PREPARATION OF POLYURETHANE FROM LIGNIN AND CRUDE GLYCEROL

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ABSTRACT: Polyurethane foam (PUF) was prepared by a novel approach, using a renewable polyol derived from only biofuel production by-products, lignin and crude glycerol. This could potentially be a high value bio-refinery application for the two byproducts from cellulosic ethanol and biodiesel production, respectively.Renewable polyols were synthesized by the liquefaction of lignin in crude glycerol.Three different technical lignins were individually employed to preparepolyols viz.: kraft lignin, lignosulfonates and organosolv lignin.Water-blown polyurethane (PU) foam was prepared by reacting the polyols with commercial diphenylmethane-4,4'-diisocyanate (MDI). The PUF had compressive strength which conform to industry requirements for thermal insulation [1]. The PUF had renewable content as high as 44 wt%.A major benefit of these renewable polyols is that PUF could be prepared without the need to add any petroleum derived polyols. Making use of lignin instead of untreated agricultural residues i.e. lignocellulose, enables the production of both biopolyols and cellulosic ethanol.The structural differences of technical lignins clearly have a significant influence on the ensuing PU properties. Biomass pretreatmentmethods and species therefore need to be selected with consideration to their effect on lignin properties if the high lignin content present in many biomass types are to be exploited.

Keywords: biodegradable, biopolymers, bioplastic, polyols.

1 INTRODUCTION

Biofuel need to be produced profitably and generate sufficient return on investment for it to become a sustainable source of energy. Apart from the revenue from biofuel itself, biorefineries can make use of production by-products to generate further income.

Lignin is a major component of lignocellulosic biomass which cannot be fermented and is removed during bioethanol production [2].Crude glycerol is a by-product of biodiesel production. About 1kg is produced per 10kg biodiesel and is of low value [3].Both lignin and crude glycerol have been studied as potential reagents for producing polyurethane which are partly renewable.

Lignin have been used both modified and unmodified as polyol component in the polyurethane formulation [4]. Modification is achieved through liquefaction in polyol solvents such as propylene oxide (PO), [5], and polyethylene glycol (PEG), [6]. More often agricultural residues i.e. lignocellulose, have been used to prepare polyols through liquefaction [7].The benefit of using lignin instead of lignocellulose during liquefaction is that cellulose and hemicellulose can still be employed for fermentation or any other application if the lignin is isolated beforehand.

A couple of studies have looked at liquefying lignocellulose[8,9] in crude glycerol to yield polyols intended for polymer synthesis. The advantage of using crude glycerol is of course its lower price compared to petroleum derived PO or PEG and the fact that it is renewable. Crude glycerol has recently even been applied successfully as sole polyol source after modification by Luoet al.[10].

Therefore in this study we investigate the combination of crude glycerol, as liquefaction solvent, with technical lignin as a novel preparation route of polyurethane with increased renewable content and potentially improved biodegradability. This is proposed as a potentially feasible route for utilizingbiofuel by-products and additionally the importance of biomass and pretreatment method selection are evaluated.

2 EXPERIMENTAL

2.1 Materials

Sugarcane bagasse was obtained from Tsb Sugar RSA (Malalane, RSA). The dried bagasse was milled to pass through a 1.5 mm sieve using a hammer mill. Hardwood calciumlignosulphonates(LS)was supplied by Sappi Saiccor mill (Umkumaas, RSA). Softwood kraft lignin(KL) was purchased from Sigma-Aldrich (Kempton Park, RSA). Sunflower oil (Crispa^{TM} gold) was purchased from Sime Darby Hudson & Knight (Boksburg, RSA). Diphenylmethane-4,4'-diisocyanate (MDI), Desmodur® 44V20L, was supplied by Bayer Material Science (Isando, RSA). Catalysts and surfactants for polyurethane preparation were supplied by Air Products South Africa (Kempton Park, RSA). PEG of average molecular weight 400 g/mol were also bought from Sigma-Aldrich. All other chemicals used were of reagent grade or purer.

