CHARACTERIZATION OF NICKEL-COATED CARBON FIBER-REINFORCED POLYPROPYLENE COMPOSITES: EFFECTS OF EXTRUSION PROCESSING METHOD

Donghwan Cho and Sebeom Jung, Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyeongbuk 39177, Korea*
**Corresponding author: dcho@kumoh.ac.kr*

Abstract

In this study, nickel-coated carbon fiber-reinforced polypropylene (NiCF/PP) composites with various NiCF contents were fabricated by extrusion and injection molding processes. H-NiCF/PP and S-NiCF pellets were produced by two different feeding routes of NiCF, hopper feeding (H) and side feeding (S), respectively. The effect of extrusion processing method on the electromagnetic, mechanical, and topological properties of the composites was characterized in terms of electromagnetic interference shielding effectiveness (EMI SE), tensile and flexural properties, fiber length distribution, and microscopic observation. The S-NiCF/PP composites exhibited the EMI SE, tensile, and flexural properties higher than the H-NiCF/PP composites. The improved properties of the S-NiCF/PP composites were explained by that they exhibited the higher aspect ratio and longer fiber distribution of NiCF remaining in the composite than the H-NiCF/PP counterparts, due to less shearing force and fiber damages occurring during twin-screw extrusion compounding. Hence, the improvement effect was somewhat restricted due to peel-off phenomenon of the nickel-coated layers from the carbon fibers in the composites occurring during the process. The characterization results were agreed with each other.

Introduction

Electromagnetic interference (EMI) has been a key issue in electric and electronic devices and in human health [1]. The EMI may cause not only operational malfunction of electronic devices, but also a negative impact on human health [2]. Metals have been widely applied for electromagnetic interference shielding materials. With the beginning of the twenty-first century, carbon materials such as carbon fiber, carbon nanotube, and graphene have attracted much attentions in imparting electromagnetic interference shielding [3,4], Most recently, many papers [5-7] have been increasingly dealing with carbon nanoparticles to improve the EMI shielding as well as to reduce the weight of industrial devices and parts. To impart plastics to electrical conductivity conductive metallic fillers have been frequently added in the polymer resins, but their mechanical performances are not satisfactorily imparted. Therefore, carbon fiber-reinforced plastics (CFRP) incorporated with conductive fillers have been studied [8-10].

Because the electrical resistivity of carbon fiber is normally higher than that of metals, a relatively large amount of carbon fibers should be used in carbon fiber-reinforced plastics for comparable electromagnetic interference shielding effectiveness (EMI SE). However, it may cause some difficulties in composite processing as well as economic problems due to high cost carbon fiber. Accordingly, to solve such the problems, carbon fibers thinly coated or plated with metals have often been used to provide the EMI SE and the mechanical properties to the composite [11,12].

General-purpose Polypropylene (PP), which is one of the most popular thermoplastics, has been widely used in automobile parts, housings for electronics, commodities, and many other industrial parts due to its many practical advantages in the mechanical, chemical, water-resistant, and thermal properties. In addition, PP is less expensive, remoldable, and recyclable. Studies on dealing with the effect of different fiber feeding routs upon fabrication of polyolefin matrix-based carbon fiber composite on the mechanical properties as well as on the EMI SE are hardly found. Consequently, the objective of the research is ultimately to study carbon fiber-reinforced PP matrix composites with high mechanical properties as well as increased EMI SE. To do so, two investigations were preliminarily performed in the present work. First, the effect of nickel-coated carbon fiber (NiCF) content on the EMISE and the tensile and flexural properties of NiCF/PP composites was investigated. Second, the effect of carbon fiber feeding methods (hopper feeding and side feeding) on the fiber length distribution, the EMISE and the mechanical properties of the composites was explored. The presentation will be given more extensively about the thermal stability, heat deflection temperature, surface resistivity, and facture surfaces, which are not described in this paper.

Materials

In this work, nickel-coated PAN-based carbon fibers (NiCF) were supplied in 8 mm-long chop form from Bullsone Advanced Materials Co., Korea and used as reinforcement for chopped carbon fiber/PP composites. The PAN-based carbon fibers (12 k, T700 Grade) were commercially produced by Toray Advanced Materials Co., Korea.

