Thermal decomposition and glass transition of industrial hydrolysis lignin

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Abstract Thermal properties of industrial hydrolysis lignin (HL) obtained from bio-ethanol production plants were investigated by thermogravimetry and differential scanning calorimetry. Thermal decomposition of HL was observed in two stages suggesting coexisting carbohydrates. Glass transition temperature (T_g) was observed in a temperature range from 248 to 363 K. T_g values were lower than that of other industrial lignins, such as kraft lignin or lignosulfate. Enthalpy relaxation was observed as sub-T_g, which is not as prominent as other industrial or laboratory scale isolated lignins. T_g of HL decreased in the presence of water and saturated at water content (W_c) of 0.18 (mass of water/mass of dry HL). The amount of bound water calculated from melting enthalpy of water and W_c was ca. 0.18. Thermal decomposition and molecular motion of as obtained industrial HL are affected by coexisting carbohydrates.

Keywords Hydrolysis lignin · Bio-ethanol · Glass transition · Enthalpy relaxation · Water

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Introduction

Bio-ethanol production has recently received considerable attention, since alternate energy resources are required in order to maintain a sustainable cycle in nature. Various bio-resources, such as corn, sugar, residual sugar cane, wood, etc. have been utilized to produce bio-ethanol in industrial scale. Among them, wood is a promising resource and hydrolysis of wood carbohydrates has been established as a method to produce monomeric fragments which are quantitatively able to ferment to alcohol [1]. In the production of bio-ethanol, a large amount of residual hydrolysis lignin (HL) has been obtained as a by-product since lignin content in wood is ca. 25–30% depending on wood species [2]. Zarubin and his coworkers [3] have extensively studied the structure of hydrolysis lignin obtained from wood hydrolysis industry. Although fundamental research has been carried out, HL has not fully been utilized, even though the amount of HL obtained as a by-product is large, for example in Russia it is 10^5 tons/year. At present, in Russia, several tens of million tons of HL are kept in land field spoiling the environment. The amount of HL production unavoidably increases due to worldwide demand for bio-ethanol.

Hatakeyama and his coworkers [4–6] have investigated utilization of "as obtained" industrial lignins, such as kraft lignin (KL), sodium lignosulfonate (LS), without any after-treatments or chemical modifications. Among various possibilities for lignin utilization, polyurethane (PU) has received particular attention [7–10], since PU is utilized in a wide range of applications. PU derived directly from industrial lignin is promising, if simple production process and characteristic properties that are required in the market are taken into consideration [4]. When industrial production of HL is considered, cost performance is a crucial

factor. Chemical modification and other after-treatments increase the total cost of production. Among various kinds of industrial lignin which can be directly transformed into PU, HL is an important candidate. In order to be competitive with products derived from petroleum in the market, it is important to investigate the characteristic properties of industrial lignin products as provided.

When new PUs derived from industrial HL are developed, the polymeric properties of industrial HL in the solid state need to be compared with those of other industrial lignins. In this study, molecular motion of industrial HL as obtained in powder form is investigated by differential scanning calorimetry (DSC) and thermogravimetry (TG) and compared with that of other industrial lignins, and the potential of HL for PU preparation is examined.

Experimental

Samples

Four kinds of HL samples were obtained; one from New Zealand (HL-1), and three from different plants in Russia, Archangelsk (HL-2), Lobinsky (HL-3), and Kirovsky (HL-4). According to the manufacturer's report, HL-2, HL-3, and HL-4 were hydrolyzed under the following conditions; concentration of sulfuric acid 0.5%, temperature of the process ~ 450 K, time of the treatment ~ 120 min, and pressure ~ 1.3 MPa.

Two kinds of industrial lignins such as kraft lignin (KL) and lignosulfonate (LS) were used as reference materials. KL was obtained from Westvaco C., US. LS (commercial name Vanilex HW, sulfone group 0.13, carboxyl group 0.26. alcoholic hydroxyl group 0.28 and phenolic hydroxyl group 0.42 ($C_6 - C_3$) mole^{-1}) was obtained from Nippon Paper Chemicals Co. Ltd, Tokyo, Japan. Cellulose powder (commercial name, KC Flock, W-100/100G and W-400) obtained from Nippon Paper Chemicals Co. Ltd, Tokyo, Japan was used as a model polymer of contaminant of HL. Industrial lignins were used without further treatments. Samples were dried at 393 K for 3 h in an oven before measurements.

