Controlling of the Interfacial Shear Strength between Thermoplastic Resin and Carbon Fiber by Adsorbing Polymer Particles on Carbon Fiber Using Electrophoresis

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Abstract

In order to control the interfacial adhesion between carbon fibers and thermoplastic resins, poly(methyl methacrylate) (PMMA) particles have been adsorbed on the carbon fiber surfaces using an electrophoresis process. The amount of PMMA particles adsorbed on the modified carbon fibers was varied using the electrophoresis technique performed in polymer colloids for a short time. Additionally, the interfacial shear strength between the modified carbon fiber and the resin was controlled by a modification of the present process. An improved interaction and a strengthened surface adhesion between the carbon fiber coated with particles and the PMMA resin were observed.

Keywords: Carbon Fiber, Polymer Colloid, Electrophoresis, Interfacial Shear Strength

1. Introduction

Carbon fiber reinforced plastics (CFRP) are one of the most well-known composite materials used in construction materials in transporter and sports equipment owing to its light and strong characteristics. Interaction between materials plays an important role in the mechanical properties of the composite materials, making the fundamental research in this area very important [1, 2]. Owing to the importance of the strength enhancement between the resin and the carbon fiber in CFRPs, the modifications of the carbon fiber surfaces have been investigated using various techniques such as polymer coating [3, 4]. The purpose of the present study is to develop a technique for controlling the interfacial adhesion between the carbon fiber and the thermoplastic resin. Adsorption of polymeric particles on the carbon fiber surfaces by electrophoresis for improving the interfacial adhesion has been investigated. Polymer colloids have been prepared by various methods. In particular, polymerization in water without using surfactants, known as soap-free emulsion polymerization [5], was carried out in order to prevent the surfaces of carbon fibers from being contaminated by surfactants used in the adsorption process. An ionic water-soluble initiator was used to enable soap-free emulsion polymerization and maintain the dispersion stability of the polymer colloids in water [6, 7].

Epoxy resins are often used as a thermosetting resin [1, 8, 9]; however, poly(methyl methacrylate) (PMMA) has been used as a thermoplastic resin since the monomers composing the film can form particulates and colloids easily in the soap-free emulsion polymerization process [10]. Additionally, thermoplastic can be recycled [11, 12]. In the present study, we investigate the adsorption of PMMA particles on the surface of carbon fibers by electrophoresis and the fragmentation testing using a tensile test apparatus to evaluate the surface adhesion between the modified carbon fiber and the thermoplastic resin.

2. Experimental

2.1 Preparation of polymer colloid

Water to be used in the soap-free emulsion polymerization reactions was purified using a purification system (WG250, Yamato Scientific) followed bubbling with nitrogen gas in order to remove any dissolved oxygen. Methyl methacrylate (MMA, Tokyo Chemical Industry) was used as a monomer in the polymerization process. MMA was selected since the thermoplastic resin contained PMMA (HBS006, Mitsubishi Rayon). 2, 2'-Azobis(2-methylpropionamidine)dihydrochloride (V-50, Sigma Aldrich) was used as a radical initiator without further purification, which enabled the particles to be positively charged. The experimental conditions employed in the polymerization process [13] 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). The polymerization reaction time was set as 6 h. As a result, the average size and zeta potential of the synthesized particle were 160 nm and 42.8 mV, respectively.

Table 1. Experimental conditions of polymerization

Water	Initiator	Monomer	Reaction temperature	Rotation speed	Reaction time
75 g	8.12 mmol/l	66.7 mmol/l	70 °C	130 rpm	6 hr

2.2 Adsorption of polymer colloids on carbon fibers by electrophoresis

Carbon fibers (HTS40, Toho Tenax) were treated with acetone in order to remove the sizing agents. The carbon fibers were immersed in the polymer colloid to allow the polymeric particles to adsorb on their surfaces with the help of an electrophoresis system (**Fig. 1**). Since positively charged particles were used in the present study, carbon fibers were attached to the negatively charged electrode of the direct-current power source (AD-

8724D, A&D) to induce efficient adsorption of the particles on the carbon fiber surfaces. The adsorption time was set as 30 s.

