Reaction of Model Compounds of Phenol Resin and Molding Materials of Phenol Resin in Supercritical Water for Chemical Recycling of Polymer Waste

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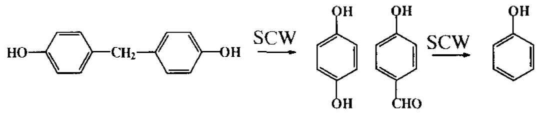
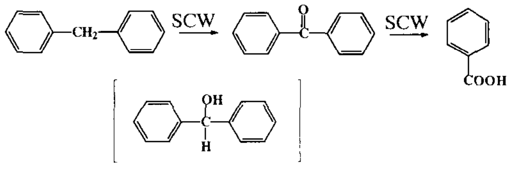
Oxygen supply reaction by supercritical water (SCW) to diphenylmethane was confirmed by the production of benzophenone. Molding materials of phenol resin were decomposed into their monomers by the reaction in SCW and addition of polycarbonate accelerated the decomposition reaction of molding material.

SCW has attracted considerable interests as chemical reaction media.[1,2] It is emerging as a medium that could provide the destruction conditions of polymeric compounds such as cellulose,[3] thermoplastic polymers,[4] and hazardous waste such as PCB.[5] Physical properties of SCW were noted because SCW can homogenize relatively large amounts of non-polar organic compounds making them available for chemical reaction.[6] However, chemical reactions of water in the decomposition reaction of polymeric compounds were hardly reported.[7]

We have already reported that prepolymers of phenol resin and substituted diphenylmethanes as the model compounds of phenol resin were decomposed into their monomers by the reaction at from 573 to 703 K in water.[8] SCW oxidation of substituted phenols were reported,[9] but the reaction of phenol compounds under non-oxygen atmosphere were hardly reported. In further reaction of *p*-bis(hydroxyphenyl)methane in SCW, we have confirmed the production of hydroquinone and *p*-hydroxybenzaldehyde. These compounds were easily converted to phenol in SCW. The production of hydroquinone and *p*-hydroxybenzaldehyde suggested the possibility of oxygen and hydrogen supply from SCW.



In this study diphenylmethane was reacted in SCW to confirm the oxygen supply reaction from SCW, because diphenylmethane doesn't have oxygen atom. Diphenylmethane was known as a thermally stable compound.[10] However, the production of benzophenone and benzoic acid in SCW at 673 K was confirmed in this study although the yield of benzophenone was only 0.6%. Benzophenone was converted to phenol in SCW. The production of benzophenone suggested the oxygen supply reaction from SCW. To confirm the reaction directly, diphenylmethane was heated in $H_2{}^{18}O$ at 703 K for 60 min. In the reaction in $H_2{}^{16}O$, molecular weight of benzophenone was 182 as shown in Figure 1, however, in the reaction in $H_2{}^{18}O$, molecular weight of benzophenone was 184. It indicated that oxygen was supplied from SCW directly. Decomposition reaction of benzophenone into benzoic acid was also confirmed. These results indicated that methylene bond of phenol resin model compound was ruptured via intermediate in which hydroxyl groups attacked methylene carbon producing carbonyl compound. In the first step of nucleophilic attack of hydroxide ion to methylene carbon, the production of benzhydrol was expected, however, benzhydrol was not detected. It was confirmed from the reaction of benzhydrol alone that benzhydrol was reactive and unstable in SCW giving benzophenone and diphenylmethane.



