EVALUATION OF THE IMPREGNATION CHARACTERISTICS OF THE CARBON FIBER REINFORCED COMPOSITES USING DISSOLVED POLYPROPYLENE

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**Keywords:** Carbon fiber reinforced thermoplastic, Polypropylene solution, Impregnation, carbon fiber sizing, Interlaminar shear strength.

1. Introduction

Fiber reinforced thermoplastic composites belong to a new class of customized composite intermediates consisting of reinforcements of carbon, glass and aramid fibres and engineering thermoplastic polymers to meet a variety of property and performance requirements in demanding environments [1]. Owing to many advantages of the carbon fiber, such as high strength, good electrical conductivity, and light weight, carbon fiber reinforced thermoplastic (CFRTP) has been used in a variety of application fields [2-3]. Especially carbon fabric is the most promising for CFRTP among various forms of fibres. Fabrics are unique in their ability to provide mechanical strength in both longitudinal as well as transverse directions. And it also offers very good specific strength, thermal conductivity [4]. However, CFRTP with fabric has a significant drawback regarding the manufacture of structural parts. The molten viscosity of thermoplastic resins is extremely high compared to that of thermoset resins, which makes it difficult to impregnate thermoplastic resin into fiber bundles [5]. Therefore a key issue is the achievement of good impregnation of the fabric with the thermoplastic polymers [6-7].

Conventionally, various methods have been used to manufacture the CFRTP such as film stacking, powder impregnation and solution impregnation. Film stacking and powder impregnation are common and easy method to make CFRTP [8-10]. However, these two methods cannot overcome the problem of poor impregnation. In our earlier work, the carbon fabric reinforced polypropylene (PP) was fabricated using the film stacking method, but PP was not impregnated into fiber bundle, as shown Fig. 1 [11]. On the other hand, solution impregnation entails solubilization of the matrix polymer at a suitable concentration and then immersion of the fiber within the solution. However, it is difficult to dissolve a large amount of PP in common solvents at room temperature because of its high solvent resistance and semi-crystalline structure. And solvent can be difficult to remove perfectly after impregnation and can cause voids [7].

![SEM topographies of the cross section of the carbon fabric/PP composites fabricated by conventional film stacking method.](image)

The solubility of the PP is low compared to other thermoplastics due to the semi-crystalline nature of the polymer. The crystals were harder to penetrate by the solvent due to the close packing found in this phase. And although there exists a concentration potential across the crystal/solvent layer, once the first fraction of solvent penetrates the crystal layer, the solvent starts to act as a barrier to keep more solvent from penetrating. On the other hand, the amorphous phase is more soluble than the crystalline phase [13-14]. Therefore PP can be easily dissolved in solvent by increasing amorphous phase. Polymer quenching is the representative method to
prevent the formation of crystals during the solidification process [15].

In this study, the novel sizing method using the PP solution impregnation was proposed to improve the degree of impregnation and interfacial characteristics between the carbon fabric and PP matrix. The PP sizing agent was fabricated by using the liquid nitrogen quenching method to impregnate the PP into carbon fiber bundles at the relatively low temperature around 50°C. After impregnation, the carbon fibers were dried by microwave, and the surface properties of PP sized fiber were characterized by x-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The carbon fiber reinforced PP composites (CFRPP) were fabricated by using film stacking method, and the degree of impregnation of PP was evaluated through the interlaminar shear strength (ILSS) of the CFRPP and SEM analysis.

