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Synthesis of vegetable-oil based polymer by terpolymerization of epoxidized soybean oil, propylene oxide and carbon dioxide

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ABSTRACT

Although carbon dioxide (CO_2) is well known as one of the major green-house gases, it is also an economical C1 resource. Thus, CO_2 has been regarded as an appealing starting material for the synthesis of polymers, like polycarbonates by the reaction with epoxides. Herein the reaction between natural epoxidized soybean oil (ESO), propylene oxide (PO) and CO_2 under high pressure (4.0 MPa) with the presence of Co-Zn double metal cyanide (Co-Zn DMC) catalyst was studied. Temperature and reaction time were varied accordingly and the products obtained were characterized by FTIR, GPC and ^{1}H NMR. The results obtained indicate the formation of polycarbonates in the samples collected with yields vary from 60 to 85%. The number average molecular weight (M_n) of the resultant polymer prepared at reaction temperature of 80 °C and reaction time of 6 h can reach up to 6498 g/mol.

1. Introduction

The rising levels of carbon dioxide (CO_2) in the atmosphere are linked to global warming and this phenomenon is becoming a pressing environmental issue. Thus continuous efforts are being made to mitigate the atmospheric CO_2 concentration via carbon capture and storage. The aforementioned technique is quite popular and received considerable attention among researchers in recent years. This technique requires CO_2 to be removed from the flue gases of large emitters such as power plant by means of membrane separation or an absorbent/adsorbent such as monoethanolamine (MEA) (Coutris et al., 2015). Following to this step, the captured CO_2 then stored in the underground reservoirs. In spite of the fact that this method has great potential in reducing the amount of CO_2 entering the atmosphere, the thought of retaining huge CO_2 reservoirs is not very appealing. In view of that, a more meaningful strategy such as utilization of CO_2 by its conversion into valuable materials and products is expected to subsidized carbon capture and sequestration processes. Furthermore the use of CO_2 as a chemical feedstock is ideal since it is abundantly available, inexpensive, non-toxic and non-hazardous (Taşcı and Ulusoy, 2012; Wang et al., 2012).

One of the popular approaches is to use CO_2 as co-monomer in polymerization reactions. In this context, the catalytic copolymerization of epoxides and CO_2 emerges as a promising technology (Sakakura et al., 2007). In the year of 1969, Inoue and coworkers have successfully synthesized poly(propylene carbonate) from propylene oxide (PO) and CO_2 by using $ZnEt_2$ and water as catalyst (Inoue et al., 1969). To date substantial amount of literatures are available revealing different types of outstanding catalyst for the copolymerization process (Ang et al., 2015; Meng et al., 2016; Trott et al., 2016) ever since their discovery. Simultaneously, a number of epoxides and diverse operating conditions for the coupling of CO_2 and epoxides have been reported by devoted researchers (Dai et al., 2016; Darensbourg and Chung, 2014; Oh and Ko, 2013; Sebastian and Srinivas, 2014; Tang et al., 2013). Despite of the countless references available in this field, very few reported on the utilization of renewable bio-resources specifically vegetable oil-based epoxide in copolymerization with CO_2.

Usage of vegetable oil-based epoxide as a starting material can be considered as an interesting strategy to enhance the green content of the polymers. Moreover, it may serve as a substitute to the traditional epoxide which is petroleum based. Owing to the heavy dependence of mankind on fossil fuels and its current consumption rates, the worldwide fossil fuel reserves are depleting rapidly (Ingrao et al., 2015). Hence, it is essential to find an alternative starting material from renewable resources since it can provide both environmental and economic sustainability.

Soybean oil, particularly, is a vegetable oil with interest in polymer since its abundant availability, reactive functionalities and competitive cost (Costa et al., 2016; Miao et al., 2014). This renewable material is composed of triglycerides, which are the major component of plant oil. Triglycerides are formed from three various fatty acid

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chains joined by a glycerol center. The major composition of fatty acid in soybean oil is linoleic acid with 53% and soybean oil has an average of 4.6 double bonds per molecule (Xia and Larock, 2010).

