THERMAL PROPERTIES OF LIGNIN- AND MOLASSES-BASED POLYURETHANE FOAMS

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Lignin- and molasses-based polyurethane (PU) foams with various lignin/molasses mixing ratios were prepared. The hydroxyl group in molasses and lignin is used as the reaction site and PU foams with various isocyanate (NCO)/the hydroxyl group (OH) ratios were obtained.

Thermal properties of PU foams were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG) and thermal conductivity measurement. Glass transition temperature (T_g) was observed depending on NCO/OH ratio in a temperature range from ca. 80 to 120°C and thermal decomposition temperature (T_d) from ca. 280 to 295°C. Mixing ratio of molasses and lignin polyol scarcely affected the T_g and T_d. Thermal conductivity of PU foams was in a range from 0.030 to 0.040 W m^{-1} K^{-1} depending on mixing ratio of lignin and molasses.

Keywords: *molasses, sodium lignosulfonate, thermal conductivity, PU foams*

Introduction

Lignin is a biopolymer with random cross-linking of the sub-structural phenyl propane units, and the physical and chemical properties are highly dependent on the isolation processes. The higher order structure of lignin is fundamentally amorphous with phenyl-propanoid units such as, *p*-coumaryl alcohol, coniferyl alcohol and/or synapyl alcohol cross-linked to produce a three-dimensional lignin polymer via a radical coupling process during its biosynthesis [1–3]. Lignin is obtained as a by-product of the chemical pulping industry. Various types of industrial lignin are obtained. Among them sodium lignino-sulfonate (NaLS) obtained from the sulfite pulping process is a polyelectrolyte, which is soluble in water and a certain number of organic solvents.

Molasses is obtained as a by-product of the sugar industry. The major components are saccharides mainly mixed with sucrose, glucose and fructose [4–6]. Both lignin and molasses are obtained as industrial residues of large-scale industries. Although they are the most promising natural resources, they have not been utilized in a broad range of practical fields. In our previous studies, we have developed lignin- and polysaccharide-based polyurethanes, polycapro-lactones, epoxy resins and biocomposites [4–18].

Among new plant-based polymers, polyurethane (PU) is one of the most useful three-dimensional polymers. Various forms of materials such as sheets, foams, adhesives and paints are obtained from PU derived from plant components. Physical properties of PU can easily be controlled by molecular design. In order to develop biocompatible materials using residual plant materials, fundamental data on physical properties is necessarily required, since the major purpose is to utilize bio-based polymers in practical fields. Thermal properties are a major factor to design biocompatible materials, which are compatible to similar kinds of materials prepared from petroleum. In this study, thermal properties of polyurethane foams derived from lignin and molasses, which were developed for housing insulation, are investigated.

Experimental

Sample preparation

Sodium lignosulfonate (LS) commercial name of Vanilex HW^R was obtained from Nippon Pulp and Paper Co., Japan. According to the manufacturer's report, molecular mass of LS was $1 \cdot 10^3 – 1 \cdot 10^4$. Molasses (ML) was obtained from Tropical Technology Center Co., Japan, Poly(phenylene methylene) poly-isocyanate (MDI) was obtained from BASF INOAC Polyurethane Co. Silicone type surfactants were obtained from Japan Unicar Co. One portion of LS or ML was solved in 2 portions of diethylene glycol (DEG) (Mitsui Chemical Co. Ltd., Japan). The above polyols were designated as LSD and MLD,
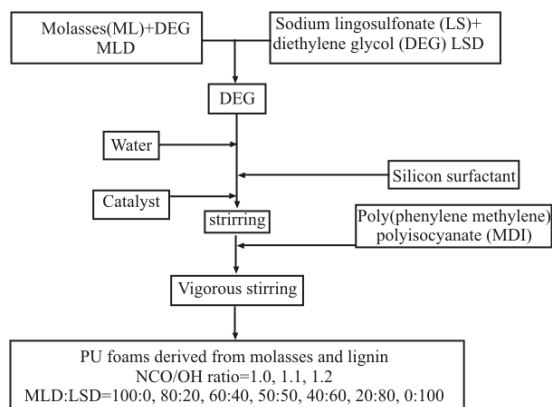
Fig. 1 Sample preparation

respectively. Two kinds of polyols were mixed with the following mixing ratios; MLD/LSD=100/0, 80/20, 60/40, 40/60, 20/80 and 0/100, respectively. As shown in the flow chart (Fig. 1), after two polyols, surfactants and catalyst (di-*n*-butyltin dilaurate) were homogeneously mixed under stirring, poly(phenylene methylene) polyisocyanate (MDI) was added under vigorous stirring. Trace amount of water is used as a foaming agent. NCO/OH ratio was varied at 1.0, 1.1 and 1.2, respectively.

