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Reactions of polymers in supercritical fluids for chemical recycling of waste plastics

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Sub- or supercritical fluids have been focused as reaction media for environmental applications from a view point of green chemistry. Chemical recycling of waste plastics is important issue. We have applied reaction in water or organic solvent in sub- or supercritical condition to convert polymers into its monomers. Condensed polymers such as polyethylene terephthalate or nylon 6 were depolymerized to its monomers by hydrolysis of alcoholysis in supercritical water or alcohol. The other polymers such as phenol resin and fiber reinforced plastics (FRP) were also decomposed to small molecules by solvolysis. In this paper, the degradation of polymers studied in our group was reviewed. *© 2006 Springer Science + Business Media, Inc.*

1. Introduction

Production of plastics in the world was 168 million tons in 1999, and it will be 210 million tons in 2010. Since treatment of plastic wastes becomes serious problem, development of recycling process has been desired. There are three types of recycling for plastic wastes, that is, material recycling, thermal recycling, and chemical recycling.

For the recycling of plastics, chemical recycling is the most desirable process where plastics are converted to its monomers. Condensed polymers could be monomerized by noncatalytic solvolysis in sub- or supercritical fluids. Condensation polymers with ether, ester, or acid amide linkages are easily decomposed to their monomers by hydrolysis or alcoholysis in near-critical water or alcohol. Polyethylene terephthalate (PET) was depolymerized in near-critical water [1, 2] or methanol [3–7]. Nylon 6, which is a polymer synthesized by ring-opening polymerization of ε-caprolactam, was depolymerized by hydrolysis in sub- and supercritical water [8]. ε-caprolactam and ε-aminocaproic acid were detected in the product liquid phase.

Decomposition of addition polymerization plastics has been also studied in supercritical water. Product distribution could be controlled for the pyrolysis in supercritical water. Watanabe *et al.* [9] observed that the pyrolysis in supercritical water is different from that in argon. Higher yields of shorter chain hydrocarbons, higher 1-alkene/n-alkane ratio, and higher conversion were obtained in supercritical water.

The recycling of thermosetting resins, which are abundantly used for electronics, is important. Phenol resin is one of thermosetting resins and has high thermal stability because aromatic units are connected by methylene bonds. We have applied degradation of printed circuit board in sub- and supercritical water [10]. Treatment of fiber reinforced plastics (FRP) is serious problem. We have used solvothermal degradation to dissolve polymers and recover fibers from FRP [11].

2. Experimental methods and materials

Batch reactors of 5–9 cm^3 inner volume were used for the depolymerization experiments. The polymer samples and solvent were charged in the reactor and purged by argon or nitrogen. The reaction was started by placing the reactor in a heating furnace or in a molten salt bath. The heating furnace has a function to shake the reactor by shaking the furnace itself. After a certain time, the reactor was cooled quickly in a water bath to quench the reaction. The products were analyzed with HPLC, GC-MS, GC-FID, and TOC analyzer.

The PET used was DIANITE PA-500 (Mitsubishi Rayon Co., Ltd., Japan) or sample provided by Mitsubishi Heavy Industries, Ltd., Japan. The nylon 6 used was

