

Characterization of Thermal and Mechanical Properties of Lignosulfonate- and Hydrolyzed Lignosulfonate-based Polyurethane Foams

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Lignosulfonate and lignosulfonate hydrolyzed under alkaline conditions were used as the polyol components in polyurethane foam formulations. Although the treatment increased hydroxyl group abundance, it did not improve the applicability of hydrolyzed lignosulfonate in polyurethane foam. Thus, the use of original lignosulfonate yielded foams of thermal stability and mechanical properties comparable to other types of bio-based foams (Young's moduli 0.95 to 4.42 MPa, 50% weight loss, and temperature ca. 500 °C). Lignosulfonates can be a renewable polyol component for the formulation of rigid, semi-rigid, and flexible foams.

Keywords: Foam; Lignin; Lignosulfonate; Renewable polyol; Polyurethane

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INTRODUCTION

To reduce the impact of industry on the environment, technologies based on renewable resources have been developed over recent years. These technologies employ research aimed at, among others things, the development of new polymeric materials. Polyurethane (PUR) is a class of polymer exhibiting a wide range of applications. Therefore, many efforts have been made to investigate the applicability of bio-based polyols in polyurethane materials; these include glycerol derivatives (Mamiński *et al.* 2012), liquefied wood (Wei *et al.* 2004; Juhaida *et al.* 2010), soy derivatives (Khazabi *et al.* 2011) and oils (Desroches *et al.* 2012; Gava *et al.* 2015). The pathways for conversion of vegetable oils into polyols for rigid and flexible foams were widely discussed by Petrović (2008). Narine *et al.* (2007) report canola, soybean, and castor oils as the raw materials for rigid PUR foams. Foams based on vegetable and animal oil-derived polyols were also investigated (Beneš *et al.* 2012; Das *et al.* 2009).

An alternative abundant renewable feedstock for PUR polymers is lignin. Its annual production from the paper industry reaches 30 million tonnes (Hatakeyama and Hatakeyama 2010). The ‘sulfite process’ generates water-soluble, amphiphilic lignosulfonates with Mg⁺⁺, Na⁺, or NH₄⁺ cations. Unfortunately, the application of lignosulfonates is limited by the sulfur content, which can be as high as 5% weight. For this reason, lignosulfonates are commonly combusted for energy production (Doherty *et al.* 2011).

Lignin and its derivatives were employed as renewable resources for flexible (Cinelli *et al.* 2013; Bernardini *et al.* 2015) and rigid (Xue *et al.* 2015) PUR foams. An extensive up-to-date discussion of the pathways for lignin conversion into polyols can be found in the review papers by Matsushita (2015) and Mahmood *et al.* (2016). Faris *et al.* (2015) synthesized polyols from oil palm wastes. Polyurethane foams prepared from liquefied, bamboo-based polyols were investigated by Xie *et al.* (2014). A series of lignin- and lignosulfonate-based foams were successfully prepared and characterized (Hatakeyama *et al.* 2003; Hatakeyama and Hatakeyama 2010). The authors showed that kraft lignin, sodium lignosulfonates, and hydrolysis lignin exhibited good solubility in glycols and some types of lignin and that they could be used in PUR foams without pretreatment.

Therefore, in the present work, PUR foams containing lignosulfonate and hydrolyzed lignosulfonate were studied so that the effect of lignosulfonate alkaline hydrolysis on the properties of PUR foams could be assessed.

EXPERIMENTAL

Materials

The following compounds were used in the experiments: sodium lignosulfonate (Borregaard LignoTech, Rothschild, WI, USA), polypropylene glycol (PPG; molecular weight of 1000, Bayer Material Science LLC, Pittsburgh, PA, USA), glycerol, polymeric methylenediphenyldiisocyanate (PMDI; 31.5% NCO; Huntsman Corp., Charlotte, NC, USA), 1,4-diazabicyclo[2.2.2]octane (DABCO® 33-LV; Sigma-Aldrich Corp., Saint Louis, MO) as a catalyst, and modified dimethylpolysiloxane Struktilon 8006 (Structol®, Hamburg, Germany) as a surfactant. Alkaline hydrolysis of lignin was performed in a 100-mL pressurized reactor (Parr Instruments, Moline, IL, USA), according to the procedure described by El Mansouri *et al.* (2006) at 170 °C for 2 h.

