Surface Modification of Carbon Fiber Using a Titania Solution and the Mechanical Properties of CFRTP Fabricated Using That Method

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Abstract

Long molding times and the impossibility of remelting or reforming carbon fiber-reinforced plastics (CFRPs) that contain thermosetting resin after molding have led researchers to focus on carbon fiber-reinforced thermoplastics (CFRTPs) made with thermoplastic resin. Compared to CFRPs, CFRTPs are easier to recycle, but they generally exhibit strength properties that are inferior to those of CFRPs due to poor adhesion between the carbon fiber and the resin. To address this issue, we devised a new surface modification method (using a titania solution) to improve adhesion between fiber and the resin. Fragmentation and tensile tests were used to evaluate the effect of the surface modification method on CFRTP adhesion. The results indicate that surface modification can enhance adhesion in CFRTP, which may improve the material’s mechanical properties.

Key Words: Thermoplastic resin, CFRTP, Strength, Titania solution, Surface modification

1. Introduction

Recently, fiber-reinforced plastics (FRPs) have seen wide use in automotive, aerospace, marine, and other industrial applications due to their relatively high specific strength, stiffness, and toughness[1, 2]. Since FRPs use thermosetting resin as a matrix, there are concerns about recyclability and high-speed molding. By contrast, fiber-reinforced thermoplastics (FRTPs) that use thermoplastic resin, which softened by melting, are attracting attention to their excellent recyclability and faster molding times [3]. To address the inferior mechanical characteristics of FRTP fabricated with continuous fiber using conventional molding methods compared to FRP, we previously developed a solution prepgreg molding method that makes possible high fiber content on par with that of FRP (i.e., mechanical characteristics on par with those of FRP)[4, 5]. The solution prepgreg molding method can also be applied to materials such as engineering plastics, super engineering plastics[6], and cellulose resins[7], broadening the range of applications in which FRTPs made using thermoplastic resin can be used. Making FRPs from strong fibers and a well-suited matrix may not necessarily result in a strong material. The fiber-matrix interface is equally important in determining the overall performance of the FRP. Reports in the literature describe how researchers have treated the surface of reinforcing fibers to improve adhesion between the fibers and the resin. For example, methods such as oxygen plasma treatment [8, 9], gamma-ray radiation [10], ammonia solution[11], gas phase oxidation[12], and thermal treatment[13] are widely used to improve the interfacial adhesion of carbon fiber to the polymer matrix. However, some of these common techniques used to increase the surface area of the fiber also destroy its surface bonding characteristics, resulting in an overall decrease in FRP performance. There is little research related to the adhesion of continuous carbon fiber and thermoplastic resin, and none on the topic of polyethylene terephthalate (PET), a general-purpose thermoplastic resin that is characterized by low cost and excellent mechanical characteristics. Surface-treated carbon fiber is used as-is so that it will adhere to epoxy in manufacturing applications; since the functional groups in epoxy resin and PET resin that determine adhesion differ, there is a need for additional study of treatment methods.

In this paper, we (a) propose titania solution formulated using titanium alkoxide with coordinated acetylacetone as a surface modification agent for carbon fiber to improve adhesion between the fiber and PET thermoplastic resin while minimizing the treatment process’s adverse impact on the strength of the reinforcing fibers caused by the surface modification process, (b) evaluate adhesion between carbon fiber and PET resin, and (c) confirm the...
effectiveness of the proposed method. We also fabricate CFRTP using continuous fiber and study the effects on its mechanical characteristics.

2. Surface modification agent for reinforcing fiber and associated formulation method

Because carbon fiber has a hexagonal structure and a relatively stable surface, researchers have had difficulty developing surface coatings for use with the material. Efforts to improve adhesion with other materials by roughening the surface of the fibers, for example by using plasma treatment, have resulted in a slight reduction in the strength of the carbon fibers. We address this issue by proposing a titania solution as a surface modification agent to cover the surface of the carbon fibers with a coating of titanium oxide (a compound of titanium), as shown in Fig. 1. Bonding at the interface between the carbon fiber and PET resin is improved by using titanium alkoxide with coordinated acetylacetone to thermally treat the fiber in an oxidizing environment (in atmospheric air) and then subjecting the material to dehydration concentration to leave the carbon fibers coated with a film of titanium oxide. Since titanium compounds cross-link readily with compounds such as epoxy resin and polyvinyl alcohol resin, they are used in synthetic resin and adhesive applications [14]. Erck[15] reported favorable adhesion when graphite was coated with a titanium compound. Although the specific reason for the improvement is not clearly understood at present, it is π-stacking interactions from π electron of coordinated complex in acetylacetone of TiO₂ compound and π electrons on the graphite surface of carbon fiber, make it possible for titanium compounds to form a coating that adheres strongly to the surface of the carbon fibers. About the interface between PET and titanium compound, PET can be inferred that the carbon fiber treated with titanium compound will absorb moisture in the air and cause hydrolysis to form a hydroxyl group. The hydroxyl group will form a hydrogen bond with the PET to improve the interface performance between carbon fiber and PET [14]. In addition, the hexagonal structure of titanium compound will form π-stacking interactions with the benzene ring of PET to improve the interface performance also.

