

Degradation of Thermoplastic Resin in Sub- and Supercritical Water

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Decomposition reactions of thermoplastic resin (polystyrene) were carried out in sub- and supercritical water at 300 ~ 400 °C for 10 ~ 420 min. Molecular weights of polystyrene clearly decreased with an increase in reaction time in the reactions in 1-methylnaphthalene and water even at 300 °C. Production of monomeric compounds such as toluene, xylene, styrene, and α -methylstyrene was confirmed in the reactions not only in 1-methylnaphthalene but also in water. In the reactions in supercritical water, yields of styrene and α -methylstyrene were larger than those of toluene and xylene. The compositions of the products in water were different with those obtained by pyrolysis reaction in 1-methylnaphthalene.

Introduction

In recent years the amount of waste plastics has increased, and it has become a serious problem because of lack of landfill sites. Therefore, the development of chemical recycling process of plastic resin has been gaining greater attention. On the other hand, supercritical water oxidation is viewed as a promising technology for hazardous waste treatment, and many decomposition reactions of hazardous compounds with oxygen gas in water were reported in which carbon dioxide and water were obtained by complete supercritical oxygenation [1]. We have already reported the decomposition reactions of polymeric compounds such as phenol resin [2] and polycarbonate [3] in which monomers were obtained effectively even in the reactions without oxygen. In this study, the decomposition reaction of polystyrene was carried out in sub- and supercritical water under argon atmosphere.

Materials and Methods

The number-average molecular weights of the polystyrene used in this study were approximately 44000 and 1100. A 10 ml tubing bomb batch reactor for the reaction was used, which was heated and cooled quickly within 2 min. Reactions were carried out for 10 to 420 min at 300 to 400 °C. After the reaction, reaction products were extracted by using ether.

The reaction products were analyzed by gas chromatography, gas chromatography-mass spectrometry and GPC chromatography to identify and quantify the reaction products.

Results and Discussions

Reactions of polystyrene were carried out in 1-methylnaphthalene and water with or without additives.

In the reaction in 1-methylnaphthalene, pyrolysis reactions were expected as the main reactions because 1-methylnaphthalene was known as thermal stable solvent.

Fig.1(a) shows changes of molecular weight of polystyrene in the reaction in 1-methylnaphthalene at 400 °C. Molecular weight clearly decreased with an increase in reaction time. Decomposition reaction of polystyrene was also observed in the reaction in supercritical water as shown in Fig.1(b). Similar molecular weight decrease was observed

even in the reaction in water, however we could not compare them by calculating mean molecular weight because 1-methylnaphthalene was included in GPC chromatograms. The same results were observed in the reactions at 300 °C.

To clarify the effect of solvents monomer compounds were quantified in the reactions at 300 ~ 400 °C. Reaction time was 60 min. The reaction products in 1-methylnaphthalene were shown in Fig.2(a). It shows that the decomposition reaction occurred at over 350 °C. In the decomposition reactions at 400 °C yields of toluene and xylene were larger than those of styrene and α -methylstyrene and the total yield reached of identified products 72.9 %. In the reactions in supercritical water, yields of styrene or α -methylstyrene were larger than those of toluene and xylene. GPC chromatogram showed that the reaction occurred even at 300 °C, however, production of monomeric

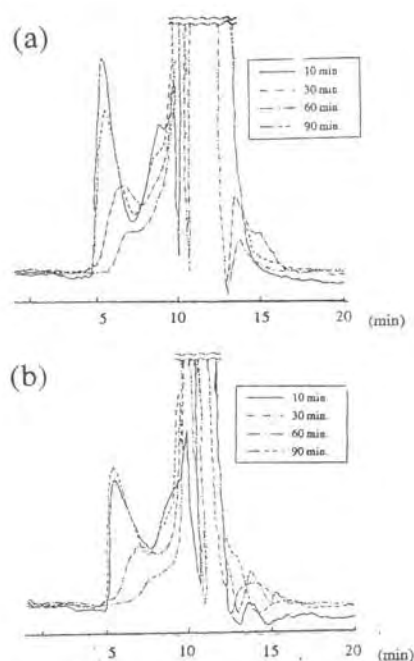


Figure 1 GPC chromatograms of the reaction products of polystyrene in (a) 1-methylnaphthalene at 400 °C for 10 ~ 90 min, and (b) water at 400 °C for 10 ~ 90 min.