Polycarbonates are a class of thermoplastic polymers with carbonate linkages in their chemical structure. Commonly, they are categorized as aliphatic or aromatic polycarbonate, depending on the structure of the R groups. The general structure of polycarbonate is shown in Fig. 1. The conventional method to synthesized polycarbonate is by the reaction between Bisphenol A (BPA) and phosgene ($COCl_2$) which results an amorphous polymer with high impact strength, toughness, heat resistance and transparency. These exceptional properties made them a versatile material with substantial industrial significance. Although BPA-based polycarbonate produced excellent properties of products, on the other hand it also has some drawbacks such as the usage of highly poisonous phosgene and chlorinated solvents. Utilization of BPA itself as a monomer caused a great anxiety regarding negative health effects due to leaching out of the polymer when in contact with food (US Food and Drug Administration, 2014). Additionally both monomers used are fossil-based compounds.

From the environmental point of view, copolymerization of natural epoxides with CO_2 may lead to significant environmental impacts since they contribute to reduce the atmospheric emissions of CO_2, circumvent the use of very toxic and hazardous phosgene in the traditional route of polycarbonate production and involve the use of renewable bio-resources like vegetable oils which will lessen the dependency on the petroleum based routes of synthesis.

Therefore in the present work, an attempt was made to terpolymerize ESO, PO and CO_2 in the presence of heterogeneous catalyst namely Co-Zn Double Metal Cyanide (Co-Zn DMC). The reaction takes place at fixed CO_2 pressure of 4.0 MPa with equal volume of ESO and PO. The reaction temperature and reaction time were varied in the range of 60–100 °C and 6–72 h and respectively. Under the conditions studied, the resultant products yield a mixture of polycarbonate, cyclic carbonate and polyether.

2. Experimental

2.1. Material

ESO with approximately 4.5 oxirane rings per triglyceride (Fig. 2) obtained from Traquisa (Barbera del Valles, Barcelona Spain) was used in this research work whereas PO (> 99%) was supplied by Sigma Aldrich. Materials, such as potassium hexacyanocobatate(III) ($K_3Co(CN)_6$), zinc chloride ($ZnCl_2$), and tertiary butyl alcohol (*tert*-butanol) were used without further purification. CO_2 with a purity of 99.99% was used as received. Other solvents such as chloroform, dimethyl sulfoxide (DMSO), hexafluoroisopropanol (HFIP), methylene chloride, methanol and toluene were of analytical reagent grade and used without further purification.

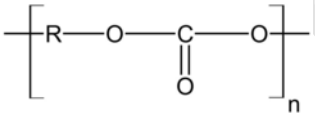


Fig. 1. General structure of polycarbonate.

2.2. Preparation of the catalyst

Co-Zn DMC catalyst was prepared in the presence of *tert*-butanol as complexing agent. The method of preparation was according to the procedure outlined by Li et al. (2011) (Li et al., 2011). Briefly, solution 1 was prepared by dissolving 6.64 g of $K_3Co(CN)_6$ in 100 mL of double distilled water meanwhile solution 2 was made by dissolving 80 g of $ZnCl_2$ in 300 mL of double distilled water and 150 mL of *tert*-butanol. Solution 1 was added dropwise to solution 2 over a period of one hour and the mixture was kept for aging at 50 °C for another two hours under vigorous stirring. The resulted white suspension was filtered and centrifuged in order to segregate the Co-Zn DMC complex. The white precipitate collected was redispersed in a solution of *tert*-butanol and water (1:1 v/v) using high speed stirring. 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 (white colour solid, yield = 3.9 g).

2.3. Polymerization of ESO, PO and CO_2

Terpolymerization was carried out in a 100 mL stainless steel reactor (Autoclave Engineers, Erie, PA USA) autoclave equipped with a mechanical stirrer and an automatic temperature controller system. The autoclave was first dried at 100 °C for at least 12 h then it was cooled down to 25 °C. Subsequently, the reactor was charged with 10 mL of ESO, 10 mL of PO and 0.1 g of dried Co-Zn DMC catalyst. Initially, the reactor was purged twice with CO_2 and next slowly pressurized to 4.0 MPa. The reaction temperature was then raised and maintained between 60 and 100 °C with a stirring speed of 500 rpm to initiate the polymerization reaction. Meanwhile the reaction time was ranging between 6 h to 72 h. Once 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.

