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Soft-type polyurethane foams derived from molasses

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Abstract Molasses (ML)-based soft-type polyurethane (PU) foams were successfully prepared by controlling evolved heat during chemical reaction. Two kinds of isocyanate, poly(phenylene methylene) polyisocyanate (MDI) and tolylene diisocyanate (TDI), and polypropylene glycol with a long molecular chain length were utilized to control the chemical reaction. The hydroxyl group in ML was used as the reaction site and soft-type PU foams were synthesized at isocyanate (NCO)/hydroxyl group (OH) ratios of 1.05. Mechanical properties of the above foams were controlled by changing the mixing ratio of MDI and TDI. Pore size and distribution were measured by scanning electron microscopy. With increasing thickness of cell wall, compression strength and modulus increased. Thermal properties of PU foams were investigated by differential scanning calorimetry, thermogravimetry, and thermal conductivity measurements. Two-step glass transition temperatures were observed at around ca. −55 and 80 °C, regardless of kind of isocyanate. The low temperature side glass transition is attributed to the molecular motion of long oxyethylene chains and the high temperature side transition is caused by rigid components including saccharide components. Thermal decomposition of PU foams started from ca. 270 °C. Thermal conductivity of soft-type PU was observed in a range from 0.034 to 0.035 J s^{-1} m^{-1} K^{-1}.

Introduction

Plant residues obtained from agriculture related industries, such as the sugar, palm oil, and food industries should be utilized in order to reduce environmental loading. At the same time, it is considered that a large amount of waste has potential as future resources if a new conversion method for industrial products is established. One of the major residual biomasses whose utilization has not been fully exploited is ML. Molasses is obtained as a by-product of the sugar industry which is one of the major industries involving agricultural crops. In the purification process of sucrose, ML is obtained as a residual component. Composition of ML is, in general, a mixture of sucrose, glucose, fructose, ash, and water, etc., although the amount of each component depends on the purification process [1]. Although ML has been used as a resource for alcohol fermentation, a large amount of residual ML is not utilized in new industrial applications due to lack of suitable methods.

Among various kinds of functionally tailored materials, polyurethane (PU) is one of the most suitable polymers for effective control of its characteristics. Recently, PU's having specific functionalities, such as scaffolds for tissue engineering [2], micro encapsulation [3, 4], and biodegradable civil construction material [5] have been developed. From plant components, PU's in various forms having a wide range of molecular properties have been prepared [1, 5–16]. In order to develop biocompatible materials using residual plant materials, fundamental data on physical properties is required. When practical application is taken into consideration, mechanical properties are major factors in the design of new materials from biowastes in order to convert biocompatible materials to similar kinds of materials prepared from petroleum.

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When saccharides are subjected to chemical reaction for the development of new polymeric materials, the major problem is their unstable nature in a temperature range of chemical reaction. Mono- and disaccharides composed of ML are decomposed easily at around 200 °C [17]. On this account, saccharide components decompose in a short time due to evolved heat of the PU foaming reaction which takes place in 1–2 min.

In our previous studies, we found that ML is dissolved in polyethylene glycol (PEG) with different molecular mass. This ML–PEG solution is designated as ML polyol (MLP) and has been used for PU preparation. MLP is a useful component for the control of physical properties of PU foams by mixing with other polyols in order to prepare foams, sheets and composites whose matrix consists of PU [10].

It is also noted that PU's derived from MLP mixture showed biodegradability, and that decomposition smoothly proceeds in soil [18]. Although semi-rigid type PU with compression strength of ca. 80 kPa has been prepared from MLP, it was difficult to prepare soft-type PU foams having suitable practical performance using only MLP. It is thought that chemical reaction was not successfully controlled due to the fact that heat was evolved during the reaction in a short period. In order to overcome the above problem and control the chemical reaction, we investigated possible reaction conditions. In this study, preparation conditions to obtain soft-type PU foams derived from ML polyol are examined. In addition, mechanical and thermal properties of soft-type PU foams derived from ML are investigated.

Experimental

Materials

Molasses was obtained from Tropical Technology Center Co. Okinawa, Japan; The above ML consists of glucose (8.5%), fructose (9.2%), sucrose (32.5), other saccharides (2.3%), ash (9.5%), and water (20.5%). Diethylene glycol (DEG) was obtained from Godo Co. Tokyo, Japan. Polyethylene glycol (PEG) #PEG200 was obtained from Lion Co. Tokyo, Japan. Polypropylene glycol (PPG) Adeka Polyether P-3000 was obtained from Adeka Co. Tokyo, Japan. Poly(phenylene methylene) polyisocyanate (MDI) was obtained from BASF INOAC Polyurethane Co. Tokyo, Japan. Tolylene diisocyanate (TDI), which is a mixture of 2,4-TDI (80%) and 2,6-TDI (20%) isomers, was obtained from Mitsui Chemical Inc. Tokyo, Japan. Silicone type surfactant SH-192 was obtained from Dow Corning Toray Co., Tokyo, Japan. Di-*n*-butyltin dilaurate (DBTDL) from Merck KGaA, Darmstadt, Germany, and Kaolizar No. 8 from Kao Co. Tokyo, Japan were used as catalysts.