2.2 Crude glycerol preparation

Crude glycerol was prepared from sunflower oil by transesterification. Reaction temperature was 60°C, duration 120 min, molar ratio of oil:bioethanol was 1:6, 1% potassium hydroxide (oil weight), stirred at 100 rpm [11,12,13]. The reaction was conducted in a stainless steel vessel with a fixed impeller and steel tubing for heating by steam. After reaction the mixture was left 24h to separate into the glycerol and fatty acid ethyl ester (FAEE) rich phases. The crude glycerol was drawn from the bottom of the reactor.

2.3 Organosolv lignin isolation

Lignin was extracted from the sugarcane bagasse by an organosolv method described byXu et al.[14]. In short: Bagasse was dewaxed with toluene/ethanol (2:1 v/v) at 9 mL/g bagasse, 73°C for 6 hours under reflux.

Bagasse was extracted with solvent: formic acid/acetic acid/water of 3:6:1 (v/v/v) at a ratio of 10 mL/g bagasse with HCl as catalyst (0.1wt% of bagasse). The mixture was stirred at 85°C for 4 hours. The filtrate was reduced under vacuum and hemicelluloseprecipitated in three volumes 95 v% ethanol. The solubilized lignin was obtained by evaporating the solvents and isolated in pH 2 water by centrifugation at 4000 rpm for 15 min. This acid insoluble lignin was freeze dried.

2.4 Liquefaction

Liquefaction was conducted in a temperature controlled glass reactor under atmospheric pressure. Catalyst, H_2SO_4, was first added to crude glycerol until pH 8 was measured. The mixture was heated to 160°C, lignin was then added at 9:1 (crude glycerol:lignin wt/wt). The reaction ran 90 min under magnetic stirring whereafter it was immediately cooled.

2.5 Yield

15 mL ethanol/g reaction mixture was added and the mixture stirred for 5 h. The solid residueand dissolved liquid (biopolyol) products were then separated by centrifugation at 4000 rpm for 10 min. The ethanol was removed from the biopolyols in a rotary evaporator at 25-30 °C.

2.6 Polyurethane foam preparation

Rigid PUF was prepared by weighing the polyol, catalysts, surfactant and blowing agent into a cylindrical beaker and mixed at 9,000 rpm for 15 s. MDI was then measured into the beaker and mixed at 9,000 rpm for 10-15 s. The foam was left to rise and cure for at least 24 h. Table I gives the KL PUF formulation. Isocyanate index of 1.05 was employed.

Table I:KL PUF formulation

Reagent	Parts (weight)
KL Polyol	100
Gelling catalyst	0.86
Blowing catalyst	0.67
Surfactant	2.50
Water	1.25
MDI	126.6

2.7 Biodegradability test

Both petroleum derived PUF, (PEG/Glycerol made up the polyol),and the KL PUF were cut into discs of 2-3 mmand buried in fertile soilsamplestaken from the local area and stored at ambient temperatures away from direct sunlight.

2.8 Characterization

Bioservices (Johannesburg, RSA) analyzed the content of glycerol, FAEE, glycerides, free fatty acids, ethanol, water, soap and salts in the crude glycerol.

Lignin was characterized by UV according to the method described bySun et al. [15]. 5 mg lignin was dissolved in 10 mL 95 v%dioxane. 1 mL of this solution was further diluted to 10 mL of 50v% dioxane. Absorbance was measured in a quartz cuvette between 190 – 360 nm.

Lignin were characterized by FTIR recording diffuse reflectance spectra of samples in a potassium bromide matrix.

The hydroxyl number of the biopolyols were determined according to ASTM D4274-11 Method D. Viscosity of the same was measured according to ASTM D4878-08.

The compressive strength of the PUF was measured according to the method described in ASTM D1621-10. Density was determined according to SANS 1383:2008. PUF samples, prepared from KL biopolyol and PEG400/glycerol respectively, were further aged in soil and the microstructure analyzed over time by scanning electron microscopy (SEM) on a FEI Quanta 250 FEG. Foam samples were sputter coated with gold/palladium and micrographs captured under high vacuum mode using the secondary electron detector and an accelerating voltage of 5kV.

Thermal gravimetric analysis (TGA) was conducted according to literature [16]. About 7 mg samples of PUF were used. The heating rate was 20°C.min^{-1}, nitrogen flow was 100 cm^{3}.min^{-1}. Heating range was 25 – 600°C.

