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Environmentally Compatible Hybrid-Type Polyurethane Foams Containing Saccharide and Lignin Components

Hyoe Hatakeyama,[1] *Tatsuko Hatakeyama*[2]

[1]Fukui University of Technology, 3-6-1 Gakuen, Fukui, Fukui 918-8505, Japan
[2]Otsuma Women's University, 12 Sanbancho, Chiyoda-ku, Tokyo 102-8357, Japan
E-mail: hatakeyama@otsuma.ac.jp

Summary: Semi-rigid polyurethane (PU) foams were prepared using lignin-molasses- poly(ethylene glycol) polyols. Two kinds of lignin, kraft lignin (KL) and sodium lignosulfonate (LS), were used. Both lignin and molasses polyols were mixed with various ratios and were reacted with poly(phenylene methylene) polyisocyanate (MDI) in the presence of silicone surfactant and di-*n*-butyltin dilaurate. A small amount of water was used as a foaming agent. The apparent density of PU foams increased with increasing lignin content. The compression strength and elastic modulus linearly increase with increasing apparent density, suggesting that mechanical properties are controllable by changing reaction conditions. The PU foams were amorphous and glass transition was detected by differential scanning calorimetry. The glass transition temperature (T_g) maintained an almost constant value, regardless of the mixing ratio. This indicates that both the phenolic group of lignin and the glucopyranose ring of molasses act as rigid components in PU crosslinking network structures, and both groups contribute to the main chain motion to the same extent. By thermogravimetry (TG), it was confirmed that PU foams are thermally stable up to around 300 ℃. By differential scanning calorimetry, T_g was observed at temperatures from 80 to 120 ℃.

Keywords: compression strength; foam; lignin; molasses; polyurethane

Introduction

Bio-based polymers have been in demand on the world market in recent years, since energy conservation is a serious problem for maintaining sustainable development. Biomass, especially that obtained from industrial residues which have not been effectively used, has received particular attention. Biomass-based polymers are not only environmentally compatible but their physical properties and market prices are competitive in comparison with ordinal polymers derived from petroleum. Major plant components, such as saccharides and lignin, contain highly reactive hydroxyl groups, which can be used as reaction sites. Using the above reaction sites, it is possible to convert saccharides and

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lignin to functional and biodegradable polymers that are environmentally compatible.[1-7] In order to obtain stable structures and reliable properties for practical application, it is necessary to establish stable and substantial systems. In this study, among various polymers related to the above chemical modification of saccharides and lignin, hybrid-type polyurethane (PU) foams with various amounts of saccharides and lignin have extensively been investigated. Semi-rigid bio-based PU's are designed in order to use them as insulation materials for house construction. Using both components--saccharides and lignin--it is possible to control the cross-linking condition by changing the number of the hydroxyl group.

Experimental

Sample preparation. Kraft lignin (KL) was obtained from West Vaco Co., Ltd. Sodium lignosulfonate (LS) was provided by Nippon Paper Industries Co., Ltd. Polyethylene glycol having a molecular weight of M_n 200 (PEG200) was commercially obtained from Daiichi Kogyo Seiyaku Co., Ltd. Poly(phenylene methylene) polyisocyanate (MDI) was commercially obtained from BASF Inoac Co., Ltd.

Lignin in powder form was dissolved in PEG at 65–75 ℃; a 33% KL-PEG system (KL polyol, KLP) and LS-PEG system (LS polyol, LSP) were prepared. Molasses (glucose 8.5%, sucrose 32.5%, fructose 9.2%) was obtained from Tropical Technology Center. Residual water in molasses was dehydrated by vaporization. Molasses was dissolved in PEG at 25 ℃ and a 33% molasses-PEG system (ML polyol, MLP) was prepared. As shown in the preparation scheme in Figure 1, KLP and MLP or LSP and MLP were mixed at various ratios and PEG was added in order to control the viscosity of the system. The total content of lignin and molasses in mixed polyols was maintained at 16.5% throughout this experiment. Silicone surfactant, di-*n*-butyltin dilaurate (DBTDL), was added as a catalyst and a small amount of water was used as a foaming agent. This pre-mixture was reacted with MDI under vigorous stirring at room temperature. The NCO/OH ratio of the KLP-MLP systems was 1.4 and that of LSP-MLP systems was 1.2. After PU foams were obtained, they were allowed to stand overnight at room temperature.

