

Preparation and Physical Properties of Sodium Lignosulfonate- and Saccharide-based Rigid Polyurethane Foams

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Abstract

Rigid polyurethane (PU) foams were prepared from polyol mixtures containing lignosulfonate polyol (LSP) (sodium lignosulfonate + polyethylene glycol) and molasses polyol (MP) (molasses + polyethylene glycol) by the reaction with polyphenyl polymethylene polyisocyanate (MDI) in the presence of a silicone surfactant, a catalyst and water. Thermal properties of the obtained PU foams were measured by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperature (T_g) did not show obvious difference with the change of LS and MOL contents. Mechanical properties of PU's were measured by compression tests. Compression strength, yielding strength and compression elasticity increased with increasing apparent density.

1. Introduction

Plant components such as lignin and saccharides are basically biodegradable. They have reactive hydroxyl groups in their molecules and have more than two hydroxyl groups per molecule. In recent years, polyurethane's (PU's) have been prepared from plant components and their physical properties studied at our laboratory [1-7]. PU's having plant components show excellent thermal and mechanical properties. They are also biodegradable [8]. Sodium lignosulfonate (LS), which is obtained as a by-product of pulp production process, can be used as a polyol component for PU's. In our previous studies, PU's derived from molasses (MOL) have already been reported [9].

In this study, PU foams were prepared from LS and MOL. Their thermal and mechanical properties were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG) and compression tests in order to establish how the changing ratio of LS and MOL affects the physical properties of PU's.

2. Experimental

2.1 Materials

LS was provided by Nippon Paper Industries Co., Ltd. MP (a mixture of MOL and PEG200, MOL%=33.3) was provided by Tropical Technology Center Ltd. Polyethylene glycol (PEG 200) having molecular weight of 200 and MDI were obtained from Tokai Rubber Industries Co., Ltd.

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2.2 Preparation

LS polyol (LSP) was obtained by dissolving LS in PEG200 under heating from 65 to 75 °C. As shown in Fig. 1, LSP and MP were mixed with PEG200. The polyol was obtained with various LS and MOL contents. The above polyol was mixed with small amounts of silicone surfactant, catalyst and water. This premixture was reacted with MDI under vigorous stirring at room temperature. After foams were obtained in plastic cups, the samples were allowed to stand overnight at room temperature.

In the above processes, the contents of LS and MOL were calculated as follows:

$$\text{LS content (\% in polyol)} = [W_{\text{LS}} / (W_{\text{LS}} + W_{\text{MOL}} + W_{\text{PEG}})] \times 100$$

$$\text{MOL content (\% in polyol)} = [W_{\text{MOL}} / (W_{\text{MOL}} + W_{\text{LS}} + W_{\text{PEG}})] \times 100$$

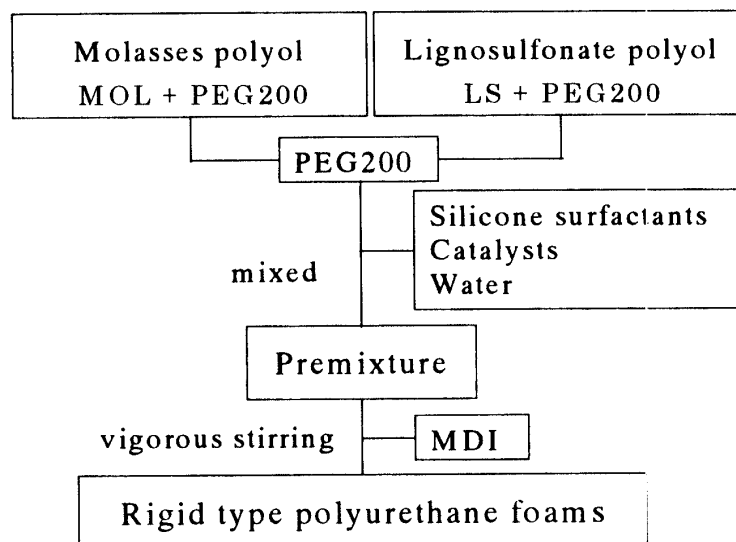
where W_{LS} is weight of LS, W_{MOL} is weight of MOL and W_{PEG} is weight of PEG. A schematic chemical structure of LS- and MOL-based PU's is shown in Fig. 2.

