Polyurethane foams from alkaline lignin-based polyether polyol

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ABSTRACT: As a byproduct produced during biorefining, alkaline lignin (AL) possesses multiple benzene ring and phenol hydroxyl groups with high chemical reactivity, and is renewable and cheaper than petrochemical products. Here, AL was liquefied in polyethylene glycol-400/glycerol and subsequently used to prepare polyurethane foams (PUFs). The results showed that the AL could be almost completely liquefied. The resulting lignin-based polyether polyol (LPP) exhibited physicochemical properties similar to a commercial polyether polyol (PP). The PUFs made from LPP presented better thermal stability and higher compressive strength than those PUFs obtained from commercial PP, suggesting this could be a viable commercial application for AL. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43261.

INTRODUCTION

Polyurethanes are a class of polymers known for their versatility produced through the condensation polymerization reactions between polyols and isocyanate. Polyols can be monomeric or polymeric and contain multiple hydroxyl functional groups that are available for organic reactions. Polymeric polyols (PP) account for about 90% of the polymeric polyols used industrially and the remaining are polyester polyols. PP contains repeating ether linkage (–R-O-R-)with two or more terminal hydroxyl functional groups able to react with other substances.[1–3] Polyurethane foams (PUFs) are important polyurethanes, and are commonly classified as flexible, semi-rigid, and rigid, depending on their mechanical performance and densities.[4,5] Since commercial polyols and isocyanates are mainly from petrochemical derivatives, one of the problems related to current polyurethanes production is their dependence on petroleum industry.[6] Due to the concern about feedstock processing, it is important to develop alternative synthesis strategies using renewable sources that are less hazardous to the environment.[5] From the point of view of the polyurethane industry, the use of polyols produced with a closed carbon cycle seems to be attractive, especially if underutilized lignins can be utilized.[5]

Lignin has hydroxyl groups on aromatic rings and side chains, which makes them a potential feedstock for preparation of PP. Zhou *et al.*[7] reviewed lignin alcoholysis pathways catalyzed by acid and alcoholic solvents in combination with lignin liquefaction fragments. These pathways could be exploited for lignin liquefaction and the generation of PP. PP could then be used for PUFs production after reaction with isocyanate.[8] Different lignins, including Kraft lignin,[9] alkaline lignin (AL),[10] and enzymatic hydrolysis lignin,[11] have been used to produce PP via oxypropylation[9] and PEG-400/glycerol liquefaction.[10,11] The main factors affecting the performance of PUFs in this process include type, content and molecular weight of lignin, and the isocyanate and NCO/OH molar ratio (Isocyanate index).[12] An report by Chen and Lu[12] showed that the PUFs based on bio-PP prepared from wheat straw liquefaction showed superior to those produced from petroleum-based PP, including higher compressive strength, thermal stability, and biodegradability.

In the biorefinery process, alkaline pretreatment is an effective method that increases the sensitivity of lignocellulose to cellulase by removing the inhibitory xylan and lignin components.[13] However, this process produces AL that could cause environmental pollution if it not effectively utilized. Transformation of lignin to polymeric materials would be a high-value application that could prevent AL from becoming waste.[14] Liu *et al.*[15] and Liu *et al.*[16] have reported that AL could be used as a reinforcing agent for PUFs synthesis. In this study, AL-based PP (LPP) was prepared through a PEG-400/glycerol system and PUFs synthesized from the LPP mixed with the commercial PP at different proportions. The PUFs prepared with LPP had better thermal

Table I. Physical Properties of Alkaline Lignin

Properties	Value
Water-solubility	no
Solid content, %, w/w	92.24
Klason Lignin content,%, w/w	86.11
Ash content, F %, w/w	1.95
Molecular weight(Mw),Da	2726
Polydispersity(PD)	2.53

stability and higher compressive strength which may be an improved application for AL.

