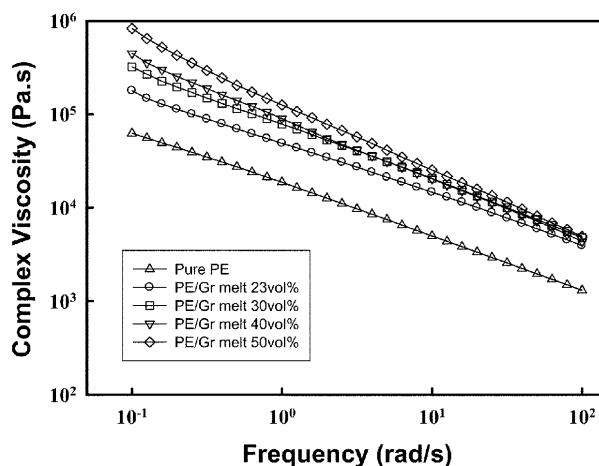


Figure 8. Complex viscosity of melt mixed polyethylene/graphite (PE/Gr) composites with filler content.

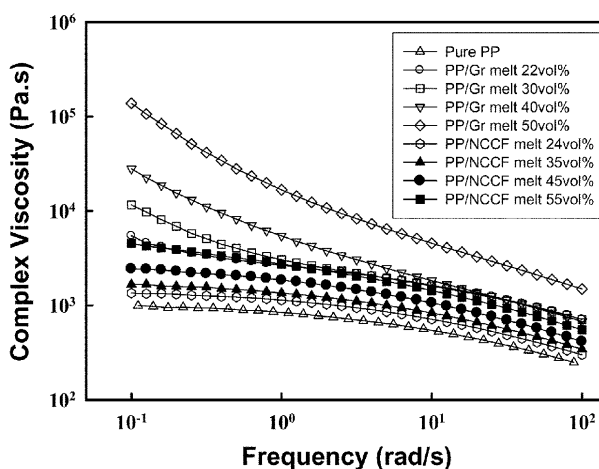


Figure 9. Complex viscosity of melt mixed polypropylene/graphite (PP/Gr) and polypropylene/nickel-coated carbon fiber (PP/NCCF) composites with filler content.

9, it is seen that the complex viscosities of the PP/Gr composites are higher than those of the PP/NCCF composites at the same filler content. This is maybe due to that the diameter of graphite particle (about 300 to 500 μm) is much larger than that of the nickel-coated carbon fiber (about 10 μm). Also, for the melt mixed PP/NCCF composites as shown in Figure 7, the fillers are oriented to 'along the flow' direction after melt mixing. Therefore, this fiber orientation was attributed to decrease the complex viscosities of the melt mixed PP/NCCF composites.

Conclusions

In this study, the electrical, morphological and rheological properties of melt and dry mixed composites for PE/Gr, PP/Gr and PP/NCCF with filler type, filler content and processing temperature were investigated. In the studies of electrical conductivity of dry mixed composites, the electrical conductivities of PP/NCCF composites were increased with the decrease of processing temperature. But, for the PE/Gr and PP/Gr dry mixed composites, the electrical conductivities of were not changed with the processing temperature. For the melt mixed PP/NCCF composites, the electrical conductivities showed higher than those of the melt mixed PE/Gr and PP/Gr composites. From the above results, it is suggested that the higher aspect ratio of NCCF can make the composites more conductive network in polymer matrix than the graphite does.

From the results of morphological studies, the fillers in the dry mixed PP/NCCF composites were more randomly dispersed with various directions in PP matrix and the degree of connectivity among the fillers appeared high. The high connectivity of the fillers after dry mixing may form improved current pathway than the melt mixed PP/NCCF composites. For the melt mixed PP/NCCF composites, the fillers were oriented to 'along the flow' direction after melt mixing on the contrary, therefore, the degree of connectivity among the fillers appeared low. From the above morphological results, it is suggested that the increased values of electric conductivities of the dry mixed composites are due to more randomly dispersed NCCF compared that of the melt mixed PP/NCCF composites.

Complex viscosities of the PP/Gr composites were higher than those of the PP/NCCF composites. This is maybe due to that the diameter of graphite particle (about 300 to 500 μm) is much larger than nickel-coated carbon fiber (about 10 μm). Also, for the melt mixed PP/NCCF composites, the fillers were oriented to 'along the flow' direction after melt mixing. Therefore, this fiber orientation was attributed to decrease the complex viscosities of the melt mixed PP/NCCF composites compared those of the melt mixed PP/Gr composites.

