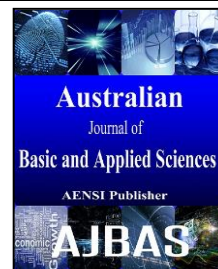




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Synthesis of poly(propylene carbonate) using biobased epoxide by the terpolymerization reaction catalyzed by Co-Zn double metal cyanide

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ABSTRACT

Background: The most common epoxides used for copolymerization with carbon dioxide (CO₂) are propylene oxide (PO) and cyclohexene oxide. However, given that the commercial productions of these epoxides are highly dependent on finite resources and the volatility of the commodity price, these have triggered great interest in finding an epoxide alternative from renewable resources. Epoxide which is derived from natural resources such as plant oils have currently become a potential candidate for the production of epoxy-based polymers. Apart from being renewable, they are abundantly available and possess excellent environmental credentials (i.e. inherent biodegradability). **Objective:** The feasibility to terpolymerize mixture of PO and epoxidized soybean oil (ESO) with CO₂ to produce polycarbonate was studied. **Method:** The terpolymerization reaction was performed in the presence of heterogeneous catalyst namely Co-Zn Double Metal Cyanide and at fixed CO₂ pressure of 40 bars. The terpolymerization conditions such as reaction temperature and reaction time were varied accordingly. **Results:** Polymer with an average molecular weight (M_n) of 6498 kg/mol and yield of 72% was obtained at reaction temperature and reaction time of 80°C and 6h respectively. FTIR and ¹H NMR spectroscopy analysis revealed the formation of poly(propylene carbonate) in the products produced together with ether unit and cyclic carbonate. **Conclusion:** The results obtained indicate the viability to synthesized renewable polymeric material from the natural epoxide specifically ESO.

INTRODUCTION

The exploration for bio-based products from agricultural resources has become a subject of interest among researchers and academia owing to the growing concern by the public on environmental issues pertaining to global warming and waste disposal. Moreover, the volatility of crude oil prices during the last decade as well as the progressive depletion of the oil reserve further stimulate the demand to use renewable counterparts in replacement of traditionally fossil based products. For instance, synthesis of bio-based material such as polymer from renewable feedstock will help to minimize the reliance on fossil fuel based feedstock predominantly petroleum. In this context, utilization of vegetable oil offers several advantageous given the fact that they are renewable, available in large quantities and also less expensive (Liu *et al.*, 2015).

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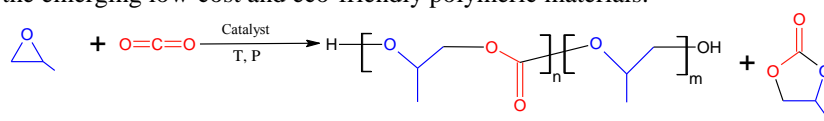


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Triglycerides which are the product of esterification of glycerol with three fatty acids are the major constituents of vegetable oils and the compositions of fatty acids chain vary depending on the source of vegetable oils (Meier *et al.*, 2007; Miao *et al.*, 2014). There are two main criteria in determining the physical and chemical properties of vegetable oils which are the fatty acid chain length and the numbers and locations of double bonds in the fatty acid chains. Commonly, the length of the fatty acid chain is between C12 and C20, with most of the fatty acids having a long straight-chain with an even number of carbons. Several different reactive sites such as double bond, ester groups, hydroxyl group and epoxy group are present on these triglycerides (Miao *et al.*, 2014).

In general the carbon-carbon double bonds in the fatty acid chains of the vegetable oils have to be converted into more reactive groups such as epoxide groups, acrylate groups or hydroxyl groups prior to the application to obtain polymeric materials. Epoxides can be obtained via the epoxidation reaction whereby oxygen atom is added to a carbon-carbon double bond (olefin) to form carbon-oxygen bonds. The coupling of epoxides, reactive products per se, with carbon dioxide (CO₂) may yields aliphatic polycarbonates, ether unit and cyclic carbonates, the latter being the thermodynamic products. Scheme 1 illustrates the copolymerization reaction between a propylene oxide (PO) and CO₂. This reaction is in the direct focus of academics as well as industry primarily due to a promising range of industrial applications. Furthermore, aliphatic polycarbonates such as poly(propylene carbonate) (PPC), the alternating copolymer of PO and CO₂, becoming more attractive since it is one of the emerging low-cost and eco-friendly polymeric materials.



