Enhancement of Surface Adhesion between Thermoplastic Resin and Carbon Fiber Using Polymer Colloids

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Abstract

To enhance the interfacial adhesion between carbon fiber and thermoplastic resin, poly(methyl methacrylate) (PMMA) particles were adsorbed on the carbon fiber. It was found that positively charged PMMA particles were readily adsorbed on the carbon fiber and the interfacial shear strength between the modified carbon fiber and the resin was enhanced. In addition, the interaction between the carbon fiber coated with particles to the PMMA resin would be improved, and the surface adhesion between them was strengthened.

Keywords: Carbon Fiber, Polymer Colloid, Surface Adhesion

1. Introduction

Carbon fibers are used to make carbon fiber reinforced plastic (CFRP), one of the most well-known composite materials. The interaction between materials plays an important role in the improvement of the mechanical properties of composite materials [1, 2]. Because of the importance of enhancing the strength between resin and carbon fiber in the case of CFRP, modifications of the carbon fiber surface have been investigated by various techniques such as polymer coating [3-5]. The purpose of the present study is improvement of the interfacial adhesion between carbon fiber and resin. We have developed an innovative technique for the adsorption of polymeric particles on carbon fibers to improve the interfacial adhesion to the resin. The role of polymer colloids is to act as a glue between carbon fiber and resin. Polymerization without surfactants, known as soap-free emulsion polymerization [6], was conducted to prevent the surfaces of carbon fibers from being contaminated by the surfactants in the adsorption process. An ionic water-soluble initiator was used to enable the soap-free emulsion polymerization, and the charge of the synthesized particle was determined by the functional group of the initiator [7, 8]. Epoxy resins are often used as a thermosetting resin in many studies [1, 9, 10]; however, in the case poly(methyl methacrylate) PMMA was chosen as a thermoplastic resin because the monomers that compose the film formed a particulate easily in the soap-free emulsion polymerization [11]. In the present research, we investigated the following: adsorption of PMMA particles with negative or positive charge on the surface of carbon fibers; fragmentation testing using a tensile test apparatus to evaluate the mechanical properties of the composite material made by the combination of modified carbon fiber and thermoplastic resin.

2. Experimental

The water used in the soap-free emulsion polymerization was purified using a purification system (RFD240NA, Advantech, Japan) with its conductivity of < $1.0X10^{-5}$ S/m, and nitrogen gas was then bubbled into the water to remove any dissolved oxygen. Methyl methacrylate (MMA, Tokyo Chemical Industry, Japan) was used as a monomer for the polymerization. The monomer was selected to correspond to the thermoplastic resin, which was a film including PMMA (HBS006, Mitsubishi Rayon). Potassium persulfate (KPS, Sigma Aldrich, Japan) and 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (V-50, Sigma Aldrich, Japan) were used as radical initiators without further purification. KPS or V-50 enabled the particles to be charged negatively or positively, respectively. Their chemical structures are shown in **Fig. 1**. Carbon fibers through the standard electrochemical oxidation method and modifications (HTS40, Toho Tenax, Japan) were used after the treatment with acetone to remove the sizing agents. The experimental conditions employed for the polymerization [12] are listed in Table 1. The temperature of the reactor and the rotation speed of the impeller in the reactor were controlled by a magnetic stirrer equipped with a heater (RCH-20L, EYELA, Japan). The carbon fibers were immersed in these polymer colloids for 1 day to allow them to adsorb the polymeric particles on their surfaces. They were then washed with water to remove the excess polymeric particles and dried at room temperature. The morphologies of the carbon fibers and particles were observed by field emission scanning electron microcopy (JSM-7500FA, JEOL, Japan). The amounts of adsorbed PMMA particles on the carbon fibers were calculated from the TG-curve by thermo gravimetry analyzer (DTG-60AH, SHIMADZU, Japan).

To evaluate the interfacial shear strength of a single carbon fiber, fragmentation tests [9] under a microscope (MS-804, MORITEX Corporation, Japan) were carried out using a tensile testing machine (10073B, JAPAN HIGH TECH). The specimen was prepared as follows: Before and after adsorption of PMMA particles, the single carbon fiber, sandwiched by two films including PMMA was hot-pressed at 180 ^{o}C for 1 min by a heater press machine (N4003-00, NPa system, Japan), and then quenched by placing the film between two steel plates cooled with water at 25 ^{o}C. Then, the film was cut into strip specimen geometry with 25 mm gauge length and 4 mm width. Specimens were tested until the fragmentation process saturated, which occurred at a tensile strain of about 15 %. The average length of the fragmentation carbon fibers ($<L>$) was measured. Fragmentation tests of a single carbon fiber were carried out for four samples with each carbon fiber. The interfacial shear strength (τ_m) between carbon fiber and resin was calculated by the following equation [13]:

