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Bio-based Polyurethane Derived from Carbon Dioxide and Epoxidized Soybean Oil

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Abstract

The synthesis of polyurethane relies on a toxic and petroleum-based isocyanate reactant. The aim of this research was to synthesize Polyurethane using environment-benign and renewable starting materials such as carbon dioxide and soybean oil. The carbonated soybean oil was first prepared from carbon dioxide (CO_2) and epoxidized soybean oil (ESBO) using zinc glutarate (ZnGA) as a catalyst but the result of FTIR indicated the absence of the peak of cyclic carbonate around 1800 cm^{-1}. Therefore, in this work, the synthesis of Polyurethane was modified from A. Lee (Lee & Deng, 2015) using tetramethylammonium bromide (TBAB) as a catalyst. The as-synthesized carbonated soybean oil (CSBO) was allowed to react with two types of substances, 3-aminopropyltriethoxysilane or diethylenetriamine with the molar ratios of cyclic carbonate:NH_2 of 1:1 with THF or DMF as solvents to obtain Polyurethanes (U1THF, U1DMF, U2THF, U2DMF). After 3 hours lignin solution was added to form a film. Raman spectra confirmed the catalyst removal from CSBO. FTIR spectra showed the peak around 1800 cm^{-1} assigned to cyclic carbonate of CSBO, and a new peak of urethane linkage around 1700 cm^{-1} (C=O stretching) of Polyurethanes. The conversion of epoxide to cyclic carbonate was also confirmed by ^{1}H-NMR. Upon adding lignin into the Polyurethanes, the lignin-urethane U1THF, and U1DMF formed films whereas U2THF, and U2DMF formed viscous liquids. In terms of applications, all four formulations can be potentially applied as bioadhesives.

Keywords: Non-isocyanate polyurethanes, Bio-based polyurethane, Epoxidized soybean oil, Bioadhesives

1. Introduction

The conventional polyurethanes are usually synthesized by a polycondensation reaction between a diol and a diisocyanate (Caraculacu & Coseri, 2001; Kathalewar, Joshi, Sabnis, & Malshe, 2013). However, isocyanates are derived from non-renewable resources and notably toxic chemicals. In addition, that is synthesized from an even more toxic substance phosgene which causes environmental hazards. The exposure to isocyanates can cause health effects (Gupta & Upadhyaya, 2014).

Due to the use of isocyanate in conventional polyurethanes, there is a substantial interest to develop alternative, environmentally friendly methods and materials for preparing polyurethanes (non-isocyanate routes). Polycondensation, rearrangement, and ring opening routes still use toxic agents such as phosgene, aziridine, acyl azide, etc. Among these routes, one of the most attractive methods is the polyaddition reaction of cyclic carbonate with amines (Cornille, Auvergne, Figovsky, Boutevin, & Caillol, 2017; Rokicki & Piotrowska, 2002). The reaction of carbon dioxide with epoxide groups to form cyclic carbonate is very effective to further the polymerization reaction such as the polymerization of copolycarbonate (Ree, Bae, Jung, & Shin, 1999; Taherimehr & Pescarmona, 2014).

Soybean oil as feedstocks for polymeric materials attracts increasing attention because they are inexpensive and available in large quantities. (Pfister, Xia, & Larock, 2011). They have been utilized to replace petroleum chemicals to produce coatings, inks, plasticizers, lubricants, and agrochemicals. (Maisonneuve, Lamarzelle, Rix, Grau, & Cramail, 2015; Rokicki, Parzuchowski, & Mazurek, 2015).

Recently, several researchers accomplished synthesizing polyurethane using soybean oil as a starting material using a non-isocyanate reaction route. In 2008, Javni et al. (Javni, Hong, & Petrović, 2008) prepared polyurethane by a non-isocyanate route by reacting carbonated soybean oil with diamines. Carbonated soybean oil was reacted with different diamines such as 1,2- ethylenediamine, 1,4-butylenediamin and 1,6-hexylenediamine. The results showed that polyurethane could be prepared with a wide range of mechanical properties which was useful for industrial applications (Javni et al., 2008; Maisonneuve et al., 2015; Rokicki et al., 2015). The Poly (butylene carbonate) can successfully be synthesized based on carbon dioxide (CO_2) and 1, 2-butylene oxide using a self-prepared zinc glutarate (ZnGA) as a catalyst as reported by Chunsakul et al. (Chunsakul, Seadan, & Suttiruengwong, 2019).

