Hydrolytic Liquefaction of Hydrolysis Lignin for the Preparation of Bio-based Rigid Polyurethane Foam

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Hydrolytic Liquefaction of Hydrolysis Lignin for the Preparation of Bio-based Rigid Polyurethane Foam

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Highlights

1. Hydrolysis lignin (HL) was liquefied in un-catalyzed water-ethanol mixture.
2. A low M_w (~1000 g/mole) LHL was obtained with high functionality/hydroxyl numbers and yield.
3. Powdered/solid LHL was derivatized into liquid polyols via oxypropylation for rigid PU foams.
4. Bio-based rigid PU (BRPU) foams were prepared with 50-70 wt.% bio-contents.
5. All BRPU foams exhibit good compression strengths and low thermal conductivity.

Abstract

Hydrolysis lignin (HL) was liquefied to low average molecular weight (M_w) intermediate employing 50/50 (v/v) water-ethanol mixture. The effects of process parameters including reaction temperature, reaction time and HL concentration were investigated and the liquefied hydrolysis lignin (LHL) products obtained were characterized with GPC, FTIR and ^{1}H NMR. The best operating conditions appeared to be at 250 ^{o}C, 1 h with 20% (w/v) HL concentration, leading to ~70 wt.% yield of LHL (M_w ~1000 g/mole and OH_{Total} ~442 mgKOH/g). The solid form LHL was derivatized into liquid polyols via oxypropylation with 50-70 wt.% bio-contents which was subsequently utilized for the preparation of bio-based rigid polyurethane (BRPU) foams. All the foams were characterized in terms of their physical, mechanical and thermal properties & morphology. BRPU foams exhibit superior compression modulus and strengths than reference foam prepared from commercial sucrose polyol provided by Huntsman Co. At a fixed formulation, i.e., fixed percentage of physical blowing agent, BRPU foams showed the following sequence in terms of their compression modulus: sucrose polyol reference foam (2695.0 kPa) <LHL50PO50 (9202.0 kPa) <LHL60PO40 (19847.0 kPa) <LHL70PO30 (21288.0 kPa). All BRPU foams were thermally stable up to approximately 200 ^{o}C and thermal conductivity was low (0.030±0.001 W/mK), making them suitable for insulation material.

Keywords: Hydrolysis lignin, liquefaction, oxypropylation, polyols, rigid polyurethane foam.

1. Introduction

Polyurethanes (PUs) are a broad class of polymers having urethane (-NH-(C=O)-O-) moieties as a main linkage that are known for their versatility. Foam materials represent the most important commercial products made of PUs and are commonly classified as flexible, semi-rigid and rigid foams, depending on cell morphology (closed or open), mechanical characteristics and densities. Among foamed polymers used commercially, rigid polyurethane (RPU) foams have the lowest thermal conductivity.[2] RPU foams have been widely utilized in appliances and the construction industry because of their unique combination of excellent thermal insulation and mechanical properties. PU foams are available in a wide range of densities from approximately 30-200 kg/m^3 depending on applications.[3] For example, the required density for thermal insulation in buildings lies in the range of 30 kg/m^3 to 45 kg/m^3.[4]

Nowadays the production of PU mostly depends on petroleum-derived feedstocks.[1] Due to the rapid depletion of petroleum reserves and increasing prices, there has been increasing interest in exploring biomass resources as an alternative to petroleum based materials.[5] The major advantages in utilizing biomass include: (1) biomass is renewable and available world-wide, (2) biomass contains negligible sulfur and other detrimental elements, and (3) biomass can be regarded as a carbon-neutral resource as the utilization of biomass does not result in a net increase in the CO_2 concentration in the atmosphere.[6] Therefore, biomass is a promising alternative source for polyols production.

Lignocellulosic biomass consists of three major components: cellulose, hemicelluloses and lignin. Cellulose comprises the largest fraction of the biomass ranging 30-50% of the total dry mass.[7] Polysaccharides, i.e., cellulose and different hemicelluloses are the primary constituents of wood and agriculture plant stems. Cellulose is a homo-polymer of D-glucose, joined by β-(1-4) glycosidic linkages, whereas the hemicelluloses are heteroglycans containing several different types of neutral (pentose and hexose) and acidic (uronic acid) monosaccharides as structural elements. Enzymatic hydrolysis of woods and pulp is an already established approach for the degradation of wood fibers. Delignification or acid pre-hydrolysis may be required in order for the enzymes to access the degradable cellulosic components in wood. During enzymatic hydrolysis the polysaccharides in the woody biomass are broken down by the enzymes and the reaction is not hindered by the presence of lignin or lipophilic extractives as long as the enzymes can come into contact with the polysaccharides. This result in the removal of most of polysaccharides and left lignin and extractives as a residual byproduct called hydrolysis lignin (HL) [8-9], composed of some unreacted cellulose, mono and oligosaccharides, with lignin comprising 50 to 60% of the mass.[10] Consequently, the cellulose and hemicelluloses in chemical pulps can be effectively hydrolyzed to monosaccharide components by enzymes. The HL is usually utilized for producing heat via direct combustion. However, lignin is a natural, aromatic complex biopolymer of three phenyl-propanols, i.e., *p*-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol,[11] can be a promising source of phenols, aromatics and polyols. The phenyl-propanols are linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., α-O-4 and β-O-4).[12] The ether linkages, especially β-O-4, under proper reaction conditions, can be easily cleaved to form two hydroxyl groups. Biomass is therefore, a promising alternative source of polyols (polymers having multiple hydroxyl groups in their structure) and via further reaction with polyisocyanates to form PUs.

The present paper focuses on the use of hydrolysis lignin (HL) – a by-product from pre-treatment processes in cellulosic ethanol plants, for the preparation of polyols and their utilization in the preparation of RPU foams with high bio-contents. In order to overcome the low reactivity of HL, which is an insoluble material with lignin still combined with residual cellulose and hemicellulose, an effective and promising approach may be the direct hydrothermal liquefaction of HL. Typical direct liquefaction processes include fast pyrolysis and solvolytic liquefaction. Solvolytic liquefaction is more advantageous than fast pyrolysis (usually above 450 ^{o}C) because it can be carried out in an organic solvents such as alcohols at much lower temperatures (<300 ^{o}C).[13] Liquefaction processes dissociate the lignin and carbohydrates and partially cleave the primary and secondary ether bonds in both lignin and high molecular weight carbohydrates (cellulose and hemicellulose) into lower molecular compounds. As a result, the insoluble solid lignocellulosic biomass is converted into a soluble OH-rich product which can potentially be used as a substitute for polyether polyol in the preparation of PU foams.[14-15]

In the literature, a number of studies have been reported for the hydrothermal liquefaction of different biomasses employing water as a solvent and their utilization for PU foams preparation.[16-20] However, the yields of desired products were low, between 25-60 %. Higher yields were obtained using organic solvents or water/solvent mixtures. Cheng et al. reported that ethanol-water mixture (50/50, v/v) proved to be more effective solvent for the liquefaction of biomass than either solvent on its own, exhibiting synergistic effect on the direct liquefaction of biomass.[5] They carried out direct liquefaction of white pine saw dust in a 50 wt.% ethanol-water medium and achieved approximately 66 wt.% bio-oil yield after 15 min reaction at 300 ^{o}C (M_w ≈1373 g/mole) and used the resulting bio-oil as a substitute for phenol in the production of phenol-formaldehyde (PF) resins. Inspired by the above research work, the present work is attempted to liquefy HL using a water-ethanol mixture to obtain liquefied HL (LHL) for the utilization in the preparation of PU foams.

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The major objectives of this work were to (1) liquefy/de-polymerize HL employing a water-ethanol mixture and investigating the effects of process parameters (reaction temperature, time and HL concentration) to find the best operating conditions, (2) oxypropylate LHL, obtained at the optimized operating conditions, to obtain liquid polyols with high bio-contents (50 wt.% - 70 wt.%), and (3) prepare and characterize BRPU foams using oxypropylated LHL. It should be noted that although with a conventional lignin de-polymerization/liquefaction route, this work focused more on valorization of liquefied hydrolysis lignin (LHL) for the production of bio-based rigid polyurethane foams with a high percentage of bio-contents i.e., up to 70 wt.%, which has not been reported in public literature to the best of our knowledge. This was achieved by the oxypropylation of liquefied lignin in the presence of acetone solvent that can not only dissolve the LHL, but also facilitate the complete transformation of the phenolic hydroxyl groups to aliphatic hydroxyl groups via the oxypropylation. Also, the moisture free mixture of (glycerol + 11% KOH) was used to avoid the formation of poly(propylene oxide) (PPO) oligomers. Thus, the submitted work was aimed not to improve the conventional depolymerization/liquefaction process, but to advance the oxypropylation process and further utilization of the oxypropylated LHL in bio-based rigid polyurethane foams.

2. Methods

2.1. Materials

The hydrolysis lignin (HL) used in this study was provided by FPInnovations and was not soluble in any solvents.[10] The HL was the residual of sugar/ethanol production from Aspen wood that is composed of 30-55 wt.%, cellulose; 15-35 wt.%, hemicellulose; and 5-31 wt.%, lignin. The novel bio-conversion process as shown in Fig. 1, outlined by Yuan et al. comprises of low- pressure mechanical refining to disintegrate biomass feedstock (aspen wood), hemicellulose extraction, enzymatic hydrolysis, sugar/lignin separation, and fermentation.[10] Lignocellulosic biomass is first subjected to mechanical refining at a set of conditions (temperature, pressure, time etc). If desired, the biomass could be subjected to a chemical treatment to obtain valuable anti-oxidants and to facilitate the separation of biomass in the subsequent fractionation process. The treated substrates are collected as pulp from the mechanical refining. Cellulose enzyme catalyzes the conversion of cellulose to glucose which can then be processed to various products, including sugar alcohols, sugar acids and biofuels. The hydrolysis of wood feedstock results in a solid residue which contains primarily lignin. Since few chemicals are employed in the process, compared to traditional kraft lignin and steam-explosion lignin, the lignin thus produced is of low inorganic impurity and sulfur free, similar to that of neutral native lignin with little degradation. The chemical components of the raw hydrolysis lignin as well as its elemental compositions are presented in Table 1.

