

# Oxidative Degradation of CFRP with NO<sub>2</sub> in sc CO<sub>2</sub> for Chemical Recycling

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An attempt was made to oxidatively degrade carbon fiber reinforced plastics (CFRP) with NO<sub>2</sub> in supercritical CO<sub>2</sub> (scCO<sub>2</sub>), in order to recover carbon fiber (CF) as well as other industrially useful chemicals from CFRP waste. An extensive series of experiments revealed that the most promising experimental conditions for the oxidative degradation of ca. 0.5 g CFRP in NO<sub>2</sub>/scCO<sub>2</sub> were reaction time of 1 h at 140°C under 10 MPa using 1.0 g of NO<sub>2</sub>. Clean CF was recovered almost quantitatively under these conditions, and it was found that the CF content of the CFRP used in this study was ~63%. Furthermore, 2,4,6-trinitrophenol, which might have been produced by the breakage of polymer main chains and subsequent nitration, was also recovered in ca. 10% yield with respect to the initial amount of CFRP. Based on IR analyses, it was surmised that the remaining residue of decomposed products was a mixture of oligomers derived from the original resin and their nitration products. A probable reaction path for the oxidative degradation of the matrix polymer was also proposed.

## INTRODUCTION

Carbon fiber reinforced plastics (CFRP) are composite materials consisting of a polymer matrix in which carbon fibers with a diameter of a few micrometers are embedded. CFRPs, which are generally lightweight, low-density materials, exhibit considerably enhanced rigidity and electrical/thermal conductivity [1]. Due to these advantageous characteristics, they are used as structural engineering materials, especially in aircraft and aerospace production. Moreover, CFRPs have recently found widespread use in the automotive industry, in motor racing, and in the manufacture of sports equipment subject to high levels of stress. They are used for making high-strength and high-rigidity parts in industrial applications, such as robot arms, reinforcements and sleeves in turbomolecular pumps, and drive shafts [2]. Consequently, worldwide demand for CFRP continues to increase. The total production of CFRP in 2008 was 40,000 tons, and in the last 5 years the demand has increased ca. 15% per year, more than 20% of which from the aircraft industry. The demand is expected to expand further in the future, and approach 70,000 tons in 2012 [3, 4]. Therefore a proportional amount of waste CFRP materials is also expected to be produced

It is widely thought that CFRP materials are difficult to recycle because they are composed of a thermosetting resin matrix containing carbon fiber. Until now, little CFRP waste has been recycled, almost all being dumped in landfills, although a few

recycling processes have been implemented. One example is the material recycling of CFRP waste, in which the waste is simply crushed and used as a concrete loading material [5]. Another is the chemical recycling of CFRP. In this process, the CFRPs are pyrolyzed and CF is reclaimed for reuse [6, 7]. However, in the latter process, there are doubts about whether the reclaimed CF has the same mechanical properties as those of virgin CF, because of the high-temperature treatment of CFRP during pyrolysis. Thus, the development of a new technique appropriate for CFRP is now desirable, in order to reclaim CF and the matrix resin, as part of a new recycling system.

Supercritical fluids (SCF) have received much attention as reaction and processing media in materials synthesis. Supercritical carbon dioxide (scCO<sub>2</sub>) is by far the most frequently used fluid because it is cheap, non-toxic and non-flammable and has a relatively low critical temperature (T<sub>c</sub> = 304 K) and pressure (7.4 MPa). Furthermore, the low viscosity and high diffusivity relative to liquids and very low surface tension of scCO<sub>2</sub> make it an ideal solvent in many types of chemical reactions. Lastly, the use of scCO<sub>2</sub> facilitates isolation of products at the end of the reaction, since CO<sub>2</sub> is a gas at ambient pressure and is eliminated completely upon depressurization.

