Advances of Polyurethane Foams Derived from Lignin

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Received December 9, 2012; Accepted January 22, 2013, Published online February 12, 2013

ABSTRACT: Lignin and saccharides are two major components of plants. Huge amounts of plant residues are obtained as by-products of large-scale industries, such as pulp and paper, bio-fuel and the food industry. In this paper, preparation of polyurethane (PU) foam directly from various kinds of industrial lignin and molasses, which have scarcely been utilized, is summarized based on our results obtained by recent investigation. A one-step reaction using hydroxyl groups of plant materials as an active site makes it possible to produce a wide variety of PU, such as foams, sheets, gels and composite matrix. In this paper, PU foams receive particular focus. By controlling reaction conditions and the combination of plant components, mechanical and thermal properties can be varied in a wide range. Furthermore, industrial products using PU's derived from lignin and saccharides are competitive with those from petroleum in both functional properties and production price.

KEYWORDS: Industrial lignin, polyurethane foam, saccharide, compression strength, TG, DSC, thermal conductivity

1 INTRODUCTION

Lignin is one of the most abundant biopolymers on earth, occurring in wood and other plant-based materials and serving as the dominant matrix phase in plant structures [1–3]. The chemical and morphological structure of native lignin in higher plants is complex and heterogeneous. Furthermore, lignin molecules are closely associated with cellulose and other polysaccharides in plant cell walls [4]. In the separation and purification of lignin from co-existing biopolymers consisting of wood, the chemical structure is considerably modified. Different industrial processes have been developed in order to prepare pulp and paper, and also, to produce bio-ethanol.

Lignin is obtained mainly from the pulp and paper industry and bio-ethanol production as by-products. Due to recent demand for new bio-energy resources, biodiesel is produced from palm oil. Oil palm cultivation has increased in countries located around the equator. Accordingly, lignin obtained as by-product of new energy resources is worthy of attention. For a long time, considerable effort has been paid to the development of new products from lignin and related plant components [5–17]. In this paper, we introduce

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DOI: 10.7569/JRM.2012.634111

J. Renew. Mater., Vol. 1, No. 2, April 2013

our recent research on utilization of industrial lignin as a starting material for PU production.

In order to develop the utilization of lignin, our research strategy is as follows; (1) renewable plant resources are used as a starting material for the preparation of industrial products, (2) industrial residues of plant resources are utilized as they are, without further modification, as a starting material taking into consideration cost performance, 3) a certain amount of contaminants is accepted, if they do not disturb the chemical reaction or characteristic properties of products, 4) however, necessary pre-treatments such as dehydration are carried out in order to proceed with the chemical reaction, 5) physical properties of obtained products are similar or better than those derived from petroleum sold on the market, 6) considering practical application, the processing facilities used in the present stage of production can be used without any modifications.

Based on the above strategy, we have carried out various trials. Among them, the most effective utilization method for attaining the above purpose is polyurethane (PU) production. In the early stage of PU production, castor oil was a major chemical. At the present, chemicals derived from petroleum are major starting materials for PU reaction, although vegetable oils are also used [18–25]. Among PU products, such as foam, elastomer, paint, adhesive, fibre, synthetic and leather, 80 % of PU is produced in a foam shape, in particular, flexible type foam is a major type due to its wide application. Flexible



type foam is used in furniture, bedclothes, and car parts. Rigid PU foam is used for insulators and housing. When energy problems and changes in life style all over the world are taken into consideration, the development of insulators for housing is an important goal in terms of practical application. If the starting materials for PU preparation are converted from petroleum to biomaterials, such as plant residues, it will contribute not only to the utilization of renewable material, but also the environmental compatibility of plastic.

In this paper, we review PU preparation from various types of industrial lignin investigated in our research group. The major characteristic of our PU preparation is that lignin was directly solved in polyethylene glycols with various molecular masses. Lignin polyol having 33 % lignin in polyethylene glycol was used as a starting material. [26]. In some cases, lignin polyol was mixed with polyol derived from molasses, which is a residual component of the sugar industry, and was utilized in order to control physical properties of PU.

2 MATERIALS

Industrial lignin and other chemicals utilized for PU foam preparation are shown in Table 1. Industrial lignins, such as kraft lignin (KL), lignosulfonate (LS)

and hydrolysis lignin (HL) were used as received without further treatment. Lignin samples were obtained in powder form. In order to simplify the process, and taking into consideration competition in the market, a certain amount of contaminants in lignin powder was accepted. The effect of contaminants found in industrial lignin on the physical properties of obtained PU foams was carefully examined in the measurement process. Molasses (ML) is also a residual component of the sugar industry. ML was also used after dehydration without further purification. Chemicals shown in Table 1 are representative ones.

3 PREPARATION OF PU FOAMS

In previous studies of PU preparation from lignin, PU reaction was carried out after modification of lignin [27, 28]. However, we found that PU reaction can be attained by one step-reaction, since lignin is soluble in polyethylene glycol with various molecular masses [26]. The hydroxyl group attached to lignin molecule is used as a reaction site of PU reaction.