Polypropylene (PP, JM-365), which was supplied in pellet form from LOTTE Chemical Co., Korea was used as matrix for the composite. It is a high impact type of PP containing ethylene-propylene rubber. According to the manufacturer's data, the melt flow index is 26 g/10 min. the density is 0.9 g/cm^3, the melting temperature is 160°C, the flexural modulus is 1,270 MPa, the Izod impact strength is 69 J/m, and the heat deflection temperature is 105°C.

Processing and Characterization

Processing of NiCF/PP Composites

NiCF/PP pellets and the composites were produced by twin-screw extrusion and injection molding processes, respectively, with an optimization of processing parameters such as barrel temperatures, screw speed, and feeding rate. "As-received' PP pellets and chopped NiCF were sufficiently dried at 80℃ over 8 hours prior to extrusion process.

In this work, two different extruders were utilized. In the case of extrusion using a main hopper for feeding both chopped NiCF and PP pellets together, a modular intermeshing co-rotating twin-screw extruder (Model BT-30-S2-421, LG Machinery Co., Korea) with the L/D ratio of 42 and each screw diameter of 30 mm was used. The extrudates were continuously cooled down through a water bath and then cut to 2-3 mm by using a pelletizer, producing NiCF/PP pellets of about 5 kg. The NiCF/PP ratios of the pellets were 0/100, 10/90, 20/80, and 30/70 by weight.

In the case of extrusion using a side feeder for chopped NiCF and a main hopper for PP pellets, a co-rotating twin-screw extruder (Model PCM30, LG Machinery Co., Korea) with the L/D ratio of 38, each screw diameter of 30 mm and a sider feeder (WCA-302) was used, as shown in Figure 1.

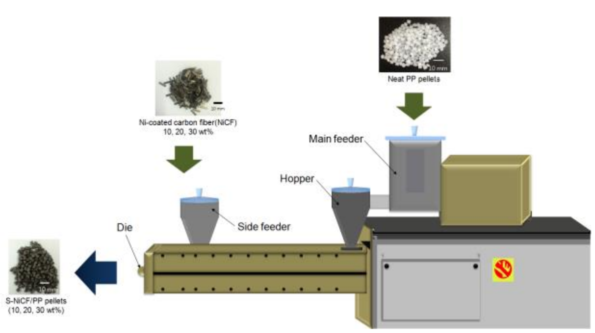

Figure 1. Twin-screw extrusion processing for producing NiCF/PP pellets through a sider feeder.

The extrudates were continuously cool down through a water bath and then cut to 2-3 mm by using a pelletizer, producing NiCF/PP pellets of about 5 kg. Here, the NiCF/PP ratios of the pellets were 0/100, 10/90, 20/80, and 30/70 by weight.

After fully drying the NiCF/PP pellets, injection molding process was performed with the pellets, which were produced using the main hopper and the sider feeder, respectively, by an injection molding machine (PRO-WD 80, Dong Shin, Korea). By injection molding NiCF/PP composites with various NiCF contents for mechanical and impact tests were obtained. Hereinafter, "H-NiCF/PP" and "S-NiCF/PP" designate the composites produced by using the main hopper (H) and the side feeder (S), respectively.

Preparation of NiCF/PP Composites for EMI SE measurement

The specimens for electromagnetic interference shielding effectiveness (EMI SE) measurement were prepared by using a hot-press (GE-122S, Kukje Scien, Co, Korea), using NiCF/PP pellets. As seen in Fig. 2, the pellets of about 15 g were placed uniformly in the mold for making an EMI-SE specimen, heated up to 220℃ for 20 min, allowing flow of melted PP resin, and then pressed up to 6.9 MPa (1000 psi). During the compression molding, a couple of debulking steps were carried out to remove pores and voids possibly existing in the composite. Each composite was cooled down to ambient temperature with the presence of applied pressure. The reference and load specimens for EMI SE measurement were finally obtained with varying the NiCF content, as shown in Figure 2.

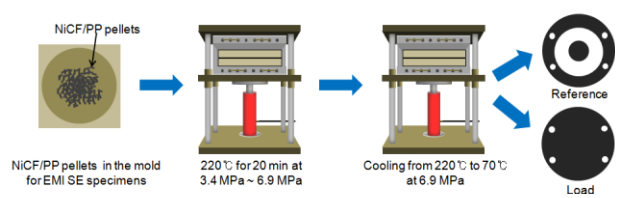

Figure 2. Compression molding process for producing NiCF/PP composite specimens for EMI-SE measurement.

