Rigid Type Polyurethane Foams Containing Saccharide and Lignin Structures in The Molecular Chain

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Abstract

Polyurethane (PU) foams with various amounts of lignin and saccharides contained in polyols were prepared by changing the ratios of kraft lignin (KL) to molasses (ML) contents in polyethylene glycol (M_w=ca.200). Thermal and mechanical properties of the above polyurethanes (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous TG and Fourier-transform infrared spectrometry (TG-FTIR) and mechanical measurements. Glass transition temperatures (T_g's) of the PU's decreased from ca.115 °C to ca. 100 °C with increasing KL/ML ratio. However, thermal degradation temperatures (T_d's) increased with increasing KL/ML ratio from ca. 290 °C to ca. 300 °C. The amount of thermal degradation products having characteristic functional groups changed according to the temperature. Compression strength of PU foams increased from ca. 650 kPa to ca. 900 kPa with increasing KL contents.

1. Introduction

Since there are reactive sites in saccharides containing alcoholic hydroxyl groups and in lignin having alcoholic hydroxyl groups and phenolic hydroxyl groups, polyurethanes (PU's) can be derived from saccharides and lignin by the reaction with isocyanates [1-9].

PU foams were prepared using molasses polyol (MLP) containing saccharides and kraft lignin polyol (KLP) containing lignins in this study. Thermal properties of PU foams were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Mechanical properties of PU foams were measured by compression tests.

2. Experimental

2.1 Materials

MLP was obtained from Tropical Technology Center. Co. Ltd. KL was commercially obtained from Westvaco, Co. Ltd. Polyethylene glycol having an average molecular weight of 200 (PEG200) was commercially obtained from Daiichi Kogyo Seiyaku Co. Ltd.

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2.2 Preparation

In order to prepare PU foams, KL was dissolved in PEG200 under heating from 65 to 75°C. As shown in Fig. 1, ML and KL were mixed with PEG200 and this premixtures were obtained by mixing KL/ML with various ratios from 16.5/0 to 0/16.5. The above polyol was mixed with a small amount of silicone surfactant, catalyst and water. This premixture was reacted in a plastic cup with polyphenyl polymethylene polyisocyanate (MDI) under vigorous stirring at room temperature. After foams were obtained in cups, the samples were allowed to stand overnight at room temperature.

In the above processes, the contents of KL and ML were calculated as follows:

KL content (%) in polyol $=[W_{KL}/(W_{KL}+W_{ML}+W_{PEG})] \times 100$

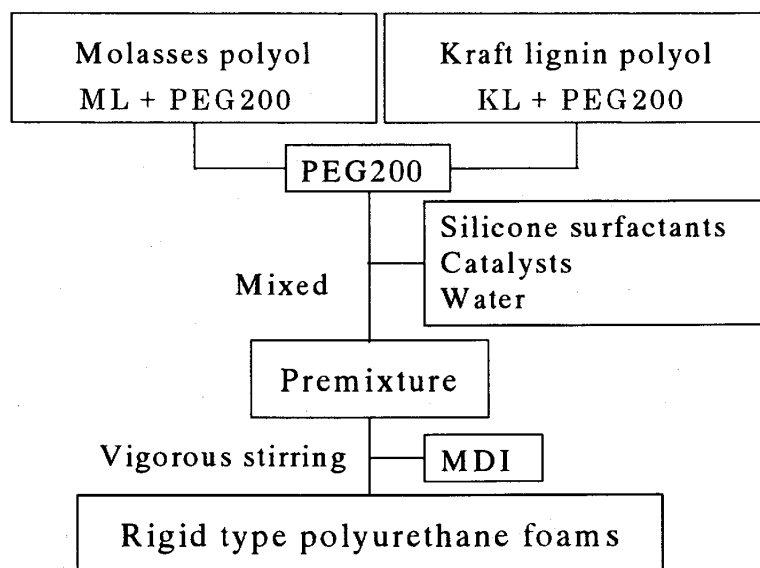ML content (%) in polyol $=[W_{ML}/(W_{ML}+W_{KL}+W_{PEG})] \times 100$

where W_{KL} is weight of KL, W_{ML} is weight of ML and W_{PEG} is weight of PEG. A schematic molecular structure of saccharide- and lignin-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. 5 mg 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. 7 mg 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-Fourier Transform Infrared Spectrometry (TG-FTIR) measurements was 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 [10].