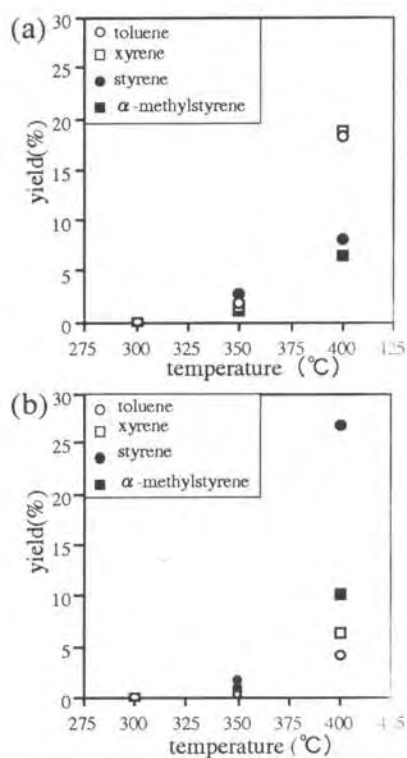


Figure 2 Products in the reactions of polystyrene in (a) 1-methylnaphthalene for 60 min. and (b) water for 60 min

compounds were not confirmed in the reactions at 300 °C, indicating that the decomposition reactions of polystyrene occurred by random scission. To clarify the reaction path, reactions were carried out at 350 °C for 60 to 420 min.

Total yields of monomeric compounds in the reactions at 350 °C were lower than those at 400 °C. In pyrolysis reactions, monomers were obtained even for short reaction time and long reaction time was not effective to increase their yields as shown in Fig.3(a). Total yields of monomeric compounds were 4.3 ~ 13.5 %. However, in the reactions in supercritical water monomer yields increased with an increase in reaction time and had the maximum values for 180 and 240 min as shown in Fig.3(b). The total yield of monomeric compounds reached 16.5 % in the reactions for 240 min.

In order to clarify the reaction mechanism, styrene and 1,4-diphenyl-1,3-butadiene were reacted as model compounds of polystyrene.

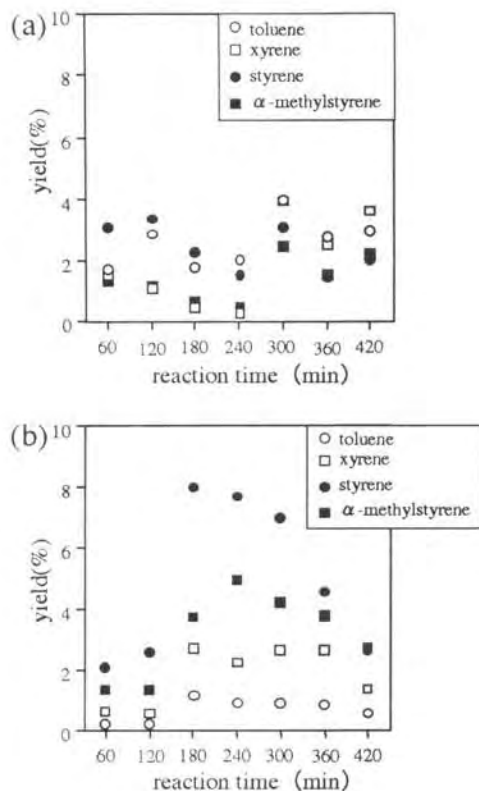


Figure 3 Reaction products in the reactions of polystyrene at 350 °C in (a) 1-methylnaphthalene and (b) water.

Styrene was not decomposed, however in the reactions in 1-methylnaphthalene, degradation was observed in the reactions in water. On the other hand, degradation of 1,4-diphenyl-1,3-butadiene to 1-phenyl dialin, and 1-phenylnaphthalene was confirmed.

As mentioned above, decomposition reactions were confirmed in the reactions not only in 1-methylnaphthalene but also in water at 300 ~ 400 °C, however, monomer yields between them were different.

Conclusions

Degradation reactions of polystyrene in sub- and supercritical water were confirmed by GPC. The tendency was similar to those in 1-methylnaphthalene, however, compositions of reaction productions sub- and supercritical water were different with those obtained by pyrolysis. We already confirmed the decomposition reaction of thermosetting resin in sub- and supercritical water. Water is excellent solvent for the treatment of plastic waste.

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