Therefore, the aim of this study was to synthesize Polyurethane using environment-benign and renewable starting materials such as carbon dioxide and soybean oil. The carbonated soybean oil was first prepared from carbon dioxide (CO_2) and epoxidized soybean oil (ESBO) using zinc glutarate (ZnGA) as a catalyst but the result of FTIR indicated the absence of the peak of cyclic carbonate around 1800 cm^{-1}. Therefore, in this work, the synthesis of Polyurethane using tetra-n-butylammonium bromide (TBAB) as a catalyst. Chemical analysis of synthesized polyurethanes was carried out using FTIR, NMR and Raman spectroscopy. The peel strength was conducted and compared with commercial pressure sensitive adhesive.

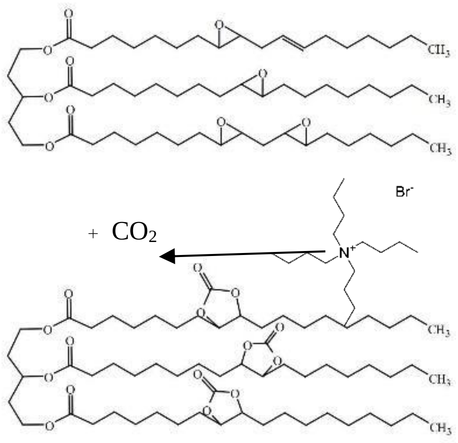
2. Materials and Method

2.1 Materials

Epoxidized soybean oil was donated by Applied DB public company LTD, Thailand. Carbon dioxide (99.8%) was purchased from MSG Company. Titanium tetrachloride (TiCl), Tetra-n-butylammonium bromide (TBAB), Lignin, alkaline, (3-Aminopropyl) triethoxysilane were purchased from Sigma Aldrich, Singapore. N,N-dimethyl-formamide (DMF) was obtained from RCI Labscan. THF was purchased from QReC. Ethyl acetate was purchased from SCHARLAU. Diethylenetriamine was purchased from FLUKA. All other chemical reagents were analytical grade.

2.2 Synthesis of Carbonate Soybean Oil (CSBO)

The ESBO (50 g) and TBAB (5 mole% with respect to the epoxy content) were first added into the reactor. The reactor was pressurized at 70 bar with CO_2. Then the reactor was stirred at 400 rpm and heated up to 140˚C. After the reaction time of 72 h, the reactor was cooled at 50˚C. The product was dissolved in ethyl acetate and then washed catalyst from product solution by adding distilled water. The mixture was separated using a separatory funnel. Both water and ethyl acetate were removed via rotary evaporator. The reaction is shown in scheme 1.



Scheme 1. Synthesis of carbonate soybean oil.

2.3 Synthesis of Polyurethane

3 g of CSBO (cyclic carbonate, measured by ^{1}H NMR) was dissolved in 20 ml with two different solvents (THF and DMF). The as-synthesized carbonated soybean oil (CSBO) was allowed to react with two types of substances, (3-Aminopropyl) triethoxysilane or diethylene-triamine with the molar ratios of cyclic carbonate: NH_2 of 1:1) with THF or DMF as solvents to obtain Polyurethanes (U1THF, U1DMF, U2THF, and U2DMF), where U1 and U2 denote polyurethane from (3-Aminopropyl) triethoxysilane and polyurethane from diethylenetriamine respectively. The reaction mixture was stirred at 70˚C for 3 h. After the reaction, the product was poured into a Teflon mold and oven at 70˚C for 7 h.

2.4 Synthesis of lignin-Polyurethane

After 3 hours of reaction for the preparation of Polyurethanes (U1THF, U1DMF, U2THF, and U2DMF), the solution of lignin alkali dissolved in two different solvents (THF/water and DMF/water) (12 ml/8 ml) was added. The reaction mixture was stirred at 70˚C for 12 hours, then the product was poured into Teflon mold and oven-sampled at 70˚C for 7 hours.

2.5 Characterization

2.5.1 Raman Spectroscopy

The catalyst was successfully removed from carbonate soybean oil which is characterized by Raman spectroscopy (Bruker, USA). The Raman spectra were recorded between 107-3781 cm^{-1} and used a laser source 785 nm with the resolution of 9-18 cm^{-1}.

2.5.2 FTIR Analysis

The chemical structure and functional groups of carbonate soybean oil, Polyurethane, and lignin polyurethane from Epoxidized soybean oil, and CO_2 were characterized with Fourier transform infrared spectrometer; FTIR (VERTEX70, Bruker, USA). The FTIR spectra were recorded in the range of 4000-400 cm^{-1} and used the resolution of 4 cm^{-1}.