EXPERIMENTAL

Materials

AL was provided by Changzhou Peaks Chemical. Its main physical parameters are shown in Table I. Compared to other lignins,[17] AL is sulphur-free with low molecular weight, moderate polydispersity, and high Klason lignins content. Because of the presence of alkali in the extraction process, the majority of chemical bonds between the lignin–carbohydrate complexes (LCC) were broken and the AL contain little carbohydrate. According to Lora and Glasser[18] and Li and Gellerstedt,[19] lignins used in polymer industry should be free of sugars and sulphur, and should have a high Klason lignin content, and AL meets this criteria as a good raw material used for PP production. Commercial PP (MJ-4110) was purchased from Lianyungang Mai Jia Chemical. This PP is synthesized from ethylenediamine and aniline. Chemical reagents, including polyethylene glycol (PEG)−400(Tianjin Yongda Chemical Reagent), glycerin, dioxane, phthalic anhydride, stannous octoate, triethylenediamine, concentrated sulfuric acid, sodium hydroxide, methanol, potassium hydroxide (Sinopharm Chemical Reagent Beijing), pyridine (Xilong Chemical), silicone oil (SD-201, Siltech New Material Corporation), dichlorofluoroethane (R141B, Shanghai 3F New Material), diphenyl-methane-diisocyanate (MDI, 44V20, Bayer Company) were used as received.

Lignin Liquefaction Procedure

AL (20 g) and liquefaction solvent (Figure 1, parameters obtained by a series of optimization experiments according to literatures[20,21]) were added to a three-necked flask (500 mL) with a condenser pipe, mechanical agitator and temperature gauge. The liquefaction was carried out at 140°C. After 5 min, the flask was placed into cold water to terminate the liquefaction reaction rapidly.
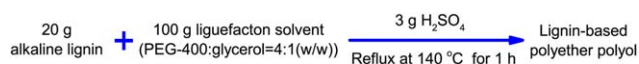
PUFs Synthesis

One-shot technique was used to synthesize PUFs.[5] For 10 g of LPP the required amount of MDI was calculated according to eq. (1):

$$\frac{[\text{NCO}]}{[\text{OH}]}=\frac{M_{\text{MDI}}\times W_{\text{MDI}}}{M_{\text{LP}}\times W_{\text{LP}}+\left(\frac{2}{18}\right)\times W_W}=1.1 \qquad (1)$$

M_{MDI}: isocyanate group mole number per gram of MDI (mol)

W_{MDI}: mass of the MDI (g)

Figure 1. The scheme of liquefaction process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

M_{LP}: mole number of hydroxyl contained in the bio-PP (mol)

W_{LP}: mass of bio-PP (g)

W_W: mass of water (g)

Stannous octoate, triethylene diamine, silicone oil, water, R141B, and LPP were added in weight percentages given by Table II into a 100-mL beaker, and stirred mechanically for 5 min. MDI was then added and stirred rapidly for 15 s. The uniform mixture was then poured into a mold (170 mm × 120 mm × 70 mm). After foaming for 15 min, the synthesized PUFs were released from the mold and sealed in a plastic bag for 24 h before measuring the physical properties.

Analysis Methods

The hydroxyl values of PP were determined by the titration method according to GB/T 12008.3 − 2009:0.5 g PP sample was dissolved in 25 mL phthalation reagent and was heated to 115°C for 30 min under reflux. It was then cooled down with ice bath followed by addition of 50 mL deionized water through the condenser to wash the reagents. Subsequently, the mixture was titrated with 1.0M NaOH solution. The indicator was 1% phenolphthalein solution in pyridine. The phtalation reagent consisted of 116 g phehalic anhydride and 16 g imidazole dissolved in 700 mL pyridine. The hydroxyl number was calculated based on eq. (2):

$$\text{Hydroxyl number}=\frac{(V1-V2)\times M\times 56.1}{W}+C \qquad (2)$$

V_1: volume of NaOH solution required for titration of blank solution (mL);

V_2: volume of NaOH solution required for titration of sample (mL);

M: molarity of NaOH (mol/L);

56.1: molar mass of KOH (g/mol);

W: amount of the sample (g);

C: acid number of sample (mg KOH/g).