Because of these advantageous physico-chemical characteristics of scCO<sub>2</sub>, it has been used in many types of chemical reactions, and even in some reactions related to CFRP recycling. The chemical recycling of glass fiber reinforced plastics (GFRP) and CFRP in subcritical benzyl alcohol [8] and the decomposition of CFRP in sub- and supercritical water [9, 10] have been reported. Recently, we have succeeded in oxidatively degrading nylon-6 and nylon-6,6 with NO<sub>2</sub> in scCO<sub>2</sub> [11]. In this study, it was revealed not only that valuable short-chain  $\alpha,\omega$ -diacids could be obtained in good yield under relatively mild conditions, but also the utility of the NO<sub>2</sub>/scCO<sub>2</sub> system for oxidation reactions of polymers. In our continued search for new types of chemical recycling of polymers, we describe herein the oxidative degradation of CFRP with this NO<sub>2</sub>/scCO<sub>2</sub> system, especially in order to recover CF, as well as to recycle the matrix resin for chemical uses.

## MATERIALS AND METHODS

**Materials.** A specimen of cured CFRP was kindly donated by Advanced Composite Materials Tochigi Co., Ltd., which manufactures body and wing parts of B747 aircraft using CFRP. The composition of the donated specimen was unknown.

Liquid CO<sub>2</sub> and liquid NO<sub>2</sub> were purchased from Hikari Sanso Co., Ltd., and Takachiho Chemical Ind., Ltd., respectively, with purities >99.8%. All other chemicals were of reagent grade and purchased from Wako Pure Chemical Ind., Ltd., and/or Aldrich Chemical Co. with purities >99.9%, and were used as received.

**Characterization.** <sup>1</sup>H-NMR spectra were recorded on a JEOL JNM-ECS500 (500 MHz) spectrometer. IR spectra of KBr pellets of the sample were measured on a Fourier-transform IR spectrophotometer (Shimadzu, FTIR 8400A). Microscopic images of CF were obtained using a JEOL JSM-T330A scanning electron microscope (SEM) with and without gold coating of specimens.

**CF recovery procedure.** Before the reactions, the rock-like CFRP sample was crushed using a Nippon Rikagaku Kikai R-8 chemical mill, and the crushed sample was used without sieving. All reactions were conducted in batch mode in a 50-cm<sup>3</sup> high-pressure stainless steel reactor with a magnetic stirrer. CFRP sample (ca. 0.5 g) was placed in

the reactor, and the inside of the reactor was purged with a small amount of CO<sub>2</sub>. After the introduction of appropriate amounts of liquid NO<sub>2</sub>, a calculated amount of liquid CO<sub>2</sub> needed to maintain a desired pressure was introduced into the reactor. Next, the reactor was heated to the desired reaction temperature using an oil bath and maintained at that temperature for a certain time. In this stage, the heating rate was of critical importance. The reaction N<sub>2</sub>O<sub>4</sub> → 2NO<sub>2</sub> is extremely exothermic [12], and care should be taken to prevent a vigorous reaction by keeping the heating rate lower than ca. 2 °C·min<sup>-1</sup>. For example, it required 1 h to reach 100 °C from ambient temperature in order safely to carry out the reaction in our NO<sub>2</sub>/scCO<sub>2</sub> system.

After a specified reaction time, the reactor was placed in an ice bath to quench the reaction. When the temperature in the reactor reached ambient temperature, the gas phase was vented slowly and the reaction product was collected by washing with acetone.

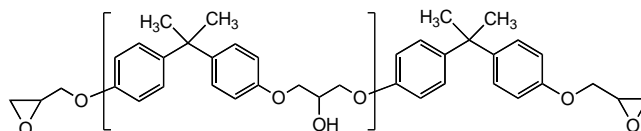
The solid residue, which was expected to contain recovered CF, was filtered off, washed with acetone, and dried in vacuo. The obtained solid residue is hereafter denoted SD-RE. The acetone extract was evaporated using a rotary evaporator. This residue was dissolved in hot water and separated into a water-insoluble residue (WIS-RE) and a water-soluble fraction, which was further extracted with ethyl acetate (EA). Evaporation of the EA phase afforded solid products, denoted EA-EX (solid extracted from EA).

