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The Use of Lignin as Cross-linker for Polyurethane Foam for Potential Application in Adsorbing Materials

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Lignin was extracted from wheat straw and used for its crosslinking function in the synthesis of polyurethane foam (PUF). The effects of lignin's addition on the cross-linking structure and macroscopic properties of the PUFs were investigated. A morphological examination, Fourier transform infrared (FT-IR) spectroscopy, and thermogravimetric analysis (TGA) were conducted to measure the performance of the polyurethanes. Kinetic models were simulated to analyze the oily solvent adsorption mechanism of the polyurethane. The results showed that an increase in the cross-linking density was conducive to an improvement of the physical properties of the polyurethane. Moreover, the process of oily solvent adsorption was in accordance with the quasi-second-order kinetic model. Both physical and chemical adsorption occurred during the adsorption process. This work demonstrated a highly effective method for imparting PUFs with an excellent performance and proper lignin content.

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INTRODUCTION

Recently, the utilization of sustainable and environmentally friendly sources for the production of green materials has generated noticeable interest from both academic and industrial fields. Of these renewable resources, biomass acts as a carbon source that can generate valuable chemicals and replace petrochemicals. The production of new value-added bio-chemicals and biomaterials from various types of industrial or agricultural residual resources was proposed by use of bio-refining approaches (Li *et al*. 2016).

Lignin is a complex, heterogeneous, and natural aromatic compound that contains cross-linked phenolic polymers (Jeong *et al*. 2013). However, lignin is only a byproduct in the paper-making industry and is most often burned as a low-value fuel. As a source of chemicals and materials, lignin can replace petroleum feedstock for many polymer products (Mahmood *et al*. 2016b). Different functional monomers (phenolic hydroxyl, aliphatic hydroxyl, and methoxyl groups) are incorporated in the macromolecular phenyl propane structure (Baillères *et al*. 1997; Vanholme *et al*. 2010). The rigid benzene ring structure and phenol hydroxyl groups in the lignin structure are promising candidates for value-added utilization (Li and Ragauskas 2012).

One method for the value-added utilization of lignin is to prepare lignin-containing copolymers (Saito *et al*. 2013). A strategic execution of copolymerization is to prepare polyurethane foams (PUFs). The PUFs are considered to be one of the most versatile and useful three-dimensional polymeric materials with applications in diverse areas, and are an

important category of expended materials (Hatakeyama *et al*. 2008; Cateto *et al*. 2014). Polyurethane foams can be applied in many areas, including as sponges in furniture manufacturing, wastewater treatment, packaging, sound absorbing materials, adhesives, *etc*. (dos Santos *et al*. 2013; Huo *et al*. 2012; Kumari *et al*. 2016).

The reactions between polyols and isocyanates during the chain propagation steps play an important role in the polymerization reactions when preparing polyurethane (Li *et al*. 2016). The lignin in polyurethane is mainly used as an additive packing/filler (Paberza *et al*. 2014), reactive agent to be cross-linked with urethane (Pan and Saddler 2013), and modified functional additive (Zhu *et al*. 2014). Cinelli *et al*. (2013) reported a green process for the synthesis of soft PUFs using kraft lignin with two types of chain extenders, which can impart PUFs with a higher flexibility. Li *et al*. (2016) noted that alkaline lignin was completely liquefied with polyethylene glycol-400/glycerol when preparing PUFs with higher thermal and physical performances. Jeong *et al*. (2013) used softwood kraft lignin as a cross-linking agent to react with polyol when preparing PUFs. The obtained PUFs showed an excellent elasticity and could be used in buffer materials.

Using lignin as an additional agent to prepare PUFs has been widely studied (Xue *et al*. 2014; Carriço *et al*. 2016; Mahmood *et al*. 2016a). The additive amount of lignin in earlier works were all higher than 5%, and amounts in excess of that cause agglomeration of lignin particles in the final products. It has been shown that micro-additive amounts of functional reagents can lead to a remarkable improvement of the mechanical characteristics of cross-linked polyurethane (Estrin *et al*. 2012). The relationship between the lignin content and cross-linking behavior has rarely been studied.

The present research investigates the effect of micro lignin contents on the cross-linking structure and physical properties of prepared lignin-based polyurethane foam (LPUF). At the same time, the physical performance, mechanical properties, and thermal behaviors were evaluated. Finally, the adsorptive properties of the LPUFs were thoroughly investigated.

EXPERIMENTAL

Materials

Lignin was extracted from the black liquor of wheat straw. The relevant data of the lignin and a more detailed description of the pulping conditions are given in the authors' previous work (Tian *et al*. 2017).

The chemical 4,4'-methylenebis phenyl isocyanate (MDI, purity ≥ 98 wt.%) was purchased from Aladdin (Shanghai, China). Polyethylene glycol (PEG, 330n, molecular weight = 5000 g/mol, OH = 33 to 37 mg KOH/g) was provided by Hengyu Chemical Co., Ltd. (Jiangsu, China). Silicone oil (Industrial reagent, IR) was supplied by Scientific and Technological Chemical Technology Co., Ltd. (Beijing, China). Benzene, toluene, xylene, ethyl acetate, triethanolamine, and dibutyltin dilaurate were all used as analytical reagents. Ultrapure water (18 MΩ • cm at 298 K) was purified with a Millipore Milli-Q (Millipore Direct-Q5, Billerica, MA, USA).

Synthesis of the lignin-based polyurethane foam (LPUF)

The PEG (20.00 g) and lignin (lignin weight present was based on the weight of PEG: 0%, 0.5%, 1%, 1.5%, 2%, 2.5%) were weighed, added to a 50-mL plastic beaker, and magnetically stirred at 25 °C for 5 min to obtain a uniform pre-mixture. The pre-mixture, deionized water (0.35 g), triethanolamine (0.20 g), silicone oil (0.40 g), and dibutyltin dilaurate (0.15 g) were accurately weighed, and stirred in a thermostat water bath at 80 °C for 5 min. The MDI (8.0 g) was added into the mixture under constant stirring conditions. The mixture was immediately poured into a mold (cubic paper container, $10 \times 10 \times 8 \text{ cm}^3$) where the mixture emitted heat and produced bubbles. Finally, the LPUFs were obtained after heating the mold for 10 h at 80 °C. A better isocyanate index was 1.1, which was reported in previous studies (Pan and Saddler 2013; Carriço *et al*. 2016). The isocyanate index was calculated according to the following formula (Cinelli *et al*. 2013),

$$\frac{n_{[NCO]}}{n_{[OH]}} = \frac{W_{\text{NCO}} \times W_{\text{NCO}}}{\sum W_{OH} \times M_{OH} + \frac{2}{18} \times W_{H_2O}} \tag{1}$$

where $n_{[NCO]}$ and $n_{[OH]}$ are the amounts of isocyanate and PEG (mol), respectively, W_{NCO} and W_{OH} are the weight of the isocyanate and polyol (containing PEG, lignin, and catalysts) (g), respectively, M_{NCO} and M_{OH} are the molar masses of isocyanate and polyol (mol/g), respectively, and W_{H_2O} is the mass of the water (g).