The gel permeation chromatography (GPC) spectrums were acquired using a high-pressure liquid chromatography system

Table II. formula of Additives for PUF Preparation

Additive	% (percentage of the total mass of mixture including mixed PP, MDI and additives)
Stannous octoate	0.2
Triethylene diamine	0.5
Silicone oil	2.5
Water	2
R141B	1.5

Table III. Properties of Mixed PP

Polyol	MJ-4110 (%)	LPP (%)	Hydroxyl value mg KOH/g	Average molecular weight (Mw, Da)
M100	100	0	430	1006
M75	75	25	438	1016
M50	50	50	446	1056
M25	25	75	454	1060
M0	0	100	462	1079

(1260, Agilent Technologies) consisting of a refractive index detector (RID; G1362A) and TSK G3000 PWXL column. Tris(hydroxymethyl)aminomethane-acetate acid (Tris-HAc) buffer solution (20 mmol L^{-1}, pH = 7.4) was used as the eluent at a flow rate of 0.50 mL min^{-1}. The column temperature was 25°C. The PP was dissolved in 1% (w/v) NaOH and then diluted with Tris-HAc buffer solution (20 mmol L^{-1}, PH = 7.4). Single needle injection volume was 20 μL. The polymer standards used for calibration were Agilent PEG-10 (PL2070-0100, MW 106-2200, Agilent Technologies).

The infrared spectra of all samples were determined using a Shimadzu FTIR-8400S Infrared Spectrometer. The infrared spectrum of solid samples was measured by the KBr tablet method, and that of the liquid samples were measured by painting method on KBr sheet. The determination range of spectra was 4000 cm^{-1} to 400 cm^{-1} with the wavenumber interval at 4 cm^{-1}. Forty scans were taken for each sample.

The density of lignin polyurethane rigid foam was measured according to ASTM D792-standard method: 2.0 ± 0.1 g PUFs with a sinker tied to a fine wire were put into a preweighed beaker. Air-free distilled water was then added until the beaker was completely full, and was weighed. The density was calculated with eq. (3):

$$\text{Density} = \frac{a}{a+w-b} \rho_w \qquad (3)$$

a: mass of PUFs (g); w: total mass of beaker, sinker, wire, and water (g); b: total mass of sample, beaker, sinker, wire, and water (g); ρ_w: water density in the test temperature (kg/m^3).

The compressive strength of polyurethane samples was measured by a microcomputer controlled universal material testing machine (WDW-100E, Ji'nan Shijin Group) The sample was cut into a cube (30 mm × 30 mm × 30 mm, length × width × thickness) and compressed to its 50% of its initial thickness at the rate of 2 mm min^{-1}. The pressure of 10% was obtained by correlating the pressure and displacement which was used as the compressive strength of the sample.

The thermal stability of the PUFs sample was measured by the ASTM-D3850 standard method. The thermogravimetric analysis (TGA) was done using a thermal analyzer (TG, SDT Q600) by heating from room temperature to 800°C at a heating rate of 10°C min^{-1} under a nitrogen flux of 200 mL min^{-1}.[22]

The PUFs sample was cut into thin slices and observed under the optical microscope (Eclipse E100, Nikon Instruments). The real-time pictures were taken by a camera connected to a 4X magnification objective lens. The total magnification of the sample's photos was 8X.

RESULTS AND DISCUSSION

Characterization of Lignin-Based Polyether Polyol

The LPP produced from the AL liquefaction was a brown viscous liquid. The water content, viscosity, and hydroxyl number of LPP were 1.75 ± 0.45%, 2654 ± 375 mPa s, and 420 ± 12 mg KOH, respectively. The AL liquefaction ratio was 99.4%. All the above values were in the range of those reported previously.[23]

To compare the performance of PUFs prepared from LPP with that of commercial PP, MJ-4110 with a hydroxyl value close to the LPP were used as a control. Mixtures of LPP and MJ-4110 at different ratios (Table III) were used as the starting material to produce PUFs.

