

Decomposition of Model Compounds of Phenol Resin Waste with Supercritical Water

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Model compounds of phenol resin waste such as prepolymers and substituted diphenylmethanes were decomposed into their monomers by the reaction at from 300 to 430 °C with water in 10 ml tubing bomb reactor. The decomposition reactions were accelerated by the addition of alkali salts such as Na₂CO₃.

The chemical recycling of waste polymers has been gaining greater attention in recent years as a means of obtaining valuable products from waste plastics.¹ Thermal cracking of thermoplastic resin is a well-known technique and fluidized-bed pyrolysis technology has been under development.^{2,3} However, chemical recycling process for thermosetting resin wastes such as phenol resin waste has not been yet reported. We have already reported that prepolymers of phenol resin were decomposed in hydrogen donor solvent at 400 - 440 °C. However, the yields of phenol were only 5.3 - 13.7%.⁴ In this study, we have found that seven prepolymers and *p*- and *o*-bis(hydroxyphenyl)methanes as model compounds of phenol resin were effectively decomposed into their monomers by the reaction with supercritical water. It is well known that water under supercritical conditions is much less polar and can homogenize substantial amounts of non-polar organic compounds.^{5,6} It is emerging as a medium that could provide the optimum conditions for a variety of chemical reactions among them the destruction of hazardous waste.⁷

Seven prepolymers whose molecular weights were 247 - 923 were reacted with supercritical water at 430 °C for 0.5 h. 10 ml tubing bomb reactor was used as the reactor in which the reaction temperature was attained in about 2 min.⁸ The typical reaction was carried out for 0.1 g of prepolymer with 1.0 ml water after flushing the reactor with argon. Prepolymers were kindly provided by Dainippon Ink & Chemicals Co., Ltd. and

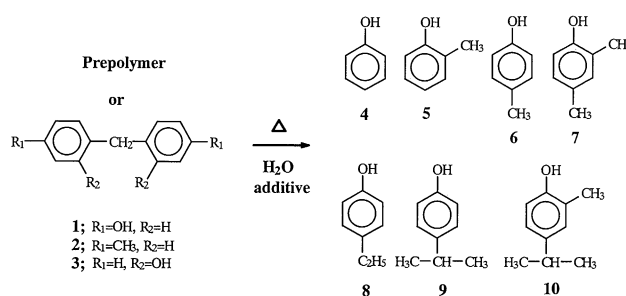
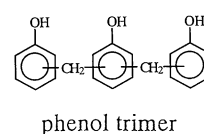


Figure 1. Reaction products of model compounds of phenol resin waste with supercritical water.

their exact compositions were unknown. Reaction products were extracted by ether and compounds **4**, **5**, **6**, **8**, **9** and **10** were identified by GC/MS as the main decomposition products as shown in Figure 1. No carbonization occurred in these reaction conditions. The yields of products depended on the kinds of prepolymers as shown in Table 1. Main decomposition products from prepolymers A and C were **4** and **9** indicating that prepolymers A and C were isopropylphenol resins. Also the main decomposition products from prepolymers F and G were **5**, **6** and **8** indicating that they were cresol resins. Total yield of identified products reached 78% in the case of prepolymer C.

To obtain information on the reaction mechanism in water, substituted diphenylmethanes, **1**, **2**, and **3** were reacted at 300 - 430 °C. Model compound **2** and diphenylmethane could not be decomposed even by the reaction at 430 °C for 1 h. By the reaction of compound **1** and **3** with water, phenol and cresol were obtained as the main products. In the reaction of compound **3**, the production of xanthene was also confirmed. Even in the neat reaction at 430 °C for 0.5h, yield of xanthene reached 21.5% although the yield of phenol was only 1.4%. It



was considered that the presence of hydroxyl groups was essential for the decomposition reaction. We have tried to add phenol in the reaction of compound **2**, however, no decomposition reaction occurred. It indicates that the reactant itself should possess hydroxyl groups. A total yield of phenol and cresol on the decomposition reaction of compound **1** was 19.5% at 350 °C for 1 h and more than 40% at 430 °C for 1 h as shown in Figure 2. Although conversion of compounds **1** and **3** reached 100% at 430 °C for 1 h, the yield of identified products was less than 50%, indicating the presence of unidentified products. We confirmed the presence of trimer of phenol by the GC/MS analysis of water soluble products, indicating the

Table 1. Decomposition reaction of prepolymers A ~ G (molecular weight) of phenol resin with supercritical water

			Yield of product (wt%)						
	H/C	Additive	4	5	6	8	9	10	Total
A (435)	1.1	none	30.7	1.3	0.1	0.2	19.2	3.3	54.8
		Na ₂ CO ₃	48.9	8.9	5.0	0.9	25.8	2.5	92.0
B (748)	1.1	none	18.0	0.4	0.2	0.0	0.0	0.0	18.6
		Na ₂ CO ₃	27.4	1.2	1.0	0.0	13.4	0.0	43.0
C (576)	1.1	none	26.6	12.0	5.0	1.3	29.3	3.7	77.9
		Na ₂ CO ₃	58.0	4.9	2.4	0.7	24.0	0.4	90.4
D (605)	0.9	none	20.0	7.0	11.6	0.7	0.0	0.0	39.3
		Na ₂ CO ₃	29.0	9.9	11.0	1.5	0.0	0.0	51.4
E (923)	0.9	none	10.5	3.8	5.9	0.8	0.0	0.0	21.0
		Na ₂ CO ₃	24.5	6.9	8.4	1.3	0.0	0.0	41.1
F (425)	1.0	none	0.6	8.4	3.3	5.4	0.0	0.0	17.7
		Na ₂ CO ₃	1.2	29.7	7.7	11.6	0.0	0.0	50.2
G (247)	1.1	none	1.6	23.7	6.7	10.8	0.0	0.0	42.8
		Na ₂ CO ₃	1.6	38.7	8.3	12.2	0.0	0.0	60.8

