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Influence of treatment with superheated steam on tensile properties of carbon fiber

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ABSTRACT

The influence of treatment with superheated steam (SHS) during the recycling of carbon fiber reinforced plastics was assessed by exposing unidirectional carbon fiber reinforced (UD) sheets to SHS under various conditions. The thermal behavior of UD sheets was identified through thermal analysis. The polymer decomposition was clarified microscopically and based on the weight reduction. Carbon fiber recovery was optimal after treatment at temperatures higher 650 °C as well as at relatively lower temperatures when 4 vol% O_2 was used. The effects of SHS on the fibers were evaluated by comparing the tensile properties of the recycled carbon fibers (r-CFs) with those of corresponding virgin ones. The strength of r-CFs exhibited appreciable scatter, despite the average strength being lower. The cross-sectional area and tensile modulus of the individual r-CFs were approximately equal to those of the virgin fibers. Statistical and fracture surface analyses were performed to elucidate the experimental results.

1. Introduction

To achieve minimal energy losses and low greenhouse gas emissions, considerable efforts are being devoted to developing lightweight composite materials. Among the various type of composites being explored, carbon fiber reinforced plastics (CFRP) have found widespread application in the aircraft and automotive industries [1,2]. The total demand for carbon fibers and CFRP is expected to increase in the next few decades, primarily owing to their suitability for manufacturing high performance lightweight structures [3,4]. However, the prohibitive cost and long manufacturing time as well as the other technical complications that arise during manufacturing have limited the applicability of CFRP. At the same time, CFRP waste has also increased, raising concerns about environmental pollution [5].

Currently, recycling is considered one of the most efficient ways of managing CFRP waste, and various innovative approaches have been introduced in recent years [6–10]. However, it is difficult to recycle carbon fibers and polymers simultaneously from the waste due to technical limitations. Conventionally, recycling can involve the decomposition of the polymer matrix with inert gases and the subsequent recovery of the carbon fibers. Recently, treatment with superheated steam (SHS) has become regarded as a potential approach for recycling CFRP because of its specific advantages over hot air, which is used in conventional processes [11–13]. SHS has high thermal capacity and thermal conductivity, which are the critical parameters determining the recycling efficiency. In addition, a recent study reported that SHS can effectively enhance the interfacial adhesion between the polymer matrix and the as-treated carbon fibers [14].

This study aimed to assess both the suitability of SHS in recycling CFRP and the effects of SHS treatments on the tensile properties of carbon fibers. The Weibull distribution was used to elucidate the correlation between the experimental results and the size distribution of critical flaws. Finally, the fracture surfaces were analyzed to confirm the presence of flaws on the carbon fibers.

2. Experimental

2.1. Materials

Virgin carbon fibers (PYROFIL TR-50S, Mitsubishi Chemical Co., Ltd., Japan) were used as the reference material. Unidirectional carbon fiber reinforced (UD) sheets in an average volume fraction of 55% were provided by the Industrial Technology Center of Fukui Prefecture, Japan, for this study. The manufacturing process of these UD sheets can be described simply in the following steps: spreading a 15K TR-50S tow

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through constant airflow, then impregnating spread filament tow to both sides of polyamide 6 (PA6) resin film.

2.2. SHS treatment and conditions

The SHS treatment equipment consists of an induction-heating (IH) SHS-generating system and a processing chamber that is equipped with a heater to provide a relatively constant temperature. Permissible maximum dimensions of the sample in SHS treatment are currently regarded as 250 × 250 × 250 mm (length × width × thickness). The SHS treatment was performed on UD sheets with dimensions of 240 × 180 × 0.044 mm (length × width × thickness) at the Japan Fine Ceramics Center, Japan. The range of treatment temperatures was 500–700 °C, with a 50 °C gradient, and the processing time for each treatment was 1 h. Both the heating and cooling rates were 10 °C/min, and the flow rate of SHS was 5 kg/h. The samples corresponding to the treatments are labeled based on the corresponding temperature in the rest of the paper.

At the same time, the thermal behavior of the UD sheets was analyzed using thermogravimetry and differential scanning calorimetry (TG-DSC; STA 449 F3 Jupiter®, NETZSCH-Gerätebau GmbH, Germany) performed with a heating rate of 10 °C/min. To identify the polymer decomposition in SHS treatment, 50 vol% water vapor with Argon as the carrier gas at a flow rate of 100 mL/min was executed.

In a previous study [14], the tensile strength of carbon fiber treated with only SHS decreased with increasing treatment temperature. Thus, a novel approach was employed to try to minimize the potential influence of the high treatment temperature on the carbon fibers. This process consisted of the following two steps: 1 h treatment at 400 °C with pure SHS and an additional 1 h SHS treatment at 500 °C in the presence of 4 vol% O_2. The selection of treatment temperatures for these two steps were on the basis of the thermal behavior of UD sheets in SHS-like condition, as shown in Fig. 1. Decomposition of PA6 began at 400 °C, thus 400 °C was selected as the temperature for first step treatment to decompose polymer matrix in a mild manner. However, an additional 1 h treatment at 400 °C was considered to be insufficient for complete decomposition of polymer residual, thus 500 °C is selected as the treatment temperature for second step. In addition, to fulfill the separation of as-treated bundle into individual single fibers, 4 vol% O_2 was added to the SHS for the second step treatment. This approach is labeled the “2-step” treatment in this study.