Figure 2 shows FTIR spectra of mixed polyol. Infrared spectroscopy is an effective technique to characterize the functional groups of substances. 3391 cm^{-1} is the main vibration absorption of hydroxyl groups.[21,24] The absorption peaks near 2850 − 2870 cm^{-1} and 2930 − 2980 cm^{-1} were mainly the
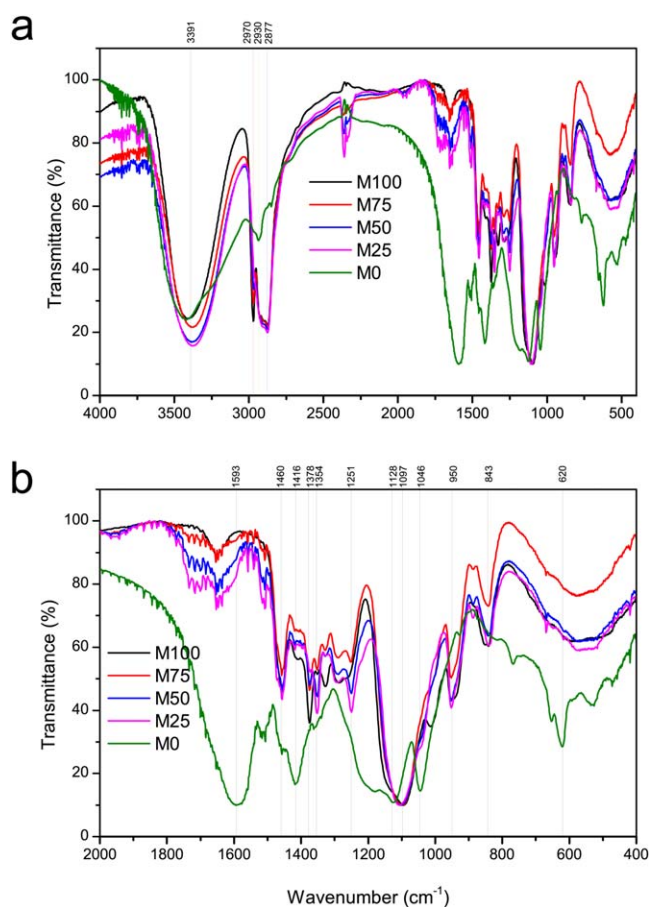

Figure 2. FTIR spectra of mixed polyol (a) full graph; (b) wavenumber between 2000 and 400 cm^{-1} M100: MJ-4110; M75: MJ-4110:LPP = 75:25; M50: MJ-4110:LPP=50:50; M25: MJ-4110:LPP=25:75; M0: lignin-based PP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
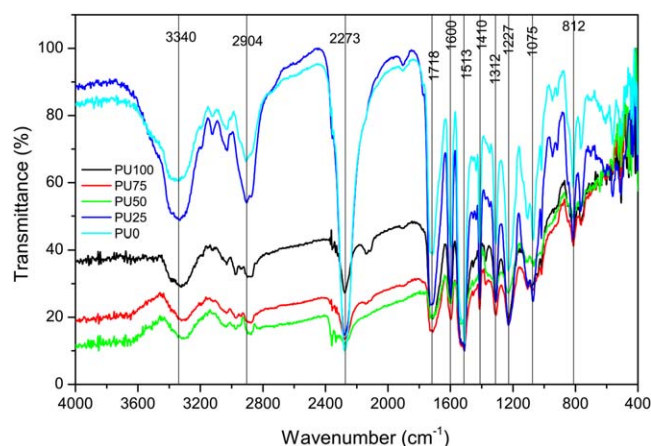
Figure 3. FTIR spectra of different PUFs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