Although the chemical recycling of waste polymers has been gaining greater attention in recent years,[11] chemical recycling reaction of thermosetting resin has not been yet reported. In this study, based on the decomposition reaction of model compounds in SCW, molding materials A and B of phenol resin were reacted. Molding materials were prepared by the reaction of prepolymers

Table 1. Decomposition reaction of molding materials A and B of phenol resin in SCW at 703 K for 15 ~ 90 min

Molding material	Time (min)	Additive (wt%)	Yield of product (wt%) 1	2	3	4	5	Total
A	15	none	1.0	1.0	1.3	0.5	0.0	3.8
A	15	Na_2CO_3 (0.1)	4.3	4.0	3.1	1.2	0.0	12.6
A	15	Na_2CO_3 (0.3)	6.1	4.5	5.4	1.6	0.0	17.6
A	15	Na_2CO_3 (0.5)	6.7	4.8	6.2	1.7	0.0	19.4
A	30	none	2.5	0.9	1.9	0.8	0.0	6.1
A	30	Na_2CO_3 (0.1)	4.7	3.4	2.2	0.4	0.0	10.7
A	30	Na_2CO_3 (0.3)	7.0	6.5	6.8	2.5	0.0	22.8
A	30	Na_2CO_3 (0.5)	7.9	5.3	5.9	1.6	0.0	20.7
A	60	none	3.6	5.1	3.9	2.5	0.0	15.1
A	60	Na_2CO_3 (0.1)	8.8	8.5	8.2	3.0	0.0	28.5
A	60	Na_2CO_3 (0.3)	7.4	7.7	7.5	2.8	0.0	25.4
A	60	Na_2CO_3 (0.5)	7.2	7.3	7.3	2.6	0.0	24.4
A	90	none	3.0	4.3	4.4	2.1	0.0	13.8
A	90	Na_2CO_3 (0.1)	5.4	6.1	6.7	2.8	0.0	21.0
A	90	Na_2CO_3 (0.3)	7.1	7.9	7.2	2.8	0.0	25.0
A	90	Na_2CO_3 (0.5)	7.4	7.6	7.7	2.7	0.0	25.4
B	15	none	1.1	1.7	1.1	0.3	0.6	4.8
B	15	Na_2CO_3 (0.1)	2.4	8.0	5.6	0.3	1.4	17.7
B	30	none	0.9	0.1	0.3	0.0	0.1	1.4
B	30	Na_2CO_3 (0.1)	3.2	3.8	4.3	0.4	2.2	13.9
B	60	none	2.2	3.6	3.5	0.6	2.1	12.0
B	60	Na_2CO_3 (0.1)	3.4	4.7	4.7	0.6	2.5	15.9
B	90	none	2.1	3.3	3.5	0.5	2.1	11.5
B	90	Na_2CO_3 (0.1)	2.9	3.2	4.0	0.3	1.9	12.3

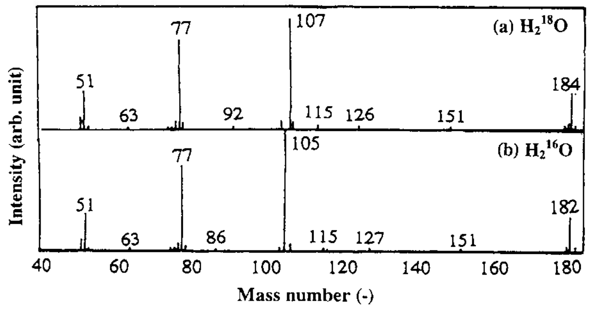
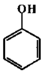


Figure 1. MS spectra of the reaction products in the reaction of diphenylmethane in SCW ((a) $H_2{}^{18}O$, (b) $H_2{}^{16}O$).

of phenol resin and bridging agent. The content of phenol resin in the molding material A was lower than 50%. And the others were fillers and bridging agent such as hexamethylenediamine.

In the reaction of molding materials A and B in SCW, production of compounds **1**~**7** and hexamethylenediamine were confirmed by GC/MS.