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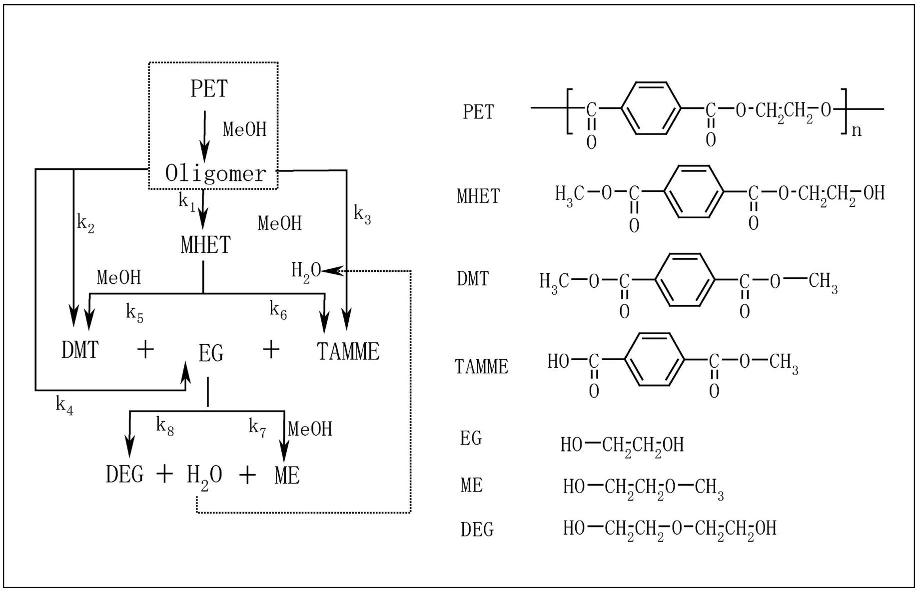

Figure 1 Reaction scheme for decomposition of PET in methanol.

purchased from Aldrich. As a phenol resin sample, electric circuit board (MCL-437G, Hitachi Chemical Co.) was used. The FRP was supplied by Hitachi Chemical Co.

As a solvent for the depolymerization, methanol was used for PET. Water was used for nylon 6 and phenol resin. For FRP, diethyleneglycol monomethylether (DGMM) and diethyleneglycol monoethylether (DG ME) were used.

3. Condensed polymerization polymers

Condensation polymers with ether, ester, or acid amide linkages are depolymerized by solvolysis. The depolymerization reaction may be hydrolysis in water and alcoholysis in alcohol. Fig. 1 shows solvolysis reactions of various polymers. When solvolysis selectively proceeds in the polymers, the polymers can be depolymerized in to its monomers.

3.1. Polyethylene terephthalate

Polyethylene terephthalate (PET) is a condensation polymer abundantly used. Various chemical recycling methods such as methanolysis in liquid methanol, glycolysis in liquid ethylene glycol, ester exchange, and hydrolysis using alkali, have been developed. Condensation polymers with ether, ester, or acid amide linkages are easily decomposed to their monomers by hydrolysis in supercritical water.

PET was depolymerized to its monomers, terephthalic acid and ethylene glycol, in sub- and supercritical water [1]. The yield of terephthalic acid reached close to100% with a purity of greater than 97% under the conditions of 673 K, 40 MPa and a reaction time of 30 min. The yield of ethylene glycol was lower because of further decomposition catalyzed by produced terephthalic acid. Yamamoto *et al.* [2] also showed the possibility of depolymerization of PET in sub- and supercritical water. Secondary products observed were benzoic acid, diethylene glycol, 1,4-dioxane, acetaldehyde, and crotonic acid.

Sako *et al.* [3] reported that the methanolysis in supercritical methanol produced both monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG) with almost 100% yield in 30 min without catalyst. We investigated reaction mechanism of the depolymerization of PET to its monomers in supercritical methanol [4–7].

As the reaction time was longer, the molecular weight of the polymer was decreased. PET with weight-average molecular weight of about 47,000 (polymerization degree: $n = 240$ to 250) was decomposed to oligomer with that of 3,000 (polymerization degree : $n = 15$) in 300 s and with that of 1,000 (polymerization degree : $n = 5$) in 600 s in supercritical methanol. The products observed after 1200 s reaction were methyl-(2-hydroxyethyl) terephthalate (MHET), DMT, and terephthalic acid monomethyl ester (TAMME). MHET is a 1:1 monomer of DMT and EG and TAMME is a by-product produced in the side reaction. After reaction time of 1200 *s*, PET decomposed to the components of monomer size, and DMT increased gradually.