Measurements

Differential scanning calorimetry (DSC)

DSC was carried out using a Seiko DSC 220C. Scanning rate was 10°C min^{-1} and N$_2$ gas flow rate was 30 mL min^{-1}. PU foams were powdered by grinding and sample mass ca. 5 mg was used for measurements. The sample was heated from room temperature to 200°C (1st heating), cooled from 200 to –50°C and heated again from –50 to 200°C (2nd heating). The 2nd heating curves were mainly used for analysis in order to erase thermal history.

Thermogravimetry (TG)

TG was performed using a Seiko TG 220 at a heating rate of 20°C min^{-1} in a nitrogen atmosphere at flow rate of 100 mL min^{-1}. Derivative thermogravimetric (DTG) curves were obtained by differential calculation of TG curves. Mass residues (MR) measured at 450, 500 and 550°C were designated as m_{450}, m_{500} and m_{550}, respectively. m_{20} refers to the mass residue at 20°C which was the amount of the material used for the TG experiments.

Thermal conductivity measurements

Anacon Detection Technology, a thermal conductivity analyzer, TCA Point 2 was used. The size of sample was 200 (length)×200 (width)×30 (height) mm. The

temperature of hot plate was 37.7°C and that of cold plate was 10°C. Polystyrene foam with thermal conductivity 0.0262 W m^{-1} K^{-1} was used as a standard.

Apparent density measurements

Apparent density [ρ=mass (*m*)/apparent volume (*V*), g cm^{-3}] was measured on samples of 15 (length)×30 (width)×10 (thickness) mm using a Mitsutoyo ABS digital solar caliper and an electric balance (Shimadzu balance EB-4300DVW). 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 Shimadzu balance.

Mechanical property measurements

Compression strength was measured using a Shimadzu Autograph AG-IS at 25°C. Sample size was 15 (length)×30 (width)×10 (thickness) mm. Applied stress was varied in order to control the rate in a range from 1.0·10^{-3} to 1.0·10^{-2} m min^{-1}. Compression strength (σ, Pa) was calculated according to Japanese Industrial Standard (JIS) K7220. Compression modulus (*E*, GPa) was determined using the initial stage of stress-strain curve.

Results and discussion

Figure 2 shows photographs of PU foams derived from molasses and lignin polyols. Colour of PU foam varied from light yellow to light brown with increasing lignin content, since NaLS powder is dark brown.

Figure 3 shows three-dimensional relationships between NCO/OH ratio, MLD/LSD ratio and apparent density (ρ). The values of ρ are in a range from 0.04 to 0.07 g cm^{-3}, which varied depending on preparation conditions. The number of intermolecular cross-linking increases with increasing NCO/OH ratio, i.e. the amount of vacancy of PU foams decreased when cross-linking density increases. As shown in Fig. 3, the maximum values are obtained when mixing ratios of MLD/LSD are in a range from 40/60 to 30/70.
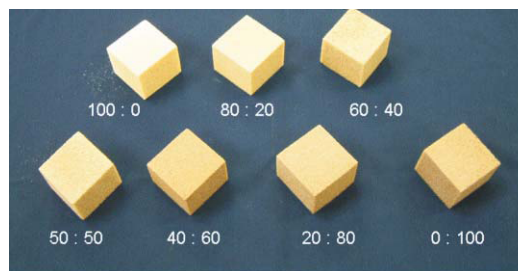

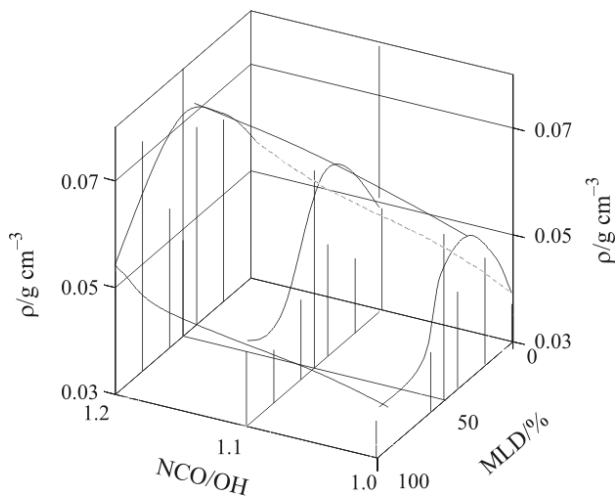**Fig. 2** Polyurethane foams prepared from MLD/LSD, NCO/OH ratio=1.2. Numerals in the figure show MLD/LSD ratio