Cross-linking density

The cross-linking density was calculated by the Flory-Rehner equation, which is given as Eq. 2 (Flory and Rehner 1943; Zhu *et al*. 2011),

$$-\left[\ln\left(1 - v_p\right) + v_p + \chi v_p^2\right] = v_s \rho_p \left(v_p^{1/3} - \frac{v_p}{2}\right) / M_e \tag{2}$$

where v_p is the volume of the polymer in the swollen PUFs (%), χ is the interaction parameter of the polymer-solvent, v_s is the molar volume of the solvent (%), and M_e is the average relative molecular mass between adjacent cross-links (g/mol).

Equation 2 is frequently rearranged and simplified, and is shown below as Eq. 3 (Fan and Xiao 2010),

$$V_e = -\frac{1}{v_s}\left[\frac{\ln\left(1 - v_p\right) + v_p + \chi v_p^2}{v_p^{1/3} - v_p / 2}\right] \tag{3}$$

where V_e is the cross-linking density of the polyurethane (mol/cm³). The variables v_p and χ were determined by Eqs. 4 and 5, respectively (Zhu *et al*. 2011),

$$v_p = \frac{m_p / \rho_p}{m_p/\rho_p + m_s / \rho_s} \times 100\% \tag{4}$$

$$\chi = \frac{v_s}{RT}(\delta_p - \delta_s)^2 \tag{5}$$

where m_p and m_s represent the masses of the polyurethane and solvent (g), respectively, ρ_p and ρ_s are the densities of the polyurethane and solvent (g/cm³), respectively, R and T are the gas constant (8.314 J/K·mol) and absolute temperature (K), respectively, and δ_s is the solubility parameter of the solvent (J/cm³). The variable δ_p (J/cm³) was determined by fitting the curves of the swelling coefficients (Q) *versus* the solubility parameter (δ) (Mathew *et al*. 2017). The corresponding abscissa value at the top of the curve was determined as δ_p in Fig. 3. (a).

Methods

Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared (FT-IR) spectra of the PUFs were recorded using a VERTEX-70 (Bruker, Karlsruhe, Germany) equipped with a digital detector. The dry samples were ground and pelletized using KBr. The spectra were then measured in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1}.

Apparent density

The apparent density was determined according to the standard ASTM D792 (2008). The samples were measured five times, and the average results were recorded.

Mechanical properties

The mechanical properties tests were performed with an Instron instrument (model 5565, Norwood, GA, USA). The tensile and compressive tests were carried out according to ASTM D1623-09 (2009) and ASTM D1621-10 (2010) (Hakim *et al*. 2011; Yu *et al*. 2014), respectively. Both the tensile and compression tests of PUFs/LPUFs were performed at the room (25 °C) and the rate of the crosshead movement was fixed at 10 mm/min. The specimens were evaluated five times, and the average values were determined.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed using a TA Q500 apparatus (TA Instrument, New Castle, USA) under a nitrogen gas atmosphere. The samples were heated from room temperature to 700 °C at a heating rate of 10 °C/min.

Adsorption tests

The methods for determination of the oily solvent and water sorption were based on the ASTM F726-99 (1999) standard test method (Li *et al*. 2012). Four types of oily solvent, benzene, methyl benzene, dimethyl benzene, and ethyl acetate, were employed to investigate the adsorption quantity of the sorbents. The sorbent was cut to the specified size and weighed accurately to determine the initial mass. Different oily solvents (50 mL) were poured into a 100-mL beaker. After immersion for 30 min, the specimen was removed and weighed immediately after it was drained for 30 s. The experimental error was controlled within plus or minus 5%, and the sorption was calculated by Eq. 6,

$$\text{Sorption(g/g)} = \frac{S_{ot} - S_0}{S_0} \tag{6}$$

where S_0 is the initial weight of the sorbent (g) and S_{ot} is the weight of the sorbent that has adsorbed oily solvent (g).

Kinetic model analysis

Lagergren quasi-first-order and quasi-second-order kinetic equations were used to analyze the polyurethane oily solvent adsorption process. The two model algorithms are shown by Eqs. 7 and 8 (Qiu *et al*. 2009; Huo *et al*. 2012),

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1 t}{2.303} \tag{7}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{8}$$

where Q_e and Q_t are the amounts of solvent adsorbed (g/g) at the equilibrium and time t (min), respectively, and K_1 and K_2 are the adsorption constants corresponding to the quasi-first-order (min^{-1}) and quasi-second-order (g/g min) kinetic equations, respectively.

The kinetic evaluation of the adsorption was also performed by using Morris-Weber model to explain the diffusion process (Qiu *et al*. 2009). The Morris-Weber model was described by Eq. 9,

$$Q_t = k_d \cdot t^{1/2} + C \qquad (9)$$

where k_d is the intraparticle diffusion constant. C represents a parameter of the function that indicated the resistance of the interfacial film (Crini *et al*. 2007).