2.4. Characterizations

The functionalization of $K_3Co(CN)_6$ and Co-Zn DMC catalyst were examined using IR spectroscopy. Absorption spectra were recorded on a Jasco 4100 spectrometer (Jasco International, Tokyo Japan) in attenuated total reflectance (ATR) mode meanwhile spectra of ESO and terpolymerization products were recorded on a

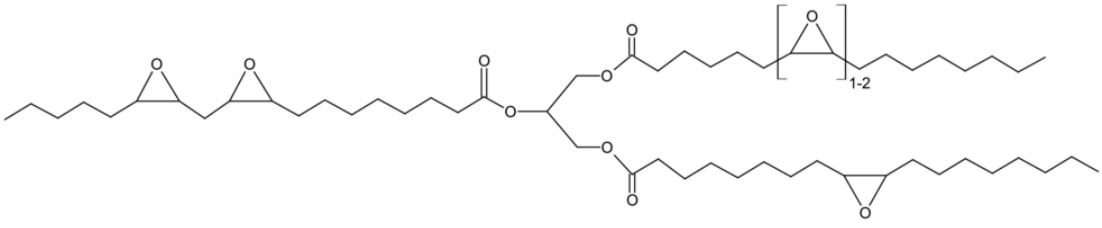


Fig. 2. Structure of ESO.

Perkin–Elmer 1000 FTIR spectrometer in the wavenumber region of 600 to 4000 cm^{-1}. ^1H NMR spectroscopic analysis of ESO and final products was recorded using a Bruker AMX-300 spectrometer at 25 °C. The equipment operated at 300 MHz and all measurements were made by using $CDCl_3$ as solvent. In Gel Permeation Chromatography (GPC) test, the number average molecular weight (M_n) and the polydispersity index (PDI) were determined using a Agilent HPLC equipped with a separation column of PLHFIP gel running at room temperature. Mobile phase is HFIP containing 2.72 $g{\cdot}L^{-1}$ of sodium trifluoroacetate to prevent polyelectrolyte effect. 100 μL will be injected and the concentration of each sample will be 0.2 w/vol%. Calibration was performed with polymethyl methacrylate (PMMA) samples.

2.5. Solubility test

A simple test was conducted to check on the solubility of the insoluble polymers. 20 mg of the samples were mixed in 2 mL of solvent which are chloroform, DMSO, HFIP and toluene at room temperature. The dissolution of the samples in solvent was observed every one hour interval for the first 6 h and later monitored once a day up to seven days.

3. Results and discussion

3.1. IR of Co-Zn DMC catalyst

In this study, the DMC catalyst composed of zinc hexacyanometalate was prepared by means of precipitation reaction in a traditional method between $K_3Co(CN)_6$ and metal salt namely $ZnCl_2$ along with *tert*-butanol as complexing agent. The incorporation of *tert*-butanol during the preparation of DMC catalyst was claimed could help to heighten the activity of the catalyst (Tharun et al., 2012; Zhang et al., 2011). Shown in Fig. 3 is the IR spectrums of $K_3Co(CN)_6$ and Zn-Co DMC catalyst. It was observed that the ν(CN) of $K_3Co(CN)_6$ shifted to higher wave number approximately 2193 cm^{-1} in Co-Zn DMC catalyst. The ν(CN) shift to higher frequency is in a good agreement with report by Dharman et al. (2008) which suggest that CN^- acts as σ-donor by donating electrons to the Co^{3+} and as a π-electron donor by chelating to Zn^{2+}, which is responsible for raising the (CN) value (Dharman et al., 2008). The presence of complexing agent *tert*-butanol, was verified by the —OH stretching vibration absorption and C—H stretching vibration absorption at approximate 3482 cm^{-1} and 2985 cm^{-1} respectively (Guo and Lin, 2014).

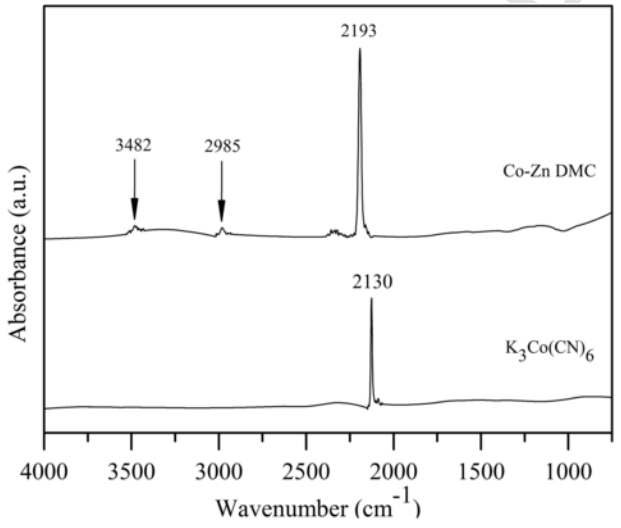


Fig. 3. IR spectra of $K_3Co(CN)_6$ and Co-Zn DMC catalyst.