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References

- (1) S. Srinivasan, *J. Electrochem. Soc.*, **136**, 41 (1989).
- (2) S. J. Lee, S. Mukergee, J. McBreen, Y. W. Rho, Y. T. Kho, and T. H. Lee, *Electrochim. Acta*, **43**, 3693 (1998).
- (3) T. R. Ralph, *Platinum Met. Rev.*, **41**, 102 (1997).
- (4) S. Srinivasan, *Fuel Cells from Fundamentals to Applications*, Springer, New York, 2006, Chap. 4
- (5) D. H. Doughty, B. Vyas, T. Takamura, and J. R. Huff, *Mater. Res. Soc.*, **393**, 151 (1995).
- (6) J. Wind, R. Spah, W. Kaiser, and G. Bohm, *J. Power Sources*, **105**, 256 (2002).
- (7) D. P. Davies, P. L. Adcock, M. Turpin, and S. J. Rowen, *J. Power Sources*, **86**, 237 (2000).
- (8) R. C. Makkus, A. H. Janssen, F. A. de Bruijn, and R. K. Maltant, *J. Power Sources*, **86**, 274 (2000).
- (9) R. Hornung and G. Kappelt, *J. Power Sources*, **72**, 20 (1998).
- (10) J. M. Park, *J. Col. Inter. Sci.*, **225**, 384 (2000).
- (11) N. Mutong, W. Weiduan, and H. Guoying, *Compos. Interface*, **15**, 1 (2008).
- (12) S. M. Hong and S. S. Hwang, *Compos. Interface*, **13**, 145 (2006).
- (13) S.-J. Park, M.-K. Seo, and J.-R. Lee, *Compos. Interface*, **13**, 249 (2006).
- (14) C. K. Kum, Y. T. Sung, M. S. Han, W. N. Kim, H. S. Lee, S. J. Lee, and J. Joo, *Macromol. Res.*, **14**, 456 (2006).
- (15) Y. T. Sung, M. S. Han, K. H. Song, J. W. Jung, H. S. Lee, C. K. Kum, J. Joo, and W. N. Kim, *Polymer*, **47**, 4434 (2006).
- (16) V. P. Privalko, D. I. Sukhorukov, and J. Karger-Kocsis, *Polym. Eng. Sci.*, **39**, 1525 (1999).
- (17) T. Das, A. K. Banthia, B. Adhikari, H. Jeong, C.-S. Ha, and S. Alam, *Macromol. Res.*, **14**, 261 (2006).
- (18) B. S. Kim, S. H. BAe, Y.-H. Park, and J.-H. Kim, *Macromol. Res.*, **15**, 357 (2007).
- (19) J.-M. Park and J.-W. Kim, *Macromol. Res.*, **10**, 24 (2002).
- (20) M. Park, J. Kim, S. H. Kim, M. B. Ko, C. R. Choe, and V. S. Mironov, *Korea Polym. J.*, **8**, 6 (2000).
- (21) S. Lee, Y. Lee, and J. W. Lee, *Macromol. Res.*, **15**, 44 (2007).
- (22) C. K. Kum, Y. T. Sung, Y. S. Kim, H. G. Lee, W. N. Kim, H. S. Lee, and H. G. Yoon, *Macromol. Res.*, **15**, 308 (2007).
- (23) Y. T. Sung, M. S. Han, K. H. Song, J. W. Jung, H. S. Lee, C. K. Kum, J. Joo, and W. N. Kim, *Polymer*, **47**, 4434 (2006).
- (24) F. Mighri, M. A. Huneault, and M. F. Champagne, *Polym. Eng. Sci.*, **44**, 1755 (2004).
- (25) J. M. Choi, T. J. Kim, M. S. Hyun, D. H. Peck, S. K. Kim, B. R. Lee, J. S. Park, and D. H. Jung, *Carbon Sci.*, **6**, 181 (2005).
- (26) G. Yu, M. Q. Zhang, H. M. Zeng, Y. H. Hou, and H. B. Zhang, *J. Appl. Polym. Sci.*, **73**, 489 (1999).
- (27) J. Feng and C.-H. Chan, *Polym. Eng. Sci.*, **39**, 1207 (1999).
- (28) G. Yu, M.Q. Zhang, H. M. Zeng, Y. H. Hou, and H. B. Zhang, *Polym. Eng. Sci.*, **39**, 1678 (1999).