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Chemical recycling of poly(*p*-phenylene sulfide) in high temperature fluids

Kenji Okubo, Taichi Sugeno, Hideyuki Tagaya*

Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata 992-8510, Japan

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ABSTRACT

Poly(*p*-phenylene sulfide) (PPS) is the engineering plastic with high thermal stability. In this study, the effective decomposition reactions of PPS were confirmed in the high temperature fluids. In high temperature water, 50% conversion was attained at 430 °C by adding the basic compound although perfect solubilization could not be attained. However, in high temperature methanol, perfect solubilization was attained by the reaction at 430 °C. It was also confirmed that even by the reaction at 370 °C, conversion reached to 75% by the reaction in methanol for 5 h. Main reaction products of PPS in high temperature fluids were oligomers and monomeric compounds such as thiophenol, diphenyl sulfide, thioanisole and dibenzothiophene.

1. Introduction

Poly(*p*-phenylene sulfide) (PPS) is the industrially important and an attractive engineering thermoplastic because of its high solvent resistance, high mechanical strength and high thermal stability [1]. Various PPS composites were prepared to achieve improvements of mechanical properties furthermore [2,3], although PPS is a plastic endowed with excellent thermal and chemical resistance [4,5]. Good flow properties and thermal stability in the molten state make PPS relatively easy to process by injection molding and extrusion. Long time operation is possible even at 240 °C, however, when heated to temperatures exceeding 300 °C, PPS undergoes cyclization, branching and cross linking processes. The degradation study on PPS is important since the processing in high temperature may induce changes that will affect the ultimate performance [6–8].

The idea of recycling of PPS has become important not only environmentally, but also economically since the production of PPS has increased firmly [9]. Mechanical recycling has been investigated as probable recycling method for engineering thermoplastic with high thermal stability such as PPS [10].

Recently, we have found that waste plastics including thermosetting resin such as phenol resin decomposed into their monomeric compounds in sub and supercritical water. The addition of basic compounds such as Na_2CO_3 was effective on the decomposition reaction. Furthermore, chemical participation of water on the reaction was suggested [11–13].

High temperature water has become the subject of wide ranging interests [14–17], because of its low dielectric constant similar to organic solvents and high thermal stability at near and above its critical point ($Tc = 374.2$ °C, $Pc = 22.1$ MPa) [18–20].

In this study, to obtain information on the decomposition reaction of PPS in high temperature fluids, PPS was treated in high temperature water or methanol by using a 10 ml tubing bomb reactor.

2. Experimental

2.1. Materials

PPS was supplied kindly from Japanese Chemical Company and used after pulverizing.

The elemental composition of the PPS was found to be carbon 66.6%, hydrogen 3.8%, nitrogen 0.1% and sulfur 28.8%. Their values are similar to the theoretical composition of carbon 66.6%, hydrogen 3.7%, nitrogen 0.0% and sulfur 29.6%.

Methanol from Yamaichi Chemical Industries was used after distillation. Model compounds of PPS such as thioanisole from Thermo Fisher Scientific, thiophenol from Kanto Chemical Co. Inc.,

* Corresponding author. Tel.: +81 238 26 3115; fax: +81 238 26 3413.
E-mail address: tagaya@yz.yamagata-u.ac.jp (H. Tagaya).

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and diphenyl sulfide from Wako Pure Chemical Industries were used as received without purification. Diphenyl from Tokyo Chemical Industry was used as the standard in GC quantitative determination. Sodium carbonate from Kanto Chemical Co. Inc., was used as the basic additive.

2.2. Decomposition reaction

Decomposition reactions in high temperature fluids were carried out by using 10 ml tubing bomb reactor with or without additive such as Na_2CO_3. Typically, 0.08 g of PPS powder and 1 ml solvent were introduced in the tubing bomb reactor and heated by IR Image Furnace which was pre-heated at the reaction temperature. The reaction was carried out at 280–430 °C for assigning reaction time. After the reaction, the reactor was cooled immediately by ice bath.

2.3. Characterization

After the filtration, obtained solid residue was dried, and analyzed by TG and SEM. The liquid product was extracted with organic solvents and identified by mass spectrometer (GC/MS, Shimadzu QP5000), and quantified by gas chromatography (GC, Shimadzu GC-14A equipped with a flame ionization detector (FID) and a Silicone SE-30 50 m column). Thermal Analyses (TG, DTG and DTA) up to 1000 °C were carried out at a heating rate of 10 °C/min in a flow of nitrogen using a Seiko SSC 6200 apparatus.

3. Results and discussion

3.1. Thermal properties of PPS

PPS is thermally stable and weight loss of PPS has started at 450 °C as shown in Fig. 1 although the residue reached to 37% even by the thermal treatment at 1000 °C. It suggested the occurrence of carbonization reaction. The amount of the recovered residue was similar to those reported [7] in which the residues taken at 800 °C from TG experiments under nitrogen of PPS were 37 and 42%.

