

Chemical Recycling of Carbon Fiber Reinforced Plastic with Sub- or Supercritical Fluids

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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 two kinds of sub- or supercritical fluids.

First, subcritical water at 300-400°C and 20MPa was used for the decomposition of epoxy resin and the recovery of phenolic monomers, where phenolic monomers mean phenol and isopropyl phenol. In the case of uncatalyzed reaction, the total yield of phenolic monomers increased with temperature and reaction time. The maximum of the total yield was 50% at 400°C and 60min. On the other hand, in the case of catalyzed reaction using 2.5wt% potassium carbonate, the total yield increased with reaction time until 45min. However, after 45min, it decreased with the reaction time because the monomers decomposed in subcritical water. The maximum of the total yield was 72% at 400°C and 45min.

Second, 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 selectively 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.

INTRODUCTION

Recently recycling is required strongly from the viewpoint of environmental protection and conservation of 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 without thermal and mechanical damage. In this work, epoxy resin was tried to decompose with two kinds of sub- or supercritical fluids. One is the decomposition by subcritical water to phenolic monomers of phenol and isopropyl phenol. The other is the decomposition and solubilization by supercritical methanol. In this case, the methanol-soluble

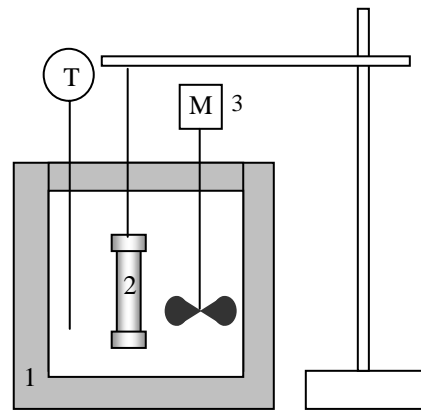
epoxy resin separates from carbon fiber and the resin can be reused as an unhardened epoxy resin.

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. It was cut into pieces of 3mm×3mm×45mm.

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 8.9cm³ in inner volume. The whole reactor was immersed into a salt bath.

The experimental procedure was as follwos. A given weight of either epoxy resin or CFRP and either water or 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, the concentration of phenolic monomers 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 water or methanol.



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

Figure 1 Batch-type experimental setup.

RESULTS

1. Decomposition of epoxy resin and CFRP with subcritical water

Figure 2 shows the dependence of the total yield of phenolic monomers on the reaction time and potassium carbonate catalyst at 400°C and 20MPa. The decomposition behavior of pure epoxy resin was similar to that of epoxy resin in CFRP for both catalyzed and uncatalyzed reactions. In the case of uncatalyzed reaction, the total yield of the phenolic monomers increased with reaction time. The total yield was 50% at 60min. On the other hand, in the case of catalyzed reaction of 2.5wt% potassium carbonate, the total yield increased with reaction time until 45min. Then it decreased with reaction time. This was because the monomers decomposed in subcritical water. From these results, the maximum total yield was 72% at 400°C, 20MPa and 45min using 2.5wt% potassium carbonate.

The carbon fiber was recovered after the decomposition of epoxy resin at 400°C, 20MPa and 45min with or without potassium carbonate catalyst. The tensile strength of the carbon fiber is shown in Figure 3. It decreased by 12-17%, comparing with virgin carbon fiber. The catalyst did not influence the strength of carbon fiber much. On the other hand, when CFRP was heated at around 400°C and 0.1MPa in air, the strength of carbon fiber hardly decreased.

As a result, the reduction of the tensile strength was caused by the contact with subcritical water for a long time. However this small reduction of the tensile strength has no problem for practical reuse. From these results, the optimum condition of CFRP recycling with subcritical water was 400°C, 20MPa and 45min using 2.5wt% potassium carbonate.