2.5.3 ^{1}H-Nuclear magnetic resonance (^{1}H-NMR)

Nuclear magnetic resonance (NMR) using NMR Spectrometer from Varian (400MHz) with ^{1}H probes. In The NMR spectroscopic measurements, chemical shifts were calibrated with the chemical shifts of the solvent used (D-chloroform).

2.5.4 T-Peel test

The T-peel test of samples (Figure 1) were measured at room temperature with a crosshead speed of 100 mm/min by a universal testing machine (NRI-TS500-5B).

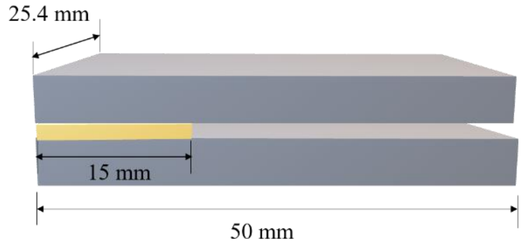


Figure 1. Sample of T-peel test.

3. Results and Discussion

3.1 Characterizations of carbonate soybean oil

The synthesized cyclic carbonates from epoxides are shown in scheme 1. Under the high-pressure condition, the tetrabutylammonium ion activates the epoxide ring followed by the nucleophilic attack by the bromide ion. Then it attacks the carbon dioxide to produce the cyclic carbonate, which simultaneously allows the bromide to leave and the catalyst to be released (Chunsakul et al., 2019; Doll & Erhan, 2005). However, the catalyst is removed using an extraction method using ethyl acetate and water.

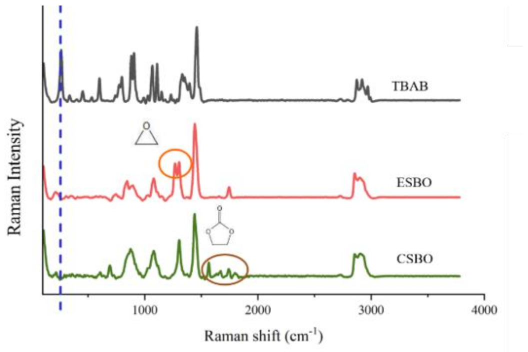


Figure 2. Raman spectra of Tetra- n- butyl ammonium bromide (TBAB), Epoxidized soybean oil (ESBO), and Carbonate soybean oil (CSBO).

The results in Figure 2 showed that Raman spectra of TBAB appears the characteristic peak of TBAB at Raman shift 265 cm^{-1}, the Raman spectra of ESBO showed a peak of the epoxy group at doublet 1260 and 1280 cm^{-1} and the Raman spectra of CSBO showed a new peak C=O of cyclic carbonate around 1600-1800 cm^{-1} but no characteristic peak of C-C stretching of TBAB and characteristic doublet peak of the epoxy group. Therefore, the result confirmed the catalyst removal from CSBO.

Figure 3 presents the FTIR spectra of ESBO, and CSBO for comparison. Table 1 and 2 list the vibration modes and wavenumbers of IR absorption peak of ESBO and CSBO respectively.

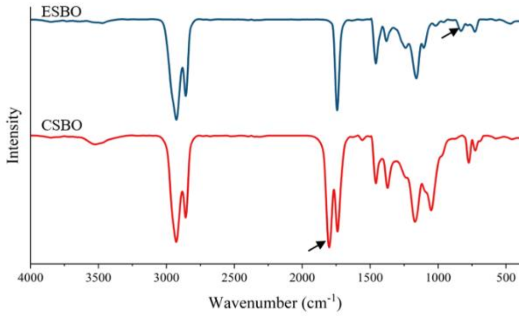


Figure 3. FTIR spectra of Epoxidized soybean oil (ESBO), and Carbonate soybean oil (CSBO).

Table 1. Vibration modes and Wavenumbers of IR absorption peaks in FTIR spectra of ESBO.

Peak value (cm^{-1})	Group
3000 - 2800	Stretching vibration of saturated C-H bond
1750 - 1700	Stretching vibration of C=O
1280 - 1200	Stretching vibration of C-O (ester bond)
825	Stretching vibration of C-O (epoxy group)

Table 2. Vibration modes and Wavenumbers of IR absorption peaks in FTIR spectra of CSBO.

Peak value (cm^{-1})	Group
3000 - 2800	Stretching vibration of saturated C-H bond
1800	Stretching vibration of C=O (cyclic carbonate group)
1750 - 1700	Stretching vibration of C=O
1280 - 1200	Stretching vibration of C-O (ester bond)

The results in Figure 3 and table 1 revealed that the peak at 825 cm-1 corresponded to the characteristic peak of C-O stretching (epoxy group). The FTIR spectra of CSBO showed the new characteristic peak corresponding to the cyclic carbonate group. The characteristic peak of cyclic carbonate (C=O) is indicated at 1800 cm^{-1} and the peak of the epoxy group disappeared.

