Hydrolysis Degradation of Polycarbonate Using Different Co-solvent Under Microwave Irradiation

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Abstract

Hydrolysis degradation of polycarbonate (PC) is one of the important chemical methods in environment. In this project PC degraded using microwave irradiation. The reaction was carried out by using various concentration of NaOH as catalyst, different amount of water as main solvent and constant amount of different kind of co-solvent (tetrahydrofuran and 1,4-dioxane) to compare the effect of them on yield of bisphenol A. The solid product (BPA) as a main monomer of polycarbonate analyzed by Fourier Transforms Infrared Spectroscopy (FTIR). The highest yield of BPA (94 %) was achieved during 12.5 min at 110 °C when using 3.5 g water as main solvent and 0.5 g NaOH as catalyst and 20 g tetrahydrofuran as co-solvent.

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1. Introduction

Polycarbonate is an important thermoplastic material among other polymers and has significant properties such as good stability, excellent flexibility and good transparency [1]. Increasing of waste polycarbonate specially to form of plastics and CDs, it is necessary to decompose it with suitable methods [2]. One of the important techniques for degradation of polymers is chemical recycling. Chemical recycling process for polymers and plastics are mainly divided into glycolysis, methanolysis, aminolysis and hydrolysis [3]. Process of conventional chemical recycling was done usually at high pressure and temperature during long time

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processing [4]. Fu-sheng et al. [5] investigate the hydrolysis degradation of PC under moderate condition to achieve pure BPA. The hydrolysis degradation of polycarbonate was done by using 1, 4-dioxane, tetrahydrofuran and N-methyl-2-pyrrolidone as co-solvent and also water as a main solvent. Using of different types of co-solvent has significant effect on yield of BPA. The yield of BPA was 70 and 68% respectively when using tetrahydrofuran (THF) and 1, 4-dioxane as co-solvent. Depolymerization of PC was done by using supercritical water and used methanol as solvent and BPA was achieved as a main monomer. BPA yields has reached to 90-93% [6]. The methanolysis of polycarbonate was carried out by CH3OH (methanol) without any solvent, the reaction time was 2 hours and the yields of BPA and DMC were not achieved. However, by using solvent such as 1, 4-dioxine, 1, 2-dichloroethane, N-methyl-2-pyrrolidone or tetrahydrofuran, the yield of monomers increased rapidly. According to their study yield of bisphenol A (BPA) reached to 78% in the present of THF as a solvent however this value increased up to 79% at the present of 1, 4-dioxane as the solvent [7]. In this project, the hydrolysis degradation of polycarbonate by using different types of co-solvent under microwave irradiation is studied. The aim of this work was compared between co-solvent to achieve the highest yield of BPA.

2. Experiment

2.1. Materials and Methods

Material which are used in experiments were pure pellet polycarbonate (PC), tetrahydrofuran and 1, 4-dioxane as co-solvent as co-solvent, sodium hydroxide as catalyst and water as main solvent. The degradation process was carried out in a Pensonic grill microwave. Small pellet of PC (5 g) were mixed with different amount of water (2, 3.5 and 5 g) and different concentration of NaOH (0.25, 0.5 and 0.75) with constant amount of co-solvent (tetrahydrofuran and 1, 4-dioxane) in PTFE mould during different time processing (10, 12.5 and 15 min). After taking out PTFE mould from the microwave, the product was filtered to separate unreacted PC from liquid phase material. The liquid phase was then distillate by distillation technique at 100°C. Equation 1 shows the reaction mechanism for hydrolysis degradation of polycarbonate to bisphenol A.

\[
\text{H}_2\text{O, NaOH, THF or 1, 4-dioxane} \rightarrow \text{PC} \rightarrow \text{BPA} + \text{CO}_2
\]

3. Design of Experiment (DOE)

In this study we used the DOE software to limit the number of samples and decrease the time of experiment and also save the materials which are used during process.

4. Results and Discussion

Table 1 shows the samples which DOE determined to achieve highest yield of BPA. Comparison between different co-solvent which is used in these experiments shows that effect of tetrahydrofuran (THF) on yield of BPA was more than 1, 4-dioxane to achieve the highest yield of BPA. Polycarbonate is polar molecules so the polar co-solvent should be used for it. Polarity of THF is more than 1, 4-dioxane because of the symmetric structure of 1, 4-dioxane in comparison with THF so leads to decrease the solubility of polycarbonate by using 1,4-dioxane. Fusheng et al. [5] have similar results of comparison between these two co-solvent as showed in table 2 when they used 5 g PC, 1.0 g NaOH and 4.9 g H2O during 8 hours time processing at 65°C.

Table 1. Comparison of different types of co-solvent on the yield of BPA
According to the table the type of co-solvent can affect the yield of BPA. The yields of BPA were as high as 94 % and 85 % by using tetrahydrofuran and 1, 4-dioxane as co-solvent, respectively. The analysis of BPA was be carried out on Perkin-Elmer (1600 series) FTIR spectrophotometer in the range of 400-4000 cm⁻¹, using kalium bromide (KBr) powder contacting 1 wt % of sample. Figure 1 and 2 shows the FTIR spectrum of obtained BPA product when using THF and 1,4-dioxane as co-solvent respectively.

Table 2. Effect of solvent on hydrolysis degradation of polycarbonate

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Solvents dosage (g)</th>
<th>Yield of BPA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>15</td>
<td>-----------</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>DMF</td>
<td>15</td>
<td>66</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>15</td>
<td>68</td>
</tr>
</tbody>
</table>
According to the figures a broad peaks observed at 3347.90 cm\(^{-1}\) and 3355.50 cm\(^{-1}\) are related to O – H cm\(^{-1}\) phenol group. The peak of C – H cm\(^{-1}\)can be found at 2965.10 cm\(^{-1}\) and 2964.76 cm\(^{-1}\) which are little and near to O – H cm\(^{-1}\)group. The approximate value of both graphs peaks are too close to each other which determine the applicability of both THF and 1, 4-dioxane as a co-solvent in hydrolysis degradation of PC. Furthermore the significant similarities between the existing peaks in above graphs (1611.69, 1598.6, 1509.1, 1362.7 1238.20, 1177.3, 827.06 and 552.35 cm\(^{-1}\)) with those of standard BPA in literatures, shows the successful process of degradation of PC to BPA as its main monomer.

5. Conclusion

Hydrolysis degradation of polycarbonate by using different kinds of co-solvent was carried out under microwave irradiation. The highest yield of BPA (94 %) was achieved by using 20 g THF as co-solvent, 3.5 g H2O as main solvent and 0.5 g NaOH as catalyst during 12.5 min. the other co-solvent which was used for depolymerization of PC was 1, 4-dioxane to give 85 % yield of BPA during similar condition with the process using THF. The obtained results show that in the same experimental condition using THF as a co-solvent lead to increase the yield of BPA in compare with 1,4-dioxane.

References