Scheme 1: Copolymerization of PO with CO₂

To date, considerable amount of literatures are available reporting on various types of epoxides (Darensbourg and Chung, 2014; Kim *et al.*, 2006) and catalyst used (Kember *et al.*, 2011; Klaus *et al.*, 2011) in the copolymerization reaction as well as different operating conditions (Wang *et al.*, 2006). For instance, common epoxides used in copolymerization with CO₂ are PO, cyclohexene oxide and epichlorohydrin. Table 1 gives list of copolymerization of epoxide with CO₂ at different operating conditions.

Table 1: Copolymerization of epoxide with CO₂ at different operating conditions

Starting Material	Catalyst	Product	Temp. (°C)	Pressure	Time (hr)	Yield (%) or Productivity (g Polymer/g catalyst)	M _n	Reference
PO	DMC with co-catalyst PEG	PPC	60	4 MPa	40	83.5%	13 532	Guo and Lin, 2014
CHO	Co - Zn DMC	PCHC	75	30 bar	11	52.8 g polymer/g catalyst	20 900	Sebastian and Srinivas, 2014
PO	nanolamellar Zn-Co(III) DMCC	PPC	60	5 MPa	10	6050 g polymer/g Zn	31 800	Zhang <i>et al.</i> , 2011
PO	Zinc glutarate	PPC	60	50 bar	40	74.2 g polymer/g catalyst	92 400	Zhong and Dehghani 2010
PO	Zinc glutarate	PPC	60	5 MPa	40	126 g polymer/g catalyst	56 100	Du <i>et al.</i> , 2004
PO	Co - DMC	PPC	90	4 MPa	10	60.6 kg polymer/catalyst	130 000	Li <i>et al.</i> , 2011
PO	Zinc glutarate	PPC	60	51.5 atm	40	64.54 g/g catalyst	343 000	Ri <i>et al.</i> , 2000
cis-2-butene oxide	Bifunctional cobalt (III)	PPC	70	20 bar	6	74.5%	13 900	Darensbourg and Chung, 2014
CHO	Cobalt porphyrin (TPP)CoCl	PC	80	50 atm	12	99%	14 500	Sugimoto and Kuroda, 2008
PO	with co-catalyst dimethylaminopyridine (DMAP)		40	50 atm	48	95%	14 500	

Note: CHO - cyclohexene oxide

PCHC - poly(cyclohexane carbonate)

PC - polycarbonate

To the knowledge of the authors, utilization of bio-based epoxide specifically epoxidized soybean oil (ESO) as the monomer in copolymerization with CO₂ has never been reported. Thus in this study, ESO derived from soybean oil has been chosen as one of the starting material in the polymerization reaction. Soybean oil is edible oil extracted from soybean seeds. It is a triglyceride oil composed of 11% palmitic (C16:0), 4% stearic (C18:0), 23.4% oleic (C18:1), 53.3% linoleic (C18:2), and 7.8% linolenic (C18:3) acids with an average number of 4.6 double bonds per molecule (Belgacem and Gandini, 2008; Xia and Larock, 2010).

This research is aimed to study the viability of utilizing ESO in the terpolymerization reaction with PO and CO₂ to produce polycarbonate. The effect of reaction temperature and reaction time in correlation with the yield and molecular weight of the resultants polymer were also studied.

Methodology:

Heterogeneous catalyst namely Co-Zn double metal cyanide (Co-Zn DMC) was prepared via conventional method by dissolving 80 g of ZnCl₂ in 300 mL of double distilled water and 150 mL of tert-butanol. 6.64 g of K₃Co(CN)₆ was dissolved in 100 mL of double distilled water and then was added dropwise into ZnCl₂ solution under vigorous stirring. The precipitate formed was constantly agitated and heated at 50°C for another two hours. The resulting white precipitate was separated by filtration and centrifugation and subsequently re-slurried in a mixture of tert-butanol and water (v/v=1/1). This step was repeated serially by increasing the volume ratio of tert-butanol to water (6:4, 7:3, 8:2, and 9:1, respectively). Finally, the solid was redispersed in pure tert-butanol, centrifuged, and vacuum dried until a constant weight was reached (Li *et al.*, 2011).

Polymerization took place in a 100 mL stainless steel reactor (Autoclave Engineers, Erie, PA USA) equipped with mechanical stirrer and an automatic temperature controller system. 0.1 g Co-Zn DMC was placed into the dried autoclave together with 10 mL of ESO and 10 mL of PO. The reactor was purged twice with CO₂ and then slowly pressurized to 40 bars. Next it was heated between 60°C to 100°C with a stirring speed of 500 rpm to initiate the polymerization reaction. Meanwhile the reaction time was varied ranging between 6h to 72h. After the reaction ends, the autoclave was cooled down to room temperature, slowly depressurized and opened. The products obtained were purified by dissolving in dichloromethane, precipitated by excess methanol and then dried at room temperature to a constant weight.

