CHEMICAL RECYCLING OF CARBON FIBER REINFORCED PLASTIC WITH SUPERCRITICAL ALCOHOL

I.Okajima[1], K.Watanabe[1], Y.Shimamura[1], T.Awaya[1] and T.Sako[1]

[1]Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan
e-mail: tiokaji@ipc.shizuoka.ac.jp

Abstract

In order to establish the recycling technique of carbon fiber reinforced plastic (CFRP), we investigated the optimum conditions to decompose epoxy resin used for matrix resin of CFRP using supercritical methanol (239°C of critical temperature and 8.0MPa of critical pressure). Supercritical methanol at 250-350°C and 10MPa was used for the decomposition and solubilization of epoxy resin at 5-120min of reaction time. In the case of uncatalyzed reaction, the crosslinked structure of epoxy resin was decomposed selectivity and the uncured resin dissolved in supercritical methanol at higher than 270°C within 1h. When the temperature decreased to 250°C, whole epoxy resin dissolved in supercritical methanol for 2h. MALDI-TOF/MS analysis of the decomposed and methanol-soluble epoxy resin indicated that the main chain of epoxy resin did not decompose and the ester bond decomposed selectively. When CFRP was treated using semi-flow type reactor, the recovered carbon fiber had no heat damage and maintained the shape of the plain fabric. On the other hand, matrix resin was solubilized in methanol and did not remain on the surface of carbon fiber.

Keywords: *CFRP, Chemical Recycling, Supercritical Alcohol*

1. Introduction

Recently recycling is required strongly from the viewpoint of environmental protection and conservation of petroleum resources. Especially much attention is attracted to the recycling techniques of waste plastics. Carbon fiber reinforced plastic (CFRP) has excellent characteristics of low density and high strength so that it has been used for several fields such as aerospace industry and aviation materials and so on. However waste CFRP is difficult to recycle because it contains thermosetting plastics such as epoxy resin. Now major waste treatment is landfill. Therefore the development of advanced recycling technique of CFRP is expected strongly.

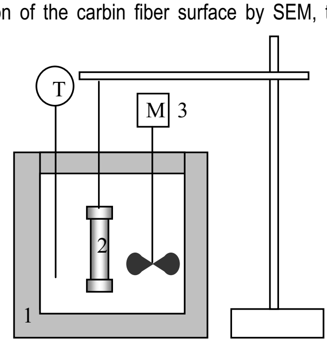
In order to establish the new recycling technique of CFRP, we investigated the optimum conditions to decompose epoxy resin used for matrix resin of CFRP and recover the carbon fiber (CF) without thermal and mechanical damage. In this work, epoxy resin was tried to decompose and solube by supercritical methanol. In this case, the methanol-soluble epoxy resin separates from carbon fiber and the resin can be reused as an unhardened epoxy resin.

2. Materials and Methods

The bisphenolA type epoxy resin and CFRP were used for the decomposition experiment. The bisphenolA type epoxy resin, which was hardened with phthalic anhydride, was crushed into peaces of about 3mm square. CFRP was made of carbon fiber and bisphenolA type epoxy resin cured with phthalic anhydride as matrix resin. In this work, two kinds of apparatuses were used.

Figure1 shows the batch-type reactor to determine the optimum condition of the recycling of CFRP. The reactor was 316 stainless steel tube of 12.7mm in diameter, 150mm in length and 8.9cm^3 in inner volume. The whole reactor was immersed into a salt bath.

The experimental procedure was as follows. A given weight of either epoxy resin or CFRP, which was cut into pieces of 3mm×3mm×45mm, and methanol were loaded into the reactor. The both sides of the reactor was sealed by caps and heated in the salt bath during a certain reaction time. It took about 90 sec to reach the reaction temperature. The reactor was taken out of the salt bath and cooled in water to stop the reaction as soon as possible. The products and carbon fiber were recovered from the reactor with methanol. Then the weight of the solid residue, molecular weight of products by TOF-MS, observation of the carbin fiber surface by SEM, tensile



1. Salt bath 2. Reactor 3. Agitator T. Thermometer

Figure 1 : Batch-type experimental setup.

strength of CF and ratio of functional groups on carbon fiber surface were measured. The reaction temperature was assumed to be equal to the temperature of the salt bath. The reaction pressure was calculated from the reactor temperature, inner volume of the reactor and the loaded weight of methanol.

Semi-flow type experimental setup had the reactor made of 316 stainless steel of 4.7L in inner volume. A given weight of CFRP (200 mm×45 mm× 2mm) was loaded into the reactor and it was sealed. Methanol was injected using a high pressure pump. Then the reactor was heated until a given reaction temperature. The starting time of the reaction was defined as the time when the temperature in the reactor was reached at the reaction temperature. After the treatment of CFRP, inside of the reactor was washed with methanol and the products and CF were recvered.