In addition, the physical appearance of ESBO was a colorless liquid but after reaction with CO_2, the product was a brown liquid, and the viscosity was increased. Therefore, it was confirmed that the synthesis of CSBO was successful.

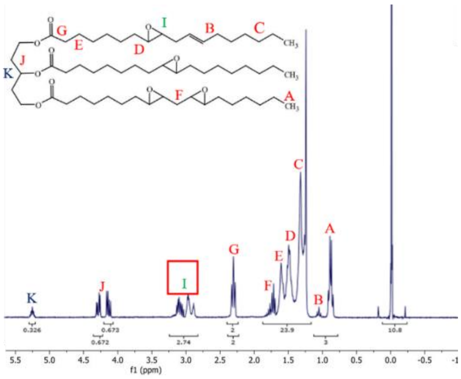


Figure 4. NMR spectra of ESBO.

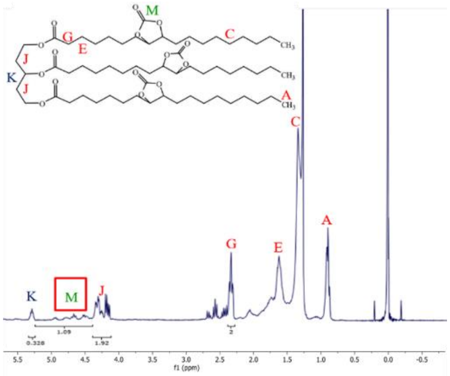


Figure 5. ^{1}H-NMR spectra of CSBO.

The ^{1}H-NMR spectra of ESBO and CSBO were used to propose the chemical structure and it confirmed the conversion of epoxide to cyclic carbonate. Figure 4 showed the NMR spectra of ESBO, where the peak at 2.80-3.20 ppm corresponded to the epoxy group. Figure 5 showed the NMR spectra of CSBO, which showed the peak at 4.20-5.10 ppm assigned to cyclic carbonate groups.

The performance of the carbonation reaction was evaluated through the conversion carbonation or yield (% Y) of cyclic carbonate. The mole of epoxide and carbonate groups were calculated from the integrals of the ^{1}H-NMR spectrum (Figure 4 and 5). The central carbon (K) signal was taken as the spectrum normalization factor. The mole of epoxide groups (Em) was calculated with the signals corresponding to epoxy rings (I) (Equation (1)). Similarly, through Equation (2), the mole of carbonate groups (Cm) was calculated from the signals (M) (González Martínez, Vigueras Santiago, & Hernández López, 2021).

Then quantitative results, 100% conversion of ESBO into CSBO was confirmed via the 1H-NMR spectrum. It was clear from Figure 5 that the original epoxy groups at 2.80 - 3.20 ppm disappeared while the new signals at 4.20 - 5.10 ppm corresponding to the cyclic carbonate group appeared. The calculated moles of the epoxy group and cyclic carbonate group are 4.26 and 2.53 respectively. The yield of cyclic carbonate was found to be 61% (Equation (3)).

$$Em = \frac{I}{2K} \qquad (1)$$

$$Cm = \frac{M}{2K} \qquad (2)$$

$$\%Y = \frac{C_m}{E_m} x\ 100 \qquad (3)$$

3.2 Characterization of Lignin-Polyurethane

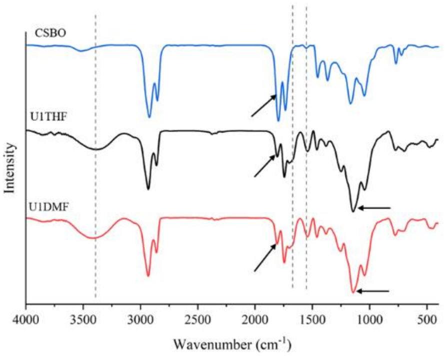


Figure 6. FTIR spectra of Carbonate soybean oil (CSBO), U1THF, and U1DMF.

Table 3. Vibration modes and wavenumbers of IR absorption peaks in FTIR spectra of U1THF and U1DMF.

