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Study on Degradation of Polycarbonate Resin by Glycolysis in Microwave Reactor

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Abstract

In this study, glycolysis process of polycarbonate (PC) resin was researched to recovery Bisphenol-A (BPA) by using Glycerol. The microwave reactor was used to decrease the reaction time. The sodium and potassium hydroxide with different concentrations were carried out for the evaluation of PC conversion and BPA yield. The result showed clearly high efficiency of using microwave on comparison with normal process, with the conversion of PC and yield of BPA reached 100% and 95% respectively within only 5 minutes. This result has shown the application ability of BPA recycling from waste of PC in electronic, medical and transportation vehicle waste.

Keywords: Polycarbonate; Waste Recycling, Bisphenol A, depolymerization

1. Introduction

Polycarbonate resins are widely used in many fields such as electronics, medical, automotive, protection, etc. [8, 9]. Optical disks are one of the most common types of electronic waste today with over 95% is polycarbonate resin. The three different routes for PC recycling are: direct recycle (mechanical recycling or blending with other materials), treatment via chemical methods and thermochemical methods (pyrolysis) [8].

Recently studies on the conversion of polycarbonate wastes into valuable raw materials have been published to show that polycarbonate can completely convert to bisphenol a monomer [9]. Oku et al. showed monomer recycling of PC resin into biphenyl-A using liquid solvents, such as DMI (1, 3-dimethyl-imidazolidin-2-one). This method was unique and proceeded with very high conversion of almost 100% of the original polymer at the reaction temperature lower than 100oC [9]. In other hand, glycerol and methanol, EG, etc. has been suggested as a glycolysis and alcoholysis used to depolymerization of PC to recover BPA. However, most of publishes must be required high temperature, high pressure and long-time reaction due to increase the dissolve of PC into the solvents [4, 10, 11].

Additionally, the base catalyst has been used for almost of the depolymerization reaction for recovery of the BPA and other valuable by-products [2, 12]. Hu et al. studied using alkali catalyst for methanolysis in methanol and toluene solvents to recovery more than 96% BPA. Tagaya et al. [5] has been investigated Na2CO3 catalysed depolymerization of PC waster by glycolysis in subcritical and supercritical water at 300oC for 10h. The phenol yield reached more than 30%.

The aim of this study was to evaluate the conversion of polycarbonate resin using microwave energy to minimize reaction time. Several catalyst concentrations were used together with several reaction times to investigate the maximize conversion in a short reaction time.

The results showed that the polycarbonate resin was able to completely conversion with alkaline catalyst in approximately 5 minutes in reaction.

2. Experimental

2.1 Materials

- Polycarbonate was obtained from Dow Chemical's virgin polycarbonate resin.

- All of chemical reagents, which were Glycerol, BPA, NaOH, ethanol, n-hexane, and toluene, were purchased from Sigma-Aldrich.

- Deionized water was obtained from Barnstead, Easy pure II instrument.

2.2. Instrument

The reaction was performed in teflon vessel (inner volume 100ml). The vessel that was contained sample (mixed of PC/Glycerol/H2O/base catalyst with different ratios) was putted in microwave MARS CEM 5 accelerated reaction system. The time and temperature of reaction was controlled for each sample with fixed 500W duty.

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The product after reaction was re-crystalled, filtered by cold water at 4oC and dried at 100oC in 3h.

Crystal sample were pressed with KBr and structure determined by FTIR 6700, wavenumber range from 3500 to 400cm-1, Thermo. Electro.

The filtered liquid phase after was extracted by toluene (with ratio of toluene/solution was 2/1) and analysed by GC, FID, Thermo. Trace GC.

The GC condition was injector SSL, TR5 column, 30m x 0,35mm x 0,25µm. Injector temperature: 200oC; detector: 275oC; temperature programmed column: 120oC hold 1 min, 220oC, ramp rate 10oC/min, 220oC hold 1 min.

Dissolve samples in CH2Cl2 for NMR analysis on 500 MHz NMR-DRX equipment, Bruker.

Conversion of PC and yield of BPA were calculated by the following formula:

Conversion of PC = (Wi−Wl)/Wi×100% (For. 1)

Yield of BPA = (WBPA/Wi)(MPC/ MBPA)×100% (For. 2)

Where:

- Wi, Wl are initial and remaining weight of PC,
- WBPA is weight of BPA recovery.
- MPC and MBPA are the molar masses of the repeating unit of PC and BPA.

3. Results and Discussion

3.1. Influence of reaction time

All of the reaction, the ratio of PC/Glycerol/H2O was fixed at 1/5/0.5. NaOH was used in 2% wt. base on all reactants.

