Thermal Stability of Bisphenol A in Sub-critical Ethanol and Methanol

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Abstract: The experiments on thermal stability of bisphenol A (BPA) with or without catalyst in sub-critical ethanol and methanol were carried out in autoclaves. The influence of experimental conditions such as temperature (150~270), pressure (2.1~9.4 MPa), reaction time (15 min), and ethanol/methanol to BPA ratio (8.0), was investigated, and the reaction products were determined by a gas chromatography coupled with a mass spectrometer. It was found that the thermal stability of BPA in sub-critical ethanol was higher than that in sub-critical methanol at the same reaction conditions, and the presence of NaOH, a catalyst used for the depolymerization of polycarbonate (PC), would decrease the stability of BPA. The results obtained enhance our ability for the selection of the optimum medium as well as the operational parameters for the depolymerization of PC.

Keywords: bisphenol A; sub-critical; thermal stability; methanol; ethanol

The chemical recycling of polymer waste has been gaining great attention in recent years as a means of obtaining valuable products from waste plastics and protecting environment [1-6]. Many existing studies focus mainly on depolymerization of polycarbonate (PC) in sub- and supercritical fluids [7-10]. Pan et al. [11] focused on the depolymerization of PC in sub- and supercritical toluene. Huang et al. [12] found that polymer degradation and the activation energy for the random scission of PC in the supercritical methanol was 97.2 kJ/mol. Hargenaars et al. [13] found that PC made by melt-transesterification underwent fast redistribution, and led to post-condensation in open systems and strong changes of molecular weight distributions (MWDs) for fractions. By depolymerization in sub- or supercritical fluids, PC can be depolymerized to bis phenol A (BPA), which is an important organic industrial chemical material mainly used to produce PC and epoxy resin.

For the sake of recycling, the valuable depolymerization products should be stable in the sub- or supercritical fluids. But few papers investigated the stability of PC depolymerization product, BPA, in sub- and supercritical fluid, although its stability is an important concern. The process could not be suitable to commercial use if the product is not stable.

In this experiment, the stabilities of BPA in sub-critical ethanol and methanol with or without the depolymerization catalyst (NaOH) were investigated. The results obtained enhance our ability for the selection of the optimum medium as well as the operational parameters for the depolymerization of PC.

1 EXPERIMENTS

The BPA used here was produced in Sinopharm Chemical Reagent Co., Ltd., the methanol was provided by Quzhou Juhua Reagent Co., Ltd., and the NaOH was bought form Hangzhou Xiaoshan Chemical Reagent Co., Ltd.

The experiment was carried out in a 0.5 L autoclave, which was equipped with a constant rotating stirrer. The BPA and ethanol/methanol were loaded into the autoclave with a ratio of 1:8 (20 g/160 ml) together with 1.0g of NaOH. The autoclave was heated in a heating collar to the reaction temperature at 3 ℃/min, and the temperatures were controlled by an XMT controller. After reaching the specified reaction temperature, the autoclave was removed from the heating collar and cooled quickly[specify how]. The products weres removed for analyses.

The residuals of BPA in sub-critical ethanol and methanol were separated and analyzed by gas chromatograph with flame ionization detector (GC-FID). The fluid products were analyzed by gas chromatography-mass spectrometry (GC-MS) qualitatively and gas chromatography quantitatively.

The stability is defined by the recovery of BPA during reaction in sub-critical medium. Recovery of BPA was defined by:

$$\text{Recovery}(\%) = \frac{\text{Weight of BPA remained after reaction}}{\text{Weight of BPA feed}}$$

2 RESULTS AND DISCUSSION

2.1 Degradation products

A typical GC analysis result of degradation products obtained in sub-critical ethanol was shown in Figure 1 and the MS-pattern of BPA in Figure 2. These figuresshow that there are three main compounds, including phenol (peak 1), p-isopropylphenol (peak 2), and 1,2,4,5-tetramethyl-benzene (peak 3). The peak 4 refers to the residual bisphenol A. The products in sub-critical methanol was almost the same as those in sub-critical methanol [something is wrong here!]and the components produced in the depolymerization with and without the presence of NaOH catalyst were also almost the same. Our results show that ethanol and methanol were only serving as the solvents and they were not reactants.