Wavenumber (cm^{-1})	**Groups**
3300	Stretching vibration of N-H (Urethane linkage)
3000 - 2800	Stretching vibration of saturated C-H bond
1800	Stretching vibration of C=O (cyclic carbonate group)
1600	Stretching vibration of C=O (Urethane linkage)
1500	Stretching vibration of C-N (Urethane linkage)
1280 - 1200	Stretching vibration of C-O (ester bond)
1078	Stretching vibration of Si-O

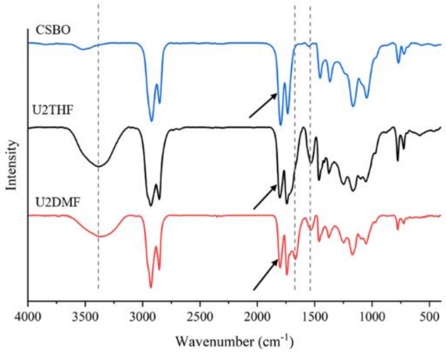


Figure 7. FTIR spectra of Carbonate soybean oil (CSBO), U2THF, and U2DMF.

Table 4. Vibration modes and Wavenumbers of IR absorption peaks in FTIR spectra of U1THF and U1DMF.

Peak value (cm^{-1})	**Group**
3300	Stretching vibration of N-H (Urethane linkage)
3000 - 2800	Stretching vibration of saturated C-H bond
1800	Stretching vibration of C=O (cyclic carbonate group)
1600	Stretching vibration of C=O (Urethane linkage)
1500	Stretching vibration of C-N (Urethane linkage)
1280 - 1200	Stretching vibration of C-O (ester bond)

The results in Figure 6 and 7 and Table 3 and 4 showed that the FTIR spectra of U1THF was similar to U1DMF. That showed the new characteristic peak corresponding to the Urethane linkage. That peak C=O stretching at 1600 cm^{-1}, C-N stretching at 1500 cm^{-1}, and N-H stretching at 3300 cm^{-1}. The characteristic peak of cyclic carbonate (C=O) was indicated at 1800 cm^{-1} was decreased. Therefore, the result can be confirmed that the ring-opening reaction turns into urethane linkage.

In addition, the characteristic of Si-O-Si stretching at 1078 cm^{-1} intensity was increased as shown in Figure 6. The appearance of Si-O-Si is due to the self-condensation of (3-Aminopropyl) triethoxysilane. (Kathalewar et al., 2013; Robles, Csóka, & Labidi, 2018). Therefore U1THF and U1DMF samples were able to form into films. However, U2THF and U2DMF samples were viscous liquid. They could not be fabricated into the film.

Upon adding lignin into the Polyurethanes, the lignin-U1THF and Lignin-U1DMF formed into films whereas lignin-U2THF and lignin-U2DMF were viscous liquid. However, U1THF and U2THF formed a heterogeneous phase. This was probably due to the distinguished solubility of lignin alkali and THF. On the other hand, the solubility of lignin alkali in DMF was better. Thus, U1DMF and U2DMF mixtures were homogeneous.

3.3 T-Peel test

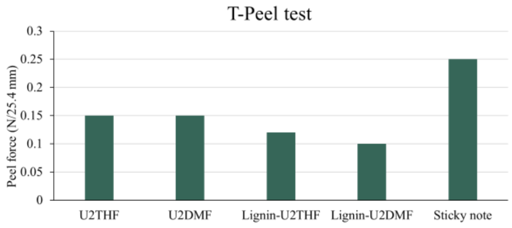


Figure 8. Peel force of viscous liquid polyurethanes compared with sticky notes.

Figure 8 showed the peel force of the samples compared to commercial sticky notes. U2THF and U2DMF have the same peel force (around 0.15 N/25.4 mm). U2THF-lignin U2DMF-lignin showed the peel forces of 0.12 N/25.4 mm and 0.10 N/25.4 mm respectively. In all cases, the peel force was lower than that of the sticky note. Without lignin, the adhesive performance was better in terms of the peel force. This may be due to the phase separation of lignin and polyurethane, which could not form the continuous phase. Although all specimens showed lower peel strengths than the commercial one. It could possibly be recommended as pressure sensitive bioadhesives.

4. Conclusion

Polyurethane was successfully synthesized using carbon dioxide and soybean oil as renewable starting materials. U1THF and U1DMF specimens could be fabricated into films whereas U2THF and U2DMF were viscous liquid. After adding lignin alkaline, U1THF-Lignin and U2THF-Lignin formed a heterogeneous phase but U1DMF-Lignin and U2DMF-Lignin were homogeneous phases. Peel strengths of all specimens were lower than the commercial one. In terms of applications, the synthesized polyurethane can be potentially applied as pressure sensitive bioadhesives.

5. Acknowledgment

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