Mechanical Properties of Injection-Molded Composites of Carbon Nanofibers in Polypropylene Matrix

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This paper describes the dispersion of carbon nanofibers (CNFs) in a polypropylene (PP) matrix and the mechanical properties of specimens fabricated by injection molding; the effects of kneading and surface treatments of CNFs are also discussed. Dispersion of CNFs in composites is quantified by determining the residual cluster rate and the maximum cluster size. The residual cluster rate is almost constant when the kneading time is 5 min or more, but the maximum cluster size decreases slightly with kneading time. The Young’s modulus of 30 wt.% vapor grown carbon nanofiber (VGNF) filled in PP matrix (VGNF/PP) increases to approximately 2.3 times that of neat PP, and the tensile strength of 30 wt.% VGNF/PP composites increases to approximately 1.4 times that of neat PP. Adding elastomer or pretreatment of CNFs with an aluminate coupling agent improves the Young’s modulus and tensile strength of CNF/PP composites.

1. Introduction

Carbon nanotube (CNT) was discovered by Iijima(1) in 1991, and will become one of the most important materials in the 21st century. Single-walled carbon nanotubes (SWCNTs)(2–4) and multiwalled carbon nanotubes (MWCNTs)(5–9) as well as vapor-grown carbon nanofibers (VGNFs)(10–12) are promising materials for reinforcing various polymer matrices (thermoplastics, thermosets and thermoplastic elastomers). Much recent nano-composite

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research has been directed towards the use of CNTs as reinforcement. VGNFs are fabricated using almost the same method used for carbon nanotubes; however, fabrication costs are lower than those for carbon nanotubes. Typically, diameters of VGNFs are in the range of 50 nm to 200 nm; therefore, VGNFs are also referred to as MWCNTs with very large diameters. CNTs and carbon nanofibers (CNFs) have excellent mechanical properties such as exceptionally high axial strength and an axial Young’s modulus on the order of several hundred GPa. When CNFs are added as reinforcement to polymer matrices fabricated by injection molding, they orient in the flow direction, therefore, it is expected that the mechanical and electrical properties of molded composites are improved with small amounts of filler in comparison with conventional carbon fillers.

The objectives of this study are the fabrication of CNF/polypropylene (PP) composites on thin plates by injection molding and the evaluation of the dispersion of CNFs and the mechanical properties of the molded specimens. The effects of the surface treatment and kneading conditions are also discussed.

2. Experimental

CNFs used in this study are graphitized vapor-grown carbon fibers (VGCFs), graphitized VGNFs and MWCNTs. All of them were fabricated by thermal chemical vapor deposition and produced by Showa Denko K.K., Japan. Table 1 shows the sizes of the carbon nanofibers used in this study. Scanning electron microscope (SEM) images of VGCFs, VGNFs and MWCNTs are shown in Fig. 1. These images show that MWCNTs are curly and that the distribution of the diameters of MWCNTs is wider than those of VGCFs and VGNFs. Transmission electron microscope (TEM) images of VGCFs, VGNFs and MWCNTs are shown in Fig. 2. A hollow center and graphite sheets in which many layers overlap are observed in all nanofibers used in this study. Figure 3 shows the Raman spectra over a wide frequency range of carbon nanofibers used in this study, and Table 2 shows the Raman spectroscopic parameters for these three samples. There is no difference between the spectra and shapes of VGCF and VGNF, but for MWCNT, the full width at half maximum values (FWHMs) of the G- and D-bands and the relative intensity, $I_D/I_G$, are larger than those of VGCF and VGNF. The MWCNTs used in this study are nongraphitized material, so they consist of graphitic structures with small disordered portions and impurities.

PP is a translucent white crystalline polymer widely used in injection molding. An injection molding grade PP (J108M, Mitsui Chemicals, Inc.) was selected as the matrix polymer. The melt flow rate (MFR) of this PP is about 45 g/10 min (JIS K 7210). The PP

<table>
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<tr>
<th></th>
<th>VGNF</th>
<th>VGCF</th>
<th>MWCNT</th>
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<tbody>
<tr>
<td>Diameter [nm]</td>
<td>80 – 100</td>
<td>100 – 200</td>
<td>20 – 50</td>
</tr>
<tr>
<td>Length [µm]</td>
<td>5 – 15</td>
<td>10 – 20</td>
<td>~ 5</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>~ 150</td>
<td>~ 150</td>
<td>~ 100</td>
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pellets were preliminarily ground into PP powder. The average particle diameter of the PP powder was 300 µm.

