

## BIO-BASED POLYURETHANE PREPARED FROM RENEWABLE FEEDSTOCKS

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### ABSTRACT

*Non-isocyanate polyurethane (NIPU)s were prepared by reacting carbonated soybean oil with kraft lignin using two pot reactions. In the first stage, epoxidized soybean oil (ESBO) reacted with carbon dioxide to form carbonated soybean oil (CSBO) with tetra-butylammonium bromide (TBAB) as the catalyst. In the second stage, urethane monomer was formed from the reaction of CSBO with 3-aminopropyltriethoxysilane (APES) and was reacted with the kraft lignin. The reaction was catalyzed by lithium chloride and the NIPU was cured both at room temperature and at 70 °C. Effects of lignin composition (20 – 50 wt%) on the NIPU mechanical properties were studied. Fourier transform infrared spectroscopy (FTIR) analysis was used to determine the structure of the lignin, CSBO, and lignin polyurethane. Tensile strength of the NIPU was much more improved when the polymer was cured at elevated temperature compared to when cured at room temperature. On the other hand, room temperature curing favoured high elongation at break.*

Keywords: Bio-based polyurethane foam, Non-isocyanate, Carbonated soybean-oil, Tensile strength  
Elongation-at-break.

### INTRODUCTION

Polyurethanes (PU)s are versatile, elastic, and segmented phase-separated polymer that consist of a chain of organic units joined together by urethane linkage (-NHCOO-). They have been used in wide array of applications such as insulation, upholstery furniture and beddings, elastomers, packagings, vehicle parts, coatings, and constructions. PU is synthesized through the step-growth polymerization reaction between a diisocyanate and a polyol, with the most widely-used diisocyanates, being diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) among the many alternatives that exist. These isocyanates are very toxic and are made from even more toxic substance, phosgene, which causes environmental hazards. Further, exposure to isocyanate can cause damaging health complications such as skin irritation and chronic asthma (David and Stanley, 1969). PU from petrochemical starting materials is susceptible to environmental degradation. They have poor chemical resistance and are hydrolytically unstable.

When used as coating, it is important to remove moisture in the PU before the coating is applied to surfaces, because the unstable carbamic acid formed from the reaction of isocyanate and water can decompose irreversibly, forming urea and carbon dioxide. Due to these drawbacks from conventional PU, several alternative environmentally friendly methods have been reported for PUs from

green resources. Some of these methods include (i) epoxidation of vegetable oils followed by carbonization to form cyclic carbonate and subsequent reaction with petrochemical isocyanate (Tanaka *et al*, 2008; Tu *et al*, 2008; Latinwo and Agarry, 2014), petrochemical diamine (Hatakeyama *et al*, 2005), or with AgNCO-based isocyanate (Çaylı and Küsefoğlu, 2008), (ii) reaction of bis(chloroformate) with diamines (Hoff and Wicker, 1945), (iii) adiponitrile carbonate with diols or polyols (Dieter *et al*, 1975), (iv) reaction of urethane diphenol with phosgene (Foti *et al*, 1983). PUs from these approaches are environmentally friendly than those from conventional method. Nevertheless, they are less preferable commercial alternatives because of low degree of polymerization.

From among the many methods for non-isocyanate polyurethane, the cyclic carbonate reaction with amine route is the most attractive. This is due to the formation of hydroxylpolyurethane containing hydroxyl group which can form intermolecular hydrogen bonding with urethane group making the polyurethane not receptive to moisture and when applied as coating is not as troublesome as conventional polyurethane coating. Additionally, polyurethane from cyclic carbonate exhibit increased resistance and high thermal stability. All these are made possible because cyclic carbonates are characterized by high boiling and flash points, low odor, low evaporation rates, low toxicity,

good biodegradability, and high solvent power (Javni *et al*, 2008). However, since the amine used is petrochemical-based, the polyurethane is not 100 % green.

With increasing awareness of environment, it is important to minimize use of environmentally unfriendly substances; hence, this study focus on preparation of non-isocyanate based polyurethane from 100% renewable resources. It has been reported (Rasmussen *et al*, 2014) that lignin, a major constituent of plants cell wall, wood, and algae and a byproduct of the kraft pulping process can be converted to polyamine by reacting with organosilane, particularly 3-aminopropyltriethoxysilane (APES) in the presence of lithium chloride catalyst to create the functional group for reaction with cyclic carbonate, thereby forming polyurethane. This approach was followed in this study.