symmetric and asymmetric C—H stretching vibration of methyl and methylene groups.[21] These two absorption peaks of LPP were smaller than the other samples, suggesting that the methyl and methylene content of LPP was relatively low, consistent with lignin being composed mainly of aromatic rings. The absorption peak intensity at 2970 cm^{-1} for other four types of PP reduced gradually with the addition of LPP, indicating that the asymmetric methyl and methylene were present more in the MJ-4110 but less in LPP. As shown in Figure 2(b), mixed polyol showed remarkable differences in the fingerprint region. Peaks at 1593, 1128, and 620 cm^{-1} were associated with the vibration of aromatic ring, while 1460, 1378, 1354 cm^{-1} were related to the vibration of methyl and methylene within the fatty chain segment. In addition, peaks at 1097 and 1046 cm^{-1} represent the symmetric and asymmetric vibration of ether bond. Therefore, the fingerprint of LPP proved that the content of lignin in LPP was relatively higher and LPP was the PP contained more symmetric ether bond.[20,25] The other samples of polyols showed stronger vibrations in the aliphatic chain segment, indicating a higher content of fatty chain segment. Moreover, the strong absorption at 1097 cm^{-1} suggests a high ether moieties content.[25]

Characterization of PUFs

FTIR. Figure 3 shows the infrared spectra of PUFs samples synthesized with different PPs. The PUFs synthesized with M100, M75, M50, M25, and M0 are represented by PU100, PU75, PU50, PU25, and PU0, respectively.

It can be inferred from Figure 3 that there are obvious differences among FTIR spectra for the various PUFs. The peak at 2273 cm^{-1} was the absorption of vibrations due to the unreacted isocyanate groups.[5] The presence of the peak at 3340 cm^{-1} was ascribed to the vibration of N—H bond.[5,11] However, some of the MDI still remained, likely because the ratio of NCO and OH at 1.1 used here caused an excess of MDI. Although the moisture in PP at 50% could consume some MDI, some remained. When LPP was used at 75% or higher, more MDI remained due to the low reaction activity of lignin in LPP. The differences for different PUFs samples at 2904 cm^{-1} was related to composition of mixed PP. The analy-

sis in 3.1 has shows that the asymmetric methyl and methylene were dominant in the control, but LPP contained more symmetric methyl and methylene, as the absorption peaks at 2904 cm^{-1} of PU25 and PU0 were enhanced significantly. The strong absorption peaks seen at 1718, 1605 cm^{-1} and 1513, 1312 cm^{-1} indicate the combination between isocyanate groups and functional groups of lignin (especially for PU25 and PU0). Since MDI itself has certain toxicity, the persistence of this residue in the PUFs may preclude its wide application. Therefore, adding the LPP at 50% might be necessary to achieve good results and conform to the requirements of polyurethane materials synthesis.

TG-DTG Analysis. Thermal stability is an important quality indicator of PUFs. Because of the presence of urethane bonds, PUFs is thermally unstable and usually starts to degrade between 150 and 220°C depending on the isocyanates and polyols used.[26] The TG and DTG curves of the PUFs prepared in this study are shown in Figure 4. Figure 4(a) shows that the heat resistance of the obtained PUFs gradually increased as LPP content increased. Polyurethane is a block copolymer with long chain diol as soft segment and polyisocyanate and extender as hard segment. The soft segment usually affects elasticity, toughness, and low temperature resistance and the hard segment determines the softening and melting temperature and mechanical properties, such as, tensile strength, hardness, and tear strength. Thus, the properties of resulting PUFs depend both on the phase structure and the micro-phase separation of soft and hard segments.[27] Kakinuma[28] made an agglomeration structure model for polyurethane soft and hard segments. The rigid structure of lignin and the crosslinked network structure formed during the preparation of PUFs can somewhat increase the heat resistance of the PUFs.[11] The pyrolysis of PUFs obtained by PP mixture can be divided into the two stages: The first stage is the degradation of the flexible chain segments in PUFs, forming a pyrolysis peak at about 330°C; The second stage is the degradation of hard chain segment, forming a pyrolysis peak around 400°C [Figure 4(b)].[12,22,29,30] Figure 4(b) shows that the pyrolysis of PUFs samples was started at 200°C, representing the
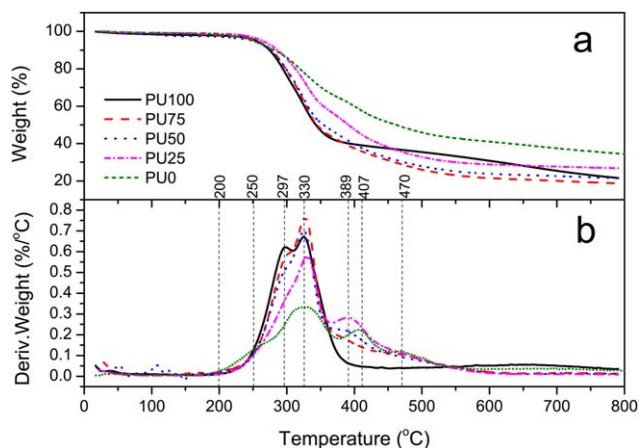