Spectroscopic analyses of products were performed using Fourier transform infrared spectroscopy (FT-IR) (Model: Perkin Elmer 1000) and a Bruker NMR spectrometer (Model: Bruker AMX 300) with ¹H probe and CDCl₃ as the solvent. Number average molecular weight (M_n) of polymer products was estimated using a gel permeation chromatography (GPC) system. Hexafluoroisopropanol was used as an eluent.

RESULT AND DISCUSSION

Effects of reaction temperature and reaction time on the yield and average molecular weights of resultant polymer:

Effects of reaction temperature and reaction time on yield and average molecular weights of resultant polymers were showed in Table 2. Yield was calculated as per following:

$$\text{Yield} = \frac{\text{Amount of products collected}}{\text{Amount of epoxides used}} \times 100\% \quad \dots(\text{Eq.1})$$

It was observed that as the reaction temperature increased from 60°C to 80°C, the yield increased from 62% to 82%. The yield of products then reach plateau at 90°C and 100°C. This trend was due to higher temperature molar equivalents of CO₂ in solution that has been claimed to lessen thus resulting a decreased in yield of the product. This observation is in agreement with report by Wang *et al.* (2012). The GPC analysis showed that the M_n recorded for sample prepared at reaction temperature of 60°C and 80°C are 2323 and 3834 g/mol respectively. On the other hand, the M_n for samples prepared at reaction temperature of 90°C and 100°C cannot be detected which could be due to the formation of cross-linked material. The conclusion was made based on the observation during GPC analysis was conducted, whereby these two samples were unable to dissolve in the solvent used.

The influence of reaction time on yields of resultant polymers was investigated (Table 2, entries 2, 5, 6 and 7). Under the desired conditions, 72% of yield was obtained in 6h. Prolonging reaction time beyond 6h helps to increase in yield of the resultant polymer. However at 72h the yield recorded decreased slightly. The M_n of resultant polymer recorded was the highest at reaction time of 6h with 6498 g/mol. Beyond the reaction time of 6h the M_n of the products were detected to reduce notably. This phenomenon could be explained owing to the formation of side products during the terpolymerization reaction between the mixtures of epoxides with CO₂. In general the copolymerization between epoxide and CO₂ will generate polycarbonate and side products such as cyclic carbonate and ether linkages (as shown in scheme 1). Under prolong reaction time; cyclic carbonate was

produced via back-biting pathway (Meng *et al.*, 2016) meanwhile polyether linkages were formed due to the consecutive insertion of epoxides (Klaus *et al.*, 2011). Therefore in this particular system, the formations of cyclic carbonate and ether unit have lowered the M_n of the resultant polymers.

Table 2: Effects of reaction temperature and reaction time

Entry	Reaction Temp. (°C)	Time (h)	Yield (%)	M_n	M_w
1	60	24	62	2323	4251
2	80	24	82	3834	4962
3	90	24	86	Crosslinked material	
4	100	24	86	Crosslinked material	
5	80	6	72	6498	8462
6	80	48	90	1983	5696
7	80	72	75	3541	4246

Operating conditions:

Pressure of $CO_2 = 40$ bars, Co-Zn DMC = 0.1 g, Volume of ESO = 10 mL and Volume of PO = 10 mL

1H NMR and FT-IR Measurements:

Fig. 1 shows the 1H NMR spectrum of the representative polymer synthesized at reaction temperature of 80°C and reaction time of 24h. The observed peaks were assigned as follows: 1H NMR ($CDCl_3$), δ (ppm) 1.3 (3H; $-CH_3$), 1.49 (3H; $-CH_3$), 3.5 (3H; $-CH_2CH-$), 4.02 (1H; $-OCH_2-$), 4.2 (2H; $-H_2C-$), 4.5 (1H; $-OCH_2-$), 4.9 (1H; $-CHO-$), 5.0 (1H; $-CH-$). These data reveal that the terpolymerization product contains PPC together with ether unit and cyclic carbonate (Tang *et al.*, 2013). It is also notable from the spectrum, signal of epoxy proton at δ 2.8-3.2 ppm which signifies the residue of epoxide. Thus under the conditions studied only a fraction of epoxide has been consumed during the terpolymerization process which further justify the results of M_n obtained in earlier section. Besides the methine proton $-CH_2-CH-CH_2-$ of the glycerol backbone at δ 5.1-5.3 ppm and methylene proton $-CH_2-CH-CH_2-$ of the glycerol backbone at δ 4.1-4.3 ppm are also detected which indicates triglyceride structure of ESO has not been disturbed (Zhang *et al.*, 2015). The spectrums of remaining products (figure not shown) illustrate the same peaks as shown in Fig. 1.