RESULTS AND DISCUSSION

FT-IR

Figure 1 shows the FT-IR spectra of lignin and PUFs. Pristine lignin showed a broad band at 3500-3000 cm^{-1}, which was attributed to the stretching of phenolic and aliphatic hydroxyl groups (Kumari *et al*. 2016). The absorption peak at 2970 cm^{-1} was associated with the C=O stretching vibration in carbonyl groups. The bonds at 2922cm^{-1} were related to asymmetric stretching vibration of methylene (-CH$_2$) and 2848 cm^{-1} were due to C-H symmetric stretching vibration in lignin molecular structure (Yang *et al*. 2015). The bands at 1622 cm^{-1}, 1508 cm^{-1}, and 1460 cm^{-1} resulted from aromatic ring stretching vibration.
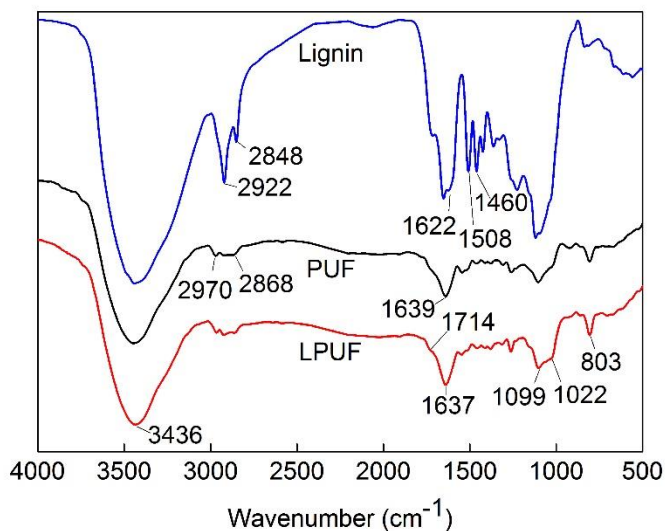

Fig. 1. FT-IR spectra of lignin, PUF and LPUF (0.5 wt.% lignin)

From the spectra of polyurethane foams, the characteristic absorption peaks that appeared at approximately 3436 cm^{-1} were assigned to the stretching vibration of the N-H bond (Santos *et al*. 2016) in polyurethane. The bands centered approximately 2970 cm^{-1} and 2868 cm^{-1} corresponded to the C-H stretching of the aliphatic chains (Rahman *et al*. 2016). The vibrancy peak observed near 1714 cm^{-1} were associated with carbonyl stretching. The peak at 1637 cm^{-1} was the characteristic absorption of urea. The bonds between 1022 cm^{-1} and 1099 cm^{-1} were ascribed to the C-O bond (Qu *et al*. 2017). The

signal that appeared at 803 cm^{-1} was attributed to the C-H deformation of the aromatic groups in the spectra. The reaction between isocyanate and lignin was evidenced by the following changes of FTIR spectra: (a) a wider band at 3436 cm^{-1} in polyurethane typical of bonded N-H increased with increasing lignin content, which was merged with the OH bond at 3300 cm^{-1} (Luo *et al.* 2013); (b) a marked increase of the absorption bands in C–O stretching region between 1022 cm^{-1} and 1099 cm^{-1} was due to the reaction between isocyanate and hydroxyl groups of lignin; (c) the peaks of urea shifted from 1639 cm^{-1} to 1637 cm^{-1} suggesting that the introduction of lignin affect the hydrogen bonds between N-H and C=O because of the interaction between lignin and isocyanate (Carriço *et al.* 2016). It was concluded that the reaction occurred between isocyanate and lignin. In addition, the addition of lignin did not change the main functional groups of the PUFs, as was shown in the FT-IR spectra.

Synthesis and Oily Solvent Adsorption of the Polyurethane Foams (PUFs)

The synthetic reaction diagram of the PUFs is shown in Fig. 2. Because of the numerous hydroxyl groups and special three-dimensional structure, the lignin added can not only extend the polyurethane molecular chain, but it can also support a skeleton in a cellular structure. Hydrogen bonds also existed in the compound molecules. The unique spatial structure of lignin was beneficial for increasing the cross-linking density and improving the physical properties of polyurethanes.
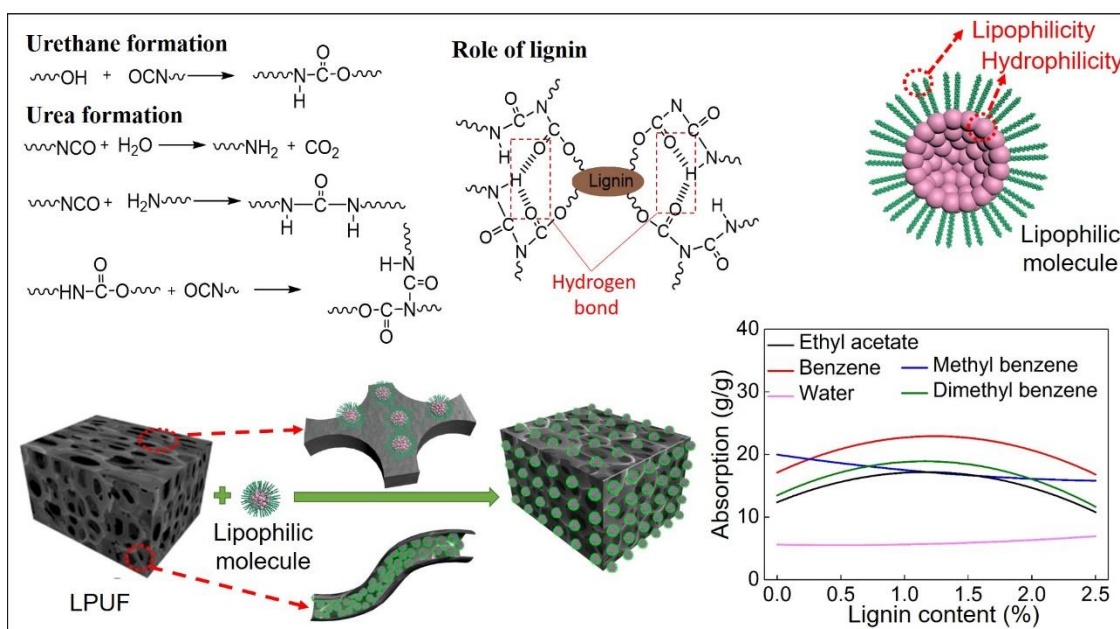

Fig. 2. Synthetic reaction and oily solvent adsorption diagram of the LPUF

The adsorption behavior of the oily solvents onto the LPUFs is also described in Fig. 2. The oily solvents were adsorbed onto the surface of the PUFs via van der Waals forces through lipophilic oily molecules. Oleophilic and hydrophobic groups, such as aroma structures, ether bonds, ester bonds, and hydrocarbon side chains, are introduced in condensation polymerization reactions. These groups exist on the surface of the foams and promote intermolecular attraction, which can enhance the oily solvent adsorptive capacity (Gui *et al.* 2011; Li *et al.* 2012). Electron transfer occurs between an adsorbent and

adsorbate during chemical adsorption and promotes the formation of new chemical bonds. When the lignin content was in the range of 0.5 wt.% to 2.0 wt.%, the maximum adsorption of benzene, dimethyl benzene, and ethyl acetate increased by 50.2%, 44.0%, and 41.5%, respectively, compared with that with no lignin addition.