Sample preparation in laboratory scale was carried out as follows. Lignin in powder form was dehydrated and one portion of lignin was solved in two portions of DEG, TEG or PEG at 60°C for 2 hours [26]. Industrial

Material	Abbreviation	Manufacturer, characteristics etc.	Country
Industrial Lignin	KL	Westvaco Co. Ltd.	US
	LS	Vnilex HW ^R from Japan Paper Chemicals Co. Ltd. Tokyo	Japan
	HL	Residue of alcohol fermentation	Russia
			NZ
Molasses	ML	Tropical Technology Center Co. Ltd. Okinawa, The above ML consists of glucose (8.5 %), fructose (9.2 %), sucrose (32.5), other saccharides (2.3 %), ash (9.5 %) and water (20.5 %).	
Polyethylene glycol			
Diethylene glycol	DEG	Mitsui Chemicals Co. Ltd.	Japan
Triethylene glycol	TEG	Mitsui Chemicals Co. Ltd.	
Poly(ethylene glycol)	PEG	Daiichi Kogyo Seiyaku Co. Ltd. Kyoto molecular mass = ca.200	
Polymeric poly- (phen- ylene methylene) polyisocyanate	MDI	BASF INOAC Polyurethanes LTD, Shinjo	Japan
Tolylene	TDI	Mixture of 2,4-TDI (80%) and 2,6-TDI (20%) isomers, Mitsui	
Diisocyanate		Chemical Inc. Tokyo	
Catalyst,	DBTDL	Merck KGaA, Darmstadt	Germany
di-n-butyltindilaurate			
Surfactant		L-5420, Nippon Unicar Co. Ltd, Tokyo	Japan
		Silicone type surfactant SH-192 Dow Corning Toray Co. Ltd. Tokyo	
Water		Distilled	

Table 1 Representative materials used for PU foam preparation.

lignin, such as KL, LS or HL can be solved in a polyethylene glycol having different molecular mass. Solubility of each lignin varied, accordingly polyethylene glycol with different molecular mass must be chosen. The above solutions were designated as lignin polyol, such as kraft lignin polyol (KLP), lignosulfonate polyol (LSP), hydrolysis lignin polyol (HLP), etc [26]. The number of hydroxyl groups in polyols was evaluated. Lignin polyols, surfactants and catalyst were homogeneously mixed under stirring at room temperature (25°C) and water was added as a foaming agent. MDI is shown as an isocyanate, however, TDI or MDI/TDI mixtures [26, 29] were also used in order to control the physical properties of obtained PU foams. NCO/OH ratio was varied from 1.0 to 1.2. The above reaction was carried out in a disposable plastic vessel (1000 cm³ in volume). The reaction proceeds as follows (1) solution became creamy by adding MDI under stirring. Stirring time (sec) was defined immediately after adding MDI until the solution reached a creamy condition, (2) creamy solution starts to foam after maintaining for a short time and cream time (sec) terminates when foaming reaction started, (3) volume increases gradually and homogeneously, and rise time (sec) was defined as the time interval from when the foaming reaction started until the increase in volume finished The total time of the reaction depends on the mixed components; Generally, the reaction was completed in 1–3 min. The samples were maintained for 24 h at room temperature in order to complete the reaction. The foams from a plastic vessel were cut into rectangular shapes using an automatic saw for measurement. PU foams thus obtained are brown and the colour depends on the kind of lignin and lignin content. Generally, the colour of PU foam became darker with increasing lignin content.

As described in the latter sections, PU foams derived from industrial lignins are rigid. In order to control the flexibility of PU foams, molasses (ML) was solved in polyethylene glycol and prepared ML polyol. ML polyol was mixed with lignin polyol with various mixing ratios and physical properties of lignin PU were controlled. By using mixed polyol derived from lignin and saccharides, molecular flexibility can be varied in a wide range. ML was dehydrated by evaporation, and then one portion of ML was solved in two portions of polyethylene glycol [29]. The above polyol containing 33 % ML was designated as molasses polyol (MLP). The number of hydroxyl group in ML polyol was evaluated by Industrial Standard (JIS) K 1557. Lignin polyol and MLP were mixed in various mixing ratios, lignin poly/MLP = 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100, respectively. Reaction was carried out in a similar manner to that of lignin polyol except for starting materials.

4. MORPHOLOGY AND APPARENT DENSITY

4.1 Morphology

Figure 1 shows representative electron scanning micrographs of the fracture surface of PU foams derived from HL. Scale bar indicates 100 μ m. Morphological observation was carried out using an electron scanning microscope (SEM) of JEOL JSM-6100. The surface of the sample was coated with gold. The cross-section of each pore was calculated assuming ellipse. A crosssection of 50–60 pores for each sample was measured and average value and standard deviation calculated. The size of pore was around 0.5mm² and standard deviation ca. 0.1 mm².

