

## The Decomposition Reaction of Plastics and Model Compound of Them in Sub- and Supercritical Water

Hideyuki Tagaya\*, Naomi Komuro, Yu-ichi Suzuki, Masa Karasu and Jun-ichi Kadokawa  
Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510 Japan  
E-mail: tc021@dip.yz.yamagata-u.ac.jp, FAX: +81-238-26-3413

Model compounds of waste plastics such as polycarbonate and phenol resin were reacted in sub- and supercritical water to make clear the mechanism of the decomposition reaction of plastics in water. Cleavage reactions of methylene bonds were confirmed in the reactions of model compounds such as bis(hydroxyphenyl)methanes in sub- and supercritical water although the methylene bond was stable in thermal reactions. It was also confirmed that sub- and supercritical water played important roles not only as a stable solvent thermally, but also as a chemical reagent.

### Introduction

In recent years, the increase of the amount of waste plastic becomes a serious problem, therefore, the chemical recycling of waste polymers has been greater attention as a means of obtaining valuable products from waste plastics [1]. Thermal cracking of thermoplastic resin is well-known technique and fluidized-bed pyrolysis technology has been under development [2,3]. We have already confirmed that waste polymers such as polycarbonate and phenol resins were decomposed into their monomeric compounds in sub- and supercritical water under argon atmosphere [4-7]. The critical temperature and pressure of water at supercritical conditions are 374.1°C and 22.1MPa, respectively. The dielectric constant of water at near supercritical conditions is small and water, organic compounds and gases are completely miscible. Water is inexpensive and non-toxic solvent, therefore, water is an attractive solvent than other organic solvent. In this study, model compounds of waste plastics such as polycarbonate and phenol resin were reacted in sub- and supercritical water under argon atmosphere to make clear the role of water on the decomposition reaction.

### Experimental

Compounds **1** to **5** were used as model compounds of polycarbonate and phenol resin in which compounds **1** to **4** had methylene bonds. Decomposition reaction in water was carried out in 10 ml tubing bomb reactor. Typically, 0.1g of model compound and 1-4 ml of water with or without additives were introduced in the reactor and the reactions were carried at 250 to 430°C for 0.25 to 24h after flushing the reactor with argon gas. Reaction products were extracted by ether. Ether extract and water soluble products were identified by GC/MS and quantified by GC and HPLC.

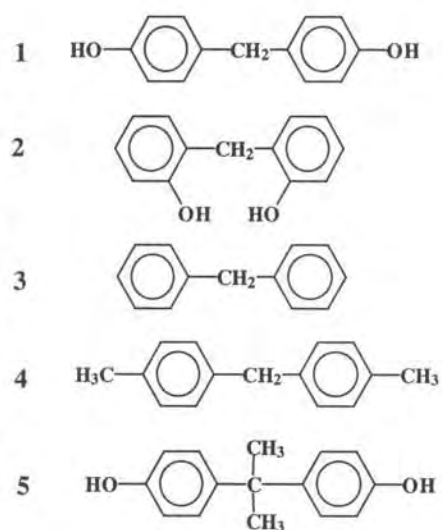


Figure 1. Model compounds **1-5** used in this study.

## Results and Discussions

Thermoplastic resin such as polystyrene and polycarbonate were decomposed into their monomeric compounds even in the reactions at 300°C in water [4]. In the reaction of polycarbonate at 430°C, yields of the identified reaction products such as phenol and bisphenol A reached more than 90 % by the addition of Na<sub>2</sub>CO<sub>3</sub>. No monomeric compounds were confirmed in the reaction of polycarbonate at 300°C without solvent, indicating that water was excellent solvent for the decomposition of polycarbonate. Also, the molding materials of phenol resin were decomposed mainly into phenol, cresols and dimethylphenol, although phenol resin was stable in the reaction in organic solvent such as 1-methylnaphthalene. In this study five model compounds as shown in Figure 1 were reacted.

Decomposition reaction of *p*-bis(hydroxyphenyl)methane The cleavage reactions of methylene bridge of *p*-bis(hydroxyphenyl)methane (model compound **1**) in sub- and supercritical water were confirmed. Phenol, *o*- and *p*-cresols were main products in the reaction at 430°C. The production of hydroquinone and hydroxybenzaldehyde was confirmed in the reaction at 300°C although they were unstable at high temperature and the yields were small. The total yield of identified products reached 20% even by the reaction at 350°C for 1h. Decomposition reactions were carried out by varying the injection amounts of water from 1 to 4ml. The yield of products increased with an increase in the injection amounts of water and the total yield reached 60% in the reaction in 4ml water at 430°C for 30min.

