

TREATMENT OF PHENOL RESIN FOAM POWDER AND PREPOLYMER IN HIGH-TEMPERATURE WATER

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Abstract: In this study waste plastics such as phenol resin foam powder were decomposed into their monomer compounds in sub- and supercritical water. Water plays important roles as stable physical medium at high temperature and reactive chemical reagents to accelerate decomposition reaction of the thermosetting resin. In the decomposition reaction, methylene bonds were cleaved easily via the ionic reaction by water. The water participating mechanism was confirmed to make clear the decomposition products of phenol resin foam.

1. Introduction

It is well known that water under sub- and supercritical conditions is much less polar and can homogenize substantial amounts of non-polar organic compounds. Also the high temperature water including supercritical water is emerging as a medium which could provide the optimum conditions for a variety of chemical reactions, among them the decomposition of polymeric compounds [1]. We have already confirmed that waste plastics such as phenol resin decomposed into their monomeric compounds in sub and supercritical water [2 ~ 7]. In this study waste plastics such as phenol resin foam powder were decomposed into their monomer compounds in sub- and supercritical water. Water plays important roles as stable physical medium at high temperature and reactive chemical reagents to accelerate decomposition reaction of the thermosetting resin. In the decomposition reaction, methylene bonds were cleaved easily via the ionic reaction by water. The water participating mechanism was confirmed to make clear the decomposition products of phenol resin foam and model compounds including prepolymer.

2. Experimental

Waste organic compounds were reacted after pulverizing. A 10ml tubular bomb reactor was used as the reactor in which the reaction temperature was attained within 2 min [8]. The typical reaction was carried out for 0.1g of waste organic compounds in 1~ 5ml of water with

or without additives. Prepolymer and 4,4'-methylenediphenol was used as model compound of phenol resin foam. NaCl, KCl, CsCl, KI, CaCl₂, NH₄OH, and Na₂CO₃ were used as the additive.

After the reaction, products were extracted by ether and measured by GC/MS and GC. The yield of products was defined by product(g)/reactant(g). Main products were phenol and alkylphenols. In the thermal analysis of organic resources, the temperature increasing rate was 10°C / min.

Prepolymer of phenol resin was prepared by the polymerization reaction of pure phenol and recovered mixtures of phenol, cresols and alkyl phenols in acidic conditions. Molecular weight distributions of prepared prepolymer were measured by GPC.

3. Results and Discussion

3.1 Decomposition reaction of phenol resin foam

Phenol resin foam was pulverized and reacted at 430°C. More than 50% of the foam was converted to monomeric compounds. To obtain information on the reactions at mild conditions, the resin was reacted at 300 to 380°C as shown in Fig.1. Conversion increased with an increase in the reaction temperature and total yields of identified monomer compounds increased with temperature.

Na₂CO₃ was more effective additive than NH₄OH on the decomposition reaction. However, high yield of oligomer was expected in the reaction adding NH₄OH.

3.2 The effects of the time on the decomposition reaction of phenol resin foam

In the reaction at 320°C, conversion gradually increased as shown in Fig. 2. It suggested the possibility to obtain high yields of the decomposition also at mild reaction conditions.