4.2 Apparent Density of PU

Apparent density $[\rho = mass (m)/apparent volume (V), gcm⁻³]$ was measured on samples of 30 (length) × 30 (width) × 30 (thickness) mm using a solar caliper and an electric balance. The average caliper values of each part of a sample were measured at three different spots and used to calculate the apparent volume (V). The mass (*M*) of each sample was weighed using the balance. 5 to 7 test pieces were measured and the



Figure 1 Scanning electron micrograph of PU foam derived from HL.

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Lignin	Solvent	ρ / g cm ⁻³	Stand. Dev.
KL	DEG	0.082	0.0023
KL	PEG	0.070	—
LS	DEG	0.070	0.0008
LS	PEG	0.049	0.0031
HL*	DEG	0.065**	—
		0.050***	0.0037
HL****	PEG	0.063	—

Table 2 Apparent density of representative PU foamsderived from various kinds of lignin.

Lignin content in polyol = 16.5 %, NCO/OH ratio = 1.2, *Russian HL (**plant 1, *** plant 2), ** **New Zealand,

— = not calculated

average value and standard deviation were calculated. Representative ρ values and the standard deviation of PU derived from KL, LS and HL are shown in Table 2. PU foams shown in Table 2 were prepared in a similar manner as described in the section on sample preparation. In general, p value mainly depends on lignin species and molecular mass of polyethylene glycol. It is clear that light foams can be obtained when PU is derived from chemical components having bulky molecular units and long oxyethylene chains. As shown in the values of standard deviation, PU foams are homogeneous. When sample preparation was varied, such as change of the amount of foaming reagent (water), and molecular mass of polyethylene glycol increased, a wide variety of PU having different apparent density were obtained. In this study, in order to control preparation conditions which can be repeatable in a stable manner, molecular mass of polyethylene glycol was chosen in a range lower than ca. 200. The amount of water (foaming reagent) was maintained at a constant.

As described in the section on sample preparation, lignin polyol was mixed with MLP in order to increase the molecular flexibility. When PU foam was prepared by using MLP, flexible type PU foams derived from MLP is ca.0.04 to 0.05 g cm⁻³ depending on the kind of isocyanate or molecular mass of polyethylene glycol. When PU foams were prepared using a mixture of lignin-polyol and MLP, no significant change in apparent density was observed as shown in Figure 2. It is thought that the size of glucopyranose or fructose ring which consists of ML is comparably similar to that of the phenolic group attaching to the methoxyl group and hydroxyl group of lignin.

If we assume that the additivity of density of air and that of PU matrix, the following equation 1 is obtained



Figure 2 Apparent densities of PU foams derived from LS/ ML and HL/ML mixtures. Closed circle; LS/ML, Closed rectangular; HL/ML Solvent; PEG, total lignin content in polyol; 33 %.

$$\rho_{\rm air} v + \rho_{\rm matrix} (1 - v) = \rho_{\rm foam} \tag{1}$$

Where ρ_{air} is density of dry air at 20°C and 101.325 kPa (=1.2041 kg m⁻³⁾. v is volume fraction of air, ρ_{matrix} is density of PU matrix and ρ_{foam} is apparent density of PU foam

As shown in Table 2, ρ_{foam} is in a range from ca. 0.05 to 0.08 g cm⁻³.When ρ_{matrix} is assumed to be ca. 1.0 to 1.3 g cm⁻³ at constant $\rho_{foam'}$ v changes in a range from 0.92 to 0.95. If ρ_{matrix} is assumed to be 1.0 g cm⁻³ and ρ_{foam} is varied from 0.05 to 0.08 g cm⁻³, v changed from 0.92 to 0.95. From the above assumed calculation, it can be said that volume fraction of air in PU foams is in a range from 0.92 to 0.95. As shown in scanning electron micrograph, each pore whose cross section is in a range from 4×10^{-3} to 5×10^{-3} cm² is separated via a thin wall. The volume fraction of matrix consisting pore wall is in a range from 0.5 to 0.8 $\times 10^{-3}$ cm².

5 MECHANICAL PROPERTIES

Mechanical properties are a crucial factor when new products are prepared. Mechanical properties of PU foams were investigated by compression test). Compression strength and modulus were measured using a Shimadzu Autograph AG-IS at 25°C. Sample size was 40 (length) × 40 (width) × 30 (thickness) mm. The rate of applied stress was 3.0×10^{-3} m min⁻¹. Three test pieces were measured and average value was used. Compression strength at 10 % stress was defined as σ_{10} (Pa) according to Japanese Industrial Standard (JISK7220). Compression modulus (*E*, GPa) was determined using the initial stage of stress-strain curve using equation 2.

$$E = \Delta P \left(\Delta L / L \right)^{-1} A^{-1} \tag{2}$$

Where ΔP is pressure, *L* is height of sample, ΔL is height at ΔP and *A* is cross section.