Scanning electron microscopy

A JEOL scanning electron microscope JSM-6100 was used. Lignin particles were spread on sample holder and the surface was coated with gold.

Thermogravimetry

A Seiko TG/DTA 220 was used. Sample mass was ca. 7 mg, heating rate 20 K min^{-1}, N$_2$ flow rate 200 mL min^{-1}.

Temperature was varied from 298 to 870 K. Samples were dried at 293 K for 3 h in an oven before measurements. Decomposition temperature was defined as reported previously [11].

Differential scanning calorimetry

A Seiko DSC/DTA 220C was used. Sample mass was ca. 5 mg, heating rate 10 K min^{-1}, N$_2$ flow rate 30 mL min^{-1}. Temperature was varied from 220 to 470 K. When thermal history of the sample was erased, the 2nd heating run was used for analysis of transition temperature. Temperature of transition was defined as reported previously [11, 12].

Results and discussion

TG of HL

Thermal degradation of various kinds of isolated lignins has been measured [13]. Although the temperature range of thermal degradation depends on isolation method and also on species of original wood, degradation gradually takes place in a broad temperature range from 520 to 670 K [13–15]. One-stage degradation is ordinarily was observed in TG curves of isolated lignin and evolved gas during thermal decomposition was identified by simultaneous measurement of TG-Fourier transform infrared spectrometry (FTIR) [16]. In contrast, as shown in Figs. 1 and 2, TG curves of several industrial lignin samples show two-stage
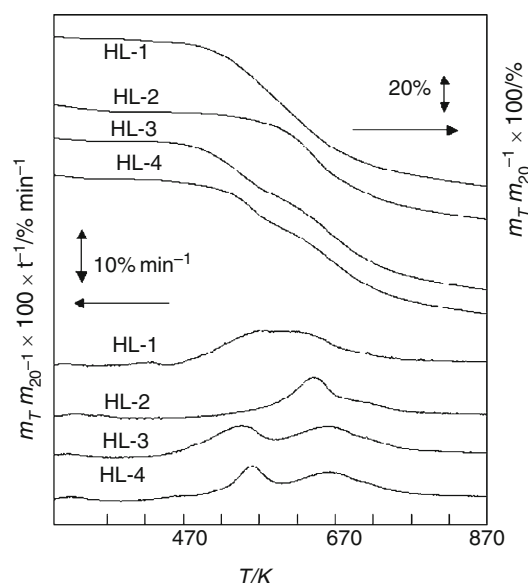
Fig. 1 TG curves of various kinds of HL. Heating rate = 20 K min^{-1}. m_{20}, mass at 293 K; m_T, mass at T; HL, hydrolysis lignin
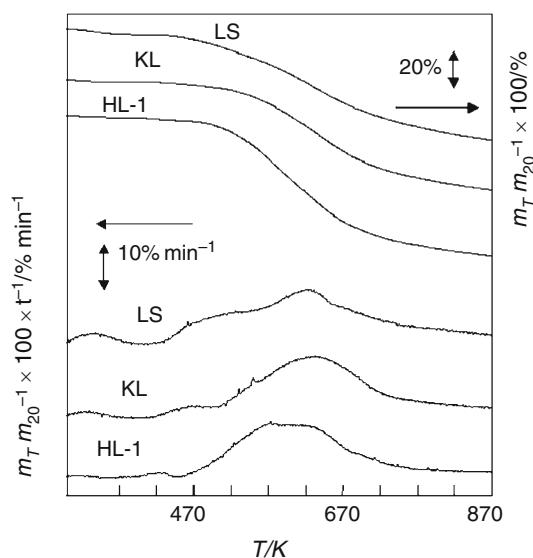
Fig. 2 TG curves of LS, KL, and HL-1. Heating rate = 20 K min^{-1}. HL, hydrolysis lignin; KL, kraft lignin; LS, lignosulfonate; m_{20}, mass at 293 K; m_T, mass at T

Table 1 Decomposition temperature of HL, KL, LS, and cellulose powder

Sample	T_d/K		ΔT_d/K		M_{773}/%
HL-1	518		576		45
HL-2		593		643	59
HL-3	493	623	551	664	45
HL-4	523	633	565	667	50
LS	453	588		624	59
KL		543		636	59
Cellulose powder*		613		648	12

* W-100/100G

Glass transition of HL

degradation. Table 1 shows thermal degradation temperature (T_d) and mass residue at 773 K of HL samples and other industrial lignins and cellulose powders.