Cross-linking Density of the PUFs

The swelling coefficients ($Q=1/v_p$) versus the solubility parameters (δ) of the LPUFs with different lignin contents are shown in Fig. 3 (a). The corresponding abscissa values at the top of the curves were fitted by Gauss and were determined as the solubility parameter (Valero *et al*. 2009; Mathew *et al*. 2017).
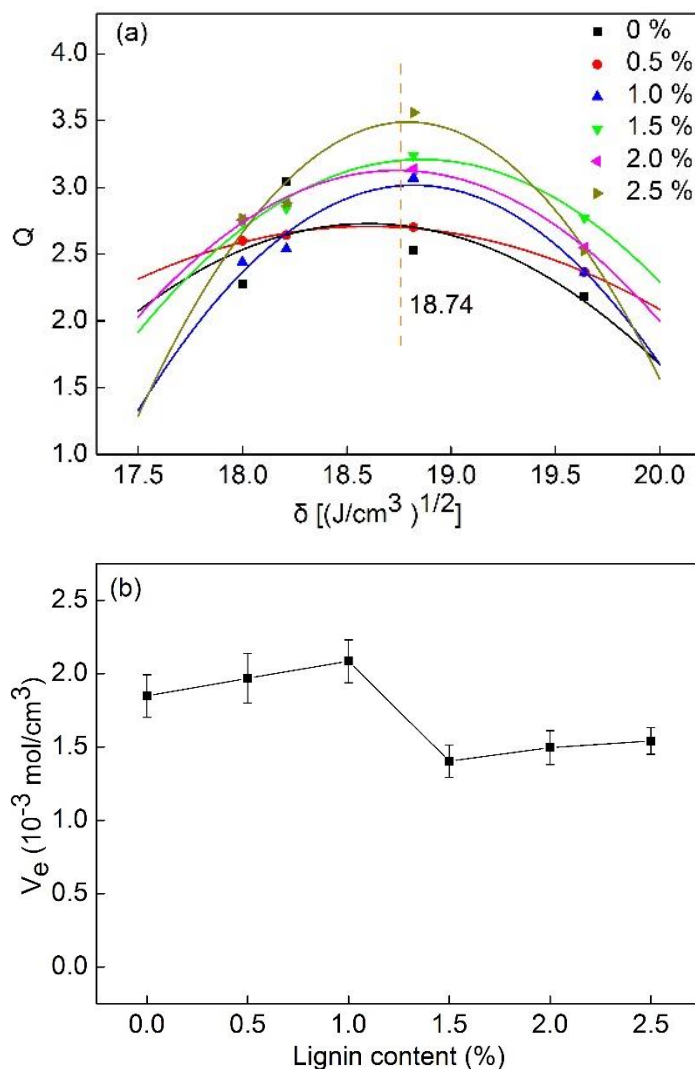

Fig. 3. (a) Fitting curves of the swelling coefficients (Q) *versus* the solubility parameters (δ) of the LPUFs with different lignin contents; (b) cross-linking density of the LPUFs

It was found that the abscissa corresponding to the maximum value of the ordinate was 18.7 $(J/cm^3)^{1/2}$(Zhu *et al*. 2011). The cross-linking density of PUFs were calculated by Eq. (3), (4), and (5). The cross-linking densities of the PUFs showed a slight increase with lignin content less than 1%. The cross-linking density of the PUFs increased with a small

addition of lignin (less than 1%), but when the lignin content increased further, the cross-linking density decreased noticeably, as shown in Fig. 3b. This was possibly due to that the cross-linking reaction between the isocyanates and hydroxyl groups distributed on the surface of lignin macromolecules caused the enhancement of cross-linking values and promoted the formation of more complex network structures in polyurethanes. However, overused lignin may produce local excessive cross-linking due to agglomeration, which leads to a decrease in the cross-linking density of PUF.