presence of condensation reactions. If the radical intermediates were produced, hydrogen donor was effective to avoid the condensation reaction. Decomposition reactions of prepolymers in hydrogen donor solvents were already confirmed as reported.⁴ Therefore, hydrogen donor, tetrahydronaphthalene, was added to the reaction with water. However, the addition of tetrahydronaphthalene was not effective. Furthermore, no reaction occurred when tetrahydronaphthalene alone was used as solvent. The addition of acid was not also effective.

The addition of alkali salts was effective and yields of reaction products increased as shown in Figure 2 indicating that the reaction was the ionic decomposition reaction. Even by the addition of small amounts of Na_2CO_3 or NaHCO_3 , a total yield of phenol and cresol reached 50% at 400 °C for 0.25 h when additive / model compound ratio was 0.02. The yields reached more than 60% at 430 °C for 0.5 h by the addition of Na_2CO_3 .

Based on the former results, decomposition reaction of prepolymers were also carried out by adding 1 wt% Na_2CO_3 for prepolymer. The yields fairly increased as shown in Table 1. In the case of isopropylphenol resin, prepolymers A and C, phenol yields increased to 48.9% and 58.0%, respectively, and the total yields reached more than 90%. Certainly, reactivities of prepolymers were larger than those of bis(hydroxyphenyl)methanes, **1** and **3**.

Hydrolysis of condensation polymers such as polyesters and polyamide has been reported.⁹ For example, polyethylene terephthalate (PET) depolymerized to monomer completely at 265 °C. However, the reactivity of aromatic compounds containing methylene bridges was fairly low even the reaction at 405 °C.⁸ This study indicates that water is excellent solvent for the decomposition reaction of methylene bridges containing in prepolymer of phenol resin. By the reaction of compound **1** at 300 °C for 15 min, productions of benzaldehyde and p-dihydroxybenzene were confirmed although the yields were small. They were unstable at high temperature and not confirmed by the reaction at over 350 °C. The results suggested the participation of water in the decomposition reaction.

To obtain information on the mechanism of the effects of alkali salt addition, neutral salt, NaCl was added. Yield of phenol increased from 7.0% to 11.0% by the addition of NaCl although the increase of yield was small. It is well known that the addition of NaCl affected the density of water at near supercritical region.¹⁰ Decomposition reactions were carried out by varying the injection amounts of water from 1 ml to 2 ml, 3 ml, and 5 ml. However, no significant change of the yields was observed, indicating that the density was not important factor for the decomposition of phenol resin model compounds in these reaction conditions. Acceleration mechanism of the addition of alkali salts for the reaction was not clear, however, effective decomposition of phenol resin model compounds was attained with supercritical water, especially by the addition of alkali salt. As described above, polyester such as PET could be hydrolyzed in supercritical water. Not only thermoplastic resin, but also thermosetting resin could be decomposed into their monomers by the reaction with supercritical water. Phenol resin involved in the molding material of phenol resin is less than 50%. In the preliminary reaction of molding materials of phenol resin at 430

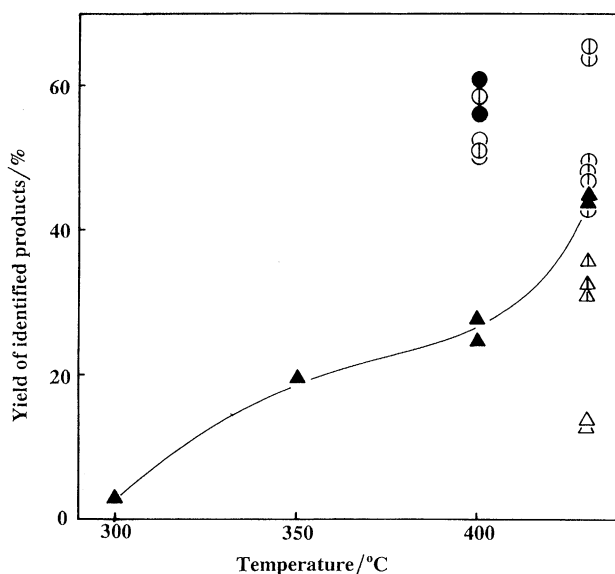


Figure 2. Yield of identified products in the reaction of model compound **1** with supercritical water. Additives were NH_4OH , NaOH , KOH , Na_2CO_3 , NaHCO_3 , and K_2CO_3 .

additive	Reaction time (h)		
	0.25	0.5	1
none	△	△	▲
alkali salt	○	⊙	●

°C for 1 h, the total yield of **4**, **5**, **6** and **7** reached 28.5%. Further application of this reaction to molding materials of phenol resin is now in progress.

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