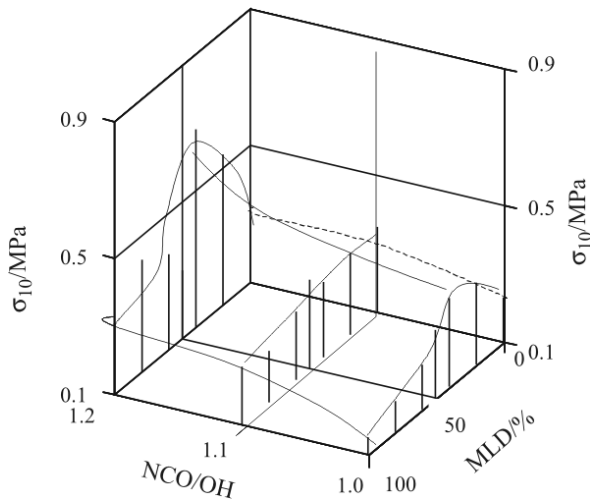**Fig. 3** Relationship between apparent density (ρ), NCO/OH ratio and MDL content

Fig. 5 Relationship between compression modulus (E), NCO/OH ratio and MDL content

Fig. 4 Relationship between compression strength at 10% strain (σ_{10}), NCO/OH ratio and MLD content

Fig. 6 DSC heating curves of PU foams derived from molasses and lignin. Numerals in the figure show MLD/LSD ratio, NCO/OH ratio=1.2, heating rate=10°C min^{-1}

Figure 4 shows three-dimensional relationship between compression strength at 10% strain (σ_{10}), NCO/OH ratio and MDL content. Compression strength is in a range from 0.2 to 0.7 MPa, which is larger than that of commercially available PU foams derived from petroleum. Figure 5 shows compression modulus (E) calculated from the initial gradient of compression *vs*. strain curves. The value of E is in a range from 5 to 20 MPa. Both σ_{10} and E values showed the maximum value at around MLD/LSD= 40/60. As described in the introduction, MLD is derived from molasses composed from mono- and disaccharides, and LSD is derived from lignin. The reason why the optimum value is obtained in the blending ratio at around 60/40 has not yet been explained, although it is known that the ratio of saccharide *vs*. lignin components in plant material is in a similar range from 70/30 to 60/40. The above re-
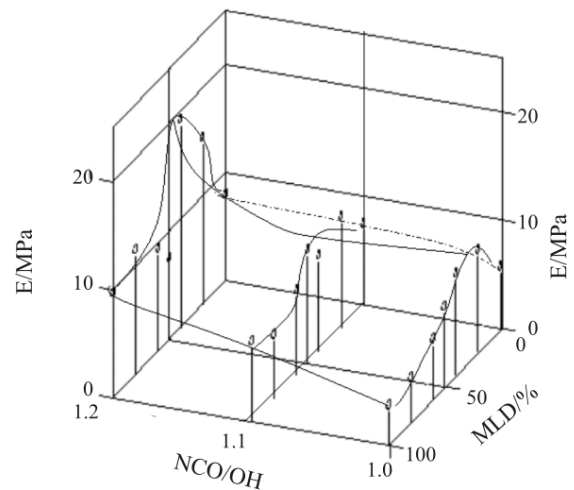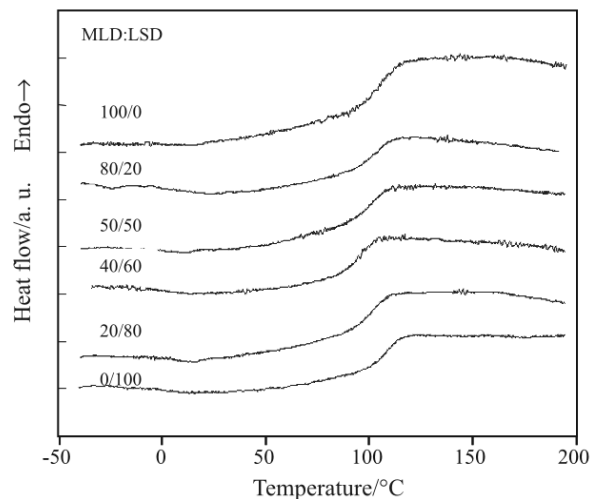
sults obtained by mechanical measurements indicate that the PU foam derived from plant component can be used for practical purposes.

