

# **Soybean Oil-based Non-Isocyanate Polyurethanes for Commercial Applications**

**Report - 1**

**(July 01, 2023 – December 31, 2023)**

**By**

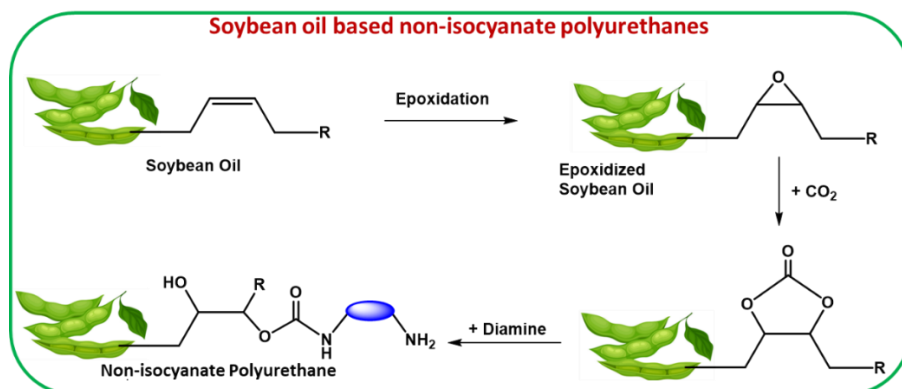
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## Summary of the Worked Performed

The main objective of this project is to provide value-added applications of soybean oil for polyurethane industries. Polyurethanes (PU) are of great interest since they represent one of the largest categories of plastics by demand, with applications ranging from construction to the automotive and furniture industries. The traditional polyurethane synthesis stems from the polyaddition reaction of diisocyanates and diols, both of which are largely derived from fossil fuel sources. The isocyanates are produced from hazardous and toxic phosgene gas by the phosgenation process. Phosgene is an extremely toxic gas. Additionally, the isocyanates are toxic and moisture-sensitive and cannot be prepared without sophisticated safety devices, thus posing serious environmental and human health risks. Consequently, a strong thrust has been directed to PUs that avoid diisocyanates and have a reduced carbon footprint.

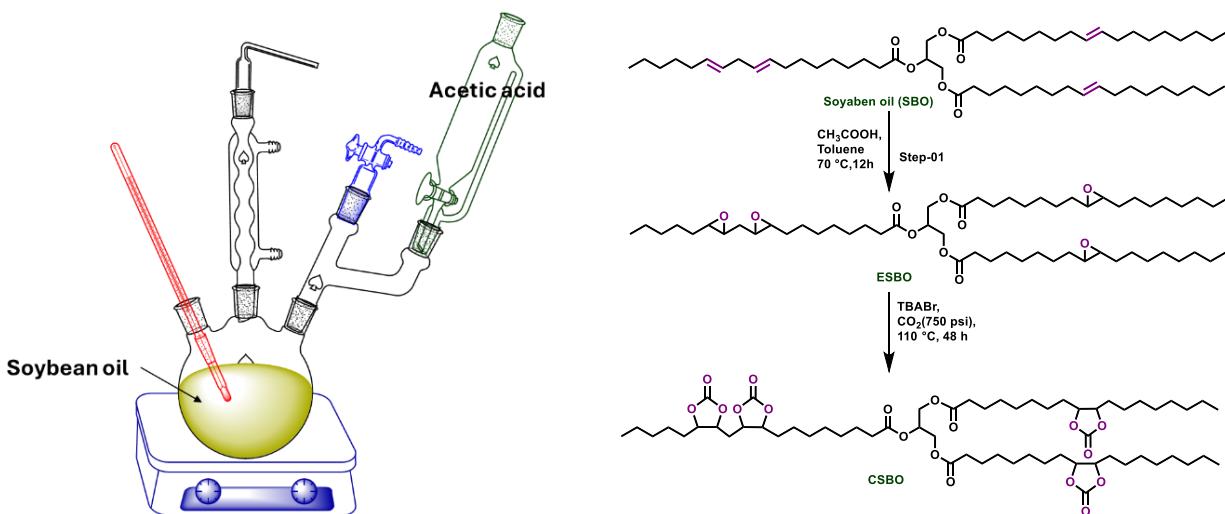
During this period, we prepared non-isocyanate polyurethanes (NIPU) using soybean oil. For this soybean oil was chemically modified to epoxidized soybean oil using a facile approach. The epoxidized soybean oil was reacted with carbon dioxide ( $\text{CO}_2$ ) to synthesize carbonated soybean oil which was used to react with a diamine to prepare non-isocyanate polyurethanes. The prepared materials were characterized using standard methods to confirm the formation of desired chemicals. The carbonated soybean oil was used to prepare non-isocyanate polyurethane foams. The properties of the non-isocyanate polyurethane foams were tuned by varying the experimental conditions. Our results suggest that soybean oil can be chemically modified to be used for the preparation of non-isocyanate polyurethane foams. The use of carbon dioxide and soybean oil for the preparation of non-isocyanate polyurethane foams will be very attractive to industries due to low cost and government/environmental agencies as it is a green synthesis process that reduces greenhouse gas.