Characterization

Electromagnetic interference shielding-effectiveness, (EMI-SE) of NiCF/PP composites produced with different feeding methods was measured at ambient temperature according to ASTM-D4935-10 standard [13] by using a Network Analysis (E5071C, Agilent, USA) and a standard test fixture of interference shielding effectiveness (EM-2017A, AELECTRO-METRICS, USA). The frequency range used was 30 MHz~1.5 GHz.

According to the ASTM D 638M standard, tensile tests were carried out with NiCF/PP composites of dog-bone shape at ambient temperature by using a universal testing machine (UTM, Shimadzu JP/AG-50kNX, Japan). The crosshead speed was 50 cm/min and the load cell of 50 kN was used. The average tensile modulus and strength were obtained from 10 specimens.

Izod impact tests were carried out with NiCF/PP composites according to the ASTM D256 standard by using a pendulum-type impact tester (Tinius Olsen, Model 892, UK). The dimensions of each specimen were 65 mm in length, 12.5 in width, and 3 mm in thickness. Each specimen has a 'V'-shaped notch (2.5 mm in depth) made using a notch cutter. The impact rate of the pendulum was 3.46 m/s. The impact distance was 610 mm. The impact energy of 12.66 J was used. The average impact strength was obtained from 8 specimens per each composite.

Results and Discussion

Fiber Length Distribution and EMI SE

Figure 3 compares the length distribution of the carbon fibers existing in the H-NiCF/PP and S-NiCF/PP composites. In the H-NiCF/PP, carbon fibers in the range of 50~200 μm long are predominant and the longest fiber length is about 484 μm. The carbon fibers existing in the S-NiCF/PP composite are in the range of 300~500 μm long and the longest fiber length is about 838 μm. It is expected that the high aspect ratio of the carbon fiber existing in the composite after processing plays a positive role in enhancing the EMI SE, mechanical, and thermal properties of resulting composites.

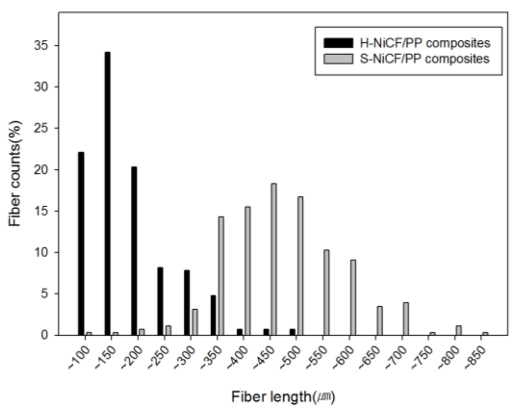

Figure 3. Fiber length distribution of H-NiCF/PP and S-NiCF/PP composites.

Figure 4 displays the effect of processing method (H and S) on the EMI SE of H-NiCF/PP and S-NiCF/PP composites with varying the NiCF content. Neat PP exhibited 0 dB in all the frequency range given, as expected. On the other hand, the EMI-SE values of the NiCF/PP composites significantly depended not only on the NiCF content but also on the processing method. With H-NiCF/PP, the EMI SE was increased with increasing the NiCF content and frequency. In the case of S-NiCF/PP, the EMI SE values were further increased, compared to those of H-NiCF/PP counterparts. The EMI SE was increased with increasing the NiCF and frequency, showing the highest value of 28 dB at 1500 MHz. It may be said that with the S-NICF/PP with 30 wt% NiCF the EMI SE did not strongly depend on the frequency range given. As a result, the S-NiCF/PP exhibited higher EMI-SE than the H-NiCF/PP. It can be explained by that the carbon fibers in the S-NiCF/PP may be subject to less fiber length degradation and fiber damages due to less shearing forces between the moving screws in the barrel during the extrusion process, resulting in the carbon fiber length longer than in the H-NiCF/PP composite. The longer carbon fibers may provide a longer pathway to connect the short carbon fibers, giving rise to an increased shielding effectiveness of electromagnetic interference.

