EFFECT OF SUPERHEATED STEAM TREATMENT ON INTERFACIAL SHEAR STRENGTH OF CARBON FIBER –EPOXY COMPOSITES

M. Wada[a*], K. Kawai[a], T. Suzuki[b], H. Hira[c]. S. Kitaoka [a]

[a]*Materials Research and Development Laboratory, Japan Fine Ceramics Center, Nagoya, Japan*
[b]*Aichi Science & Technology Foundation, Toyota, Japan*
[c]*Department of Integrated Mecanical Engineering, Daido University, Nagoya, Japan*
**m_wada@jfcc.or.jp*

Keywords: CFRP recycling, Superheated steam, Interfacial shear strength, Surface chemical states

Abstract

The both recovery of carbon fiber from carbon fiber reinforced plastic (CFRP) and surface modification of the recovered fiber would result in further lowering of the CFRP production costs by the use of recovered carbon fibers without additional surface modification processes. Thus, the effect of superheated steam (SHS) treatment on the mechanical properties and chemical states of virgin carbon fiber was investigated. The interfacial shear strength between the treated fiber and epoxy resin was improved by SHS treatment at temperatures up to 600 ºC, above which it became constant. In contrast, SHS treatment with N_2 gas resulted in an increase of the shear strength with increasing treatment temperature. SHS treatment with N_2 addition, which increases the basicity of the fiber surface, is effective for the promotion of interfacial adhesion between the fibers and resin.

1. Introduction

Superheated steam (SHS) is dry steam at ordinary pressure and at a temperature above the boiling point of water. It has a high heat transfer coefficient and enables rapid and uniform heating. Therefore, SHS has received much attention in recent years. In addition, SHS provides a low oxygen partial pressure environment. Considering these features, the SHS treatment of carbon fiber reinforced plastic (CFRP) waste has the potential to effectively decompose the matrix resin and to enable the recovery of carbon fiber without the degradation by oxidation. In fact, investigations of carbon fiber recovery from CFRPs using SHS have been reported in recent years [1,2]

Commercial carbon fibers are typically applied to surface treatment and then coated with a sizing agent in order to improve adhesion between the carbon fiber and resin. SHS treatment should remove the sizing agent on carbon fiber with removal of CFRP matrix resin, whereas it could introduce many active sites for the adhesion of resin on fibers. Thus, if SHS treatment enables the simultaneous removal of matrix resin from CFRPs and surface modification of the recovered fiber, further lowering of the CFRP production costs could be expected by the use of recovered carbon fibers without additional surface modification processes.

In an attempt to develop such a scheme, we focused on the part of surface modification of carbon fiber by SHS treatment. The purpose of the present paper is to clarify the effect of SHS treatment on the mechanical and adhesion properties of carbon fibers and the chemical states of the fiber surface using virgin carbon fiber. In addition, we attempted to evaluate the influence of process gas addition, such as N_2 gas, to SHS.

2. Experimental

TORAYCA®T700 carbon fiber (Toray Industries Inc., Tokyo, Japan) without a sizing agent (unsized fiber) was used as the test specimen. Carbon fiber coated with a sizing agent (sized fiber) was also evaluated as a reference specimen.

Unsized fiber bundles were exposed to SHS at a flow rate of 5 kg/h with and without the addition of 4 vol% N_2 gas. The specimen was placed in the process chamber at 400 ºC and held for 5 min at 500–800 ºC. Removal of the specimen was conducted at 400 ºC. Both the heating and cooling rate was 20 ºC /min.

The diameter and surface morphology of the treated carbon fibers were examined using field emission-scanning electron microscopy (FE-SEM).

Tensile strength specimens were prepared by fixing a monofilament onto a paper holder with adhesive. The specimen was set up in the testing machine and the paper holder was then cut into two parts before testing. The gauge length was 20 mm and the crosshead speed was 0.5 mm/min. All tests were conducted at room temperature. Twenty or fifty specimens were tested for the treated fiber or unsized and sized virgin fibers, respectively.

The interfacial shear strength (IFSS) between the carbon fiber and resin was determined by single fiber fragmentation tests [3,4]. Flat bone-shaped single fiber composite specimens for the evaluation were prepared using bisphenol-A type epoxy resin (#828, Mitsubishi Chemical Corp., Tokyo, Japan) and triethylenetetramine (Mitsubishi Chemical Corp., Tokyo, Japan) as the matrix resin and curing agent, respectively. Three specimens were tested for all carbon fibers.