2.3 Measurements

Differential scanning calorimetry (DSC) was performed in nitrogen flow using a Seiko DSC 220 C. Samples of ca. 5mg were placed in aluminum open pans and measurements were carried out at a heating rate of 10 °C /min in nitrogen flow. Glass transition temperature (T_g) was observed as an endothermic shift of the baseline in the DSC curve [10]. A Seiko TG/DTA 220 was used for thermogravimetry (TG). Samples of ca. 7mg were placed in platinum pans and measurements were carried out at a heating rate of 20 °C/min in the temperature range from room temperature to 600 °C in nitrogen flow. Thermal degradation temperature (T_d) was observed in TG curves according to the method shown in the literature [10]. TG-FTIR measurements were carried out using a Seiko TG/DTA 220 thermobalance equipped with a Jasco FT/IR 420 spectrometer. The gases evolved during thermal degradation were analyzed simultaneously by FTIR [7].

Apparent density (ρ = weight / apparent volume: g/cm³) was measured using a Mitsumoto ABS digital solar caliper and an electric balance. Apparent volume was calculated using a sample with ca. 40 mm (length) × ca. 40 mm (width) × ca. 30 mm (thickness).

Compression tests were carried out using a Shimadzu Autograph AG-2000D according to JIS K7220 at room temperature. 3 sample pieces were used for each test. Sample size was ca. 40 mm (length) × ca. 40 mm (width) × ca. 30 mm (thickness). Compression speed was 3.0 mm/min. The compression strength was detected at 10% strain. The yielding strength was evaluated as the maximum strength from each stress-strain curve. The compression elasticity was calculated from the gradient of the first straight line of stress-strain curves according to JIS K7220.