## MATERIALS AND METHOD

### Materials

Epoxidized soybean oil (ESBO) with epoxy oxygen content (EOC) of 6.8 g /100g corresponding to 4.0 epoxy groups per triglyceride was purchased from Spectrum Chemicals. Carbon dioxide was supplied by Air gas. 3-aminopropyltriethoxysilane, Tetrabutylammoniumbromide (TBAB), and lithium chloride were supplied by Sigma-Aldrich and used as received. Kraft lignin was purchased from Cognis Ltd.

### Method

#### Synthesis of carbonated soybean oil

Carbonated soybean oil (CSBO) was prepared by weighing 100 g of ESBO and placed in a 500 mL three necked reactor. 6.5 g/100g ESBO of the catalyst TBAB and carbon dioxide at a rate of 0.2 mL/s were added. The reactor was then heated in a oil bath to 140 °C at atmospheric pressure with continuous stirring at the speed of 700 rpm for 72 h. The reaction was monitored by means of IR and was terminated when there was complete conversion.

#### Synthesis of non-isocyanate polyurethane (NIPU)

12 g of CSBO was weighed and placed in 100 mL Erlenmeyer flask. 7 mol % of lithium chloride was dissolved in 20 mL tetrahydrofuran (THF) and then added to the flask. The reaction mixture was mixed thoroughly for 4 min, thereafter; 3-aminopropyltriethoxysilane in ratio 1:1 with CSBO was dropped into the reaction mixture. The reaction mixture was heated at 70 °C for 3 h with constant stirring, then, various contents of Kraft lignin (20 – 50 wt %) in powder form dissolved in THF/water solution in 60/40 v/v was added to the reaction mixture and stirred for 12 h. The resulting mixture was poured into a cup mold and dried for 2 h. It was then cured at 70 °C for 6 h.

#### Characterization

FTIR spectroscopy was performed on a Perkin-Elmer FTIR spectrometer using attenuated total reflectance (ATR) technique for recording. The total number of scans was 32 and the resolution 4 cm<sup>-1</sup>.

Tensile properties were determined according to ASTM D 882-97 using an Instron testing machine (Hampden Co., UK) with a load cell of 5 kN with self-tightening grip. The test specimens were 45 x 12 x 12 mm<sup>3</sup> in dimension. The tests were carried out at the speed of 5 mm/min.

#### Results and Discussion

Preparation of Carbonated soybean oil (CSBO) and functionalization with organosilane

The synthesis steps for the preparation of CSBO are shown in Figures 1 and 2. In the first step (Figure 1), ESBO was modified through chemical fixation of CO<sub>2</sub> on the epoxide groups to form cyclic carbonate in the presence of TBAB catalyst. The epoxide ring of the soybean oil was attacked by the bromide of the catalyst to effect ring opening. This was followed with nucleophilic attack of the catalyst alkoxide at the carbon dioxide. Ring closure of the carboxylate produce the five-membered cyclic carbonate (Tamani *et al*, 2004). In Figure 2, the cyclic carbonate was reacted with APES to form the polyamine group that reacted with the kraft lignin, forming the polyurethane (Figure 3).

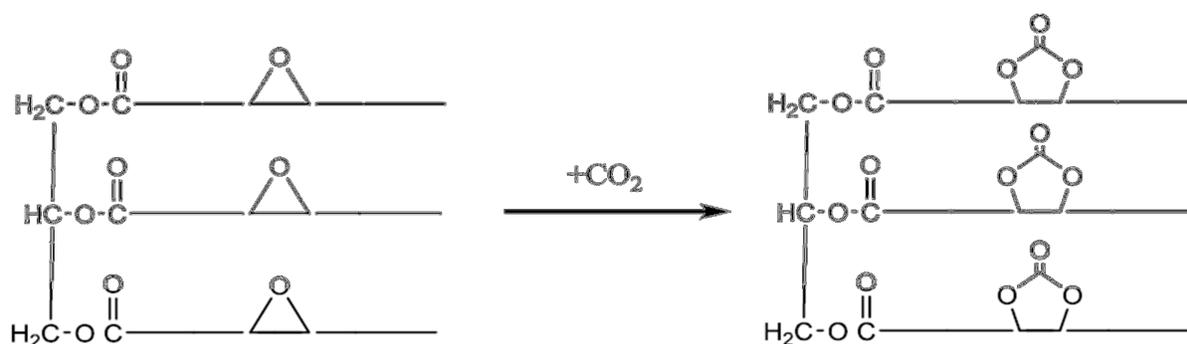


Figure 1: The scheme for the Formation of Cyclic Carbonate from Reaction of ESBO and CO<sub>2</sub>