The morphologies of the carbon fibers with particles were examined by field emission scanning electron microcopy (FE-SEM, JSM-7500FA, JEOL). The specimen was coated with a thin osmium film by vapor deposition (Osmium Plasma Coater OPC60A, Filgen) before performing the FE-SEM measurements. To calculate the amounts of the

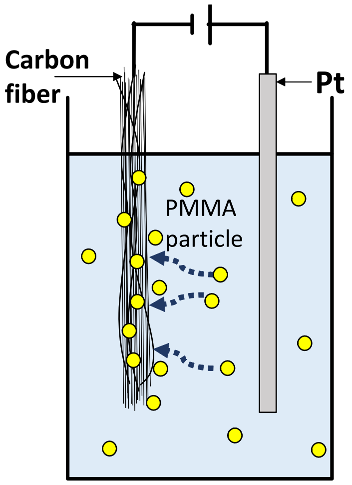

Fig. 1 Adsorption on carbon fiber system using polymer colloid and electrophoresis.

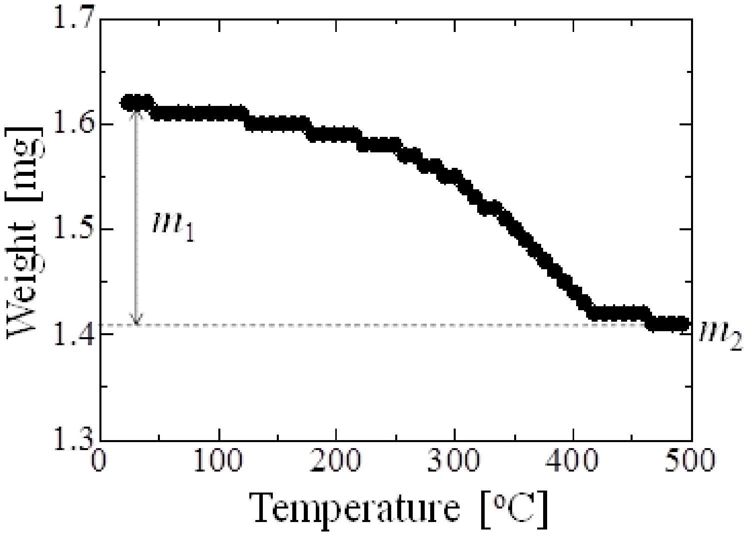

Fig. 2 TG curve of the modified carbon fibers with PMMA particles.

adsorbed PMMA particles on the carbon fibers, a thermal gravimetric analyzer (TG, DTG-60AH, SHIMADZU) was used at a heating rate of 10 ^{o}C/min to heat the sample up to 500 ^{o}C. The TG-curve is shown in **Fig. 2**. The morphologies of the carbon fibers after TG measurements were observed by FE-SEM. As a result, the PMMA particles were removed from the surfaces of the carbon fibers. Hence, the decrease in the weight observed corresponds to the amount of PMMA particles adsorbed on the carbon fibers (m_1). The amount of PMMA particles present on the unit surface area of the carbon fibers (M) can be calculated using the equation (1).

$$M = \frac{\rho S m_1}{D \pi m_2} \qquad (1)$$

, where ρ, S, D, and m_2 are the density, sectional area, average diameter, and the mass of the carbon fiber, respectively.

2.3 Evaluation of the surface adhesion between the carbon fiber and the thermoplastic resin

To evaluate the surface adhesion between a single carbon fiber and the thermoplastic resin, fragmentation tests [8] under a microscope (MS-804, MORITEX Corporation) were carried out using a tensile testing machine (10073B, JAPAN HIGH TECH) for calculating the interfacial shear strength of the carbon fiber. The specimen was prepared as follows: The single carbon fiber sandwiched between two films containing PMMA was hot-pressed at 180 ^{o}C for 1 min by a heater press machine (N4003-00, NPa system) followed by quenching by placing it between two steel plates cooled with water at 25 ^{o}C. Then, the film was cut into strips with a gauge length of 25 mm and a width of 4 mm.

Specimens were tested until the fragmentation process was saturated, which occurred at a tensile strain of about 15 %. The average length of the fragmentation carbon fibers (<*L*>) was measured. The interfacial shear strength (τ_m) between the carbon fiber and the thermoplastic resin was calculated using the following equation [14, 15]:

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

, where the effective length (l_c) could be given by

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

The average diameter of the carbon fiber (D) was measured from the diffraction of a He-Ne laser beam from the fiber, 7.26 μm. The tensile strength (σ_f) of the carbon fibers (the lengths of which were taken to be l_c) was estimated using the Weibull analysis, which was utilized for the analysis of fracturing single fiber [16], of the single fiber tensile tests results [17]. The tensile tests were performed using a tensile testing machine (SDW-1000SS-E-SL, IMADA SEISAKUSHO). The testing machine was operated at a gauge length of 25 mm and a crosshead speed of 1 mm/min according to ASTM C-1577-03 standards.