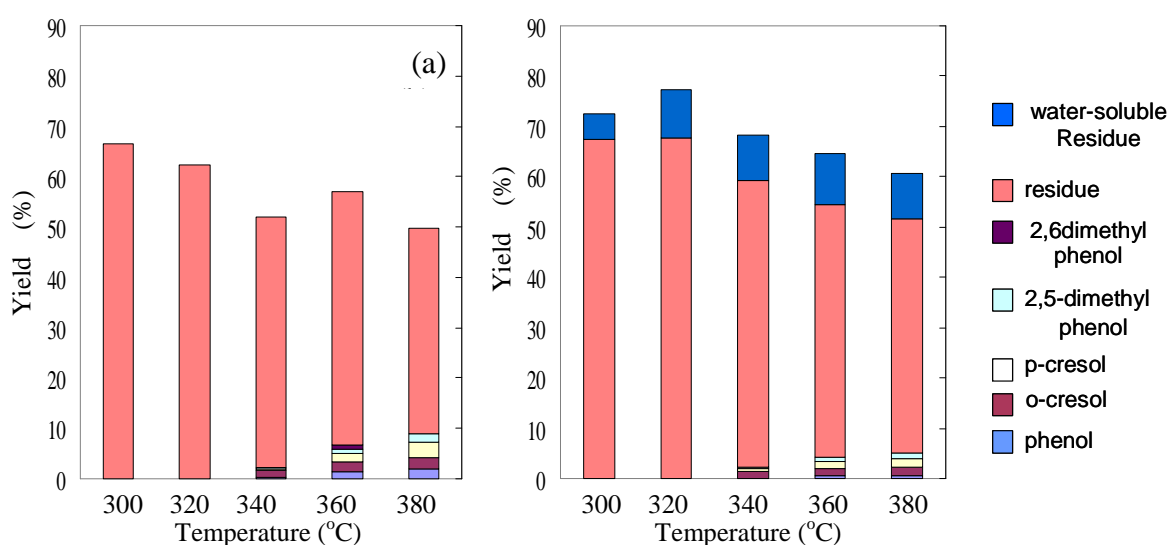


Fig. 1. The effect of temperature and additive on the decomposition reaction of phenol resin foam (a) Na₂CO₃, (b) NH₄OH

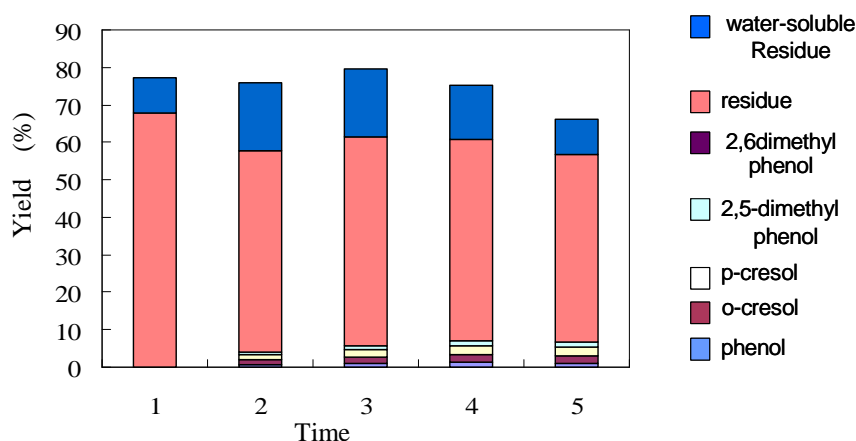


Fig. 2 Decomposition reaction of phenol resin foam at 320 °C

3.3 Decomposition reaction of 4,4'-methylenediphenol

To attain information on the decomposition reaction mechanism of phenol resin, model compound of resin, 4,4'-methylenediphenol was reacted. Conversion and yield of monomeric compounds increased when temperature increased as shown in Fig.3. Phenol yield was fairly small in the reaction at below 250 °C. Products were obtained in the row of phenol, *p*-cresol, and *o*-cresol. However, the total product yields are too small to explain the conversion. Therefore, 4,4'-methylenediphenol was converted to unidentified products which can not be observed in GC and GC-MS spectra. It was considered the presence of dehydrogenation condensation reaction. We already found the production of trimer of phenol [9].

3.4 Effects of inorganic additives on the decomposition reaction

Effects of inorganic additives on the decomposition reaction of 4,4'-methylenediphenol were studied. We have already confirmed that the addition of neutral salts such as NaCl was effective for the decomposition reaction. To obtain information on the positive effect of neutral salts, decomposition reactions by adding various alkali halides were carried out. Addition of alkali halide increased conversion of 4,4'-methylenediphenol and yields of phenol and *p*-cresol. NaCl was the best additive among them.