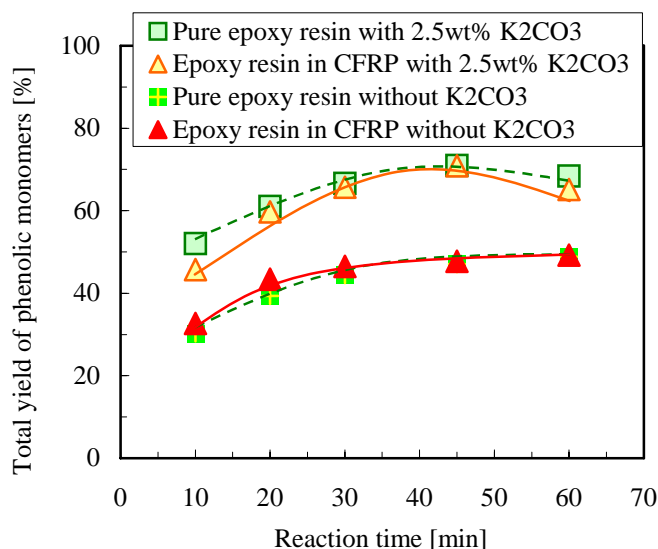


Figure 2 Reaction time dependence of total yield of phenolic monomers at 400°C and 20MPa.

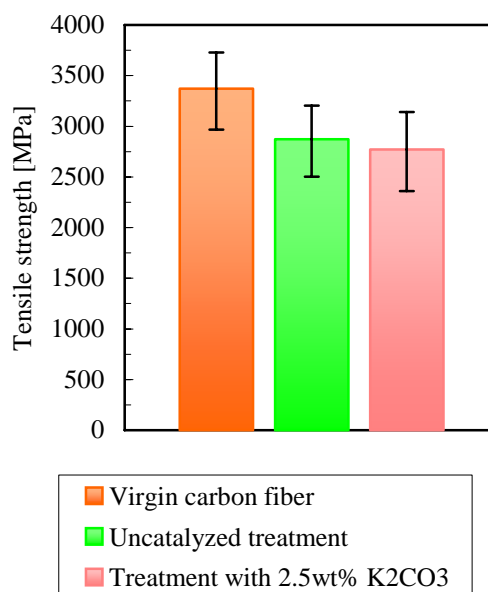


Figure 3 Tensile strength of carbon fiber treated at 400°C, 20MPa and 45min.

2. Decomposition of epoxy resin with supercritical methanol

Figure 4 shows the dependence of the residual ratio of the epoxy resin on reaction temperature and reaction 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 the weight 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.

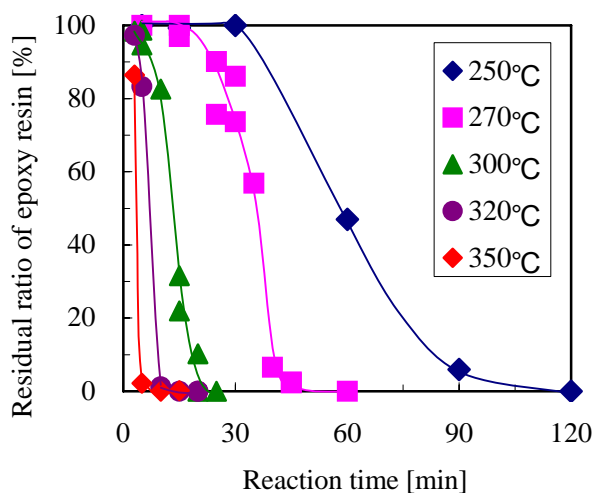


Figure 4 Dependence of residual ratio of epoxy resin on reaction temperature and reaction time at 10MPa without catalyst.

Figure 5 shows the analytical result of MALDI-TOF/MS of the decomposed and methanol-soluble epoxy resin at 270 and 350°C, 10MPa, 60min. The molecular weights of the decomposition products decreased with 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.

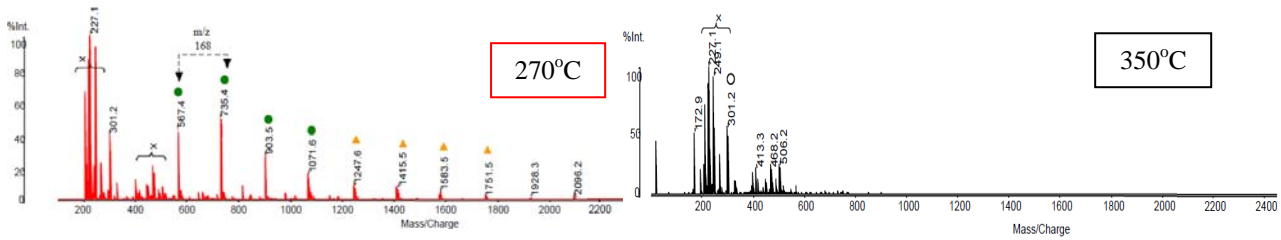


Figure 5 Analytical result of MALDI-TOF/MS of methanol-soluble epoxy resin at 270 and 350°C, 10MPa, 60min. (×: Matrix resin)