Figure 4. TG and DTG curves of PUFs, (a) TG; (b) DTG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
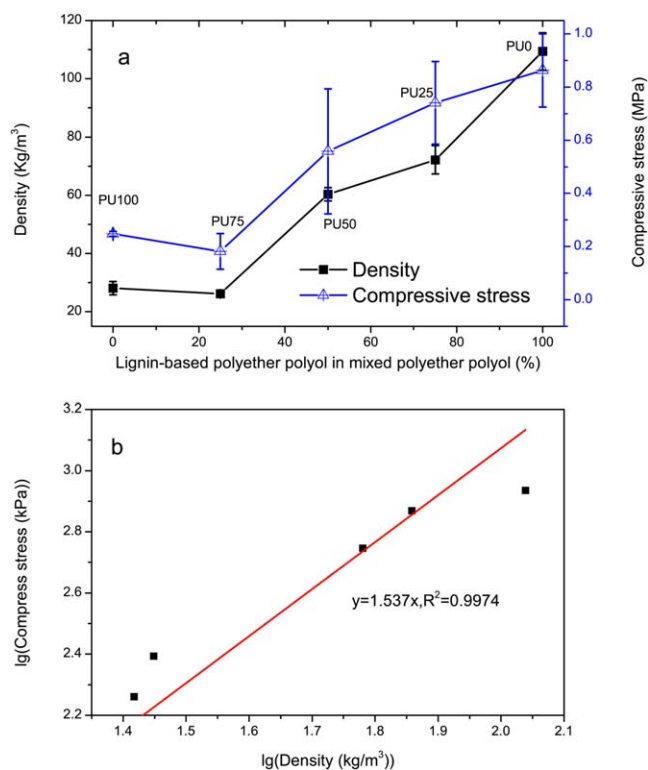
Figure 5. Relation between density and compress stress of PUFs, (a) the dependence of density and compress stress on quantity of LPP in mixed PP (Data shown as average value ± standard deviation); (b) the dependence of compress stress on density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

breakage of the urethane bond. With increased LPP content, the pyrolysis rate of the obtained PUFs gradually decreased. The pyrolysis pattern was also changed: PU100 and PU75 showed one pyrolysis peak, PU50 and PU25 had two, and PU0 had three peaks. This is likely due to lignin having a wide range of pyrolysis temperature $(160 - 900°C)$. In addition, the highly cross-linked structure of lignin increased the crosslinking degree of the polyurethane, leading to a slow pyrolysis rate.