The other chemicals used in the study were NaOH, acetone, pyridine, acetic anhydride, HCl, dibromomethane, ethanol, polymeric MDI, sucrose polyol (JEFFOL SD-361), triethanolamine, triethylene diamine (TEDA), stannous octoate, silicon oil, glycerol etc., All were reagent grade, purchased from Sigma-Aldrich, and used as supplied.

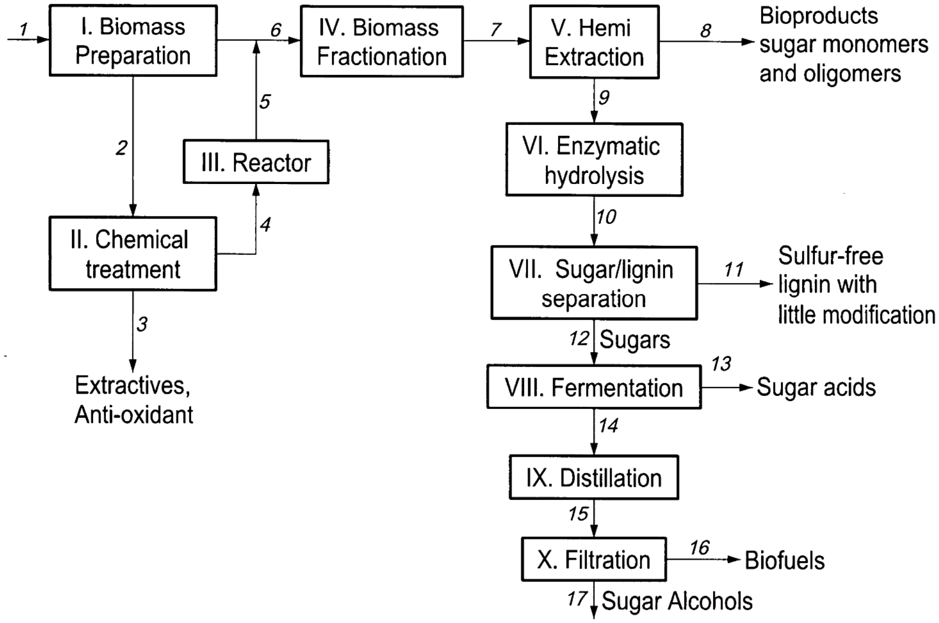

Fig. 1. Schematics of the fractionation process for the production of value-added products from lignocellulosic biomass

Table 1.Chemical and elemental composition (d.a.f) of hydrolysis lignin (HL) [10]

Component	Mass fraction (%)
Lignin %	56.7
Carbonhydrates %	29.8
Ash %	1.2
Others, %	12.3
Carbon, %	62.8
Hydrogen, %	6.1
Nitrogen, %	4.0
Others, %	28.3

2.2. Hydrolysis lignin liquefaction

The liquefaction of HL was carried out in a 500 mL stainless-steel autoclave reactor equipped with a stirrer and a water-cooling coil. In a typical run, the reactor was loaded with 60 g of HL and 300 mL of denatured ethanol-water (50/50 v/v) co-solvent. The reactor was sealed, purged and was subsequently pressurized to 2 MPa with nitrogen to prevent the reactive material from boiling over the course of the heating process. The reactor was heated to the reaction temperature (in 30 min) and kept at the desired temperature for 60 min before cooling. Once the reactor had cooled to room temperature, the negligible gaseous products were vented into the fume hood. The liquid products and solid residue (SR) were rinsed from the reactor with acetone, and the resulting suspension was filtered under vacuum through a pre-weighed Whatman No. 5 filter paper. The SR products and filter paper were dried at 105 °C for 24 h before weighing. The organic solvents in the filtrate were then removed by rotary evaporation under vacuum at 40-50 °C. The yields of LHL and SR were calculated as the mass fraction of each product relative to the mass of the HL loaded into the reactor. Each experiment was performed twice or thrice to reduce the experimental error to ± 5%.

2.3. Oxypropylation of LHL

The LHL obtained at the best operating conditions, still in solid form, was transformed into a liquid polyol by oxypropylation and used as a bio-based polyol, as a feedstock for the preparation of PU foam. Oxypropylation of LHL was carried out in a 100 mL Parr reactor. In a typical run, 18.9 g of LHL, 21.21 g

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propylene oxide (PO), 2.31 g of anhydrous glycerol & KOH (%KOH in mixture was 11 wt.%) and 16.8 g of acetone. After all the ingredients were loaded, the reactor (under atmospheric pressure) was heated up to 150 °C. Initially, the pressure in the reactor increased to a maximum of 150 psig and then decreased to a stable pressure of ~14.7 psig (or 1.0 atm-g) after 2 h reaction, implying complete consumption of PO or completion of the reaction. After cooling the system to room temperature, the reactor contents were completely rinsed into a beaker using acetone followed by neutralization of the reaction mixture using sulfuric acid. The neutralized reaction mixture was then filtered through a Buchner funnel to separate the solid residues from the acetone soluble phase. The acetone soluble filtrate was transferred to a pre-weighed flask and the acetone and unreacted PO (if any) were removed by rotary evaporation at 60 °C.

2.4. Rigid polyurethane foam (RPUF) preparation

All of the foam samples were prepared in 455 mL plastic cups using a one pot method. Typically, the rigid PU foam formulation in this study includes a polyol combined with 10% (w/w) glycerol (a co-crosslinking agent), a physical blowing agent (acetone at 20% (w/w)), equal amounts of stannous octoate and triethylene diamine at 2% (w/w) as catalyst, surfactant at 2% (w/w) and water at 2% (w/w). For comparison, reference foam was prepared using sucrose polyols. The amounts of the blowing agent, catalyst, surfactant and water were determined with respect to the total weight of polyol used. PMDI was added at a NCO/OH ratio of 1:1. The foam preparation procedure used was comprised of the following steps: (1) the polyols, catalysts and blowing agents were all weighed into a cup and mixed at 550 rpm for 10-12 s to obtain a homogeneous mixture and (2) a predetermined mass of PMDI was then added to the cup and the mixture was stirred vigorously for another 12-15s. The mixture was then placed on a level surface in a fume hood and the foam was allowed to rise at ambient temperature (23±2 °C). All of the foam samples were left in the fume hood for 24-48 h for curing before the sample was collected for analysis. Foam shrinkage, structural uniformity, stability and cell appearance could be observed at this point. Then, the foam samples were conditioned for a minimum of 24 h to a maximum of 1 week prior to further characterization, depending on requirements.

2.5. Product Characterization

The relative molecular weights of the liquefied HL (LHL) and oxypropylated LHL were measured with a Waters Breeze GPC–HPLC (gel permeation chromatography–high performance liquid chromatography) instrument (1525 binary pump, UV detector at 270 nm; Waters Styrylgel HR1 column at a column temperature of 40 °C) using tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min using linear polystyrene standards for molecular weight calibration. The functional groups of the HL, LHL and oxypropylated LHLs were analyzed by Fourier Transform Infrared Spectroscopy (FTIR). Proton nuclear magnetic resonance (^{1}H-NMR) spectra for the LHL and oxypropylated LHLs were acquired at 25°C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from -2 ppm to 14 ppm (sw =9000.9 Hz). Quantitative ^{1}H-NMR analysis was realized using acetylated samples of LHL and oxypropylated LHL. Briefly, 1 g of dried sample was dissolved in a 1:1 (v/v) mixture of pyridine (5 mL) and acetic anhydride (5 mL) followed by stirring for 24 hr. The mixture was then transferred into a beaker containing 100 mL of ice-cooled 1 wt.% HCl solution. The resulting precipitates of the acetylated samples were washed with distilled water to pH ≈7. The samples were then vacuum dried at 60 °C for 24 hr to remove residual water prior to the quantitative ^{1}H-NMR analysis. Dibromomethane (CH_2Br_2) was used as an internal standard with a characteristic peak at 4.9 ppm for hydroxyl number estimation of the LHL and oxypropylated LHL by ^{1}H-NMR spectra. The samples were prepared by dissolving 30.0 mg of the acetylated LHL or oxypropylated LHL and 15.0 mg of the internal standard in *d*-chloroform (≈1000-1500 mg) then transferred into a 5 mm NMR tube via a transfer pipette for analysis. Solid state NMR spectra for the foam sample were acquired while spinning at 13.5 kHz. As a comparison, hydroxyl numbers of the oxypropylated

LHL samples were also measured as per ASTM D4274-99 using a Potentiometric Titrator (Titroline 7000 Titrator). The two results coincided very well. The filtered sample of freshly prepared LHL was dissolved in acetone to make a homogeneous solution of a concentration of approx. 0.1 wt.% for GC-MS analysis. GC-MS analysis was conducted with an Agilent 7890B GC coupled with a 5977A MSD using a 30 m × 0.5 mm × 0.25 µm DB-35ms column with temperature programming as follows: a 2 min hold at an initial temperature of 60 ^{o}C followed by a 10 ^{o}C min^{-1} ramp to the temperature of 120 ^{o}C with a 0 min holding time and finally the temperature was raised to 280 ^{o}C with a 8 ^{o}C min^{-1} ramp with a 5 min hold. The viscosity of the oxypropylated LHL sample was measured by using BROOKFIELD CAP 2000+VISCOMETER at 80 ^{o}C.

