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Recycling of fiber reinforced plastics using depolymerization by solvothermal reaction with catalyst

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Abstract Fiber reinforced plastics (FRP) have been widely used as a high strength material. However, it is well known that the FRP is one of the most difficult materials to fractionate into elemental components, namely fiber, filler, and polymers in the waste recycling process. Therefore, the wastes are treated in the incineration or landfilling without any recycling approaches. We have developed a new recycling method using subcritical fluids where unsaturated polyester (UP) resin in FRP can be efficiently depolymerized to separate glass fiber from filler and polymer. Reactions were carried out with or without a catalyst (K_3PO_4) in diethyleneglycol monomethylethter (DGMM) and benzyl alcohol under their subcritical state at temperatures 463–623 K for 1–8 h in a batch reactor. The conversion of UP became fast as the catalyst/solvent molar ratio increased and it was enhanced in the presence of K_3PO_4 catalyst in subcritical BZA. The glass fiber recovered after the FRP treatment in subcritical BZA was relatively long, while it became short and somewhat damaged at temperature higher than 573 K. The similar trend was observed when DGMM was used as a solvent.

Introduction

Plastics have been used in various situations and the consumption is increasing year by year. Plastics production in Japan was 6,100,000 ton in 2005. Therefore, efficient technology for recycling of waste plastics has been seriously desired. Currently, landfilling and incineration are extensively used for waste plastics. Only a fraction of waste plastics have been recycled by material recycling or thermal energy recovery. Therefore, new technologies for waste plastics recycling have been expected to develop because conventional methods have problems.

Recycling methods of waste plastics are three types, that is, material recycling, thermal recycling, and chemical recycling. Material recycling is the method for reuse as material without chemical change. Owing to deterioration in quality, this method is not ideal recycling. Thermal recycling is the method to recover energy by incinerating waste plastics. This method is easily applicable for a mixture of waste plastics. However, carbon resource could not be recycled, although this method is extensively used.

Chemical recycling of waste plastics has attracted great attention from the environmental view point in recent years. Chemical recycling is classified into thermal decomposition, depolymerization (monomerization), and partial oxidation (gasification).

Although several technologies have already been commercialized, they have drawback such as apparatus corrosion caused by strong acid catalyst and slow reaction rate. Recently, sub- and supercritical fluid has been applied to recycle waste plastics. Polyethylene terephthalate (PET) was depolymerized in sub- and supercritical water [1, 2] or methanol [3–7]. Depolymerization of Nylon 6 in sub- and supercritical water has been studied [8–10].

Fiber reinforced plastic (FRP) has been widely used as a high strength material in recent years. FRP is a composite material manufactured by laminating unsaturated polyester resin with glass fiber and filler. FRP has been used in various industries such as petrochemistry, construction,

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automobiles, and environment business because of its heat-resistance, anti-corrosion properties, and mechanical strength. FRP has a specific gravity that is 1/5 of iron where the lightness of it enhances easy carriage. Lower thermal conductivity (1/180 of iron) does not require thermal insulation. Corrosion resistance of FRP, which is one of the most important chemical properties for any compounds, behaves with different character against acid, alkali, salt, and solvent.

On the other hand, it is well known that the FRP is one of the most difficult materials to fractionate into elemental components, namely fiber, filler, and polymers, resulted in the incineration or landfill of used FRP materials without any recycling approaches.

Until now, a few recycling technology of FRP have been studied. Sugeta et al. [11] studied the decomposition of FRP in sub- and supercritical water using a batch-type reactor. FRP was almost completely decomposed at 653 K and 5 min. Fukuzawa et al. [12, 13] investigated the dissolution process of the resin part of FRP by "ambient pressure dissolving method" using various solvents with or without catalyst in order to develop the recycling technology of FRP. They reported the inference of catalyst and solvent on depolymerization of FRP. The highest conversion was observed when K_3PO_4 was used as a catalyst and using diethyleneglycol monomethylethter (DGMM) as a solvent. The second highest conversion was observed for benzyl alcohol (BZA).