The Boehm titration method [5,6] was used to determine the concentration of acidic and basic functional groups on the carbon fibers. The specimens were mixed with aqueous solutions of 0.05 N NaOH and the excess base in the supernatant solutions was then titrated against 0.05 N HCl. The total acidity of the carbon fiber was quantified according to the consumption of NaOH. Similarly, the concentration of total basic sites on the fiber surface was determined by mixing the specimen with 0.05 N HCl and back-titration of the obtained supernatant solutions with 0.05 N NaOH.

3. Results and Discussion

The diameters of carbon fibers treated by by SHS with or without N_2 gas at 500–800 ºC were approximately 7 μm and almost the same as those of the virgin fibers. The surface morphology of the carbon fibers was examined by SEM observation at a low acceleration voltage of 1 kV. Figure 1 shows the SEM images of the unsized virgin fiber and the fiber after

SHS treatment with or without N_2 gas at 800 ºC. The surface smoothness of the treated fibers is similar to that of the non-treated fiber.

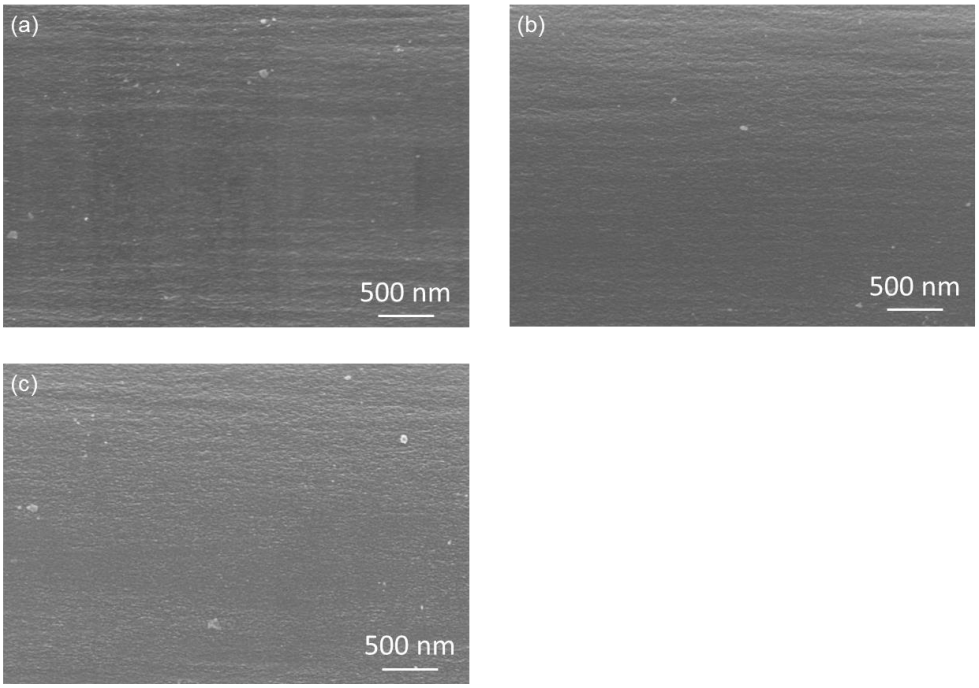

Figure 1. SEM images of the (a) unsized virgin fiber and fibers after SHS treatment (c) without and (e) with N_2 gas addition at 800 ºC.

Table 1 shows the average tensile strength of single carbon fibers. The strength of the fiber treated by SHS only at 500 ºC maintained the initial level, whereas it was reduced to lower than that of the unsized virgin fiber after treatment above 600 ºC. On the contrary, when N_2 gas was added during the SHS treatment, the fiber treated at 600 ºC maintained the initial level of strength. Therefore, the N_2 gas addition effectively inhibited the deterioration of fiber strength during SHS treatment.

Fibers	Treatment conditions		Tensile strength / GPa
	Atmospheres	Temperature (ºC)	
Sized	Non-treatment		3.90 (0.69)
Unsized	Non-treatment		3.72 (0.76)
	SHS	500	3.87 (0.94)
		600	3.53 (0.94)
		700	3.29 (0.91)
		800	3.13 (0.75)
	SHS + 4 vol% N_2	500	4.08 (0.99)
		600	3.86 (0.83)
		700	3.51 (0.89)
		800	3.45 (0.97)

Table 1. Tensile strength of carbon fibers treated by SHS with and without N_2 gas addition. The results for the unsized and sized virgin fibers are also shown for reference. Standard deviations are indicated between parentheses.

Table 2 shows the IFSS between the carbon fiber and epoxy matrix resin measured using the single fiber fragmentation test. The IFSS was improved by SHS treatment without gas at temperatures up to 600 ºC, above which it became constant. In contrast, SHS treatment with

N_2 gas resulted in an increase of the IFSS with increasing treatment temperature. In particular, the IFSS after SHS treatment with N_2 gas above 700 ºC was higher than that of a commercial sized fiber.