Figure 3 (a) Relationships between compression strength (σ_{10}), LS content in polyol and polyethylene glycol having different molecular mass, (b) Relationships between compression modulus (*E*), LS content in polyol and polyethylene glycol having different molecular mass LSD; LS solved in DEG, LST; in TEG, LSP; in PEG, NCO/OH ratio = 1.2.

The effect of lignin content in polyol on compression strength and modulus is not remarkable as shown in Figure 3(a) and (b). In Figure 3, σ_{10} and *E* of LSPU are representatively shown. PU foams derived from KL and HL showed similar values as LSPU when molecular mass of polyethylene glycol is the same. σ_{10} values of HLPU depend on location of ethanol production, since the amount and kinds of contaminants in received HL powder showed a wide variety depending on different plants.

The effect of molecular mass of polyethylene glycol is not significant when DEG, TEG and PEG (molecular mass = ca. 200) were used for preparation. , However, when the molecular mass of polyethylene glycol increased by more than several thousands, molecular flexibility increased. For example, when polyethylene glycol with molecular mass 4000 was used, σ_{10} values are observed in a range from 0.15 to 0.4 MPa. In this case, the rigid structure of lignin affects compression strength. Both σ_{10} and *E* values increased with increasing KL content [32].

Compression strength and modulus of PU foams linearly depend on apparent density. As shown in Figure 4, σ_{10} increases linearly with increasing apparent density, regardless of types of lignin. As shown in Table 2, when molecular mass of polyethylene glycol increases, apparent density decreases. Accordingly, σ_{10} of PU foams derived from lignin polyols with PEG show low values, while those with DEG show high values in Figure 4.

The effect of molasses polyol on mechanical properties was clearly observed. When polyol derived from LS was mixed with ML, values of σ_{10} markedly decreased, as shown in Figure 5. The scale of z-axis of Figure 3(a) and Figure 5 is the same. The values of σ_{10} are observed at around 0.3 to 0.4 MPa.



Figure 4 Relationship between apparent density (ρ) and compression strength (σ_{10}) of KLPU and LSPU Open circle; KLD, open rectangular; KLT, open triangle; KLP Closed circle; LSD, closed rectangular; LST, closed triangle; LSP.



Figure 5 Effect of ML polyols on σ_{10} of LSPU foams.



Figure 6 (a) Analysis of TG curve and derivative TG curve of PU foams derived from industrial lignin T_{d} ; decomposition temperature, DT_{d} ; peak temperature of derivative TG curve, m_{25} ; mass at 25°C, m_{450} ; mass at 450°C, m_{500} ; mass at 500°C, (b) TG and DTG curves of PU foams derived from HLP/MLP mixtures with various mixing ratio Numerals in the figure show mixing ratio (=HLP/MLP).

The flexibility of molecular chains affects the mechanical response of applied stress and stress recovery, since a thin wall constructs three dimensional structure. The above facts indicate that mechanical properties can be designed for practical purposes by changing lignin and molasses polyol. By mixing lignin and molasses, rigid or semi-rigid PU foams can be obtained.

6 THERMAL PROPERTIES

6.1 Thermal Stability

Among various techniques of examining thermal stability of polymers, thermogravimetry is a representative and well established method [33]. In this section, representative TG results of PU foams derived from industrial lignin are introduced. Measurements were carried out in a similar manner in order to compare decomposition behavior of PU foams from various resources. Thermogravimetry (TG) was carried out using an SII Nanotechnology thermogravimeter-differential thermal analyzer, TG-DTA 220. Sample mass was ca. 7 mg, heating rate was 20°C min⁻¹, and N₂ flow rate was 100 cm³ min⁻¹. Temperature range was varied from 25 to 600°C. Decomposition temperature (T_d) was determined

from TG curve and its derivative curve. Figure 6(a) shows representative TG and derivative TG curve (DTG) of PU foam derived from HLP. In this study, $T_{\rm d}$ was defined as shown with an arrow. This PU foam decomposes in one stage, however, when decomposition took place in more than two stages, $T_{\rm d}$ was numbered from the low to high temperature. Peak temperature of DTG curve was defined as $DT_{\rm d}$. Residual mass of decomposed component was defined as $(m_T/m_{25}) \times 100$ (%), where m_T is mass at temperature T and m_{25} is mass at 25°C. In this study, $(m_T/m_{25}) \times 100$ (%) was calculated at 450, 500°C.

Figure 6(b) shows representative TG curves of PU foams derived from HLP/MLP mixtures. It is clearly seen that decomposition takes place in one step. T_d and D T_d of representative PU foams derived from various kinds of lignin are shown in Table 3. T_d is observed at around 300°C, regardless of kind of lignin and D T_d is found at around 320°C. As reported previously, a major decomposition of lignin is observed at around 300°C [11, 14, 17]. Simultaneous measurements of TG-Fourier transform infrared spectrometry (FTIR) of PU derived from lignin indicate that the amount of evolved gas of PU derived from lignin is smaller than that of PU without lignin [11]. On this account, the major thermal decomposition of lignin and scissions



derived from various kinds of lignin.

