AN ECONOMICAL AND ENVIRONMENTALLY FRIENDLY CFRP RECYCLING SYSTEM THAT RECOVERS BOTH CARBON FIBER AND RESIN

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ABSTRACT

Recycling of carbon fiber reinforced plastics (CFRP) is a highly demand research topic in recent years. In this research, we focused on an environmentally friendly recycling method using nitric acid, which could decompose epoxy resin under relatively mild condition which is 80℃ under atmospheric pressure. Moreover decomposed epoxy resin in nitric acid solution could be recovered by liquid-liquid extraction process using ethyl acetate. Therefore, when applying this recycling method to CFRP, both carbon fiber and resin could be recovered, which is a unique feature that cannot be achieved in other recycling methods. In this research, the CFRP waste sample used was automobile prototype parts. Following the decomposition of CFRP sample in nitric acid at 80°C, recycled carbon fiber were recovered without degrading its quality, moreover showed 1.4 times higher tensile strength compared to virgin carbon fiber. In this report, in order to develop this recycling method into practical use, two research results will be reported. First of all, we studied a new recycling scheme to recover carbon fiber in short recycling time. As a result, following the immersion of CFRP in an alkaline solution after nitric acid decomposition, the resin residue was removed quickly, and shorten the recycling time from the original 24 hours to 8.5 hours. Next, in order to consider the effective usage of the recycled carbon fiber, it was processed into non-woven fabric and molded into a CFRP plate. Evaluating the mechanical properties of the CFRP plate, recycled CFRP plate showed higher bending modulus and tensile modulus than that of virgin one. The possibility of applying recycled carbon fiber to CFRP products where it needs high quality was shown, which could realize closed-loop recycling.

1 INTRODUCTION

Carbon fiber reinforced plastics (CFRP) is a lightweight and high-strength material expanding its usage in global market size. However, due to its difficulty of recycling, no suitable method of processing scrapped CFRP has currently been established [1]. Therefore it is important to establish recycling methods utilize limited and valuable resources, before large volumes of scrapped CFRP will be disposed of in the future.

As one of the CFRP recycling method, we focused on a recycling method using nitric acid, which could decompose the resin under relatively mild condition such as at 80°C under atmospheric pressure [2-6]. According to our previous research, carbon fibers recovered from the CFRP using this nitric acid recycling method showed higher value of tensile strength and interfacial shear strength compared to virgin carbon fibers [5, 6]. This was considered that the nanosize voids and defects existing on the carbon fiber surface decreased along with the recycling treatment, and the increase in interfacial strength is thought to be due to oxidation and nitration on fiber surface [6]. In addition, epoxy resin dissolving into HNO_3 could be recovered by liquid-liquid extraction process using ethyl acetate which is a characteristic of this recycling method, while resin could not be recycled in other CFRP recycling method. Therefore, it could be expect to recycle both carbon fiber and resin in this method.

In this study, in order to develop this recycling method into practical use, the results of two studies will be reported. First of all, we studied a new recycling scheme to recover carbon fibers in short recycling time despite mild condition. Secondly, in order to examine the effective usage of the recycled carbon fiber, recycled carbon fiber was formed into non-woven fabric and molded to a CFRP plate, then the mechanical properties were compared to virgin one.

2 EXPERIMENTS

2.1 CFRP materials

Waste from a CFRP prototype automotive parts, molded from carbon fiber sheet and epoxy resin (Bisphenol A type epoxy resin and polyamine as hardener), was used as a sample in this research. In the first study, in order to proceed the recycling in a test tube scale, CFRP sample cut into 20×30×2 mm in size were used. In the second study, to fabricate a non-woven fabric in an aligned fiber length of 50 mm, CFRP sample cut into around 50×50×2 mm was used (Fig.1).

