RECOVERY OF USEFUL MATERIALS FROM THERMOSET COMPOSITE MATERIALS BY LIQUEFACTION

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Abstract

Liquefaction of fiber reinforced plastics (FRP) was carried out in three solvents (cresol mixture solvent, benzyl alcohol, and 1-methyl pyrrolidone) with small amount of additives at 200 °C. FRP was liquefied almost completely in the cresol mixture solvent with 0.05 mmol/g of sulfuric acid for 240 min under atmospheric pressure. Total weight of liquefied FRP was increased than that of plastics in original FRP. The results indicate solvent was incorporated into products with liquefaction of FRP. Yield of residue in thermal decomposition of the once liquefied FRP at 600 °C was almost equal as well as thermal decomposition of original FRP. Effect of pretreatment by liquefaction was not observed in thermal decomposition of FRP. FRP could be liquefied almost completely in the liquid products derived from thermal decomposition of the once liquefied FRP. These experimental results suggest that recovery of glass fiber from waste FRP is feasible by using recycle solvent derived from the once liquefied FRP.

Keywords: *FRP, solubilization, reuse, recycle cresol*

1. Introduction

Fiber reinforced plastics (FRP) have been used widely in a lot of industrial products due to their distinguished material property light and strong. On the other hand, most of the waste FRP are incinerated or landfilled, because conversion from the used FRP to useful products was very difficult. FRP tank for liquefied propane (LP) is lighter and more convenient than a conventional steel tank, and we are expecting to be used widely in Japan as well as in EU countries. However, not only convenience but also environmental friendliness is very important to create a new market of the FRP-LP tank. In this work, we developed a recovering technology of glass fiber from the FRP-LP tank by liquefaction using recycle solvent derived from FRP itself.

2. Materials and Methods

RIPOXY (Showa Denko K.K., Japan); photopolymerized polyvinyl ether; was used as FRP sample. Cresol mixture (mixture of o-cresol, m-cresol, and p-cresol), benzyl alcohol, n-methylpyrrolidone, tripotassium phosphate (K_3PO_4), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were purchased from Tokyo Chemical Industry Co., Ltd. or Wako Pure Chemical Industries Ltd., respectively as special grade for chemical experimental.
FRP sample (3.0 g) was liquefied in various solvents (100 g) with additives by using a glass flask (300 ml) connected to water cooling reflux condenser. Liquefaction was carried out at boiling point of each solvent for 60 – 360 min with stirring by the magnet. After the reaction, glass fibers were separated from solvent, the fibers were washed by tetrahydrofuran (THF) and by distilled water to remove solvent and additives. The recovered glass fibers were dried at 50°C for 10 hours under vacuum. Solubilization rate was calculated from equation (1). Liquefied FRP was derived from of the liquid products by distillation of solvent at 220 °C. Thermal decomposition of the liquefied FRP was carried out in a Pyrex reactor which was heated up to 600 °C in 30 min, and the temperature was kept for 30 min. Gaseous products were collected into a gas bag, and were analyzed by GC.

Solbilization rate [%] = (1 – (a-c)/ (b-c)) × 100 (1)

a:weight of unliquefied products,

b:weight of FRP, c:weight of glass fiber in FRP

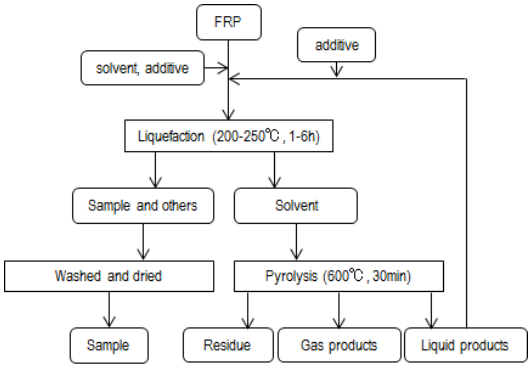

Fig.1 Procedure of liquefied FRP in this study

3. Results and Discussion

Solubilization rates of FRP using three different solvents; cresol mixture, benzyl alcohol, and 1-methyl pyrrolidone; with/without sulfuric acid were shown in Fig.2. Without sulfuric acid, solubilization rates of the FRP for 60 min using cresol mixture solvent, benzyl alcohol, and N-methylpyrrolidone were 47%, 45% and 65%, respectively, and the liquefaction rates were increased with reaction time. Solubilization of the FRP was accelerated significantly in each solvents in the presence of sulfuric acid, in particular the solubilization rate in cresol mixture solvent reached to 99% at 240 min by the addition of sulfuric acid.