Apparent density (ρ = weight / apparent volume: g/cm^3) was measured using a Mitsutoyo 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 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.

KL/KLP = 33%, ML/MLP = 33%
NCO/OH ratio = 1.4
KL content / % = [KL/(KL+ML+PEG200)] × 100 = 0~16.5%
ML content / % = [ML/(KL+ML+PEG200)] × 100 = 16.5~0%
PEG200 is constantly 83.5%

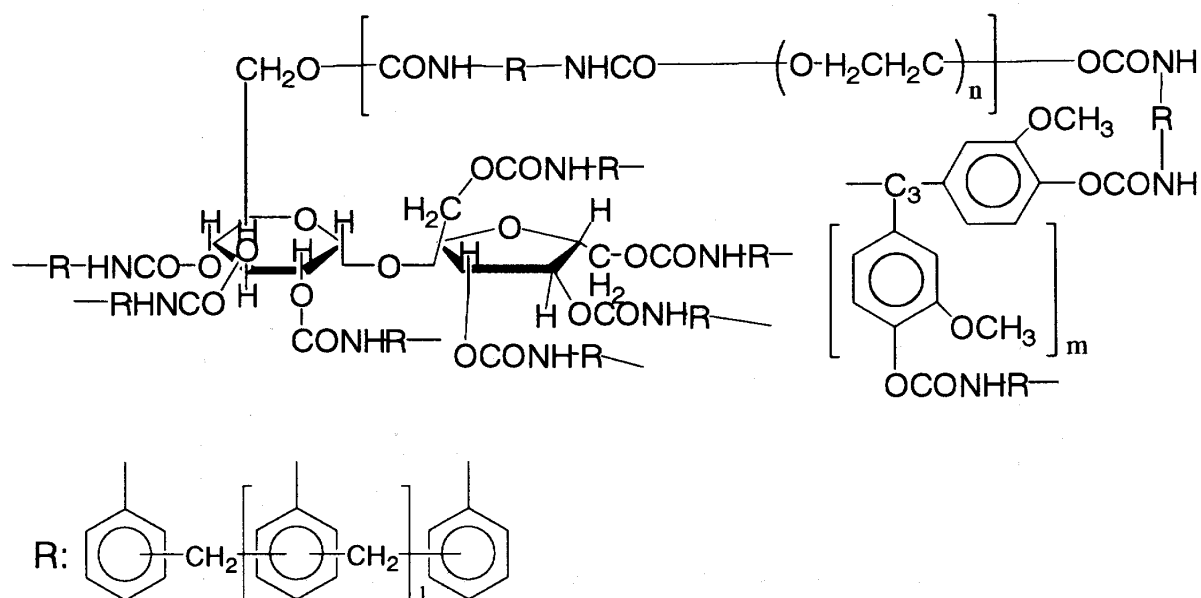Fig. 1 Preparation of KL- and ML-based rigid PU foams

Fig. 2 Schematic molecular structure of saccharide- and lignin-based PU

3. Results and discussion

3.1 DSC

Fig. 3 shows DSC heating curves of PU's with various KL and ML contents. Fig. 4 shows the relationship between glass transition temperature (T_g), heat capacity difference between the glassy and the rubbery states (ΔC_p) and KL contents of PU's prepared from KL-ML-PEG200-MDI system. T_g decreased with increasing KL content. Saccharides, which have rigid pyranose and furanose rings, have reaction sites more than lignin. Accordingly, it is considered that the number of crosslinking points decreased with the increase of KL/ML ratio. The cross-linking density of PU increases with the increase of ML content.