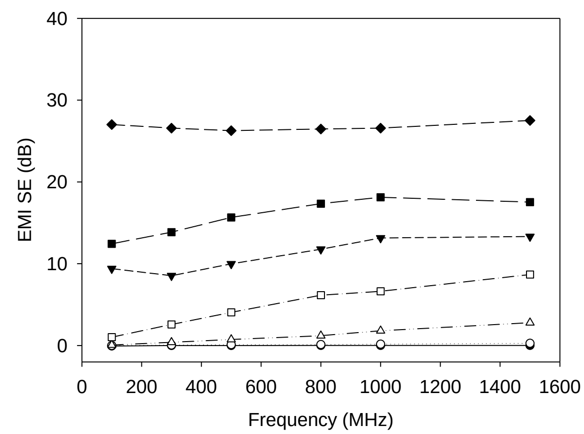

Figure 4. EMI SE as a function of frequency measured with H-NiCF/PP and S-NiCF/PP composites with various NiCF contents.

Mechanical Properties

Figure 5 shows the difference in the tensile modulus and strength of resulting NiCF/PP composites between the hopper (H) feeding and the side (S) feeding methods, depending on the NiCF content. Neat PP indicates the tensile modulus of 1355 MPa. With increasing the NiCF content from 10 to 30 wt%, the tensile modulus of H-NiCF/PP composites is considerably increased about 275% from 2515 to 5001 MPa due to a reinforcing effect by the NiCF, whereas the modulus of S-NiCF/PP composites is increased up to 6354 MPa, indicating a dramatic increase of about 370% even with the NiCF of 30 wt%, compared to that of neat PP. It is obvious that the S-NiCF/PP composite exhibits the tensile modulus higher than the H-NiCF/PP counterpart.

The improvement of the tensile strength of the composite is also significant with the increasing NiCF. The tensile strengths of both H-NiCF/PP and S-NiCF/PP composites are higher than that of neat PP, showing the gradual increase with increasing the NiCF content. The improvements at 30 wt% NiCF are 42% with the H-NiCF/PP (34 MPa) and 55% with the S-NiCF/PP (38 MPa), compared to the tensile strength (24 MPa) of neat PP. It is mentioned that the tensile properties of S-NiCF/PP composites are higher than those of H-NiCF/PP composites.

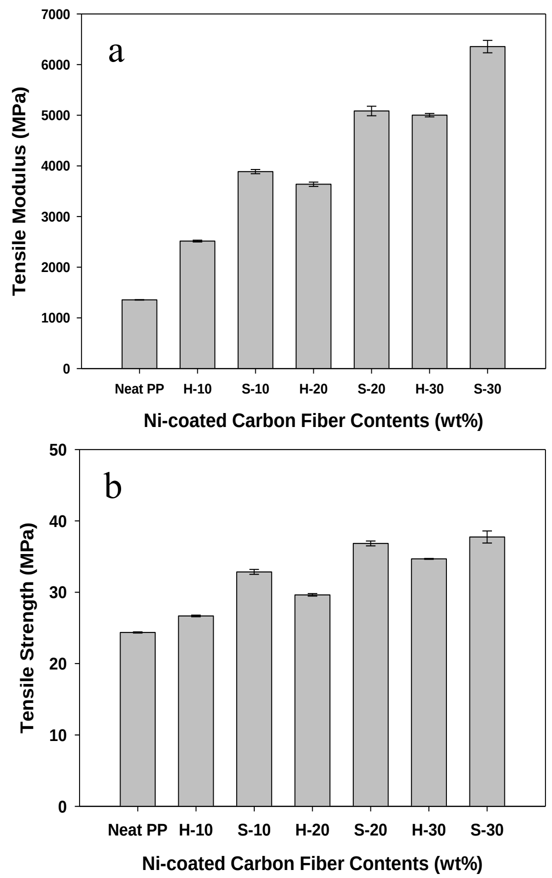

Figure 5. The tensile modulus (A) and strength (B) of H-NiCF/PP and S-NiCF/PP composites with various NiCF contents.