The PP matrix composites were obtained by kneading with a twin screw kneader to disperse CNFs in the PP matrix. PP powder and CNFs were mixed and supplied to the kneader. After kneading, they were cut and crushed into pellets for injection molding. The filler content in the composites was varied from 0 to 30 wt.%. Tensile test specimens were fabricated by injection molding. The dimensions of the specimens are shown in Fig. 4.

The mechanical properties of the composites were evaluated by tensile tests in the flow direction. The tensile tests were carried out at room temperature at a testing speed of 5 mm/min. The elastic modulus of the composites, $E_c$, was determined for 0.5% deformation. The density of the molded specimens, $\rho$, was measured by the Archimedes method.
Fig. 2. TEM images of VGCF, VGNF and MWCNT.

Fig. 3. Raman spectra of carbon nanofibers used in this study.
3. Results and Discussion

3.1 Dispersion of CNFs

3.1.1 Quantification of the dispersion of CNFs

In order to observe the dispersion of CNFs in the composites, 0.4 wt.% VGCF/PP samples were taken out of the kneader at different kneading times. Then, the samples were compressed to form films approximately 100 $\mu$m thick using a hot press. The samples were observed using an optical microscope with transmitted light. The binarized optical microscope images of the samples are shown in Fig. 5. The black areas in the binarized images are residual clusters, and the residual clusters with diameters of 5 $\mu$m to 30 $\mu$m are observed between dispersed VGCFs. It can be assumed that these residual clusters are mixtures of multiple VGCF clusters and carbon impurities that were not removed from the VGCFs. In order to quantify the dispersion of CNFs, two parameters are employed as follows: (1) the rate at which residual clusters occupied an image (residual cluster rate); and (2) the maximum cluster size.\(^{(17)}\) These parameters are calculated from the binarized optical microscope images using image-analysis software. Figure 6 shows these dispersion parameters as functions of kneading time. The residual cluster rate decreases in the range from 0 to 5 min, after which it becomes constant. The maximum cluster size drastically decreases in the range from 0 to 5 min, and it decreases slightly after that. These data show that large clusters were decomposed by the shear stress due to the rotation of the two screws and became small clusters and individual fibers; therefore, the dispersion of VGCFs improves.

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Table 2

Results of fitting Raman spectra for VGCF, VGNF and MWCNT.

<table>
<thead>
<tr>
<th></th>
<th>Wave number [cm$^{-1}$]</th>
<th>FWHM [cm$^{-1}$]</th>
<th>Wave number [cm$^{-1}$]</th>
<th>FWHM [cm$^{-1}$]</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGCF</td>
<td>1568.8</td>
<td>29.7</td>
<td>1347.6</td>
<td>51.6</td>
<td>0.1004</td>
</tr>
<tr>
<td>VGNF</td>
<td>1574.4</td>
<td>28.9</td>
<td>1350.8</td>
<td>47.8</td>
<td>0.1214</td>
</tr>
<tr>
<td>MWCNT</td>
<td>1560.7</td>
<td>45.2</td>
<td>1331.9</td>
<td>60.1</td>
<td>0.3966</td>
</tr>
</tbody>
</table>

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Fig. 4. Dimensions of tensile test specimens (Thickness = 2 mm).
3.1.2 Effect of surface treatment of CNFs

In order to investigate the effect of surface treatment on the dispersion of CNFs, two types of surface treatment were used; one was the addition of elastomer in the kneading of the composites, and the other was pretreatment of CNFs using an aluminate coupling agent.

Fig. 5. Binarized optical microscope images of 0.4 wt.% VGCF/PP composites at different kneading times.

Fig. 6. Dispersion indexes of VGCF in the PP matrix as functions of kneading time.
In the case of adding elastomer, 5 wt.% of the elastomer, 0.4 wt.% of VGCFs and the balance of powdered PP were introduced into the kneader simultaneously. The kneading time was 20 min. The residual cluster rate and the maximum cluster size were investigated. In the case of the pretreatment of CNFs with an aluminate coupling agent, CNFs are dispersed in the organic solvent by magnetic stirring, after which an aluminate coupling agent (10 wt.% to CNFs) was added to the solvent, the mixture stirred to volatilize the organic components, and the residual substances dried. Pretreated VGCF (0.4 wt.%) and the powdered PP were introduced into the kneader together, and the residual cluster rate and the maximum cluster size were calculated after kneading for 20 min.