The solubilization rate of FRP increased with concentration of sulfuric acid as shown in Fig.3. The rate reached 99% at 0.05 mmol/g of the sulfuric acid, and it was saturated more than 0.05 mmol/g.

Weight of the liquefied FRP which was derived from liquid products by distillation of solvent was much larger than that of original FRP. The increase of liquid products indicated that the solvent was incorporated into the liquefied FRP or polymerization of solvent proceeded during liquefaction of FRP. On thermal decomposition of the once liquefied FRP at 600 °C, yield of residue and gas was 21% and 5%, respectively. These yields were almost equal to the distribution of products derived from thermal decomposition of original FRP. Effect of pretreatment by liquefaction was not observed in thermal decomposition of FRP.

FRP could be liquefied almost completely in the liquid products derived from thermal decomposition of the once liquefied FRP as shown in Fig.4. These experimental results suggest that reusing liquid products derived from thermal decomposition of the once liquefied FRP as solvent is feasible.

4. Conclusions

FRP was liquefied in cresol mixture solvent, benzyl alcohol and 1-methylpyrrolidone, respectively. Particularly, the FRP was liquefied almost completely in cresol mixture solvent for 240 min by addition small amount of sulfuric acid. On the thermal decomposition of the once liquefied FRP, similar yields of gas or residue were observed as well as direct decomposition of original FRP. FRP was liquefied almost completely in liquid products derived from thermal decomposition of the once liquefied FRP. These experimental results suggest that recover of glass fiber from waste FRP is feasible by using recycle solvent.

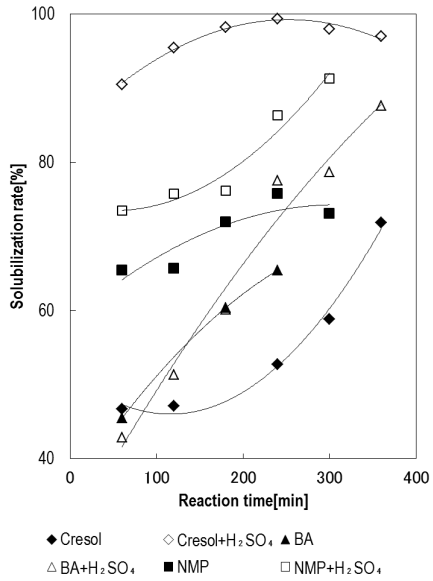

Fig.2 Effects of solvents and sulfuric acid on solubilization rate (H_2SO_4:0.05 mmol/g)

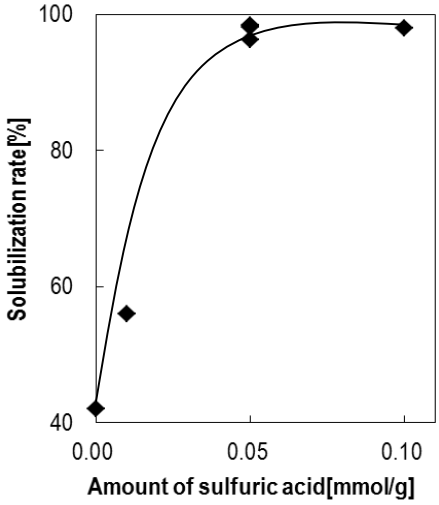

Fig.3 Effect of sulfuric acid concentration in cresol mixture solvent on solubilization rate

Fig.4 Recovered glass fiber from FRP using recycle solvent derived from the once liquefied FRP.
H_2SO_4 (0.05 mmol/g) , 250°C, 240 min.