NCO/OH ratio = 1.2

Fig. 1 Preparation of LS- and MOL-based rigid PU foams

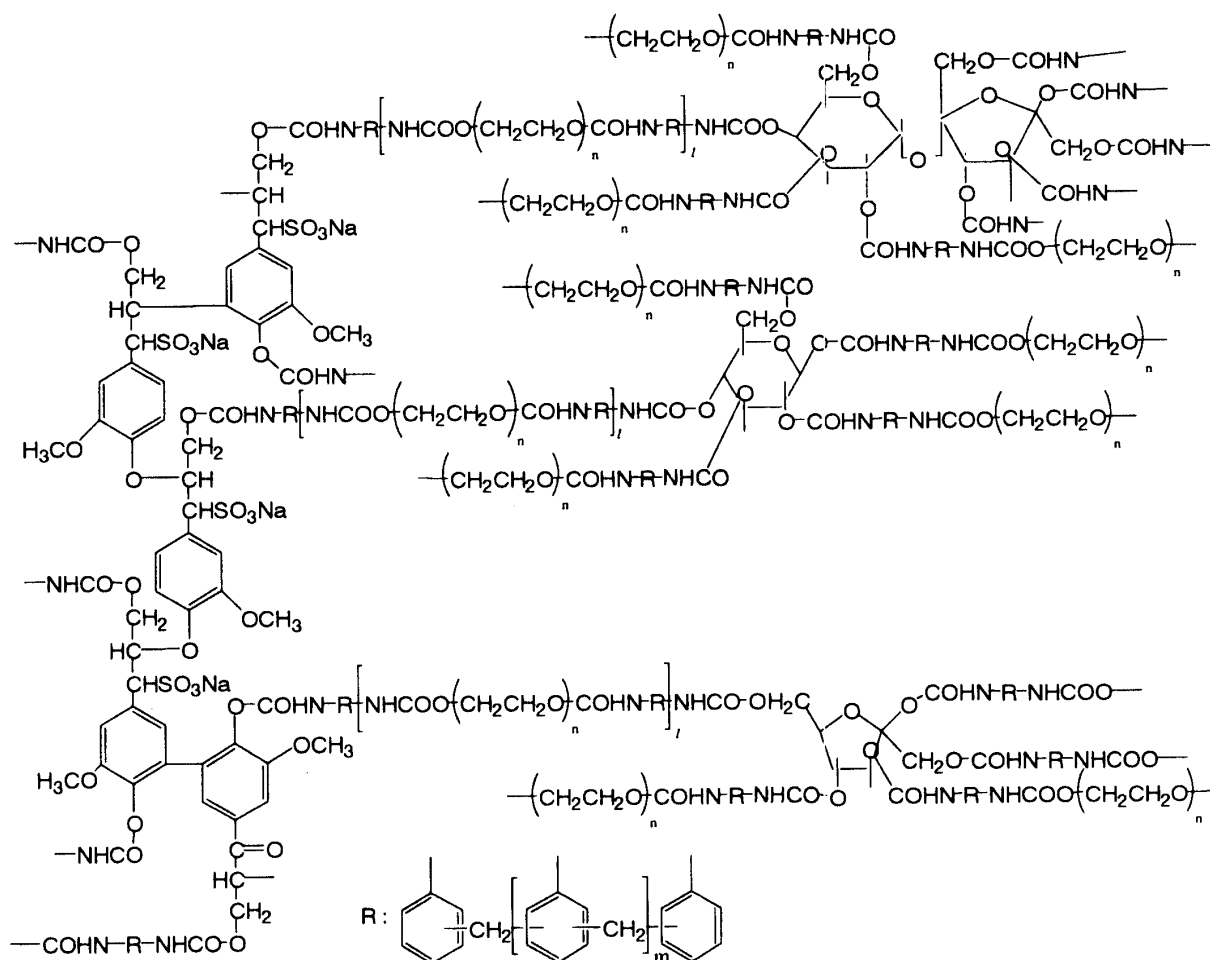


Fig. 2 Schematic chemical structure of LS- and saccharide-based PU

3. Results and discussion

3.1 DSC

Fig. 3 shows DSC curves of PU's prepared from the LS-MOL-PEG200-MDI system. Fig. 4 shows the relationship between glass transition temperatures (T_g 's) and heat capacity differences (ΔC_p) at T_g . The T_g and ΔC_p of the above PU's did not show obvious difference with the change of mixing ratios of LS and MOL. Saccharides, which have inflexible pyranose and furanose rings, have more reaction sites than lignin, while lignin has very rigid aromatic rings in the molecular structure. Accordingly, the effect of saccharide and lignin structures on T_g and ΔC_p of the prepared PU foams seemed to create a balance between the molecular characteristics of saccharides and lignins.

3.2 TG

Fig. 5 shows TG curves and DTG curves of PU's prepared from the LS-MOL-PEG200-MDI system. T_d , DT_{d1} and DT_{d2} were observed. From the results of TG-FTIR, DT_{d1} is identified as the thermal degradation of urethane bond and ether bond, since the absorbance bands of NCO (2277 cm^{-1}) and C-O-C (1128 cm^{-1}) were observed in the evolved gases. DT_{d2} is identified as the thermal degradation of benzene rings, since the absorbance bands of C=C (1510 and 1620 cm^{-1}) were observed. Fig. 6 shows the change of thermal degradation temperatures (T_d 's) and mass residues at 450°C (MR_{450} 's) with LS contents and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system. T_d and MR_{450} did not show obvious changes with increasing LS content. It is considered that the changes in LS content and MOL content in PU's did not affect markedly the T_d and MR_{450} .