Figure 7 shows the relationship between the residual cluster rate and the kneading time for each surface treatment. Adding elastomer decreases the residual cluster rate to less than half of that from adding nontreated CNFs, but the pretreatment of CNFs using an aluminate coupling agent increases the residual cluster rate to 1.5 times or more than that from adding nontreated CNFs. In the case of adding elastomer, the kneading torque was smaller than that in kneading nontreated CNFs: therefore, the melt viscosity was decreased by adding elastomer. In the case of pretreatment of CNFs using an aluminate coupling agent, although the kneading torque was almost the same as that in kneading nontreated CNFs, the dispersion of CNFs became worse compared with the case of adding nontreated CNFs. CNFs pretreated using an aluminate coupling agent agglomerate easily: therefore, large clusters of CNFs are formed by aluminate coupling pretreatment and the kneading conditions are not sufficient to break the large clusters of agglomerated CNFs.

3.2 Mechanical Properties

3.2.1 Effect of kneading conditions

In order to investigate the effects of kneading conditions on mechanical properties, the kneading time \((t)\), the rotation speed of screws \((r)\) and the kneading temperature \((T)\) were varied.

Fig. 7. Residual cluster rates of VGCF/PP composites as functions of kneading time for each surface treatment.
First, the effect of kneading time was investigated. Figure 8 shows the density, Young’s modulus and tensile strength of the molded specimens as functions of kneading time when the rotation speed of the screws was 50 rpm and the kneading temperature was 200°C. After kneading for 10 min, the density of the molded specimens became constant and the variation in Young’s modulus decreased: therefore, the composites became almost homogeneous in 10 min. However, when the kneading time was 10 min or longer, the Young’s modulus and tensile strength of the composites decreased. The reasons for this are the fracture of CNFs by shear force during the kneading of the composites, and the heat degradation of PP as a result of long kneading times. When the kneading time is too short, the composites become inhomogeneous, and when the kneading time is too long, the mechanical properties of the composites decrease. Therefore the optimal kneading time is 10 min.

Fig. 8. Relationships between mechanical properties and kneading time when the rotation speed of the screws was 50 rpm and the kneading temperature was 200°C. (a) Young’s modulus and density of VGNF/PP composites. (b) Tensile strength and density of VGNF/PP composites.
Second, the effect of the rotation speed of the screws was investigated. Figure 9 shows the density, Young’s modulus and tensile strength of the molded specimens as functions of kneading speed, when the kneading time was 5 min and the kneading temperature was 200°C. The density, Young’s modulus and tensile strength of the molded specimens increased as the rotation speed of the screws increased. Since the shear force which the composite receives in kneading increases with the increasing rotation speed of the screws, agglomerates of CNFs are destroyed and the dispersion of CNFs improves. The optimal rotation speed of the screws is 150 rpm.

Finally, the effect of the kneading temperature was investigated. Figure 10 shows the density, Young’s modulus and tensile strength of the molded specimens as functions of kneading temperature, when the kneading time was 5 min and the rotation speed of the screws was 50 rpm. When the kneading temperature is low, since the viscosity of the composites is high, the shear force which the composites receive increases and the
agglomerates of CNFs are destroyed easily. However, the continued dispersion of the CNFs is difficult since the viscosity of the composites is high. On the other hand, when the kneading temperature is high, since the viscosity of the composites is low, the dispersion of CNFs can progress easily; however, the PP matrix is easily deteriorated by heating, therefore a short kneading time is desirable.

From the results, the optimal kneading conditions for improving the mechanical properties are as follows: a kneading time of 10 min, a rotation speed of screws of 150 rpm, and a kneading temperature of 210°C.

3.2.2 Effect of the kind of CNFs

Figure 11 shows the Young’s modulus and tensile strength of PP matrix composites filled with various carbon nanofibers as functions of filler content. Regardless of the kind of CNF, the Young’s modulus increases as the CNF content increases. When VGNFs with a diameter
Fig. 11. Young’s modulus and tensile strength of PP matrix composites filled with various carbon nanofibers as functions of filler content. (a) Young’s modulus. (b) Tensile strength.

of 80 nm and VGCFs with a diameter of 150 nm were filled, almost no difference was observed between the composites, and the Young’s modulus of the composites increased to about 2.3 times that of neat PP. However, when MWCNTs were filled, the Young’s modulus of the composite was slightly smaller compared with those of composites filled with the same content of VGCF or VGNF. Since many impurities were contained in MWCNTs compared with VGCFs and VGNFs, the reinforcement effect was not fully achieved. When the CNF content was from 0 wt.% to 20 wt.%, the tensile strength of the composites was almost constant. However, when the CNF content was 30 wt.%, the strength increased, especially in 30 wt.% VGNF/PP composites.