Obtained industrial lignin samples were in powder form, and morphological observation was carried out by scanning electron microscopy (SEM). When HL powder was spread on the sample holder of SEM, wood fragments were observed for HL-1, HL-2, and HL-3. Particle size of fragments was in a range from 1 to 10 μm depending on the portion of supplied samples. The exact amount of woody fragments could not be determined, since fractionation was unsuccessful because the swollen lignin portion could not be fully separated from micro-order wood particles in solution. In other industrial lignins, KL, LS, and HL-1, no detectable woody particles were observed by SEM.

Due to the difference in the hydrolysis in industrial processes, the presence of contaminants is apparently seen. The low temperature side peak observed in TG derivative curves for HL-1, HL-3, and HL-4 strongly indicates that residual component is hemicellulose, such as xylan [13]. When cellulose particles were measured under the same condition by TG, decomposition was observed as one stage and T_d value is shown in Table 1. When TG curves of HL and cellulose are compared, the sharp TG derivative curve of HL-2 indicates the coexistence of cellulose. A small peak detected in LS at a temperature around 373 K suggests that water strongly restrained by LS could not be completely dried at 393 K for 3 h. Low temperature side peak is attributed to water strongly restrained by LS.

The polymeric properties of isolated lignin in solid state have been investigated by various experimental techniques over the last 40 years [6, 17–22]. Although the values of reported glass transition temperate (T_g) are found in a wide temperature range, depending on preparation method and wood species, it can be said that T_g values of lignin isolated in laboratory scale are higher than those of industrial lignin. At the same time molecular motion of in situ lignin has been observed at a temperature lower that that of isolated lignin [23, 24]. The above results suggest the amorphous structure of lignin is affected by coexisting component of wood and also thermal and mechanical history. As shown in Fig. 3, T_g of industrial HL samples was observed from 348 to 363 K. It is clear that T_g of HL is lower than that of other types of industrial lignin, such as KL and LS. Among HL samples, T_g values are found to be
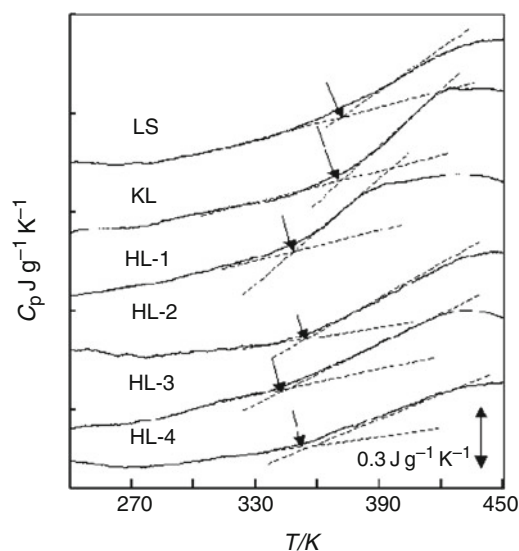
Fig. 3 DSC heating curves of LS, KL and HLs. Heating rate = 10 K min^{-1}. HL, hydrolysis lignin; KL, kraft lignin; LS, lignosulfonate

similar regardless of different production plants. As already reported, T_g of lignin in situ is observed at a temperature lower than that of isolated lignin. HL is obtained at a milder chemical process compared with that of other industrial lignins. This may explain why T_g of HL is close to that of lignin in situ.

In many other amorphous polymers, heat capacity difference between glassy state and rubbery state at T_g (ΔC_p) is used as an index of molecular mobility [25, 26]. However, in HL, ΔC_p cannot be used for discussion of molecular mobility, since the amount of lignin is not exactly calculated due to residual cellulose and hemicellulose.