3.2. Properties and characterization of terpolymerization products

The properties of individual products obtained from terpolymerization reaction are tabulated in Table 1. As shown in Table 1, at reaction temperature of 60 °C and 80 °C the yield of polymerization products are 62% and 82% respectively and reach plateau at 90 °C with a maximum yield of 86% meanwhile the productivity was observed to increase from 112 g product/g catalyst to 154 g product/g catalyst as the temperature raised from 60 °C to 90 °C. However, at 100 °C the productivity decreased slightly to 151 g product/g catalyst. Meanwhile for the effect of reaction time, in general the longer the reaction time, the higher the yield and productivity. When the reaction time varied from 6 h to 72 h, the yield recorded ranging between 72 and 90% whereas productivity was in-between 129 and 161 g product/g catalyst.

Analysis of the products by GPC revealed the M_n for all samples prepared ranges between 1983 g/mol to 6498 g/mol. These values are comparable with the M_n reported elsewhere (Dai et al., 2016; Guo and Lin, 2014; Wei et al., 2013). Considering the starting material used for this reaction comprises of a mixture of natural ESO and commercial PO, thus this has shown a good indication of the viability of natural ESO as a precursor for the synthesis of vegetable oil based polymer. However, two samples prepared at 90 and 100 °C were unable to be characterized by GPC perhaps due to the formation of a cross-linked material.

To further validate the possibility of the formation of a cross-linked material, a simple solubility test was conducted. From the observation, the two samples prepared at higher temperature were insoluble in all solvent (chloroform, DMSO, HFIP and toluene). These results confirm that the probability of the two samples obtained at higher temperature is both cross-linked materials.

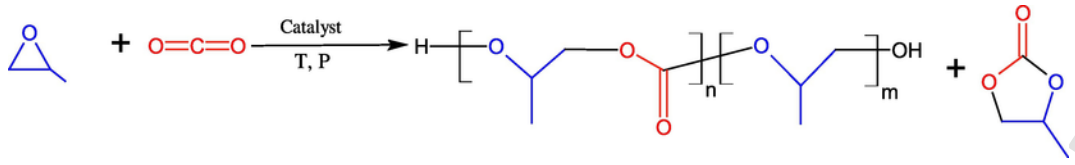
3.3. Analysis of products

Polycarbonates and cyclic carbonates are the two types of products generally produced from the reaction of CO_2 with epoxide (Scheme 1). In an ideal copolymerization reaction, an alternating insertion of CO_2 and epoxide will take place in the growing polymer chain. However, the consecutive insertion of two epoxides may also happen and leads to the formation of ether bonds in the copolymer which typically is undesired. The consecutive insertion of two CO_2 molecules has never been observed as this is strongly disfavored from a thermodynamic perspective (Coates and Moore, 2004).

Table 1
Data on the terpolymerization of ESO, PO and CO_2 under Co-Zn DMC catalyst.

Entry	Reaction temp. (°C)	Time (h)	Yield (%)	Productivity g product/g catalyst	M_n/M_w/PDI
1	60	24	62	112	2323/4251/1.8
2	80	24	82	142	3834/4962/1.3
3	90	24	86	154	Crosslinked material
4	100	24	86	151	Crosslinked material
5	80	6	72	130	6498/8462/1.3
6	80	48	90	161	1983/5696/2.9
7	80	72	75	129	3541/4246/1.2

Reaction conditions: volume of ESO = 10 mL, volume of PO = 10 mL, Co-Zn DMC amount = 0.1 g, pressure of CO_2 = 4.0 MPa.



Scheme 1. Copolymerization of CO_2 and epoxide.

In this work, the vegetable oil based polymer synthesized from the terpolymerization reaction of ESO, PO and CO_2 with the presence of Co-Zn DMC catalyst is a polycarbonate, specifically a poly(propylene carbonate). At the same time, cyclic carbonate and polyether linkages were also detected. The extent of carbonate and ether backbone could be easily traced by IR and ^{1}H NMR spectroscopies of the resultant polymers. Fig. 4 shows the FTIR spectra of terpolymerization product prepared at reaction temperature and reaction time of 80 °C and 6 h respectively. It was pronounced from the spectra the intense C═O asymmetric vibration absorption peak at approximately 1745 cm^{-1}. Together with this, the presence of absorption peak around 1256 cm^{-1}, which correspond to C—O stretching vibration absorption, provides confirmation for the presence of both carbonate and ether backbone in the resultant terpolymer. Besides, the characteristic absorption peak of the C═O stretching vibrations of cyclic carbonate was detected at 1810 cm^{-1}. The FTIR spectrums of the remaining samples prepared illustrate the same characteristic peaks and given in Supplementary A1 and A2.