Figure 6 shows representative DSC heating curves of PU foams derived from molasses and lignin. Glass transition is clearly observed as heat capacity difference of the baseline at around 100°C [19]. We reported that the main chain motion of lignin in the solid-state is observed by broad-line nuclear magnetic resonance spectrometry (b-NMR) in 1970 [20]. The molecular enhancement of lignin is also found by electron spin resonance spectroscopy (ESR). Spin probe method was applied to various types of lignin, since radicals are trapped in natural and extracted lignin [21]. Glass transition of various kinds of industrial lignins in solid-state was firstly reported using DSC in 1972 [22]. It was found that glass transition of lignin

depends not only on wood species, extraction method [22], and molecular mass [23, 24] but also markedly on thermal history, since distribution of relaxation times is broad, reflecting a complex molecular structure. Chemical structure affecting the molecular relaxation of lignin was investigated by b-NMR, viscoelastic measurement by torsion braid analysis and DSC using a series of synthesized amorphous model polymers having syringyl and guiacyl group. It is well known that hard wood or soft wood can be distinguished by the location of methoxyl and hydroxyl groups in the phenyl group of lignin [4, 25, 26]. The above studies strongly suggested that the previous theory that lignin molecules are densely cross-linked via intramolecular linking was not correct [1–4, 27, 28]. It was found that lignin is an amorphous random copolymer [4]. A small amount of cross-linking of lignin scarcely affects the free molecular motion of the main chain. Heat capacity of lignin was reported and heat capacity difference at T_g was almost the same as that of synthetic amorphous linear polymers [29].

Molecular enhancement is depressed by inter- and intramolecular cross-linking. As shown in Fig. 6, heat capacity difference of PU at T_g was 0.1 to 0.15 J g^{-1} K^{-1}, indicating that molecular motion is strongly restricted by urethane cross-linking, since the value is smaller than that of ordinary amorphous polymers [29]. As reported previously [29], ΔC_p of amorphous linear polymers decreases with increasing T_g, if we accept the iso-configurational entropy theory, as opposed to the iso-free-volume theory, of glass transition. However, this general rule is not applicable to ΔC_p–T_g relationship of physically or chemically cross-linked amorphous polymers, such as PU's. No reliable relationship between ΔC_p and T_g was obtained for PU foams prepared in this study.

Figure 7 shows three-dimensional relationships between T_g, NCO/OH ratio and MLD content in MLD/LSD blended polyol. As previously reported, T_g of LS is generally observed at a temperature higher than that of non-ionic lignins, such as kraft lignin, alcoholysis lignin and mildwood lignin, since sodium ions are introduced to the side chains [22, 30]. At the same time, temperature range of transition of LS is observed in a wide range from 100 to 180°C depending on differences in industrial processing and original plant. When the molecular mass is small, part of the lignin starts to decompose immediately after the completion of glass transition. The above facts are attributed to the inhomogeneous structure of LS and to intrinsic characteristics of polyelectrolytes in completely dry state. When a trace amount of water is added to solid polyelectrolytes, molecular motion can easily be detected [31]. On this account, it has been thought that the chemical reaction of LS is difficult.

For this reason, a large amount of LS obtained as a by-product of the pulp and paper industry was not utilized, except for a certain amount of LS that was mixed with concrete as a dispersant without further chemical modification. However, we found that PU could be successfully prepared from LS by improvement of reaction conditions [32].