Lignin	Polyethylene glycol	$T_{\rm d}/^{\circ}{ m C}$	$D T_d / C$
KL	PEG	298	321
LS	PEG	286	320
HL	PEG	294	330

Table 3 Decomposition temperature of PU foams



Figure 7 Decomposition temperature of PU foams derived from HLP/MLP mixtures Closed triangle; D T_d of LSP/MLP, closed rectangle; D T_d of HLP/MLP, Open triangle; T_d of LSP/MLP, open rectangle; T_d of HLP/MLP.

between the isocyanate groups and the alcoholic OH groups in lignin.

As shown in Figure 6(b), thermal decomposition of PU foams derived from HLP/MLP takes place in one step and no significant difference is found by adding MLP. Both T_d and D T_d showed no large variation when mixing ratio was changed as shown in Figure 7. Furthermore, it is s noteworthy that T_d and D T_d of PU foams derived from HLP/MLP and LSP/MLP show similar values. Residual mass at 450°C was 38 % and that of 500°C was 35 %. TG results indicate that PU foams derived from lignin are thermally stable.

6.2 Glass Transition

Glass transition, molecular enhancement of main chain, is a relaxation process and glass transition temperature (T_g) depends on the kind of lignin, chain length of attached flexible segments such as polyoxyetylene and polyoxypropylene units and also thermal history of glassy state [7, 12, 14, 34, 35]. Lignin is an amorphous polymer and glass transition behavior is clearly observed by various experimental techniques, such as viscoelastic measurement and differential scanning calorimetry (DSC) [12, 14]. Compared with glass transition of synthetic amorphous polymer, such as polystyrene and poly(methyl methaclyate), the



Figure 8 (a) Analysis of DSC heating curve, **(b)** Representative DSC heating curves of PU foams derived from LSP prepared by various NCH/OH ratios LS content in polyol=33 %. Numerals in the figure show NCO/OH ratio, scale bar indicates $0.2 \text{ J g}^{-1} \text{ K}^{-1}$.

molecular motion of lignin, is restricted by crosslinking of main chains. Accordingly, molecular flow at a temperature higher than $T_{\sigma'}$ which is ordinarily observed in synthetic amorphous polymers, is not found. The molecular restriction of lignin can be detected as a low value of heat capacity difference between glassy state and the molten state (ΔC_{μ}), and low value of dynamic loss modulus at T_{a} . As reported, T_{a} of industrial lignin such as KL and LS is observed at around 120–160°C [12, 14, 35], although T_{a} of HL is lower than T_{a} of KL and LS [34]. Rigid phenyl groups in the main chain and intermolecular hydrogen bonding are attributable to the high T_{α} value. It is known that heat capacity difference at T_{α} (ΔC_{μ}) depends on T_g [36]. ΔC_p values of PU foams derived from lignin are in a range from 0.1 to 0.2, This clearly indicates that the molecular mobility of PU foams is in a limited range, if it is considered that ΔC_n values of typical synthetic amorphous polymers, whose T_{a} is observed in a similar temperature range of PU foams, is 0.3 to 0.4 J g^{-1} K⁻¹.

Figure 8 shows representative DSC heating curves of PU foams derived from LSD polyol. LS content in polyol was 33 % and NCO/OH ratio was varied from 1.0 to 1.2. Measurement was carried out using an SII Nanotechnology differential scanning calorimeter DSC 220 Cat a heating rate of 10°C min⁻¹ in N₂ atmosphere whose flow rate was 30 ml min⁻¹. T_g , T_{gi} and ΔC_p were determined as schematically shown in Figure 8(a). As shown in DSC heating curves in Figure 8(b), change of heat capacity is clearly observed. Values of T_g , T_{gi} and ΔC_p

40

are found in Table 4. From Figure 8 and Table 4, it is clearly seen that molecular motion of PU foams is restricted by increasing NCO/OH ratio. The effect of cross-linking is significantly observed from the facts that T_{gi} and T_{g} shift to the high temperature side and ΔC_{p} decreases with increasing NCO/OH ratio. The fact that the molecular motion of PU foam prepared at NCO/OH ratio 1.0 starts from ca. 50°C suggests movable components remain in the reaction system. Accordingly, in our studies, NCO/OH ration was mainly chosen as 1.2.

Figure 9 shows the effect of LS content and molecular mass of polyethylene glycol on T_g of PU foams. As clearly seen, the effect of lignin content on T_g is not significant, in contrast the molecular mass markedly affects T_g . Oxyethylene chain acts as a flexible component in the network structure of PU. With decreasing molecular mass, molecular enhancement is restricted and T_g shifts to the high temperature side. When PU foams are used at around room temperature, temperature difference between T_g and the room temperature is an important factor, since molecular mass of polyethylene glycol should be chosen for the design of PU products [37, 38]. Figure 10 shows relationship between T_g of PU foams derived

Table 4 T_{g} and ΔC_{p} of PU foams derived from LSD

NC/OH Ratio	T _{gi} /°C	$T_{\rm gi}^{\prime m o} { m C}$	$\Delta C_{\rm p}/{\rm J}~{\rm g}^{-1}~{\rm K}^{-1}$
1.0	50	75	0.25
1.1	73	82	0.14
1.2	76	88	0.12



Figure 9 Relationships between glass transition temperature (T_g) of PU foams derived from LSD, LST and LSP DSC heating rate=10°C min⁻¹.