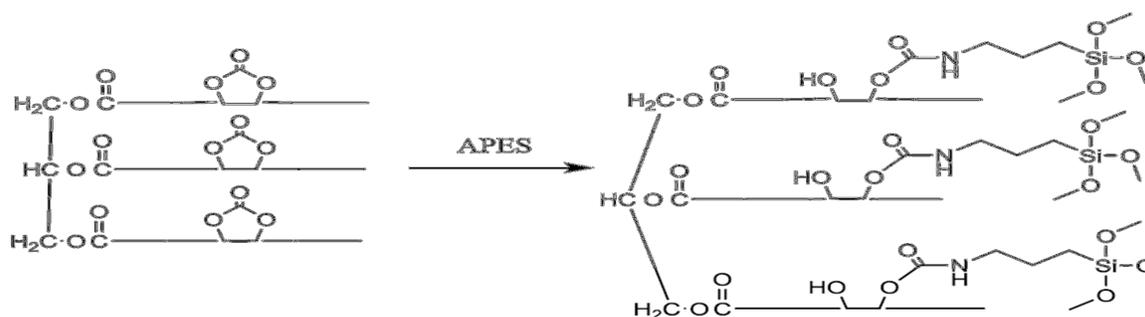


Figure 2: The scheme for the Formation of Urethane Monomer from Reaction of Cyclic Carbonate and APES

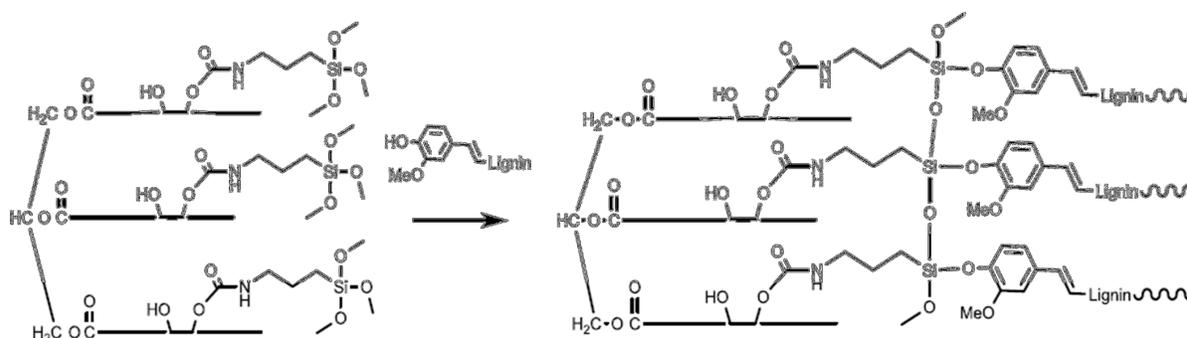


Figure 3: The Scheme for the Formation of Polyurethane

The conversion of epoxide to cyclic carbonate occurred at 140 °C and was monitored by IR. Figure 4 shows the FTIR spectroscopy of the conversion with TBAB as catalyst. It can be seen in the FTIR spectra of ESBO and CSBO, that the peak at 833 cm<sup>-1</sup> indicating presence of epoxy group in the ESBO has disappeared in the spectrum for CSBO and replaced with a new peak at 1803 cm<sup>-1</sup> corresponding to absorption for cyclic carbonate carbonyl. This shows that the ESBO has been converted to CSBO.

### Preparation and Characterization of non-isocyanate polyurethane (NIPU)

In this study, NIPU was synthesized from CSBO reacted with APES which afford cyclic carbonate ring opening producing the urethane monomer which was further reacted with lignin. The optima condition for the urethane monomer formation to go to completion without any residual epoxide group was selected as 3 h (Javni *et al.*, 2008). Concentration of lignin in the reaction for NIPU formation was varied from 20 - 50 wt%. It has been reported that if the reaction for urethane monomer

formation is stopped sooner than the 3 h optimum, there would be residual epoxide in the NIPU which cannot react with lignin if the time was below 3 h and if the reaction was taken beyond 3 h before addition of lignin, the urethane monomer would polymerize itself and would be incapable of forming NIPU with lignin (Javni *et al*, 2008; Bähr and Mülhaupt, 2012). Therefore, it was taken that the NIPU produced in this study do not contain any residual epoxide group.