All polymers were subjected to ^{1}H NMR analysis in $CDCl_3$, and a representative spectrum of the polymer produced by Co-Zn DMC catalyst at 80 °C and 6 h is shown in Fig. 5, together with that of ESO monomer for the comparison. In general, based on the ^{1}H NMR analysis it was confirmed that the resultant products from the terpolymerization of ESO, PO and CO_2 consist of chain of poly(propylene carbonate) bonded to the triglyceride. At the same time the presence of polyether linkages and cyclic carbonate are also detected in the products. As mentioned by Zhang et al. (2014), the formation of the ether units is usually thermodynamically favorable during Co–Zn(III) DMCC catalysis (Zhang et al., 2014). The peaks at δ 2.8–3.2 ppm region related to epoxy proton are apparent in both spectra of ESO and the polymer product. The signal of epoxy proton in the resultant polymer signify that a fraction of epoxide was unreacted during the polymerization reaction probably due to the steric hindrance owing to the long chain structure of triglyceride. Also notable are the methine proton –CH_2–C**H**–CH_2– of the glycerol backbone at δ 5.1–5.3 ppm and methylene protons –C**H**$_2$–CH–C**H**$_2$– of the glycerol backbone at δ 4.1–4.3 ppm which revealed triglyceride structure of ESO is not disturbed (Liu et al., 2013).

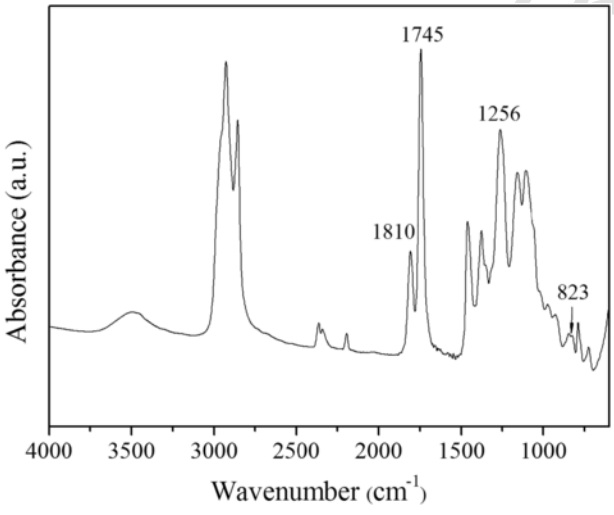


Fig. 4. FTIR spectra for purified sample prepared at T = 80 °C and t = 6 h (entry no. 5 in Table 1).

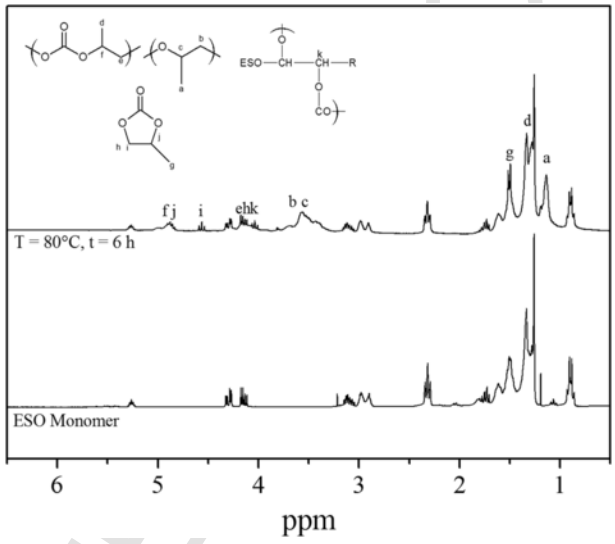


Fig. 5. ^{1}H NMR spectra for purified sample prepared at T = 80 °C and t = 6 h (entry no. 5 in Table 1).