**Figure 1.** Synthesis of non-isocyanate polyurethanes using soybean oil.

## Detailed Report of the Work Performed

For the preparation of non-isocyanate polyurethane foams, soybean oil was used as the starting material. Soybean oil was purchased from a local Walmart in Pittsburg, KS. Soybean oil was epoxidized using a facile approach. For this, a molar ratio of soybean oil: acetic acid: hydrogen peroxide of 1:0.5:1.5 was used. 300 g of soybean oil, 75 g of amber lite resin, and 150 ml of toluene were thoroughly mixed at room temperature for 15 to 20 minutes using a mechanical stirrer in a three-neck round bottom flask attached to the condenser and thermometer. After cooling down the system to 5-10 °C 43.9 ml glacial acetic acid was added to the mixture in the dropwise manner and stirred the mixture for another 30 minutes. After adding 180 ml of peroxide (30%) the mixture was again stirred for 7 hours at 70 °C. Following the mixture was allowed to cool down to room temperature and the amber lite resin was decanted and filtered out. After that, the soybean oil and aqueous layers were separated by gravity while being washed 7 to 8 times with 10% brine solution. To remove the excess solvent in the soybean oil the anhydrous sodium sulfate was used as a drying agent, followed by, rotary evaporation to dry the synthesized epoxidized soybean oil.



**Figure 2.** (Left) Reaction setup for the synthesis of epoxidized soybean oil, and (Right) Reaction scheme for the carbonated soybean oil using soybean oil.

For the synthesis of carbonated soybean oil, the synthesized epoxide soybean oil and CO<sub>2</sub> were reacted in the presence of tetrabutylammonium bromide as a catalyst (**Figure 2**). For this, 300 g of epoxide soybean oil and 12.5 g of tetrabutylammonium bromide were transferred into the Parr

reactor under a CO<sub>2</sub> pressure of 3.79 MPa. The reaction was carried out for 48 hours at 110° C and 1100 rpm stirring speed.