The FTIR of CSBO, lignin, and polyurethane containing lignin (NIPU) is shown in Figure 5. By the peak at  $1801\text{ cm}^{-1}$ , the carbonyl carbon of the cyclic carbonate of CSBO disappeared.

A new peak at  $1710\text{ cm}^{-1}$  assigned to urethane linkage (-NHCOO-) appears and it can be seen that vibrations at  $1043\text{ cm}^{-1}$  assigned to Si-O-Si overlaps with the peaks of CSBO. Further, the position shift of aromatic bands around  $1600\text{ cm}^{-1}$  can explain the covalent linkage between the aromatic lignin and APES (Rasmussen *et al* 2014). Therefore, in Figure 6 a clear evidence of the covalent bond formed between phenolic -OH of lignin and APES is given by the position shift the lignin aromatic bands from (1, 2) to (3, 4).

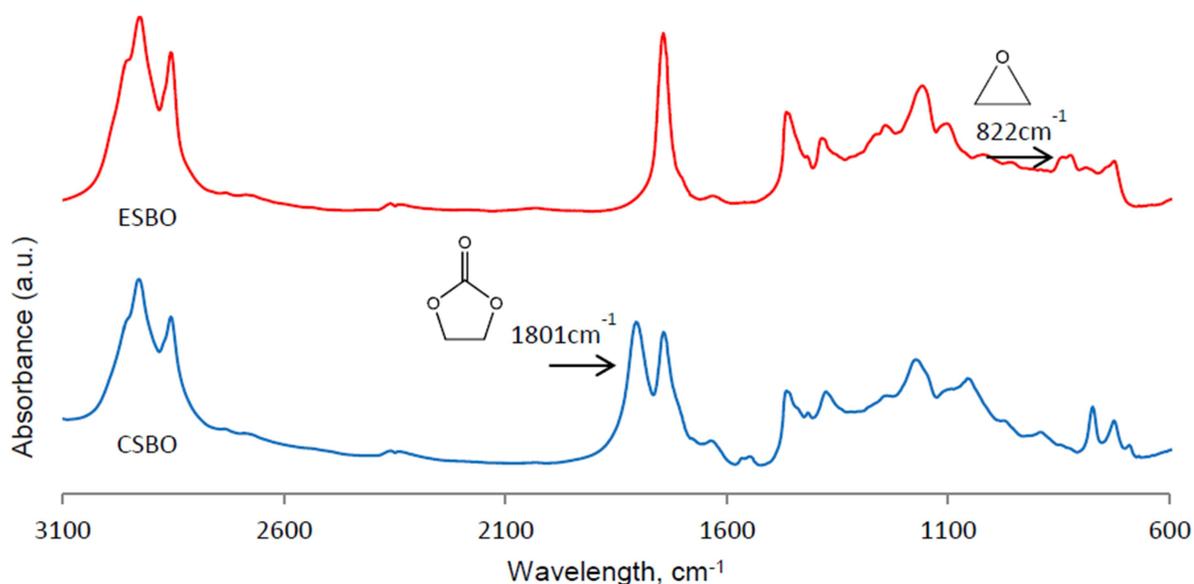


Figure 4: FTIR Spectrum of ESBO (top) and CSBO (bottom)

