INFLUENCE OF RECYCLING PROCESS ON THE TENSILE PROPERTY OF CARBON FIBER

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ABSTRACT

To evaluate the viability of superheat steam (SHS) treatment on recycling carbon fiber reinforced plastics (CFRP), unidirectional impregnated sheets were treated by SHS with the temperature range from 500 to 700 °C. The residual of polymer matrix was considered as a criterion of the evaluation, and it was assessed by the microscopic observation. Desirable recovery was observed at 650 and 700 °C with 1 hour SHS treatment. The influence of SHS treatment was elaborated by comparing the tensile property of recycled carbon fibers (RCF) to that of same type of fresh unsized fibers. Results of single-filament tensile tests indicate the strength of recycled fibers is lower than that of fresh, however, relatively stable property was observed in the case of RCF by considering the coefficient of variation (CoV). In addition, experimental results denote that the strength of both RCF and fresh fiber decreases with the growth of gauge length during the test. Tensile modulus was calculated in accordance with the ISO 11566:1996 standard. Comparing with the deviation shown in the strength, relatively slight variance was noticed in the mean of modulus. In addition, corresponding consequence was obtained by applying statistical distribution on the strength of carbon fiber.

1 INTRODUCTION

To meet the requirement of energy saving and low greenhouse gases emission, considerable efforts have been devoted to develop lightweight composite materials. Among the various type of composites, CFRP have been attracted tremendous attention, and widespread application is found not only in the aircraft and automotive industry, but in sports and leisure fields. Market report of carbon fiber also mentioned that the total demand of CFRP is expected to increase primarily for light-weight structure manufacturing [1]. However, due to the high cost, long manufacturing time and other technical complications in manufacturing carbon fiber, CFRP have been had constraints to apply as a potential sort for high-end usage. At the same time, CFRP waste also increased with the concern of environmental issues.

Currently, there is no sufficient way to manage CFRP waste except recycling. Various type of innovative recycling processes have been introduced in recent years [2, 3]. However, due to the technical limitation, it is hard to recycle carbon fiber and polymer simultaneously from the waste. Conventionally, recycling can be summarized as decomposing polymer matrix at inert gas atmosphere and recovering carbon fibers. Recently, SHS treatment is considered as a potential approach for recycling CFRP, because of its specific advantages compared to the hot air used in conventional processes. The dry steam generates by SHS treatment shows high thermal capacity, and it induces high thermal conductivity which is an essential parameter for improving the efficiency of recycling. In the meantime, a recent research suggested that the SHS can sufficiently improve the interfacial adhesion between polymer matrix and as-treated carbon fibers [4].

In this study, the viability of SHS treatment in recycling CFRP was assessed by treating unidirectional impregnated sheets at variable treatment temperature and detecting the residual of polymer matrix. The degradation on the mechanical property was evaluated by comparing tensile property of RCF to that of same series of fresh fibers. In addition, Weibull distribution was employed to quantitatively describe the strength measured by single-filament tensile test, and the probability of failure of carbon fiber at indicated stress.

2 EXPERIMENTAL

2.1 Materials

Fresh carbon fiber (PYROFIL™TR-50S, Mitsubishi Rayon Co., Ltd., Japan) without sizing agent was selected as reference material. Unidirectional impregnated (UD) sheets, which is manufactured by impregnating the same type of carbon fiber in polyamide 6 (PA6) resin, with an average thickness of 44 micro-meters were provided by Industrial Technology Center of Fukui Prefecture for SHS treatment.

2.2 SHS treatment

UD sheets with the dimensions of 180×240 mm^2 were treated at Japan Fine Ceramics Center, Japan. Temperature was range from 500 to 700°C with 50°C gradient, and the time of treatment is 1 hour for each condition. The weight of UD sheet was carefully measured before and after the treatment, also the weight reduction ratio for each treatment condition was carried out. After the treatment, decomposition or residual of polymer matrix (PA6) was examined by JSM-IT300LV scanning electron microscope (SEM).

2.3 Specimen preparation

Single filament carbon fibers were randomly selected from the fresh fiber bundles and as-treated UD sheets respectively. To prevent misalignment of the filament during the experiment, grid paper was chosen as the sheet for preparing specimen mounting. To perform the experiments at three different gauge length, a slot with length of 10, 20, and 30 mm were initially prepared on each specimen mounting. And the carbon fiber filament was place on the center of slot, and it was firmly bonded on the mountings by a drop of strain gauge adhesive (NP-50B, Tokyo Sokki Kenkyujo Co., Ltd). After the preparation, all of the specimens had been preserved in desiccator for minimizing environmental effects on the evaluation.