The surface modification agent was formulated and applied as follows:

1) First, 100 mmol of Ti[(O(CH₂)₂CH₃)]₄ (“TTnB”) was mixed with isopropanol (IPA) (123 mmol) and acetylacetone (100 mmol). Next, a mixed solution of hydrazine monohydrochloride (4 mmol), water (180 mmol), and ethanol (52.94 mL) was added gradually to facilitate a reaction between the acetylacetone and the TTnB, with the IPA serving as a catalyst. The result of this step was a titanium alkoxide solution.

2) Carbon fiber sheets were immersed in the titanium alkoxide solution. Then the sheets were removed and heat-treated in an atmospheric air environment at 400 ℃ to prompt dehydration concentration, forming a titanium oxide (titanium compound) coating on the surface of the carbon fibers.

Elemental analysis was performed on the surface of the surface-modified sample. EDS(Energy dispersive X-ray spectrometry, JEOL Ltd.) was used, and the photo are shown in Fig. 2. The results are summarized in Table 1, and O₂ and Ti increased on the fiber surface due to fiber surface modification.

3. CFRTP material composition and molding

To mold continuous fiber CFRTP, carbon fiber fabric (Toray Industries, Inc.; T300; 198 g/m²) was used as the reinforcing fiber, and copolyester (Abbreviation: PET; Toyobo Co., Ltd.; Vylon SI-173) as the thermoplastic resin. For comparison purposes, epoxy

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Table 1  EDS measurements after fiber modification.

|       | Mass [%] | Mol [%] |
|-------|----------|---------|
| C     | 84.04    | 89.93   |
| O     | 10.82    | 8.69    |
| Ti    | 5.14     | 1.38    |

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Fig. 1  Adhesion of carbon fiber and PET resin.

Fig. 2  Element distribution of fiber surface.
(Nagase ChemteX Corporation, XNR 6815) was also used as a thermosetting resin.

CFRTP was molded using the solution prepreg molding method[4], which yields high fiber content. PET resin was dissolved in an N-methylpyrrolidone (NMP) solution to create a PET resin solution with a mass fraction of 18 %, as shown in Fig. 3. This solution was impregnated into a sheet of continuous carbon fiber fabric, which was then heated in a vacuum to volatilize the solution. The resulting prepreg was laminated into a mold and pressed using a vacuum hot press to fabricate the CFRTP.

4. Experimental results and observations

4.1 Effects of surface modification on fiber strength

A tensile test was conducted on single fibers to assess how surface modification changed the mechanical characteristics of the carbon fiber. The test was carried out using the EZ-S50N (Shimadzu Corporation) with a sample span of 20 mm, a tensile speed of 1 mm/min., and 30 samples. Single fibers were extracted from carbon fiber fabric (“Blank”). The surface of some fibers was treated with corona discharge (PS-1M, Shinko Electric and Instrumentation Co., Ltd., Processing condition: 12 KV, Speed 10 mm/sec) (“Corona”), while other fibers were treated using the proposed titania solution (“Titania”). The fiber diameter after treatment was measured using an SEM. Fig. 4 are the plots of the Weibull probability of the tensile strengths of carbon fibers for different surface modification methods. F is a probability of fiber failure. From the Weibull diagram, the expected value and the variance of the strength of untreated carbon fiber (Blank) are 2.54 GPa and 0.122 GPa, respectively. The carbon fiber strength by corona treatment are 1.85 GPa and 0.234. The carbon fiber strength by titania treatment are 2.62 GPa and 0.134. Whereas corona discharge resulted in a decrease in the strength of the carbon fibers after surface modification, fibers treated with the titania solution maintained about the same strength, indicating that there was no damage to the fibers.

4.2 Evaluation of adhesion between fiber and resin

Bundles of fibers were removed from the carbon fiber fabric, combined with PET resin, and fractured. Fig. 5 provides a cross-sectional SEM photograph of the fracture surface. Compared to fibers that did not undergo surface modification, fibers that underwent treatment with the titania solution exhibited greater resin adhesion, indicating the effectiveness of the surface modification method.