3.2 TG

Fig. 5 shows TG curves of PU's with various KL and ML content. Fig. 6 shows the change of thermal degradation temperature (T_d) and mass residue (MR_{450}) at 450 °C with KL contents of PU's prepared from the KL-ML-PEG200-MDI system. T_d increased with increasing KL content, since lignin is thermally stable compared with saccharides. MR_{450} decreased with increasing KL content, number of hydroxyl groups in each saccharide unit such as pyranose and furanose structure is more than that of lignin. Accordingly, the amount of MDI which reacts with the hydroxyl group increases with increasing amount of molasses. MDI is known to form thermally stable structure at high temperature [12]. Therefore, the increase of MDI seems to cause the increase of MR_{450} with increasing amounts of saccharides in polyol.
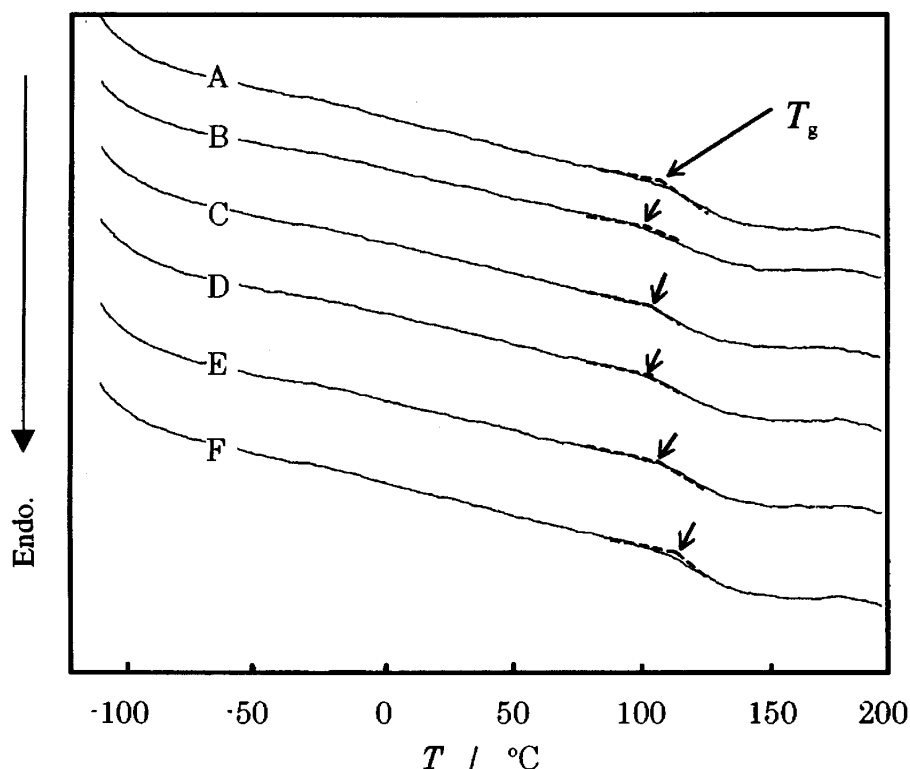

