Effects of maleic anhydride content on mechanical properties of carbon fibers-reinforced maleic anhydride-grafted-polypropylene matrix composites

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Received 21 April 2016
Accepted 25 August 2016

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DOI: http://dx.doi.org/
10.5714/CL.2016.20.039

Abstract
In this work, the effects of maleic anhydride (MA) content on mechanical properties of chopped carbon fibers (CFs)-reinforced MA-grafted-polypropylene (MAPP) matrix composites. A direct oxyfluorination on CF surfaces was applied to increase the interfacial strength between the CFs and MAPP matrix. The mechanical properties of the CFs/MAPP composites are likely to be different in terms of MA content. Surface characteristics were observed by scanning electron microscope, Fourier transform infrared spectroscopy, and single fiber contact angle method. The mechanical properties of the composites were also measured by a critical stress intensity factor ($K_{IC}$). From the $K_{IC}$ test results, the $K_{IC}$ values were increased to a maximum value of 3.4 MPa with the 0.1 % of MA in the PP, and then decreased with higher MA content.

Key words: carbon Fibers, oxyfluorination, maleic anhydride, maleic anhydride-grafted-polypropylene

1. Introduction

In recent years, carbon fibers are widely used as advanced reinforcing fiber materials in polymer matrix composite, due to their good mechanical, thermal and electrical properties. And carbon fibers/polymer matrix composites are widely used in automobile, aerospace engineering, sporting goods, and transportation industries as well as civil industries for structural applications [1-4].

Polypropylene (PP) is one of the most widely used commodity thermoplastics, especially in automotive, electric, packaging and consumer applications. The reason for these can be found in its excellent properties, such as good processing, heat distortion temperature, recycling ability and favorable price/volume/performance ratio [5-7].

Carbon fibers/thermoplastics composites are attractive compared to traditional materials, such as steel, aluminum, and thermoset composites, due to their high specific strength, environmental resistance, handling, damage tolerance, corrosion resistance, superior impact resistance, high toughness, possibility to re-melt and reprocess compared with thermosetting composites, and ease of shaping and recycling [8,9].

However, despite these advantages, as-produced carbon fibers have poor interaction with most of the polymers due to the low surface energy and chemically inert surface with less reactive functional groups and are composed of highly crystallized graphitic basal planes with inert structure. This leads to poor interface adhesion with a matrix resulting in more defects and low mechanical properties of the composites. The improvement of interfacial adhesion between carbon fibers and thermoplastic matrix are attributed to the presence of polar functional groups (-OH and -COOH) on the carbon fibers surface, which are able to interact with
the active functional groups presented in the thermoplastic matrix. As a result, the interfacial bonding strength between fibers and polymer matrix is low, and good mechanical performance of composite cannot be achieved [10-13].

To improve the surface properties and surface functional groups on carbon fibers, various surface treatments can be applied, including oxidation treatments, the use of coupling agents, plasma processing, coating process, fluorination or oxyfluorination and so on [14-19]. Among the diverse treatments, oxyfluorination is known to be effective for improving interfacial adhesion and increasing wettability of carbon fibers. Oxyfluorination is a surface treatment method for carbon fibers using an oxygen-fluorine gas mixture. In the presence of oxygen, surface wettability increases as a result of the introduction of polar groups (-C-F, C=O, -COF, -RO2, COOH) [20,21].

The various methods that have been studied to improve the interfacial adhesion of composites, by modifying the matrix surface, have included the use of maleic anhydride-grafted-polypropylene (MAPP), grafting matrix polymer with hydrophilic functional group, chemical modification of matrix surface. MAPP with various maleic anhydride (MA) content, which is a very effective compatibilizer for fibers and matrix at the interface, has been used to improve interfacial adhesion. The MA-grafted-thermoplastic polymer can increase the polarity which leads to better adhesion with the fibers. Furthermore, improvements in mechanical properties attributed to fiber/matrix interface enhancement interaction by addition of MA have been evident [22-26].

The objective of this work is to investigate and compare the effects of MA content on mechanical properties of oxyfluorinated carbon fibers-reinforced MAPP matrix composites. The mechanical and morphological properties of carbon fibers/MAPP composites are likely to be different from those of MAPP in terms of MA content.