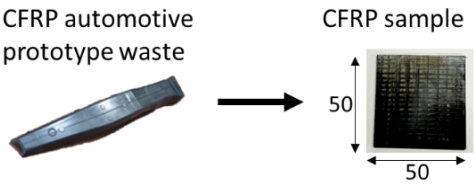

Fig.1 CFRP sample cut into 50×50 mm in size from a CFRP automotive prototype waste

2.2 Recovering recycled carbon fibers

(a) Recycling scheme-1

Procedure of recycling scheme-1, which is the original recycling method, is described in Fig.2 (a). Nitric acid (Kanto Chemical Co., Inc., special grade) was used to decompose the epoxy resin of the CFRP sample. The CFRP sample the size of 20×30×2 mm, was immersed in a test tube containing nitric acid aqueous solution adjusted to 8 M concentration by fixing the CFRP sample using a PTFE tube (with an inner diameter of 6 mm and an outer diameter of 8 mm). When immersing the CFRP sample 50×50×2 mm in size, 200 ml beaker was used instead of the test tube. The amount of the nitric acid aqueous solution was adjusted to 16 mL per 1 g of the CFRP sample. When the test tube was set in a constant-temperature bath at 80°C, decomposition of the epoxy resin by the nitric acid proceeded over time. After immersion for 2- 48 h, the solid residue, were removed from the test tube or from the beaker and collected as recovered carbon fibers. The solid residue was thoroughly rinsed with deionized water, and the recycled carbon fibers (rCF-1) were obtained by removing the residual moisture from this using a dryer (80°C, 48 h).

The decomposed resin dissolved in the aqueous nitric acid solution was recovered by liquid-liquid extraction at room temperature using ethyl acetate. We have confirmed that the resin could also be recovered from the CFRP samples as well as neat resin [2, 3], however the analysis for recycled resin will be discussed in the further research.

(b) Recycling scheme-2

A new recycling scheme-2, the procedure described in Fig.2 (b), was studied. Four test tubes containing 8 M nitric acid were prepared and a CFRP sample the size of 20×30×2 mm was fixed with a PTFE tube and immersed in each. In a similar way as the procedure shown in Section 2.2(a), when immersing the CFRP sample 50×50×2 mm in size, 200 ml beaker was used instead of the test tube. Each test tube or the beaker was set in an 80°C constant-temperature bath. After 8 h, the CFRP samples were taken out from the nitric acid aqueous solution and thoroughly rinsed with deionized water. Then, each specimen was immersed in sodium hydroxide (Kanto Chemical Co., Inc., special grade) aqueous solutions adjusted to pH 12, pH 10, or pH 8 or in a sodium hydrogen carbonate (Kanto Chemical Co., Inc., special grade) aqueous solution adjusted to pH 8, respectively. The amounts of the sodium hydroxide and sodium hydrogen carbonate aqueous solutions were adjusted to be 20 mL for a mass of 1 g of the CFRP specimens before the immersion in the nitric acid aqueous solution. After immersion in alkaline solutions for 1- 60 min, under the 80°C constant-temperature bath, the carbon fibers were taken out from the test tubes or the beaker, thoroughly rinsed with deionized water, and dried to obtain recycled carbon fibers (rCF-2).

2.3 Time Change of Epoxy Resin Decomposition Ratio

The resin decomposition rate R_d (mass%) of the CFRP specimen was calculated using equation (1), where m_0 is the sample mass before immersion in the nitric acid aqueous solution, m_t is the sample mass after immersion in the nitric acid aqueous solution for 2– 48 h, fully rinsed with deionized water and

completely dried according to the procedure explained in Section 2.2, and F_m is the mass fraction of resin in the CFRP specimen.

$$R_d = \frac{(m_0 - m_t)}{m_0 \times F_m} \times 100 \quad (1)$$

The mass fraction of the resin in the CFRP specimen (F_m) was experimentally evaluated as confirmed that F_m showed a value of 40.0% [6].

2.4 Fabrication of carbon fibers to non-woven fabric

Virgin carbon fibers (vCF) and rCF were processed into non-woven fabric by dry fabrication method. The vCF which an epoxy sizing agent are applied and the number of filaments 50 K were used, which is the same model of vCF used in the original CFRP sample described in Section 2.2. In order to process a constant non-woven fabric, fiber opening was performed using a sample opener (Daiwakiko Corp.). Opened carbon fibers were processed through a roller card machine (Toa non-woven machinery Corp.) to stretch the fibers to a sheet form and layer machine (Toa non-woven machinery Corp.) was used to fold the fiber sheets and the carbon fiber density was controlled to 150 g/m^2 by adjusting the number of folding times. Finally, needle punching machine (Daiwakiko Corp.) was used to bundle the carbon fiber sheets. Non-woven fabric processed from vCF, rCF-1, and rCF-2 are expressed as vCF-NF, rCF-NF-1, and rCF-NF-2, respectively.