2. Experimental

2.1 Fabrication of PP sizing agent

PP sizing agent was fabricated by using isotactic PP (i-PP) (427888, Sigma-Aldrich Co. LLC., USA). The i-PP should be dissolved in solvent at high temperature because of its high solvent resistance. Accordingly, the i-PP was dissolved in ortho-dichlorobenzene at 130°C for 1 hour to prepare a solution at 20 wt.% in the i-PP solution dissolved at high temperature, however, re-crystallization and solidification of PP was easily occurred as temperature decreases. Therefore, the heated PP solution was quenched by pouring liquid nitrogen to maintain the amorphous state of PP at low temperature. Quenched PP solution was kept in the freezer for 24 hours at -16°C to obtain the amorphous PP gel [16]. This PP gel comes to be re-dissolved more easily in solvent and maintained amorphous phase in solvent at lower temperature compared to i-PP pellet of semicrystalline phase. Therefore the PP gel was re-dissolved in ortho-dichlorobenzene at 50°C of minimum dissolvable temperature to make the PP sizing agent. In the re-dissolving process, it is important that re-dissolving temperature should be remained constant to prevent crystallization by drop in temperature. If ortho-dichlorobenzene is heated directly, the specific heat of ortho-dichlorobenzene is so low that it is tough to maintain the temperature of ortho-dichlorobenzene. Therefore, PP sizing agent was fabricated by heating the solution in water bath for 2 hours at 50°C as shown in Fig. 2.

XRD (X’pert Powder, PANalytical, Netherlands) analysis was used to investigate crystallinity of the quenched PP gel to assess the formation of the amorphous PP gel. 10 wt.% and 20 wt.% PP solutions were quenched by liquid nitrogen and dried them in the vacuum chamber for 12 hours at room temperature.

To check the influence of fabrication process of the PP sizing agent on the mechanical properties of the i-PP, tensile test with the film type specimen was performed by using quenched PP gel and re-dissolved PP solution. To remove the solvent completely, PP gel and re-dissolved solution were dried in the vacuum chamber for 12 hours at 30°C, respectively, and 0.07mm-thick PP film was made by using hot press at 220°C under 1 MPa. Tensile strength of the PP film was measured using a universal testing machine (INSTRON 5567A, MA, USA) based on the ASTM D638, standard test method for tensile test of polymers.

2.2 Sized Fiber Preparation

The PP sizing agent was applied on PAN-based CF fabric (12k plane weave, AKSA, Turkey) already sized with bisphenol A diglycidyl ether epoxy by the manufacturer. To remove existing epoxy sizing, the carbon fiber was heated in the vacuum condition for 3hour at 550°C. To analyze the effect of sizing process on the carbon fiber, carbon fiber surface was investigated by X-ray Photoelectron Spectroscopy (XPS) (K-Alpha, Thermo Scientific, UK), and tensile strength of the carbon fiber with respect to heat treatment time was measured by the single filament tensile test. The tensile strength of a single carbon filament was measured using a universal testing machine (INSTRON 5567A, MA,
USA) based on the ASTM D 3379-75, standard test method for high-modulus materials.

130mm×130mm area of carbon fabrics were immersed in the PP sizing agent for 10 minutes to fully impregnate the carbon fabric with PP sizing agent, and the temperature of the sizing agent during impregnation remained constant at 50°C. And then the carbon fabric impregnated with the PP sizing agent was dried by using microwave (using an effective intensity per unit mass of 12 kW/kg at 2.4 GHz) for 15 minutes to remove ortho-dichlorobenzene. Fig. 3 shows a specific diagram of the carbon fiber sizing and microwave drying process. After microwave drying, analyses with XRD and TGA (Thermogravimetric Analysis, Q600, TA instruments, USA) were performed to check the crystallization state of PP sizing agent and effect of residual solvent. TGA samples were heated at 10°C/min from 40°C to 600°C under nitrogen. The degree of impregnation using the PP sizing was investigated by SEM (JSM-5900, Jeol, Japan).

![Fig. 3 Schematic diagram of the carbon fiber sizing and microwave drying process.](image)

2.3 CFRPP composite fabrication

The CFRPP composites were fabricated using the film stacking method. i-PP pellets were used to make a PP film of 0.2 mm thickness using a hot press. 7 sheets of the PP film and 6 sheets of the CF fabric were stacked alternately and then pressed at 220 °C under 10MPa of pressure for 10 min. Fig. 4 shows the molding cycle of the CFRPP composite. If high pressure is abruptly applied, the PP cannot be impregnated into the fabric bundles but squeezed out through the inter-layer of the carbon fabric. Therefore, pressure was applied steadily during the cycle.