Fig. 3 DSC curves with various KL and ML contents of PU's prepared
from the KL-ML-PEG200-MDI system
KL and ML contents for PU's are as follows.
A = 16.5%KL, 0%ML   B = 13.2%KL, 3.3%ML   C = 9.9%KL, 6.6%ML
D = 6.6%KL, 9.9%ML   E = 3.3%KL, 13.2%ML   F =0%KL, 16.5%ML
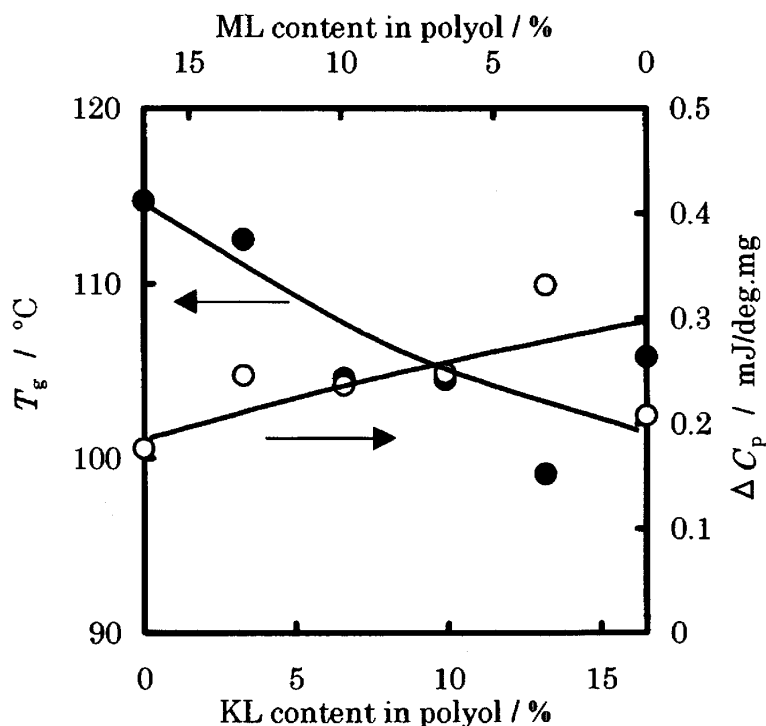
Fig. 4 Change of glass transition temperature (T_g) and heat capacity gap $(\Delta\ C_p)$ between the glassy state and the rubbery state with ML and KL contents of PU's prepared from the KL-ML-PEG200-MDI system
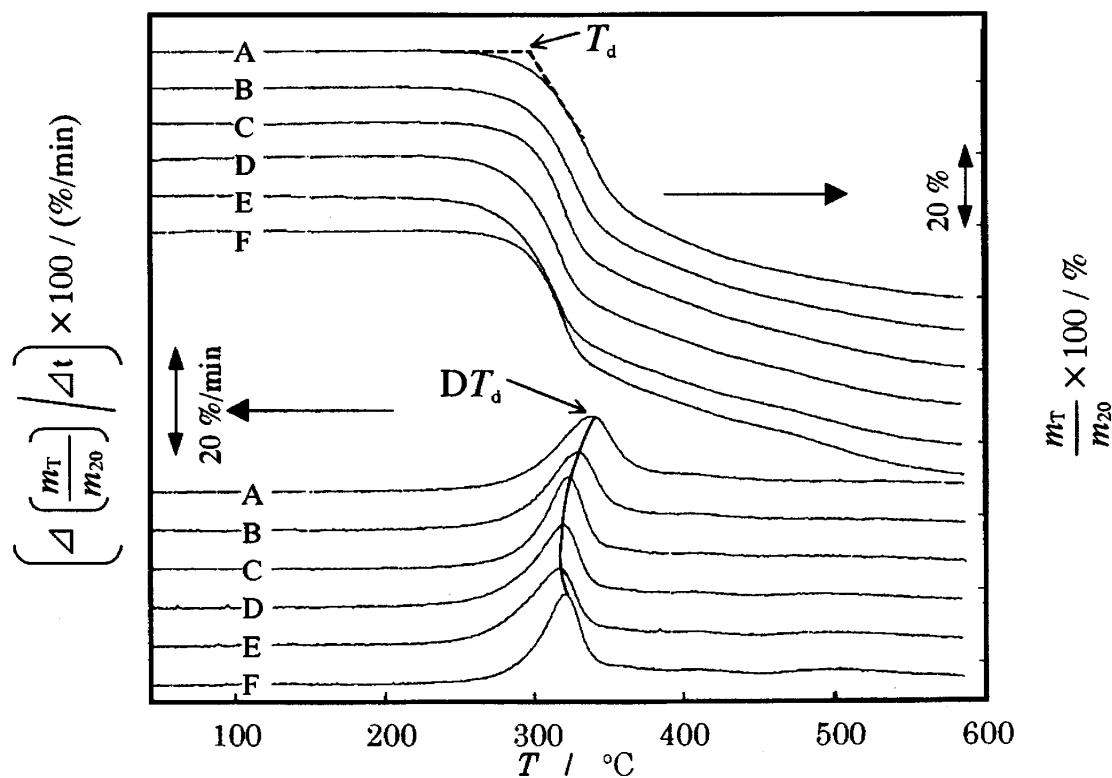
● T_g ○ $\Delta\ C_p$

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

KL and ML contents for PU's are as follows.