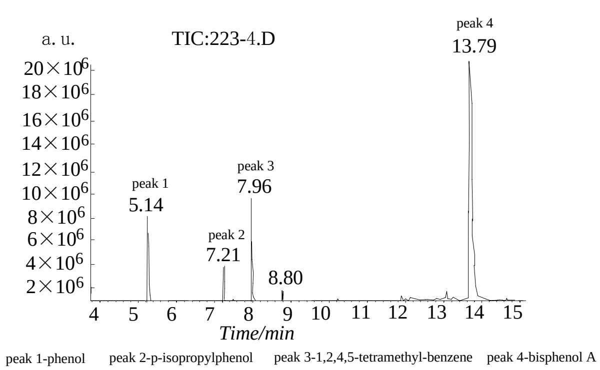

Fig. 1 GC of products in supercritical ethanol without NaOH

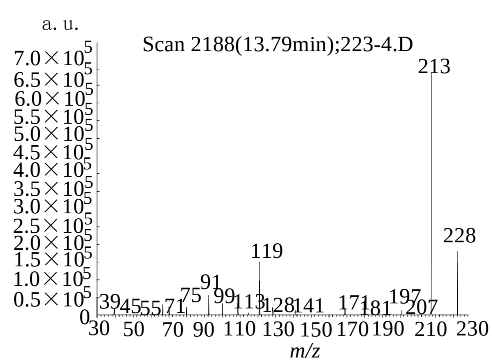

Fig. 2 MS pattern of recovered BPA

2.2 Thermal stability of bisphenol A in sub-critical ethanol

The effect of temperature on the thermal stability of BPA in sub-critical ethanol was depicted in Figure 3. It can be found that the thermal stability of BPA decreased as the reaction temperature increased, and the degradation rate was accelerated by the presence of NaOH. Without NaOH, the recoveries of BPA were 98.9% at 150 , 91.5% at 210 , and 69.6% at 270 . However, with the presence of NaOH, the recovery of BPA at 150 , 210 and 250 were 98.7%, 28.8% and 6.9%, respectively. Our results show that BPA was not stable in sub-critical ethanol at temperatures higher than 210 , and the recovery difference between the experiments with and without NaOH was up to 62.7% at 210 , indicating that the presence of NaOH reduced the stabilityof BPA substantially.

2.3 Thermal stability of bisphenol A in sub-critical methanol

The effect of temperature on the thermal stability of BPA in sub-critical methanol was shown in Figure 4. The thermal stability of BPA decreased as the reaction temperature increased, and the depolymerization rate was increased by the addition of NaOH. Without NaOH, the recovery of BPA is 93.5% at 150 , 72.8% at 210 , and 27.0% at 250 . On the other hand, in the presence of NaOH, the recovery of BPA at 150 , 210 , 250 were 75.3%, 22.1% and 2.5%, respectively. The recovery difference between experiments with and without NaOH was up to 50.7% at 210 , indicating that the stability of BPA in sub-critical methanol was affected by the presence of NaOH.

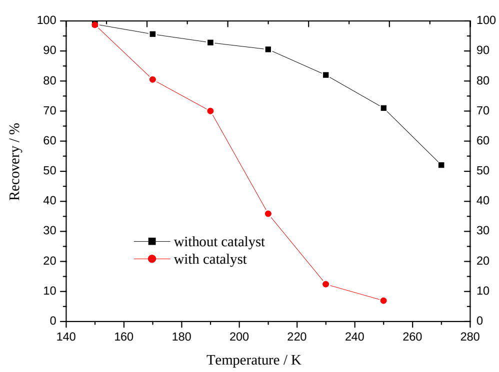

Fig. 3 Stability of BPA in sub-critical ethanol

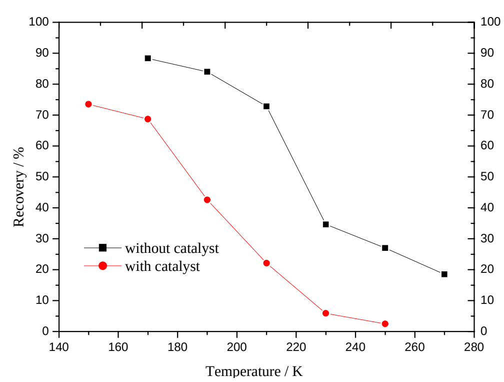

Fig. 4 Stability of BPA in sub-critical methanol

3 CONCLUSIONS

1) The thermal stability of BPA in sub-critical ethanol/methanol decreased as temperature increased with or without the presence of NaOH, which was used as a catalyst in the depolymerization of polycarbonate.

2) BPA was more stable in sub-critical ethanol than that in sub-critical methanol at the same reaction conditions.

3) The presence of NaOH decreases the thermal stability of BPA; the maximum difference of the thermal stability at 210 between experiments with and without NaOH was 62.7% in ethanol and 50.7% in methanol.

Acknowledgments

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