SEM Analysis of PUFs

The micrographs, mean pore diameter, and spatial network skeleton thickness derived from the normal PUF and LPUFs are presented in Fig. 4.
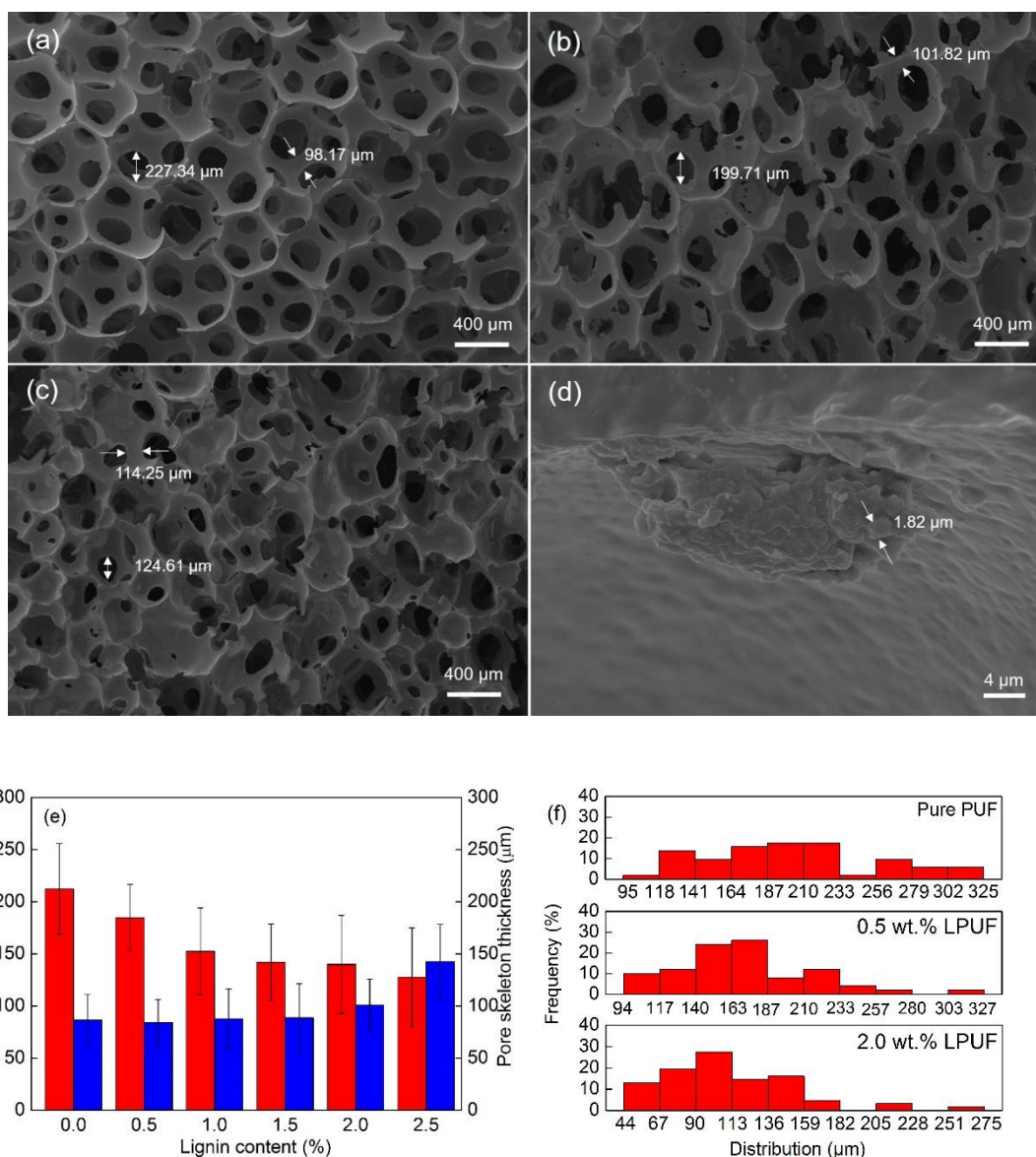

Fig. 4. Micro images of the PUFs: (a) pure PUF, (b) 0.5 wt.% LPUF, (c) 2.0 wt.% LPUF, and (d) flocculation of lignin; (e) mean pore diameter and spatial network skeleton thickness of the LPUFs (f) The pore size frequency distribution of pure PUF, 0.5 wt.% LPUF and 2.0 wt.% LPUF

The pure PUF was relatively uniform and had larger open-pores, as shown in Fig. 4a. However, irregular and disorganized holes appeared when lignin was added. The pore size and structure of the PUF/LPUFs were closely related to the lignin content in the samples. The alteration in the interior spatial network and skeleton morphology was most likely because of the fact that lignin may affect the process of cell nucleation during the synthesis of polyurethane (Xue *et al.* 2014). The amount of lignin in the polyurethane has a great effect on the structure of the cells (Li *et al.* 2011). The irregular and inhomogeneous distribution of lignin in the LPUFs was attributed to the chemical bond attraction between the reactive chemical groups that persisted on the surface and the flocculant caused by the multidimensional mesh structure of natural lignin, which can be seen in Fig. 4d. A similar situation did not occur when the amount of lignin added was more than 1.5 wt.%. Smaller pores and a thicker cellular skeleton occurred in the LPUFs, as shown in Fig. 4e. The pore size frequency distribution of pure PUF, 0.5 wt.% LPUF and 2.0 wt.% LPUF are shown in Fig. 4f. It was found that larger pore size and wide distribution occurred in pure polyurethane foam, and the pore size was obviously reduced after blending lignin. Hence, more complex pores and thicker cellular skeleton were formed when added lignin in the PUFs. The observed smaller and more complex pores and thicker cellular skeleton can thus explain the improvement of the physical and mechanical properties. For cells with a similar wall thickness, the density increases as the cell size decreases, which influences the mechanical properties (Cateto *et al.* 2014).

Mechanical Properties of the PUFs

The apparent density of the PUFs is considered to be an important criterion for measuring its performance, and it affects the pore structure and mechanical properties of the PUFs (Dworakowska *et al.* 2014). With the addition of lignin, the apparent density of the polyurethane first decreased, and then it gradually increased, as shown in Fig. 5a. A possible explanation for the decreased density was that a small amount of lignin dispersed uniformly and crosslinked with the macromolecules in the LPUFs. This process promoted the formation of stable foam skeleton and bubble structures in the polyurethane. The foam structure was formed, and larger volumes and lower densities were obtained. Increasing the dosage of lignin to over 1 wt.% resulted in local excessive cross-linking due agglomeration, which led to aggregation and adhesion of the lignin particles.

The elongation at break and specific compressive strength are also shown in Fig. 5. The results showed that the elongation at break increased slightly, and then decreased with increased amounts of lignin. The high values for the 0.5 wt.% lignin content were because of the polyol flexible segments. Once the lignin amount exceeded 1 wt.%, the elongation at break decreased noticeably.

According to Fig. 5b, the compressive and specific compressive strengths of the LPUF with a 0.5 wt.% lignin content were both higher than for the pure PUF. The compressive strength of the 0.5 wt.% LPUF increased 40.8%, and the specific compressive strength increased 61.3% compared with the pure PUF.

The following reasons explained the enhancement of the physical behaviors: (1) plasticized lignin decreases the cross-linking density of LPUFs, which increases the apparent density and compressive strength (Zhang *et al.* 2015); (2) the natural rigid structure of lignin may disrupt the macromolecular structure, which decreases the elongation and enhances the physical properties (Putz *et al.* 2008); (3) the hydrogen bonding between –NH and –C=O in LPUFs may cause a decrease in elongation, and Huang and Lai (1997) established that an increase in the hydrogen bonding index can increase the