The apparent densities of foam samples were measured according to ASTM D1622-03. The mechanical properties of PUF samples were measured at ambient conditions on an ADMET Universal Testing Machine (Model SM-1000-38). Modulus of elasticity (Young's modulus or compressive modulus) (initial linear slope of the stress-strain curve) and compressive strength at 10% deformation, were determined by performing the stress-strain tests according to ASTM D 1621-00. Thermal conductivities of the foam samples were measured using a KD2 PRO thermal properties analyzer with SH-1 dual needle sensor (1.3 mm diameter x 3 cm long, 6 mm spacing) capable of measuring thermal conductivity in the range of 0.02 to 2.00 W/mK. The specimen size used for thermal conductivity analysis was 40 mm x 40 mm x 20 mm. Thermal stability and thermal decomposition of the foams were measured using a *Pyris*^{TM} Diamond, Perkin–Elmer Thermogravimetric analyzer (TGA), under a N_2 and air flow (20 mL/min) respectively, from 30 ^{o}C to 800 ^{o}C at 10 ^{o}C/min. The glass transition temperature (T_g) of the foam samples was determined using a DSC (differential scanning calorimeter: Mettler Toledo DSC 1) under a N_2 flow (50-60 mL/min) where the sample was heated at a heating rate of 10 ^{o}C/min from 50-350 ^{o}C. Morphology of the foams was observed by a Hitachi S-4500 field emission cross beam scanning electron microscope (SEM). After examination by SEM, selected locations on the foam surface were subjected to a cross-sectional cut and the sample was coated with osmium, and imaged using a focused ion beam LEO (Zeiss, Thornwood, NY, USA) 1540XB SEM.

3. Results and discussion

3.1. Liquefaction of HL: Effects of process parameters

3.1.1. Effects of reaction temperature

Temperature is the most critical parameter for the liquefaction of lignocellulosic materials in a water/organic solvent. When biomass was heated in hot compressed water, solvolysis of hemicellulose and lignin begins to occur at temperature >190 ^{o}C, and all of the hemicellulose and much of the lignin is dissolved in water at 220 ^{o}C.[21-22] The effects of reaction temperature (from 150 ^{o}C to 300 ^{o}C) on the liquefaction of HL employing a 50/50 (v/v) water-ethanol mixture are illustrated in Fig. 2. As seen in the Fig. 2, and similar to the results observed by Cheng et al.,[5] increasing the reaction temperature from 150 ^{o}C to 250 ^{o}C increased yield of LHL from ~56 wt.% to ~70 wt.%, indicating the acceleration of liquefaction. However, contrary to the findings of Cheng et al., [5] increasing the reaction temperature to 300 ^{o}C did not further increase the yield of desired product. Rather, the LHL yield decreases to ~66 wt.%. The weight loss could be due to the decomposition and dehydration of carbohydrates and HL to small molecules which were removed with solvent. The yield of solid residues (SR) was found to decrease steadily from ~28 wt.% to ~3 wt.% with increasing reaction temperature.

Increasing reaction temperature (from 150 ^{o}C to 250 ^{o}C) resulted in a decrease in the M_w of the LHL (from ≈1440 g/mole to ≈1000 g/mole. respectively). This M_w decrease can be attributed to the increased availability of energy necessary to cleave the ether linkages in both carbohydrates and lignin. Further increase in temperature to 300 ^{o}C, resulted in increased M_w. This increase may be due to increased repolymerization/condensation reactions at higher temperature which needs more activation energy. Liquefaction and repolymerization reaction occur concurrently during liquefaction. Initially, at lower temperature, liquefaction reactions predominate and lead to the formation of lower M_w products.[23] However, as temperature increases, repolymerization/condensation reactions are gradually enhanced due to the increased concentration of intermediate products in the reaction system. The yield of SRs did not increase at 300 ^{o}C, indicating the complete liquefaction of the biomass. The remaining mass (other than LHL and SRs) could be attributed to the volatile products (monomers, aldehydes, esters and ethers, alcohols, etc.) , understanding that the yield of gases usually formed due to the cleavage of aliphatic propane chain and removal of ring substituents was relatively

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low in this work (≤ 1 wt.%).[24] For simplicity % average yield of others (other than LHL and SRs) was calculated by difference and reported. The GC-MS result of the LHL obtained at 250 °C is presented in Table 2. The relative area percent of TIC (total ion current) for each compound is also shown in Table 2. As shown in Table 2, the detectable compounds are mainly phenolic compounds, various types of ethers and esters, and substituted 5 aldehydes such as benzaldehyde. Given these results, the best reaction temperature for the liquefaction of HL in water-ethanol co-solvent mixture with respect to both yield and M_w of the LHL products, appeared to be 250 °C.

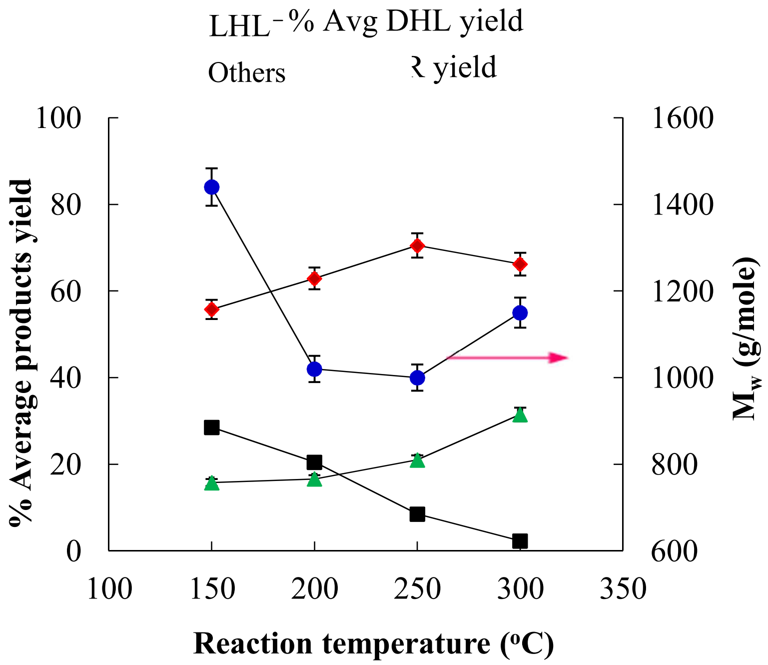

Fig. 2. Effects of reaction temperature on yield and M_w of LHL from HL liquefaction (Other reaction conditions: 10 60 min, 20% (w/v) substrate concentration, EtOH/water ratio of 1.0 and initial-system pressure: 2.0MPa)

Table 2. GC-MS analysis of LHL obtained from HL depolymerization at the 250 °C (Other reaction conditions: 60 min, 20% (w/v) substrate concentration, EtOH/water ratio of 1.0 and initial-system pressure: 2.0 MPa)

Peak number	Retention time (min)	Relative content by percent area	Compound name
1	-	-[a]	-
2	13.0615	17.1	Phenol, 2,6-dimethoxy-
3	13.6532	5.1	Undecanoic acid, 10-methyl-, methyl ester
4	14.3212	8.4	Dodecanoic acid
5	14.5821	11.5	Dodecanoic acid, ethyl ester
6	15.4091	6.6	Hydroquinone mono-trimethylsilyl ether
7	16.497	8.4	2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester
8	17.2668	5.0	Tetradecanoic acid, ethyl ester
9	18.1639	5. 7	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
10	18.3738	14.8	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-
11	19.748	7.1	Hexadecanoic acid, ethyl ester
Total area (%)		89.7	

[a]: *Not including the small peaks with an area less than 2% of the total area.*

3.1.2. Effects of reaction time

The experiments in this section were carried out to examine the effects of reaction time on hydrolytic liquefaction of HL at 250 °C in (50/50, v/v) water-ethanol reaction mixture. The product (LHL and SR) yields and the M_w of LHL obtained from HL liquefaction after various reaction times (30-120 min) are illustrated in Fig. 3. At 250 °C, increasing the reaction time from 30 min to 60 min increased the yield of LHL from ~60 wt.% to ~70 wt.% and was accompanied by a decrease in SR (from ~15.5 wt.% to ~8 wt.%). Further increasing the reaction time to 120 min resulted in the lower yield of LHL (~57 wt.%) accompanied by an increase in SR (~16.0 wt.%). The increased SR indicates pronounced cross-linking reactions between the reaction intermediates. There was almost no change in the M_w of the LHL between 30 min and 60 min. However, prolonged reaction time resulted in a slight increase in M_w, from 1000 g/mole to 1100 g/mole, which may be due to repolymerization/condensation reactions at 250 °C. Thus, based on the yield and M_w of the LHL, 60 min appears to be the optimum reaction time.