2. Experimental

2.1. Materials

Carbon fibers (TANSOME, H2550, 12K; Hyosung, Seoul, Korea) were used as a reinforcing material and the properties in Table 1. The fluorine gas used was supplied from Messer Griesheim GmbH, Bad Soden, Germany (purity 99.8%, balanced by nitrogen gas). The types of MAPP (Homan Petrochemical Co., Yeosu, Korea) was employed as a matrix with various MA content. Compositions of all samples are listed in Table 2. Oxyfluorination of the carbon fibers were performed using an oxygen and fluorine gas mixture (F2:O2 = 1:1) at 100°C and 1 bar for 1 min. The carbon fibers were surface-treated in a nickel bath. After treatment, the reaction chamber were fully purged by N2 gas in order to prevent additional reaction with oxygen in air.

<table>
<thead>
<tr>
<th>MA content (%)</th>
<th>Specimen</th>
<th>Polypropylene</th>
<th>Modified CFs/MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PP</td>
<td>CFsPP</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>MA1</td>
<td>OFCFsPP</td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>MA3</td>
<td>OFCFsMA3</td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>MA5</td>
<td>OFCFsMA5</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>MA10</td>
<td>OFCFsMA10</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>MA20</td>
<td>OFCFsMA20</td>
<td></td>
</tr>
</tbody>
</table>

CFs, chopped carbon fibers; MA, maleic anhydride; PP, polypropylene.

2.2. Carbon fiber and matrix surface measurement

The single fiber contact angle measurements of oxyfluorinated carbon fibers were carried out using the Wilhelmy balance method.
Effects of MA content on mechanical properties of CFRP

Table 3. Characteristics of liquid probes

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_1$ (mN/m)</th>
<th>$\gamma_2$ (mN/m)</th>
<th>$\gamma_3$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (Ström)</td>
<td>72.8</td>
<td>51</td>
<td>21.8</td>
</tr>
<tr>
<td>Diodomethane (Donnet)</td>
<td>50.8</td>
<td>0.38</td>
<td>50.42</td>
</tr>
</tbody>
</table>

od, using a Krüss K-100SF (Krüss Ltd., Hamburg, Germany) with 1 μg weight resolution. The Wilhelmy balance method can be carried out to follow the sorption behaviors as shown in Fig. 1. The fiber is assumed to be a right angle to the liquid surface. The advancing angle of a single carbon fiber was measured by the immersion of the fiber in a distilled water and diiodomethane solution. The contact angle for wettability and the dispersion and polar component of the surface free energies, calculated according to the Owens-Wendt-Rabel-Kaelble theory by following eq 1:

$$\gamma_i (1 + \cos \theta_i) = 2 \sqrt{\gamma_d \gamma_s} + \sqrt{\gamma_i \gamma_s}$$  \hspace{1cm} (1)

where $\theta_i$ is the measured contact angle of testing liquids; $\gamma_i$ is surface tension of testing liquids; $\gamma_d$, $\gamma_s$ is polar and dispersion energy of testing liquids; $\gamma_d$, $\gamma_s$ is polar and dispersion energy of carbon fiber surface. The test wetting liquids used in this study are described in Table 3 [27-29].

Surface functional groups of the oxyfluorinated carbon fibers and MAPP were measured by Fourier transform infrared spectroscopy and attenuated total reflectance (FT-IR, ATR; Nicolet is10, Thermo, USA), respectively. The contact angle measurements of MAPP were obtained to calculate surface free energy of the matrices themselves by using a Phoenix 150 (SEO, Suwon, Korea) with micro-syringe steel needle of 0.5 mm diameter. For contact angle measurement, contact angle specimen with dimensions of 50 × 30 × 2 mm were prepared. The droplet of test wetting liquids of Table 3 was placed on the sample surface. The syringe needle was positioned 0.2 mm from the surface of the MAPP plate, and a drop of the test liquid (2 μL) was dispensed at a rate (1.75 μL/s) in order to obtain static contact angle results. After dispensing, the drop shape was monitored with a digital camera inside 3 s, and contact angle was recorded. The contact angle was taken as the average angle after the contact angle has reached a stability at 3 s.

The morphology of fracture surfaces of the fiber and composites was observed by a scanning electron microscope (SEM; Hitachi, Tokyo, Japan) with field emission gun and accelerating voltage of 10 and 15 kV. Prior to the SEM observation, a few nanometer platinum was coated on the fiber and composite surfaces.