The reaction scheme of PET decomposition in supercritical methanol is shown in Fig. 1. The main products in PET depolymerization were DMT and EG. Some amount of MHET, bis-hydroxyethyl terephthalate (BHET), TAMME, diethylene glycol (DEG) and 2-methoxyethanol (ME) were also detected. TAMME,

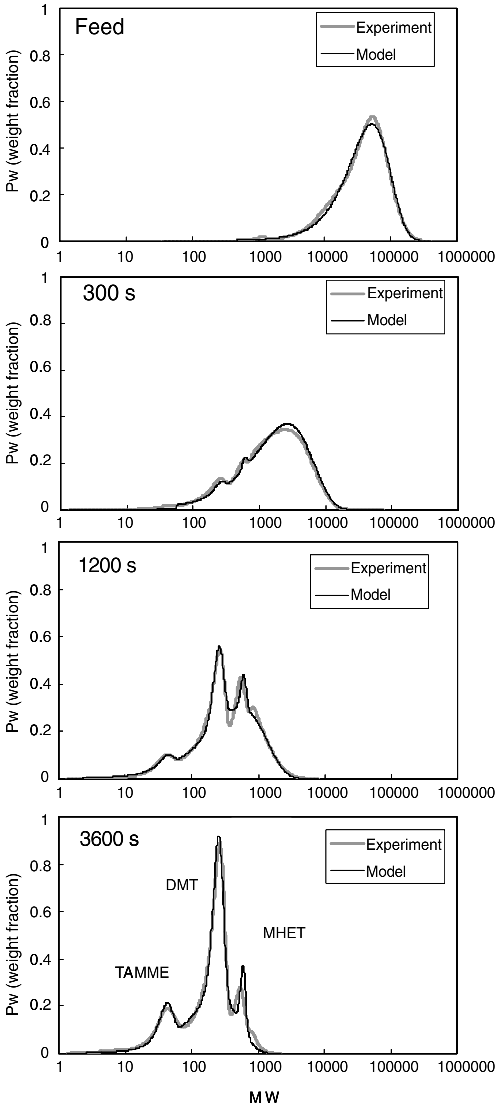

Figure 2 MWD of products of PET depolymerization in methanol.

DEG and ME may be produced by the following side reactions. Dimerization of EG might produce DEG. ME might be produced by the reaction of EG and methanol. TAMME might be also produced from polymer, oligomer, or MHET in the presence of water. The yield of monomers is defined as moles of specific products divided by moles of PET units.

PET is degraded by random scission to polymer of smaller MW. Then it is continuously depolymerized to yield MHET, DMT, and EG by end scission. Produced MHET reacts further with methanol to produce DMT and EG.

We have developed a continuous mixture kinetics to analyze the depolymerization of PET [11]. Fig. 2 shows the comparison of estimated molecular weight distribution (MWD) and experimental MWD obtained by SEC. The monomer yield changes were also calculated and compared as a function of reaction time.

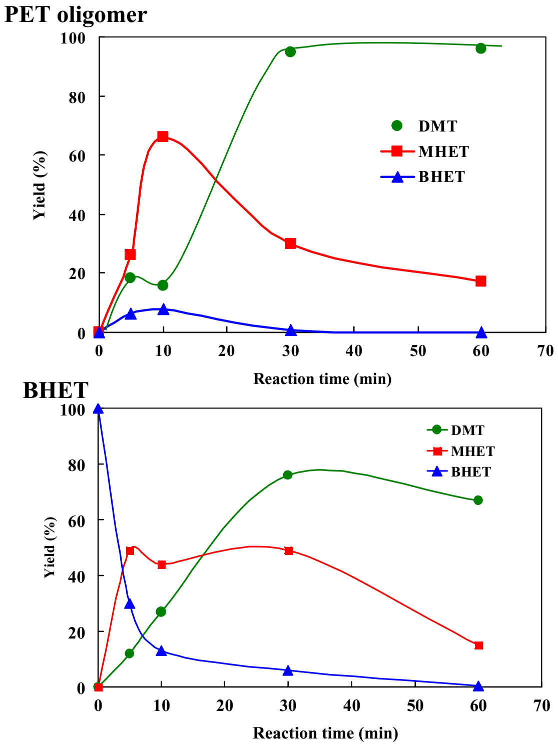

Figure 3 Relationship between the yields of products and the reaction time in decomposition of BHET and PET oligomer.