Yields of each of the isolated products (SD-RE, WIS-RE, and EA-EX) were expressed as a mass% with respect to the initial amount of CFRP sample used.

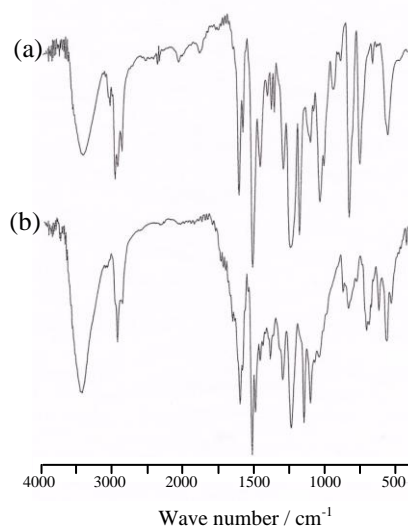
## RESULTS

**Composition [Is this correct?] of the CFRP sample.** The composition of the matrix resin donated by ACM Tochigi Co., Ltd., was not divulged by the manufacturer. In order to obtain structural information on the resin, therefore, its IR spectrum was measured. In general, it is well known that thermosetting resins such as epoxy resin, polyamide resin and phenol resin are mainly used for the CFRP matrix. Therefore, we also measured the IR spectra of these commercially available resins, and compared them with the spectrum of the CFRP sample used in this study.

Figure 1 shows the IR spectra of our CFRP sample (1b) and poly(bisphenol A-co-epichlorohydrin) (Mn = 4,000 g/mol, Aldrich reagent, see Scheme 1). Although the spectra were not exactly the same, there were major similarities. Thus, it was postulated that the matrix resin of the donated CFRP sample was similar to a bisphenol A type epoxy resin. However, the identity of the curing agent and the mass % resin remained unknown.



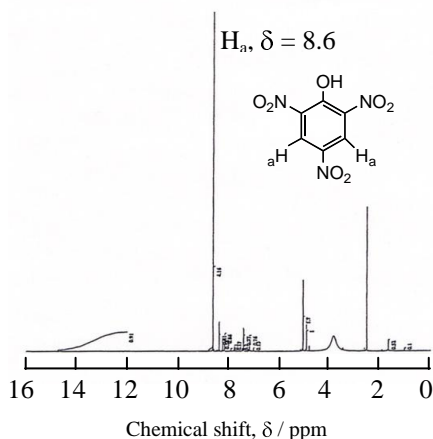
**Scheme 1.** Chemical structure of poly(bisphenol A-co-epichlorohydrin).



**Figure 1.** IR spectra of (a) poly(bisphenol A-co-epichlorohydrin) and (b) CFRP sample.

**Characterization of decomposition products.** The appearance of the SD-RE, which was simply separated from the reaction mixture obtained after oxidative degradation of CFRP in the  $\text{NO}_2/\text{scCO}_2$  system, indicated that it was undoubtedly CF, possibly containing some residual resin.

Figure 2 shows the  $^1\text{H-NMR}$  spectrum of EA-EX. Since it was not possible to separate the EA-EX mixture into its components or to purify the EA-EX, its  $^1\text{H-NMR}$  spectrum was measured without further treatment. The spectrum indicated that EA-EX might contain more than two components. One sharp and strong singlet peak at  $\delta = 8.6$  could be assigned to aromatic protons at 3- and 5-carbons ( $\text{H}_a$  in the figure). Furthermore, a small singlet peak at  $\delta \sim 4.9$  (1H) corresponded to a phenolic proton. Considering that the CFRP sample underwent oxidative decomposition upon treatment with  $\text{NO}_2$  in  $\text{scCO}_2$ ,  $\text{NO}_2$  substitution probably took place during the decomposition of the matrix resin. Thus, the spectrum provided almost conclusive confirmation that the major product in EA-EX was 2,4,6-trinitrophenol (picric acid).