Effects of additives on the decomposition reaction of model compound **1** In the reaction of model compound **1** at 430°C for 1h, conversion reached more than 70%. But the yield of the identified products was less than 50%, indicating the presence of unidentified products. The presence of the trimer of phenol resin was confirmed by the GC/MS analysis of the water soluble products. The presence of trimer suggested the presence of undesirable condensation reactions. To avoid condensation reaction, hydrogen donor compound, tetralin was added. However, by the addition of tetralin, yield of reaction products were not improved in the reaction of model compound **1**, indicating that the radical reaction was not important. If the ionic decomposition reactions occurred, the addition of acid or alkali salts might be effective to avoid the condensation reaction. Although the addition of acid was not effective, the addition of alkali salts was effective and the yields of the reaction products increased as shown in Table 1. Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were more effective additives than NH<sub>4</sub>OH, NaOH, KOH and K<sub>2</sub>CO<sub>3</sub>. These results indicated that the reaction proceeded via ionic processes. Even with the addition of small amounts of Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub>, the total yield of phenol and cresol reached 60% at 430°C for 30min when the additive/model compound ratio was 0.06.

Table 1 The effect of additives on the yield of phenol and cresol at 430°C

| additive                        | time (min) | yield (%) |        |
|---------------------------------|------------|-----------|--------|
|                                 |            | phenol    | cresol |
| none                            | 15         | 7.1       | 5.7    |
| none                            | 30         | 21.7      | 14.3   |
| NH <sub>4</sub> OH              | 15         | 14.2      | 6.2    |
| NH <sub>4</sub> OH              | 30         | 23.8      | 19.6   |
| NaOH                            | 30         | 31.9      | 14.5   |
| KOH                             | 30         | 31.9      | 16.4   |
| Na <sub>2</sub> CO <sub>3</sub> | 15         | 16.4      | 6.4    |
| Na <sub>2</sub> CO <sub>3</sub> | 30         | 42.3      | 23.5   |
| NaHCO <sub>3</sub>              | 30         | 51.2      | 12.5   |
| K <sub>2</sub> CO <sub>3</sub>  | 30         | 37.6      | 11.7   |

Even in the reactions at 350°C for 60min, the total yields of identified products reached 50% by adding Na<sub>2</sub>CO<sub>3</sub>.

To obtain information on the mechanism of the effects of alkali salt addition, a neutral salt, NaCl, was added and the yields were compared. The yield of identified products in the reaction of model compound **1** increased from 2% to 19% at 430°C for 15min by adding NaCl as shown in Figure 2. It is reported that the addition of NaCl had the same effects to increase the density of water in the reactions at near supercritical region. However, the yields of identified products in the reactions with NaCl were smaller than those with Na<sub>2</sub>CO<sub>3</sub> as shown in Figure 2. One speculation suggested the presence of the important role of water other than physical effects.

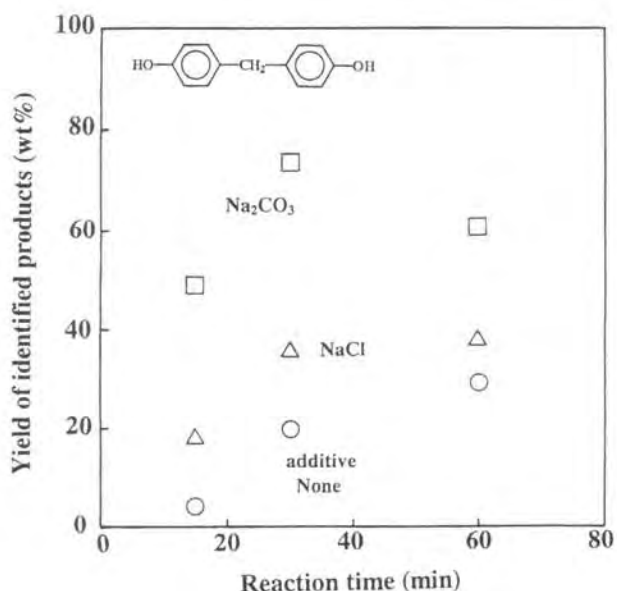


Figure 2 Decomposition reaction of model compound **1** with NaCl or Na<sub>2</sub>CO<sub>3</sub> at 430°C.

#### Decomposition reaction of model compounds **2** to **5**

Model Compound **2** (*o*-bis(hydroxyphenyl)methane) was also decomposed to monomeric compounds such as phenol and cresols and xanthene in the reactions in supercritical water.

Furthermore, we have confirmed the production of benzophenone and dimethylbenzophenone by the reactions of model compound **3** (diphenylmethane) and model compound **4** (di-*p*-tolylmethane) as shown in Figure 3.

The production of oxygen containing compounds indicated presence of chemical participation of water on the decomposition reaction of model compounds because model compounds **3** and **4** did not have oxygen.

To confirm the chemical participation of water directly, diphenylmethane was reacted in H<sub>2</sub><sup>18</sup>O and benzophenone was obtained. GC/MS chart of obtained benzophenone indicated the inclusion of <sup>18</sup>O confirming the incorporation of water oxygen directly.