Enthalpy relaxation of HL, comparison with DL

In previous studies of synthetic and natural amorphous polymers, it is clear that enthalpy level of the glassy state of amorphous polymers is governed by rate of glassification. The magnitude of enthalpy relaxation can be detected as the heat capacity overshoot at T_g by DSC. In order to control the glassification process, ordinarily the samples were annealed at a glass transition temperature region [26].

In the case of isolated lignin, the annealing effect was clearly seen by heat capacity measurement [21]. At the same time, sub-T_g can be observed in various kinds of lignin by annealing at a low temperature than T_g [20, 21]. Sub-T_g of lignin accords well with that of synthetic polymers [27] i.e., the sub-T_g peaks are asymmetric with long low-temperature tails; peaks increase in magnitude and shift to the high temperature side with increasing annealing time and temperature. By long time annealing at high temperature, sub-T_g peaks merge with the glass transition. Sub-T_g peak is observed in various HL samples, as shown in Fig. 4.

The temperature where endothermic deviation of sub-T_g peak starts is designated as T_{gl} and the high temperature side was designated as T_{gh}. Figure 5 shows DSC curves of HL-1 annealed at various annealing temperatures and times. T_{gl} and T_{gh} values are also shown in Fig. 6. T_{gh} shifts to high temperature side with increasing annealing time and temperature. However, temperature shift of HL is not prominent when the DSC curve of HL is compared with those of isolated lignins [20, 21] or synthetic polymers, such as polyvinyl chloride [27], i.e., sub-T_g of HL is not a distinct peak, although it can be observable. The results shown in Figs. 4–6 strongly suggest that HL consists of a broad range of polymeric molecules having different first- and second-order structures. This suggests that a different higher order structure having wide distribution of relaxation time is frozen in the glassy state of HL. On this account, it is appropriate to consider that lignin molecules in the glassy state, rubbery state, and partly enhanced state coexist when HL is annealed at a certain temperature.
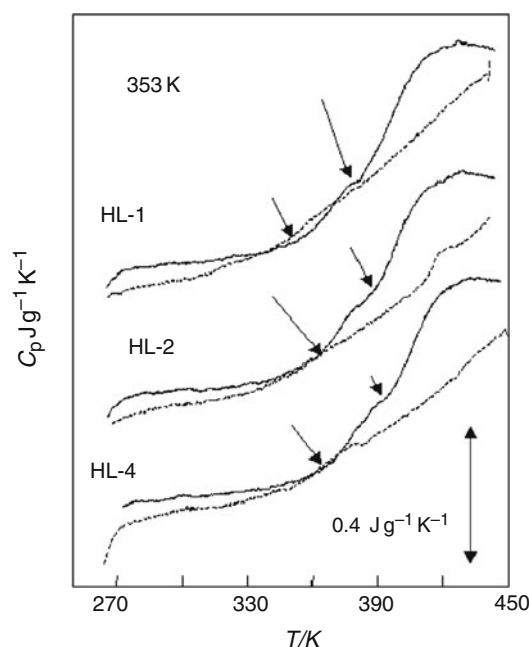
Fig. 4 Enthalpy relaxation of HL samples annealed at 353 K for 4 h. *Solid line*, annealed sample; *broken line*, original sample. HL, hydrolysis lignin

Water–HL interaction

The softening of polymers consisting of plant such as wood in moist conditions has been investigated since molecular motion of those polymers is an important characteristic for the utilization of fiber products [for example 28, 29]. Among various kinds of wood component, lignin in situ in moist conditions has received particular attention due to T_g decrease is not as high as compared with other carbohydrate components [23]. Glass transition behavior of isolated hydrolyzed lignin obtained by acid hydrolysis of softwood in 1,4-dioxane (DL) was studied by DSC in the presence of different amounts of water [30]. T_g of isolated DL decreased from 423 to 333 K by adding 20% water. The above results indicate that molecular motion of isolated lignin varies more markedly in the presence of water when T_g variation is compared with that of lignin in situ. Figure 7 shows representative DSC heating curves of HL-1 with various water contents. When $W_c = 0.10$, no first-order phase transition is observed. Glass transition is clearly seen. From $W_c = 0.15$, endothermic peak due to melting of ice and glass transition can be observed.