2.5 Molding CFRP

In order to mold CFRP from non-woven fabric, 6 layers of non-woven fabric were stacked and set into the 250×200 mm mold. Epoxy resin which is the same type as the original CFRP automobile prototype waste, was impregnate using the hot press under mold temperature 120°C, curing time 5 min and molding pressure 20 ton. CFRP which was mold from vCF-NF, rCF-NF-1, and rCF-NF-2 are expressed as vCFRP-NF, rCFRP-NF-1, and rCFRP-NF-2, respectively.

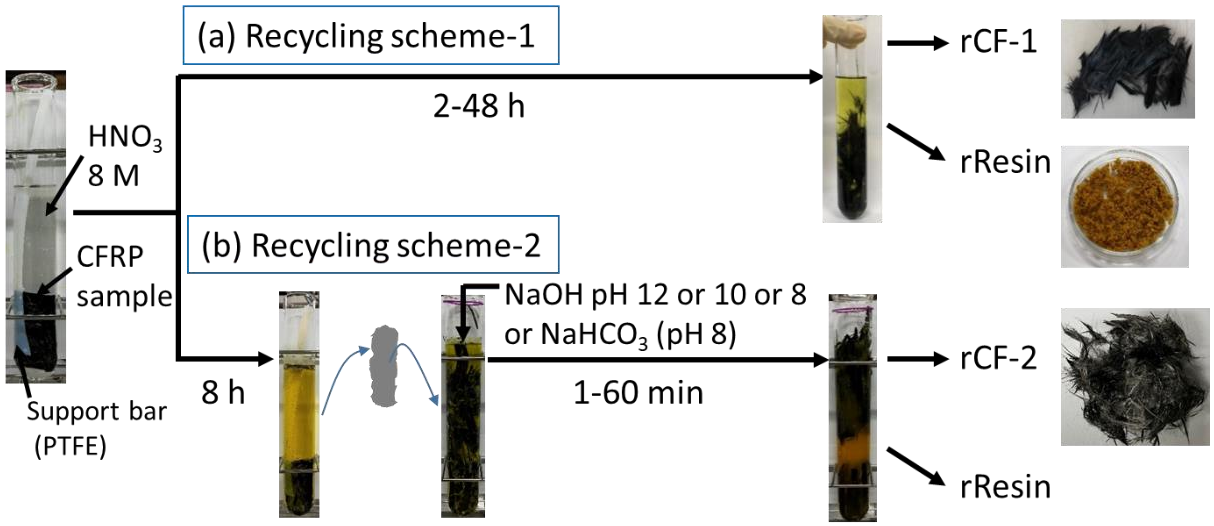

Fig.2 (a) Recycling scheme-1: recovering recycled carbon fiber from immersing CFRP sample to 8 M HNO_3 at 80°C for 2-48 h and, (b) Recycling scheme-2: recovering recycled carbon fiber from immersing CFRP sample from alkaline solution NaOH (pH 12 or 10 or 8) or $NaHCO_3$ (pH 8) at 80℃ for 1-60 min, after immersing to 8 M HNO_3 at 80°C for 8 h.

2.6 Evaluation and analysis of CFRP

(a) Measurement of CFRP

Fiber content ratio V_f of the CFRP was calculated from the equation (2), where M_1 is the mass of CFRP molded plate (g), M_2 is the mass of non-woven fiber before resin impregnation (g), ρ is the specific density of epoxy resin, 1.15 g/cm^3, and L_1 is the thickness of CFRP (mm).

$$V_f = 1 - \frac{(M_1 - M_2)}{\rho \times 1000 \times \frac{1}{250 \times 200 \times L_1}} \quad (2)$$

(b) Three-point bending test

Three-point bending test of CFRP specimen were performed using testing machine AGX-100 (Shimadzu Corporation). CFRP specimen for the bending test were prepared according to JIS K 7074-1988, which the length l_1 is 100 mm and the width b_1 is 15 mm. Specimen was fixed to the testing machine and the gauge length was set to L_1= 40×h_1 (mm), where h_1 (mm) is the thickness of the CFRP specimen. Bending speed was set to 5 mm/min and at least n=3 specimen were tested for each group. The maximum load at the breakpoint P_1 (mN) was recorded and calculated the bending strength σ_1 (GPa) using equation (3) and the bending modulus E_1 (GPa) was calculated using equation (4), where $\Delta\lambda_1$ (mm) is the displacement when the specimen fractured.