160

140

Figure 10 Relationships between glass transition temperature(T_g) of PU foams derived from KLD and LSD and lignin content in polyol NCO/OH ratio=1.2, DSC heating rate=10°C min⁻¹.

LSD

from KLD and LSD. The kind lignin seems to affect T_{g} value, when PU foams are prepared from lignin polyol.

However, when MLP was mixed with lignin polyol, the characteristic feature of each kind of lignin disappeared. Figure 11(a) shows stacked DSC heating curves of PU foams derived from LSD and MLD mixtures. T_g obtained from Figure 11(a) is shown in Figure 11(b) together with T_g of HLP/MLP and LSP/MLP. When mixed polyol is used, T_g can be controllable only by the mass of polyethylene glycol.

Glass transition behaviour of PU foams can be controlled by changing the molecular length of the flexible component. The effect of the kind of industrial lignin is not negligible, however, by mixing with ML polyol, the difference is normalized and stable thermal behavior can be obtained.

6.3 Thermal Conductivity

Thermal conductivity (TC) is an important index when rigid PU foams are used for insulators. Air is one of the most effective insulation materials, whose TC is around 0.024 J m⁻¹ K⁻¹sec⁻¹(0 °C), 0.026 (20°C) and 0.027 (40°C). TC of commercially available PU foams derived from petroleum is in a range from 0.035 to 0.14 J m⁻¹ K⁻¹ sec⁻¹. As shown in Figure 12, TC of PU foams derived from various types of lignin was observed at around 0.035 to 0.037 J m⁻¹ K⁻¹ sec⁻¹. When additivity of TC of air and matrix PU is calculated, taking into account apparent density, TC of PU matrix is ca. 0.20 J m⁻¹ K⁻¹ sec⁻¹. This value is reasonable when TC of polymeric materials is in a similar value.

Figure 13 shows TC of PU foams derived from lignin-molasses mixed polyol. TC values are almost similar to those of PU foams derived from lignin polyol. The effect of ML polyol was not significant. The difference of lignin is also negligible. TC of PU foams derived from oxypropylated lignin is reported



Figure 11 (a) DSC heating curves of PU foams derived from LSD and MLD mixtures NCO/OH ratio = 1.2, Numerals in the figure show LSD/MLD ratio. Heating rate =10°C min⁻¹, **(b)** Glass transition temperature (T_g) of PU foams derived from LSD/MLD, HLP/MLP and LSP/MLP mixed polyol. Closed circle; LSD/MLD, closed rectangle; HLP/MLP, closed triangle; LSP/MLP.



Figure 12 Thermal conductivity of representative PU foams derived from lignin supplied by various industrial plants A; LSD, B-D; HLD from different plants, E; KLP, F; HLP, G; LDP.



Figure 13 TC of PU foams derived from lignin-molasses mixed polyol. Closed circular; PU foam derived from LSP/MLP, closed rectangular; from HLP/MLP.

PU foams derived from lignin shows preferable characteristics. The above TC values of PU foams derived from various types of industrial lignin indicates that lignin is a useful material for the preparation of insulators.

0.02 J m⁻¹ K⁻¹ sec⁻¹ [27], which indicates that rigid

CONCLUSIONS

In this paper, we showed that (1) lignin as a renewable plant resource can be used as a starting material for the preparation of PU (2) lignin is utilized as it is without further modification as starting material taking into consideration cost performance, 3) a certain amount of contaminants is accepted, since they do not disturb the chemical reaction or characteristic properties of products, 4) however, necessary pre-treatments such as dehydration were carried out in a limited range, 5) mechanical and thermal properties of obtained PU foams are similar or better than those derived from petroleum sold on the market, 6) characteristic properties can be designed by changing the composition of starting materials. It is concluded that PU foams derived from various kinds of industrial lignins have appropriate characteristics for practical applications.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Clive S. Langham, Nihon University, for his helpful comments and advice. The authors also thank Mr. Daisuke Kawabiki, Fukui University of Technology for his helpful assistance.