The modulus of discontinuous-fiber-reinforced composites is expressed by Halpin-Tsai’s model. The modulus of randomly oriented discontinuous fiber composites, $E_c$, can be calculated from the following equations\(^8\)

\[ E_c = \frac{E_f V_f + E_m (1 - V_f)}{1 - V_f (1 - E_m/E_f/2)} \]
\[
E_c = \left[ \frac{31 + 2(l_{NF}/d_{NF}) \eta_e V_{NF} + 51 + 2\eta_e V_{NF}}{8(1 - \eta_e V_{NF})} \right] E_{pp},
\]

(1)

\[
\eta_e = \frac{(E_{NF}/E_{pp}) - 1}{(E_{NF}/E_{pp}) + 2(l_{NF}/d_{NF})},
\]

(2)

\[
\eta_T = \frac{(E_{NF}/E_{pp}) - 1}{(E_{NF}/E_{pp}) + 2},
\]

(3)

where \( E \) represents the tensile modulus, \( l_{NF} \) is the length of nanofibers, and \( d_{NF} \) is the outer diameter of the nanofibers (80 nm). The modulus of CNF, \( E_{NF} \), is known to strongly depend on the diameter, and the modulus of CNF is reported to be in the range of 100 – 600 GPa\(^{(18)}\) so in this study the modulus of CNF is assumed to be 300 GPa. The calculated results, when \( d_{NF} \) is 80 nm and \( l_{NF} \) is 1 \( \mu \)m and 5 \( \mu \)m, are shown in Fig. 11. CNFs in the injection-molded CNF/PP composites can be considered as oriented discontinuous fibers\(^{(16)}\) however, the experimental results for the Young’s modulus are extremely small compared with calculated results. The reasons are as follows: (1) the interfaces between the CNFs and the matrix polymer do not adhere completely, although it is assumed that the interfaces adhere completely in the calculation, and (2) the CNFs are quite short. Therefore, in order to obtain sufficient reinforcement, it is essential to improve the adhesion strength of the interfaces between the CNFs and the matrix polymer.

### 3.2.3 Effect of surface treatment of CNFs

Figure 12 shows the Young’s modulus and tensile strength of PP matrix composites filled with VGNFs, to which various surface treatments have been applied, when VGNF content was 10 wt.%\(^{\circ}\). In the case of adding elastomer, the Young’s modulus and tensile strength were 1.1 times larger than those in the case of adding nontreated VGNF. On the other hand, in the case of adding CNFs pretreated with an aluminate coupling agent, the Young’s modulus was 1.3 times larger than that in the case of adding nontreated VGNF, and the tensile strength was 1.2 times larger than that in the case of adding nontreated VGNF. The dispersion of CNFs was better than that in the case of adding nontreated VGNF, and the adhesion strength of interfaces between CNFs and matrix was improved.

### 4. Conclusions

Polypropylene matrix composites filled with carbon nanofibers were obtained by kneading with a twin-screw kneader and the specimens were fabricated using injection molding. The dispersion of CNFs and the mechanical properties of the molded specimens were evaluated, and the effects of surface treatment and kneading conditions were observed. The results are as follows:
Using a twin-screw k kneader, CNFs are dispersed in the matrix. Adding elastomer reduces the residual cluster rate, so the dispersion of CNFs is improved. Pretreatment of CNFs with an aluminate coupling agent increases the residual cluster rate.

The mechanical properties of the molded specimens are changed by changing kneading conditions: the kneading time $t$, the rotation speed of the screws $r$, and the kneading temperature $T$. Optimal kneading conditions for improving the mechanical properties are as follows: a kneading temperature of 170°C, a rotation speed of the screws of 150 rpm, and a kneading time of 10 min.

The Young’s modulus of 30 wt.% VGNF/PP composites increases to about 2.3 times that of neat PP, and the tensile strength of 30 wt.% VGNF/PP composites increases to about 1.4 times that of neat PP. Adding elastomer or pretreatment of CNFs with an aluminate coupling agent improves both the Young’s modulus and tensile strength of CNF/PP composites.
References