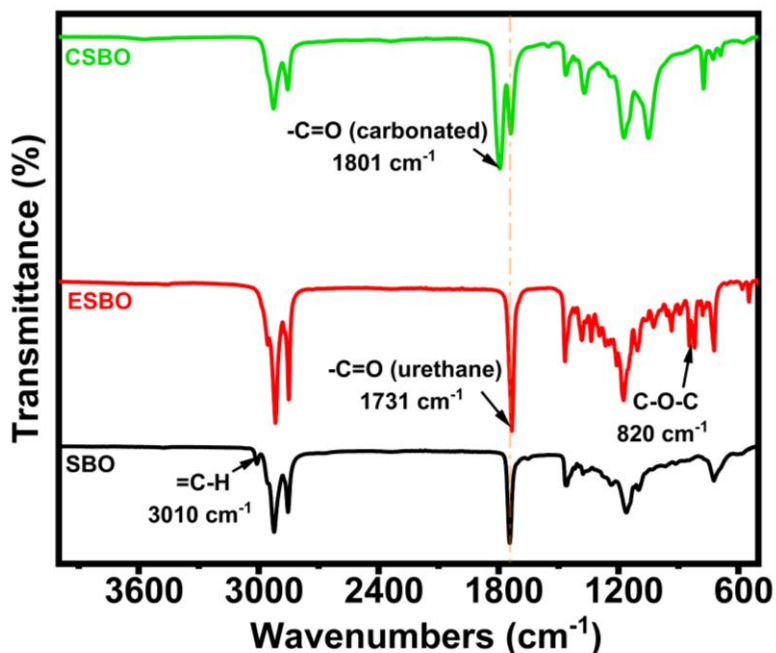
International Organization for Standardization (ISO) and American Society for Testing and Materials (ASTM) methods were used to characterize the synthesized epoxide and carbonated soybean oil. The Hanus method based on IUPAC 2.205 was used to determine the iodine value of the soybean oil and epoxidized soybean, which was 127.01 and 3.01 g I<sub>2</sub>/100g, respectively. The reduction in the iodine value indicates the successful modification of soybean oil. The percentage of oxirane oxygen was measured using glacial acetic acid and tetraethylammonium bromide and crystal violet indicator for epoxide soybean oil and carbonated oil which was 7.10% for synthesized epoxidized soybean oil but after modification, the value was decreased to 0.28%. The hydroxyl number was determined by the phthalic anhydride pyridine (PAP) method based on IUPAC 2.241. The hydroxyl value of carbonated soybean oil was almost zero. To determine the acid value, an indicator method was used according to the IUPAC 2.201 standard, and the observed acid value for soybean oil, epoxide soybean oil, and carbonated soybean oil was 0.69, 0.86, and 5.38 mg KOH /g accordingly. Using an AR 2000 dynamic stress rheometer (TA Instruments, New Castle, Delaware, USA), the viscosity was examined by raising the shear stress from 1 to 2000 Pa. The rheometer came with a cone plate with a 2° angle and a 25 mm diameter cone. The viscosity of soybean oil, epoxidized soybean oil, and carbonated soybean oil was 0.033, 0.17, and 215 Pa.s, respectively. The details of the characteristics of soybean oil, epoxidized soybean oil, and carbonated soybean oil are provided below.

**Table 1:** Some important characteristics of soybean oil, epoxidized soybean oil, and carbonated soybean oil.

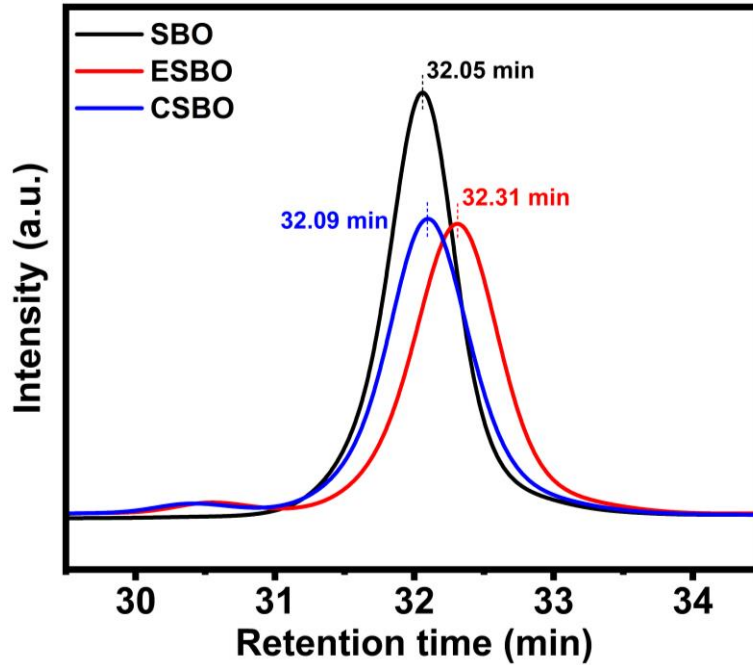
Test Name	Unit	Soybean Oil (SBO)	Epoxidized Soybean Oil (ESBO)	Carbonated Soybean Oil (CSBO)
Iodine value	g I <sub>2</sub> / 100g	127.01	3.01	
Epoxy oxirane content	%	-	7.10	0.09
Hydroxyl value	mg KOH /g	-	-	-
Acid value	mg KOH /g	0.69	0.86	5.38
Viscosity @25 °C	Pa.s	0.033	0.17	215

The synthesized epoxidized soybean oil and carbonated soybean oil were structurally characterized using Fourier-transform infrared (FT-IR) spectroscopy and Gel Permeation Chromatography (GPC) spectroscopy. FT-IR spectroscopy was used to determine the presence of functional groups. A PerkinElmer Spectrum Two FT-IR Spectrometer was used to determine the changes in the structure of soybean oil after the modification into carbonated soybean oil (**Figure 3**). The stretching vibration of =C-H at  $3010\text{ cm}^{-1}$  wavelength corresponds to the carbon-carbon double bonds (C=C) in the soybean oil. This peak disappeared in the epoxide soybean oil after the epoxidation process and a new peak of the epoxy ring (C-O-C) was observed at  $820\text{ cm}^{-1}$  which indicates the successful modification of soybean oil into epoxide oil. After the modification of CSBO from ESBO the new sharp peak was observed at  $1801\text{ cm}^{-1}$  wavelength which corresponds to the (-C=O) carbonyl group and the peak of the epoxide group disappeared after the conversion which indicates the successful modification of CSBO from ESBO.