Methods

The hydroxyl number (L_{OH}) determination (Mamiński *et al.* 2012) is not applicable to lignosulfonates; therefore, the L_{OH} values for Borregaard lignin (BCA) and hydrolyzed lignin (HZ) were estimated by adjusting the equivalent PMDI/lignosulfonate ratio under Fourier transform infrared (FTIR) spectrometry control. The results corresponded to an L_{OH} of 63 and 77 mg KOH/g for BCA and HZ, respectively.

Foams varied with the PPG / glycerol / lignin ratios. The respective formulations and sample names are given in Table 1. The amounts of catalyst and surfactant were 0.3% and 2%, respectively, and were based on the entire mixture weight. The water amount was 3% based on the polyol mixture weight (*i.e.* 0.03 g). The general procedure was as follows: lignin was vigorously stirred for 10 min with polyols (Table 1), water, catalyst, and surfactant. Then, PMDI was added and the whole formulation was mixed for 10 to 15 s and poured into a cast mould. The amount of isocyanate was calculated using Eq. 1,

$$X = \left(\frac{a \cdot L_{OH}}{56100} + \frac{y}{R_w} \right) \cdot R_{iso} \quad (1)$$

where X is the mass of isocyanate (g), a is the mass of the polyol mixture (g), LOH is the average hydroxyl number of the polyol mixture in mg KOH/100 g, y is the mass of water (g), R_w is the relative amount of water (9 in this formulation), and R_{iso} is the relative amount of isocyanate (135). The isocyanate index was 1.07 for all of the formulations.

Foam was conditioned for 24 h in a laboratory, and then the cubic samples ($50 \times 50 \times 50 \text{ mm}^3$) were cut and placed in an oven ($80 \text{ }^\circ\text{C}$ for 72 h) for dimensional stability evaluation. Shrinkage was calculated using Eq. 2,

$$\Delta V = \frac{V - V_0}{V_0} \cdot 100\% \quad (2)$$

where ΔV is the volume change (%), V is the sample volume after heating (cm^3), and V_0 is the sample volume before heating (cm^3).

Density was calculated for a specimen of dimensions *ca.* $30 \times 30 \times 30 \text{ mm}^3$ measured with a caliper and weighted. The measurement was done in triplicate, and the presented apparent density is a mean value.

T_g was determined from the TMA expansion curve. The onset technique was used to define the temperature at which the sample expands and the curve shape changes.

The analysis of variance (ANOVA) of the means was carried out using Design-Expert[®] 6.0.10 (Stat-Ease, Inc., Minneapolis, MN, USA) software.

Instrumentation

Prior to the thermal analysis experiments, the foam's porous structure was disintegrated by grinding in liquid nitrogen. Thermogravimetric analysis (TGA) was carried out on a TGA7 thermogravimetric analyzer (PerkinElmer, Waltham, MA, USA) using 5 to 7 mg of sample in a nitrogen atmosphere and heated from 50 to $900 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C}/\text{min}$. Thermomechanical analysis (TMA) was carried out on a TMA7 thermomechanical analyzer (PerkinElmer, Waltham, MA, USA) using a compression probe in the temperature range of -50 to $200 \text{ }^\circ\text{C}$ in a nitrogen atmosphere, with a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$. The SEM micrographs were made using Quanta 200 ESEM (FEI Company, Hillsboro, OR, USA) instrument. Pressure 0.75 Torr , applied voltage 25 kV . Fifteen cell dimensions were recorded and averaged. Fourier Transform Infrared spectra were recorded (400 to 4000 cm^{-1} and 32 scans at a resolution of 4 cm^{-1}) on an Avatar 380 spectrometer (Thermo Nicolet, Thermo Fisher Scientific Co., Waltham, MA, USA), operating in the total attenuated reflection (ATR) mode (ZnSe).

Young's modulus (E – the slope of the linear elastic phase at the steepest slope) was measured on a 5500-1122 universal testing machine (Instron Corp., MA), at $2.0 \text{ mm}/\text{min}$ compression rate and analyzed with Bluehill[®] version-3 software (Instron Corp., MA, USA). The compression of the samples ($20 \times 20 \times 20 \text{ mm}^3$) was evaluated in the direction of foam growth.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy was applied to the original (BCA) and hydrolyzed lignosulfonate (HZ) to show chemical differences from hydrolysis (Fig. 1). It can be clearly seen that the intensities of the bands at 3376 cm^{-1} (O–H stretch), 2934 cm^{-1}

(C–H stretching in methylene groups of the side chains), and 1595 cm^{-1} (aromatic skeletal vibrations) (Pohjanlehto *et al.* 2013; Zhou *et al.* 2013) increased, while the sulfonate ($\text{R-SO}_2\text{-O}^-$) at 1044 cm^{-1} and ether at 1113 cm^{-1} (Hu *et al.* 2012; Faix 1992) decreased upon alkaline treatment. These changes indicate an increase in hydroxymethyl group abundance and ether bond scission resulting from the alkaline hydrolysis of lignin (El Mansouri *et al.* 2006).