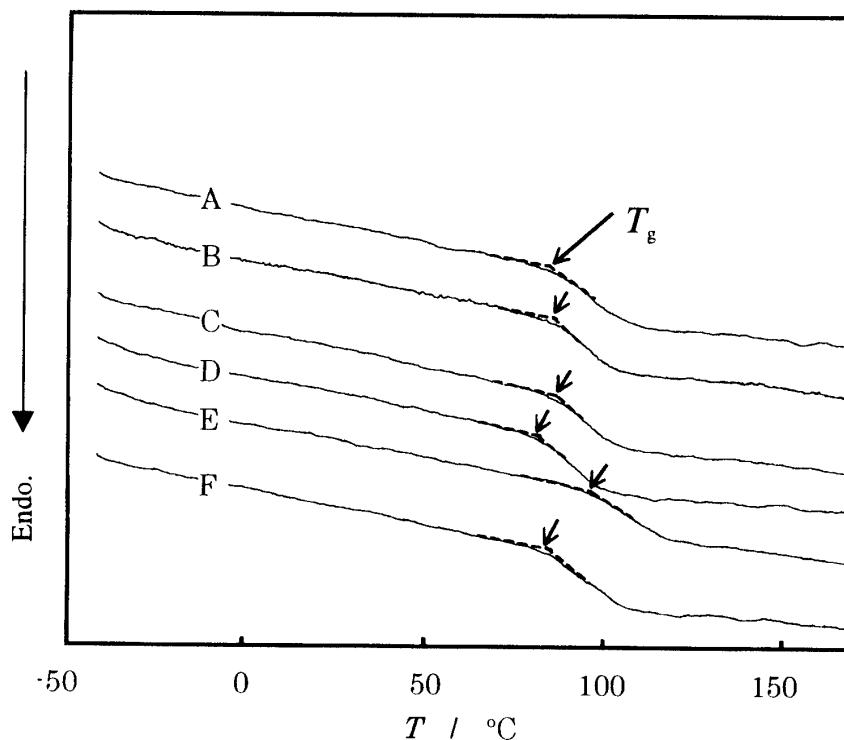


Fig. 3 DSC curves with various LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system

The LS contents and MOL contents of each curve are as follows.

A = 16.5%LS, 0%MOL B = 13.2%LS, 3.3%MOL C = 9.9%LS, 6.6%MOL
D = 6.6%LS, 9.9%MOL E = 3.3%LS, 13.2%MOL F = 0%LS, 16.5%MOL

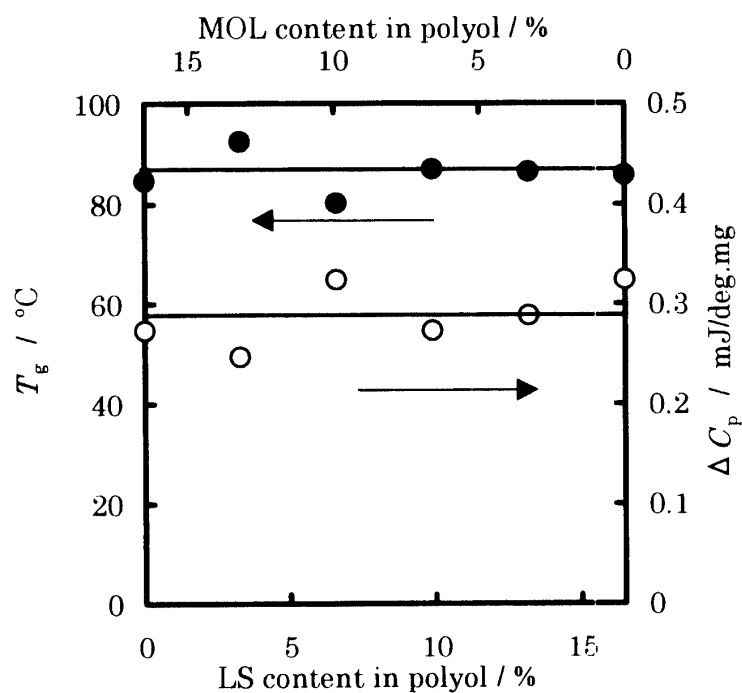


Fig. 4 Change of glass transition temperature (T_g) and heat capacity gap (ΔC_p) at T_g with LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system
● T_g ○ ΔC_p