3.2. The reaction of PPS in water

In the reaction of PPS in water alone, no conversion was attained by the treatment at 350 °C for 2 h as shown in Fig. 2. However, in the reactions at over 400 °C, conversions reached to more than 35%. The positive effects of the addition of basic compound on the conversion were observed. It indicates the presence of the ionic process through the decomposition reaction.

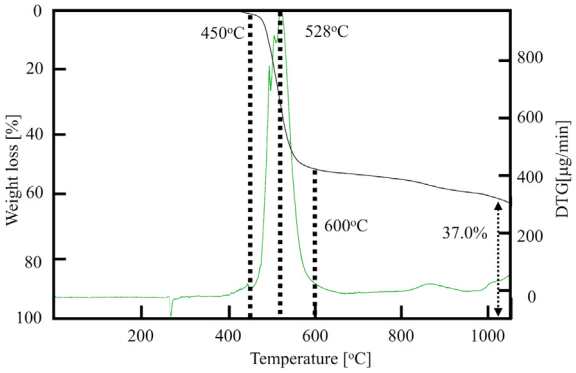

Fig. 1. Thermal characteristics of PPS resin.

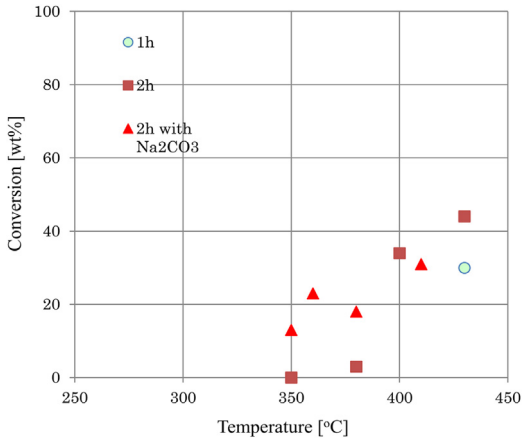

Fig. 2. Conversion of PPS resin in the reaction in water with or without Na_2CO_3.

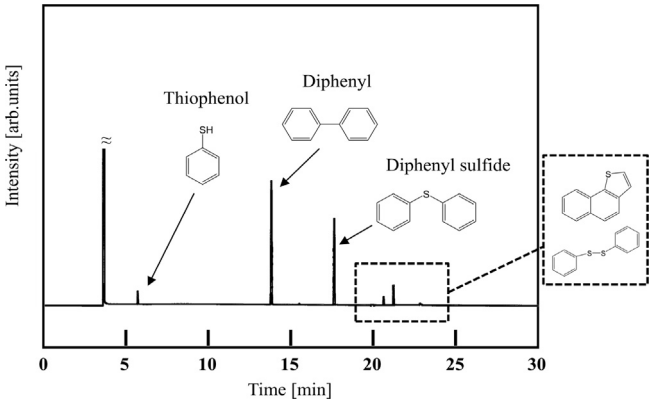

Fig. 3. GC spectrum of the reaction product obtained by the reaction of PPS resin in water at 430 °C for 2 h.

Ether soluble compounds were analyzed by GC and GC/MS as shown in Fig. 3. It shows the production of thiophenol and diphenyl sulfide in the reaction at over 430 °C. Yields of these monomeric materials were shown in Fig. 4. By the addition of Na_2CO_3, the yield of diphenyl sulfide reached more than 10% in the reaction at 430 °C for 2 h. High temperature water with the basic compound was effective for the reaction of PPS, however the perfect dissolution in organic solvent could not be attained.

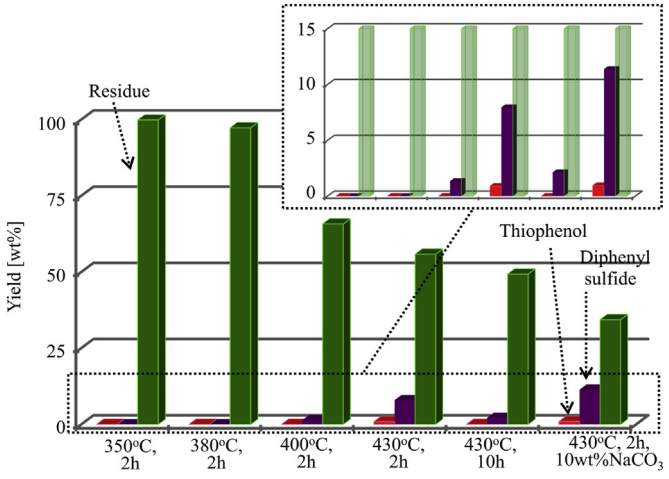

Fig. 4. Reaction of PPS resin in water at 350 °C to 430 °C.