To improve the precision of the reaction kinetics model, we investigate the PET depolymerization mechanism in supercritical methanol. BHET, which is a compound of terephthalic acid and two ethylene glycols combined with ester linkage and is a structural unit of PET, and PET oligomer (trimmer) were used as a reactant for model compound of PET. Fig. 3 shows the yield of DMT, MHET, and BHET as a function of reaction time at 543 K and 14.7 MPa with applying swing to the reactor during the reaction. The swinging the reactor was intended to stir the fluid in the reactor to improve the mass transfer. The yield of MHET increased initially and then decreased. However the yield of DMT was low for short reaction times, it was increased with the decrease of the yield of MHET. This behavior of the yield of DMT is coincidence with that of PET depolymerization as shown in Fig. 4. The results suggest that reaction existence of MHET as a reaction intermediate in PET depolymerization in supercritical methanol. The results also suggested that the depolymerization of PET would apparently occur in a successful manner as the molecular weight of the reactant. Based on our experimental results, the whole reaction scheme of the PET depolymerization could be represented as shown in Fig. 1.

Mitsubishi Heavy Industries, Ltd. (MHI) has been developing a chemical recycling process for depolymerizing post-consumer PET bottles into monomers for use as feed stocks for manufacturing PET resin, by using

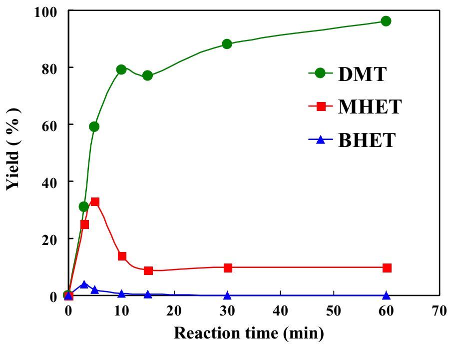

Figure 4 Relationship between the yields of products and the reaction time in decomposition of PET.

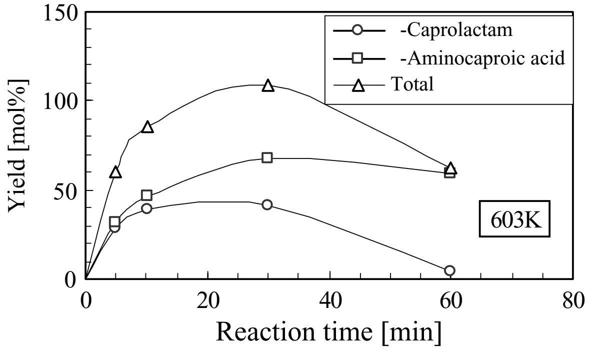

Figure 5 Decomposition of nylon 6 in subcritical water.

supercritical methanol [12, 13]. The process consists of mainly 4 sections; the PET bottle shredding section, the depolymerization with supercritical methanol section, the separation and purification section and hydrolysis section. Post-consumer PET bottles are recycled into its monomers as pure terephthalic acid (PTA) and EG, in this process.

MHI recovered high purity monomers whose qualities are equivalent to those of virgin monomers. MHI is now operating the pilot plant in order to acquire the plant operation data for designing a commercial plant.

3.2. Nylon 6

Nylon 6, which is a polymer synthesized by ring-opening polymerization of ε-caprolactam, was depolymerized by hydrolysis in sub- and supercritical water [8]. ε-caprolactam and ε-aminocaproic acid were detected in the product liquid phase. Fig. 5 shows the yields of monomer components. The total yields of these monomers were about 100% for reactions at 573 K in 60 min and at 603 K in 30 min. The yield of ε-aminocaproic acid decreased rapidly as reaction time increased. Nylon 6 was decomposed by hydrolysis to ε-aminocaproic acid followed by cyclodehydration to ε-caprolactam or decomposition further to smaller molecules.