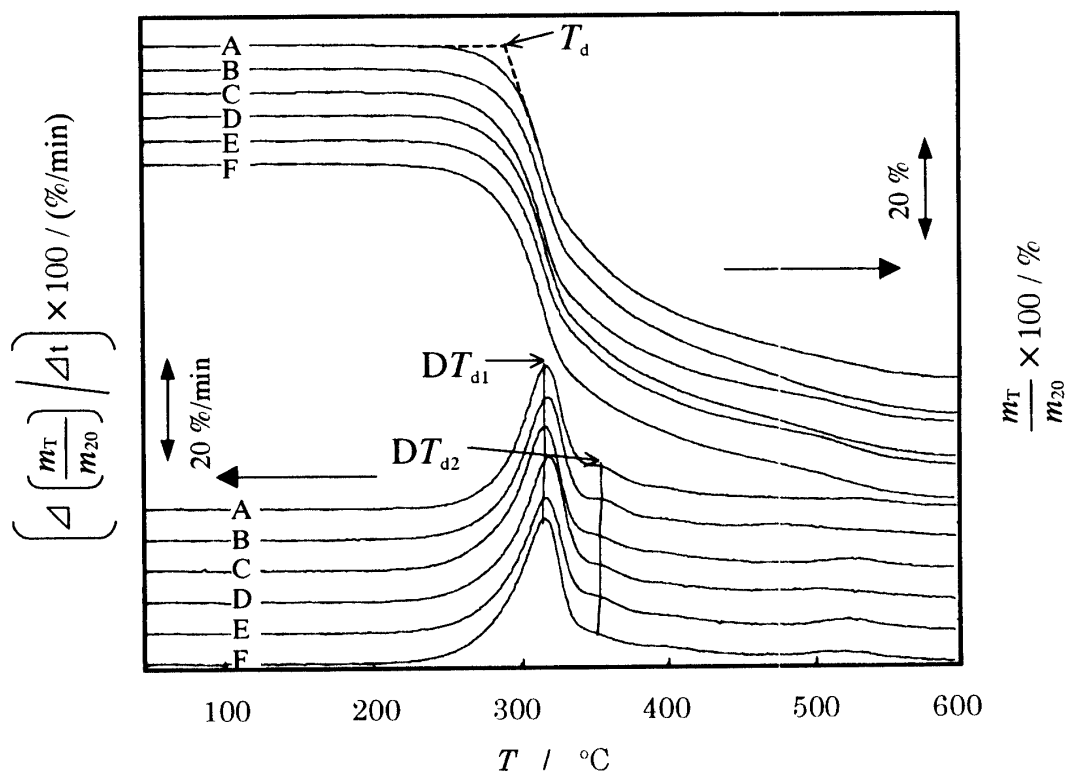


Fig. 5 TG and DTG curves with various LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system

The LS contents and MOL contents of each curve are as follows.
A = 16.5%LS, 0%MOL B = 13.2%LS, 3.3%MOL C = 9.9%LS, 6.6%MOL
D = 6.6%LS, 9.9%MOL E = 3.3%LS, 13.2%MOL F = 0%LS, 16.5%MOL