3. Results and Discussion

3.1 Control of the amount of particles adsorbed on the carbon fiber by electrophoresis

To investigate the effect of applied voltages on the adsorption of PMMA particles on the carbon fibers, morphologies of the modified carbon fibers were examined. SEM images of the carbon fibers modified with polymer colloids at applied voltages of 6.5 V and 20 V are shown in **Fig. 3**. An increased number of positively charged PMMA particles are adsorbed on the carbon fibers with an increase in the applied voltage. To evaluate the adsorption quantitatively, effects of the applied voltage on the amount of PMMA particles adsorbed on the carbon fibers were examined using TG-curves (**Fig. 4**). The amount of the particles adsorbed on the carbon fibers linearly increases with an increase in the applied voltage. Assuming that the surfaces of the carbon fibers are completely covered with PMMA particles as a mono-layer, the amount of PMMA particles could be calculated as 0.114 g/m^2. These results imply that the PMMA particles would be adsorbed as multi-layers when the applied voltages are higher than 25 V. In this way, the electrophoresis carried out for a short time could control the amount of adsorbed particles.

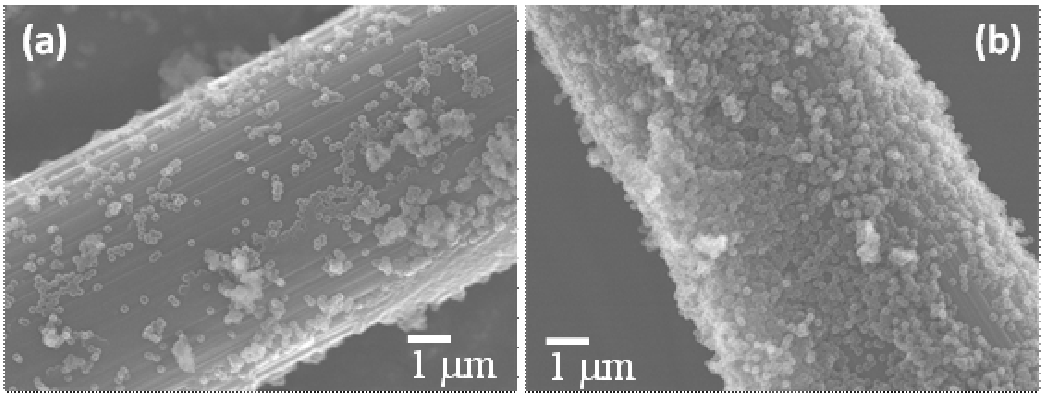

Fig.3 SEM images of carbon fibers modified by polymer colloids at an applied voltage of (a) 6.5 V, (b) 20 V.

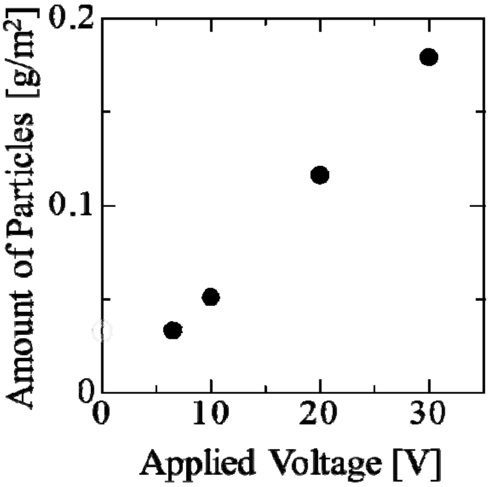

Fig.4 Effect of applied voltage on the amount of PMMA particles adsorbed on the carbon fibers.

3.2 Controlling surface adhesion between the carbon fiber and the thermoplastic resin

The carbon fiber modified with polymer colloids was placed between thermoplastic films by hot pressing for preparing the specimen for the fragmentation tests. The experimental results were listed in Table 2. When the amount of particles adsorbed on the carbon fibers was less than that of particles with which the surface of the carbon fibers could be covered completely as a mono-layer, l_c showed the variations because some areas of the surfaces of the carbon fibers were uncovered with the PMMA particles. The relationship between the interfacial shear strength between the carbon fiber and thermoplastic resin and amount of adsorbed particles can be seen from **Fig. 5**. As the amounts of PMMA particles adsorbed on the carbon fiber increase, the interfacial shear strength increases and reaches a constant value. As the thermoplastic resin film contains PMMA, the interaction between the modified carbon fiber and the resin is improved by the adsorbed PMMA particles on the carbon fiber. The multi-layers formed at the applied voltages higher than 25 V is not effective in enhancing the interfacial affinity between the carbon fiber and the resin. The interfacial shear stress could be controlled by electrophoresis.