$$\sigma_1 = \frac{3P_1L_1}{2b_1{h_1}^2} \quad (3)$$

$$E_1 = \frac{{L_1}^3}{4b_1{L_1}^2} \times \frac{P_1}{\Delta\lambda_1} \quad (4)$$

(c) Tensile test

Tensile test of CFRP specimen were performed using testing machine AGX-100 (Shimadzu Corporation). CFPR specimen for tensile test were prepared according to JIS K 7083-1993, which the length l_2 is 200 mm and the width b_2 is 25 mm. Specimen was fixed to the testing machine using a 5696 (Instron Corporation) in a gauge length λ_2=25 mm. Tensile speed was set to 2 mm/min and at least n=3 specimen were tested for each group. The tensile strength σ_2 (GPa) and the elastic modulus E_2 (GPa) was calculated using equation (5) and (6), where P_2 is the maximum load at the breakpoint (mN), h_2 is the thickness of the CFRP specimen (mm), and ε_2 is the fracture strain which is $\varepsilon_2 = \Delta\lambda_2/\lambda_2$, where $\Delta\lambda_2$ is the displacement when the specimen fractured.

$$\sigma_2 = \frac{P_2}{b_2h_2} \quad (5)$$

$$E_2 = \frac{\sigma_2}{\varepsilon_2} \quad (6)$$

3 RESULTS AND DISCUSSION

3.1 Time Change of Epoxy Resin Decomposition Ratio

Resin decomposition ratio of each recycling scheme calculated using equation (1) are summarized in Fig.3. In recycling scheme 1, resin decomposition ratio R_d reached 95 mass% in 24 h, and almost no changes were observed after 24 h, as reported in the previous research [5].

On the other hand, remarkable improvement of resin decomposition ratio was observed in recycling scheme 2 as shown in Fig.3 (a) and (b). When immersing to NaOH pH 12 after immersion to nitric acid, which is strong alkaline solution, R_d reached 98% within 1 min, and within 10 min when immersing to NaOH pH 10. Weak alkaline solution also showed improvement of resin decomposition ratio. Among the weak alkaline solution, $NaHCO_3$ was more effective for removing resin rapidly since R_d reached 96% within 15 min and finally reached to 99% within 20 min. Since NaOH pH 8, which is also a weak alkaline solution, showed improvement of resin decomposition ratio compared to HNO_3, however not as much as $NaHCO_3$ though same pH condition. This was considered that carbonic dioxide gas generated

from $NaHCO_3$ through chemical reaction between $NaHCO_3$, HNO_3, and resin, helped removing resin physically.

Carbon fiber surfaces observed by using SEM are showed in Fig.4. No resin residue to the carbon fiber surface which was collected from recycling scheme 2 was observed. Hereafter, when immersing the sample to HNO_3, even extending the immersing time to 48 h, resin residue was observed partially, however using alkaline solution after immersing to HNO_3 for 8 h, alkaline helped removing resin residue from the carbon fiber surface. Therefore we selected recycling scheme 2 and used $NaHCO_3$ for the alkaline solution in this research.