T_g of PU containing LS was easily detected compared with original LS. It was also found that the temperature range of transition became narrower. T_g of PU is observed at around 70 to 115°C due to the introduction of molasses and flexible oxyethylene chains, depending on cross-linking rate (NCO/OH ratio). The effect of NCO/OH ratio is clearly seen in Fig. 7. MLD/LSD ratio scarcely affected T_g. In our previous studies, the effect of molecular mass (in Fig. 7, the number of oxyethylene group (n) was used) of flexible components of PU was systematically examined [10, 33]. It is clear that the molecular mobility increases with increasing n. On this account, T_g decreases with increasing molecular mass of ethylene glycol. In this study, DEG was chosen as a solvent for polyols in order to obtain rigid PU's. For the development of insulators for housing, T_g of PU should be higher than atmospheric temperature. The short length of oxyethylene chains is a crucial factor in increasing T_g. The mixing of polyols is also important to stabilize the cross-linking reaction, although the effect of MLD/LSD ratio on T_g was not distinct. From DSC data, it can be said that the rigid phenylpropane ring in lignin and the glucopyranose ring in saccharides similarly contribute to the main chain motion of PU, while cross-linking density markedly affects the T_g.

Figure 8 shows representative TG and DTG curves of PU foams derived from molasses and lignin with various MLD/LSD ratios at NCO/OH ratio=1.2. The mass of PU foams decreases in the two steps as shown in TG
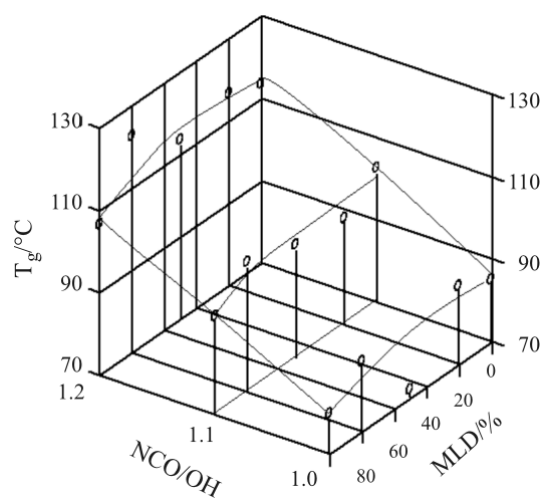

Fig. 7 Relationship between glass transition temperature (T_g), NCO/OH ratio and MDL content
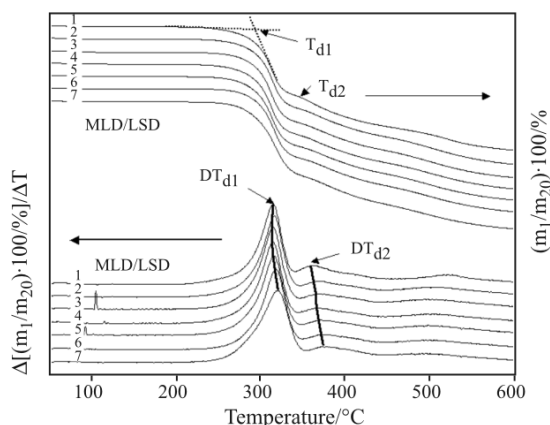
Fig. 8 TG an DTG curves of PU foams derived from molasses and lignin MLD/LSD, 1 – 100/0, 2 – 80/20, 3 – 60/40, 4 – 50/50, 5 – 40/60, 6 – 20/80, 7 – 0/100, NCO/OH ratio=1.2, heating rate=20°C min^{-1}

and DTG curves of Fig. 8. The low side decomposition (T_{d1}) is in a temperature from 285 to 295°C depending slightly on NCO/OH ratio and MLD/LDS ratio.

Figure 9 shows three-dimensional relationships between T_{d1}, NCO/OH ratio and MLD content in MLD/LSD blended polyol. The high temperature side decomposition (T_{d2}) is observed in a temperature from 355 to 365°C. T_{d2} values were scattered when plotted *vs.* MLD/LSD ratio in comparison with those of T_{d1}. DTG curves in Fig. 8 indicate that the low temperature side peak (D T_{d1}) is far higher than that of the high temperature side peak (D T_{d2}). The mass residue at 500°C was in a range from 40 to 45% regardless of NCO/OH ratio or MLD/LSD ratio. The above results suggest that the major part of PU foams decomposes at the first step.