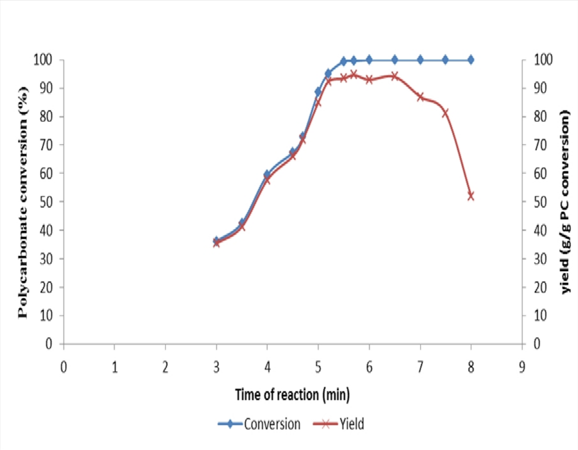

Fig. 1. Influence of reaction time on the degradation of PC in microwave reactor at 160^{o}C, 500W duty

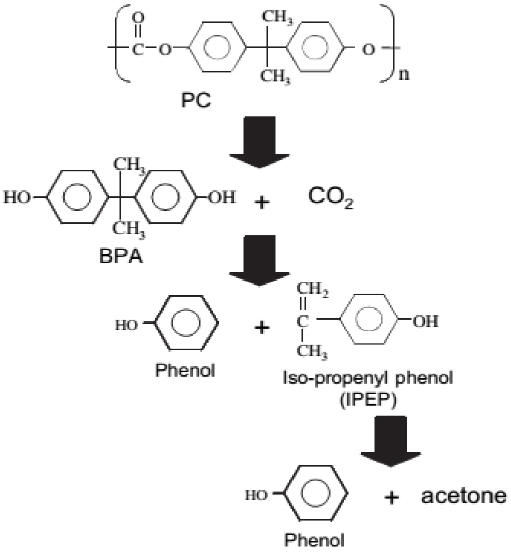

Fig. 2. Reaction scheme of PC and BPA conversions [4]

Table 1. BPA Monomer's recovery from different chemical recycling methods of PC

Recovery rate of monomer (max) (% BPA)	Time of reaction (min) (minutes)	Reaction condition	Reference
95.0	120	in autoclave with a stirrer at 90^{o}C	Liu, F. et al. [1]
90.0	70	75–180^{o}C and pressures from 2 to 25 MPa	Pinero et al. [2]
100	45		Mohammad et al [13]
80.0	10	saturated pressure of water at 573 K	Watanabe et al. [4]
97.0	600	subcritical and supercritical water	Tagaya et al. [5]
40	30	in autoclave at temperatures from 533 to 613 K	Huang et al. [6]
100	10	180^{o}C and atmospheric pressure	Oku. et al. [9]
100	5	in microwave reactor, 500W duty, 160 ^{o}C	This study

The percentage recovery of BPA from the aforementioned chemical recycling methods presented by different authors is summarized in Table1. In most of the studies were referred in Table 1, for conversion up to 100%, the reaction time usually exceeds 30 minutes in high pressure condition. Results in table 1 of experiments showed that when using microwave energy, the rate of reaction was rapidly increased compare to similar research from other group. In Fig.1, the research result also was showed that the conversion and yield BPA recovery was reached 100% and 95% at 5.5 min of reaction, respectively. After that, the BPA's yield was rapidly decreased when the reaction time was prolonged. Reaction scheme of PC and BPA conversions in Fig. 2 were suggested relationship between these reaction products, and indicated that BPA was intermediate product and decomposed into other substances. In high pressure high temperature water, BPA is known to decompose into phenol and iso-propenyl phenol (IPEP) at the first stage of the reaction, and subsequently, IPEP decomposes into acetone and phenol. In case of the study, determination of phenol and IPEP products by gas chromatography in the extracted samples was also proved for degradation of BPA to phenol and IPEP.

In addition to investigating the effect of catalyst concentration on degradation of PC in microwave reactor, the PC conversion and yield of BPA was evaluated. Fig. 4 shows that 2% by weight was optimized concentration of NaOH catalyst which was converted 100% PC and 96% of BPA yield. Additionally, that result was showed which alkali catalysts also was promoted for BPA decompose reaction when yield BPA decreased when catalyst concentration increased more than 2%.

In case of KOH catalyst that showed in Fig. 5, the BPA yield was down quickly than NaOH catalyst. It was proved that KOH more active than NaOH for BPA decompose to by-products. This suggests that a high base catalyst concentration also assists the mechanism of reaction where the BPA converts to by-products.