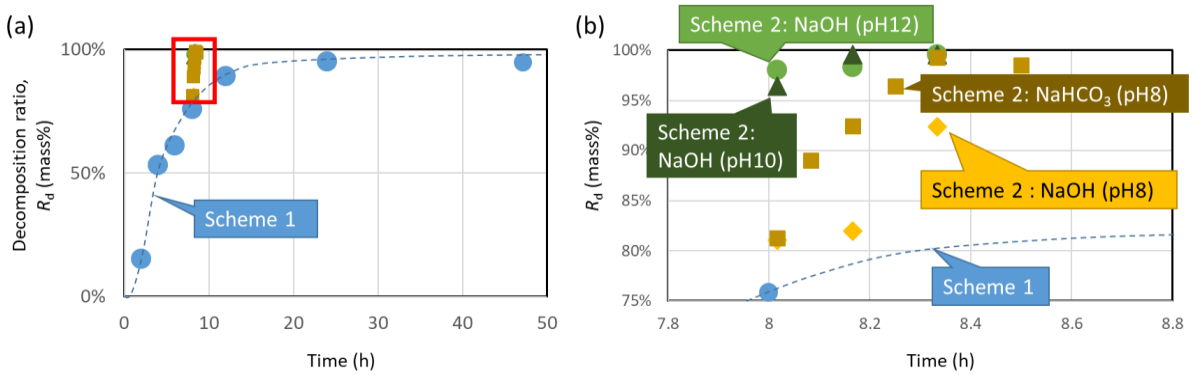

Fig.3 Resin decomposition ratio of recycling scheme 1 and 2, (a) time scale 0-48 h and (b) time scale 7.8 –8.8 h, where ●: Resin decomposition ratio of scheme 1, resin decomposition ratio of scheme 2 using ●: NaOH (pH 12), ▲: NaOH (pH 10), ♦: NaOH (pH 8) and ■: $NaHCO_3$ (pH 8) for the alkaline solution.

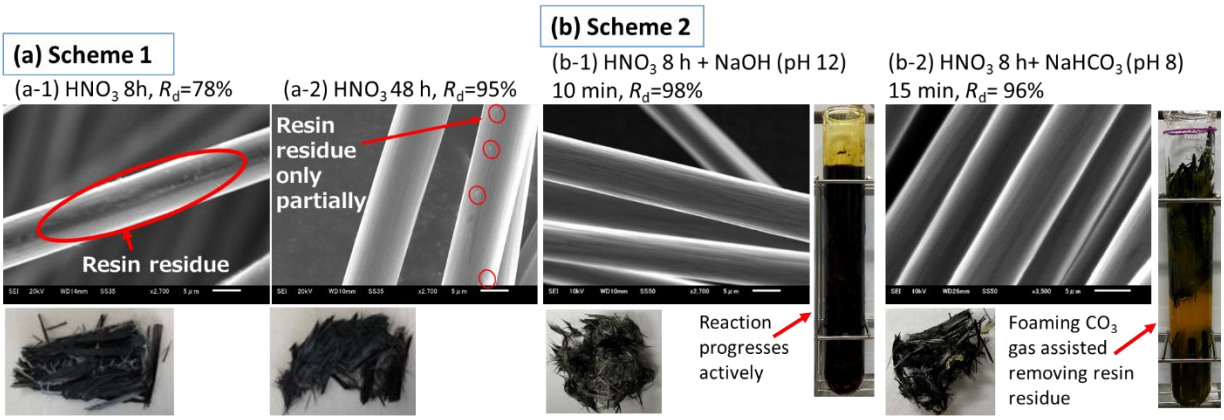

Fig.4 Carbon fiber surface observed by SEM and the picture of the recycled carbon fibers (a) in recycling scheme 1 and (b) in recycling scheme 2 along with the picture of the chemical reaction with the alkaline solution in the test tube.

3.2 Evaluation of non-woven fabric

SEM images of carbon fiber after processed through fiber opener are shown in Fig.5. Wan et al. reported that CFRP mold from a fully opened carbon fiber expressed superior mechanical properties than a CFRP mold from a carbon fiber without opened [7]. As shown in Fig.5, carbon fibers were not unwind sufficiently when processed through fiber opener only once, so it was processed twice. As shown in Fig.5 (b), entanglement of fibers were observed along with the increase of the number of fiber openings only to the sample (b) rCF-1. Moreover from the SEM image in Fig.5 (b), resin residue was observed partially on the carbon fiber surface especially on twice open fiber, which shows that resin residue spread through the fiber opening process. On the other hand, as shown in Fig.5 (c), the fibers unravel along with the fiber openning. Furthermore from the SEM image, no resin residue nor damage to the fiber was observed in sample (c).

Fiber fabricated into non-woven fabric are shown in Fig.6 (a). Uniform non-woven fabrics were obtained in carbon fiber weight 150 g/m^2. Conspicuous fluff was not observed in any of the non-woven fabrics, however sparseness was observed from the non-woven fabric (b). This was considered to be occurred due to the entanglement of carbon fiber.