Abbreviations

DBTDL = di-*n*-butyltindilaurate

- ΔC_p = heat capacity difference between glassy state and the molten state
- DEG = diethylene glycol
- DSC = differential scanning calorimetry
- DT_d = peak temperature of derivative curve of thermogravimetry
- E =compression modulus, Pa

HL = hydrolysis lignin

- HLD = hydrolysis lignin polyol solved in diethylene glycol
- HLT = hydrolysis lignin polyol solved in triethylene glycol
- HLP = hydrolysis lignin polyol solved in polyethylene glycol
- KL = kraft lignin
- KLD = kraft lignin polyol solved in diethylene glycol
- KLT = kraft lignin polyol solved in triethylene glycol
- KLP = kraft lignin polyol solved in polyethylene glycol LS = lignosulfonate
- LSD = lignosulfonate polyol solved in diethylene glycol
- LST = lignosulfonate polyol solved in triethylene glycol
- LSP = lignosulfonate polyol solved in polyethylene glycol
- MDI = phenylene methylene polyisocyanate ML = molasses
- MLD = molasses polyol solved in diethylene glycol
- MLT = molasses polyol solved in triethylene glycol
- MLP = molasses polyol solved in polyethylene glycol
- PEG = polyethylene glycol
- PU = polyurethane

 ρ = apparent density g cm⁻³

- σ_{10} = compression strength at 10 % strain, Pa
- SEM = scanning electron microscopy
- TC = thermal conductivity
- TEG = triethylene glycol
- TG = thermogravimetry
- T_{α} = glass transition temperature, °C
- T_{A}° = decomposition temperature, °C

TDI = tolylenediisocyanate

REFERENCES

- K.V. Sarkanen and C.H. Ludwig: *Lignins, Occurrence, Formation, Structure and Reactions,* Wiley-Interscience, New York (1971).
- S.Y. Lin and C.W. Dence: Methods in Lignin Chemistry, Springer, Berlin (1992).
- 3. T.Q. Hu: Characterization of Lignocellulosic Materials, Blackwell, Oxford (2008).

- 4. M.Y. Balakshin, E.A. Capanema, and H-M. Chang, Recent Advances in the Isolation and Analysis of Lignins and Lignin-carbohydrate Complexes, in *Characterization of Lignocellulosic Materials*, T.Q. Hu (Ed.), pp. 148–170, Blackwell, Oxford (2008).
- M.J. Donnelly, In vitro enzymatic synthesis of polymers containing saccharides, lignins, proteins or related compounds: a review. *Polym. Int.* 47, 257–266 (1998).
- A. Gandini and N.M. Belgacem, Recent advances in the elaboration of polymeric materials derived from biomass components. *Polym. Int.* 47, 267–276 (1998).
- A. Gandini, M.N. Belgacem, Z.X. Guo, and S. Montanari, Lignins as Macromonomers for Polyesters and Polyurethanes, in *Chemical Modification*, *Properties*, and Usage of Lignin, T.Q. Hu (Ed.), pp. 57–80, Academic/ Plenum, New York (2002).
- 8. V.P. Saraf, W.G. Glasser, and G. Wilkes, Engineering plastics from lignin. VII. Structure property relationships of polybutadiene glycol-containing polyurethane networks. *J. Appl. Polym. Sci.* **30**, 3809–3823 (1985).
- H. Hatakeyama, S. Hirose, and T. Hatakeyama, Highperformance Polymers from Lignin Degradation Products, in *Lignin, Properties and Materials*, W.G. Glasser and S. Sarkanen (Eds.), pp. 205–218, ACS Symp. Ser. 397. Am. Chem. Soc, Washington DC (1989).
- H. Hatakeyama, Polyurethane Containing Lingin, in Chemical Modification, Properties and Usage of Lignin, T.Q. Hu (Ed.), pp. 41–56, Kluwer Academic/Plenum Publishers, New York (2002).
- 11. H. Hatakeyama, Thermal analysis of environmentally compatible polymers containing plant components in the main chain. *J. Therm. Anal. Cal.* **70**, 755–955 (2002).
- 12. T. Hatakeyama and H. Hatakeyama: *Thermal Properties* of *Green Polymers and Biocomposites*, Kluwer Academic, Dordrecht (2004).
- H. Hatakeyama and T. Hatakeyama, Environmentally compatible hybrid-type polyurethane foams containing saccharide and lignin components. *Macromol. Symp.* 224, 219–226 (2005).
- H. Hatakeyama and T. Hatakeyama, Lignin structure, properties and application. Adv. Polym. Sci. 232, 1–63 (2010).
- S. Hirose, K. Nakamura, and T. Hatakeyama, molecular Design of Linear Aromatic Polymers Derived from Phenols Related to Lignin, in *Cellulose and Wood*, C. Schuerch (Ed.), pp. 1133–1144, John Wiley Sons, New York (1989).
- K. Nakamura, R. Mőrck, A. Reimann, K.P. Kringstad, and H. Hatakeyama, Mechanical properties of solvolysis lignin derived polyurethanes. *Polym. Adv. Technol.* 2, 41–47 (1991).
- K. Nakamura, T. Hatakeyama, and H. Hatakeyama, Thermal properties of solvolysis lignin-derived polyurethanes. *Polym. Adv. Technol.* 3, 151–155 (1992).
- G. Guo, I. Javni, and Z. Petrovic, Rigid polyurethane foams based on soybean oil. J. Appl. Polym. Sci. 77, 467– 473 (2000).
- Y.H. Hu, Y. Gao, D.N. Wang, C.P. Hu, S. Zhu, L. Vanoverloop, and D. Randall, Rigid polyurethane foam prepared from a rape seed oil based polyol. *J. Appl. Polym. Sci.* 84, 591–597 (2002).

