Effective Depolymerization Waste FRPs by Treatment with DMAP and Supercritical Alcohol

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Waste FRP, fiber-reinforced plastic, was readily depolymerised by treatment with supercritical MeOH in the presence of catalytic amounts of DMAP and the decomposed mixture was separated into three portions, monomeric portion, polymeric portion, and inorganic residue, by simple manipulation; the recovered organic and inorganic materials were readily used for further recycling use.

Recently, waste plastics cause a serious environmental problem all over the world. Plastics, which were once invented as a dream material that was widely used owing to their advantageous points such as no bio-degradable, no rusting, and robustness. FRPs, fiber-reinforced plastics, are recognized one of the most excellent materials so that they have been utilized for building materials, fishing boats and septic tanks. After almost 30 years has passed since these products were made, their lifetime is almost running out. These advantages now turn into formidable demerits when the FRPs are treated as a waste material. Waste FRPs are recognized as the most difficult plastics for depolymerization, and major practical solutions to date are landfill and incineration. To achieve effective chemical recycling of waste FRPs, a useful and convenient method for depolymerization of FRPs has been urgently desired. Additionally, as FRPs are composite material, every component in the waste FRPs such as monomers, glass fibers, and fillers should be separated to achieve practical chemical recycling. There have been several attempts for chemical degradation of the waste FRPs so far,[1,2] but all of them are just useful for recycling only one of the components; other components are just thrown away. This is still a big problem. Supercritical fluid often shows high and unique reactivity and has recently been used in various fields of chemistry including organic synthesis.[3] During the course of our investigation for the use of supercritical alcohol for developing a new chemical recycling process,[4] we have succeeded to find a novel practical method for depolymerization of FRPs, in which DMAP, *N*,*N*-dimethylaminopyridine, known as a good catalyst for esterification and amidation,[5] acted as an excellent catalyst to make all of organic ingredients in waste FRPs soluble in organic solvent. With this method, the waste FRPs were completely degraded and separated into organic monomeric compounds, polymeric materials, and inorganic additives, all of which were ready for recycle use. To the best of our knowledge, this is the first report that solved the longstanding problem and provided a practical perfect way to treat and recycle waste FRPs. We have also succeeded in preparing recycled plastics by using the recovered monomers coming from actual waste FRPs treated with the present decomposition reaction.

We firstly examined depolymerization of unsaturated polyesters with known contents under supercritical alcoholic conditions. The results are summarized in Table 1. Treatment of the unsaturated polyester, which was made from 26.9% of phthalic anhydride, 17.8% of maleic anhydride, 29.0% of propylene glycol, and 24.2% of styrene monomer, in supercritical methanol (275 °C/10 MPa) resulted in partial decomposition of polymer; about half amount of the polymer became to be solved in MeOH while the rest remained as insoluble solid (run 1). Addition of DMAP as a catalyst changed the result dramatically; it was observed that most of the polyester gradually lost its own shape and was finally dissolved in the reaction mixture. After opening the autoclave, we succeeded in obtaining three decomposition products, most of which were MeOH-soluble oil (49 wt %) and $CHCl_3$-soluble solid (48 wt %) (run 2). The latter mainly consisted of polystyrene that was used as a linker in the polyester. The amounts of the remaining insoluble residue were less than 3 wt % thus almost complete depolymerization of polyester unit was achieved. Prolonged reaction time gave a similar result (run 3). This decomposition reaction seemed temperature-sensitive because the reaction at 250 °C decreased an efficiency of the decomposition (run 4). So we concluded the optimized decomposition condition was 275 °C/10 MPa/5 h, which is much milder conditions than the reactions in supercritical water often employed in other decomposition method of waste plastics. EtOH also became supercritical phase under similar conditions, so we examined for the present reaction (run 5). Supercritical EtOH was also useful for the decomposition reaction with the presence of DMAP, although the reaction needed longer time for complete decomposition.

Table 1. Decomposition reaction of unsaturated polyester in alcohol

Run	Solvent	Temp /°C	Pressure /MPa	Time /h	DMAP /wt %	MeOH /wt %	$CHCl_3$ /wt %	Residue /wt %
1	MeOH	275	15	3	0	45	0	55
2	MeOH	275	10	3	5	49	48	3
3	MeOH	275	10	5	5	60	39	1
4	MeOH	250	10	3	5	42	1	57
5	EtOH	275	7.5	12	5	71	27[a]	2

[a]Dissolved with THF.