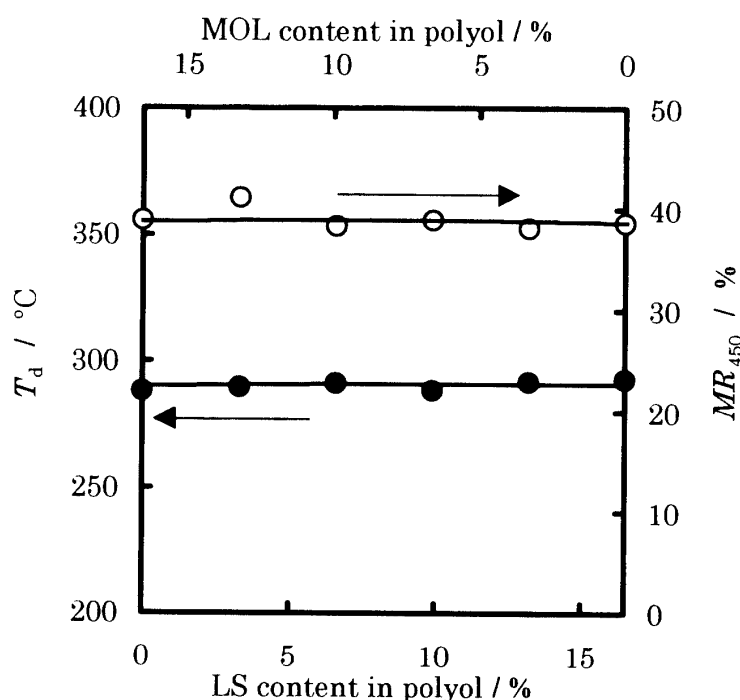


Fig. 6 Change of thermal degradation temperature (T_d) and mass residue at 450°C (MR_{450}) with LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system
 ● T_d ○ MR_{450}

3.3 Apparent density

Fig. 7 shows the relationship between ρ , LS contents and MOL contents in PU's prepared from the LS-MOL-PEG200-MDI system. The ρ of PU foams slightly increased with increasing LS content. The value of ρ changed from ca. 0.06 to ca. 0.09 g/cm³.

3.4 Compression tests

Fig. 8 shows the change in compression strength at 10% strain (σ_{10}), yielding strength (σ_y) and compression elasticity (E) with LS contents and MOL contents in PU's prepared from the LS-MOL-PEG200-MDI system. The values of σ_{10} , σ_y and E increase with LS content. The σ and E of the rigid PU foams increase with increasing LS content.

Fig. 9 shows the change of σ_{10} , σ_y and E with ρ of PU's prepared from the LS-MOL-PEG200-MDI system. The values of σ_{10} , σ_y and E increase markedly with the increasing ρ . This result suggests that the mechanical properties depend on ρ [11, 12].

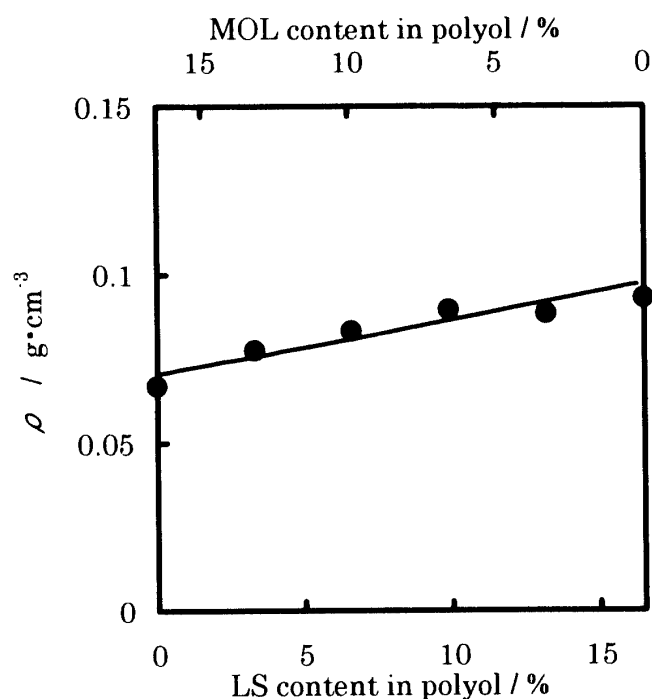


Fig. 7 Change of apparent density (ρ) with LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system