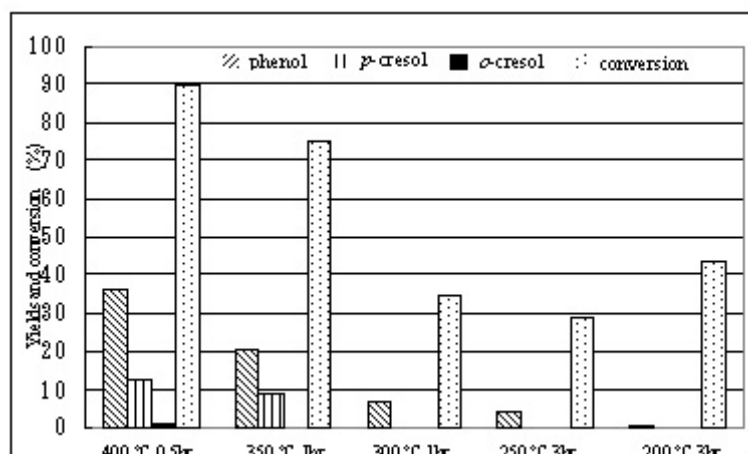


Fig. 3 Decomposition reaction of 4,4'-methylenediphenol

3.5 Dehydrogenation reaction in supercritical water

To obtain information on the decomposition reaction mechanism, dehydrogenation reaction in supercritical water was studied. 1-naphthol and methanol were reacted in supercritical water as shown in Fig.4. Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, methylnaphthol, and dimethylnaphthol were produced. Naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene were produced through decomposition reactions by water. Methylnaphthol and dimethylnaphthol were produced through dehydrogenation reaction by methanol. These kind of dehydrogenation reaction might occur in the decomposition reaction of 4,4'-methylenediphenol.

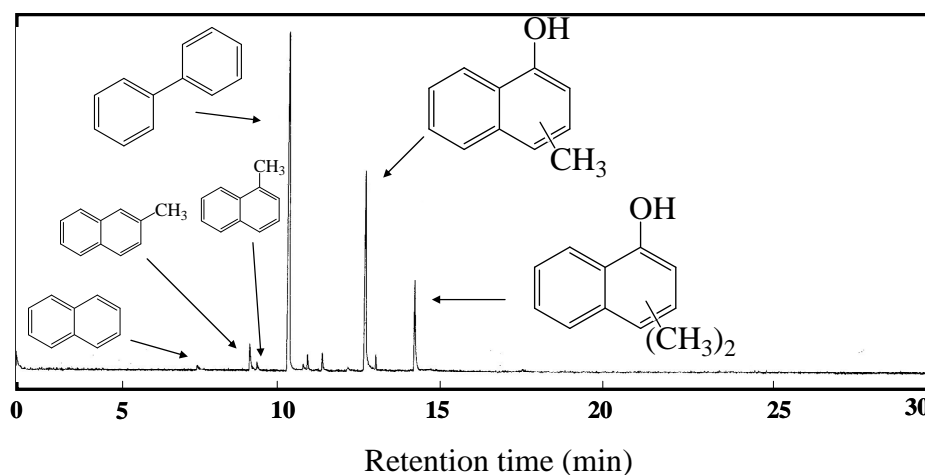


Fig. 4 GC-MS analysis of dehydrogenation reaction of 1-naphthol in supercritical water

3.6 Synthesis of Phenol Resin by Using Decomposition Products of Waste Polymers

The prepolymer of phenol resin was prepared by the conventional preparation method from the decomposition products. Two kinds of the prepolymer of phenol resin were prepared by using the pure phenol and decomposition products of polycarbonate. Formaldehyde and the hydrochloric acid are added to the phenol or decomposition products, and then were heated at 85°C with stirring for 2h. The obtained products were cooled, and were heated at 175°C to remove un-reactive materials. Thus, the molecular weights of solid products were determined by GPC analysis.

The prepolymer yield prepared by using pure phenol was 71.0% while the yield using decomposition products was 51.2%. The molecular weight of products prepared by using decomposition products was almost equal to the molecular weight of the prepolymer synthesized from the pure phenol, suggesting that the prepolymer of phenol resin can be synthesized by using decomposition products.

4. Conclusions

We have studied decomposition reaction of phenol resin foam and 4,4-methylenediphenol to make clear the decomposition reaction mechanism of phenol resin

in high temperature water. From the effect of reaction temperature, we have concluded that the reaction which produces phenol and the reaction which produces *p*-cresol and *o*-cresol do not occur at the same time. This suggestion is supported by the effect of reaction time. From the tendency of efficiency of salts as catalyst, water molecule attacks to methylene bond of 4,4'-metylenediphenol was suggested. This suggestion is supported by the effect of concentration of water which is used for this reaction. Under these conditions, not only decomposition reactions, but also condensation reactions occur. This fact was supported by the fact in the reaction of methanol and aromatic compounds.

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