Isolation of the degraded products in the MeOH-soluble oil was carried out with usual flash silica-gel chromatographic treatment. MeOH-soluble oil coming from run 3 experiment (2.756 g), for example, was subjected into flash chromatography to give pure dimethyl phthalate in 1.097 g. The decomposition experiment of run 3 started with 3.815 g of unsaturated polyester that would theoretically give 1.344 g of dimethyl phthalate. The yield of dimethyl phthalate in the present decomposition reaction was calculated to be 84%. Thus, most of monomeric phthalate was recovered as dimethyl ester that was potentially useful for recycling use. The decomposition reaction employing EtOH (run 5) also gave diethyl phthalate in 95% of isolated yield.

With the optimized reaction conditions in hand, we examined the present method for the depolymerization of actual waste FRP. Pieces of roughly grinded waste FRP (5.052 g) were put into a solution of DMAP (0.157 g, about 3 wt %) in methanol (40 mL) in an autoclave. The mixture was heated to 275 °C under 11 MPa for 6 h. After cooling down, resulting mixture was separated into three components, which were MeOH-soluble oil, $CHCl_3$-soluble solid, and insoluble inorganic residue. As expected, the first oil, 1.469 g, contained mainly dimethyl phthalate and propylene glycol. GC-analyses indicated that amounts of dimethyl phthalate and propylene glycol were 0.541 and 0.254 g, respectively. NMR observation indicated that second solid, 0.844 g, mainly consisted of polystyrene which came from linker units in the waste FRP. The sum of these two organic components reached 2.313 g that occupied about 46 wt % of the starting waste FRP. The last insoluble residue, 3.164 g, consisted of glass fiber and filler, calcium carbonate. Combustion test of the residue showed that this inorganic residue only contained less than 3% of organic unit. Thus, the present method realized complete separation of the decomposed FRP by simple filtration and washing manipulation.

It should be mentioned that the efficiency of the present degradation depended on the amounts of DMAP employed. Progress of the reaction was estimated by the amounts of insoluble residue. We examined several reactions in the presence of various amounts of DMAP. The results are summarized in Table 2. All of reaction were carried out at 275 °C under 11 MPa. The reaction without DMAP resulted in insufficient decomposition of FRPs and left 81% of insoluble residue which was an inseparable mixture of polymers and glass fibers (run 1). Treatment of FRP in the presence of 3 wt % of DMAP needed 6 h of reaction time to achieve complete decomposition (run 2 and 3). The reaction time was shortened to 3 h when 10 wt % of DMAP was used (run 4). These results clearly showed that the reaction rate and efficiency depended on the amounts of DMAP. The use of much amounts of DMAP accelerated the reaction and resulted in the complete decomposition of FRP within short reaction time.

The recovered glass fiber still maintained its strength after high temperature treatment of the present method. For example, the recovered glass fiber showed about 17 g of the strength that was as strong as a new fiber in the same diameter. Indeed comparison of SEM picture clearly showed that no significant defects on the surface of the recovered fiber were observed except for some tiny scratches in surface. Thus, the fiber recovered by this method should be instantly useful for further recycling use (Figure 1).

We examined to prepare recycled plastics with depolymerized materials. Treatment of the MeOH-soluble oil, which contained phthalic ester, with ethylene glycol and maleic anhydride, followed by addition of initiator and virgin polymeric material gave recycled plastics efficiently. Hardness of the recycled polymer depended on the amounts of virgin polymers mixed (Figure 2). For example, a 9:1 mixture of recycled and virgin polymer mixture was relatively soft and showed some sticky property after appropriate duration of polymerization reaction. The 1:1 mixture of recycled and virgin material improved the hardness of the polymer; compared with a plastic made by virgin material, this plastic was sufficiently hard so it should be potentially useful. Although we have just examined a preliminary experiment, this finding is promising to provide a new way for chemical recycling of waste FRPs.

Table 2. Decomposition reaction of FRPs in supercritical MeOH

Run	Time /h	DMAP /wt %	MeOH /wt %	$CHCl_3$ /wt %	Residue /wt %
1	3	0	19.3	0.3	81.0
2	3	3	25.3	6.6	75.8
3	6	3	28.2	16.2	62.6
4	3	10	32.9	18.8	60.4

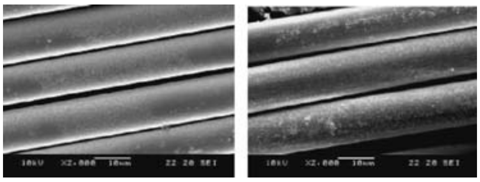

Figure 1. SEM pictures of new glass fiber (left) and recovered glass fiber from waste FRP (right).

Figure 2. Recycled polymers: recovered: virgin = 1:1 mixture (left), 9:1 mixture (right).

In conclusion, we have succeeded to develop a novel and convenient method for complete decomposition and separation of the waste FRPs which opens a new perspective for chemical recycling of FRPs. Further study on the present method is now underway in our research group.

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