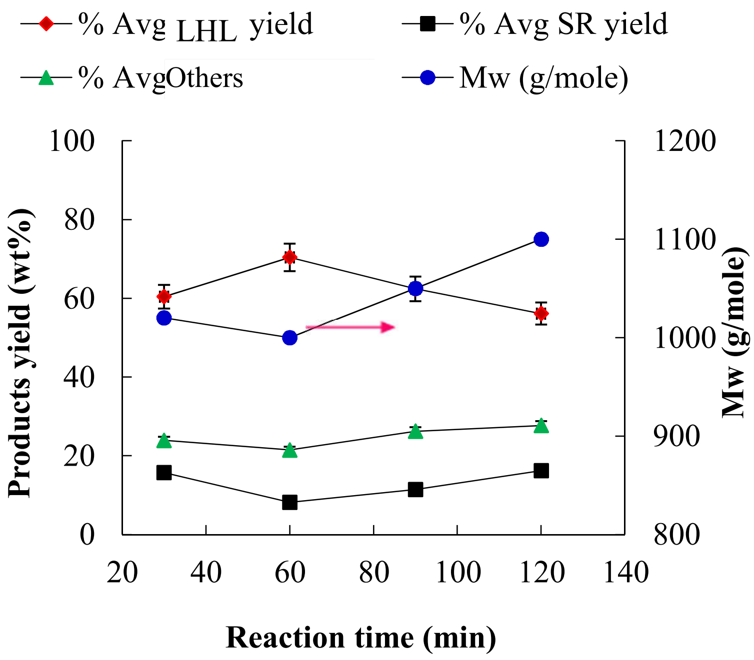

Fig. 3. Effects of reaction time on yield and M_w of LHL (Other reaction conditions: 250 °C, substrate concentration ~20% (w/v), and initial system pressure: 2.0 MPa)

3.1.3. Effects of HL substrate concentration

Feedstock concentration is another important parameter in the hydrothermal liquefaction of biomass, as higher feedstock concentrations improve the overall economics of the process.[25] The effects of solvent to biomass ratio (HL substrate concentration) were investigated by conducting the liquefaction at 250 °C for 60 min using water-EtOH mixture. The product (LHL and SR) yields and the M_w of LHL for different substrate concentrations (5% (w/v) to 30% (w/v)) are illustrated in Fig. 4. From Fig. 4, it can be clearly seen that with the increase in HL concentration from 5% (w/v) to 20% (w/v) the yield of LHL increased from ~54 wt.% to ~70 wt.% and then decreased to ~46 wt.% with a further increase in HL concentration to 30% (w/v). The opposite trend was observed for SR yield. The yield of SR decreased as HL concentration was increased to 20% (w/v) but then increased as the HL concentration further increase. This increase may be due to insufficient solvent to keep the reaction system homogeneous at higher concentrations. This situation would favor the occurrence of pronounced condensation and crosslinking reactions of intermediate products. The M_w of the LHL was found to increase significantly from 850 g/mole to 2250 g/mole as the HL concentration increased from 5% (w/v) to 30% (w/v). This could also be due to the promotion of repolymerization/condensation reactions. Fig. 4 suggests that

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in order to obtain low M_w LHL products, lower HL concentrations (≤ 20% (w/v)) are preferred. However, for process efficiency and economics, it is always better to conduct the experiments at as high concentration as possible. Although, lower substrate concentrations result in lower M_w, the product yields are also lower which would significantly increase the number of runs required to obtain a given amount of LHL product, thus increasing costs. Therefore, to keep balance for high product yield and low M_w, a 20% (w/v) substrate concentration was selected for further runs.

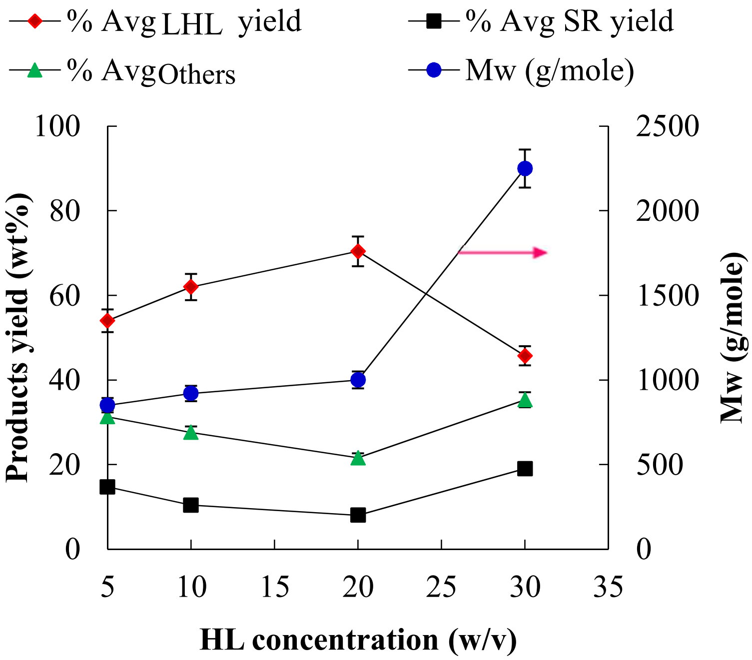

Fig. 4. Effects of HL concentration (w/v) on yield and M_w of LHL (Other reaction conditions: 250 ^{o}C, 60 min, and initial system pressure: 2.0 MPa)

In conclusion, with respect to both yield and M_w of the LHL, the optimal operating conditions for HL liquefaction appears to be at 250 ^{o}C, for 1 h with a 20% (w/v) HL concentration in water-ethanol mixture, leading to ~70 wt.% yield of LHL (M_w ≈1000g/mole and total hydroxyl number ~442 mgKOH/g) with a SR yield ~8 wt.%.

The detailed kinetic analysis for the hydrothermal liquefaction of hydrolysis lignin is very difficult because of the involvement of several parallel (competitive) and consecutive chemical reactions and the formation of tens or even over hundred intermediates and final products. It is impossible to identify and model the individual reactions occurring during liquefaction. Especially in case of hydrolysis lignin the major components are lignin, cellulose and polysaccharides/hemicelluloses. The major liquefaction reaction takes place via the cleavage of ether linkages between lignin-cellulose, lignin-hemicellulsoe and in lignin itself which results in the production of low molecular weight products. Generally, hemicelluloses hydrolyzed much faster than cellulose. Lignin ether bond cleavage also occurs simultaneously with the reaction time and can also lead to the production of intermediates or free-radical fragments which can be condensed via condensation or repolymerization reaction. Also during the liquefaction of hydrolysis lignin the acidity of the reaction media changes from neutral to acidic in the course of the reaction, which catalyze the subsequent reaction. Considering these facts, the liquefaction rate of each component could be significantly different, which in turn would cause the liquefaction rate to change as the reaction proceeds. Therefore, it is very challenging to investigate the reaction kinetics of the multi depolymerization and recondensation reactions.

3.2. Oxypropylation of LHL

LHL obtained at the above best operating condition was used for further experimentation. To obtain a large sample of LHL, a 16 L reactor was used and the products were characterized in terms of M_w, hydroxyl number and yields. The results were found similar to the ones obtained using the 100 mL reactor.

The LHL, although containing a lot of hydroxyl groups and soluble in a number of organic solvents, could be a prepolymer for polyurethane synthesis, was still in liquid form. A number of attempts were made to utilize reasonable amount (20-50 wt.%) of LHL in combination of commercial sucrose polyols for the synthesis of PU foams was not successful due to the poor solubility of LHL. Thus, a chain extension was designed to convert LHL to liquid form through oxypropylation. Also due to the poor solubility of LHL, direct oxypropylation of LHL with propylene oxide gave products of very wide molecular weight distribution and some insoluble product. Several solvents were tested for dissolving LHL in oxypropylation; finally acetone was selected as an ideal solvent. Oxypropylation of LHL was carried at three levels of bio-contents i.e., 50 wt.%, 60 wt.% and 70 wt.%. Oxypropylated samples were analyzed in terms of their M_w, hydroxyl number and viscosity (Table 3). These samples were then further used for the preparation of RPU foams.

Table 3. Characteristics of LHL and oxypropylated samples

Sample ID	M_w (g/mole)	Total Hydroxyl number (mgKOH/g)	Viscosity at 80 °C (Pa.s)	State
LHL	1000	442.0	-	Solid powder
LHL50PO50	1780	221.4	0.39	Viscous Liquid
LHL60PO40	1320	235.8	0.48	
LHL70PO30	1270	253.7	0.64	

The GPC curves of LHL at the best operating condition and its oxypropylated samples with three different bio-contents are provided in Fig. 5. FTIR spectra of sucrose polyol, original HL and LHL at the best reaction condition along with oxypropylated LHLs at different bio-contents are shown in Fig. 6. The spectra were normalized to the intensity of the lignin aromatic ring vibration at 1600 cm^{-1}. In all of the spectra, the O-H stretching vibration at ~3450 cm^{-1} can be easily seen.[26] The oxypropylation for grafting PO onto the lignin is evidenced by the following FTIR observations:(a) an increase in the bands at 2971-2870 cm^{-1} attributed to the stretching of CH_3, CH_2 and CH aliphatic groups; (b) reduction in the intensity of the carbonyl (in lignin) peak at 1714 cm^{-1}; (c) a marked increase of the absorption bands in the ether C-O stretching region (1000-1100 cm^{-1}); and (d) an increase in the band at 1371 cm^{-1} confirming the introduction of CH_3 groups.[27]

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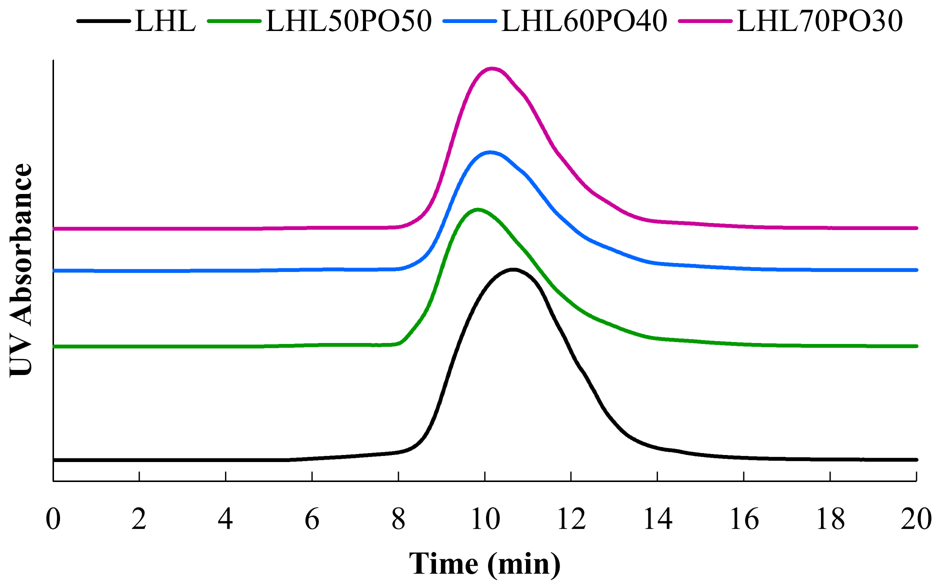