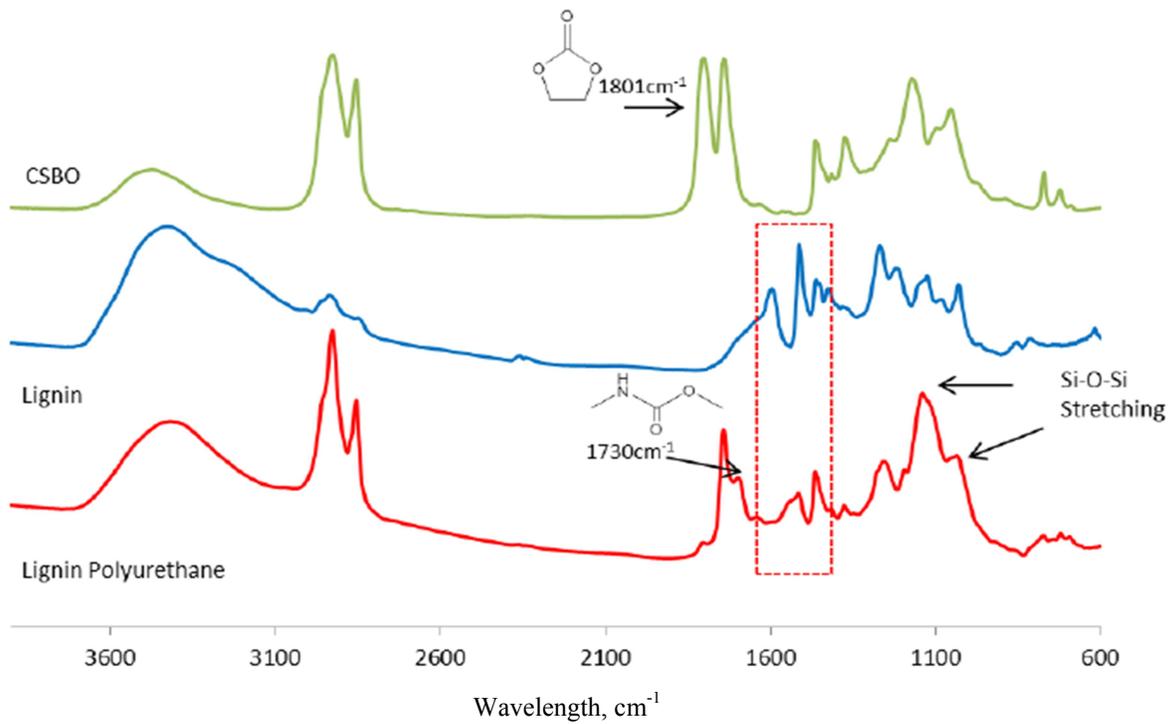


Figure 5: FTIR Spectra of Lignin Polyurethane (NIPU), Lignin, and Carbonated Soybean Oil