The appearances of epoxy resins are shown in Figure 6. The recovered and uncured epoxy resin was black and had high viscosity. The recovered epoxy resin was cured by adding more than 20wt% of acid anhydride. The hardness of the recovered and cured epoxy resin is shown Figure 7, where y-axis is the ratio of the strength of recovered and cured epoxy resin to that of virgin epoxy resin. The curing reaction was carried out at 150°C and 30h. The strength ratio increased with the amount of curing agent a little bit. The strength of re-cured epoxy resin was the same or a little higher than that of virgin resin. From these results, it was indicated that epoxy resin treated with supercritical methanol at 270°C and 1h was able to reuse as pre-polymer before hardening.

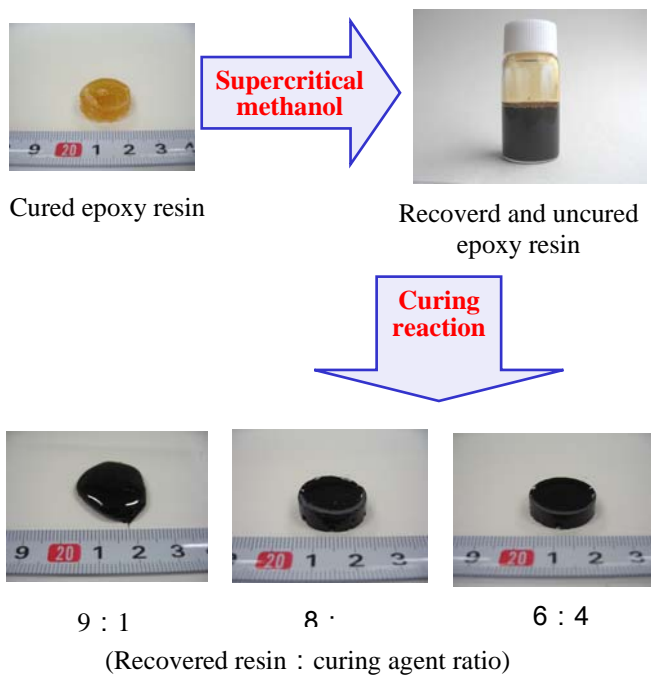


Figure 6 Appearances of epoxy resins.

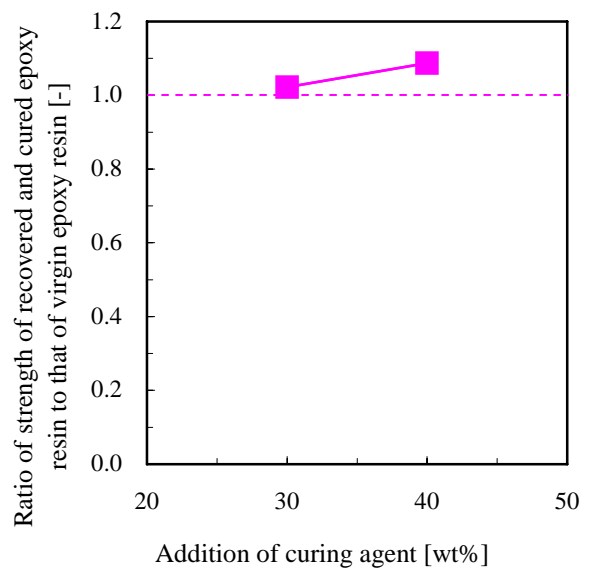


Figure 7 Hardness of recovered and cured epoxy resin.

CONCLUSION

We investigated the optimum conditions to decompose epoxy resin used for the matrix resin of CFRP. The following useful results were obtained:

- (1) When epoxy resin or CFRP was treated with subcritical water, the maximum total yield of phenolic monomers was 72% at 400°C and 45min using 2.5wt% potassium carbonate. At the same time, carbon fiber without epoxy resin was recovered. The tensile strength of carbon fiber decreased by 12-17%, comparing with that of unused carbon fiber.
- (2) When epoxy resin was treated with supercritical methanol without catalyst, the crosslinked points of the epoxy resin was decomposed selectively and dissolved in supercritical methanol within 1h above 270°C. Furthermore the recovered and cured epoxy resin indicated the strength similar to virgin epoxy resin.