3 RESULTS AND DISCUSSION

3.1 Byproducts

Table II shows the composition of the crude glycerol. Glycerol and FAEE are the main constituents.

Table II: Crude glycerol composition

Constituent	Content (wt%)	Method
Glycerol	42.7	AOACS Ca 14-56
FAEE	36	EN14103
Monoglycerides	2.2	EN14105
Diglycerides	0.9	EN14105
Triglycerides	0.8	EN14105
Free fatty acids	0.87.	AOCS Ca 5a-40
Ethanol	4.2	ASTM D975
Water	0.546	ASTM D6304
Soap	3.43	AOCS Cc 17-79
Salt	0.77	AOAC 963.05

Fig. 1 shows the FTIR spectra of the three lignin types.

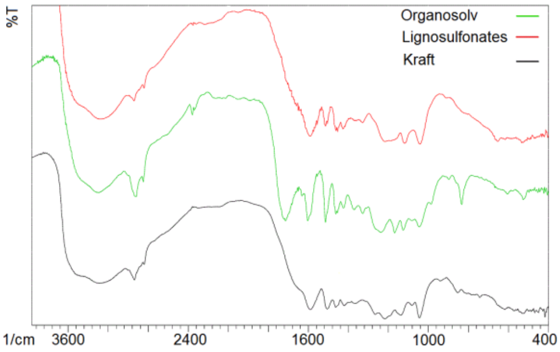

Figure 1: FTIR comparison of the three lignins

The spectra of the organosolv lignin and lignosulfonates are similar to that of the synthetically isolated kraft lignin. There are however variation of the peaks in some areas of the spectra which would be due to the difference in plant species and extraction method [17].

3.2 Biopolyols

Table III shows the liquefaction results. The OL gave a higher yield than the other lignins. The difference in yields indicate that lignin did react with the crude glycerol constituents because if there was no reaction, the three lignins should give similar yields.The hydroxyl numbers

Table III: Liquefaction yield and biopolyol properties

Lignin	KL	OL	LS
Biopolyol yield (g polyol. g crude glycerol^{-1})	0.62±0.16	0.73±0.06	0.61±0.07
Hydroxyl number (mgKOH.g^{-1})	412±27	224±10	592±18
Viscosity (mPa.s)	610±10	80	210±30

of the biopolyols in Table III are similar to those of commercial petroleum derived polyols [18], which includes polyols with a range of values for properties such as hydroxyl number and viscosity. It is also clear that a wide range of hydroxyl numbers can be obtained by liquefying different lignin types.
The three lignin type biopolyols have differing viscosities. The values are low but still comparable to a certain class of “low viscosity” commercial products [18].

3.3 Polyurethane foam

The properties of the polyurethane foams prepared from the biopolyols are given in Table IV. The compressive strength values of the PUF do fall within the usual range of PUF used for thermal insulation and packaging material, which can be as low as 110 kPa depending on the application[18]. The KL PUF lies at the higher end of the range, which of course is encouraging.

Table IV: Polyurethane foam properties

Foam type	KL PUF	LS PUF
Compressive strength (kPa)	345±63	215±58
Density (kg.m^{-3})	78±26	160±24
Renewablecontent(wt%)	44	38

Fig. 2 show photographs of the three lignin foams.

Figure 2: KL PUF (left), LS PUF (middle), OL PUF (right)

The renewable content of PUF prepared from polyols obtained through liquefaction of lignocellulose or lignin in petroleum derived solvents is generally below 20 w% [19,20,21]. As can be seen in Table IV the renewable content can be substantially increased if a “green” solvent such as crude glycerol is used.

The results of the TGA are shown in Fig. 3. The foams display initial mass loss between 150-200°C. There is a second stage of weight loss visible in the KL PUF above 300°C. The urethane bonds in polyurethane normally break at 150-220°C [22].As mentioned the KL PUF exhibit a curve with a unique shapeand onset of mass loss occurs at a higher temperature. The higher thermal stability of the KL PUF corresponds to the higher compressive strength measured for the same. An increased degree of cross linking in the KL PUF could possibly cause the higher thermal stability [19].