Figure 8 shows relationship between T_g and W_c. As clearly seen T_g decreases in initial stage and then reaches constant value. T_g of HL is slightly lower than that of DL [31]. As already mentioned in the previous section, industrial HL contains cellulose and hemicellulose. The hydroxyl groups of cellulose and hemicellulose restrain water molecules via hydrogen bonding. On this account,
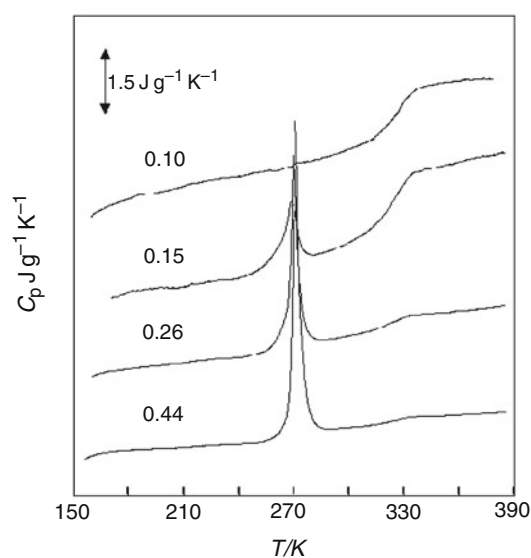
Fig. 5 DSC curves annealed HL-1 at various temperatures and times. *Numerals* in the figures show annealing time (h)
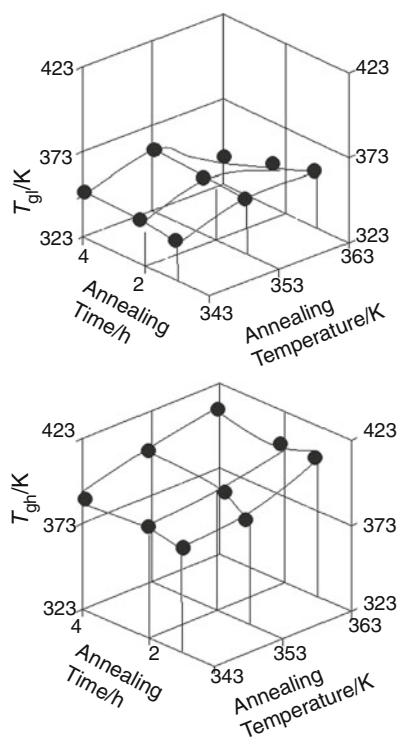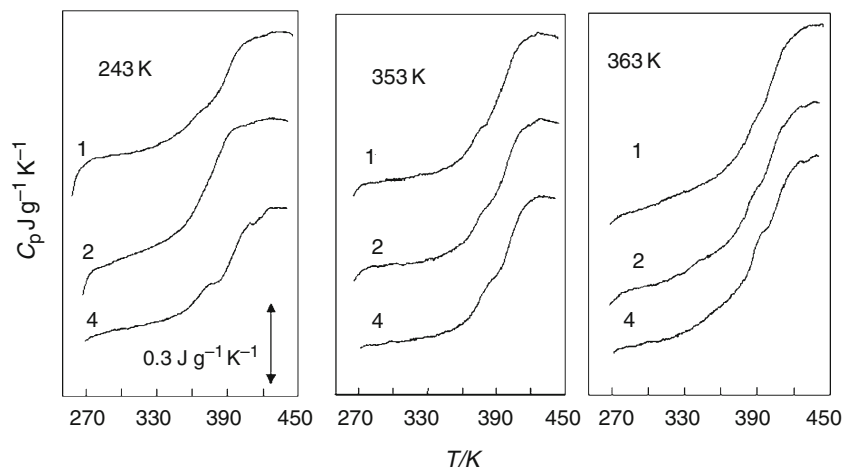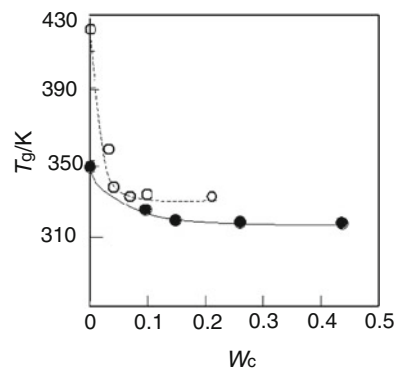