Fig. 5. GPC curves of LHL and oxypropylated LHL samples

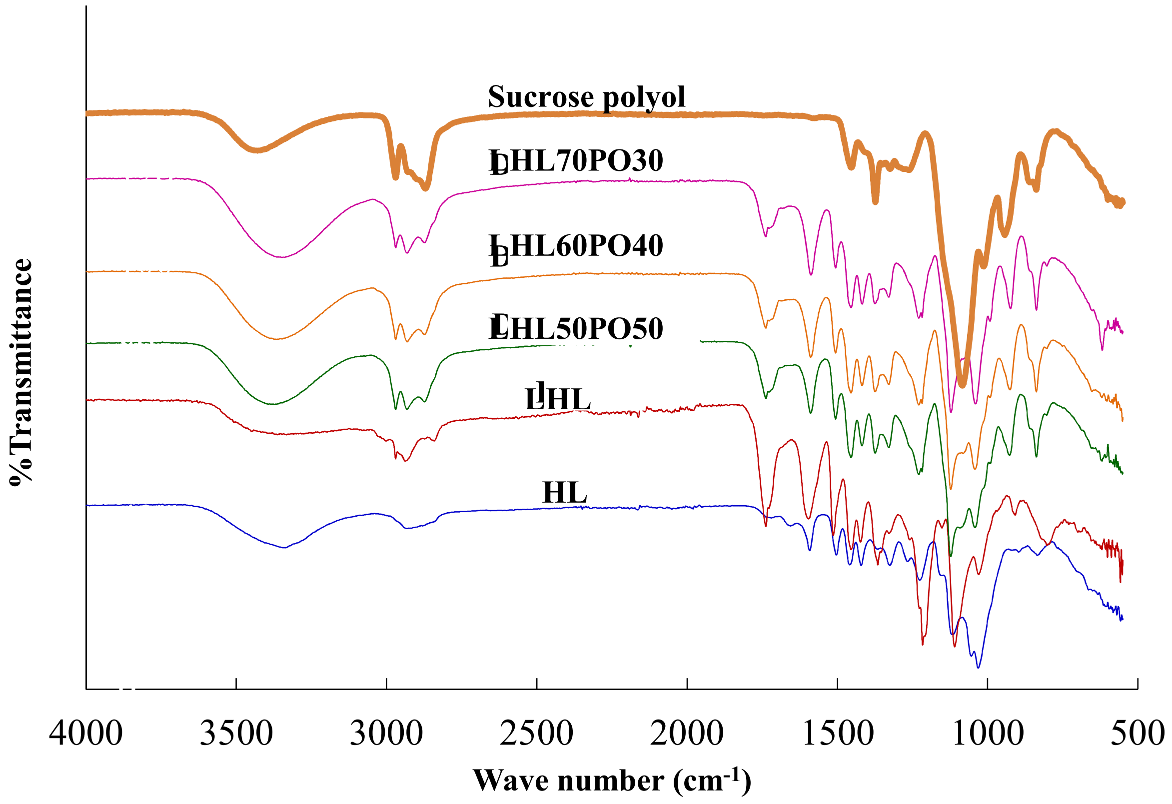
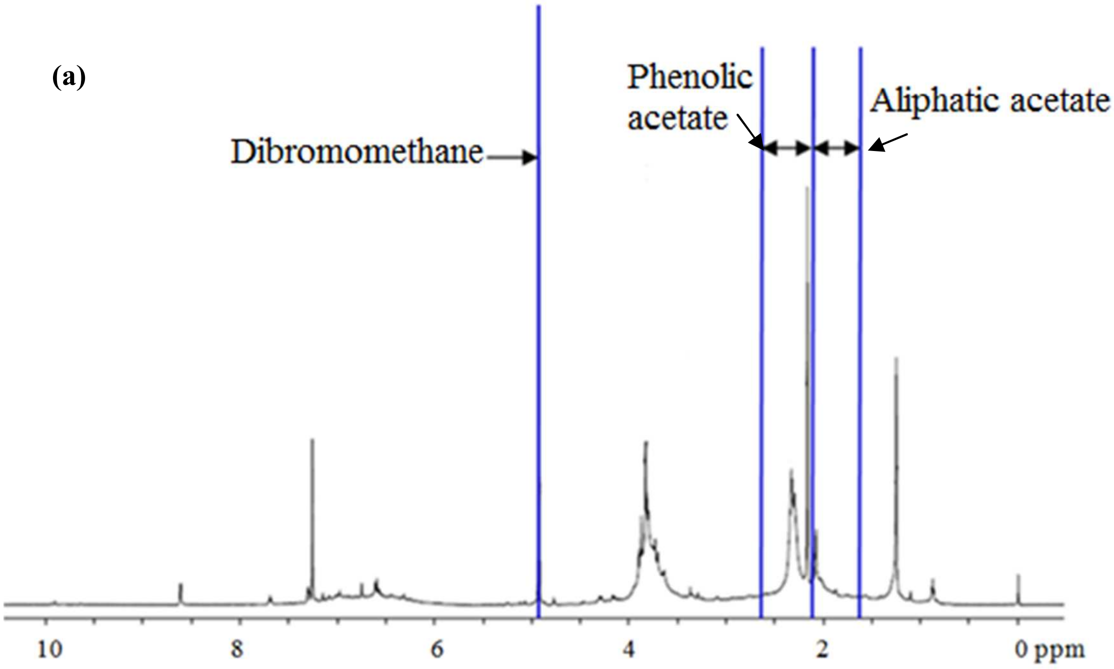


Fig. 6. FTIR spectra of sucrose polyol, HL, LHL and oxypropylated LHLs

Hydroxyl number defined as milligram of KOH per gram of sample is an important index for PU synthesis. Quantitative ^{1}H-NMR analysis of acetylated LHL and oxypropylated LHL was conducted for estimation of hydroxyl number. Dibromomethane was used as internal standard which has ^{1}H-NMRsignal at 4.9 ppm. The signals associated with aliphatic and phenolic acetates are seen at 1.6-2.05 ppm and 2.1-2.6 ppm, respectively which represent original aliphatic and phenolic hydroxyls respectively. ^{1}H NMR spectrum of acetylated LHL is shown in Fig.7a, where oxypropylated samples are shown in Fig.7b and Fig.7c representing acetylated samples of LHL50PO50 and LHL70PO30, respectively. It can be seen that after oxypropylation there were no phenolic -OH groups left (Fig.7b and Fig.7c) when compared to LHL (Fig.7a) which has both aliphatic and phenolic groups, proving that oxypropylation resulted in the complete transformation of the phenolic groups into aliphatic groups in both case. Because phenolic OH is more acidic than aliphatic OH, the catalyst potassium glycerolate was converted phenolate immediately when contacting with lignin which subsequently initiates propylene ring opening polymerization to convert phenolic OH to aliphatic OH. After all the phenolic OH converted, the chain continues to grow to extend the chain. Since PU formed with phenolic OH is not stable and reversible, thus, oxypropylation actually converted unusable phenolic OH for PU synthesis to usable aliphatic OH.



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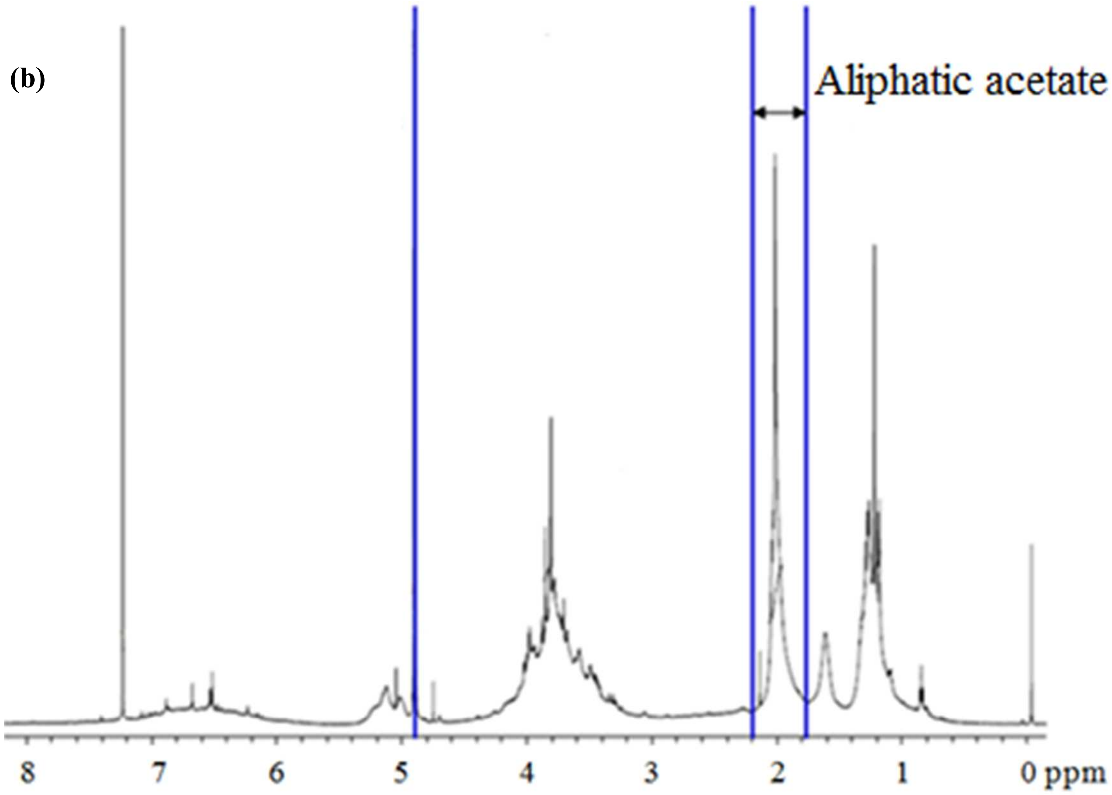