Figure 6 shows the effect of NiCF content and NiCF feeding method on the flexural modulus and strength of H-NiCF/PP and S-NiCF/PP composites. Neat PP exhibits the flexural modulus of 762 MPa. With increasing the NiCF content, the flexural modulus of H-NiCF/PP composites is largely increased about 350% from 2515 to 6096 MPa, whereas the modulus of S-NiCF/PP composites is increased up to 8917 MPa, indicating a tremendous increase of about 1070% even with the NiCF of 30 wt%, compared to that of neat PP. It is found that the S-NiCF/PP composite exhibits the flexural modulus much higher than the H-NiCF/PP counterpart.

The flexural strength of the composite also strongly depends on the fiber feeding method as well as on the NiCF loading. The flexural strengths of both H-NiCF/PP and S-NiCF/PP composites are, of course, higher than that of neat PP, showing the gradual increase with increasing the NiCF content. The improvements at 30 wt% NiCF are 100% with the H-NiCF/PP (38 MPa) and 132% with the S-NiCF/PP (44 MPa), compared to the tensile strength (19 MPa) of neat PP. It is mentioned that the flexural properties of S-NiCF/PP composites are higher than those of H-NiCF/PP composites.

The remarkable enhancement of the tensile and flexural properties in the NiCF/PP composites can be explained in terms of metal-coated carbon fibers, shearing force and fiber moving distance during compounding and extrusion. First, the presence of the coated metal on the fiber surface makes the carbon fiber stiffer than the corresponding carbon fiber without nickel-coating. Second, the chopped NiCF are influenced by the shearing force existing between the barrel and the screws during the compounding. Third, the moving distance of the NiCF mixed with melted PP in the presence of the shearing forces during the extrusion process is longer with the H-NiCF (from the hopper to the die) than with the S-NiCF (from the side feeder to the die). As a result, the NiC can shortened and damaged during the extrusion. Such the damage and length degradation of the carbon fibers may occur more severely in the H-NiCF than in the S-NiCF, resulting in a decreased fiber aspect ratio in the composite. The decreased aspect ratio in the H-NiCF/PP composite is responsible for the decreased tensile modulus and strength.

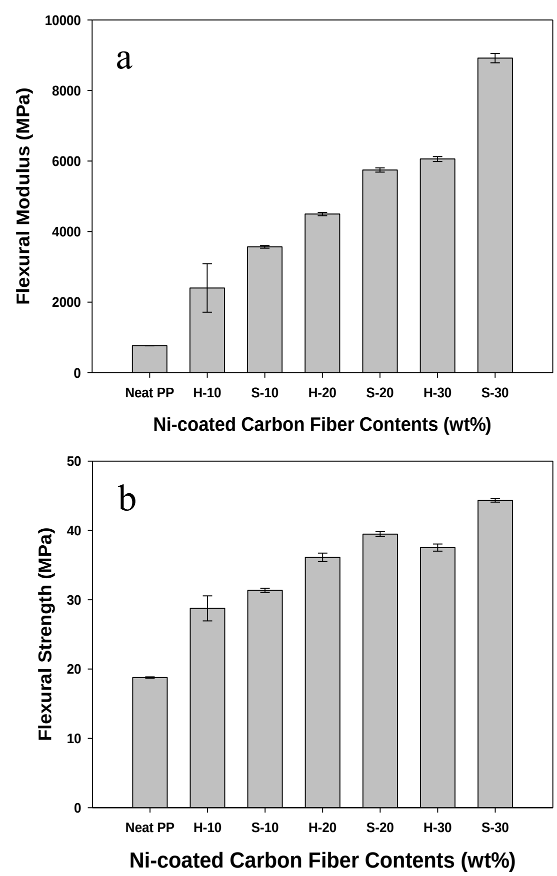

Figure 6. The flexural modulus (A) and strength (B) of H-NiCF/PP and S-NiCF/PP composites with various NiCF contents.

As mentioned earlier, the fiber length distribution result also supports the mechanical result. The NiCF existing in the S-NiCF/PP composite is longer than those in the H-NiCF/PP composite, reflecting the effect of the aspect ratio of the carbon fibers therein.