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modulus and decrease the maximum elongation of LPUFs; and (4) the imbalance between the gel and foaming rates is caused by the excessive lignin content in the synthesis process, which leads to a decrease in the cross-linking density and seriously affects both the compressive and specific compressive strengths.
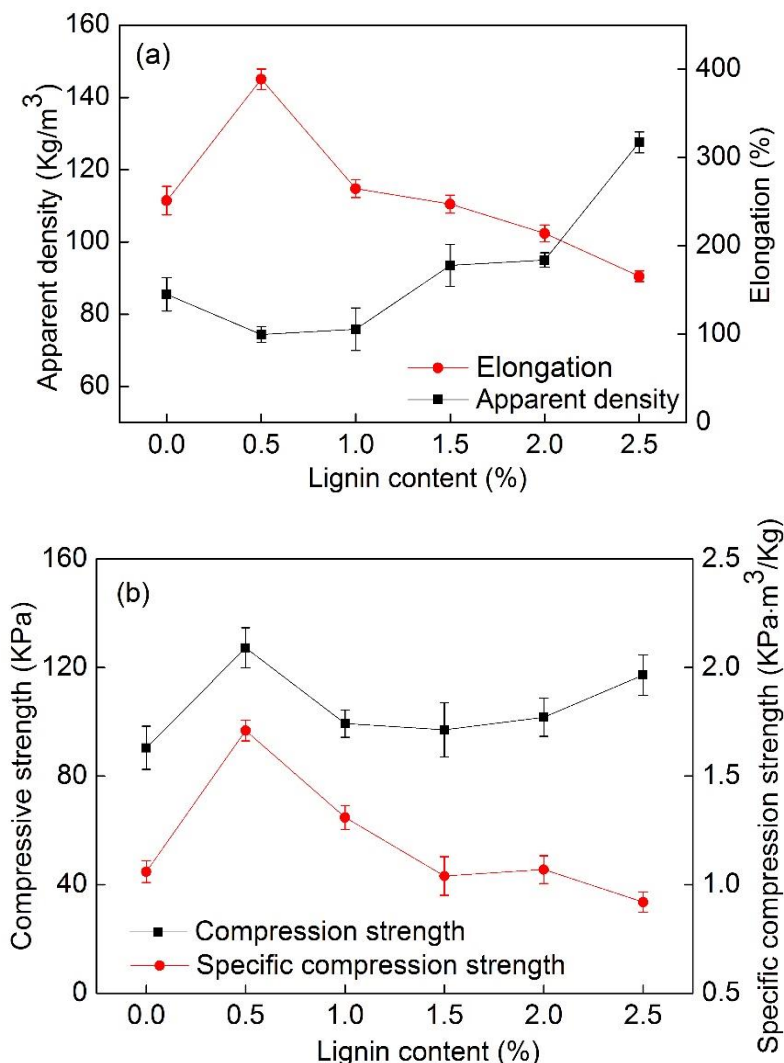

Fig. 5. (a) Apparent density and elongation of the polyurethanes; (b) compressive strength and specific compressive strength of the polyurethanes

Thermal Gravimetric Analysis

The TGA and DTG of lignin and PUFs were performed to investigate the effect of the lignin amount on the thermal behavior of the PUFs. It was observed that for lignin, the TGA curve of lignin showed a rapid mass loss before 150 °C, which was due to higher moisture content in the sample. The final thermal degradation temperature of lignin was higher than that of PUF/LPUFs. Thermal degradation of the PUFs occurred in almost the same way in three steps, as shown in Fig. 6 (a) and (b). The initial mass loss at temperatures lower than 250 °C was attributed to the evaporation of water and the loss of some small organic molecules in the PUFs (Carriço *et al.* 2016). The second mass loss observed at approximately 305 °C was related to the decomposition of hard segments urethane groups.

The third degradation event at 372 °C was probably due to the depletion of C-C bonds (Santos *et al*. 2016). Moreover, the skeleton of the foam was arranged to be more compact, due to the change of crosslinking density and mobility of the polymer chains in PUFs. In addition, the degradation temperature for LPUF was higher because of the addition of lignin (Oribayo *et al.* 2017). As expected, the TGA thermograms and DTG curves confirmed that the thermal stability of the foam was improved after blending with lignin. According to Fig. 6a and b, the thermogravimetric parameters of the PUFs shown in Table 1, it was revealed that the thermal decomposition temperature of the PUFs was effectively improved by introducing lignin into the PUF system. A possible explanation for this was that the introduction of lignin molecules increased the cross-linking density during the reaction. Moreover, the skeleton of the foam was arranged to be more compact, which was related to the change of crosslinking density and mobility of the polymer chains in PUFs (Santos *et al*. 2016). It was concluded that the thermal resistance of PUFs was improved through the incorporation of lignin.
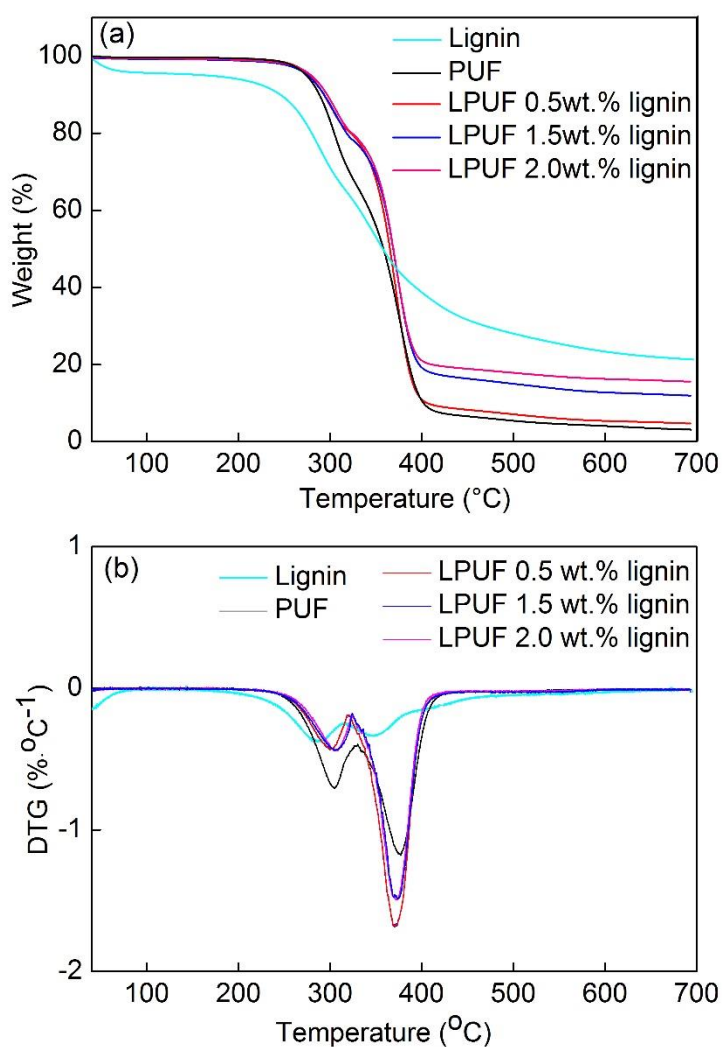

