A new recycling process for recycled plastic production from glass fiber reinforced plastics

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Abstract. The decomposition of glass fiber reinforced plastics (GFRP) with ethylene glycol monoallyl ether (EGMA) and benzyl alcohol (BnOH) by non-catalytic transesterification under high pressure, microwave irradiation was investigated. The decomposition product of GFRP with EGMA (EGMA-P) has a high reactivity for the cross-linking reaction to unsaturated polyester (UP) compared to the product of GFRP with BnOH (Bn-P) because of the presence of many allyl groups derived from EGMA. Therefore, the hardened material (EGMA-HM) with high thermal stability was prepared from EGMA-P, unsaturated polyester, and curing agent. Finally, the recycled GFRP with high bending breaking point was produced from EGMA-P.

1. Introduction

GFRP is a composite made of polymer reinforced with glass fiber. Unsaturated polyester is generally used as thermosetting resin composites and styrene resin behaves as a binder for the cross-linking polymerization. GFRP composites are widely used in many industries including windmill, automobile, shipbuilding, construction and bathtub as a hard material. Nowadays, annual production volume of GFRP in Japan is about 250,000 ton and the annual generation volume of GFRP waste is about 200,000 ton. Most GFRP wastes (ca. 95 %) end up in a landfill. The remaining GFRP wastes (ca. 5 %) become an alternative fuel in the cement industry. The mechanical recycling process of waste GFRP was difficult because of high hardness property of GFRP [1].

To realize the sustainable society, chemical recycling of GFRP has been attracted much attention from many researchers in academia and industry. The decomposition method of GFRP in supercritical or subcritical fluid without catalyst required high-temperature and high-pressure operation [2-4]. The reaction pressure was able to be reduced in supercritical methanolysis of GFRP with N,N-dimethyl-4-aminopyridine catalyst [5]. Furthermore, solvothermal decomposition of GFRP was demonstrated under ordinary pressure in the presence of tripotassium phosphate as an alkali catalyst for a prolonged time (12 hr.) [6]. The reproduction of the decomposed resin was performed through the transesterification or dehydration esterification of oxygen-containing groups in the resin with strong acid catalyst. The reproduced polyesters became black colored materials in almost all cases.

The desired full conversion of GFRP to a recycle polymer was not accomplished until now despite many efforts. We proposed the convenient solvolysis process of GFRP without catalyst under high pressure and microwave heating [7]. In this study, more developed solvolysis process of GFRP with
Figure 1. Postulated reaction schemes: (a) decomposition of GFRP resin by EGMA-solvolysis and (b) cross-linking reaction of allyl groups of EGMA-P with UP.

ethylene glycol monoallyl ether (EGMA) under high pressure and microwave heating was investigated. After the solvolysis, the recycle polymer was obtained through the cross-linking reaction of decomposition products having allyl group with unsaturated polyester (UP) as shown in figure 1. Finally, the recycled GFRP was produced from EGMA-P.

2. Experiments

2.1 Decomposition of GFRP

The piece of GFRP used in this study consists of 65 % network resin and 35 % glass fiber from the combustion test. GFRP 3.33 g and EGMA 15.0 g, were added in a 10 mL sealed tube equipped with a stir bar. Microwave was irradiated to the tube attached in the microwave apparatus (Initiator+8 with single mode microwave irradiation, Biotage AB). The reaction temperature of 300°C and the reaction pressure of 3.0 MPa were achieved by the maximum irradiation (2.45 GHz, 300 W) of the microwave apparatus for 3 h. After the microwave irradiation, the products were thermally extracted from the reaction mixture using chloroform (90 mL). The chloroform solution was separated by vacuum filtration from the glass fibers and the unreacted resin of GFRP. Chloroform was evaporated from the solution and then the remaining high-boiling solvent was distillated under reduced pressure to obtain the product (EGMA-P) as a tarry residue (Figure 2). The decomposition ratio of the GFRP was calculated from the weight reduction of GFRP as follows.

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\text{Decomposition ratio of resin} = \frac{\text{reduction amount of GFRP}}{\text{initial amount of GFRP}} \times 100
\] (1)

GFRP was decomposed with benzyl alcohol (BnOH) for comparison to give the product (Bn-P) under the same condition with EGMA experiment. The products were identified by IR, NMR, and GPC analysis.
2.2 Preparation of hardened material (HM) by curing
The EGMA-hardened material (EGMA-HM) was produced by the curing reaction of EGMA-P (5.0 g) with UP (15 g), and curing agent (methyl ethyl ketone peroxid; 0.30 g) at room temperature according to the standard preparation method. The BnOH-hardened material (Bn-HM) was prepared from Bn-P with UP and curing agent. The styrene-hardened material (St-HM) as a standard substance was formed with pure styrene with UP. The thermogravimetric analysis of hardened materials was performed by TG-DTA apparatus (30-500°C, 1.0°C / 1.0 min., Thermo plus TG8120, Rigaku Co.).