3.3 Evaluation of CFRP molded plate

CFRP plates which were molded from vCF-NF, rCF-NF-1, and rCF-NF-2 are shown in Fig.6. The experimental data through the molding which is the number of CF sheets, mass of CF and resin, V_f calculated using equation (2) and the thickness of the plate are summarized in Table 1. V_f showed around 30% in all CFRP plate, which is rather low compared to CFRP mold from continuous carbon fiber sheets.

The results of the three-point bending test and tensile test are shown in Fig. 7. As shown in Fig. 7, rCFRP-1 and rCFRP-2 did not decrease its bending strength and tensile strength, moreover, showed higher bending modulus and tensile modulus than virgin one.

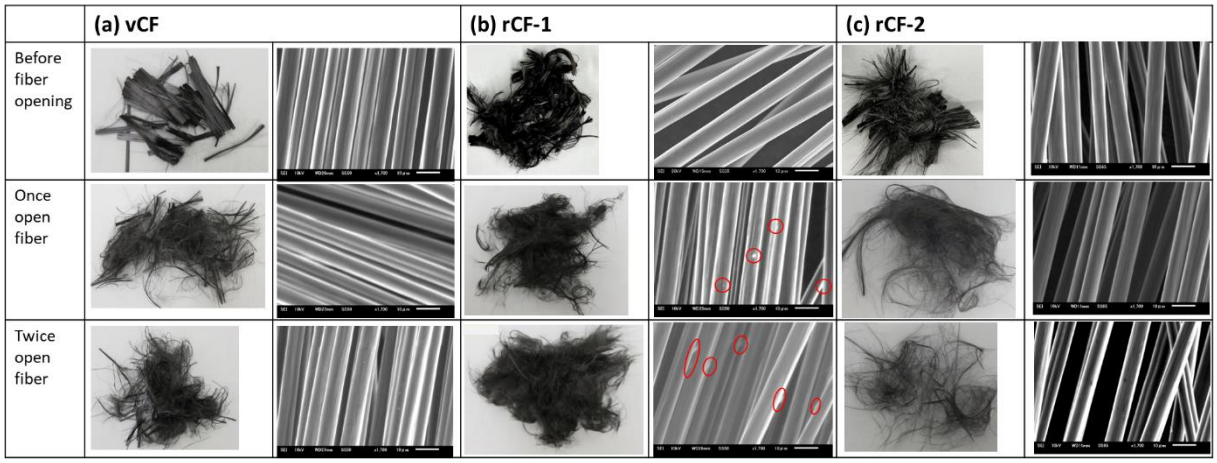

Fig.5 Picture and SEM image of the carbon fibers before fiber opening and once or twice opened fiber for (a) virgin carbon fibers, (b) recycled carbon fibers taken from CFRP after immersion to 8 M HNO_3 for 24 h under 80°C, which red circle represents the resin residue, and (c) recycled carbon fibers taken from CFRP after immersion to $NaHCO_3$ pH 8 for 15 min after immersion to 8 M HNO_3 for 24 h under 80°C.

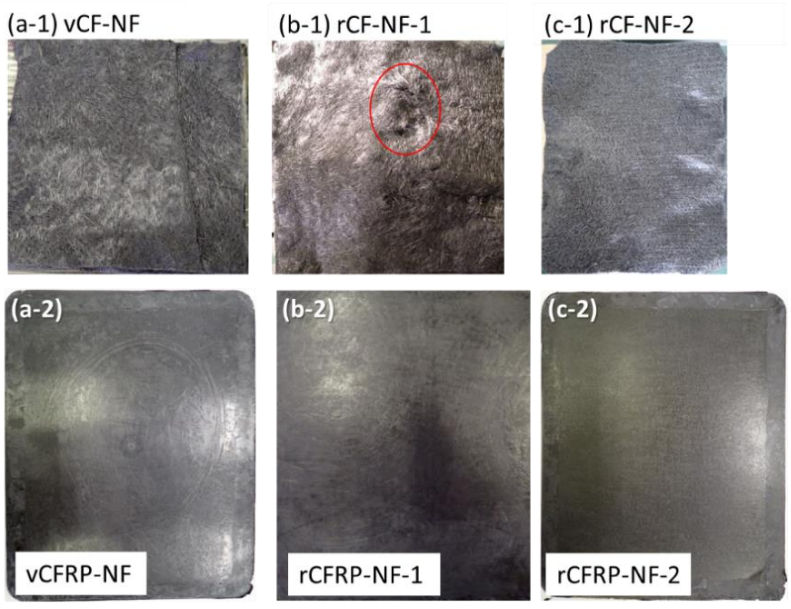

Fig.6 Non-woven fabric and CFRP plate molded under 20 ton pressure, where red circle represents the sparseness of the fabric.