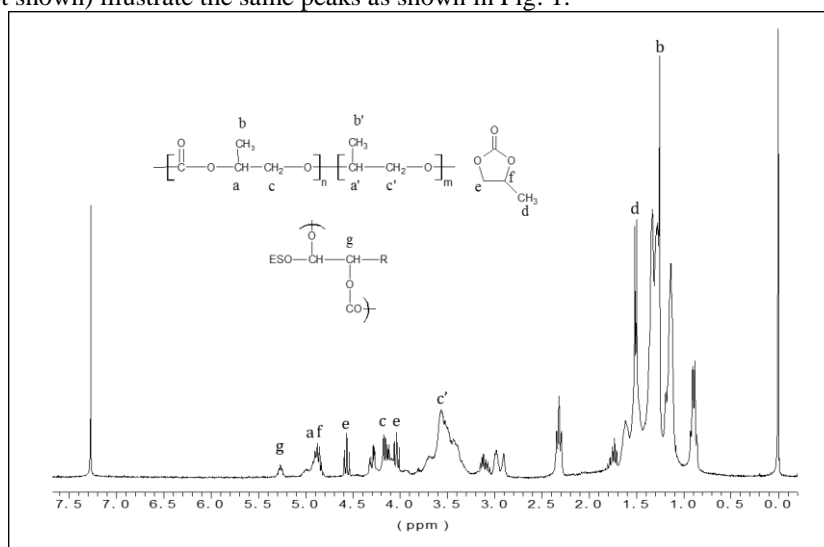


Fig. 1: 1H NMR spectra of sample prepared at $T = 80^\circ C$ and $t = 24h$ (entry no. 2 in Table 2)

To further validate the component in the terpolymerization products, the FT-IR analysis was performed. In general, the FTIR spectrum of all products prepared in this study demonstrated characteristic absorption of ester group at 1745 cm^{-1} ($C=O$). Also prominent are peaks around 1264 cm^{-1} ($C-O$) which give evidence for the presence of both carbonate and ether backbone. Last but not least is the characteristic absorption peak at 1807 cm^{-1} ($C=O$) which corresponds to cyclic carbonate was detected in the IR spectrum. The FT-IR spectrum of representative polymer synthesized at reaction temperature of 80°C and reaction time of 24h is shown in Fig. 2.

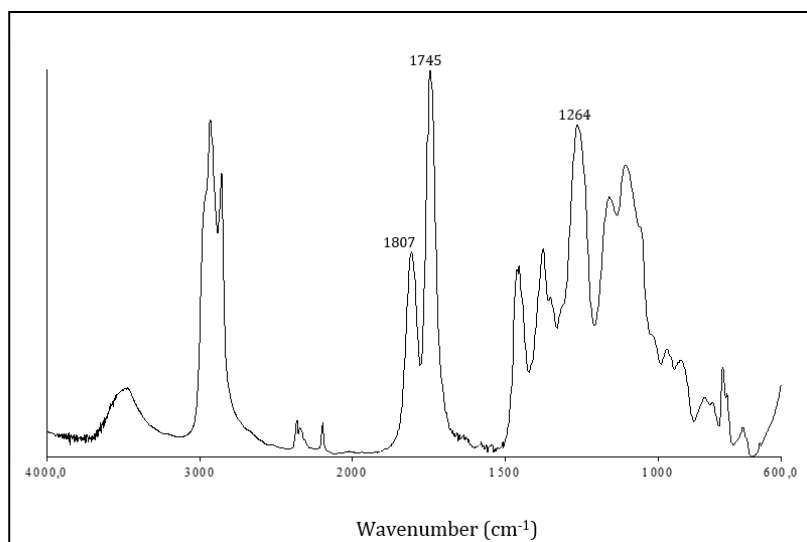


Fig. 2: FTIR spectra of sample prepared at $T = 80^{\circ}\text{C}$ and $t = 24\text{h}$ (entry no. 2 in Table 2)

Conclusion:

This study revealed the feasibility to synthesize PPC by utilizing bio-based epoxide specifically ESO. However under the conditions studied, the terpolymerization of PO, ESO and CO_2 also generate side products such as ether unit and cyclic carbonate. The presence of each component in the resultant products was verified by means of ^1H NMR and FT-IR analysis. The M_n of PPC obtained was the highest at reaction temperature and reaction time of 80°C and 6h respectively. It is also proven that both reaction temperature and reaction time affect the yield and M_n of the resultant polymer.

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