Fig. 6. TGA (a) and DTG (b) curves of the PUF and LPUFs

Table 1. Thermogravimetric Parameters of the PUFs

Lignin Content (%)	Temperature (5% of Mass Loss) (°C)	Temperature (50% of Mass Loss) (°C)
0	272.14	358.80
0.5	277.43	365.21
1.5	279.98	368.88
2.0	280.47	368.97

Quasi Dynamic Model Analysis

The PUFs are cellular materials that have a major role in the adsorption performance of an adsorbent. The adsorption experiments were performed with the 0.5 wt.% LPUF as the adsorbent and with oily solvents (ethyl acetate, benzene, methyl benzene, and dimethyl benzene) as the adsorbate at 25 °C. Adsorption isotherms can determine the relationship between the adsorbate in the bulk solution and the amount adsorbed on the PUFs at a certain temperature. From Fig. 7, it was seen that the adsorption capacity increased rapidly in the first 5 min, and then gradually increased until an equilibrium was reached. Figure 7 also revealed that the LPUF had a stronger adsorption capability than the PUF.

Adsorption kinetic analysis can offer valuable information on the adsorption mechanism by determining the adsorption rate that governs the equilibrium time of the whole adsorption process. To study the adsorption mechanism, quasi-first-order and quasi-second-order kinetic models were used to fit the experimental data. The kinetic models are shown in Fig. 7, and the corresponding parameters and the coefficients of determination (R^2) are listed in Table 2. Methyl benzene was the solvent that swelled the polyurethane networks the most, as reported by Ferrer *et al*. (2008).

Table 2. Kinetic Model Parameters for Oily Solvents Adsorption onto the Foams

Type	Oily Solvent	Q	Quasi-first-order Model			Quasi-second-order Model		
			K_1 (min^{-1})	Q_e^f (g/g)	R^2	K_2 (g/g min)	Q_e^s (g/g)	R^2
	Ethyl acetate	2.18	0.208	4.621	0.961	0.162	13.280	0.999
	Benzene	2.52	0.129	4.141	0.830	0.152	12.903	0.998
	Methyl benzene	3.04	0.071	3.038	0.585	0.127	18.255	0.996
	Dimethyl benzene	2.27	0.220	1.748	0.830	0.512	19.861	0.999
	Ethyl acetate	2.37	0.237	5.115	0.869	0.186	17.637	0.999
	Benzene	2.70	0.181	9.099	0.705	0.070	21.664	0.996
	Methyl benzene	2.64	0.291	11.455	0.603	0.071	19.857	0.995
	Dimethyl benzene	2.60	0.120	1.862	-0.003	0.238	19.179	0.999

^{f} represents the quasi-first-order kinetic model; ^{s} represents the quasi-second-order kinetic model

It was noted that the values obtained for the PUF and LPUF at the adsorption equilibrium with the quasi-first-order model (Q_e^f) were quite different from the actual values in the experiments (Q_e). This indicated that the adsorption process did not conform to the quasi-first-order kinetic model. In contrast, the values calculated from the quasi-second-order kinetic model (Q_e^s) were sufficiently close to the Q_e values. It was concluded that the oily solvents adsorption processes of the PUF and LPUF conformed to the quasi-second-order kinetic model. This situation may be attributed to a chemical activation between oily molecules with the functional groups of the polyurethane foams (Bilir *et al*. 2013). The results also showed that the oily solvents adsorption process of the polyurethane

was controlled by physical and chemical adsorption (Dufresne and Belgacem 2013; Góes *et al*. 2016).
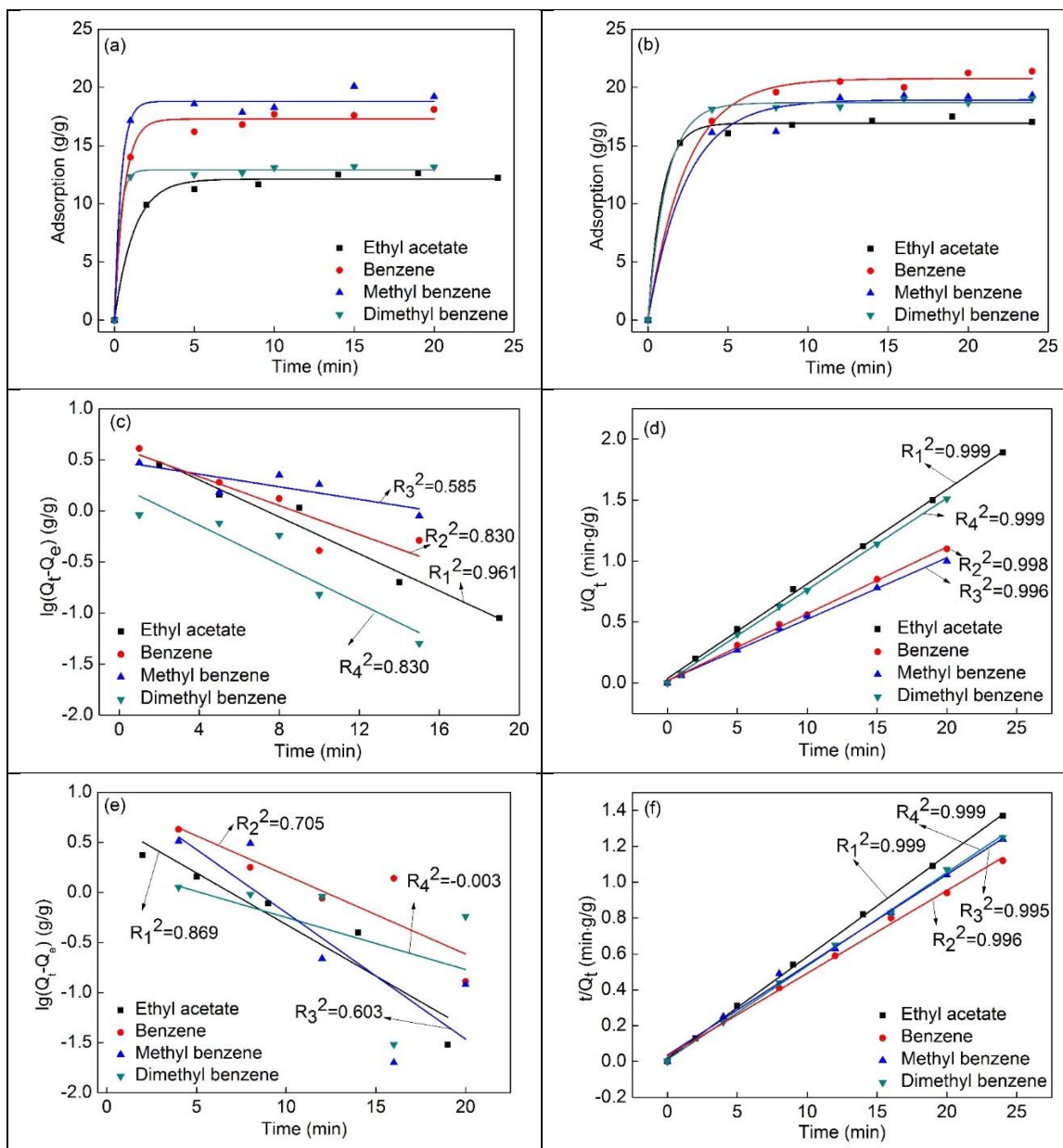