The morphology changes occurring on heating the carbon fiber modified with polymer colloids were examined using FE-SEM. **Fig. 6** indicates that the carbon fiber surfaces are extremely smooth as compared with that of the unmodified carbon fibers, which exhibit several striations as seen in Fig. 3a. PMMA particles melt and deform on the carbon fiber while heating to 200 °C. Carbon fibers are uniformly coated with the PMMA polymers. Hence, with an increase in temperature and pressure, the surface adhesion between the modified carbon fiber and the thermoplastic resin is strengthened.

Using nylon film (CM-1001, TORAY) and nylon powder (SP-500, TORAY) as matrix and polymer particle, respectively, the interfacial shear strength between the modified carbon fiber and the resin was increased up to 73.4 MPa by the present method. This method of using polymer colloids and electrophoresis is useful for controlling the surface adhesion between the thermoplastic resin and the carbon fiber, thereby improving the mechanical properties of carbon fiber reinforced thermoplastics (CFRTPs).

Table 2. Effect of amount of PMMA particles adsorbed on carbon fibers on l_c.

Amount of PMMA particles [g/m^2]	0.000	0.0258	0.0374	0.0562	0.0798	0.152
Effective length, l_c [mm]	2.56 ± 0.63	1.96 ± 0.55	1.85 ± 0.50	1.69 ± 0.41	1.70 ± 0.59	1.56 ± 0.16

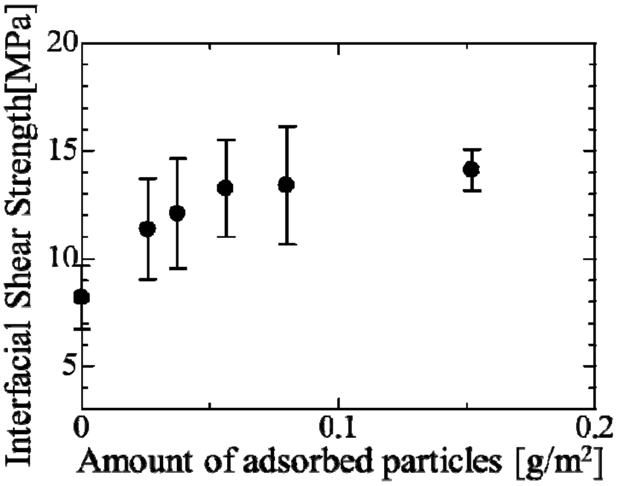

Fig. 5 Effect of particle amounts adsorbed on the modified carbon fibers on the interfacial shear strength.

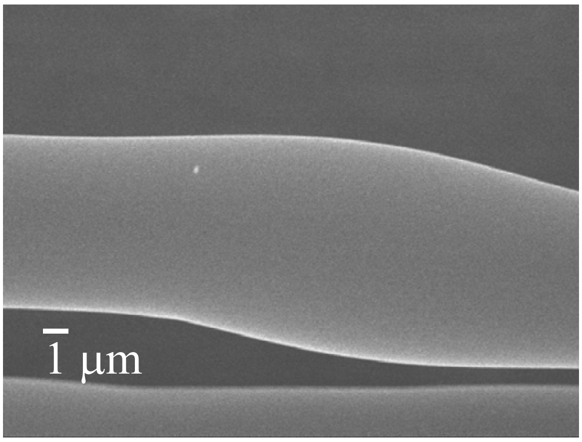

Fig. 6 SEM image of the carbon fiber modified with PMMA particles after heating.

4. Conclusions

In order to control the surface adhesion between carbon fibers and the resin in CFRTPs, polymeric particles were adsorbed on the carbon fiber surfaces by performing electrophoresis in polymer colloids. With an increase in the applied voltage, the particles were readily adsorbed on the carbon fiber within a short time and the interfacial shear strength between the modified carbon fiber and the resin was enhanced. The interaction between the carbon fiber and the resin was improved by the adsorbed PMMA particles, thereby strengthening the surface adhesion between them. The adsorption of particles using electrophoresis could be used for controlling the mechanical properties of CFRTPs.

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