The results above were fully matching with the research of Pinero [2] group. They investigated the alkali-catalysed depolymerization process of PC wastes by alcoholysis in supercritical or near critical conditions, for recovery of the monomer BPA and dimethyl carbonate (DMC) as a valuable by-product using methanol as solvent/reagent and NaOH as alkali catalyst.

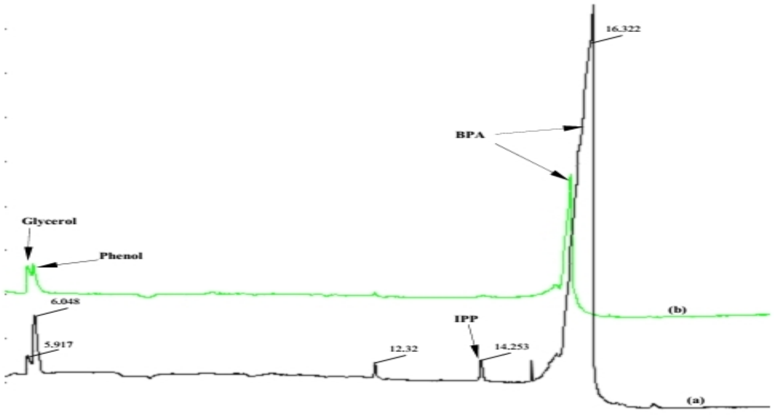

Fig. 3. GC analysis result of BPA samples.
a) Purified BPA solid sample diluted in ethanol, 2% wt/ml. b) Sample of toluene extraction

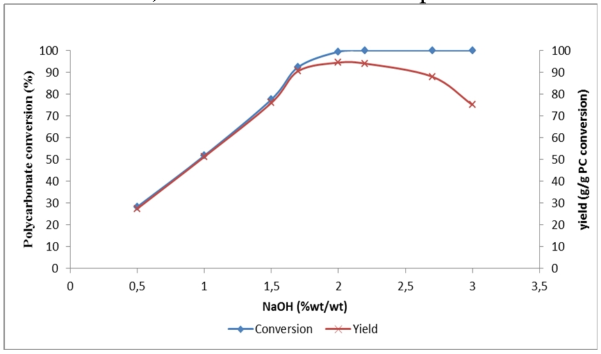

Fig. 4. Influence of NaOH catalyst concentration on the degradation of PC in microwave reactor at 160°C, 500W duty, time of reaction: 5.5 minute.

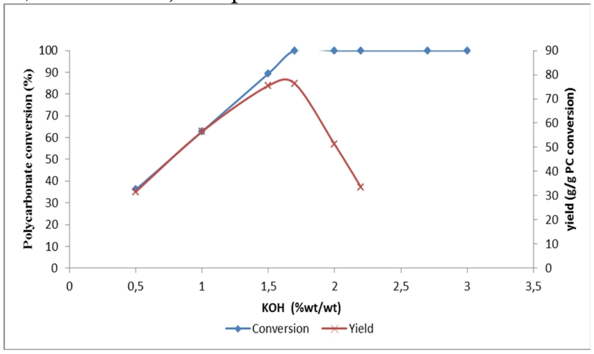

Fig. 5. Influence of KOH catalyst concentration on the degradation of PC in microwave reactor at 160°C, 500W duty, time of reaction: 5.5 minute.

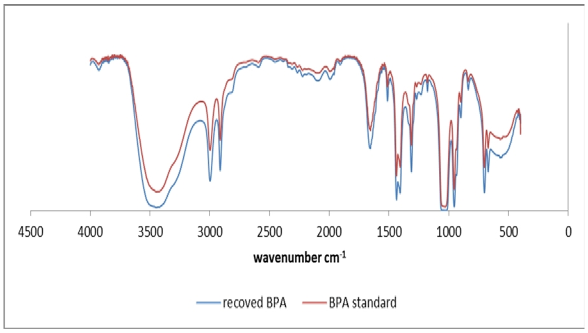

Fig. 6. FTIR result of both standard pure bisphenol A and the crystallized product obtained from the PCs recycling.

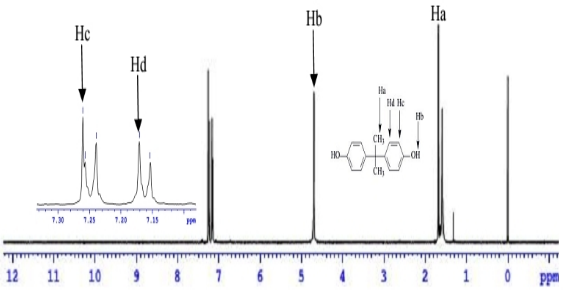

Fig. 7. ^{1}H NMR spectrum of recovered BPA from PC.