In our previous study, we have used solvothermal degradation to dissolve polymers and recover fibers from FRP [14]. In this study, we have developed a new recycling method that unsaturated polyester (UP) resin in FRP can be efficiently depolymerized and separate glass fiber from filler and polymer at subcritical conditions. We investigated the influence of reaction temperature, reaction time, amount of catalyst, and quantity of solvent on the degree of fractionation.

Experimental

The experimental apparatus (AKICO Co. Japan) is shown in Fig. 1. The apparatus consists of a batch-type reactor (about 9 cm^3 inner volume) and a heating electric furnace. FRP sample was supplied by Hitachi Chemical Co. The size of the FRP is 30.0 × 10.0 × 2.0 mm. FRP consists of three elements, that is, glass fiber, unsaturated polyester (UP) resin, and filler ($CaCO_3$). The contents of glass fiber, UP, and filler are 22.5%, 38.75%, and 38.75%, respectively. DGMM with purity more than 98%, BZA with purity more than 99% and K_3PO_4 with purity more than 95% were purchased from Wako Pure Chemical Industries, Ltd. The critical parameters for DGMM and BZA are $T_c = 608$ K, $P_c = 3.4$ MPa and $T_c = 676$ K, $P_c = 4.57$ MPa, respectively.

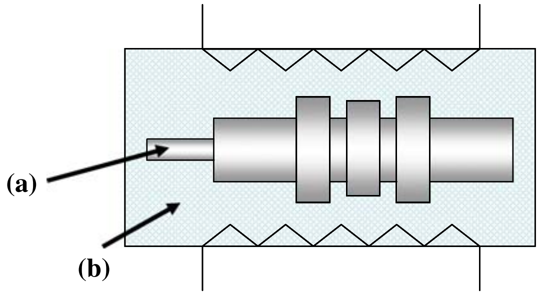

Fig. 1 Experimental apparatus (a) Batch reactor, (b) Electric furnace

The reactions were carried out at temperatures between 463 K and 623 K under catalyst/solvent ratio of 0.07–0.35 w/w and solvent/FRP ratio of 1.1–3.3 w/w for reaction times of 1–8 h.

About 1.8 g of FRP sample, dried catalyst, and dehydrated solvent were charged into the reactor. The remaining air in the reactor was purged with argon gas. The reactor was set in the electric furnace, which is previously heated to the desired temperature. The furnace has a special function to swing the reactor to immerse the whole FRP in solvent (swing span: 2 cm, frequency of swing: 60 Hz). After a certain time, the reactor was quenched quickly by immersing water and the products were collected into test tubes.

The reaction product was filtered into solid and liquid phases. The solid product was washed, dried, and then weighed. The liquid product was analyzed with a gas chromatograph mass spectrometry (GC-MS). The column was Agilent HP-5MS of 30.0 mm × 250 μm × 0.25 μm.

Results and discussion

Products

Figure 2 shows pictures of the solid phase products treated at 573 K in BZA. For 1 h treatment, FRP retained its original form. UP of the surface of FRP was slightly depolymerized. For 2 h treatment, UP of the surface of FRP was partly decomposed and fiber in FRP was appeared. For 3 h treatment, UP of the surface of FRP was completely depolymerized, although polymer in inner part remained. Therefore, fiber was not dissected out because fiber was hardened by UP. After 4 h treatment, UP of inner side of FRP was almost depolymerized and fiber could be dissected out. The glass fiber recovered by the treatment in subcritical BZA was relatively long and clean without any damage.