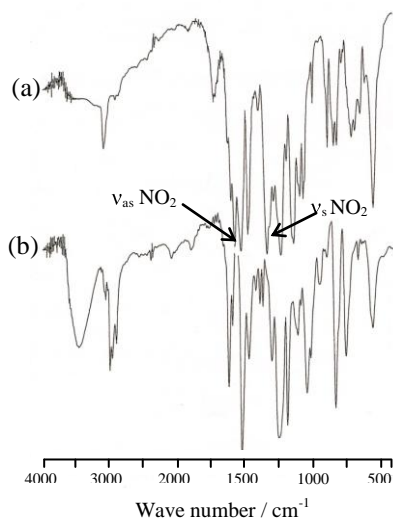


**Figure 2.**  $^1\text{H-NMR}$  spectra of EA-EX in  $d_6$ -DMSO.

In addition, there were some other characteristic peaks at  $\delta \sim 5$ ,  $\delta \sim 7 - 8$  and  $\delta \sim 13$ . The peaks at  $\delta \sim 7 - 8$  suggested the existence of aromatic rings, possibly indicating that the oligomeric products resulted from the decomposition of the main chains of the matrix resin. Also, the peaks at  $\delta \sim 5$  and  $\delta \sim 13$  suggested the presence of aliphatic carboxylic compounds such as succinic acid or malonic acid in the decomposition product, since the former peaks might be from methylene protons and the latter from carboxylic protons. The production of aliphatic carboxylic compounds was not surprising, because a prior literature report has detailed the formation of aliphatic dicarboxylic acids such as adipic, glutaric and succinic acids during oxidative degradation of nylons in the  $\text{NO}_2/\text{scCO}_2$  system [11].

Figure 3 shows the IR spectra of solid WIS-RE (a) and of poly(bisphenol A-co-epichlorohydrin) (b), for comparison. Both spectra were very similar except for a few peaks. For example, the peaks near  $1540 \text{ cm}^{-1}$  and  $1346 \text{ cm}^{-1}$ , corresponding to  $\nu_{\text{as}} \text{NO}_2$  and  $\nu_{\text{s}} \text{NO}_2$ , respectively, are absent in Figure 3(b). Therefore, it was surmised that WIS-RE consisted of  $\text{NO}_2$ -substituted oligomers of poly(bisphenol A)-type resin.

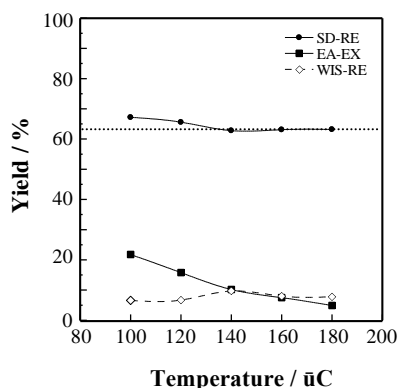
It should be emphasized that no peaks corresponding to amine group vibrations such as  $\nu \text{ N-H}$  or  $\nu \text{ C-N}$  were seen in the IR spectra of WIS-RE. Since amines are typically used as curing agents in the production of CFRP, amine vibration peaks would have been expected in the WIS-RE spectra if the CFRP sample used in this study was amine-cured. The absence of such peaks indicated either (i) that the  $\text{NO}_2$  attacked not only aromatic rings but also the N-H and N-C moieties of any amine bonds in the polymer backbone, or (ii) that amine derivatives were not used for curing the CFRP.