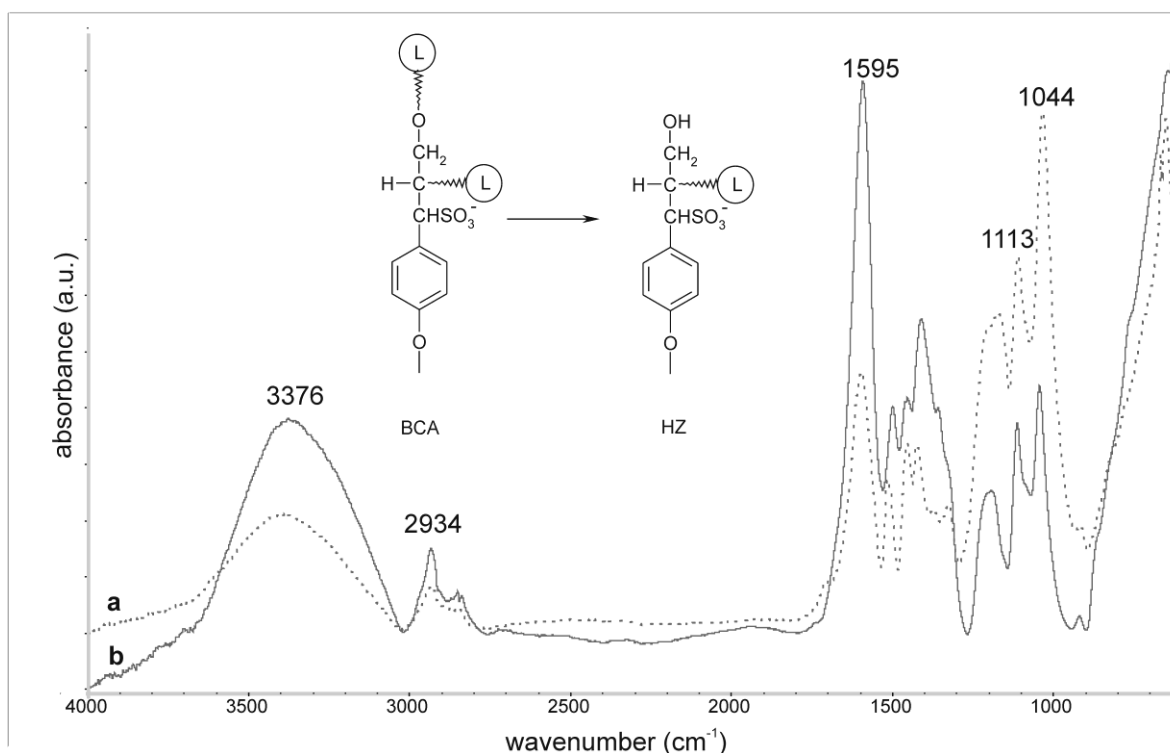


Fig. 1. Fourier transform infrared spectra of (a) lignosulfonate Borregaard lignin and (b) hydrolyzed Borregaard lignin. Proposed structures of BCA and HZ.

Table 1. Formulations and Physical Properties of the Lignin-based Foams

Sample name	PPG	Glycerol	Lignin	PMDI	Surfactant	Catalyst	Foaming start time	Tack free time	Density	Average pore size
	g						s	min	kg.m ⁻³	mm
REF	10.0	0	0	7.2	0.34	0.052	50	6	17	0.29
BCA1	0	0	10.0	5.9	0.32	0.048	70	7	20	0.43
BCA2	7.0	0	3.0	6.8	0.34	0.050	130	60	18	0.61
BCA3	6.0	1.0	3.0	11.2	0.42	0.063	170	60	36	0.60
BCA4	6.0	2.0	2.0	15.6	0.51	0.077	300	65	22	0.41
BCA5	7.0	1.0	2.0	11.3	0.43	0.064	150	60	20	0.40
HZ1	0	0	10.0	6.3	0.33	0.049	350	70	–	–
HZ2	7.0	0	3.0	6.9	0.34	0.051	240	60	13	0.43
HZ3	6.0	1.0	3.0	11.3	0.43	0.064	270	30	11	0.35
HZ4	6.0	2.0	2.0	15.7	0.51	0.077	120	7	19	0.42
HZ5	7.0	1.0	2.0	11.4	0.43	0.064	210	9	18	0.32