2.3. Mechanical properties

For mechanical characterization, $K_{IC}$ test specimen with dimensions of 50 × 10 × 5 mm were prepared. All samples were prepared by a compression molding at 10 MPa. The mechanical interfacial properties of the composites were investigated using the analytical expression for $K_{IC}$ and were characterized using a single-edge notched (SEN) beam fracture toughness test in 90° three-point bending flexure. The SEN beam fracture toughness test was conducted on an Instron model universal testing ma-

3. Results and Discussion

3.1. Oxyfluorination carbon fiber analysis

The surfaces of the fiber specimens were examined by SEM to compare the surface morphologies with respect to the surface before and after oxyfluorination as shown in Fig. 2. It was observed from SEM photographs that carbon fiber roughness increased after oxyfluorination. As-received carbon fiber surface was clean and smooth and no other significant groove was observed. On the other hand, oxyfluorinated carbon fiber surface appeared shallow longitudinal grooves. This result indicates that the fiber surface was significantly etched due to the exposing to the fluorine gas.

![SEM images of carbon fibers before and after oxyfluorination](attachment:carbon_fiber_SEM.jpg)

Fig. 2. Scanning electron microscope images of carbon fibers before and after oxyfluorination. Oxyfluorination of the carbon fibers; oxygen/fluorine gas mixture (O$_2$/F$_2$ = 1:1), 100°C, 1 bar, 1 min.
in oxyfluorinated carbon fibers was higher than those of the as-received carbon fiber. This increase might be explained by the fluorine in the reaction gas atmosphere. Additional absorbance peaks at 2800–3000 cm⁻¹ were decreased, which indicates introduction of fluorinated and oxygenated species. The FT-IR spectra results indicate that the newly formed groups were spontaneously generated without the application of a catalyst or energy because of the high reactivity of O₂-F₂ molecules. Consequently, the oxyfluorinated carbon fibers have a higher peak intensity than that of the as-received carbon fibers, especially the intensity of the carbon-fluorine group of fibers. This result can affect the surface characteristics of the fibers, resulting in oxyfluorination of carbon fibers is largely used to improve their adhesive properties and/or wettability between the fibers and the matrix due to the increase in specific polarity and the formation of Oₓ-Fₓ bonding of the oxyfluorinated carbon fiber surfaces [30,31].

Fig. 4 show the plots of dynamic single fiber contact angle results of carbon fiber before and after oxyfluorination and their surface free energy. The similar sensitivity is likewise involved in surface free energy (gs), which consists of polar (γp) and dispersive (γd) component, and its polar component is determined by the interaction of the polar groups in the surface layer. Fig. 4a shows advancing contact angle of the mass-vs-immersion depth of the carbon fibers before and after oxyfluorination. The oxyfluorinated carbon fiber has slightly higher than that of the as-received carbon fiber in the water test due to the increase polarity between polar water and treated carbon fiber. Whereas, the carbon fiber before and after oxyfluorination showed almost

Fig. 3. Fourier transform infrared spectroscopy spectra of carbon fibers before and after oxyfluorination. Oxyfluorination of the carbon fibers; oxygen/fluorine gas mixture (O₂:F₂ = 1:1), 100°C, 1 bar, 1 min.

Fig. 4. Results of single-fiber contact angle of oxyfluorinated carbon fibers; (a) water-probe, (b) diiodomethane-probe, and (c) surface free energy.
unconverted in the diiodomethane probe as seen Fig. 4b. After the advancing contact angle of two test liquids have been obtained the surface free energy components can be determined. According to the Owens-Wendt-Rabel-Kaelble theory, the total surface free energy of the carbon fiber were calculate roughly to be (54.2 mN/m) [32]. Accordingly, the fibers surface were relatively change on hydrophilic from hydrophobic by oxyfluorination. This result indicates that the surface of the oxyfluorinated carbon fibers were highly converted to the polar surface, resulting in good surface energetics after oxyfluorination as also confirmed by Fig. 4c [33]. It shows that the surface free energy of the oxyfluorinated carbon fibers differed from those of the as-received carbon fibers. Both of polar and dispersive components of the carbon fibers increased after oxyfluorination. This result indicates that the oxyfluorinated carbon fibers lead to an increase in the surface free energy, which is mainly affected by the polar component. In addition, the dispersive component of the fibers increased. Normally, the dispersive component has a strong relation with surface roughness, meaning that the surface roughness varies according to the treatment, resulting in surface roughness after oxyfluorination as also confirmed by Fig. 2.