Short beam shear test was performed to evaluate ILSS of CFRPP, and cross-section of composites was observed by SEM to check impregnation state of PP between fibres. The ILSS of the CFRPP composites was measured using a universal testing machine (INSTRON 5969, MA, USA), based on the ASTM D2344. The short beam specimen size is about 6.5 mm x 24 mm x 4 mm of the width, the length, and the thickness. The loading speed was 1 mm/min. The maximum shear stress (τ) was calculated according to the following equation:

\[ \tau = 0.75 \times \frac{P_m}{bh} \]

where \( P_m \) is the maximum load during the test (N), \( b \) is the specimen width (mm), and \( h \) is the specimen thickness (mm).

![Fig. 4 Molding cycle for fabricating the CFRTP.](image)

3. Results and discussion

Fig. 5 shows the XRD patterns of specimens with respect to fabricating step for the PP sizing agent; PP pellet, quenched PP gel, dried PP gel in the vacuum chamber at 30°C for 12 hours.

![Fig. 5 XRD patterns of the specimens with respect to the fabrication step for the PP sizing agent.](image)

The dried PP gel specimens showed the same crystal structure with the PP pellet. Crystallinity of the PP pellet, 10 wt.%, and 20 wt.% dried PP gel
was 47.5%, 36.2% and 51.6%, respectively. The 20 wt.% dried PP gel showed higher crystallinity compared to the 10 wt.% dried PP gel at the same drying condition because of the initial solvent concentration difference. Generally, the amorphous PP cannot be obtained from the melted PP phase through the ordinary cooling process because crystallization rate of i-PP is faster than the cooling rate. In case of the PP solution before quenching, solvent already penetrated into the polymer chains and they were solidified simultaneously during the quenching process. Therefore, the stable amorphous state of the PP gel is obtained at room temperature [16].

Fig. 6 shows the tensile test result of PP films fabricated by using PP pellet, quenched PP gel and re-dissolved solution. Tensile strength of the film made of PP gel was similar to that of PP pellet, but tensile strength of the film made of re-dissolved PP solution slightly decreased by 0.7% compared to that of the PP pellet. In the films made of the quenched PP gel and the solution, deviation of tensile strength increase because the crystallization of the PP was occurred unevenly during the film fabricating process.

![Graph](image)

Fig. 6 Tensile strength of the PP films with respect to fabrication step for the PP sing agent.

To check the influence of heat treatment on the carbon fiber to remove the epoxy sizing, chemical composition change on the fiber surface and tensile strength of the carbon fiber were characterized by XPS and single filament tensile test. The XPS spectra of the carbon fiber surface, corresponding to binding energies between 0 eV and 1350 eV, are shown in Fig. 7.

![Graphs](image)

Fig. 7 XPS spectra of CF surfaces with respect to heat treatment time; (a) untreated, (b) 1h, (c) 2h, (d) 3h, (e) 4h.

Table 1. Ratio of C1s to with O1s respect to the heat treatment time.

<table>
<thead>
<tr>
<th>Treatment time</th>
<th>Untreated</th>
<th>1h</th>
<th>2h</th>
<th>3h</th>
<th>4h</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s/C1s</td>
<td>23.2</td>
<td>15.0</td>
<td>13.7</td>
<td>8.1</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The carbon and oxygen peak was mainly detected on the carbon fiber surface, and the ratio of carbon to oxygen decreased as heat treatment time increased as shown in Table 1. This means that the epoxy sizing which has high oxygen radical was removed effectively. Therefore, sizing removal effect was the highest in 4 hours heat treatment. However, long heat treatment at high temperature could damage to the carbon fiber. Fig. 8 shows the single filament tensile test results with respect to heat treatment time. The tensile strength of the carbon fiber decreased with heat treatment time. The tensile strength of the carbon fiber treated for 4
hours decreased by 15.8 % compared to that of the untreated carbon fiber, and this was caused by thermal degradation of the carbon fiber. On the other hand, the tensile strength of the carbon fiber treated for 3 hours decreased by 8.15 % compared to that of the untreated carbon fiber, but this value was not significantly different with that of the carbon fiber treated for 2 hours. Therefore, heat treatment for 3 hours was selected as the desizing method of the carbon fiber based on the XPS and tensile test results.

Fabricated PP sizing agent was applied on epoxy sized and desized carbon fabrics, respectively. And the PP sized carbon fabrics were dried by using microwave to remove the solvent of the PP sizing agent.