PPG – Polypropylene glycol; REF – Reference foam; BCA – Borregaard lignin containing foam; HZ – Hydrolyzed lignin containing foam

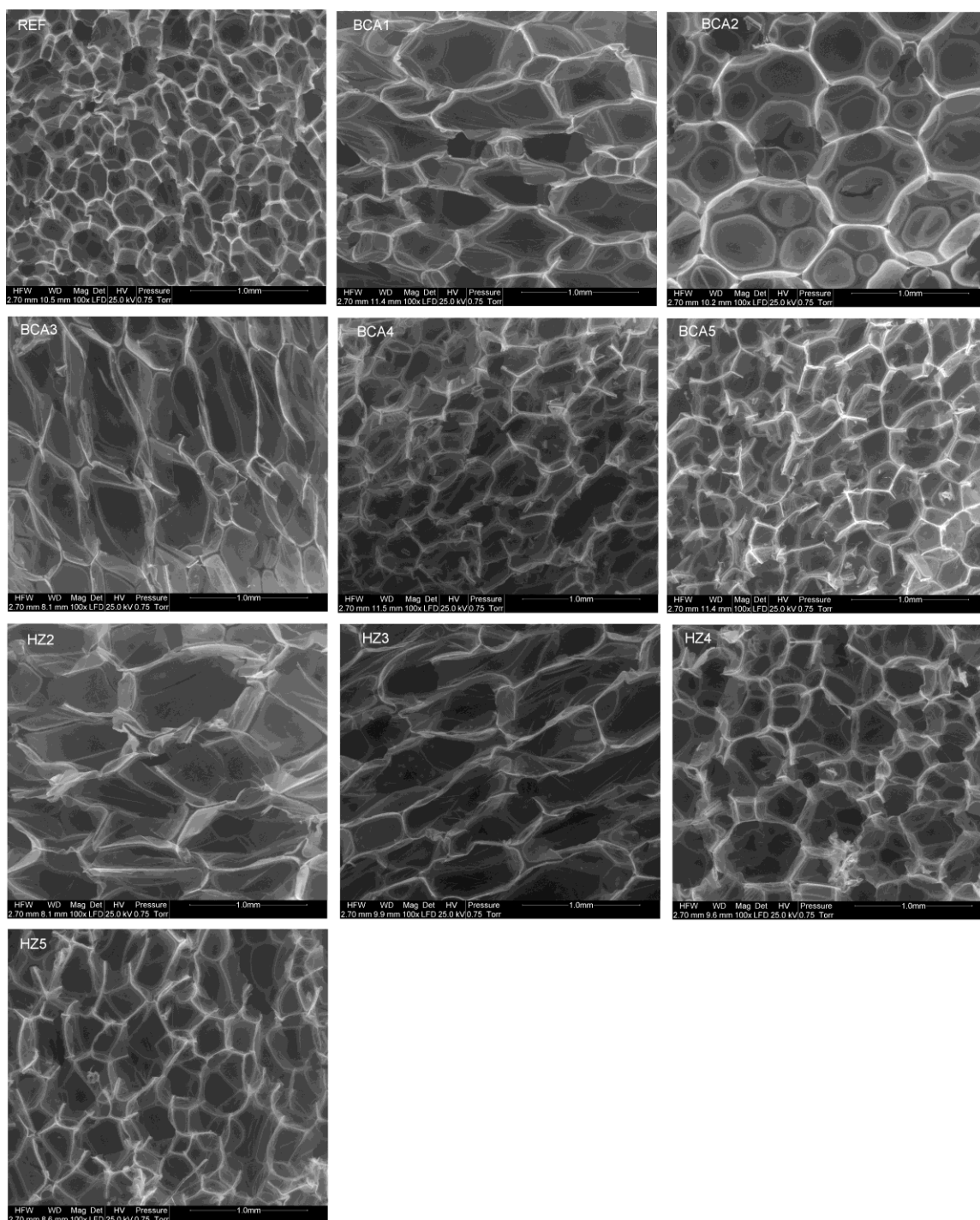


Fig. 2. SEM micrographs of the investigated foams

The data in Table 1 indicate that the foaming start time and tack free time varied widely depending on the polyol composition, which resulted from the variables in the reactivity of the formulations. For the one-component formulations (REF, BCA1, and HZ1), the foaming and tack free time were strongly dependent on the innate reactivity of a specific polyol component. Thus, easy accessibility of the hydroxyl groups in PPG and