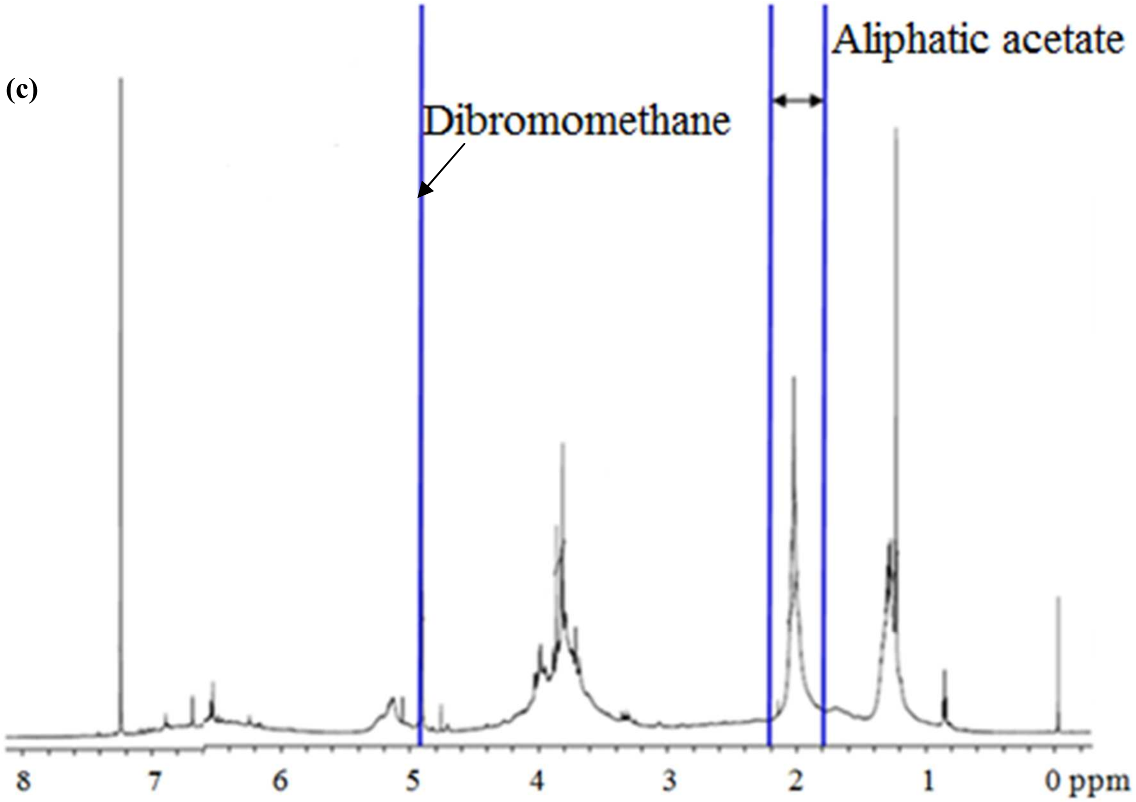

Fig. 7. ^{1}H NMR spectra of acetylated LHL (a), LHL50PO50 (b) and, LHL70PO30 (c)

3.3. Rigid PU foam (RPUF) from oxypropylated LHL

Polyurethane synthesis is essentially the formation of urethane linkages [–NH-(C=O)-O-] by the reaction of polyols (-OH) and isocyanates (-NCO). However, linkages other than urethane bonds, such as allophanate bonds, which can arise from the reaction of excess diisocyanates with NH in urethane groups, may also form. Moreover, isocyanate dimerization and trimerization reactions can also occur.[26] Density is reported as the main property of RPU foams as it also affects mechanical properties of foam.[28] In this study BRPU foams were prepared with oxypropylated LHL polyols with50-70 wt.% lignin contents via two approaches; (1) under fixed percentage of physical blowing agent (20% (w/w)); and (2) under varying percentages of physical blowing agent (20-26% (w/w)) to keep the final density approximately the same. The reaction scheme and possible chemical structure of LHL, oxypropylated LHL and the end product i.e., PU foam is shown in Scheme 1.

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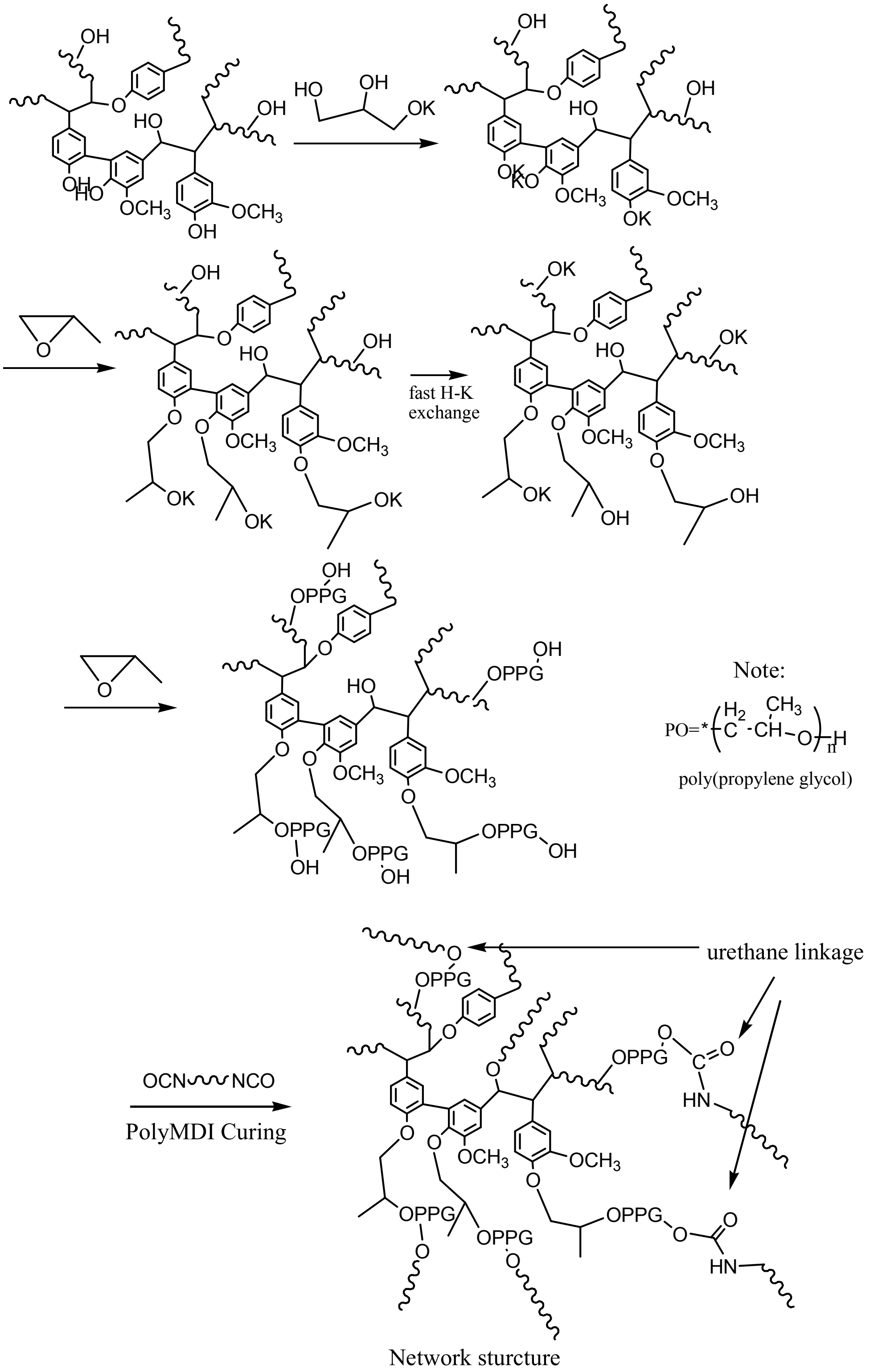

Scheme 1. Reaction scheme and possible chemical structure of LHL, oxypropylated LHL and PU

The density of BRPU foams prepared with polyols containing 50-70 wt.% LHL with a fixed percentage of physical blowing agent (20% (w/w) increased with increasing bio-content (Table 4). Consequently, the compressive strength of BRPU foams was also found to increase. The reason for this trend could be that LHL70PO30 has a structure containing multiple short chains when compared to LHL50PO50, which may leads to enhanced chemical cross-linking, and, therefore, more highly cross-linked, denser foam with increased compressive modulus and strength was obtained. When BRPU foams were prepared with polyols containing 50 wt.% - 70 wt.% bio-contents and efforts were made to keep the final density of foam approximately the same to compare mechanical characteristics directly, more physical blowing agents was introduced in the foam's formulation for higher bio-content LHL polyols. The results are also shown in Table 4. It was a tedious task to control the foam density exactly, for the sake of comparison of mechanic properties of the foams made from LHL polyols of different bio-contents with close average foam density (varying between 38.5-44.7 kg/m^3). It can be seen from Table 4, that the density of the foams prepared with polyols of high LHL contents could be slightly lower than that of the foam prepared with polyol of lower LHL by increasing the amount of physical blowing agent. The SEM images of LHL50PO50, LHL60PO40 and LHL70PO30 at varying percentages of physical blowing agent are shown in Fig. 8. It can be seen from Fig.8 that for BRPU foam prepared at 50 wt.% bio-contents average cell size was ~115 µm. However; increasing bio-content percentage to 60 wt.% to 70 wt.% (and the associated increase in physical blowing agent) resulted in an increase in average cell size to ~418 µm to ~876 µm, respectively. Increased cell size means fewer cells, enclosing larger voids form within a given volume leading to decreased foam density and, consequently, decreased Young's modulus and strength. Thus, foam morphology has a greater direct effect on foam strength than density.