Fig. 6 Change of T_g of HL-1 as functions of annealing temperature and time. T_{gl}, temperature where endothermic deviation of sub-T_g peak starts; T_{gh} the high temperature side endothermic deviation starts

Fig. 7 DSC heating curves of HL-1 in the presence of water. *Numerals* in the figure show water content

Fig. 8 Relationships between T_g and W_c. *Filled circle*, hydrolysis lignin (HL); *open circle*, dioxane lignin (DL)

the molecular motion of industrial HL enhanced at a temperature lower than that of isolation lignin.

As shown in Fig. 7, DSC heating curve of HL with $W_c = 0.1$ shows no melting peak of water, indicating that a part of water in lignin is in nonfreezing state [31]. In our previous studies, it was shown that numbers of water molecules which directly form hydrogen bonding with the hydrophilic group of polymers are not freezable even when the temperature decrease is lower than crystallization temperature of water [6]. This kind of strongly bound water to hydrophilic group is categorized as nonfreezing water.
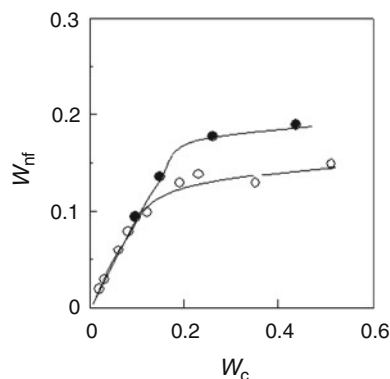
The amount of nonfreezing water (W_{nf}) can be obtained from the amount of total water content (W_c) and amount of freezing water (W_f) calculated forms the enthalpy of

Fig. 9 W_{nf} of industrial HL and isolated DL as a function of W_c. *Filled circle*, hydrolysis lignin (HL); *open circle*, dioxane lignin (DL)

melting. In various hydrophilic and biocompatible synthetic polymers [32–34], phase transition of bound water is observed at a low temperature side of free water. In the case of lignin, freezing bound water is observable for isolated lignin [30]. The values are in a range 0.03–0.04 [30]. However, in the case of industrial HL, a clear endothermic peak showing freezing bound water was not distinctly observed. On this account, in this study, W_{nf} values were calculated from the following equation

$$W_c = W_{nf} + W_f. \tag{1}$$

Figure 9 shows the relationship between W_{nf} and W_c of industrial HL and isolated DL. The W_{nf} value of HL is larger than those of DL. This is caused by (1) presence of carbohydrate polymers contaminated with HL-restrained water, since the number of the hydroxyl group of carbohydrate is more than that of lignin, and accordingly, W_{nf} value of cellulose [31] is larger than that of lignin, (2) a certain amount of bound water is formed as freezing bound water in DL, and this decreases the total amount of W_{nf}.

Conclusions

Thermal stability of industrial HL is almost similar to that of other industrial lignins, although coexisting carbohydrate affects decomposition behavior. Glass transition temperature of HL was observed in a temperature range from 348 to 363 K which is lower than that of isolated lignin. Enthalpy relaxation was not prominent, suggesting broad distribution of relaxation time. T_g variation in the presence of water indicates that the coexisting carbohydrate increases the amount of restrained water molecules. The amount of nonfreezing water was larger than that of isolated lignin. From the above results, it can be said that industrial HL is not a homogeneous material; however, this is not a serious factor when HL is utilized as a component of polyurethane

preparation, i.e., (1) thermal decomposition of HL samples depends on hydrolyzed processes of each bio-ethanol production plant; however, the temperature range of decomposition is almost similar to that of other industrial lignins which have been utilized for PU preparation, (2) T_g values of HL can be controlled by changing PU preparation conditions, (3) coexisting carbohydrates must be used as they are. This indicates that PU will be obtained as microscale bio-composites. It can be concluded that HL has a potential to be utilized as PU preparation resource.

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