2.3 Preparation of GFRP
The hand lay-up method was used for the preparation of GFRP. The weight composition ratio of recycle polymer, styrene, UP, curing agent and glass fiber was fixed at 3:2:15:0.3:10, respectively according to the standard preparation of GFRP including 65 % resin and 35 % glass fiber. GFRPs prepared from EPMA-P and Bn-P was called as GFRP-E and GFRP-B, respectively. Standard GFRP was synthesized from styrene (5.0 g), UP (15 g), the curing agent (0.30 g), and fresh glass fiber cloth (10 g). According to JIS K 7017, the bending breaking points of GFRPs were determined from three-point point bending test of GFRPs with AG-Xplus (Shimadzu Co.).

3. Results and discussion
GFRP resin was easily non-catalyzed decomposed by transesterification with EGMA and BnOH under high pressure, microwave heating. The both products (EGMA-P and Bn-P) were tarry brownish oils. Table 1 presents the decomposition ratio of GFRP evaluated from the weight reduction of GFRP. These decompositions were carried out using direct microwave heating apparatus with high pressure (at 300°C, 3.0 MPa, Initiator + 8 and Biotage AB). The decomposition ratio in EGMA (69.3%) was almost the same as that in BnOH (70.7 %) for 3-hour reaction. After the filtration, the recovered solid was fully identified as glass fiber. This means the complete esterification of GFRP was achieved in EGMA and BnOH regardless of aliphatic and aromatic alcohol. Figure 3 shows the NMR spectra of EGMA-P and separately-synthesized EGMA oligomer. The molecular weight distribution of EGMA-P is 1200-17000. The NMR analysis of EGMA-P indicated the existences of allyl groups of EGMA-P suggesting the occurrence of the cross-linking reaction to UP.
Table 1. Decomposition of GFRP resin by direct microwave heating with high pressure

| Entry | GFRP / g | Solvent | Time / h | Product | Decomposition ratio of resin / % |
|-------|----------|---------|----------|---------|---------------------------------|
| 1     | 3.11     | BuOH    | 3        | Bz-P    | 70.7                            |
| 2     | 3.33     | EGMA    | 2        | EGMA-P  | 67.2                            |
| 3     | 3.40     | EGMA    | 3        | EGMA-P  | 69.3                            |

Figure 3. The NMR spectra of: (a) EGMA-P and (b) EGMA-oligomers.

EGMA-P containing EGMA oligomers reacted with UP by using curing agent at room temperature overnight to give the EGMA-HM with a sufficient hardness. Figure 4 shows the TGA curve of EGMA-HM, Bn-HM, and St-HM. The total weight loss of Bn-HM and St-HM reached almost 100% at 500 °C. Meanwhile the weight loss of EGMA-HM at the temperature of more than 300 °C was low indicating the highest heat resistance among them. These results strongly suggested that EGMA-P, which was decomposed under high pressure, microwave irradiation, has the sufficient cross-linking reactivity to UP. The bending breaking point of GFRP-E was the same as that of standard GFRP prepared without recycle polymer. Meanwhile the bending breaking point of GFRP-B was about 14 % lower than that of GFRP-E due to the insufficient cross-linking of UP with Bn-P having no double bond. EGMA-P was found to behave alternative linker instead of styrene for the preparation of GFRP.

The complete recycling process of waste GFRP was achieved and EGMA-P with the cross-linking reactivity was prepared by the transesterification of EGMA [8]. Finally, the regenerated GFRP prepared from EGMA-P indicates sufficient hardness.
Figure 4. Thermogravimetric analysis curves of HMs.

Conclusion
The decomposition of GFRP with EGMA and BnOH readily was performed by non-catalytic transesterification under high-pressure microwave irradiation. The EGMA-P with many allyl groups had a high reactivity for the cross-linking reaction to UP compared to the product of GFRP with Bn-P. The EGMA-HM had a high thermal stability. The recycled GFRP had a high bending breaking point by using EGMA-P. The complete recycling process of waste GFRP by using EGMA solvolysis could be achieved in future.

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