In this study, we focused on the degree of fractionation of FRP. The degree of fractionation of FRP was defined as:

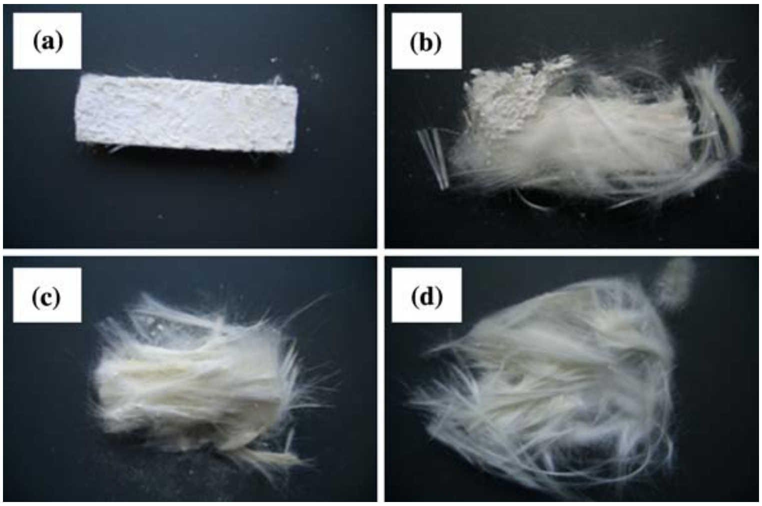

Fig. 2 Solid phase products obtained by the treatment for (**a**) 1 h, (**b**) 2 h, (**c**) 3 h, and (**d**) 4 h

$$\text{Degree of fractionation } (\%) = (\mathrm{A} - \mathrm{B})/\mathrm{C} \times 100 \qquad (1)$$

where A, weight of FRP before the treatment (g); B, weight of FRP after the treatment (g); C, weight of UP and filler before the treatment (g)

The influence of catalyst and solvent on depolymerization of FRP in BZA

Figure 3 shows the degree of fractionation as a function of catalyst/solvent ratio and solvent/FRP ratio at 523 K and 4 h. In every condition, the degree of fractionation increased with the increase in catalyst/solvent ratio. However, when the catalyst/solvent ratio was more than 0.14 w/w, the degree of fractionation became lower. This result suggested that other factors such as reactor volume, amount of FRP, and amount of solvent influenced the reaction although the amount of catalyst was important factor. Therefore, catalyst has the optimal amount in the depolymerization of FRP. Additionally, the degree of fractionation increased with the increase in solvent/FRP ratio at all catalyst/solvent ratios. Thus, reaction rate increased with increasing quantity of solvent.

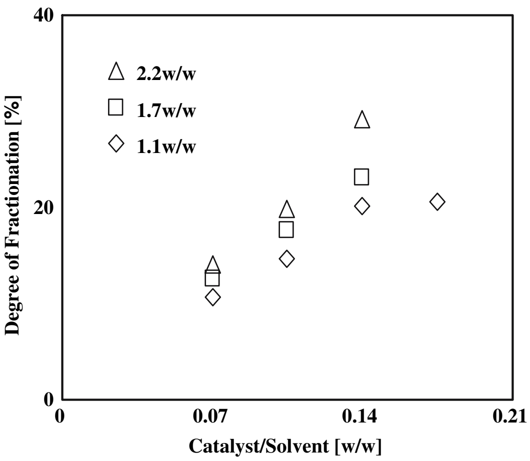

Fig. 3 Influence of catalyst and solvent on the degree of fractionation of FRP with a parameter of solvent/FRP ratio

Next, we discuss about the influence of the parameters. When amount of catalyst was doubled, the degree of fractionation became twice. When quantity of solvent was doubled, the degree of fractionation increased 1.5 times. Thus, influence of catalyst was more than that of solvent, although the effect of catalyst has a limit as described above. Therefore, this reaction is favored at larger amount of catalyst and larger amount of solvent.

As described above, the reaction is accelerated by K_3PO_4. Although we used the term "catalyst" for K_3PO_4 in this paper, the role of K_3PO_4 is not cleared yet. The alkoxide produced from BZA and K_3PO_4 may be involved in the reaction. However, the most of the K_3PO_4 in the reactor remained as a solid phase and the amount of it influences the reaction. Therefore, the role of the catalyst is not simple in this reaction system.