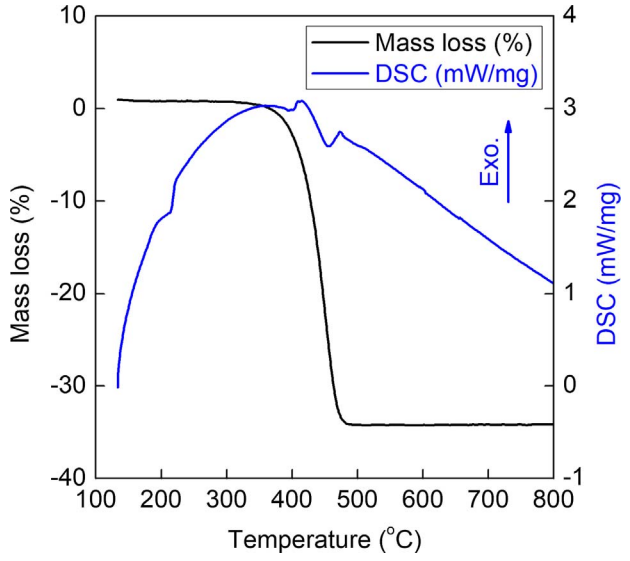

Fig. 1. TG and DSC curves of UD sheets with a heating rate of 10 °C/min in H_2O-Ar flow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Characterization

The weight reduction at each condition was calculated by measuring the weight of the UD sheets before and after the corresponding treatment. The residue of the polymer matrix (PA6), which is one of the most significant criteria for assessing the viability of the SHS treatment for recycling CFRP, was examined using a scanning electron microscopy (SEM) system (JSM-IT300LV, JEOL, Ltd., Japan).

The effects of the SHS treatments on the tensile properties of the carbon fibers were evaluated by performing tensile tests on individual carbon fibers. To prepare the specimens for the tests, single fibers were selected at random from the bundle of virgin carbon fibers and the as-treated UD sheets. In this study, 1 mm Cartesian graph paper was used for mounting the specimens to prevent misalignment between the filaments and the loading direction. To perform the tensile tests at three different gauge lengths, slots with lengths of 10, 20, and 30 mm were initially fabricated on the specimen mountings. Subsequently, a single carbon fiber was placed at the center of the mounting and then firmly bonded to the mounting using a drop of adhesive (NP-50B, Tokyo Sokki Kenkyujo Co., Ltd., Japan). After preparation, all the test specimens were kept in a desiccator to minimize the effects of the environment on the test results.

The diameter of each single-fiber specimen was measured using laser diffraction spectroscopy (μ-EYE, Tohei Sangyo Co., Ltd., Japan). The cross-sectional areas of the fibers were calculated based on the average diameter, which was obtained by irradiating a laser beam on the filament along seven radial directions at an axial gradient of 20°. A desktop tension system (Tokai Testing Machine Mfg. Co., Ltd., Japan) with a 20 N load cell was employed to measure the force and displacement during the tensile testing of the single-fiber specimens. During the experiments, the specimen mounting was clamped with grips. Then, both sides of the mounting were cut in the middle. The test was performed at a cross-head speed of 0.5 mm/min until failure. A total of 60 specimens from the virgin and recycled carbon fiber (r-CF) samples subjected to the SHS treatments were evaluated, since it is recommended that at least 20 measurements be performed at each gauge length for evaluating the tensile properties. All the tests were performed at room temperature under identical experimental conditions. The tensile strength and modulus values of the individual fibers were calculated in accordance with ISO11566:1996 [15] using Eqs. (1) and (2), respectively:

$$\sigma = \frac{F}{A_f} \tag{1}$$

$$E = \frac{\left(\frac{\Delta F}{A_f}\right)\left(\frac{L}{\Delta L}\right)}{1-K\left(\frac{\Delta F}{\Delta L}\right)} \times 10^{-3} \tag{2}$$

where A_f is the cross-sectional area of a single carbon fiber and F is the maximum tensile force applied during the test; ΔF and ΔL are the differences in the force and extension, respectively; and L is the gauge length of the specimen. The system compliance (K) contributes to calibrating the instrument error, including that related to the load train and gripping system, and its value is equal to the intercept of the linear regression line on the ordinate axis.

3. Results and discussion

3.1. SHS treatment

Fig. 1 shows the thermal behavior of the UD sheets in SHS-like condition. The upward and downward convex peaks indicate exothermal and endothermal reactions respectively. The overall upward convex behavior is considered to be affected by carbon fiber. The peak at 215 °C reflects the melting of PA6, and the peaks between 400 and