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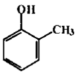

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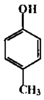

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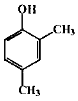

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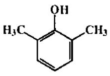

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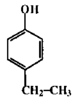

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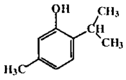

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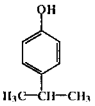
Substituted diphenylmethanes were decomposed even in the reaction at 573 K. However, two molding materials A and B of phenol resin were not decomposed in the reaction at 573 K probably because of high bridging. In the case of molding material A, yields of identified products reached 15.1% in the reaction at 703 K for 60 min as shown in Table 1 although the yields of compounds **6** and **7** were small. We have already clarified that the addition of alkali salts was effective in the decomposition reaction of model compounds of phenol resin, indicating that the reaction should be ionic.[8] Even by the addition of small amounts of Na_2CO_3, a total yield of identified products reached 28.5% in the reaction for 60 min. In the reactions for 15 min and 30 min, yields increased with an increase in the amounts of Na_2CO_3. However, in the reaction for 60 min, further addition of Na_2CO_3 was not effective. The yield of 28.5% means that more than 55% of phenol resin in the molding material A was decomposed into their monomers. Molding material B was less reactive than A and yields of identified products were less than 20% even by the reaction adding Na_2CO_3. Production of compound **5** indicated that the resin in molding material B was cresol-type.

Table 2. Decomposition reaction of prepolymers of polycarbonate in water at 503 K to 573 K for 1 ~ 24 h

Temp (K)	Time (h)	Additive (wt%)	Yield of product (wt%) 1	8	9	Total
503	24	none	0.3	0.0	0.0	0.3
503	24	Na_2CO_3 (0.4)	44.7	3.4	3.3	51.4
503	24	NaCl (0.4)	0.4	0.6	1.6	2.6
523	2	none	0.0	0.0	0.0	0.0
523	2	Na_2CO_3 (0.1)	14.3	10.5	18.0	42.8
523	2	NaCl (0.1)	0.0	0.0	0.2	0.2
573	1	none	7.0	5.0	8.2	20.2
573	1	Na_2CO_3 (0.1)	56.6	3.3	0.0	59.9
573	1	NaCl (0.1)	31.6	10.1	0.3	42.0

Thermoplastic resin such as polycarbonate was also decomposed in water. By the reaction of prepolymers of polycarbonate in water, production of compounds, **1**, **8** and **9** was confirmed. In the reaction at 573 K for 1 h, the total yield of **1**, **8** and **9** reached 20.2% as shown in Table 2 indicating that reactivity of polycarbonate was fairly larger than those of molding materials of phenol resin. The addition of Na_2CO_3 was effective for the decomposition reaction of prepolymers of polycarbonate, and the yield reached 59.9%.



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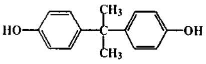

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Expecting positive effect of polycarbonate addition on decomposition reaction of molding materials, polycarbonate was mixed with molding material A. Decomposition didn't occur in the reaction at 573 K. However, in the reaction at 703 K for 3 h, yield of identified products increased from 2.2% to 26.1% by the addition of prepolymer of polycarbonate as shown in Table 3. It was considered that the reaction intermediates produced by the reaction of prepolymers of polycarbonate might accelerate the decomposition reaction of molding material.

Table 3. Decomposition reaction of mixture of molding material A of phenol resin and prepolymers of polycarbonate in SCW at 703 K for 3 h

ratio[a]	Additive	Yield of product (wt%) 1	2	3	4	5	6	7	Total
10:0	none	0.2	0.0	1.2	0.8	0.0	0.0	0.0	2.2
8.3:1.7	none	2.3	1.0	3.5	0.6	0.8	0.0	0.5	8.7
8.4:1.6	Na_2CO_3	8.6	4.3	9.1	2.6	0.3	0.3	0.9	26.1

[a] Ratio of molding material A of phenol resin to polycarbonate.

In the industrial chemical recycling process of polymer wastes, various plastic wastes may be mixed because of difficulty in their separation. Water is inexpensive and non-toxic solvent. To clarify the reaction between plastics in SCW is very important to establish effective decomposition process.

References and Notes

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