The influence of reaction temperature on depolymerization of FRP in BZA

Figure 4 shows time courses of the degree of fractionation for the treatment at 523 and 573 K. The higher is reaction temperature, the higher is the degree of fractionation. When temperature was 573 K and reaction time was 4 h, FRP was almost decomposed where the degree of fractionation reached 90%. On the other hand, when temperature was 523 K and reaction time was 8 h, the degree of fractionation reached only 60%. Therefore, high degree of fractionation was observed at shorter reaction time when reaction temperature was high.

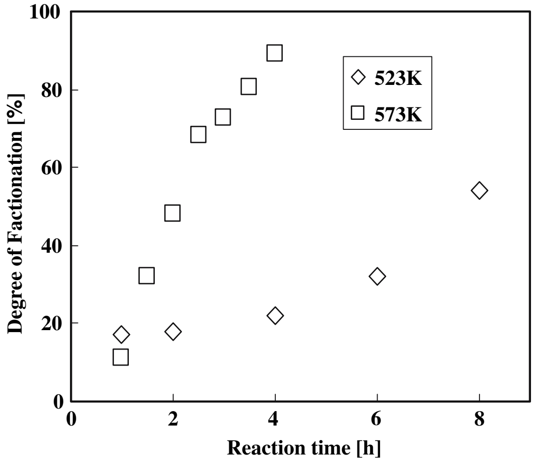

Fig. 4 Time courses of the degree of fractionation at 523 and 573 K

The comparison of the degree of fractionation in terms of difference of solvent

Figure 5 shows the degree of fractionation as a function of reaction temperature at catalyst/solvent ratio of 0.14 w/w, solvent/FRP ratio of 2.2 w/w, 4 h using BZA and catalyst/solvent ratio of 0.175 w/w, solvent/FRP ratio of 1.1 w/w, 4 h using DGMM. The degree of fractionation increased with increasing reaction time. The degree of fractionation increased with increasing reaction temperature. Especially, the degree of fractionation at 573 K was about twice as high at 523 K that was about 80%. This result suggested that reaction temperature is more influential than amount of catalyst and quantity of solvent or reaction time in the depolymerization process of FRP.

Figure 6 shows time course of the degree of fractionation at catalyst/solvent ratio of 0.14 w/w, solvent/FRP ratio of 2.2 w/w, 523 K using BZA, catalyst/solvent ratio of 0.35 w/w, solvent/FRP ratio of 1.1 w/w, 573 K using BZA and catalyst/solvent ratio of 0.175 w/w, solvent/FRP ratio of 1.1 w/w, 573 K using DGMM. The degree of fractionation increased with increasing reaction time. The similar trend was observed at 573 K in DGMM and BZA. In the previous study [12, 13], it is reported that the degree of fractionation in DGMM is higher than that in BZA at 473 K for the same amount of catalyst. In this study, reaction temperature was 573 K and the reaction in BZA required large amount of catalyst than in DGMM. Therefore, the degree of fractionation has same value. This result indicated that DGMM has higher reactivity than BZA. However, since the ignition temperature of DGMM is lower than that of BZA, BZA is more practical solvent than DGMM.