Figure 7 displays SEM images of the H-NiCF and S-NiCF remaining after the PP matrix was removed from the NiCF/PP composites by pyrolysis in an inert gas environment. It was clearly observed that part of the nickel-coated layers surrounding the carbon fibers were removed or peeled off from the surfaces by the shearing force during the extrusion process. It seems that peeling-off in the H-NiCF took place more frequently than that in the S-NiCF, which can be ascribed to the difference in the shearing force between the carbon fiber feeding methods. Also, it is observed that the fiber length of the S-NiCF remains longer than that of the H-NiCF. This peel-off phenomenon may influence the EMI SE and the mechanical properties. That is, the peel-off of the nickel-coated layers may somewhat restrict further enhancement of the EMI SE, tensile, and flexural properties. Accordingly, it is suggested that optimal processing conditions may play a significant role in further enhancing the EMI SE as well as the mechanical properties of resulting carbon fiber composites.

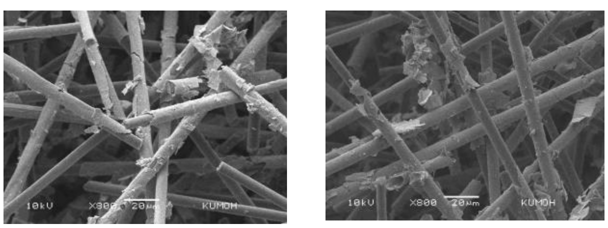

Figure 7. SEM Images of H-NiCF (A: x300, C: x800) and S-NiCF (B: x300, D: x800) remaining after PP removal from NiCF/PP pellets.

Conclusions

In the present study, as a result of characterization of the properties of NiCF/PP composites with various NiCF contents, which were produced through injection molding process via either hopper feeding or side feeding of NiCF during extrusion process, the following conclusions were obtained.

1. The S-NiCF/PP composites exhibited the wider fiber length distribution containing longer carbon fibers than the H-NiCF/PP composites.
2. The EMI SE was higher in the S-NiCF/PP than in the H-NiCF composites, with increasing with the NiCF content.
3. The tensile and flexural properties of the NiCF/PP composites were remarkably increased than those of neat NiCC, showing a gradual increase with the NiCF content.
4. The tensile modulus and strength of the S-NiCF/PP composite with 30 wt% NiCF were about 27% and 12% higher than those of the H-NiCF/PP counterpart, respectively. The flexural modulus and strength of the S-NiCF/PP composite with 30 wt% NiCF were about 46% and 16% higher than those of the H-NiCF/PP counterpart, respectively.
5. It is suggested that the side feeding of NiCF during extrusion prefers to the improvement of the carbon fiber length, the EMISE, and the mechanical properties of the resulting composites.

Acknowledgement

This work was supported by a research fund from Kumoh National Institute of Technology, Gumi, Korea.

References

[1] P. Verman, P. Saini, and V. Choudhary, *Mater. Design*, **88**, 269 (2015).
[2] Y.J. Yim, D. C. Chung, and S.J. Park, *Carbon Lett.*, **22**, 36 (2017).
[3] D.D.L Chung, *Carbon*, **39**, 279 (2001).
[4] Q. Liu, D. Zhang, T. Fan, J. Gu, Y. Miyamoto, and Z. Chen, *Carbon*, **46**, 461 (2008).
[5] B.J. Kim, K.M. Bae, Y.S. Lee, K.H. An, and S.J. Park, *Surf. Coat. Technol.*, **242**, 125 (2014).
[6] Y. Li, x. Pei, B. Shen, W. Zhai, L. Zhang, and W. Zheng, *RSC Adv.*, **5**, 24342 (2015).
[7] M.H. Al-Saleh, Synth. Metals, 217, 322 (2016).
[8] W. Tang, L. Lu, D. Xing, H. Fang, Q. Liu, and W.S. Teh, *Composites Part B*, **152**, 8 (2018).
[9] S. Hwang, Composites Part B, 98, 1 (2016).
[10] J.T. Kim, CW. Park, and B. Kim, *Synth. Metals*, **223**, 212 (2017).
[11] T. Chen, P. Xue, and M. Jia, *Polym. Compos.*, **38**, 157 (2015)
[12] J. Li, S. Qi, M. Zhang, and Z. Wang, *J. Appl. Polym. Sci.*, **132**, 42306 (2015).
[13] ASTM D4935-10, Standard test method for measuring the electromagnetic shielding effectiveness of planar.