Separation and purification of bisphenol A was achieved by crystallization, further filtration and drying. The structure of the final BPA crystals was verified quality by FTIR, NMR and the quantitative of the BPA crystal was also assessed by GC compare with standard sample that collected from Sigma-Aldrich code 1002273681. The 1HNMR spectrum of recovered BPA is presented in Fig. 7. The peak at 1.6 ppm corresponds to methyl hydrogen, the peak at 4.7 ppm is relative to hydroxyl groups and the peaks at 7.0-7.2 ppm correspond to aromatic hydrogen's [13]. All 1HNMR data was similar to data from a commercial sample that reveals successful recovering at this proposed experimental conditions.

4. Conclusion

Polycarbonate degradation by glycolysis was carried out in microwave reactor. Conversion of PC and yield of BPA was reached 100% and 95%, respectively. The research also was showed that BPA will decompose to by-products when reaction time was too long or catalysis activity was too strong. Polycarbonate degradation by glycolysis was carried out in microwave reactor. Conversion of PC and yield of BPA was reached 100% and 95%, respectively. The research also showed that BPA can be decomposed to by-products when reaction time was too long or catalysis activity was too strong.

Experimental results in microwave condition indicate that the alkali-catalysed glycolysis of PC can be considered as a green process, it allows the essential raw material to be recovered for the environmentally friendly manufacturing of PC and also minimized time and energy for treatment.

Acknowledgement

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References

[1]. Liu, F., Li, L., Yu, S., Lv, Z., Ge, X.: Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]. J. Hazard. Mater. 189, 249–254 (2011)

[2]. Pinero, R., Garcia, J., Cocero, M.J.: Chemical recycling of polycarbonate in a semi-continuous lab-plant: a green route with methanol and methanol-water mixtures. J. Green Chem. 7, 380–387 (2005)

[3]. Sato, Y., Kondo, Y., Tsujita, K., Kawai, N.: Degradation behavior and recovery of bisphenol-A from epoxy resin and polycarbonate resin by liquid-phase chemical recycling. J. Polym. Degrad. Stab., 89, 317–326 (2005)

[4]. Watanabe, M., Matsuo, Y.,Matsushita, T., Inomata, H., Miyake,T., Hironaka, K.: Chemical recycling of polycarbonate in high pressure high temperature steam at 573 K. J. Polym. Degrad. Stab., 94, 2157–2162 (2009)

[5]. Tagaya, H., Katoh, K., Kadokawa, J., Chiba, K.: Decomposition of polycarbonate in subcritical and supercritical water. J. Polym. Degrad.Stab., 64, 289–292 (1999)

[6]. Huang, Y., Liu, S., Pan, Z.: Effects of plastic additives on depolymerization of polycarbonate in sub-critical water. J. Polym. Degrad. Stab., 96, 1405–1410 (2011)

[7]. Hu, L.C., Oku, A., Yamada, E.: Alkali- catalysed methanolysis of polycarbonate. A study on recycling of bisphenol A and dimethyl carbonate. J. Polymer, 39, 3841–3845 (1998)

[8]. E. V. Antonakou, D. S. Achilias. Recent Advances in Polycarbonate Recycling: A Review of Degradation Methods and Their Mechanisms. J. Waste Biomass Valor (2013) 4:9–21

[9]. A. Oku, S. Tanaka, S. Hata. Chemical conversion of poly (carbonate) to bis (hydroxyethyl) ether of bisphenol A. An approach to the chemical recycling of plastic wastes as monomers. J. Polymer 41 (2000) 6749–6753

[10]. Kim, D., Kim, B.K., Cho, Y., Han, M., Kim, B.S.: Kinetics of Polycarbonate Methanolysis by a Consecutive Reaction Model. J. Ind. Eng. Chem. Res. 48, 6591–6599 (2009)

[11]. Chen, L., Wu, Y., Ni, Y., Huang, K., Zhu, Z.: Degradation kinetics of polycarbonate in supercritical methanol. J. Chem. Ind. Eng., 55, 1787–1792 (2004)

[12]. Jie, H., Ke, H., Qing, Z., Lei, C., Yongqiang, W., Zibin, Z.: Study on depolymerization of polycarbonate in supercritical ethanol. J. Polym. Degrad. Stab. 91(10), 2307–2314 (2006).

[13]. Mir Mohammad Alavi Nikje, Mohammad Askarzadeh. Chemical recycling of polycarbonate wastes into bisphenol A by using green solvent composition. J. Polimery 292-294, 2013, 58, nr4