$$\tau_m = \frac{D\sigma_f}{2l_c}, \qquad (1)$$

where the effective length (l_c) is given by

$$< L >= \frac{3}{4} l_c . \qquad (2)$$

The average diameter of the carbon fiber (D) was measured using the diffraction of a He-Ne laser beam from the fiber. The tensile strength (σ_f) of the carbon fibers (the lengths of which were taken to be l_c) was estimated from Weibull analysis using the results of the single fiber tensile tests [14]. The tensile tests were carried out using a tensile testing machine (SDW-1000SS-E-SL, IMADA SEISAKUSHO, Japan). The testing machine was operated at a gauge length of 25 mm and a crosshead speed of 1 mm min^{-1} according to ASTM C-1577-03 standards.

3. Results and discussion

To investigate the adsorption ability of polymeric particles on the carbon fiber, polymer colloids were prepared by soap-free emulsion polymerization using KPS or V-50. MMA is well known as a typical monomer and was used for the polymerization. **Fig. 2** shows the SEM images of the carbon fibers modified with the two kinds of polymer colloids. It was found that many more positively charged polymeric particles, synthesized with V-50, were adsorbed on the carbon fibers than were negatively charged polymeric particles, synthesized with KPS. This implies that the carbon fibers are negatively charged in water and that the attractive force might originate from the electrostatic interaction between the fiber and particles. Other researchers have reported the zeta potential of carbon fibers as being negative [15]. Positively charged polymer colloids were effective in being adsorbed onto the surface of the carbon fibers. At that time, the amount of the PMMA particles adsorbed on the carbon fiber was calculated to be 0.056 g/m^2 from the TG-curve.

The one carbon fiber before and after the modification using polymer colloids charged positively was between the films using the hot press machine to make the specimen for the fragmentation tests. As a result, the interfacial shear strength between the carbon fiber and resin was 8.18 ± 1.73 MPa and 13.3 ± 3.40 MPa for the carbon fiber and PMMA-coated carbon fiber, respectively. The data of the experiments was listed in Table 2. It was found that the interfacial shear strength between the carbon fiber and thermoplastic resin was enhanced by the adsorption of PMMA particles on the surface of the carbon fiber.

Because one of the components of the resin was MMA, the interaction between the modified carbon fiber and the resin was improved by the adsorbed PMMA particles on the carbon fiber. Additionally, PMMA particles adsorbed on the carbon fiber was observed in the air at the rate of temperature increase, 50 ^{o}C/min, by a digital microscope (KH-8700, HiROX, Japan) as shown in **Fig. 3**. It was clear that PMMA particles were melted to be deformed and coated the surface of the carbon fiber uniformly. Hence, in making the modified carbon fiber and the resin composited by increasing the temperature and pressure, the surface adhesion between them was strengthened.

Particles were adsorbed easily on the carbon fiber due to electrostatic forces, and this method was useful for enhancement of surface adhesion between thermoplastic resin.

4. Conclusions

To enhance the surface adhesion between carbon fibers and resin in CFRTP, polymer colloids were used to induce adsorption of polymeric particles on the surface of the carbon fibers. Positively charged PMMA particles were readily adsorbed on the carbon fiber because of the electrostatic force on the carbon fiber and the interfacial shear strength between the modified carbon fiber and the resin was enhanced. Because of the PMMA particles on the surface of the carbon fibers, the interaction between the carbon fiber and the resin was improved by the adsorbed PMMA particles and the surface adhesion was strengthened.

Acknowledgement

This study was supported financially in part by Grant-in-Aid for Scientific Research (C) from the MEXT of Japan, (No. 25420817). The acrylate films were given from

Mitsubishi Rayon Co., LTD. Dr. Tadashige Ikeda and Mr. Ryo Hashimoto in Nagoya University helped to make composite materials.