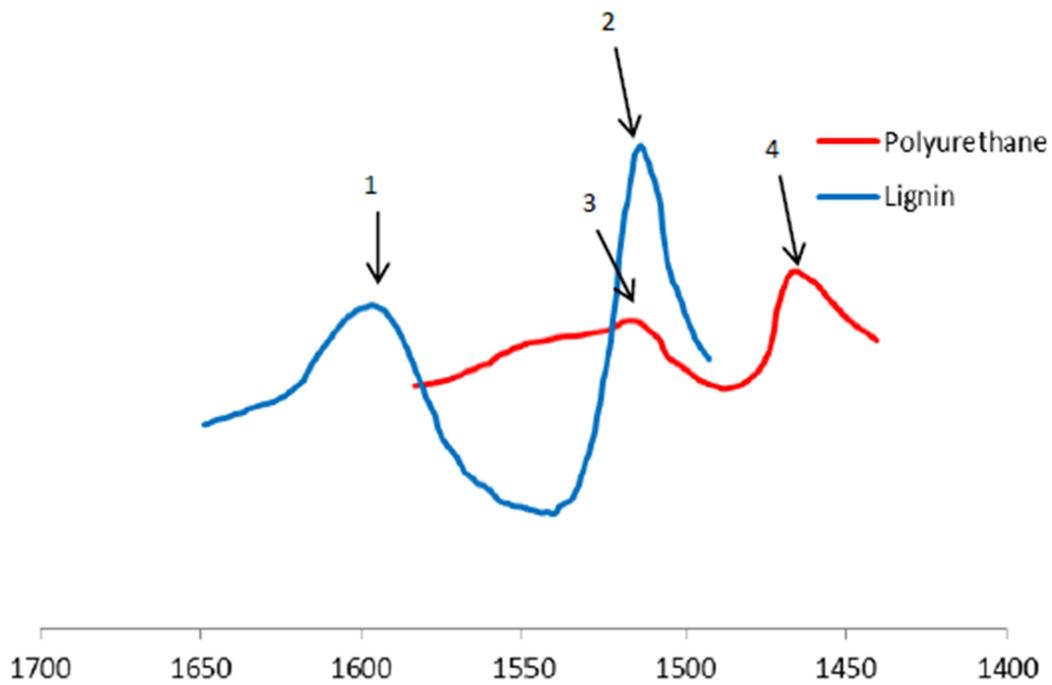


Figure 6: FTIR Spectrum of Polyurethane and Lignin at 1650-1450 cm⁻¹ Region

### Mechanical properties of NIPU

The tensile strength of non-isocyanate polyurethanes prepared at room temperature and at a curing temperature of 70 °C is shown in Figure 7. As can be seen the tensile strength of the NIPU cured at 70 °C increases as the lignin content in the NIPU is increased, while the tensile strength of the NIPU prepared at room temperature did not show any appreciable improvement with increase in lignin content. For all the NIPU cured at a higher temperature, the formation of three dimensional space networks as a result of the rigid aromatic structure of the lignin and its crosslinking characteristics resulted in the high tensile strength. This observation is similar to those reported by other studies on the relation of lignin content and tensile strength of polyurethane (Chung and Washburn, 2012; Bähr and Mülhaupt, 2012). Further, Bähr and Mülhaupt reported that hydrogen bonds formed between hydroxyl groups and carbonyl group of the urethanes accounted for higher water absorption, improved resistance to organic solvents, increased Young's modulus, and higher tensile strength in NIPUs compared to conventional polyurethane (PU) and that NIPUs exhibit improved thermal stability because of the absence of labile biurets and allophanes (Figovsky and Shapovalov, 2002) which are common occurrence in conventional PU.

Figure 8 shows the elongation at break of the NIPUs, where it can be seen that the property increased with the lignin contents when the NIPUs

are prepared at room temperature compared to the elevated temperature of 70 °C. This observation could be explained as follows: at low temperature the lignin rather than acting as a crosslinking agent and react with the urethane monomer instead blends with the monomer, thus many free silanols are available to react with each other and form siloxane bonds (-Si-O-Si-) which are known to be flexible as a result of large bond angles and lengths. Siloxane bonds act as soft segment in polymer networks (Plueddemann, 1991), consequently, in the NIPU prepared in this study, the cross linked polymer contain more siloxane bonds than lignin contributing to the increased higher flexibility. This is contrary to established phenomenon of how lignin affects the elongation at break of polymer which is to reduce the property and act as hard segment as lignin content is increased. It is surprising to note that the opposite is what results from this work. As the lignin content is increased, less and less space is available in the polyurethane at high lignin content for free silanols to react with each other and form three dimensional siloxane but would rather form linear -Si-O-Si-bridges, which would form high flexibility polymer as a result of low cross link density. Though, much space will be available for free silanols to react at low lignin content, the NIPU polymer also exhibit high flexibility at low lignin content. This is because the free silanols are very likely to react with higher probability, forming complex three dimensional siloxane networks and ultimately forming higher cross link density.