![Fig. 8 Single filament tensile strength of the CF with respect to heat treatment time.](image)

![Fig. 9 TGA curve of dried PP sizing agent on the carbon fiber.](image)

![Fig. 10 XRD patterns of the PP sizing agent applied on the carbon fibre.](image)

To investigate the crystallinity of the PP sizing agent impregnated into the carbon fabric and its impregnation state with and without the epoxy sizing, XRD and SEM analyses were performed. Fig.10 shows XRD patterns of the PP sizing agent dried by microwave on the carbon fiber surface. Crystallinity and crystal structure of the PP sizing agent was almost same regardless of epoxy sizing, because PP sizing agent didn’t react with epoxy sizing on the carbon fiber surface during the microwave heating. On the other hand, different morphologies according to existence of epoxy sizing were observed in the SEM results shown in Fig. 11. In the epoxy sized carbon fibre, the PP sizing and the carbon fibres were separated each other as shown in Fig. 11(a). In case of de-sized carbon fibre, PP sizing was stuck on the carbon fiber surface, and it was connected with the carbon fibre by large numbers of fine bridges
that de-sized carbon fiber surface have the advantage over the epoxy sized carbon fiber surface to improve interfacial characteristics with the PP sizing agent.

Fig. 11 SEM topographies of the PP sized carbon fiber: (a) untreated carbon fibre (epoxy sized), (b) desized carbon fibre.

Fig. 12 shows short beam test results of the CFRPP composite specimens with respect to surface treatment methods. The ILSS of the specimen reinforced with de-sized carbon fibre increased by 46.1% compared to that of the specimen reinforced with untreated (epoxy sized) carbon fibre. This implies that epoxy sizing is not only ineffective in improving the interfacial strength between carbon fiber and the PP matrix, it also works as defect because the interface between the PP and the epoxy sizing is weak. In case of the PP sized specimen without epoxy de-sizing, the ILSS increased by 33.6% compared to that of untreated specimen. This is caused by partial improvement of the wettability between the epoxy sized carbon fibre and PP matrix due to the PP sizing agent. On the other hands, the specimen reinforced with PP sized carbon fibre after epoxy de-sizing showed the highest ILSS compared to the others and it increased by 102.4% compared to that of the untreated specimen.

Fig. 12 ILSS of the CFRPP composite specimens with respect to the surface treatment.

Fig. 13 shows the SEM results of the composites cross-section area to check impregnation state of the PP matrix between the fibres. Untreated specimen was not impregnated into the carbon fiber tow as shown in Fig. 13(a). But the specimens reinforced with the de-sized or PP sized carbon fibres showed slightly improved impregnation state as shown Fig. 13(b) and (c). In the specimen reinforced with the PP sized carbon fibres after de-sizing process, the best impregnation state was observed as shown in Fig. 13(d), which led to the highest ILSS in the short beam test. This might be caused by the pre-impregnated PP sizing agent into the tow.
4. Conclusions
In this study, new sizing method using the PP sizing agent and the microwave drying was suggested and each processes to fabricate the PP sizing agent and the CFRPP were evaluated. The following conclusions were derived from the results.
1. Amorphous PP gel was obtained by quenching the PP solution using nitrogen, which can be re-dissolved by the solvent around 50°C.
2. The fabricating process of the PP sizing agent did not affect the tensile strength of the i-PP.
3. The tensile strength of the carbon fiber heat treated for 3 hour decreased by 8.15 % compared to that of untreated carbon fiber. And epoxy sizing was effectively removed by heat treatment for 3 hour without serious damage.
4. The residual solvent in PP sizing agent was effectively removed by microwave drying.
5. In the specimen reinforced with the PP sized carbon fibres without epoxy de-sizing, ILSS increased by 33.6% compared to that of the specimen reinforced with the untreated carbon fibres.
6. ILSS of the specimen reinforced with the PP sized carbon fibres after epoxy de-sizing was higher than those of the others and increased by 102.4% compared to that of the specimen reinforced with the untreated carbon fibres.

From this study, it was concluded that the new sizing method using the PP sizing agent and microwave drying is promising way to improve the degree of impregnation and interfacial strength of the CFRPP.

References