The percentage incorporation of ESO in the polymer was calculated from the integrated peak areas taking the terminal methyl signals as an internal reference standard. Eq. (1) was used in the calculation as per following:

$$F_{ESO} = \frac{A_{\text{reacted epoxy}}}{A_{\text{reacted epoxy}} + A_{\text{polycarbonate}} + A_{\text{ether unit}}} \times 100 \quad (1)$$

where, $A_{\text{reacted epoxy}}$ is the integrated area of the methine epoxy proton at δ 4.07–4.16 ppm (Salih et al., 2015) meanwhile the $A_{\text{polycarbonate}}$ and $A_{\text{ether unit}}$ are the integrated peak area of the methine proton of polycarbonate unit (δ 5.10 ppm) and ether unit (δ 3.5 ppm) respectively. Note that the peak of reacted epoxy overlapped with the peaks of cyclic carbonate and methylene protons of the glycerol backbone, thus these peaks areas were subtracted in the calculation. The percentage incorporation of ESO in the polymer is only 7.8% at the shortest reaction time and in general the amount is found to be decreasing with the elevation of reaction temperature and prolonged reaction time (Table 2). The amount of ESO incorporated in the polymer obtained is quite low as ESO is less reactive than PO. Even so, considering that this is the first attempt utilizing ESO as one of the starting material in the polymerization reaction with CO_2, thus the re-

Table 2
Percentage incorporation of ESO and amount of cyclic carbonate in the terpolymerization products.

Entry	Reaction temp. (°C)	Time (h)	F_{ESO} [a] (%)	W_{CC} [b] (wt%)
1	60	24	6.7	20.6
2	80	24	6.0	18.8
3	90	24	0.8	10.4
4	100	24	0.0	9.5
5	80	6	7.8	14.1
6	80	48	3.2	9.1
7	80	72	6.2	12.6

Reaction conditions: volume of ESO = 10 mL, volume of PO = 10 mL, Co-Zn DMC amount = 0.1 g, pressure of CO_2 = 4.0 MPa.

[a] F_{ESO} (%) indicates the molar fraction of ESO incorporated in the polymer product.

[b] W_{CC} (wt%) indicates the weight percentage of cyclic carbonate in the total product.

sults gave a good sign of utilizing renewable bio-resources for this particular reaction in the future.

The weight percentage of cyclic carbonate, (W_{CC}) can be determined using the formula as below:

$$W_{CC} = \frac{\text{Mass}_{\text{cyclic carbonate}} \times A_{\text{cycl}}}{\text{Mass}_{\text{ether unit}} \times A_{ether\ unit} + \text{Mass}_{\text{cyclic carbonate}} \times \left(A_{cyclic\ Carb}\right) \times 100}$$

where, $A_{\text{cyclic carbonate}}$, $A_{\text{ether unit}}$ and $A_{\text{polycarbonate}}$ are the integrated areas of $-CH_3$ protons of cyclic carbonate (δ 1.50 ppm), polyether (δ 1.14 ppm) and polycarbonate (δ 1.33 ppm) accordingly meanwhile A_{ESO} represents by the area of terminal methyl protons of ESO (δ 0.89 ppm). The calculated results are tabulated in Table 2. Surprisingly in this study, the weight percentage of the cyclic carbonate in the product was found to decrease with increasing reaction temperature. This is in contrast with the report mentioned elsewhere where stated that the formation of thermodynamically stable cyclic carbonate is highly favored at higher reaction temperature (Li and Niu, 2011). Another important finding was that the signal of ether unit becomes more significance at higher reaction temperature (Supplementary A3). A possible explanation for this might be that the homopolymerization of epoxides are more dominant during the terpolymerization reaction considering that the concentration of CO_2 supplied was fewer as the temperature raised from 60 °C to 100 °C (Henry's law) whilst the amount of both epoxides were kept constant (Tang et al., 2013).

4. Conclusions and outlook

The results of this study demonstrated that under the reaction conditions studied, the resultant terpolymerization products comprise of a mixture of poly(propylene carbonate), cyclic carbonate and polyether unit. The constituent of the resultant products have been verified by the FTIR and ^1H NMR analysis. Polymeric product with yield of 72% and M_n of 6498 g/mol was recorded at reaction temperature of 80 °C and reaction time of 6 h. The resultant polymer obtained through this research work has proven the viability of utilizing natural epoxide, namely ESO for the production of bio-based polymer.

In order to incorporate the green material in the formulation, initially the use of natural epoxide was presented as partial replacement of petroleum based epoxide. However, with persistent and extensive research effort, natural epoxide may compete well with their petroleum based counterparts in terms of properties, performance and applications. The prospect of using ESO as a substitute to the petroleum based epoxide may as well provide solutions to increasing environmental and energy concern. Nevertheless, countless challenges must be overcome to develop better vegetable oil-based polymers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.04.184.

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