- 20. I. Javni, Z.S. Petrovic, A. Gua, and R. Fuller, Thermal stability of polyurethanes based on vegetable oils. *J. Appl. Polym. Sci.* **77**, 1723–1734 (2000).
- J.F. Jin, Y.L. Chen, D.N. Wang, C.P. Hu, S. Zhu, L. Vanoverloop, and D. Randall, Structures and physical properties of rigid polyurethane foam prepared with rosin-based polyol. *J. Appl. Polym. Sci.* 84, 598–604 (2002).
- J.John, M. Bhattachaiya, and R.B. Turner, Characterization of polyurethane foams from soybean oil. J. Appl. Polym. Sci. 86, 3097 (2002).
- 23. X. Kong and S.S. Narine, Physical properties of polyurethane plastic sheets produced from polyols from canola oil. *Biomacromol.* **8**, 2203–2209 (2007).
- 24. R Tanaka, S. Hirose, and H. Hatakeyama, Preparation and characterization of polyurethane foams using a palm oil-based polyol. *Bioresour. Technol.* **99**, 3810–3816 (2008).
- H. Hatakeyama, H. Matsumura, and T. Hatakeyama, Glass transition and thermal degradation of rigid polyurethanes foams derived from castor oil-molasses polyols. J. Therm. Anal. Cal. (DOI 10.1007/s10973-012-2501-5) (2012).
- H. Hatakeyama, S. Hirose, and S. Yano, USP 4987213 (1991); S. Hirose, H. Hatakeyama, and Nakamura K. JP 1791797 (1993); S. Hirose and H. Hatakeyama, JP 2675997 (1997); H. Hatakeyama and S. Hirose, JP 2663390 (1997); S. Hirose, H. Hatakeyama, and K. Nakamura, JP 3101701 (2000); S. Hirose and H. Hatakeyama, JP 3341115(2002); S. Hirose and H. Hatakeyama, JP 4019346 (2007), ZL 02816051.7 (2009).
- H. Nadji, C. Bruzzèse, M.A. Benaboura, N. Belgacem, and A. Gandini, Oxypropylation of lignins and preparation of rigid polyurethane foams from the ensuing polyols. *Macromol. Mat. Engin.* 290, 1009–1016 (2005).
- C.A. Cateto, M.F. Barriro, A.E. Rodrigues, and M.N. Belgacem, Optimization study of lignin oxypropylation in view of the preparation of polyurethane rigid foams. *Ind. Eng. Chem. Res.* 48, 2583–2589 (2009).

- 29. H. Hatakeyama and S. Hirose, JP 2836004 (1998), H. Hatakeyama and S. Hirose, JP 2883271 (1999), S. Hirose and H. Hatakeyama, JP 3837623 (2006).
- 30. H. Hatakeyama, R. Kosugi, and T. Hatakeyama, Thermal properties of lignin and molasses-based polyurethane foams. *J. Therm. Anal Cal.* **92**, 419–424 (2008).
- H. Hatakeyama, T. Marusawa, and T. Hatakeyama, Soft type polyurethane derived from molasses. *J. Mat Sci.* 465, 7475–7481 (2011).
- 32. K. Nakamura and H. Hatakeyama, New types of polyurethanes from plant materials. *Japan Tappi*, 44, 849–855 (1990).
- T. Hatakeyama and F.X. Quinn, thermal Analysis, Fundamentals and Applications to Polymer Science, 2nd ed, John Wiley (1999).
- 34. H. Hatakeyama, Y. Tsujimoto, M. Ja, Zarubin, S.M. Krutov, and T. Hatakeyama, Thermal decomposition and glass transition of industrial hydrolysis lignin. *J. Therm. Anal. Cal.* 101, 289–295 (2010).
- H. Hatakeyama and T. Hatakeyama, Thermal Properties of Isolated and *in situ* Lignin, in *Lignin and Lignans*, C. Heitner, D. R. Dimmel and J. A. Schmidt (Eds.), pp. 301–319, CRC Press, USA (2010).
- T. Hatakeyama and H. Hatakeyama, Effect of chemical structure of amorphous polymers on heat capacity difference at glass transition temperature. *Thermochim. Acta* 267, 249–257 (1995).
- 37. T. Hatakeyama, Y. Asano, and H. Hatakeyama, Mechanical and thermal properties of rigid polyurethane foams derived from sodium lignosulfonate mixed with diethylene-triethylene-and polyethylene glycols. *Macromol. Symp.* **197**, 171–180 (2003).
- 38. T. Hatakeyama, Y. Matsumoto, Y. Asano, and H. Hatakeyama, Glass transition of rigid polyurethane foams derived from sodium lignosulfonate mixed with diethylene, triethylene and polyethylene glycols. *Thermochim. Acta* **416**, 29–33 (2004).