**Figure 3.** IR spectra of (a) WIS-RE sample and (b) poly(bisphenol A-co-epichlorohydrin).

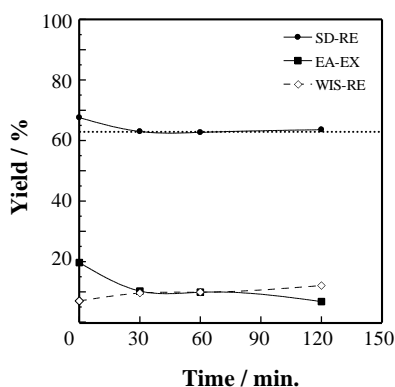
**Effect of experimental conditions on product yields.** Figure 4 shows the effect of temperature on product yields. It is very interesting to note that  $\text{NO}_2$  in  $\text{scCO}_2$  is a strong oxidizing agent that can degrade the CFRP matrix resin. Even at temperatures as low as  $100 \text{ }^\circ\text{C}$ , almost all of the CF (i.e., SD-RE) was completely recovered. Since our  $\text{NO}_2/\text{scCO}_2$  system contained such a strongly degrading environment, the reaction

temperature did not greatly affect the yield of SD-RE; the yield of CF was almost constant in the 100 - 180 °C range. However, the yield of EA-EX (predominantly picric acid) decreased with increasing temperature. This might imply that the degradation of polymer main chains occurred at the aromatic rings in these chains, with simultaneous NO<sub>2</sub> substitution. On the other hand, because of the strong oxidizing power of the NO<sub>2</sub>/scCO<sub>2</sub> system, picric acid and the other byproducts might themselves have been subject to decomposition, and consequently the yield of EA-EX decreased rapidly with increasing temperature.

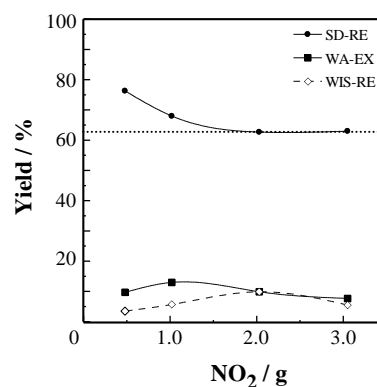


**Figure 4.** Effect of temperature on the yields. (CFRP: 0.5 g; 1 h; 10 MPa; NO<sub>2</sub>: 2.0 g)

The effects of varying reaction time are displayed in Figure 5. As shown in the figure, increasing the reaction time did not greatly affect the yield of recovered CF. Thus, we found our NO<sub>2</sub>/scCO<sub>2</sub> system to be quite effective for the decomposition of CFRP and the reaction might have been spontaneous under these conditions. However, as expected, the yield of EA-EX decreased gradually with increasing reaction time.