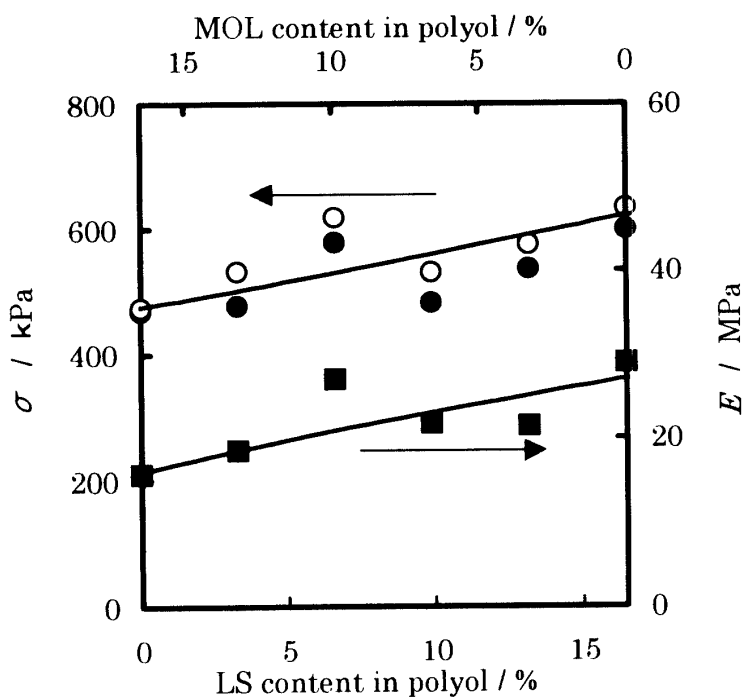


Fig. 8 Change of compression strength at 10% strain (σ_{10}), yielding strength (σ_y) and compression elasticity (E) with LS and MOL contents of PU's prepared from the LS-MOL-PEG200-MDI system

● σ_{10} ○ σ_y ■ E

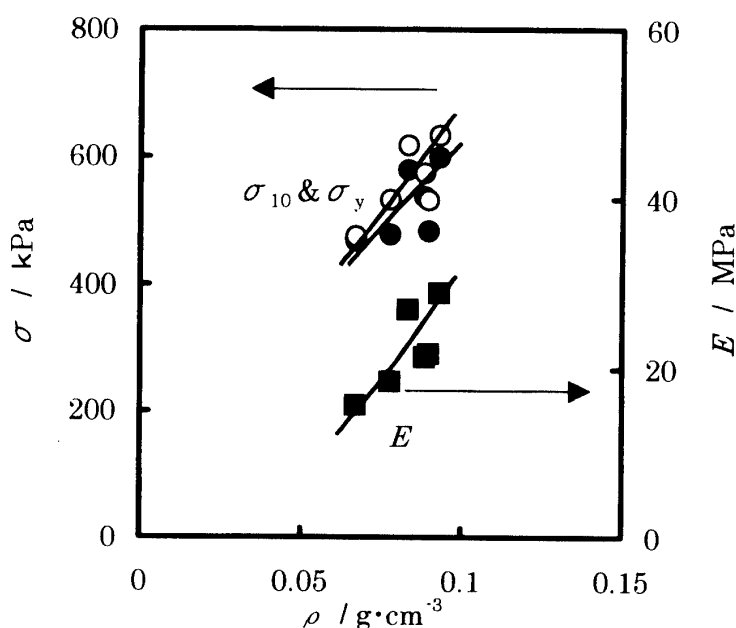


Fig. 9 Change of compression strength at 10% strain (σ_{10}), yielding strength (σ_y) and compression elasticity (E) with ρ of PU's prepared from the LS-MOL-PEG200-MDI system

● σ_{10} ○ σ_y ■ E

4. Conclusions

Rigid polyurethane foams were prepared using LSP consisting of sodium lignosulfonate, polyethylene glycol (PEG) and molasses polyol (MP) consisting of molasses and PEG. Glass transition temperature (T_g) did not show obvious difference with the change of LS and MOL contents. The compression strength (σ) and the compression elasticity (E) increased with increasing apparent density (ρ).

5. References

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