Thermal decomposition behaviour of biopolymers from plants has been investigated mainly by TG [4, 7, 9, 28] and TG-Fourier transformed infrared spectrometry (FTIR) [6, 35]. In application domains, TG and TG-FTIR data of wood and wood compo-
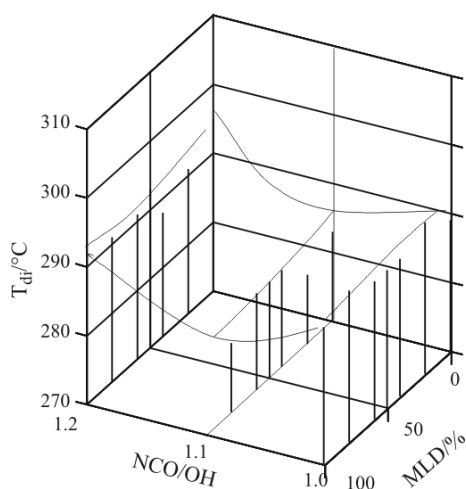
nents, such as cellulose, hemicelluloses and lignin has been utilized for material design for housing, wood processing, cigarette industry, etc. Gas evolution of wood components in dry state starts at around 300°C. Compared with synthetic polymers, the above biopolymers are thermally stable and the temperature range of thermal decomposition is wide. The amount of residual component, mainly charcoal, is 20 to 40% depending on plant species, portion of plant, extraction method, etc. When another chemical component is introduced to biopolymers by chemical reaction, thermal stability generally decreases. This strongly indicates that the higher order structure of biopolymers evolved in the long term and attained adaptable characteristics in nature.

As reported previously, a major decomposition of lignin is observed at around 300°C [8, 33–35]. Simultaneous measurements of TG-Fourier transform infrared spectrometry (FTIR) of polyurethanes derived from LS indicate that the amount of evolved gas is smaller than that of PU without LS and that thermal decomposition of PU with LS occurs in a narrower temperature range compared with that of PU foams without LS [8]. On this account, the major thermal decomposition detected as T_{d1} in Fig. 8 is attributable to decomposition of LS and scissions between the isocyanate groups and the alcoholic OH groups in LS. T_{d2} may be attributed to the miscellaneous scissions of various chemical bonds in the PU, although the fraction detected as the higher temperature side decomposition is small, as shown in Fig. 8.

In order to utilize PU foams for insulation materials, it is necessary to know the thermal conductivity of the sample. Figure 10 shows relationship between thermal conductivity and MLD content. The temperature difference between the two plates which sandwiched the PU foam was 27.7°C. Time maintained for the equilibration did not affect the results, when it exceeded 20 min. With increasing MLD content, thermal conductivity decreased slightly and was maintained at a constant value of 0.032 W m^{-1} K^{-1}. The above results were

Fig. 9 Relationship between decomposition temperature (T_{di}), NCO/OH ratio and MDL content
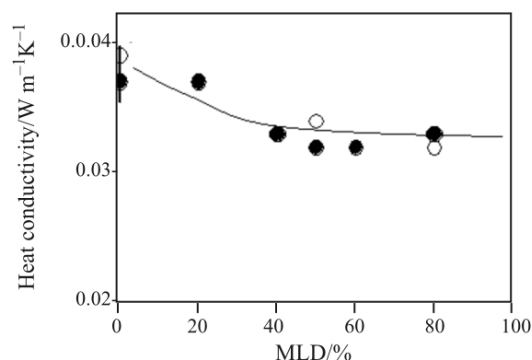

Fig. 10 Relationship between heat conductivity and MLD content. Time maintained for the equilibration, ● – 20 min, ○ – 40 min. NCO/OH ratio=1.2

Table 1 Comparison of heat conductivity of PU foams prepared in this study and commercially obtained foams

Sample	Heat conductivity/ $W\ m^{-1}\ K^{-1}$
Polyurethane foam (commercial 1)	0.136
Polystyrene foam (commercial 2)	0.035
Lignin/molasses foam	0.037–0.032

compared with commercial grade polystyrene foams. The results are shown in Table 1. The data suggests that the thermal conductivity of PU foams derived from lignin and molasses can be used as alternative materials for foams derived from petroleum.

Conclusions

New types of PU foams derived from lignin and molasses were prepared. Apparent density of PU foams was in a range from 0.04 to 0.07 g cm^{-3}, which varied depending on preparation conditions. Compression strength was in a range from 0.2 to 0.7 MPa and compression modulus (E) was from 5 to 20 MPa. Glass transition temperature of PU foams was observed in a temperature from ca. 80 to 120°C and thermal decomposition temperature from ca. 280 to 300°C depending on NCO/OH ratio. Thermal conductivity of PU foams was in a range from 0.030 to 0.040 W m^{-1} K^{-1} depending on mixing ratio of lignin and molasses. The above results indicate that PU foams derived from biopolymers can be used as insulation materials.

Acknowledgements

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