Sample preparation

Molasses was dehydrated, and then one portion of ML was solved in 2 portions of PEG 200 [19, 20]. The above polyol containing 33% ML was designated as MLP. The number of hydroxyl groups in the MLP was evaluated according to the methods shown in the Japanese Industrial Standard (JIS) K 1557. As shown in the flow chart (Fig. 1), polyol was mixed by stirring 30% MLP, 65% PPG, and 5% DEG at room temperature (25 °C). Two kinds of isocyanate were prepared with the following mixing ratios; MDI/TDI = 100/0, 90/10, 80/20, 70/60, and 60/40, respectively. Polyols, surfactants, and catalysts were homogeneously mixed under stirring, and then the mixture of MDI/TDI was added under vigorous stirring. A trace amount of water was used as a foaming agent. NCO/OH ratio was maintained at 1.05 throughout this experiment. Obtained PU foams were left at room temperature in order to complete the reaction overnight and then used for further investigation.

Scanning electron microscopy

Morphological observation was carried out using a JEOL scanning electron microscope JSM-6100. The surface of the sample was coated with gold using a JEOL JFC-1100E. The cross-section of each pore was calculated assuming ellipse. A cross-section of 50–60 pores for each sample was measured and average value and standard deviation calculated.

Apparent density measurements

Apparent density [ρ = mass (m)/apparent volume (V), g/cm^3] was measured for samples of 40 (length) × 40 (width) × 30 (thickness) mm using a Mitsutoyo ABS digital solar caliper and an electric balance (Shimadzu

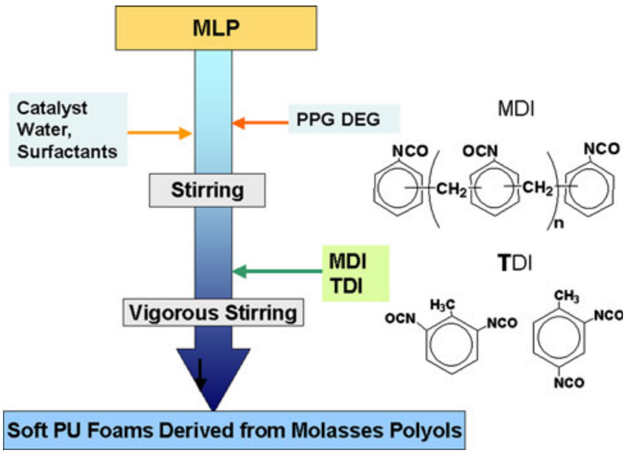


Fig. 1 Flow chart of sample preparation. *MLP* ML polyol, *PPG* polypropylene glycol, *DEG* diethylene glycol, *MDI* poly(phenyl ethylene) polyisocyanate, *TDI* tolylene diisocyanate

balance EB-4300DVW). The average values of three samples, whose size was measured at three different spots, were used for the calculation of apparent volume (*V*). The mass (*M*) of each sample was weighed using a Shimadzu balance.

Mechanical property measurements

Compression strength was measured using a Shimadzu Autograph AG-IS at 25 °C. Sample size was 40 (length) × 40 (width) × 30 (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) at the 25% strain was calculated according to JIS JISK6400 and JISK7220 Compression modulus (E, Pa) was calculated using the initial stage of stress–strain curve based on JISK7220. Three specimens were tested and the average value calculated.

Differential scanning calorimetry (DSC)

A Seiko DSC 220C was used to measure glass transition. Scanning rate was 10 °C min^{-1} and N_2 gas flow rate 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 (first heating), cooled from 200 to −50 °C and heated again from −50 to 200 °C (second heating). The second heating curves were mainly used for analysis in order to erase thermal history. Glass transition temperature (T_g) was determined as reported previously [21]. Reproducibility of T_g values measured by DSC is found elsewhere [22].

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}. When decomposition was observed in two stages, decomposition temperature (T_d) was designated as T_{d1} and T_{d2} from low to high temperature. Derivative thermogravimetric (DTG) curves were obtained by differential calculation of TG curves. The peak temperature of DTG curves was designated as DT_{d1} and DT_{d2} from low to high temperature. Mass residues (MR) were measured at 450, 500, and 550 °C. The mass of dry sample at 20 °C was used as the original amount in TG experiments. Reproducibility of T_d values measured by TG is found elsewhere [23].

Thermal conductivity measurements

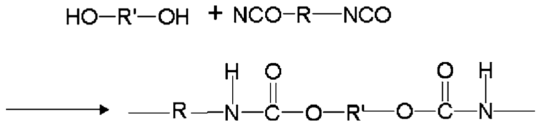
Anacon Detection Technology, a thermal conductivity analyzer, TCA Point 2 was used. The size of sample was 200 (length) × 200 (width) × 30 (height) mm. The temperature of hot plate was 37.7 °C and that of cold plate 10 °C. Polystyrene foam with thermal conductivity of 0.0262 J s^{-1} m^{-1} K^{-1} was used as a standard.