Table 4. Physical, mechanical and thermal properties of reference and BRPU foams

Foam ID	Density (kg/m^3)	Compressive Modulus (kPa)	Compressive strength at 10% deformation (kPa)
Sucrose reference foam	42.5±0.5	2695.0±100.0	182.0±45.0
At fixed percentage of physical blowing agent (20%, w/w)			
LHL50PO50	44.7(±2)	9202.0±100.0	385.0±25.0
LHL60PO40	61.0(±2)	19847.0±75.0	1088.0±30.0
LHL70PO30	64.5(±1)	21288.0±50.0	1151.0±20.0
At varying percentages of physical blowing agent (20% - 26%, w/w)			
LHL50PO50	44.7(±2)	9202.0±100.0	385.0±25.0
LHL60PO40	40.0(±2)	2315.0±120.0	181.0±35.0
LHL70PO30	38.5(±2)	1651.0±85.0	120.0±47.0

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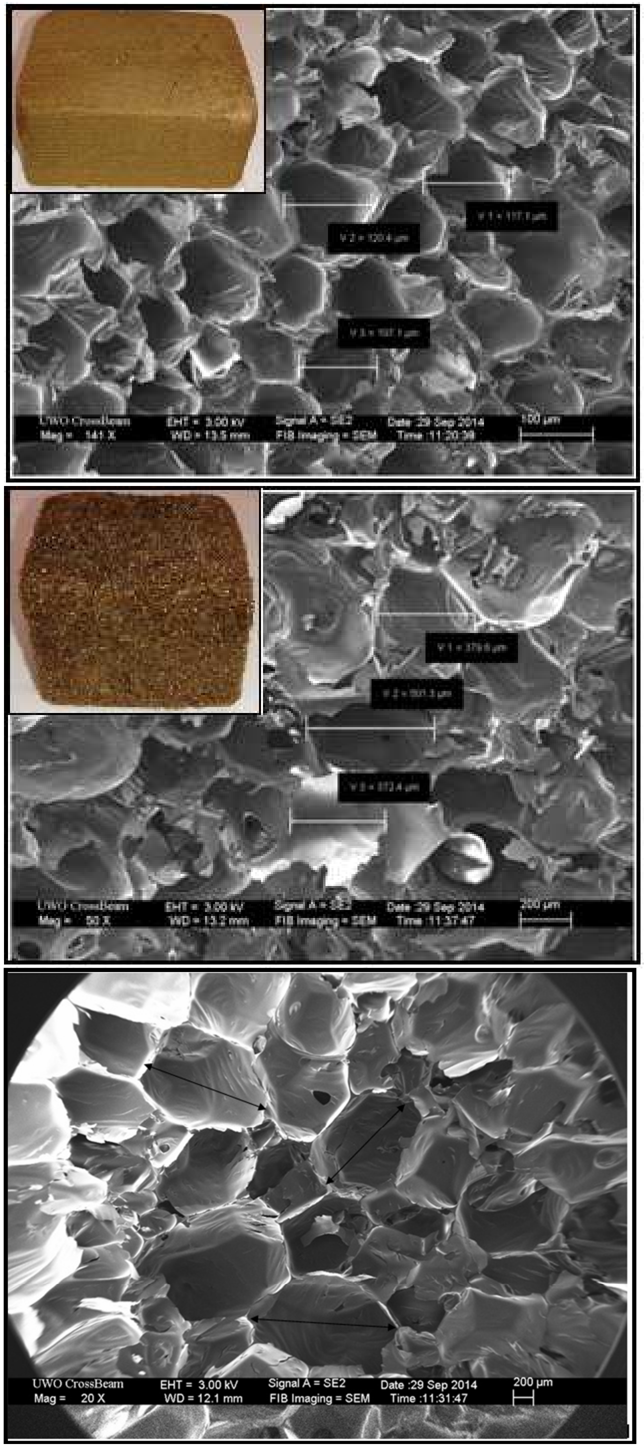

Fig. 8. SEM images of LHL50PO50 (top), LHL60PO40 (middle) and LHL70PO30 (bottom) at varying percentages of physical blowing agent

Table 5. Thermal characteristics of RPUF from oxypropylated samples

Foam ID	Density (kg/m^3)	Glass transition temperature (^oC)	Thermal conductivity (W/m-K)
At fixed percentage of physical blowing agent (20%, w/w)			
LHL50PO50	44.7(±2)	282(±2)	0.029(±0.0010)
LHL60PO40	61.0(±2)	293(±2)	0.030(±0.0010)
LHL70PO30	64.5(±1)	310(±2)	0.030(±0.0010)
At varying percentages of physical blowing agent (20% - 26%, w/w)			
LHL50PO50	44.7(±2)	282(±2)	0.029(±0.0010)
LHL60PO40	40.0(±2)	-	0.032(±0.0010)
LHL70PO30	38.5(±2)	-	0.034(±0.0010)

The glass transition temperature (T_g*'s*) of the BRPU foams, as shown in Table 5 were found to increase with increased bio-contents. This could be attributed to the increased aromatic contents in foams which could lead to a greater number of rigid/hard segments and a consequent increase in T_g of the associated BRPU foams. Thermal conductivity is the key thermal property that governs insulation applications for RPU foam. Thermal conductivity is closely related to cell morphology. Low thermal conductivity results from small average cell size and high closed cell contents. In this work, as shown in Table 5, the thermal conductivity of the BRPU foams was found to vary between 0.029 and 0.034 W/mK at 50-70 wt.% bio-content, which is satisfactory taking into account that the density of the foams is towards the higher limits of common polyurethane construction foams (thermal conductivities between 0.020 and 0.030 W/mK for densities ranging from 30-100 kg/m^3).[29]Also some of the specifications available on rigid polyurethane foam report that thermal conductivity of most common insulation materials ranges between 0.02 W/mK and 0.05 W/mK.[30]

The reference and all BRPU foams were analyzed by FTIR and shown in Fig. 9. In the spectra, residual or unreacted isocyanate group (NCO) can be identified at the band of 2253.6 cm^{-1}. The N-H stretching in urethane linkage which is in the PU hard segment region is identified at 3454.53 cm^{-1}. 1710 cm^{-1} (C=O stretching)) and 1408.84 cm^{-1} and 1098.30 cm^{-1} (C-N coupled, C-O stretch) indicates the existence of the urethane linkage.[1, 29, 31]Other characteristic bands, the N-H deformation signal at 1519 cm^{-1} of isocyanurate (resulting from reactions between isocyanate and urethane groups), conjugated and unconjugated C-O stretching at 1216 and 1064 cm^{-1}respectively and CH deformation of aromatic groups in the range of 800-600 cm^{-1} are also noted in the spectrums.[29]

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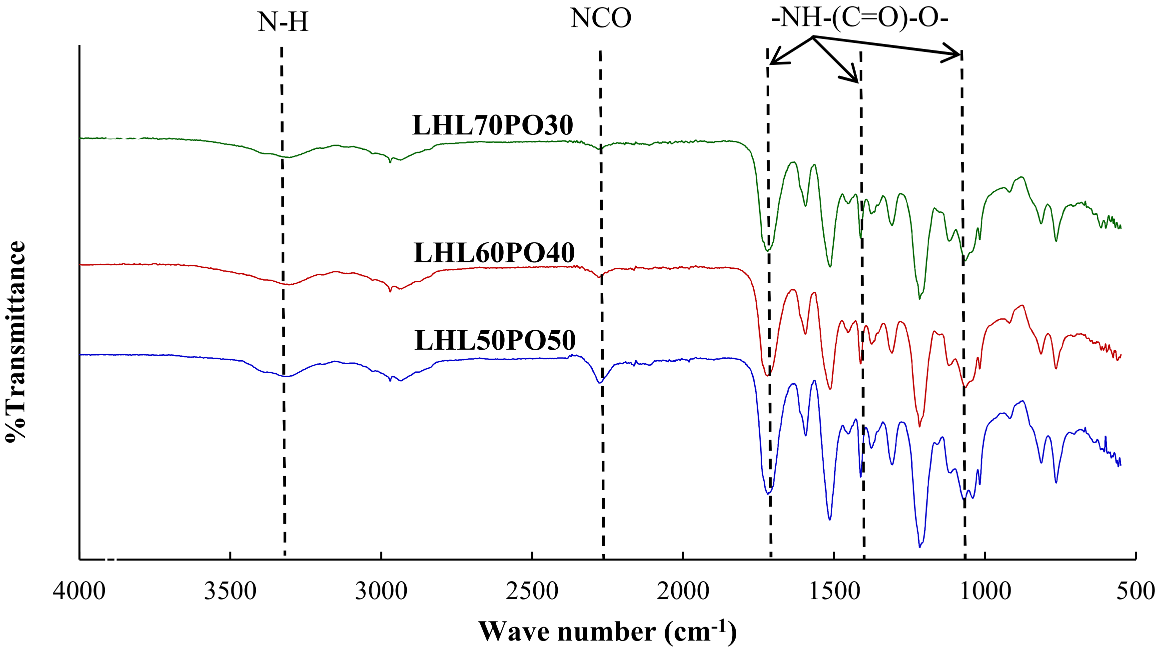