3. Results and Discussion

Figure 2 shows the dependence of the residual ratio of the epoxy resin on reaction temperature and time using supercritical methanol. The reaction pressure was constant at 10MPa. The residual ratio of the epoxy resin is defined as the ratio of the weight of methanol-insoluble residue after the decomposition to that of charged epoxy resin. For the uncatalyzed reaction, whole epoxy resin decomposed and dissolved in supercritical methanol within 1h at higher than 270°C and for 2h at 250°C.

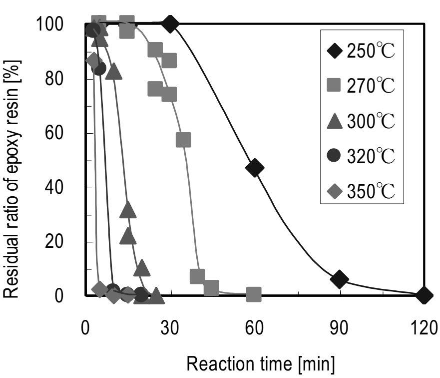


Figure2: Dependence of residual ratio of epoxy resin on reaction temperature and time at 10MPa without catalyst.

Figure 3 shows the analytical result of the decomposed and methanol-soluble epoxy resin at 270 and 350°C, 10MPa, 60min by MALDI-TOF/MS. The molecular weights of the decomposition products decreased with reaction temperature. For example, the maximum molecular weight was 2073 at 270°C and 483 at 350°C. Methanolysis reaction was accelerated at higher temperature. Furthermore, judging from the analytical result of the products, the main chain of the epoxy resin did not decompose and ester bond combining each epoxy resin segment decomposed selectively. The decomposed and methanol-soluble epoxy resin was used as an uncured resin material.

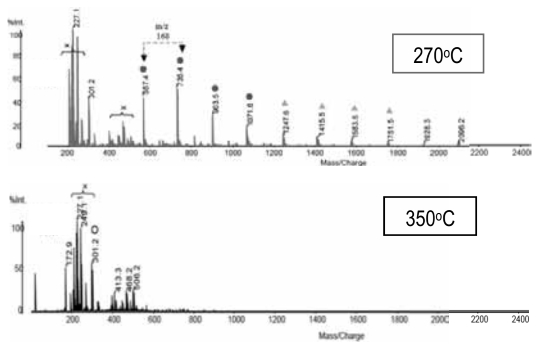


Figure 3:Analytical result of methanol-soluble epoxy resin at 27(and 350°C, 10MPa, 60min by MALDI-TOF/MS. (×: Matrix resin)

When CFRP was treated with supercritical methanol at 270°C, 10MPa, 60min, the tensile strength of the recovered CF was about 5% lower than that of virgine CF. This decrease of tensile strength was no problen for reuse of carbon fiber. On the other hand, a part of the oxygenated functional group on the surface of CF, such as carbonyl and hydroxy groups, was removed. From this resurt, the oxydation treatment of CF surface is necessary when the recovered carbon fiber is reused.

Next, CFRP was treated using semi-flow type reactor. The appearance of recovered CF was shown in Figure 4. Matrix resin of CFRP was soluble in methanol commpletely at the same reaction condition as the batch type setup. The recovered CF maintained the shape of the plain fabric and the matrix resin was not remain on the surface of CF.

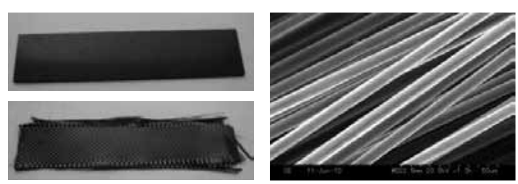


Figure 4:Appearances of CF. (upper left: CFRP before treatment, lower left: recovered CF after supercritical methanol treatment, right: SEM image of recovered CF)

4. Conclusions

We investigated the optimum conditions to decompose epoxy resin used for the matrix resin of CFRP. When epoxy resin was treated with supercritical methanol without catalyst, the crosslinked bridge of the epoxy resin was decomposed selectively and dissolved in supercritical methanol within 1h above 270°C. The recovered and cured epoxy resin indicated the strength close to virgin epoxy resin. Furthermore, the recovered CF kept the plain fabric when CFRP was treated with supercritical methanol using semi-flow reactor.

Acknowledgment

We thank the support from The New Energy and Industrial Technology Development Organization (NEDO).