Fibers	Treatment conditions		IFSS / MPa
	Atmospheres	Temperature (ºC)	
Sized	Non-treatment		52.2 (10.0)
Unsized	Non-treatment		24.0 (1.2)
	SHS	500	33.8 (4.7)
		600	45.5 (11.4)
		700	45.5 (2.8)
		800	43.8 (8.3)
	SHS + 4 vol% N_2	500	33.5 (1.5)
		600	37.9 (7.6)
		700	58.8 (22.8)
		800	67.2 (19.9)

Table 2. Interfacial shear strength (IFSS) between carbon fibers treated by SHS, with or without N_2 gas addition, and epoxy resin. The results for the unsized and sized virgin fibers are also shown for reference. Standard deviations are indicated between parentheses.

Table 3 summarizes the concentration of acidic and basic properties on the surface of the carbon fibers as determined by Boehm titration method. The unsized virgin fiber, the fiber treated by SHS only at 700 ºC and that treated by SHS with 4 vol% N_2 gas at 700 ºC were evaluated. The total amount of acidic functionality on the fiber treated by SHS only was larger than that on the unsized virgin fiber, whereas that of basic functionality was not changed after the treatment. Therefore, the improvement in IFSS after SHS treatment should be caused by the increase of acidity on fiber surface. In contrast, SHS treatment with N_2 gas addition resulted in an increase of the total basicity, in addition to the increase of total acidity. The basicity of the fibers treated by SHS with N_2 gas addition is increased, so that interfacial adhesion between the fibers and resin is effectively promoted.

Treatment conditions		Amount of surface functional groups / meq/g	
Atmospheres	Temperature (ºC)	Total acidic group	Total basic group
Non-treatment (Unsized fiber)		0.073	0.097
SHS	700	0.131	0.097
SHS + 4 vol% N_2		0.124	0.144

Table 3. Surface acidic and basic properties of unsized fiber with and without SHS treatment determined by Boehm titration method.

4. Conclusions

Virgin carbon fiber was exposed to superheated steam (SHS) with and without N_2 gas in the temperature range of 500 to 800 ºC and the effect of SHS treatment on the mechanical properties and chemical states of fiber was investigated. The tensile strength of single carbon fiber treated with SHS only was reduced to lower than the initial level after treatment above 600 ºC. On the other hand, when N_2 gas was added during the SHS treatment, the fiber treated at 600 ºC maintained the initial level of strength. The interfacial shear strength (IFSS) between the treated fiber and epoxy resin, as measured by single fiber fragmentation tests, was improved by SHS treatment without additional gas at temperatures up to 600 ºC, above which it became constant. In contrast, SHS treatment with N_2 gas resulted in an increase of

the IFSS with increasing treatment temperature. The chemical titration method indicated that only the total acidity on the carbon fiber surface increased after SHS treatment. In contrast, when N_2 gas was added to SHS during treatment, the total basicity on the fiber increased, in addition to the increase of the acidity. Therefore, SHS treatment with N_2 addition, which increases the basicity of the fiber surface, is effective for the promotion of interfacial adhesion between the fibers and resin.

Acknowledgement

This study was supported by "Knowledge Hub Aichi, Priority Research Projects".

References

[1] J. Shi, K. Kemmochi and L. Bao. Research in Recycling Technology of Fiber Reinforced Polymers for Reduction of Environmental Load: Optimum Decomposition Conditions of Carbon Fiber. *Adv. Mat. Res.*, 343-344: 142-149, 2012.

[2] S. Y. Ye, A. Bounaceur, Y. Soudais and R. Barna. Parameter Optimization of the Steam Thermolysis: A Process to Recover Carbon Fibers from Polymer-Matrix Composites. *Waste Biomass Valor.*, 4 (1): 73-86, 2013.

[3] B. Yavin, H.E. Gallis, J. Scherf, A. Eitan and H. D. Wagner. Continuous Monitoring of the Fragmentation Phenomena in Single Fiber Composite Materials. *Polymer Composites*, 12 (6): 436-46, 1991.

[4] Y. Miwa, M. Kasebe, K. Goda, J. Ohgi, S. Nagatsuka and H. Kodama. Strength and reliability of Unidirectional CFRPs with Different Fiber Surface Properties. *Journal of Society of Materials Science, Japan*. 53 (1): 50-56, 2004.

[5] H.P. Boehm. Chemical Identification of Surface Groups. *Advances in Catalysis*, 16 (2): 179-274, 1966.

[6] H.P. Boehm. Surface Oxides on Carbon and Their Analysis: a Critical Assessment. *Carbon*, 40 (2): 145-149, 2002.