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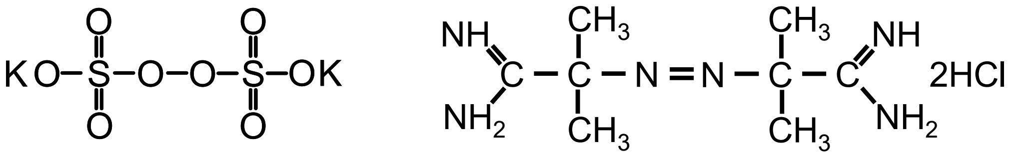
TABLE 1. Experimental conditions of polymerization

Water	Initiator	Monomer	Reaction temperature	Rotation speed	Reaction time
15 g	2.03 mmol/l	64 mmol/l	70 °C	130 rpm	6 hr



(a) KPS (b) V-50

FIG.1 Chemical structures of the initiators: (a) KPS, (b) V-50.

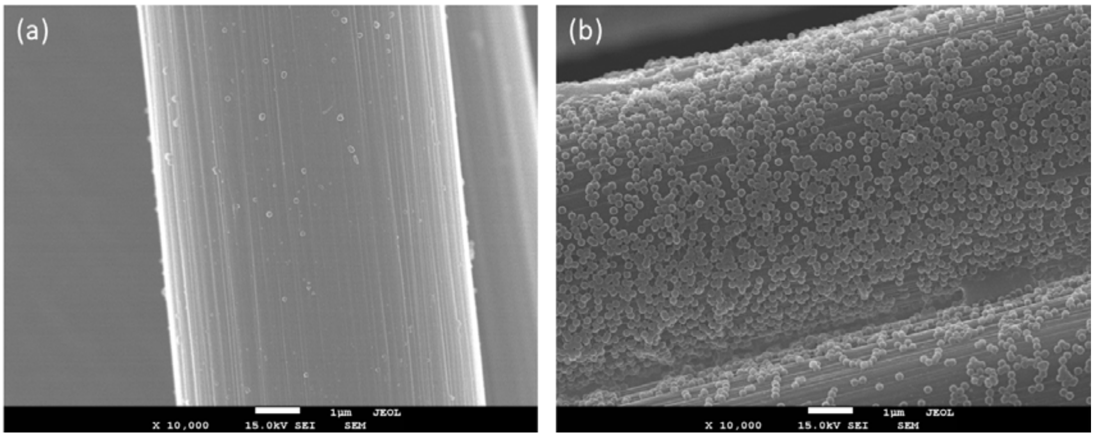


FIG. 2. SEM images of the carbon fibers after the adsorption process using the following polymeric particles: (a) negatively charged PMMA synthesized by KPS; (b) positively charged PMMA synthesized by V-50.

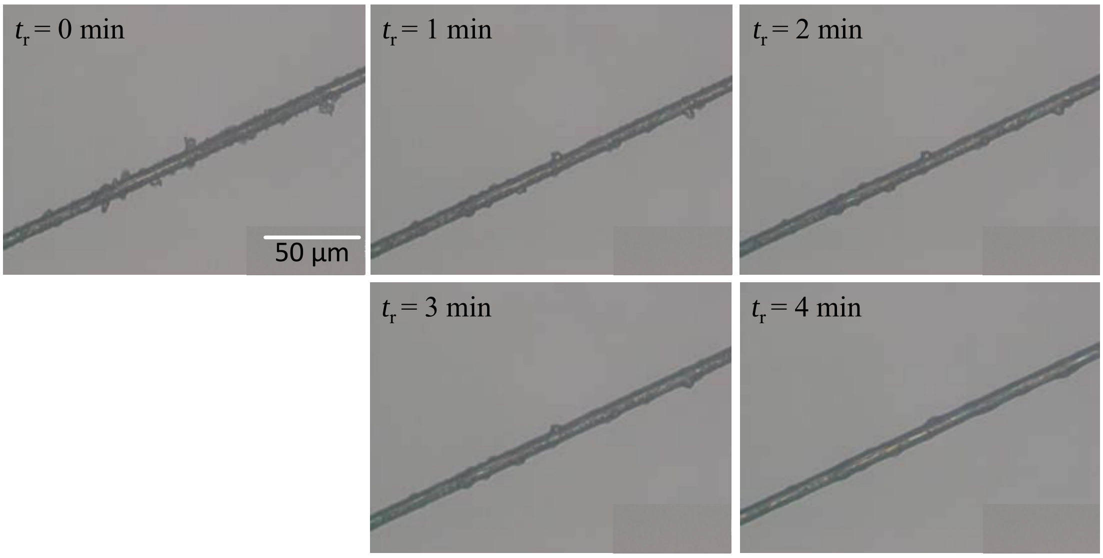


FIG. 3. Observation of melting process of PMMA particles adsorbed on the carbon fiber in the air at the rate of temperature increase, 50 ^{o}C/min, by a digital microscope. t_r meant the elapsed time since the increase of temperature of the system.