BCA provide fast foam curing. When neat hydrolyzed lignosulfonate was used (HZ1), a curing of the system occurred, but no foaming was observed. Moreover, the polymer produced from neat hydrolyzed lignin (HZ1) was dense, mechanically weak, and brittle; thus, it was excluded from further tests. The results indicated that the hydrolysis did not appreciably enhance the material as polyol. Thus, it corresponds to what was previously claimed, which is that some lignin types might work as polyols without any modification (Hatakeyama and Hatakeyama 2010). The ANOVA results (Table 2) rendered no significant effect for either BCA or HZ lignin in the formulation on the foam density or pore size; however, it is worth noting that in all of the series, pore size was higher than that of the REF series when PPG was the only polyol. The phenomenon comes from variability in the viscosity of the formulations and overall reactivity of the system that subsequently affected carbon dioxide entrapping and the foam-shape fixation conditions. The pore sizing, shown in Table 1 and Fig. 2, was comparable to those reported in other works for bio-based PUR foams, *e.g.*, 0.28 to 0.40 mm (Khazabi *et al.* 2011).

The selected thermal and mechanical properties of the foams are tabulated in Table 3. The dimensional stability is an important feature of foams. It is usually evaluated by foam conditioning at 80 °C for 72 h. It was observed that some of the investigated foams exhibited excellent dimensional stability well below 1.0%. However, it must be noted that the formulations containing neat BCA as the only polyol exhibited the highest shrinkage value of 4.4%. Statistical analysis showed that BCA exhibited a dominating effect on shrinkage. The additions of PPG and glycerol to the formulations lowered the shrinkage to below 0.5%.

Table 2. Analysis of Variance Results for the Physical, Mechanical, and Thermal Properties of the Foams (significance level $\alpha = 0.05$)

Property	DF		F-value		p-value		Model significance	
	BCA	HZ	BCA	HZ	BCA	HZ	BCA	HZ
Density	2	2	4.70	1.02	0.14	0.46	No	No
Pore size	9	2	0.65	4.03	0.73	0.14	No	No
1 st Degradation onset	5	2	35.55	10.15	< 0.0001	0.046	Yes	Yes
$T_{50\%}$	2	2	6.08	109	0.019	0.002	Yes	Yes
T_g	5	2	1.08	2.24	0.45	0.25	No	No
T_s	2	2	27	0.018	< 0.0001	0.98	Yes	No
Young's modulus	2	2	5.71	6.18	0.022	0.09	Yes	No
Shrinkage	5	2	6.95	0.077	0.018	0.93	Yes	No

DF – Degree of freedom; $T_{50\%}$ – 50% Weight loss temperature; T_g – Glass transition temperature; T_s – Softening point

More apparent relationships were found for foam formulation and thermal properties (Table 3). The 1st onset degradation temperature and 50% weight loss temperature ($T_{50\%}$) of the BCA-based foams were directly and inversely proportional to the content of BCA lignin. The ANOVA analysis indicated that the softening point (T_s) was lowered by glycerol and PPG, while T_s increased with BCA or HZ content. On the other hand, no significant (p-values 0.45 and 0.25, respectively for BCA and HZ) effect of the formulation on the glass transition temperatures (T_g) was found. These values remained in the range of 21 to 62 °C and 36 to 56 °C for the BCA- and HZ-series,

respectively (Table 3). In general, the results were in agreement with the data found for biopolyol-based PUR (Hakim *et al.* 2011). However, Hatakeyama *et al.* (2003) found that T_g increased with increasing lignosulfonate content. Outstanding results were found for the reference PPG-based (REF) and HZ2 (PPG/HZ = 0.7/0.3 w/w) foams exhibiting $T_g = 100$ °C. The observed 1st degradation onset was above 220 °C, which confirmed higher stability of the foams than that of the lignosulfonate-based foams described by Hu *et al.* (2012).