The Density and Compressive Strength of PUFs. Figure 5 shows the relationship between the density and compressive strength of PUFs and the amount of LPP. The density and compressive strength of PUFs were 20-100 kgm^{-3} and 0.2-0.9 MPa, respectively, consistent with published values with a density range of 25-70.7kgm^{-3},[9,11,31,32] and a compressive strength range of 0.223-0.420 MPa.[32] As shown in Figure 5, with increased LPP, the density and compressive strength of obtained PUFs exhibited first decreased slightly and, then gradually increased. When the dosage of LPP reached 25%, the density and compressive strength of the PUFs were reduced. There are several possible explanations for this observation. Firstly, lignin was liquefied by PEG-400 and the glycerin and polyether reaction occurred between the hydroxyl in lignin and PEG-400/glycerol. PEG-400 has a longer aliphatic chain segment and acted as the soft segment during PUFs synthesis, relaxing the rigidity of the lignin benzene ring, which made the PUFs soft and resilient.

Secondly, the excessive PEG-400 and glycerin may have acted as soft segments in PUFs independent of reaction with lignin. Lastly, the hardness of the chain segment formed by MJ-4110 might be intermediate to the hard chain segment and soft chain segment formed by LPP. Therefore, the density and compressive strength were increased with increased LPP. Power law can correlate the compressive strength and density of PUFs,[33] which was used to fit the data in the present study [Figure 5(b)]. The result was expressed as compressive strength (kPa)=Density $(kg/m^3)^{1.5}$.[37] The correlationcoefficient of R^2 was 0.9974, indicating that the hard segments formed by the lignin were significant when the amount of LPP exceeded 25%. Further, when the amount exceeds 50%, lignin could be clearly observed as fillers in the crosslinking structure (Figure 6). In fact, when the amount of the LPP was more than 50%, the properties of PUFs met the national standards of polyurethane rigid foams (density≥55 kgm^{-3}, GB8813-88; compressive strength≥0.3 MPa, GB/T6363-95). This result differs from the findings of Li et al.[11] who reported that the compressive strength of PUFs increased then decreased with increased amounts of LPP.

The foaming effect of PUFs was better and the toughness was enhanced when the LPP dosage was 25%. This would be suitable for the preparation of semi-soft materials such as automotive interior components for insulation and cushioning. When the addition was up to 50%, the density and compressive strength increased significantly (P <0.05), reached the national standard of polyurethane rigid foams.