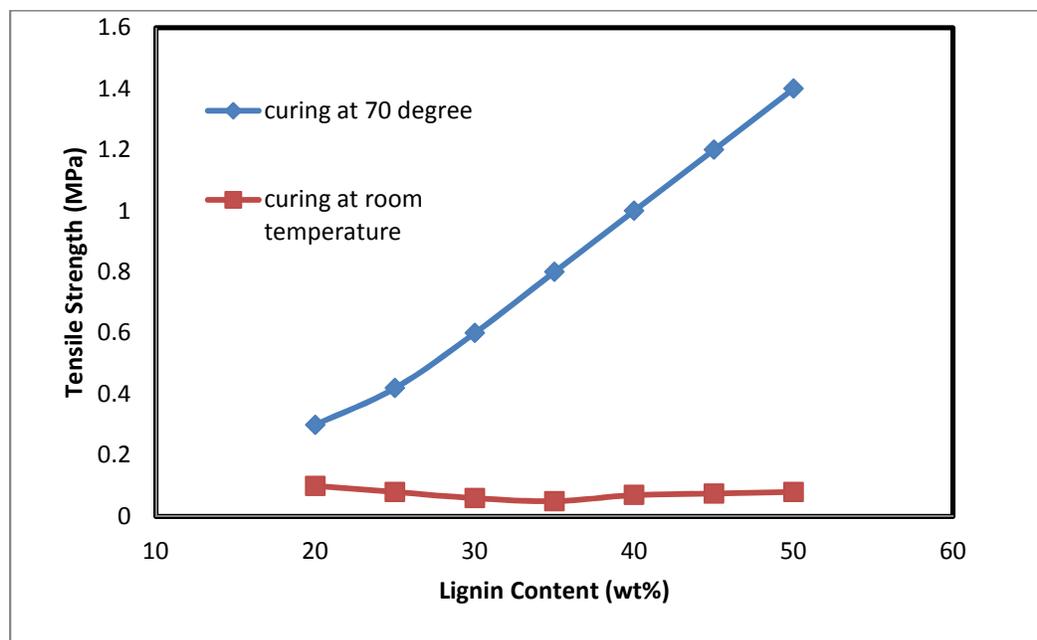


Figure 7: Tensile Strength of NIPUs with Different Lignin Contents

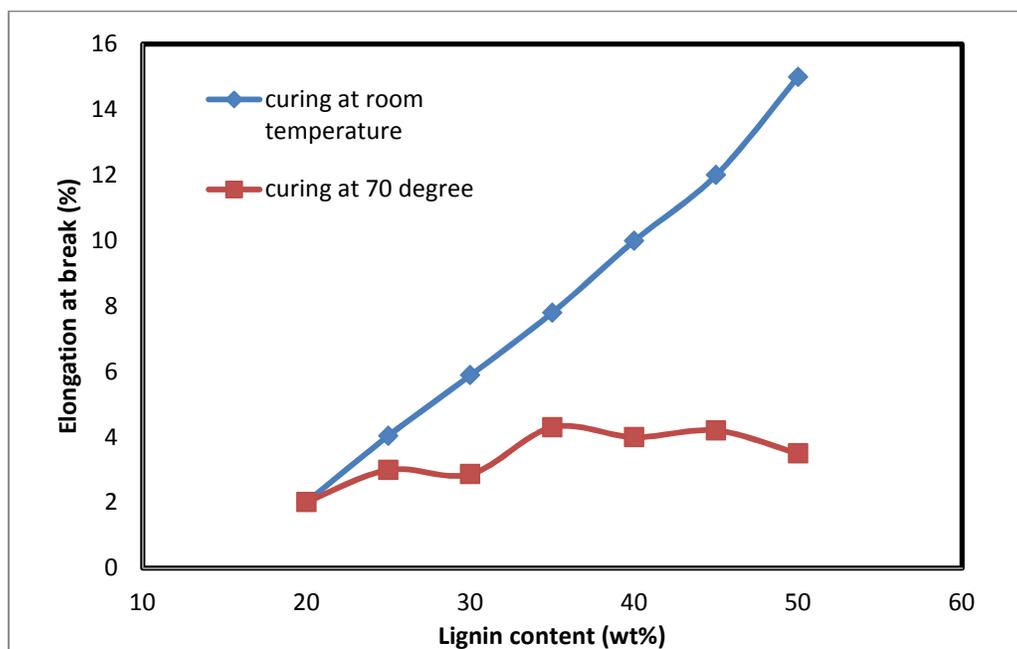


Figure 8: Elongation at Break of NIPUs with Different Lignin Contents

## CONCLUSION

The use of purely renewable resourced materials-CSBO and lignin as the starting materials for non-isocyanate polyurethane has been studied. CSBO was reacted with APES in the presence of TBAB catalyst to produce the urethane monomer. The urethane monomer was then reacted with kraft lignin with lithium chloride as catalyst. The kraft lignin content was varied from 20 – 50 wt%. The essence was to produce polyurethane that is hydrolytically stable and resistant to organic solvents with resultant immobilization of carbon dioxide by the green process employed. Effect of lignin content on tensile strength and elongation at break of NIPUs were studied. The following observations were made:

- i. This study confirmed the technical feasibility of synthesizing non isocyanate polyurethane from renewable agricultural resources as replacement for conventional polyurethanes.
- ii. The lignin content and curing temperature strongly affect the tensile strength and elongation at break of the NIPUs.
- iii. The NIPU properties can be altered from highly rigid to highly elastic by controlling the temperature and lignin content. For example, if desired product is a rigid lignin thermoplastic, then high contents of lignin should be used and cured at higher

temperature in order to achieve high tensile strength.

- iv. Sustainable implementation of the green process can contribute to the avoidance of the use of toxic and environmentally hazardous materials and can be performed in wide range of applications such as coatings, adhesives, sealants, paintings, and elastomers.

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