Fig. 9. FTIR analysis of BRPU foams prepared from oxypropylated samples of LHL at three different percentages of bio-contents

Thermogravimetric analysis was performed to investigate the effect of LHL contents on the thermal behavior of BRPU foam under inert atmosphere. Fig.10 shows the thermal stability curve of BRPU foam containing 50 wt.% bio-contents compared to the a reference foam. Thermal degradation of BRPUs is a complicated process involving the dissociation of the initial polyol and isocyanate components. Thermal decomposition can lead to the formation of water, amines, small transition components, and carbon monoxide and dioxide.[32] The mass loss up to 150 °C is considered to be due to the evaporation of water. Pyrolysis of PU foam under nitrogen atmosphere starts at ~170 °C and intensified at ~200 °C. Significant decomposition of RPU occurred between 200-450 °C. The decomposition of polyurethane polymer chain, around 350 °C produces compounds including diisocyanates and polyols along with other decomposition products such as amines, olefins and carbon dioxide.[33] The carbon residues at 800 °C was 30% and 25% for reference foam and BRPU foam with 50 wt.% bio-contents, respectively. The reduction in the amount of carbon residues for the BRPU foam may be due to the losses of numerous side chains from LHL.

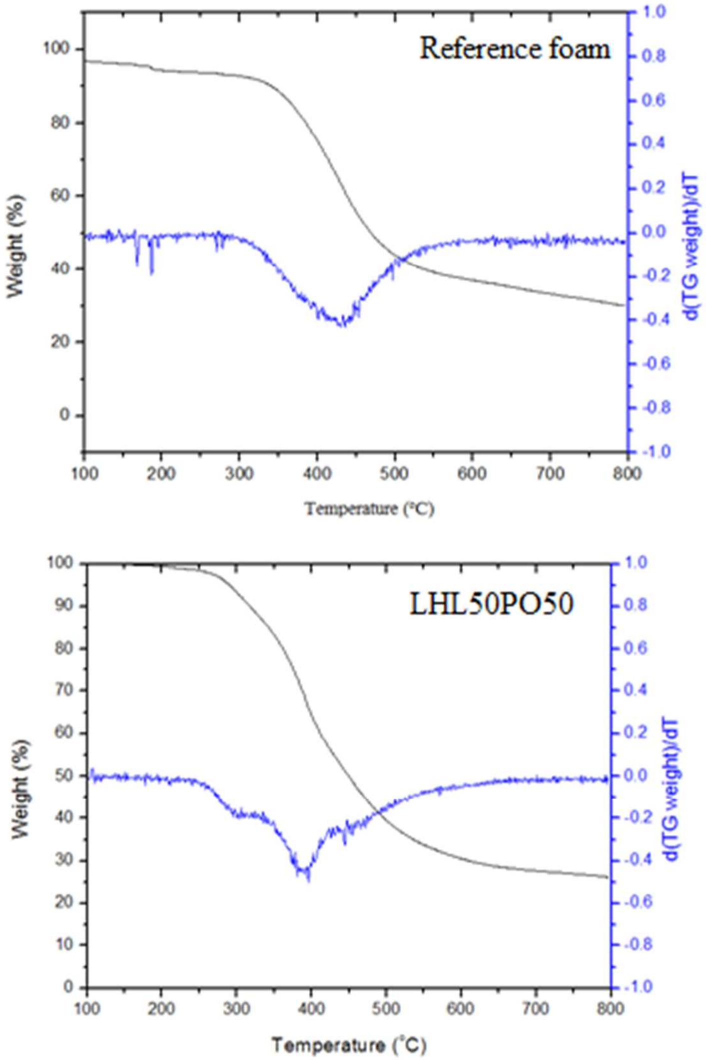

Fig.10. Degradation curve and the rate of weight loss of reference foam and BRPU foams containing 50 wt.% bio-contents

^{13}C NMR spectrum of the BRPU foam prepared with 50 wt.% bio-contents shown in Fig. 11 can provide a very useful information on the composition of foam. The peak centered at 153.5 ppm shows three distinct peaks. Theoretically, a urethane bridge C=O with an aromatic ring should appear between 152 ppm to 155 ppm. Thus, three peaks indicate the presence of urethanes having formed with all of these groups, and centered around 153.5 ppm. The 136.4 ppm peak is that of just aromatic carbons.[34]At 128-130 ppm, there is a superposition of several signals explaining the intensity of this peak; thus the signal of O(C=O)-NH- is superimposed on the 127 ppm of unreacted –N=C=O group, while the 118.8 ppm one pertains to the Ar(C) in ortho position to the –N=C=O group. The confirmation of the urethane bridge comes from peak at 70 ppm. Effectively, the –CH_2– is involved in the urethane bridge between 4,4'-dimethyl methane diisocyanate (MDI) and –CH_2OH group. The 60.5 ppm peak is –CH_2– of CH_2OH group and the peak at 55.3 ppm is due to methoxy group. [35] The 39.9 ppm peak is of –CH_2– inner bridge of MDI. CH_3 resonance was identified at 16.3 ppm.

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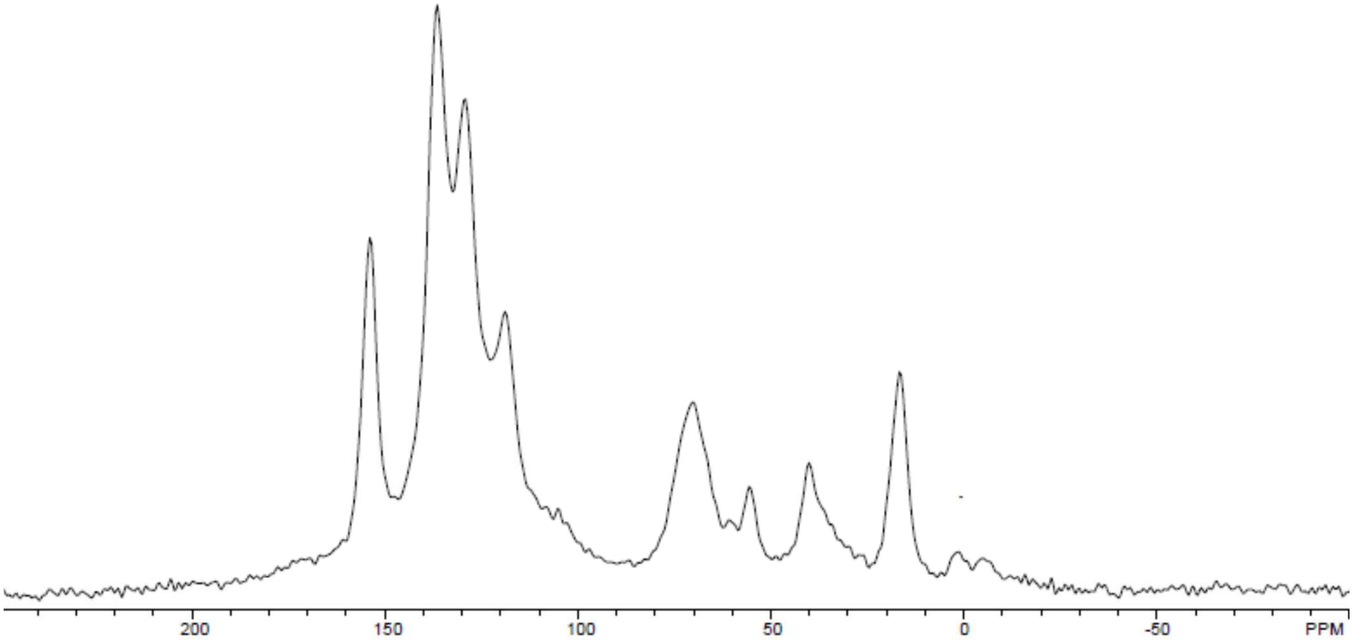

Fig. 11. Solid state ^{13}C NMR spectrum of LHL50PO50BRPU foam

4. Conclusions

High bio-content (50-70% wt.%) liquid polyols were synthesized by liquefaction of HL followed by oxypropylation. The optimal operating conditions for HL liquefaction was determined at 250 °C, for 1 h with a 20% (w/v) HL concentration in water-ethanol mixture, leading to ~70 wt.% yield of LHL with $M_w \approx 1000$ g/mole and total hydroxyl number ~442 mgKOH/g. LHL based polyols were prepared by oxypropylation with propylene oxide using potassium glycerolate as an initiator at 150 °C. A series of unique formulations were explored to utilize the oxypropylated LHL for the preparation of bio-based rigid polyurethane (BRPU) foams. Physical, mechanical and thermal property characterization results show that the foam properties were strongly dependent on the percentage of bio-contents of the LHL based polyols and percentage of physical blowing agent. All the bio-based foams exhibit high compression strengths and showed thermal conductivity between 0.029 W/mK and 0.034 W/mK. All BRPU foams were thermally stable up to approximately 200 °C and showed closed cell morphology, making them suitable for insulation and construction materials. This study showed that the HL can be effectively liquefied and is a promising alternative source for the production of low molecular weight product (LHL) which can be a suitable precursor for polyols/polyurethanes. Further studies are needed to scale-up the HL liquefaction- oxypropylation processes for large-scale production of BRPU foams, and to further improve the thermal properties of the BRPU foams.

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Graphical Abstract