The Micro Morphology of PUFs. The physical properties of PUFs are not only related to the hardness of polymer blends but also relevant to its foam structure.[22,34] Figure 6(a) shows that with increased LPP content, the foam size of PUFs increased, and the regularity decreased and foam skeleton became thicker. This is because LPP reactivity is relatively weak compared with commercial PP, which resulted in more MDI being allowed to react with water to produce a large amount of gas and increasing the size of foam. Additionally, the nonuniform of lignin resulted in a nonuniformity reaction and nonuniform foam. With the increase of LPP, some lignin acted as fillers in the polymers and reinforced the PUFs.[11] This enhanced variability in foaming and the formation of bigger bubbles. The foam cell sizes distribution statistical analysis was carried out, and the results were shown in Figure 6(b). The foam cell sizes of all samples fallen into $30 - 50$ μm (length) at the highest frequency. However, the distributions of cell sizes of samples were significantly different. PU100 had a minimum distribution range, relatively, PU75 had the largest distribution range, and the maximum cell size achieved 327 μm. When the amount of LPP was 25%, the prepared PU75 had regular cells and better color. Although the regularity of the cell structure of PU50 decreased, its structure was similar level to PU100. The density of PU50 with significant characteristics of polyurethane rigid foam was significantly different from PU100 $(t = -14.17, p < 0.05)$. Although PU25 and PU0 had qualities of rigid PUFs, the toughness of these materials needed improvement.
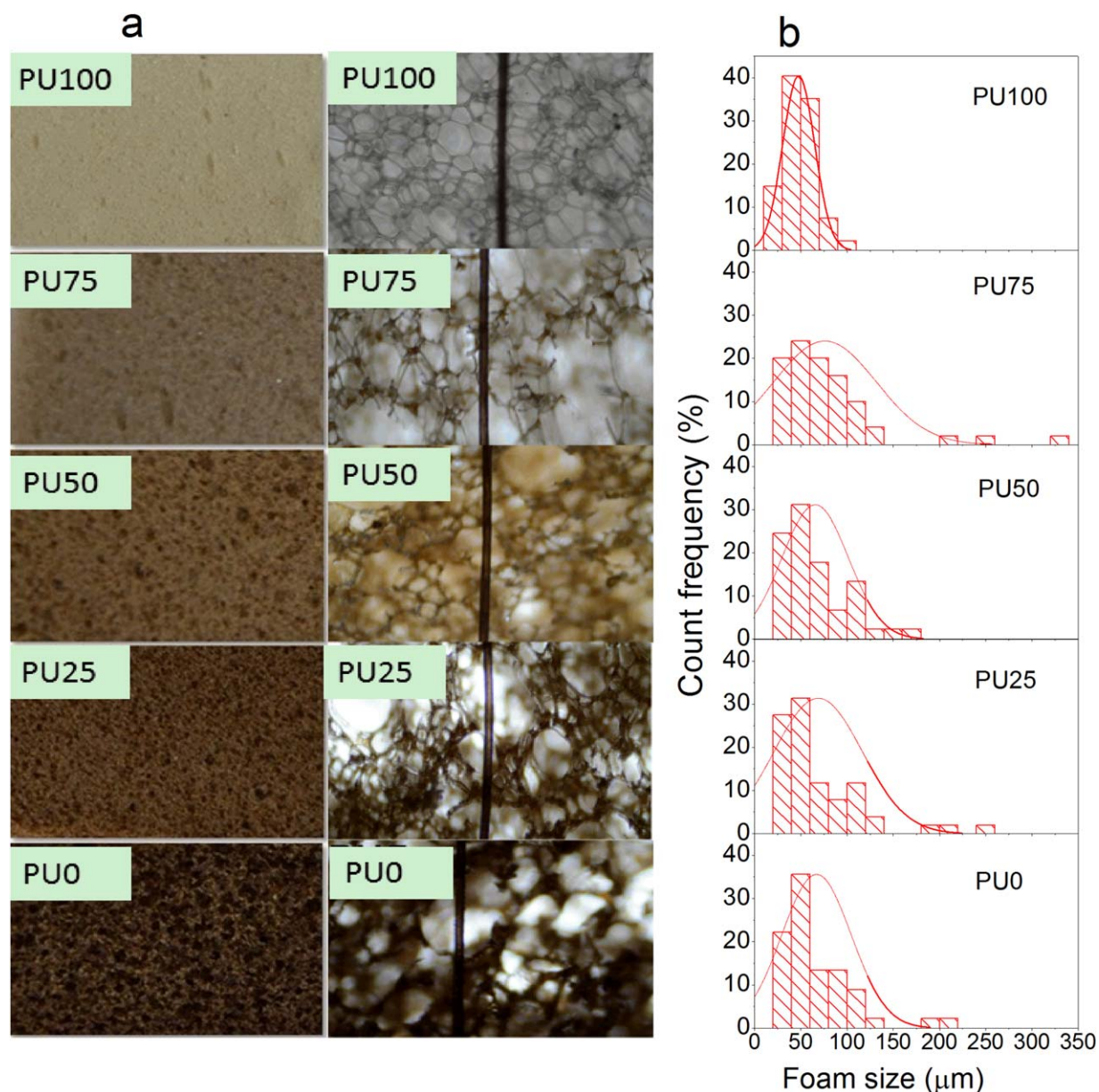
Figure 6. Microstructure of PUFs synthesized from different polyol, (a) Left: photographs taken by camera; Right: photographs taken by microscope at ×8 magnification, a 20 μm diameter wire was used as a scale; (b) foam size distribution frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

AL was liquefied with the PEG-400/glycerol system. The prepared LPP had a higher hydroxyl value (462 mg $KOHg^{-1}$) than commercial PP. PUFs prepared with LPP had better thermal stability, higher compressive strength and density than the PUFs synthesized by commercial PP. However, PUFs prepared with different mixtures of the two PP exhibited some better material properties.

ACKNOWLEDGMENTS

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