Table 1 Experimental data of non-woven carbon fiber fabric molded into CFRP.

	Number of CF sheet layers	Mass of CF (g/m^2)	Mass of resin (g/m^2)	V_f (vol%)	Thickness (mm)
vCFRP-NF	6	2,177	1,550	51.0 %	2.31
rCFRP-NF-1	6	791	1,366	27.1 %	1.57
rCFRP-NF-2	6	778	1,216	26.8 %	1.61

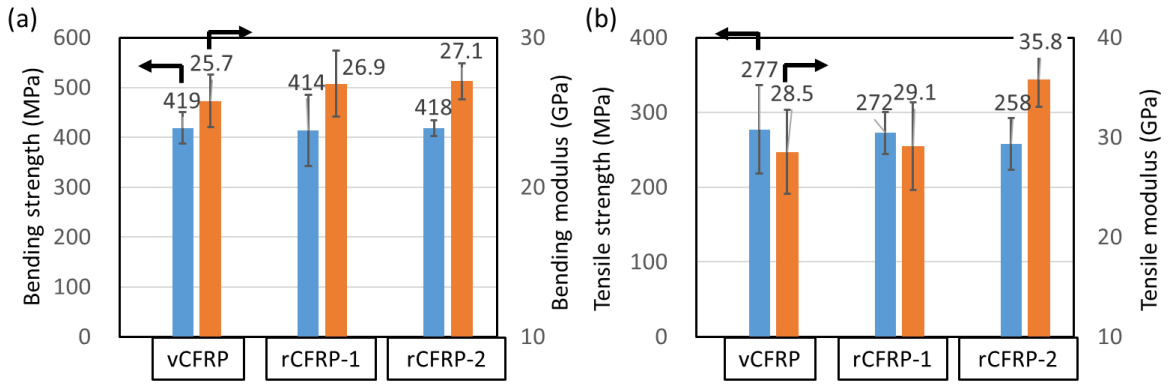

Fig.7 (a) Bending strength and modulus and (b) Tensile strength and modulus for CFRP plate.

4 CONCLUSION

In this report, in order to develop a practical recycling method which is environmentally friendly, the following two points focusing on nitric acid recycling method were conducted. First of all, new recycling scheme was studied in order to recover carbon fiber in short recycling time. Secondly, evaluated the mechanical properties of CFRP plate molded from recycled carbon fibers, to discuss the effective way to use recycled carbon fibers. The conclusions of this study are as follows.

1) Comparing the recycling scheme between the original recycling scheme 1; immersing to nitric acid to decompose resin from the CFRP, and a new recycling scheme 2; immersing CFRP sample to alkaline aqueous solution after immersion to nitric acid for 8 h, resin free carbon fiber was obtained from any alkaline aqueous solution in short time. Among the alkaline aqueous solution, $NaHCO_3$ (pH 8) was selected which showed a significant effect obtaining resin free carbon fiber in short time and also from the safety point of view. This new recycling scheme 2 using $NaHCO_3$ successfully reduced the recycling time into 8.3 h, which achieved 16 h reduction compared to original recycling scheme 1. The detailed mechanism that $NaHCO_3$ effectively removes the resin will be discussed in our further research.

2) Secondly, recycled carbon fibers were processed into non-woven fabric. A uniform non-woven fabric was obtained from recycled carbon fiber which was recovered through recycling scheme 2. Evaluating the mechanical properties of CFRP mold from non-woven fabric, CFRP mold from recycled materials did not decreased its bending strength and tensile modulus compared to CFRP mold from virgin materials. Moreover, imcreased its bending modulus and tensile modulus than virgin one.This result showed that recycled materials could likely be applied to CFRP products where high quality requires and replace virgin materials, which is a novel approach to realizing closed-loop recycling.

The economical and environmental effect to reuse recycled materials will be discussed in our future research.

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