The KL, LS and ML content in polyols were calculated using the following equations.

$$\text{KL content / \% in polyol} = \left(\frac{W_{KL}}{W_{KL} + W_{ML} + W_{PEG200}}\right) x100 \qquad (1)$$

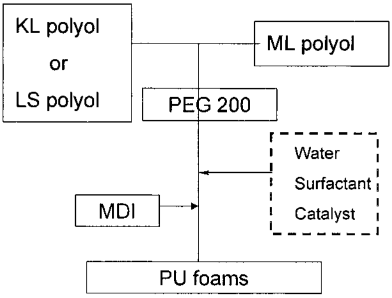

Figure 1. Preparation scheme of polyurethane foam derived from lignin-molasses polyol systems. KL=kraft lignin, LS=sodium lingosufonate, ML=molasses, PU=polyurethane, MDI=poly(phenylene methylene) polyisocyanate.

$$\text{LS content / \% in polyol} = \left(\frac{W_{LS}}{W_{LS} + W_{ML} + W_{PEG200}} \right) x100 \tag{2}$$

$$\text{ML content / \% in polyol} = \left(\frac{W_{ML}}{W_{ML} + W_{KLorLS} + W_{PEG200}} \right) x100 \tag{3}$$

Apparent density. A sample piece of 40 (width, mm) x 40 (length, mm) x 30 (thickness, mm) was prepared. The size of the samples was measured using a caliper, and sample mass was measured using a balance. The apparent density (ρ_a) of three pieces for each sample was measured and the mean value was calculated.

Mechanical measurement. Stress-strain measurements were carried out using a Shimadzu Autograph AG-2000D. The sample size was 40 (width) x 40 (length) x 30 (thickness) mm, with a compression rate of 30 mm min^{-1}. The compression stress (σ_{10}) at 10% strain, compression yielding stress (σ_y) and elastic modulus (E) were calculated from the stress-strain curve.

Thermogravimetry. A Seiko Instrument thermogravimeter-differential thermal analyzer TG-DTA 220 was used. Sample mass was 7 mg, heating rate was 20 ℃ min^{-1}, and N_2 flow rate was 100 mL min^{-1}. The temperature range was varied from 25 to 600 ℃. Decomposition temperature (T_d) was determined from the TG curve and its derivatives curve. When the decomposition took place in two stages, T_d was numbered from the low to high temperature.

Differential scanning calorimetry. A Seiko Instruments differential scanning calorimeter

DSC 220C was used. Sample mass was 5 mg, heating rate was 10 ℃ min^{-1} and N_2 flow rate was 30 ml min^{-1}. The glass transition temperature (T_g) and heat capacity difference at T_g were defined as reported previously.[8]

Results and Discussion

Figure 2 shows the schematic chemical structure of polyurethane derived from a lignin-molasses polyol. When the molasses content is large, intermolecular linking increases, since the number of the hydroxyl group of saccharides is far larger than that of lignin. At the same time, both the phenolic ring and glucopyranose ring act as rigid segments in the main chain of PU. The apparent density of foams generally corresponds to the number and size of pores. When the amount of foaming agent is large, PU contains a large number and volume of pores. Accordingly, pore structure is controlled by reaction conditions. In PUs prepared by the procedure described in the experimental section, the apparent density increased with increasing KLP or LSP content and linearly decreased with MLP content. This suggests that the hydrophylicity of ML is strongly related to the amount of water used as a foaming agent.

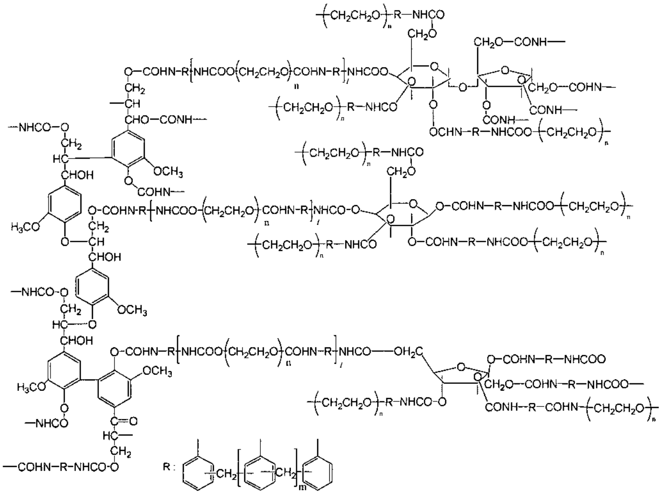

Figure 2. Schematic chemical structure of polyurethane derived from lignin-molasses polyol.