A = 16.5%KL, 0%ML   B = 13.2%KL, 3.3%ML   C = 9.9%KL, 6.6%ML
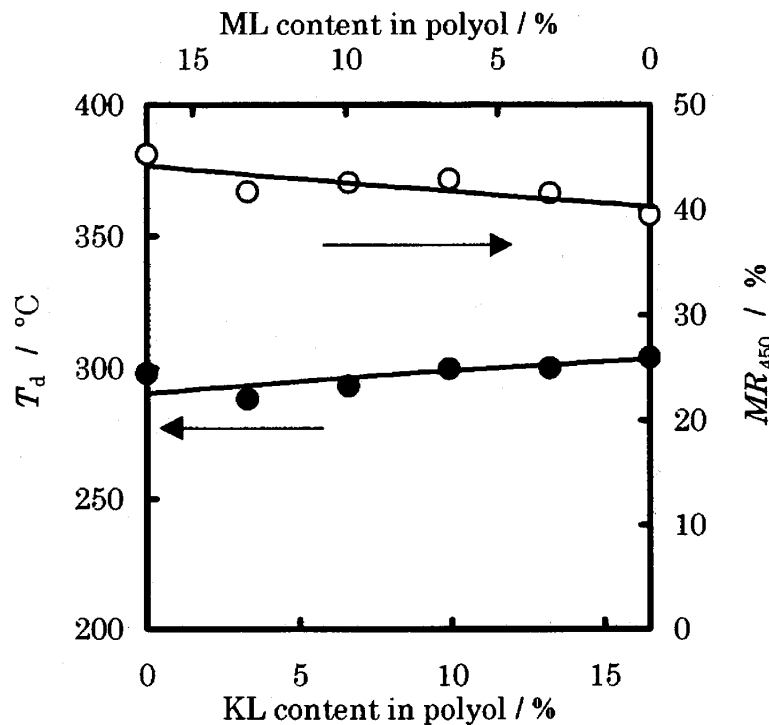D = 6.6%KL, 9.9%ML   E = 3.3%KL, 13.2%ML   F =0%KL, 16.5%ML

Fig. 6 Relationship between thermal degradation temperature (T_d), mass residue at 450°C (MR_{450}), ML and KL contents of PU's prepared from the KL-ML-PEG200-MDI system

● T_d　○ MR_{450}

3.3 Apparent density

Fig. 7 shows the relationship between apparent density (ρ) and KL contents in PU's prepared from the KL-ML-PEG200-MDI system. The ρ of PU foams increases with increasing KL content. The value of ρ changes from ca. 0.08 to ca. 0.11 g/cm^3.

3.4 Compression tests

Fig. 8 shows the relationship between 10% compression strength (σ_{10}), yielding strength (σ_y), compression elasticity (E) and KL contents in PU's prepared from the KL-ML-PEG200-MDI system. The values of σ_{10}, σ_y and E increase with increasing KL content. This result suggest that the mechanical properties depend on the apparent density [11, 12]. Actually, the values of σ_{10}, σ_y and E increase with increasing ρ, as shown in Fig. 9.
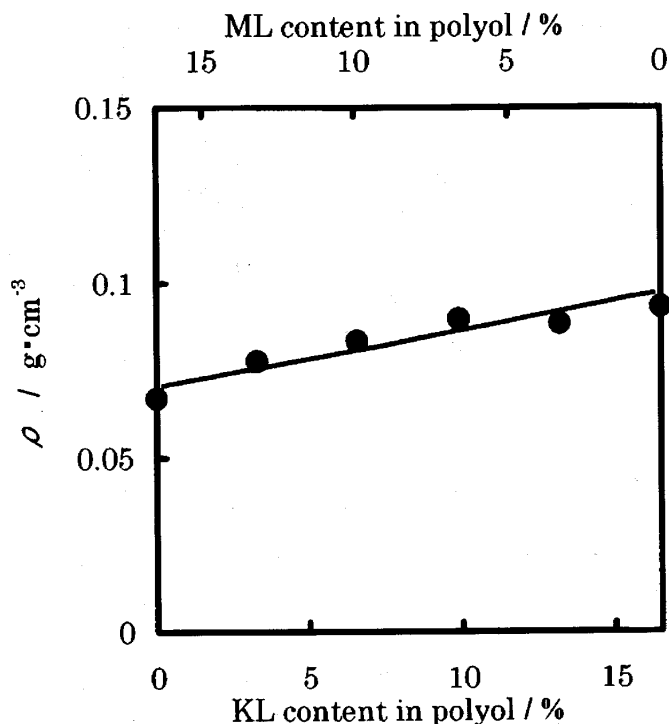
ML content in polyol / %