2.4 Tensile test on single filament

Tensile property of fresh carbon fiber and the fibers from the treatment was measured by Desktop Tension System (Tokai Testing Machine Mfg, Co., Ltd.) with a 20N load cell. At the initial stage of test, the specimen mounting was clamped by the grips, then both side of the mounting was cut at middle. Cross-head speed of 0.5mm/ min was carried out until failure. Force and displacement of the grips were recorded to establish the correlation between load and extension of each specimen. At least sixty specimens had been used in one case such as fresh and fibers from treatment, since 20 measurement is recommended for each gauge length, and even some specimens would be failed during clamping. Tensile strength and modulus was calculated in accordance with ISO11566:1996 [5].

3 RESULT AND DISCUSSION

3.1 SHS treatment

Table 1 shows mass change rate of UD sheets before and after the SHS treatment. Mass change of the sheets was mainly determined by the temperature, since the time of treatment for each temperature range was 1 hour. It is clear that the mass change increases with the growth of treatment temperature.

Table 1. Mass change rate of UD sheets

Temperature (°C)	500	550	600	650	700
Mass change rate (%)	-33.1	-34.3	-35.2	-35.6	-36.1

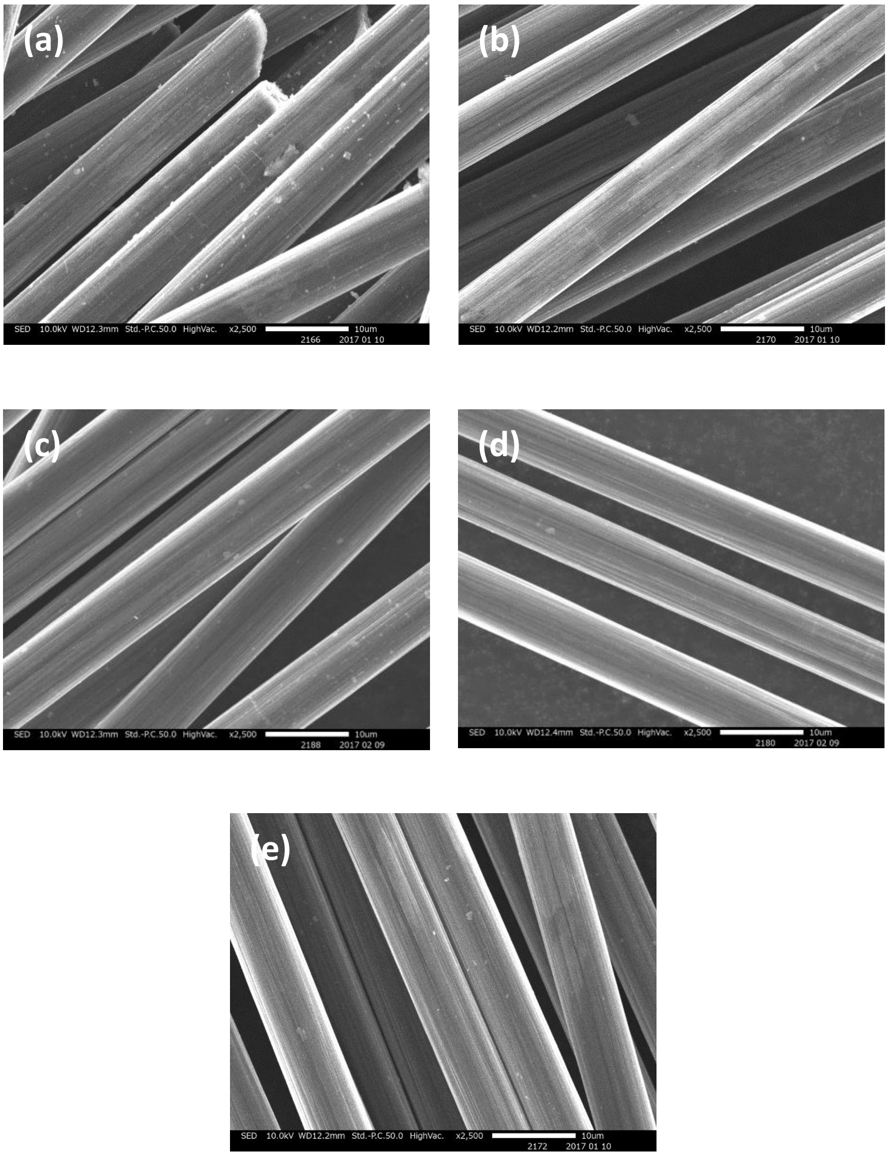

Figure 1. SEM micrographs of carbon fibers from SHS treatment at variable temperature: (a) 500°C, (b) 550°C, (c) 600°C, (d) 650°C, (e) 700°C.