A fragmentation test was carried out to provide a quantitative evaluation of adhesion between the carbon fiber and the resin. Fig. 6 provides an overview of the testing process. A resin solution was poured into a mold to which a single carbon fiber had been secured using tape, and the NMP was volatilized gradually so as
to avoid surface irregularities at a temperature of 150 °C over 24 hours. Next, the resin was completely hardened in a vacuum dryer and cut into samples. The samples were placed under tension in a small material tester (IMC-90FD, Imoto Machinery Co., Ltd.) until the fiber in the resin fractured, and the fiber fracture length was measured under a microscope. The interfacial shear strength (IFSS) was then calculated using the formula $\text{IFSS} = \frac{3D\sigma_f}{8\bar{L}}$ in accordance with JIS K 7176 using the average of the measured fiber fracture length values, $\bar{L}$; the fiber diameter (as measured by SEM), $D$; and the fiber tensile strength, $\sigma_f$, as measured in 4.1. Single fibers were then cut from a piece of carbon fiber fabric to create samples to test adhesion with PET resin. Some were left untreated (“PET”), while others were subjected to corona surface modification (“PET [Corona]”) or treated with the titania solution (“PET [Titania]”). For comparative purposes, a number of single fibers were also extracted from the carbon fiber fabric to test for adhesion with epoxy resin (“Epoxy”) (Denatite XNR 6815, Nagase Chemtex Corporation). Twelve samples were prepared for each type.

Fig. 7 presents the measured adhesion results. Whereas corona discharge treatment provided little increase, surface modification with the titania solution increased adhesion between the fiber and the resin while maintaining the fiber’s innate mechanical characteristics and without damaging the surface of the fiber. As a result, the interfacial shear strength was 25.4 MPa, an increase of about 42 % compared to the PET sample. The PET (Titania) samples exhibited interfacial shear strength on par with that of the epoxy thermoplastic resin samples (Epoxy), indicating that treatment with titania solution is a fairly effective surface modification technique.

4.3 Mechanical properties of CFRTP

Tensile testing was performed in accordance with JIS K7073 (Correspond with ASTM D3039) in order to evaluate the mechanical characteristics of CFRTP using samples prepared both with and without titania solution surface modification. In the tensile test, the tensile direction was along the warp direction of the fabric.

Samples measured 120 mm (L) by 15 mm (W) by 1 mm (thickness), and the tab length was 30 mm. An Auto Graph AG-20 KND (Shimadzu Corporation) was used to perform the test. The sample speed $V$ was 1.0 mm/min, and 5 samples of each type were prepared: untreated fiber from carbon fiber fabric (“CFRTP”), molded CFRTP treated with titania solution (“CFRTP [Ti]”), and CFRP fabricated using epoxy thermoset resin and the VaRTM method (“CFRP”). As previously mentioned, the surface modification method of fibers is as same as presented in section 2.

Fig. 8 provides a photograph showing where CFRTP treated with titania solution fractured during tensile testing. The brittle nature of the fractures is likely the result of the surface modification.

Fig. 9 provides an example tensile load-displacement curve for CFRTP treated with titania solution as measured during the tensile test. The material’s tensile strength was calculated using the maximum value from that curve. In addition, the tensile modulus was calculated from output of the strain gauges on the sample.
Fig. 10 summarizes the tensile modulus for each sample type. To facilitate comparison, each sample was molded to have fiber content as close to 45% as possible. Based on the fiber reinforced plastic’s rules, the strength of FRP is proportional to the fiber content. To facilitate comparison, each sample was molded to have fiber content as close to 45%. As can be seen from Fig. 10, all samples exhibited approximately the same tensile modulus, regardless of whether they were fabricated from thermoplastic resin, and regardless of whether they underwent surface modification. This similarly in results is because the tensile modulus reflects the conditions at the initial stage of tensile load, which are primarily determined by fiber content.

Fig. 11 summarizes each sample’s tensile strength. The CFRTP treated with titania solution was 75% stronger than untreated samples. This significant increase in strength indicates the effectiveness of the titania solution surface modification method. However, the surface-treated CFRTP exhibited mechanical characteristics that were inferior to those of CFRP (94.2% of the CFRP value). Future investigation will be required in order to determine whether that difference is the result of insufficient adhesive force between the fiber and resin or an effect of the PET resin.

5. Conclusion

We proposed treating the surface of carbon fibers with titania solution in order to develop a continuous fiber-reinforced thermoplastic plastic with good recyclability and mechanical characteristics. We then investigated the effectiveness of that method using PET thermoplastic resin and carbon fibers.

Surface modification of carbon fibers with titania solution significantly increased adhesion between the two materials while causing little damage to the fibers. In addition, CFRTP molded using surface-treated carbon fibers exhibited tensile strength that was 75% higher than control samples, indicating the effectiveness of the method.

We plan to investigate whether this treatment method can be applied to other thermoplastic resins.

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