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Evaluation of the impregnation characteristics of carbon fiber-reinforced composites using dissolved polypropylene

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ABSTRACT

Owing to the many advantages of carbon fiber, such as its high strength, good electrical conductivity, and light weight, carbon fiber-reinforced thermoplastics (CFRTPs) have been used in a variety of applications. However, the use of CFRTPs in fabrics suffers a significant drawback regarding their manufacture. 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. Therefore, a key issue is the achievement of good impregnation of the fabric with the thermoplastic polymers. In this study, a novel sizing method using polypropylene (PP) solution impregnation was proposed to improve the degree of impregnation and the interfacial characteristics between the carbon fabric and PP matrix. After impregnation, the carbon fibers were dried by microwave, and the surface properties of the PP sized fibers were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The carbon fiber-reinforced PP (CFRPP) composites were fabricated using a film stacking method. The interlaminar shear strength (ILSS) was measured using the three point bending test. From the test results, the ILSS of the specimen reinforced with the PP sized carbon fibers after epoxy de-sizing increased by 102.4% compared to that of the specimen reinforced with the untreated carbon fibers.

1. Introduction

Fiber-reinforced thermoplastic composites belong to a new class of customized composite intermediates consisting of reinforcing materials, such as carbon, glass and aramid fibers, and thermoplastic polymers, to meet a variety of performance requirements in demanding environments [1]. Owing to the many advantages of carbon fiber, such as its high strength, good electrical conductivity, and light weight, carbon fiber-reinforced thermoplastics (CFRTPs) have been used in a variety of applications [2,3]. In particular, carbon fabric is a promising field for the application of CFRTPs with various forms of fibers. Fabrics are unique in their ability to provide mechanical strength in both the longitudinal and transverse directions; they also offer very good specific strength and thermal conductivity [4]. As the use of CFRTPs increases, many studies dealing with the mechanical properties and failure mechanism of CFRTPs under a wide range of conditions have been published [5–8]. De Baere et al. investigated the in-plane shear fatigue behavior of a carbon fabric-reinforced PPS by performing and comparing three-rail shear experiments and tensile experiments with $[\pm 45^\circ]_{4s}$. However, the use of CFRTPs in fabrics suffers a significant drawback regarding their manufacture. 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 [9]. Therefore, a key issue is the achievement of good impregnation of the fabric with the thermoplastic polymers [10].

Conventionally, various methods have been used to manufacture CFRTPs, such as film stacking, powder impregnation and solution impregnation. Film stacking is one of common methods to make CFRTPs [11–13]. Powder impregnation was developed to promote fiber impregnation and this method is appropriate when the diameter of polymer particles is similar to that of the fiber. But this is difficult to achieve, as the particle size is frequently limited by economic considerations and the effectiveness of the method used to prepare the powder [14]. On the other hand, solution impregnation entails solubilization of the matrix polymer at a suitable concentration followed by the immersion of the fiber within the solution. Wu et al. investigated a solution processing technique and the mechanical properties of carbon fiber reinforced polyethersulfone composites [15]. However, this method 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. Additionally, the solvent can be difficult to completely remove after impregnation and can cause voids.

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The solubility of PP is low compared to other thermoplastics due to the semi-crystalline nature of the polymer. The crystals are harder to penetrate by the solvent due to the close packing found in this phase. 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 [16–18]. Therefore, PP can be easily solubilized by increasing the amount of amorphous phase. Polymer quenching is the standard method to prevent the formation of crystals during the solidification process [19]. However fully amorphous isotactic PP can only be obtained by cooling the equilibrium liquid at a rate of about 1000 K/s, or faster, to a temperature lower than the glass transition temperature. Therefore, it is difficult to obtain amorphous PP through existing quenching method [20].