**Figure 5.** Effect of time on the yields. (CFRP: 0.5 g; 140 °C; 10 MPa; NO<sub>2</sub>: 2.0 g)



**Figure 6.** Effect of NO<sub>2</sub> amount on the yields. (CFRP: 0.5 g; 140 °C; 1 h; 10 MPa)

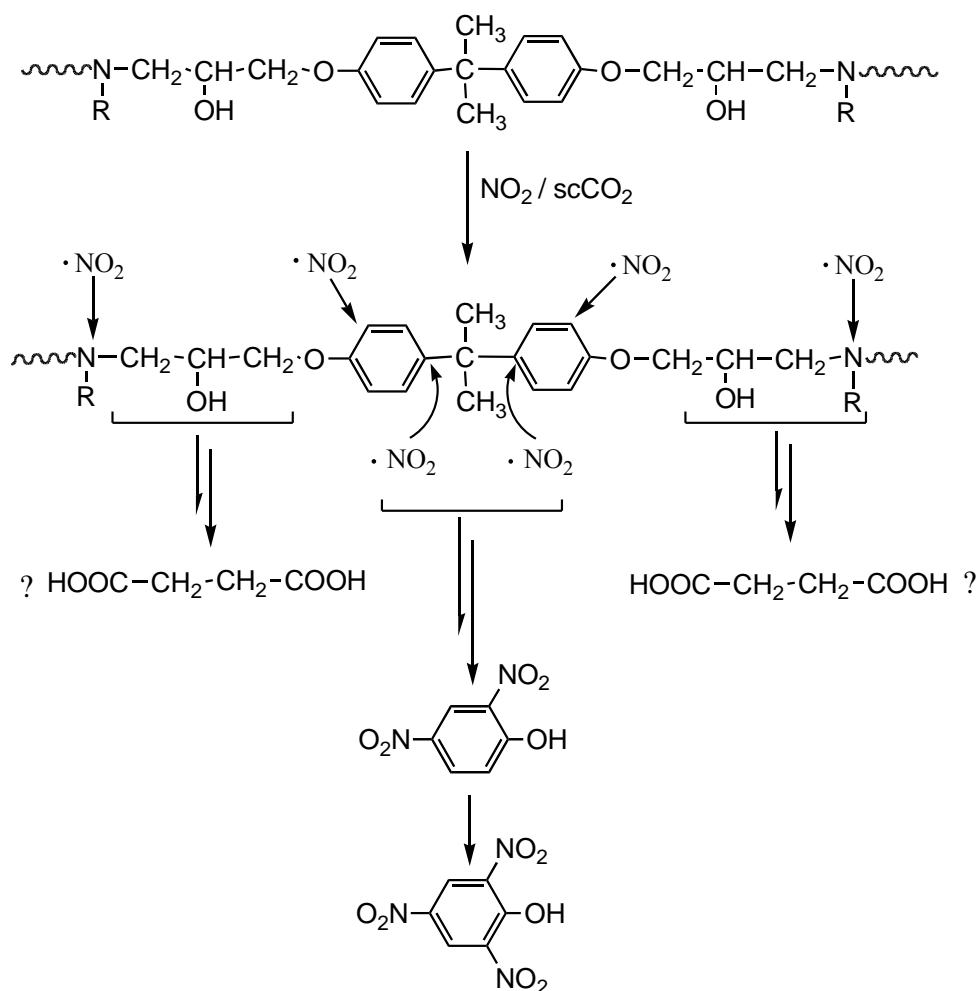
Control of the amount of NO<sub>2</sub> used was critical to obtaining good yields of SD-RE, and was the most important experimental parameter, as shown in Figure 6. The yield of SD-RE (from 0.5 g CFRP starting material) decreased with increasing amounts of NO<sub>2</sub>, reaching a constant value of ~63% when the amount of NO<sub>2</sub> used in the reaction

mixture exceeded 2.0 g. The yield of WA-EX was not strongly affected by the quantity of  $\text{NO}_2$  used.

In light of these results, it was concluded that the most promising experimental conditions (i.e., to recover the most CF by oxidative degradation of CFRP) in the  $\text{NO}_2/\text{scCO}_2$  system were a reaction time of 1 h, temperature of 140 °C, pressure of 10 MPa and 2.0 g of  $\text{NO}_2$  for every 0.5 g CFRP. Under these conditions, the amount of recovered CF was almost constant, suggesting that the CF content of the original CFRP sample was ca. 63%. In addition, ~13% of picric acid (with respect to the initial amount of CFRP used) was obtained.

***A proposed reaction pathway for oxidative degradation of CFRP in  $\text{NO}_2/\text{scCO}_2$ .***

Based on the experimental results obtained in this study, we propose the mechanism shown in Scheme 2 for the degradation of the polymer matrix of CFRP in  $\text{NO}_2/\text{scCO}_2$ .



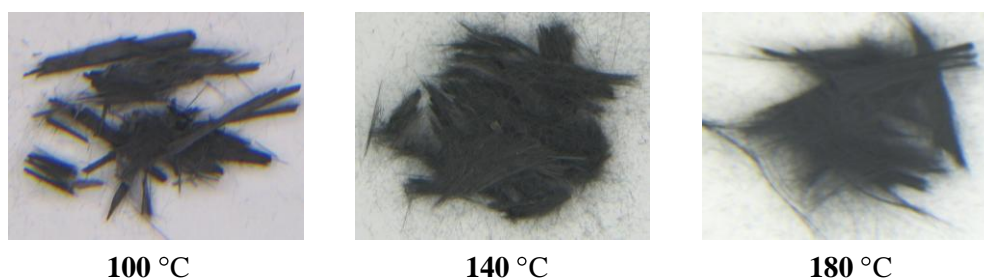
**Scheme 2.** A postulated pathway for the oxidative degradation of matrix resin in the  $\text{NO}_2/\text{scCO}_2$  system.