Contribution of SHS in recycling was demonstrated by detecting residual of polymer matrix on the fibers. Figure 1 shows SEM micrographs of fibers from SHS treatment at variable temperature. As shown in Figure 1 (a), large amount of polymer matrix had been found on the fibers after 500°C treatment. Compared with 500°C, the efficiency of resin decomposition by SHS at 550 and 600°C had been improved (Figure 1 (b) and (c)), however those conditions are still insufficient for separating the bundle into single filament of carbon fibers. Among the various temperature, desirable recovery was obtained at 650 and 700°C with 1 hour SHS treatment (Figure 1 (d) and (e)). However, the probability of carbon fiber degradation could be increased with increasing processing temperature [4]. Hence, to achieve complete decomposition of polymer matrix with minimal degradation on the mechanical property of carbon fiber, 650°C with 1 hour SHS treatment was selected as the ultimate condition for recycling.

3.2 Tensile property

Tensile property of single filaments was measured at 10, 20, and 30 mm gauge length respectively. As an essential parameter for calculating tensile property, diameter of the carbon fiber was measured by laser diffraction spectroscopy (μ-EYE, Tohei Sangyo Co., Ltd). Figure 2 shows tensile strength of fresh and RCF from 650°C SHS treatment. It is obvious that the mean strength of RCF is lower than that of fresh fibers. Degradation is reasonable due to the strength of single filament is mainly influenced by the flaw [6], and the treatment condition such as high processing temperature increases probability of flaw or defect on the fibers [7]. Increased probability also induced higher possibility to establish more uniform distribution of the flaws on fiber, thus the CoV of RCF is relatively lower than the fresh fibers. Comparing tensile strength at three different gauge length denotes that the probability of failure also increases with the growth fiber length.

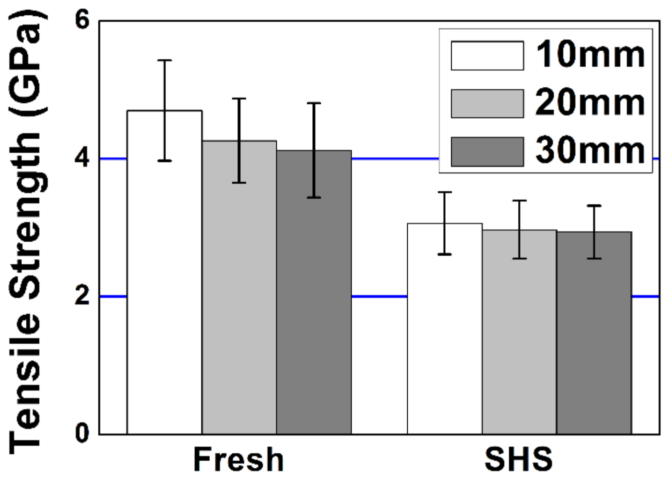

Figure 2. Tensile strength of fresh unsized fiber and recycled fiber from SHS treatment. The error bars result in the standard deviation of experiment results.

Calculating tensile modulus (E) of carbon fiber followed the method suggested in ISO11566:1996 standard, as shown below:

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

where ΔF and ΔL are the difference in force and extension respectively. These two parameters can be derived from the correlation between load and extension. A is the cross section area of the filament, L is the gauge length of the specimen in Eq. (1). System compliance (K) contributes to calibrate the instrumental error such as load train and gripping systems, and it is equal to the intercept of fitted line on axis of ordinate. System compliance 0.16 was applied in calculating tensile modulus of fresh and

RCF respectively. As shown in Table 2, increased probability of flaw also results in the degradation of modulus and higher CoV. Comparing with the deviation shown in the tensile strength, relatively lower variance was observed in the mean of modulus between fresh and RCF.

Table 2. Tensile property of fresh and recycled carbon fiber

		Tensile Strength			Tensile Modulus
		10	**20**	**30**	
Fresh	Mean (GPa)	4.70	4.26	4.12	207
	CoV (%)	15.5	14.3	16.6	5.7
SHS [650°C]	Mean (GPa)	3.06	2.97	2.94	208
	CoV (%)	14.7	14.1	13.0	15.9

3.3 Weibull distribution

Statistical method, especially Weibull distribution is generally applied in describing the tensile strength of carbon fiber obtained by single-filament tensile test [8–10]. Correlation between the stress and probability of failure of carbon fiber can be expressed by the cumulative density function (CDF) of the Weibull distribution [11]:

$$F(\sigma_i) = 1 - \exp\left[-\left(\frac{\sigma_i}{\sigma_0}\right)^m\right] \tag{2}$$

where m is the Weibull modulus, which is also known as shape parameter of the distribution. σ_0 is characteristic stress (scale parameter) of carbon fiber. $F(\sigma_i)$ is cumulative probability of failure of carbon fiber at indicated stress (σ_i). Based on the Eq. (2), linearized form of CDF is expressed by following equation:

$$ln\left[ln\left(\frac{1}{1 - F(\sigma_i)}\right)\right] = mln\sigma_i - mln\sigma_0 \tag{3}$$