Fig. 7. Isothermal adsorption curves of the PUF and LPUF with different oily solvents at 25 °C: (a) normal PUF and (b) LPUF (0.5 wt.% lignin); (c) quasi-first-order and (d) quasi-second-order kinetic models of the PUFs; (e) quasi-first-order and (f) quasi-second-order kinetic models of the LPUF

The foams prepared in the present work had almost full-hole structures, which can be observed in the SEM images. The open-holes that existed complexly in the foams, as shown in Fig. 4, provided abundant "capillary-channels" and "shelters" for the entry and adsorption of oleophilic molecules. Moreover, the network skeleton can effectively support the weight of the adsorbed oily solvents and ensure an efficient retention capacity. A small amount of lignin (less than 1.0 wt.%) increased the spatial cross-linking density, which

made the pores smaller and the spatial network structure more complex. These complex skeleton structures facilitated the development of a capillary effect, which helped to achieve the purpose of oil storage. These behaviors undoubtedly increased the adsorption capacity of the adsorbate onto the polyurethane. Therefore, when the foam was in contact with the oily solvents, not only were van der Waals forces and chemical bond forces formed, but also the capillaries formed by the capillary condensation phenomenon on the surface of the polyurethane affected the oily solvents retention.

Morris-Weber Model

The fitted curves of the Morris-Weber model for the adsorption of pure PUF(a) and LPUF with 0.5 wt.% lignin (b) are shown in Fig.8. If a straight line was obtained when $t^{1/2}$ was plotted against Q_t, a diffusion process was active in controlling the adsorption kinetics. Furthermore, if the straight line passed through the origin, it indicated that the intraparticle diffusion was the rate-controlling step to control the adsorption process. If the origin was not passed, the adsorption process was partly controlled by diffusion, along with other adsorption stages (Vinhal *et al*. 2015). From Fig. 8 (a) and (b), it is apparent that the fitted line did not pass through the origin. This indicated that the adsorption process was controlled by intraparticle-diffusion and other adsorption mechanisms.
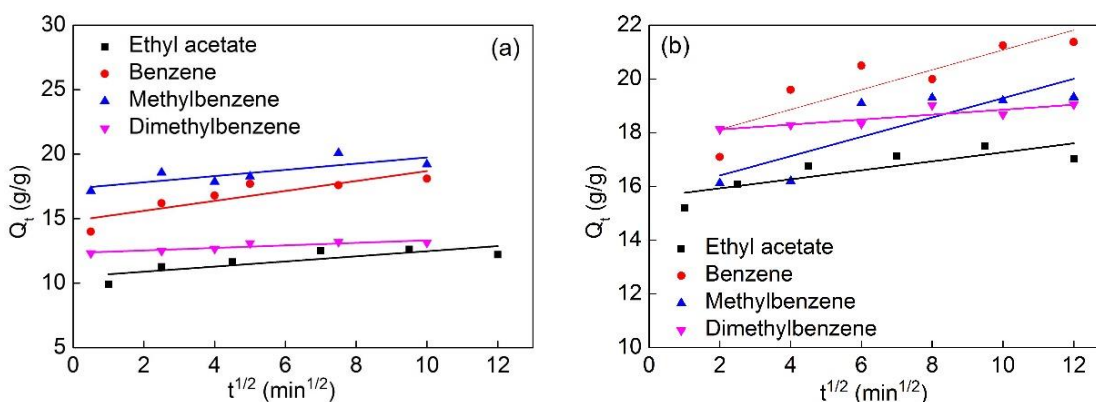

Fig. 8. Application of the Morris-Weber model for the adsorption of pure PUF (a) and LPUF with 0.5 wt.% lignin (b).

CONCLUSIONS

1. Lignin extracted from wheat straw was added to the synthesis process of polyurethane as an additive. No remarkable differences were observed in the FT-IR spectra, which was because the small lignin content did not change the main chemical functional groups of the LPUFs.

2. The lignin content affected the cross-linking behavior and macro performances, and led to an amicable physicochemical property of the polyurethane with a suitable lignin content. Microscopic images showed smaller bubbles and thicker cellular skeletons with increased lignin content, which was associated with the increase in the cross-linking density caused by adding lignin within a proper range. The results of the TGA indicated that the thermal stabilities of the LPUFs were slightly enhanced.

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3. The mechanical tests showed that the increase in the cross-linking density was conducive to an improvement of the physical performances of the polyurethane. The compressive strength of the 0.5 wt.% LPUF increased 40.8%, and the specific compressive strength increased 61.3%, compared with the normal PUF.

4. The adsorptive behaviors of the polyurethanes conformed to the quasi-second-order kinetic model. The process also involved intraparticle-diffusion. The open-holes that existed complexly in the foams provided abundant "capillary-channels" and "shelters" for the entry and adsorption of oleophilic molecules. It was concluded that LPUFs could potentially be used as adsorbing materials.

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