The conversion of the soybean oil into epoxidized soybean oil and carbonated soybean oil was further confirmed using gel permeation chromatography. As per the GPC curves, the retention time of soybean oil was 32.05 min which was lower than the epoxidized soybean oil 32.32 min which suggests a change in the soybean oil after epoxidation and carbonation (**Figure 4**).



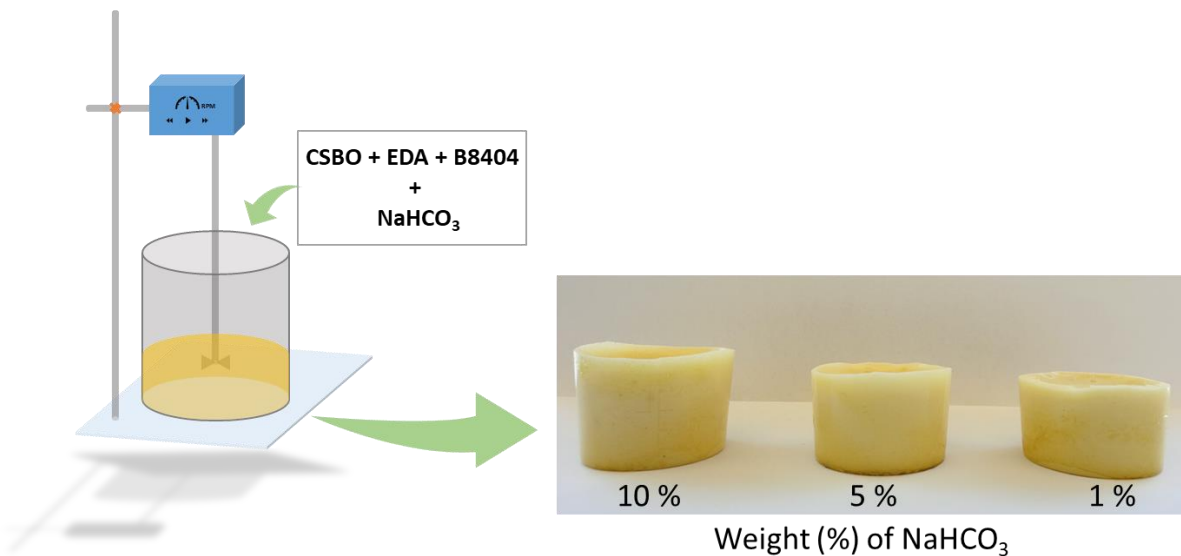
**Figure 3.** FT-IR spectra of soybean oil, epoxidized soybean oil, and carbonated soybean oil.



**Figure 4.** GPC spectra of soybean oil, epoxidized soyabean oil, and carbonated soyabean oil.

#### Synthesis of Non-Isocyanate Polyurethane Foams:

After the successful synthesis of epoxidized soyabean oil and carbonated soyabean oil, non-isocyanate polyurethane foams were prepared (**Figure 5**).



**Figure 5.** Preparation of non-isocyanate polyurethane foams using soybean oil.

For this, 10 g of carbonated soybean oil (CSBO) was taken in a hard plastic cup followed by the addition of 10 wt.% surfactant B8404, 20 wt.% of ethylene diamine (EDA), and different wt.% of  $\text{NaHCO}_3$  (1 wt.%, 5 wt.% and 10 wt.%) (all weight percentage was taken in respect of CSBO) was added and vigorously stirred the mixture by using mechanical stirrer for 2 min. After the homogenous mixture, the reaction mixture was allowed to room temperature for 24 hours, for batter curing foam was cured in the oven for a further 24 hours at  $\sim 50^\circ\text{C}$ . The characterization of the foams is ongoing and a detailed report will be provided in the next six-monthly report. The project is going very well and is on schedule.