As shown in Figure 3, Weibull modulus (m) of the strength distribution can be estimated from the linear regression of aforementioned expression (Eq. (3)). Weibull modulus of fresh and RCF are 7.33 and 7.94 respectively. According to the shape and scale parameter, CDF was established for illustrating the correlation between probability of carbon fiber failure and strength (Figure 4). It is clear that the probability of failure of RCF at an indicated stress is higher than that of fresh carbon fiber. That also means recycling process increased probability of flaw on carbon fiber since failure of carbon fiber filament is mainly determined by the flaw. Additionally, upper and lower limits of the strength for inducing complete survival to failure indicate corresponding scattering of the tensile strength obtained by single-filament tensile test.

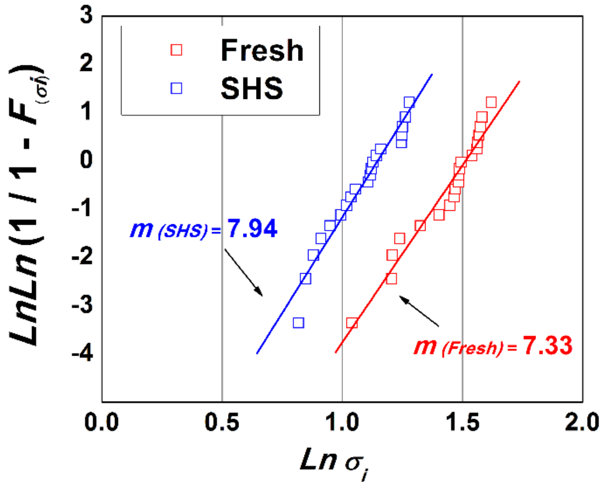

Figure 3. Weibull distribution of the tensile strength of fresh and recycled carbon fibers

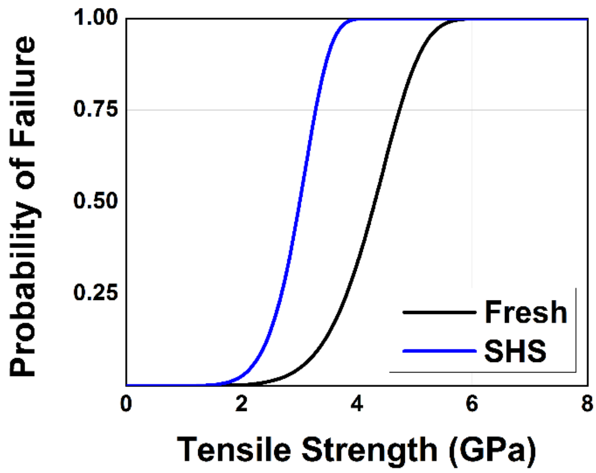

Figure 4. Probability of failure of fresh and recycled carbon fibers at indicated stress

4 CONCLUSION

As a potential approach for recycling CFRP, viability of SHS treatment was evaluated by processing UD sheets at variable conditions. Residual of polymer matrix (PA6) was assessed, and it was considered as a criterion. Micrographs demonstrate that the desirable recovery of carbon fiber was obtained at the temperature above 650°C. Ultimate aim of employing SHS treatment in recycling is to attain complete decomposition of resin with relatively lower degradation of carbon fiber. Thus, 650°C and 1 hour was selected as the potential condition for recycling, and the fibers recovered from that condition was examined. Fresh carbon fibers without sizing agent was selected as reference material for the comparison. Tensile property of both fresh and RCF was measured by single-filament tensile test with identical experiment parameters. Appreciable degradation of carbon fiber was observed, and that is reasonable due to the strength of single filament carbon fiber is mainly influenced by the probability and distribution of flaws, and the treatment condition such as high processing temperature and decomposition of polymer matrix increases probability of flaw or defect on the fibers. CoV of the strength of RCF is lower than that of fresh fibers since increased probability resulted in the uniform distribution of flaws. Comparing the tensile strength at three different gauge length reveals the probability of failure increases with the growth of fiber length. On the other hand, system compliance for calibrating instrumental error was derived, and tensile modulus was calculated in accordance with ISO11566: 1996 standard. Mean value of tensile modulus of RCF is comparable to fresh fibers, and the scattering shown in modulus attributes to the uncertainty of the flaws. Conclusively, Weibull distribution was employed to statistically describe the tensile strength of fresh and RCF. Correlation between the probability of failure of carbon fiber and indicated stress was established to illustrate the degradation and scattering of tensile property obtained by the experiments.

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