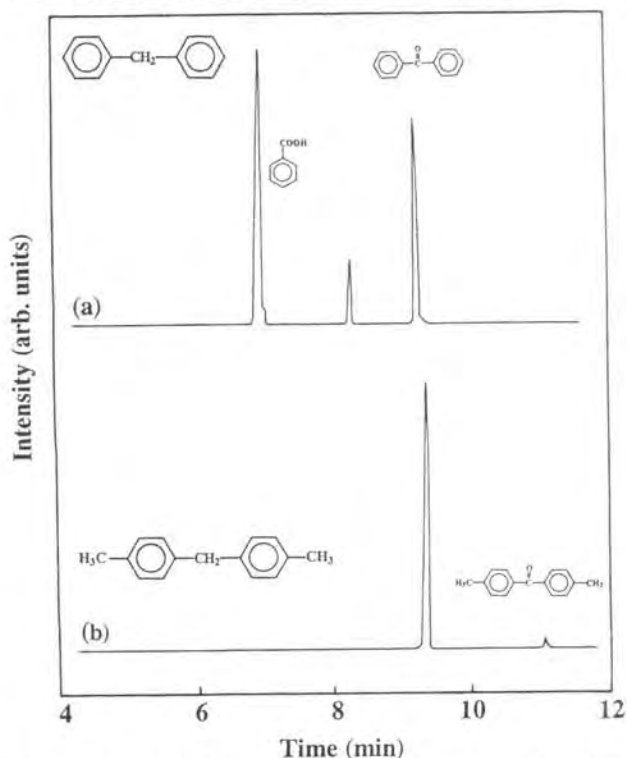


Figure 3 GC/MS charts of the decomposition products of (a) diphenylmethane and (b) di-*p*-tolylmethane.

It was also confirmed the decomposition reaction of dihydroxybenzophenone leading to the formation of phenol and hydroxybenzoic acid. Hydroxybenzoic acid was reactive and the production of phenol in the reaction of hydroxybenzoic acid was confirmed.

From these results, decomposition reaction of phenol resin including chemical participation of water was considered as shown in Figure 4. The methylene bond was oxygenated in the first step giving a carbonyl compound in water. The carbonyl compound decomposed into carboxylic acid and phenol compound.

Compound **5** was model compound of polycarbonate. Model compound **5** was decomposed to phenol, isopropenylphenol and isopropylphenol in supercritical water. Hydrogenation of isopropenyl phenol to isopropylphenol was observed in supercritical water suggesting the possibility that hydrogen was supplied by water.

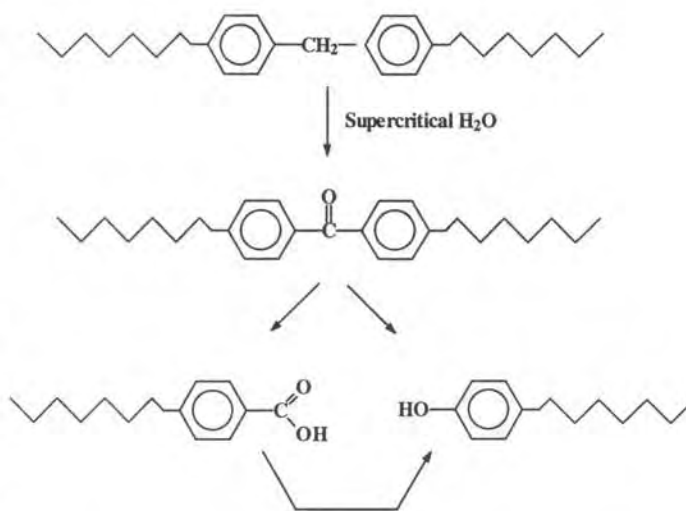


Figure 4 Decomposition reaction of phenol resin in sub- and supercritical water

## Conclusions

In this study we have clarified that water is an excellent solvent for the decomposition reaction of compounds containing methylene bridges. The addition of alkali salts was effective for the decomposition reactions of *p*-bis(hydroxyphenyl)methane and *o*-bis(hydroxyphenyl)methane and a significant increase of yield was observed by the addition. It was clarified that water density was an important factor for the decomposition of the phenol resin model compounds such as *o*-bis(hydroxyphenyl)methane and *p*-bis(hydroxyphenyl)methane under these reaction conditions. The acceleration mechanism of alkali salt addition for the reaction was not clear, however, effective decomposition of the model compounds of phenol resin was attained by the reaction with supercritical water, especially when adding an alkali salt.

## References

1. Bisio, A. L.; Xanthos, M. "How to Manage Plastics Waste," Hanser, New York, 1995.
2. Kaminsky, W.; Schlesselman, B.; Simon, C. *J. Anal. Appl. Pyrolysis*, 1995, **32**, 19.
3. Kastner, H.; Kaminsky, W. *Hydrocarbon Processing*, 1995, **74**, 109.
4. Tagaya, H.; Suzuki, Y.; Kadokawa, J.; Karasu, M.; Chiba, K. *Chem. Lett.* 1997, 47.
5. Tagaya, H.; Suzuki, Y.; Asou, T.; Kadokawa, J.; Chiba, K. *Chem. Lett.* 1998, 937.
6. Tagaya, H.; Katoh, K.; Kadokawa, J.; Chiba, K. *Polymer Degradation and stability* 1999, **64**, 289.
7. Suzuki, Y.; Tagaya, H.; Asou, T.; Kadokawa, J. Chiba, K. *Ind. Eng. Chem. Res.* 1999, **38**, 1391.