This indicates that cyclodehydration reaction proceeds in water near the critical temperature. According to this result, 3-aminocaprolactam was synthesized from L-lysine by cyclodehydration in subcritical water [14].

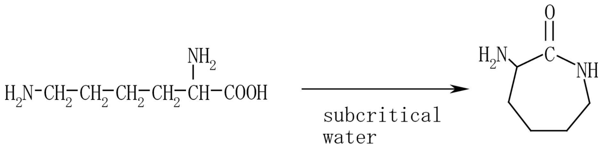

Figure 5

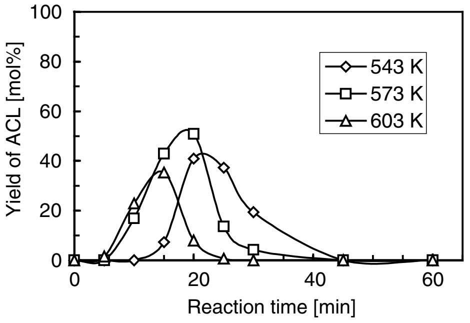

Figure 6 Yield of 3-amino-ε-caprolactam (ACL) for reaction of L-lysine in subcritical water.

As the reaction time increased, the reaction product colored yellow more deeply. At higher temperature, yellow or green colored oil phase was observed. In the products, 3-aminocaprolactam was identified by LC-MS. Lysine was cyclodehydralyzed to 3-aminocaprolactam and then further decomposed to smaller molecules in subcritical water. Lysine was completely reacted in 30 min at 633K. The highest yield of 3-aminocaprolactam was 51% in 20 min at 603K as shown in Fig. 6. For longer reaction, the yield of 3-aminocaprolactam decreased due to further decomposition. Therefore, sub- and supercritical water was found to be excellent reaction media for cyclodehydration.

4. Addition polymerization polymer

Decomposition of plastics of addition polymerization has been also studied in supercritical water. Product distribution could be controlled for the pyrolysis in supercritical water. Watanabe *et al.* [9] observed that the pyrolysis in supercritical water is different from that in argon. Higher yields of shorter chain hydrocarbons, higher 1-alkene/n-alkane ratio, and higher conversion were obtained in supercritical water. The difference was explained by the difference in the reaction phase. The enhancement of the polyethylene decomposition by supercritical water was considered to be due to dissolution of high molecular weight hydrocarbons into supercritical water and diffusion of water into the molten polyethylene phase.

4.1. Phenol resin

The recycling of thermosetting resins, which are abundantly used for electronics, is important. Phenol resin is one of thermosetting resins and has high thermal stability because aromatic units are connected by methylene bonds. Prepolymers of phenol resin were decomposed into their monomers by reactions at 523-703 K under an Ar atmosphere in sub- and supercritical water [15]. The total yield of identified products depended on the kind of prepolymers, and the maximum yield reached 78% in the reaction at 703 K for 0.5 h. The decomposition was accelerated by the addition of Na_2CO_3, and the yields of identified monomers reached more than 90%. Molding material of phenol resin was also decomposed mainly into phenol and cresols in supercritical water.

We applied subcritical and supercritical water technology for chemical recycling of printed circuit board wastes into chemical resources. The circuit board was used as a reactant after removing cupper coating. A batch reactor was used to evaluate the conversion and yields of monomers [10].

The reaction products consisted of liquid, gas, and solid phase. The liquid phase was initially colorless and gradually colored brown. The solid residue was black colored and covered by tar-like material at higher reaction temperature. The conversion was calculated from the mass of solid residue. By decomposition in supercritical water, about 80% of feed was transformed into liquid phase or gases. About 20% was remained in solid phase as residue. Higher conversion was obtained for longer reaction time and at higher temperature. Even in 20 minutes of the reaction, conversion was more than 60% at 723 K.

Elemental analysis of the feed sample gave the composition as H 6.82%, C 56.0%, and N 2.41%. The ratios of H to C and N to C in the solid residue were lower than the feed sample. The H/C ratio was lower at higher reaction temperature and longer reaction time. This indicates that the solid is carbonated in supercritical water with reaction proceed. However, N/C ratio was close to the feed value for longer time and at higher temperature.