3.2. MAPP analysis

Fig. 5 shows the ATR-IR spectrum and structure of PP and MAPP. Fig. 5, compares absorption spectra for both PP and MAPP in the range of 500–4000 cm$^{-1}$. For MAPP compatibilizer, new peaks in range of 3500–3800 cm$^{-1}$, 1500–1800 cm$^{-1}$, 1260 cm$^{-1}$, 1000–1100 cm$^{-1}$, 806 cm$^{-1}$ were found to belong to the MA functionality. The possible chemical reaction on such interfacial bond formation between MA and PP was shown in Fig. 5 (right side). Additional absorbance peaks at 3500–3800 (-OH) cm$^{-1}$, 1500–1800 (C=O, COO-, anhydride group), 1260 cm$^{-1}$ (oxygen in the ring) and 1000–1100 cm$^{-1}$ (-OH, C-C-O), 806 cm$^{-1}$ (=C-H) were observed indicating related to the conversion of acid group to anhydrides due to the heat treatment by physical mixture [34-36]. These functional groups can lead good mechanical interfacial strength between oxyfluorinated CFs and Polarized MAPP matrix.

Fig. 6 shows the water contact angle and polar component as a function of the content of MA of MAPP. MA, maleic anhydride; MAPP, MA-grafted-polypropylene.

3.3. Mechanical properties and cross-section observation

Fig. 7 shows the illustration of proposed molecular interaction between oxyfluorinated carbon fiber and MAPP. The reaction between the carbon fiber and MAPP is explained in the following reaction. The OH group of the fibers reacts with the anhydride group and maleic acid group of MAPP forming a
It was found that $K_{IC}$ value increased up to the samples treated at OFCFsMA10 and then diminished. That is, the $K_{IC}$ value is increased with increasing the MA content on PP surface. As checked in Fig. 6, MA10 caused the lowest water contact angle due to the dramatically enhanced polar component, and theoretically confirmed in Fig. 9. But, the $K_{IC}$ value of OFCFsMA20 were decreased. These results can be thinkable that the $K_{IC}$ value decreased were indicates that the surface of PP were covered with excessive MA may form a weak layer resulting in decrease in interfacial adhesion due to the formation of new weak interface between the carbon fiber and matrices. Furthermore adding redundant MA may cause increased radical depolymerization of the PP molecule chains, thereby leading to the reduction of the mechanical properties [38]. In addition, theoretical calculations have the oxyfluorinated carbon fibers/PP composites have a higher work of adhesion than that of the other composites.

4. Conclusions

This study showed an increase on mechanical properties of composites as a result of the addition of MA modified PP to carbon fiber-reinforced MAPP composites. The oxyfluorination introduced much higher oxygen and fluorine content on the fiber surface increase to the surface free energy including polar and dispersive component of carbon fibers than as-received carbon fiber. The structure of PP consists of organized non-polar hydrocarbon chains, and PP generally have very poor wettability. While, after the MA reaction, it was observed that the oxygen functional group was formed at the interface by reaction between PP and MA, such polar component tended to grow with the MA contents. In conclusion, mechanical properties was found that $K_{IC}$ value increased up to the samples treated at OFCFsMA10. But, the $K_{IC}$ value of OFCFsMA20 were decreased. It was probably due to excessive MA-contents can be decreased mechanical properties of composites. In conclusion, surface treatment of carbon fiber and modified matrix plays an important role in improving the adhesion between fiber and matrix. The degree of theoretical (work of adhesion) and practical experiments ($K_{IC}$).

Fig. 7. Illustration of proposed molecular interaction between oxyfluorinated carbon fiber and maleic anhydride grafted-polypropylene.

Fig. 8. Scanning electron microscope image of the fracture surfaces of composites; (a) CFsPP, (b) OFCFsPP, and (c, d) OFCFsMA10.

Fig. 9. Work of adhesion and $K_{IC}$ of oxyfluorinated carbon fibers/maleic anhydride grafted-polypropylene composites. $K_{IC}$, fracture toughness.
polarity was improved by incorporating a MAPP. The addition of MAPP led to the enhancement of the fiber/matrix interfacial adhesion and hence mechanical properties.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

This study was supported by the “National Research Foundation of Korea (Project no.2015M3A7B4049716)” funded by the Korea government (MSIP), Republic of Korea.

References