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

2. Experiments

2.1. Fabrication of the PP sizing agent

The PP sizing agent was fabricated using isotactic PP (i-PP) (427888, Sigma–Aldrich Co. LLC., USA). The i-PP should be dissolved in solvent at a high temperature because of its high solvent resistance. Accordingly, the i-PP was dissolved in *ortho*-dichlorobenzene at 130 °C for 1 h to prepare a solution at 20 wt%. In the i-PP solution dissolved at a high temperature, however, the re-crystallization and solidification of PP easily occurred as the temperature decreased. Therefore, the heated PP solution was quenched by the addition of liquid nitrogen to maintain the amorphous state of PP at low temperature. The quenched PP solution was kept in the freezer for 24 h at −16 °C to obtain an amorphous PP gel [21]. This PP gel is re-dissolved more easily in solvent and maintained its amorphous phase in solvent at lower temperatures compared to a semi-crystalline i-PP pellet. Therefore, the PP gel was re-dissolved in *ortho*-dichlorobenzene at 50 °C, the minimum dissolvable temperature to make the PP sizing agent. In the re-dissolving process, it is important that the temperature be kept constant to prevent crystallization caused by a drop in the temperature. If the *ortho*-dichlorobenzene is heated directly, its specific heat is so low that it is difficult to maintain its temperature. Therefore, the PP sizing agent was fabricated by heating the solution in a water bath for 2 h at 50 °C, as shown in Fig. 1.

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

To check the influence of the fabrication process of the PP sizing agent on the mechanical properties of the i-PP, the tensile test with a film-type specimen was performed using the quenched PP gel and the re-dissolved PP solution. To remove the solvent completely, the PP gel and the re-dissolved solution were dried in a vacuum chamber for 12 h at 30 °C, and a 0.07 mm thick PP film was made using a hot press at 220 °C and 1 MPa. The tensile strength of the PP film was measured using a universal testing machine (INSTRON 5567A, MA, USA) based on ASTM D638, the standard test method for the tensile test of polymers [22].

2.2. Sized fiber preparation

The PP sizing agent was applied on a PAN (polyacrylonitrile) based CF fabric (12k plane weave, AKSA, Turkey) already sized with bisphenol A diglycidyl ether epoxy by the manufacturer. In this study, we used plain woven carbon fabrics without any change of stacking sequence and concentrated on the effect of degree of impregnation on the mechanical properties with respect to the impregnating methods. To remove the existing epoxy sizing, the carbon fabric was heated under vacuum for 3 h at 550 °C. To analyze the effect of the de-sizing process on the carbon fiber, the carbon fiber surface was investigated by X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific, UK), and the tensile strength of the carbon fiber as a function of the 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 ASTM D 3379, the standard test method for high-modulus materials [23]. The loading speed was 0.5 mm/min. The specimen was pulled to failure and the tensile strength and modulus were calculated from the usual formulas.

A 130 mm × 130 mm area of carbon fabric was immersed in the PP sizing agent for 10 min to fully impregnate the carbon fabric with the PP sizing agent, and the temperature of the sizing agent during impregnation was kept constant at 50 °C. The carbon fabric impregnated with the PP sizing agent was then dried by microwave (using an effective intensity per unit mass of 12 kW/kg at 2.4 GHz) for 15 min to remove any excess *ortho*-dichlorobenzene. Fig. 2 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 morphology of the PP sizing agent and the effect of any residual solvent. TGA samples were heated at 10 °C/min from 40 °C to 600 °C under a nitrogen atmosphere. The degree of impregnation using the PP sizing agent was investigated by SEM (JSM-5900, Jeol, Japan).

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. Seven sheets of the PP film and six sheets of the CF fabric were stacked alternately and then pressed at 220 °C under 10 MPa of pressure for 10 min. Fig. 3 shows the molding cycle of the CFRPP composites. If high pressure is abruptly applied, the PP is not impregnated into the fabric bundles but is instead squeezed out through the inter-layer of the carbon fabric. Therefore, pressure was applied steadily during the cycle.

A short beam shear test was performed to compare the interlaminar failure resistance of the CFRPP composites with respect to the fabricating methods. But, the short-beam shear test measures the "apparent" inter laminar shear strength of composite materials. Thus, the short-beam shear method is not appropriate for generating design allowables but it provides information about the quality of the adhesion at the fiber/matrix interface [24]. The ILSS of the CFRPP composites was measured using a universal testing machine (INSTRON 5969, MA, USA), based on ASTM D2344 [25]. The short beam specimen size was approximately