Based on our experimental evidence, together with the fact that the equilibrium  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2\bullet$  shifts to the right with increasing temperature [12], it was very probable that the  $\text{NO}_2$  radical attacked many positions, such as the quaternary carbon substituted ipso carbon on the aromatic ring, the 2- and 4-carbons on the aromatic ring, and the N atoms of the amine moieties. This was supported by the fact that during the degradation of certain nylons with  $\text{NO}_2$  in  $\text{scCO}_2$ , the  $\text{NO}_2$  radical exclusively attacked the NH moiety of each amide bond on the polymer backbone, with oxidation of the  $\alpha$ -carbons to carbonyl groups, to form  $\alpha,\omega$ -diacids as the final products of oxidative degradation [11].

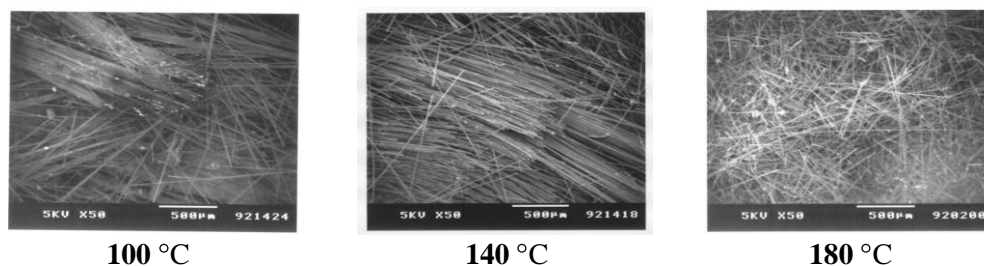
The degradation of CFRP in this study appeared to follow a similar reaction pathway to that of nylon. Thus, the matrix polymer chains were decomposed by a radical chain reaction initiated by  $\text{NO}_2$ , ultimately resulting in 2,4,6-trinitrophenol and succinic acid, even though the latter compounds could not be isolated. A similar mechanism has been proposed for the photo-oxidation of low-density polyethylene by zip depolymerization [13].

**Fiber characterization** SEM images were only taken of those recovered CF samples which had been obtained using optimized experimental conditions, i.e., reaction time of 1 h at 10 MPa using 2.0 g of  $\text{NO}_2$  per 0.5 g CFRP, and mainly to determine the influence of reaction time on the surfaces of the recovered fibers.

Figure 7 shows images of the recovered CF samples obtained at various temperatures. As mentioned before, at reaction temperatures higher than 140 °C, the yield of SD-RE, i.e., CF, was almost unchanged (see Fig. 4). Therefore, CF recovered at temperatures higher than 140 °C was not expected to be coated with the matrix resin, as indicated by the data of Figure 4. The images of CF recovered at 100 °C showed bundles of fibers still tightly bonded to each other, whereas the more fluffy CF recovered at elevated temperatures seemed to consist of separate fibers. The influence of temperature on the recovered CF surface was even more clearly observed in SEM photographs (Figure 8), even at magnifications as low as 50x.