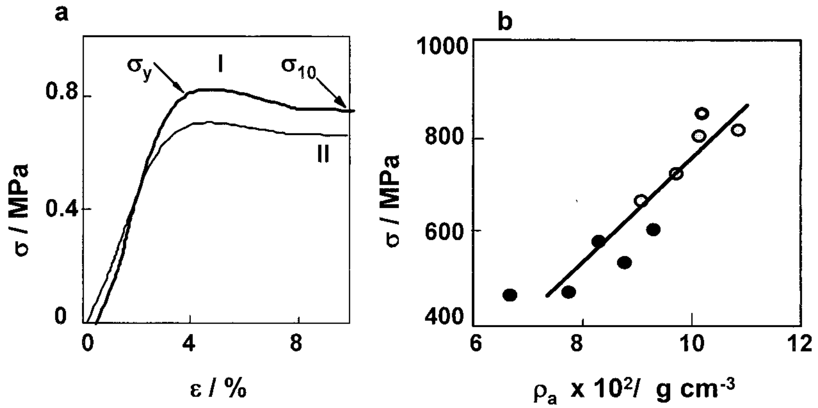

Figure 3. (a) Representative compression curve of PU foam derived from lignin-molasses polyol systems showing strength at 10 % compression (σ_{10}) and yielding strength (σ_y). I:KLP-MLP PU, II; LSP-MLP PU. 3. (b) Relationships between compression strength (σ_{10}) and apparent density (ρ_a).

Figure 3-(a) shows representative compression curves of PU foams derived from a lignin-molasses polyol system. A similar pattern of compression curves was obtained regardless of kinds of lignin or the mixing ratio of lignin and molasses. Compression strength at 10% strain (σ_{10}) and yielding strength (σ_y) were calculated as shown in this figure. The relationship between σ_{10} and, ρ_a .is shown in Figure 3-(b). It is clearly seen that ρ_a increases linearly with increasing ρ_a. Values of σ_y also showed a similar tendency as σ_{10}, although σ_y values are higher than those of σ_{10} in a whole range of apparent density.

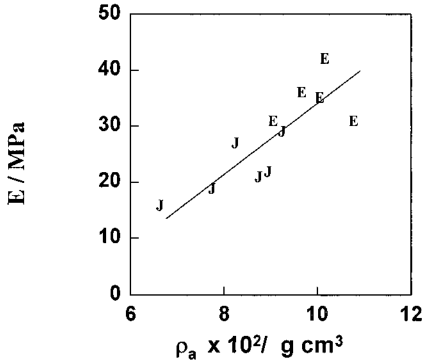

Figure 4. Relationships between elastic modulus (E) and apparent density (ρ_a).

The elastic modulus (*E*) was calculated using the linear gradient portion of the stress-strain curve. The relationship between *E* and ρ_a of PU foams derived from KLP-MPL and LSP-MLP is shown in Figure 4. *E* increases linearly with increasing ρ_a. The above facts indicate that mechanical properties of PU foams can be defined mainly by changing the mixing ratio of different types of polyols. In the systems used in this study, mechanical strength increases when the amount of lignin increases. The molasses polyol acts contrary to lignin polyol, since the number of the hydroxyl groups attaching to saccharides necessarily affects foaming conditions.

Thermal stability of PU foams was examined using TG. Figure 5-(a) shows representative TG curves of lignin-MLP PU systems. By the observation of TG curves, it seems that thermal decomposition takes place smoothly at around 290 ℃; however, in TG derivative curves, a large peak at around 320 ℃ and a small peak at 350 ℃ are recognized. This suggests that the second step decomposition is masked in an abrupt decrease of TG curves. Both T_d and DT_{d1} increased when KL content increased. In contrast DT_{d2} maintains a constant value and no difference is observed if the kind of lignin is varied. By the observation of TG-FTIR as reported in previous reports, thermal decomposition of urethane bonding between phenolic hydroxyl groups and isocyanate groups occurred at a lower temperature than that of urethane bonding between alcoholic hydroxyl groups and isocyanate groups. DT_{d1} was found to correspond with the thermal degradation of urethane bond and ether bond, since absorbance bands of NCO (2277 cm^{-1}) and C-O-C (1138 cm^{-1}) were observed in the evolved gases. DT_{d2} was found to correspond with the thermal degradation of aromatic rings, since the absorbance bands of C=C (1519 and 1620 cm^{-1}) were observed.

TG results show that thermal decomposition occurs in a limited temperature range, although the mixing ratio changed in a wide range. Mass residue of the above PU foams at 500 ℃ is ca. 40%, regardless of lignin and mixing ratio. For practical purposes, this fact is advantageous, since the mixing ratio can be changed without taking into consideration the thermal stability in order to prepare designed mechanical properties.