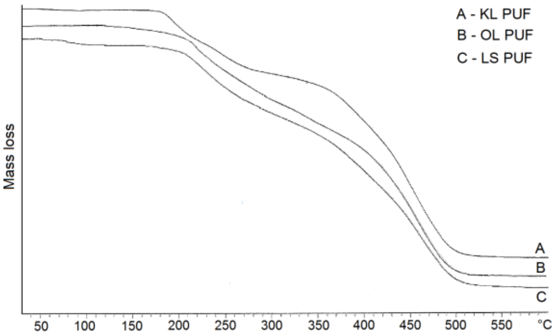

Figure 3: TGA of the byproduct derived PUF

3.4 Biodegradability

Fig. 4 and Fig. 5 show SEM micrographs of the foams before and after aging in soil. The KL PUF structure appears different after 6 months. The surface of the foam showed perforations in certain areas (Fig. 4). The number of pores visible in the cross section of the cell walls increased substantially (Fig. 5). The PEG/glycerol PUF appears unchanged after 6 months (Fig. 4). From the above alone it cannot be concluded that the foam is broken down by microorganisms, but Amaral et al. [23]foundsimilar results and in combination with respirometry tests concluded that PUF, prepared with oxypropylated lignin, showed improved biodegradability.

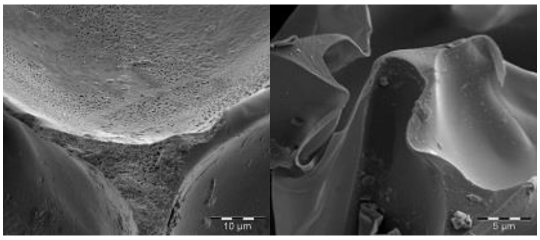

Figure 4: KL PUF (left) and PEG/glycerol PUF (right) after 6 months aging in soil

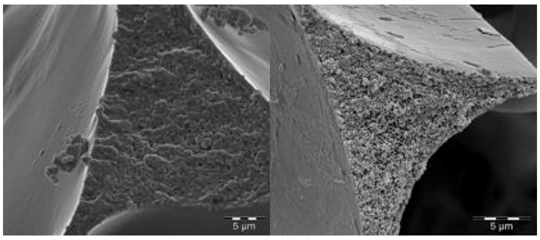

Figure 5: KL PUF before (left) and after (right) 6 months aging in soil

3.5 Polyol cost comparison

Table V display a very basic cost comparison between petroleum derived polyols and the biopolyolsderived from crude glycerol and lignin. Clearly the concerned biopolyols possess a potential cost advantage due to the low cost of crude glycerol and a further, morecomprehensive economic feasibility study is therefore warranted.

Table V: Polyol cost comparison

Description	Cost (€/ton)	Ref./Note
Polyols:		
Petroleum derived	1760-2050	[24,25](1)
PO/biomass	1000-1500	[25]
Lignin	50-1200	[4]
Crude glycerol	190-365	[26,27](2)
KL polyol	724	(3,4)

4 CONCLUSIONS

The liquefaction of technical lignin in crude glycerol yielded polyols which was successfully reacted with MDI to yield rigid polyurethane foam.The polyols had hydroxyl numbers and viscosities comparable to those of commercial petroleum derived polyols.

By employing crude glycerol as solvent, renewable content of up to44 wt% was achieved in the PUF.

The KL PUF structure appeared damaged after a period of soil incubation. Petroleum derived PUF did not show any signs of damage. The byproduct derived PUF might therefore present improved biodegradability.

A very basic cost comparison revealed that the raw materials to prepare the concerned renewable polyols would be roughly€724 /ton which is lower than the selling price of commercial polyols.

It was found that different technical lignins significantly influence the final PUF properties. Pretreatment method and species selection in thebiorefinery context shouldtherefore take into consideration the specific intended use of lignin by-products to maximizeprofitability.

5 NOTES

(1) Exchange rate of $1.10/€ was assumed.
(2) Refined crude glycerol: 80 wt% glycerol.
(3) 9:1 Crude glycerol/lignin (wt/wt). Liquefaction polyol yield as per Table III.
(4)Based on €1200/ton lignin and €365/ton crude glycerol.

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8 LOGO SPACE