The HZ-containing foams exhibited significant models for the effect of polyol composition on their final properties. The 1st degradation temperature and 50% weight loss temperature ($T_{50\%}$) were significant (p-values 0.046 and 0.002, respectively), while T_s remained relatively unchanged. As far as the sample residual weight was concerned, the PUR foams exhibited thermal stability close to those reported for bio-based PUR foams (Hakim *et al.* 2011), but lower than PF foams containing 20% of the phenolated lignosulfonate, *i.e.*, 61% at 800 °C (Hu *et al.* 2012). From the statistical analysis it was found that an increasing content of HZ lignin resulted in an increased 1st degradation temperature. The major decomposition starts at approximately 280 °C, which corresponds to the dissociation of urethane linkages formed from phenolic hydroxyls (Hatakeyama *et al.* 2003). The effect of PPG, glycerol, and HZ on $T_{50\%}$ was the opposite.

From the data presented in Table 3, it is clear that the compression Young's modulus (E) of the BCA-based foams varied depending on the formulation, while the additions of HZ had no effect. Because of the variations in the density of the foams, a specific E ($E/\text{density}$) was computed. The specific E of rigid BCA1 and BCA2 (*ca.* 0.21 MPa/g·cm⁻¹) was even higher than that reported by Del Saz-Orozco *et al.* (2012) for lignin-reinforced phenol-formaldehyde foams (0.16 MPa/g·cm⁻¹). The ANOVA results indicated that the polyol composition was significant (p-value 0.022) for the mechanical properties of the foams. Thus, the formulations, BCA1 and BCA2, without glycerol and 100% and 30% lignosulfonate, respectively, provided rigid foams with E of 4.42 MPa and 3.81 MPa, respectively. These were the highest specific E values of all the foams. All of the other foams were semi-rigid or flexible.

Table 3. Compression Young's Modulus (E) and the Thermal Properties of the Foams

Series	E	Specific Young's modulus	Shrinkage 72 h at 80 °C	50% Weight loss	1 st Degradation onset	T_g (from TMA)	T_s (from TMA)
	MPa	MPa/g·cm ⁻¹	%	°C	°C	°C	°C
REF	1.62 ± 0.33	0.09	1.47	462	272	100	153
BCA1 ^a	4.42 ± 0.66	0.22	4.40	531	227	29	184
BCA2 ^a	3.81 ± 0.45	0.21	0.71	525	286	23	153
BCA3	1.11 ± 0.11	0.03	0.04	507	280	48	156
BCA4	0.95 ± 0.10	0.04	0.10	502	281	21	150
BCA5	3.11 ± 0.52	0.16	0.05	510	284	62	153
HZ1	–	–	–	–	–	–	–
HZ2	0.46 ± 0.12	0.03	0.10	512	232	100	155
HZ3	0.90 ± 0.08	0.08	0.10	492	231	41	155
HZ4	0.86 ± 0.17	0.04	7.0	506	284	36	156
HZ5	0.84 ± 0.20	0.05	15	516	283	56	136

^a Rigid foam; $T_{50\%}$ – 50% Weight loss temperature; T_g – Glass transition temperature;

T_s – Softening point; TMA – Thermomechanical analysis

CONCLUSIONS

1. The alkaline hydrolysis of lignosulfonate resulted in an increase in hydroxyl abundance. However, the treatment did not improve the applicability of hydrolyzed lignosulfonate in PUR foams.
2. The use of original lignosulfonate turned out to be more practical when compared to the hydrolyzed lignosulfonate, since it provided PUR foams of higher mechanical properties without any treatment of the raw material.
3. Some formulations yielded foams that exhibited a thermal stability and mechanical performance comparable to other types of bio-based foams.
4. It has been demonstrated that lignosulfonates can be used as a polyol component in the formulation of rigid, semi-rigid, or flexible foams.
5. Further work should investigate the optimization of the foam properties and the maximum lignin content in the formulation.

ACKNOWLEDGMENTS

The authors would like to thank the U.S. Department of State and Polish-American Fulbright Commission for funding this project by a Senior Research Grant.

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Article submitted: February 4, 2016; Peer review completed: March 30, 2016; Revised version received and accepted: May 10, 2016; Published: July 14, 2016.

DOI: 10.15376/biores.11.3.7355-7364