A heat capacity gap due to the glass transition of semi-rigid foam of PU is observed at around 100 °C in the DSC heating curve, as shown in Figure 6-(a). Figure 6-(b) shows that glass transition temperatures (T_g's) of KLP-MP PU foams slightly decrease with increasing lignin content and those of LSP-MP PU foams maintain at an almost constant

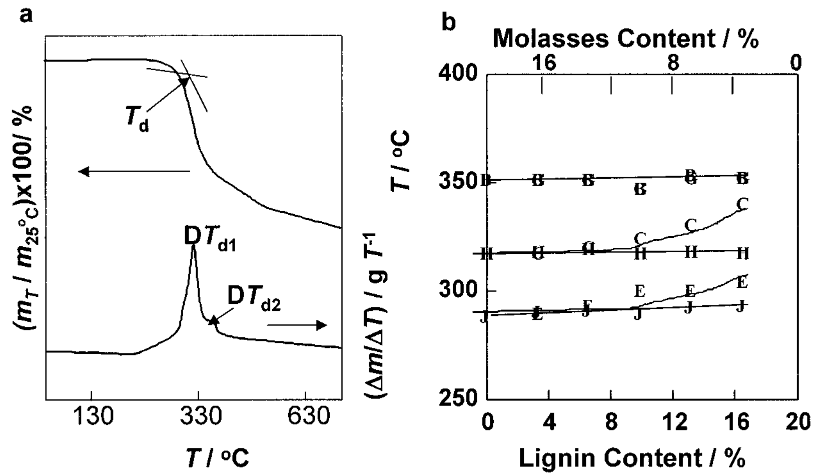

Figure 5. (a) Representative TG and derivative TG curve of PU foams derived from lignin (LS)-molasses polyol systems showing decomposition temperature (T_d), peak temperature of the first decomposition step (DT_{d1}) and the second step (DT_{d2}) in a derivative TG curve. 5 (b) Relationships between T_d, DT_{d1}, DT_{d2} and lignin or molasses content in PEG T_d ;E=KLP-MP, J=LSP-MP, DT_{d1}; C=KLP-MP, H=LSP-MP, DT_{d2}; G=KLP-MP; B=LSP-MP.

value. The above results indicate that molecular motion of PU foams is restricted by both factors, i.e., cross-linking density and NCO/OH ratio and number of rigid segments in the main chains. As described in the experimental section, the total amount of lignin and molasses in polyol is maintained at a constant value, regardless of mixing ratio; however, the number of cross linking increases with increasing ML content. The MLP content affects the T_g value in the case of KLP-MP PU foams; however, the effect of MLP is masked in the case of LDP-MP PU foams by cross-linking network structures, as the case of LSP-MP PU foams.

The T_g of semi-rigid PU foams ranges in temperature from 80--120 ℃. T_g values are reasonable when it is considered that T_gs of amorphous polymers synthesized from petroleum are observed in a similar temperature range. A stable characteristic is thought to be preferable for practical applications.

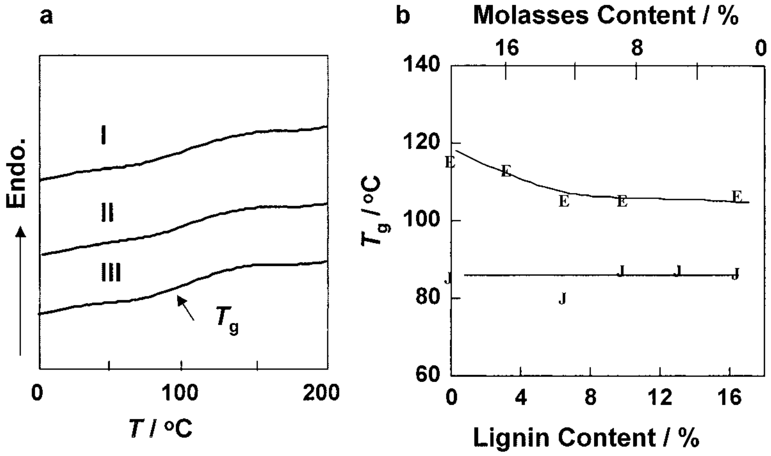

Figure 6. (a) Representative DSC heating curves of KLP-MLP PU foams: I; KLP=0, MLP=16.5%, II; KLP=6.6, MLP=9.9%, KLP=16.5, MLP=0%, 6. (b) Relationship between glass transition temperature (T_g) and lignin content in polyol: E; KLP-MP, J ; LSP-MP.

Conclusion

Simi-rigid PU foams are prepared using lignin-molasses-poly(ethylene glycol) polyols. By changing the mixing ratio of lignin polyol and molasses polyol, apparent density was controlled. It was found that mechanical properties depend directly on apparent density. By TG, it is confirmed that PU foams are thermally stable up to around 300 ℃. By DSC, glass transition is observed at temperatures from 80 to 120 ℃.

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