Fig. 7 Change of apparent density (ρ) with KL and ML contents of PU's prepared from the KL-ML-PEG200-MDI system
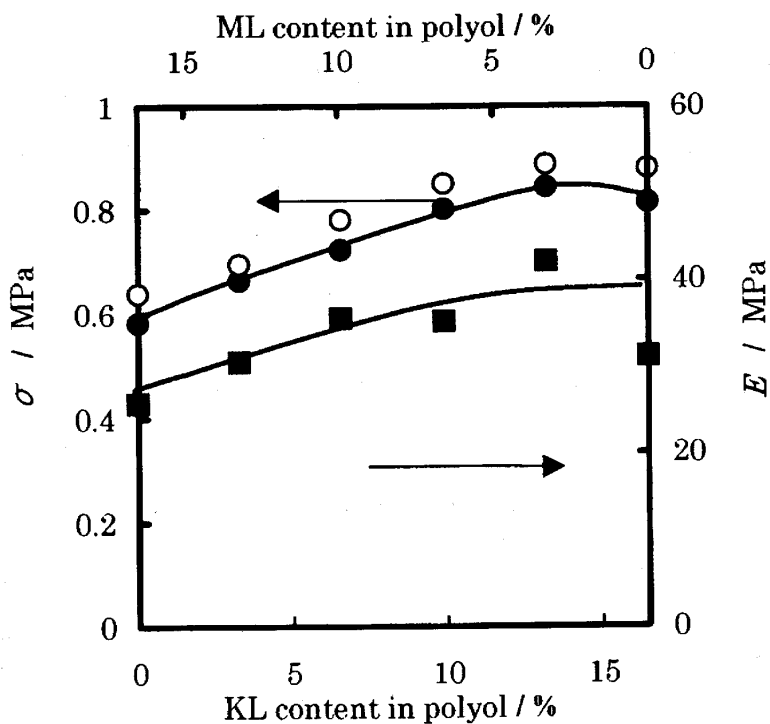
ML content in polyol / %

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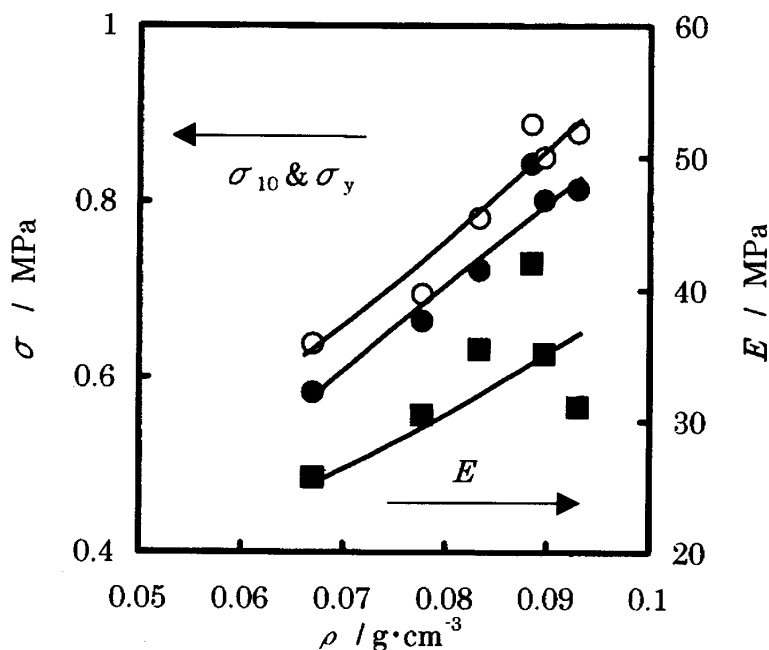
● σ_{10} ○ σ_y ■ E

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 KL-ML-PEG200-MDI system

● σ_{10} ○ σ_y ■ E

4. Conclusions

Rigid polyurethane foams were prepared using KLP consisting of kraft, polyethylene
glycol (PEG) and molasses polyol (MLP) consisting of molasses and PEG. Glass transition
temperature (T_g) did not show obvious difference with the change of KL and ML contents.
The compression strength (σ) and the compression elasticity (E) increase with increasing
KL content and with increasing apparent density (ρ).

5. References

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