According to GC-MS analysis, phenol, o-cresol, p-cresol were found as main components in liquid phase. Phenol was the largest peak in the chromatogram. Similar phenolic compounds were also observed in small quantity. In the chromatogram, the unknown larger molecules are observed. Immediately after the reactor was opened, liquid phase color was changed from colorless to mars brown, and then sediment of the same color was observed. This may be due to the fact that the phenolic compounds exist more than their solubility in water.

The yield of phenol and cresols was higher for longer reaction time and at higher temperature. The yield reached up to around 5% at 733 K in 80 min. Since the circuit board sample contains phenol resin about 27.5% in weight, the yield corresponds to 18% of phenol resin. The yields of cresols were similar to phenol and the highest yield was around 3%, which corresponds to 11%. Therefore, about 30% of phenol resin part was converted to phenol and cresols in this experimental condition.

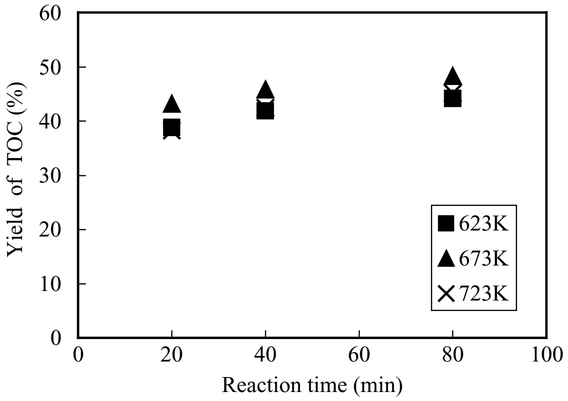

Figure 7 TOC yield of liquid phase products for degradation of phenol resin in sub- and supercritical water.

Total organic carbon (TOC) was measure for liquid phase products. The TOC yield was defined as mass of organic carbon in liquid phase products divided by carbon mass in feed sample. As shown in Fig. 7, about 48% of carbon in feed sample was converted into small molecules dissolved in liquid phase. The TOC yield was maximum at 673 K and the yield at 723 K was lower than that at 673 K. This may be owing to the progress of the conversion into gas phase. From the total carbon analysis, inorganic carbon was not observed in liquid phase.

The distribution of carbon was evaluated from the results of elemental analysis of solid phase and TOC of liquid phase. As shown in Fig. 8, larger amount of carbon was distributed in liquid phase and gas phase with progress of the reaction. At lower temperature, carbon existed in solid phase was larger fraction.

The fraction of phenol and cresols calculated based on carbon balance in liquid phase carbon is evaluated. About 30% of carbon exists as phenolic monomers. Since fraction of phenol resin in feed sample is less than 50%, the results indicate that phenol resin is effectively converted to its monomers.

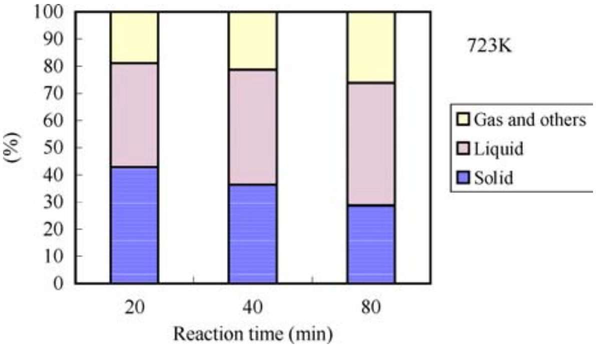

Figure 8 Distribution of carbon in solid, liquid, and gas phases for degradation of phenol resin in sub- and supercritical water.