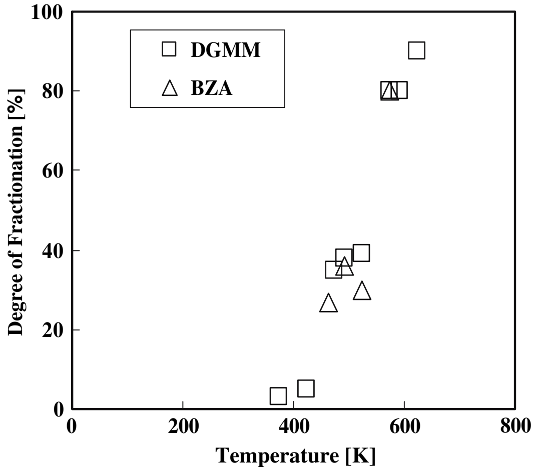

Fig. 5 Comparison of solvent between BZA and DGMM as a function of temperature

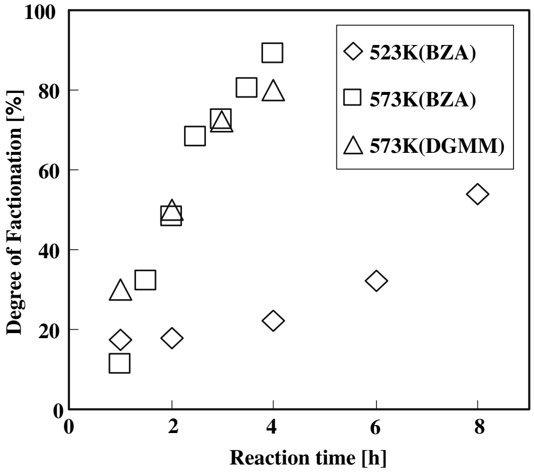

Fig. 6 Time course of degree of fractionation for the solvent of BZA and DGMM at 523 and 573 K

The influence of FRP structure

The imaginary structure of FRP is shown in Fig. 7. FRP decomposition process proceeds by removing the filler as well as depolymerization of UP. At milder reaction condition, filler remains in treated FRP because UP depolymerization rate is slow. Therefore, the degree of fractionation is low.

The degree of fractionation increased significantly between 6 h and 8 h at 523 K in BZA and between 2 h and 3 h at 573 K in BZA. Since UP was depolymerized considerably in this time region, majority of filler was removed.

Analysis of liquid phase by GC-MS

Liquid phase after the treatment at 573 K and 4 h using BZA was analyzed by GC-MS. The main components

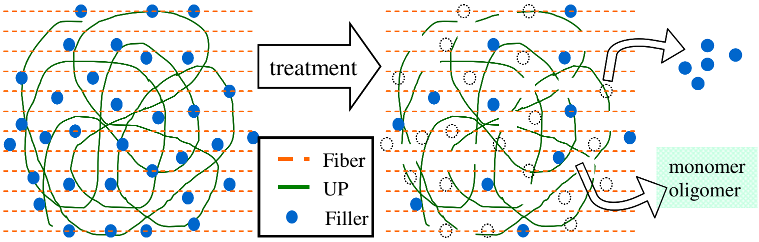

Fig. 7 Imaginary structure of FRP decomposition

detected in liquid phase were benzaldehyde, BZA (solvent), benzoic acid, hydrocinnamylalcohol, phenylethyl alcohol, and dibenzyl ether. The miner components were styrene derivative and 1,3,5-cycloheptatriene. The content of benzoic acid was only decreased with increase in reaction time. The other components were increased with increase in reaction time. This indicates that benzoic acid is intermediate product and secondary reaction occurred in longer reaction time where benzoic acid decomposed.

Conclusion

We investigated the influence of reaction temperature, reaction time, amount of catalyst and quantity of solvent on the degree of fractionation.

At all reaction conditions the degree of fractionation increased with the increase of catalyst/solvent and solvent/FRP ratio. When amount of catalyst was doubled; the degree of fractionation was twice. When quantity of solvent was doubled, the degree of fractionation was 1.5 times. Therefore, influence of catalyst was more than that of solvent. However, effect of catalyst has a limit. Therefore, amount of catalyst and at the same time increased quantity of solvent is more effective in this reaction.

The higher is reaction temperature, the higher is the degree of fractionation.

The main peaks in liquid phase were benzaldehyde, BZA (solvent), benzoic acid, hydrocinnamylalcohol, phenylethyl alcohol, and dibenzyl ether. The miner peaks were styrene derivative and 1,3,5-cycloheptatriene. The peak of benzoic acid was decreased with increase reaction time.

The results indicated that the fibers recovered could be used to re-produce the FRP, because the fiber is not damaged during the reaction.

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