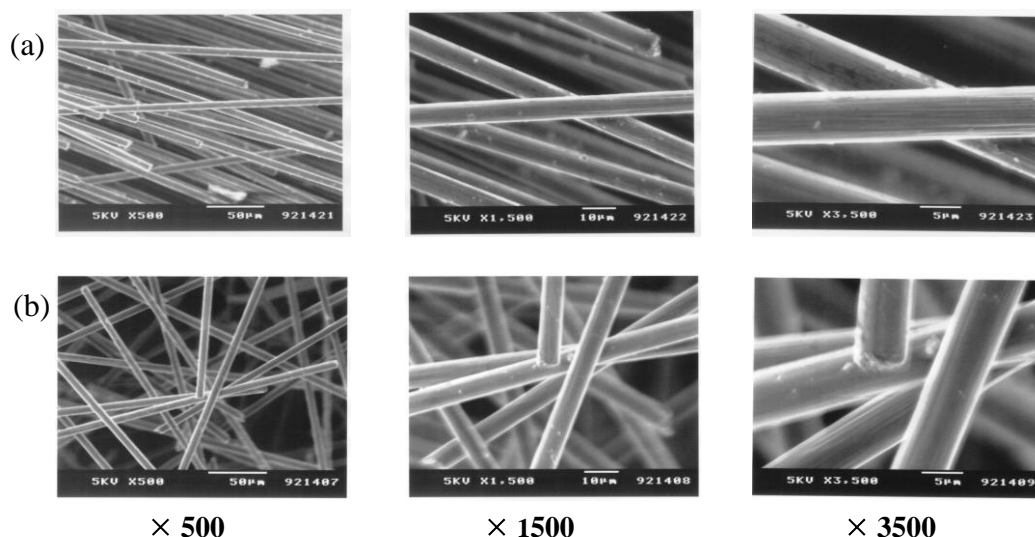
**Figure 7.** Images of recovered CFs. (sample: 0.5 g; 10 MPa;  $\text{NO}_2$ : 2.0 g)



**Figure 8.** SEM images of recovered CFs at 50x magnifications (sample: 0.5 g; 10 MPa;  $\text{NO}_2$ : 2.0 g).



Figures 7 and 8 show the obvious influence of degradation temperature on the fiber surface. However, in order to optimize the process temperature, the fiber surface was observed at various magnifications, since lower temperatures were expected to result in less thermal deterioration of the CF surfaces. Figure 9 presents SEM images of CF samples recovered at 140 °C and 180 °C, under 500x, 1500x and 3500x magnifications.



**Figure 9.** SEM images at various magnifications of CFs recovered at (a) 140 °C and (b) 180 °C (sample: 0.5 g; 10 MPa; NO<sub>2</sub>: 2.0 g).

Fibers recovered at 140 °C still showed some thermally degraded matrix resin present, whereas the images of fibers recovered at 180 °C showed nearly clean, smooth fiber surfaces. Thus, it was concluded that a reaction temperature of at least 140 °C was needed for the degradation of CFRP in order to obtain clean fibers with a minimum of oxidation damage.

## CONCLUSIONS

In this study, the high potential of oxidative degradation with an NO<sub>2</sub>/scCO<sub>2</sub> system to recover CF from CFRP scrap was successfully demonstrated. Optimized experimental parameters were determined from detailed experiments varying reaction time, temperature and concentration of NO<sub>2</sub>. Of these system parameters, the temperature and the NO<sub>2</sub>-to-CFRP ratio played important roles in recovering clean, smooth fibers. Finally, it was concluded that the optimum experimental conditions required reaction time of 1 h at 140 °C under 10 MPa using 2.0 g of NO<sub>2</sub> for every 0.5 g CFRP. SEM observation of the fiber surface showed that the fibers underwent no serious damage. Consequently, CF recovered in this manner might be suitable for use in other processes. Furthermore, in the present study, valuable chemicals such as picric acid were also recovered from the CFRP sample.

Thus, the NO<sub>2</sub>/scCO<sub>2</sub> system could be used to recover CF under relatively mild experimental conditions, offering a new method for chemical recycling of CFRP scraps.

However, the decomposition products obtained from the degradation of the matrix resin were not completely identified in this study. Future research will focus on the precise identification of these products as well as mechanical testing of the recovered CF.

## ACKNOWLEDGMENT

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