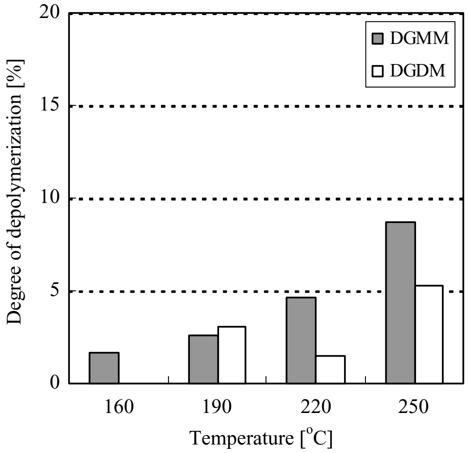

Figure 9 Depolymerization of UP in FRP. (Solvent: DGMM or DGDM; Reaction time: 4 hrs; Catalyst: No).

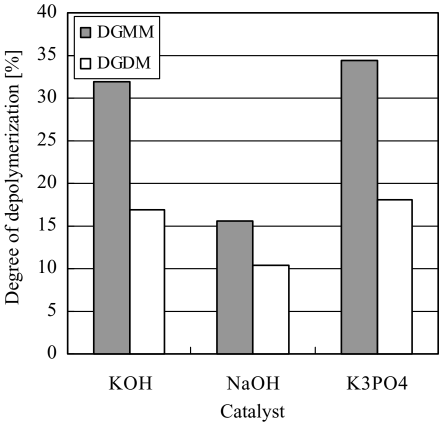

Figure 10 Effect of catalyst on the degree of depolymerization of UP in FRP at 220°C for 4 hrs.

4.2. Fiber reinforced plastics (FRP)

Among the wastes present in the world, the waste FRP can be considered as the resource in which it can be separated between unsaturated polyester resin (UP) and fiber and recovered its component. The FRP treatment in organic solvents at high-temperature and high-pressure was carried out by using a batch reactor and the effects of the operating factors (temperature, reaction time, catalysts and density of solvent) on the degree of depolymerization of UP in the FRP were experimentally investigated [11–17].

Non-catalytic degradation of FRP in diethyleneglycol monomethylether (DGMM) or diethyleneglycol dimethylether (DGDM) was carried out in a reaction time of 4 hrs and temperatures between 433 and 523 K. Fig. 9 shows the relationship between the degree of depolymerization of UP in the FRP and the reaction temperature. At 433 and 463 K, the degrees of depolymerization of UP were very small (1.7 and 2.6%, respectively). Even if the temperature was increased up to 523 K, the degree of depolymerization of UP was 8.7%.

In the case that DGDM solvent was employed as a reaction solvent, the degree of depolymerization of UP was 5.3% in maximum, which was lower than that in the case of DGMM solvent at 523 K. Previously, Fukuzawa *et al.* [18, 19] reported that UP in the FRP could be readily depolymerized in DGMM using K_3PO_4 catalyst and the degree of depolymerization of UP reached up to about 40% by the treatment at 463 K and ambient pressure for 4 hrs. Considered from these results, it was concluded that UP could be hardly depolymerized in the absence of any catalyst even if the reaction atmosphere is pressurized during the treatment of FRP.

For exploring operating conditions where the degree of depolymerization of UP in the FRP becomes high, catalytic depolymerization experiments of FRP in DGMM (or DGDM) solvent were conducted at 433–523 K, 4 hrs and 0.333 mol-cal./g-solvent. Three kinds of catalysts, namely KOH, NaOH and K_3PO_4 were used. Fig. 10 shows the effect of type of catalyst on the degree of depolymerization of UP. The degree of depolymerization was high when DGMM was employed as a reaction solvent. The degree of depolymerization reached about 35% when K_3PO_4 was used for the treatment, suggesting that K_3PO_4 was found to be the best catalyst for effective depolymerization of UP under high-temperature and high-pressure conditions.

5. Conclusions

Supercritical fluids are promising reaction media for green chemistry. The degradation of various polymers in sub- or supercritical water, alcohol, ether was studied. Condensed polymers such as PET and nylon 6 were easily depolymerized by solvolysis. The other polymers such as phenol resin and FRP were also degradated into small molecules. Theory based on continuous kinetics was applied to analyzed depolymerization of PET.

Acknowledgements

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