Results and discussion

Sample preparation and morphology

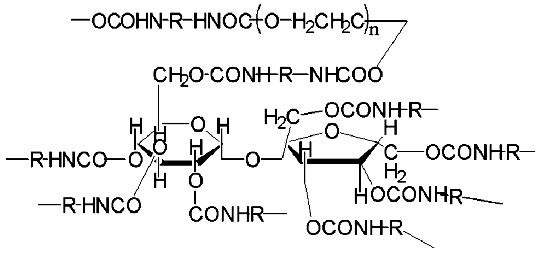
Polyurethanes were formed through polyaddition by reacting MDI and TDI containing isocyanate functional groups (R in Scheme 1) with glucose, fructose, sucrose, PEG, and PPG containing more than two hydroxyl groups (R′ in Scheme 1) in the presence of a catalyst. In this study, it is notable that the hydroxyl group of glucose, fructose, and sucrose was used as the reaction site. The schematic structure of PU is shown in Scheme 2.

It is known that thermal decomposition of mono- and disaccharides consisting of ML starts at around 200 °C [17]. On this account, saccharide components in MLP decompose in a short time due to the evolved heat of PU foaming reaction which ordinarily takes place in 1–2 min. When reaction time was less than 30 s, homogeneous PU could not be prepared and ML started the decomposition which causes carbonization that occurred in PU foams. Accordingly, it is important to control the reaction conditions to diffuse evolved reaction heat. In this study, in order to decrease reaction rate and increase reaction time, two kinds of isocyanate, MDI and TDI, were mixed and suitable conditions were investigated by changing the MDI/TDI mixing ratio. From the chemical structure shown in Fig. 1, TDI accelerates reaction time. MDI works as a rigid component and retards the reaction process. The mixing ratio was varied from 100/0 to 60/40 and it was found that



$$\mathrm{HO{-}R'{-}OH} + \mathrm{NCO{-}R{-}NCO} \longrightarrow \mathrm{{-}R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}}$$

Scheme 1 Reaction scheme. *R* MDI or TDI, *R′* glucose, fructose, sucrose, PEG, or PPG



Scheme 2 Schematic structure of PU derived from ML polyol

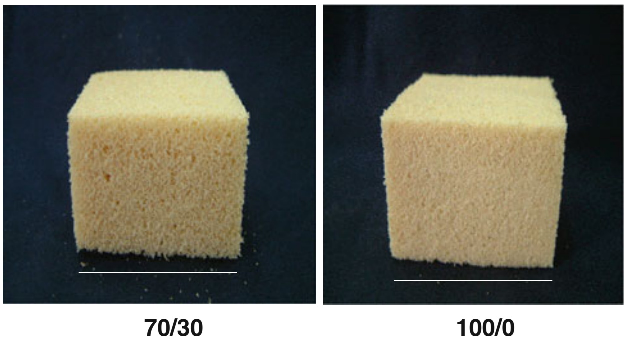


Fig. 2 Photographs of representative PU foams derived from ML. *Numerals* in the figure show MDI/TDI ratio. *Scale bar* indicates 40 mm

homogeneous and neat PU foams could be obtained in the above range of mixing ratio. When TDI content exceeded 40%, the reaction was not well controlled. When foaming was carried out under the conditions described in the experimental section, the reaction was completed in around 90 s.

Figure 2 shows photographs of PU foams derived from ML. The color of PU foams is light yellow and PU with a slightly sweet fragrance has a smooth, soft surface. Figure 3 shows representative scanning electron micrographs of PU foams prepared by MDI/TDI mixtures at 80/20 and 90/10. Ellipse pores with thin cell walls are observed. It is seen that pore size and size distribution increase with increasing MDI content. Moreover, cell wall becomes thicker when MDI content increases. Morphological architecture of foams affects directly mechanical properties as described in the latter section.

Figure 4a shows the relationship between the average values of cross-section of pore (mm^2) and MDI content (%) in MDI/TDI mixtures. Although data is scattered to a certain extent, it is clearly seen that the cross-section of pores increases with increasing MDI content. Figure 4b shows relationship between apparent density (ρ) (g cm^{-3}) and MDI content (%) in MDI/TDI mixtures. The values of ρ are found in a range from 0.036 to 0.042 g cm^{-3}, regardless of MDI content, i.e., the amount of vacancy of PU foams is almost constant. From the results, it is quite reasonable to consider that the cell wall becomes thicker with increasing MDI. This fact is also confirmed from mechanical properties shown in the next section.

Mechanical properties

Figure 5a shows relationship between compression strength at 25% strain (σ_{25}) and MDI content (%) in MDI/TDI mixtures. Compression strength is in a range from 1 to 4 kPa. Figure 5b shows compression modulus (E) calculated from the initial gradient of compression stress versus strain curves. The value of E is in a range from 5 to 20 ka. Both σ_{10} and E values increase with increasing MDI content. As described in "Sample preparation and morphology" section, the fact that the thickness of cell wall increases when MDI content in isocyanate increases suggests that mechanical properties can be controlled by changing MDI/TDI mixing ratio. The above results obtained by mechanical measurements indicate that the PU foams derived from ML can be designed for practical purposes by controlling reaction conditions.

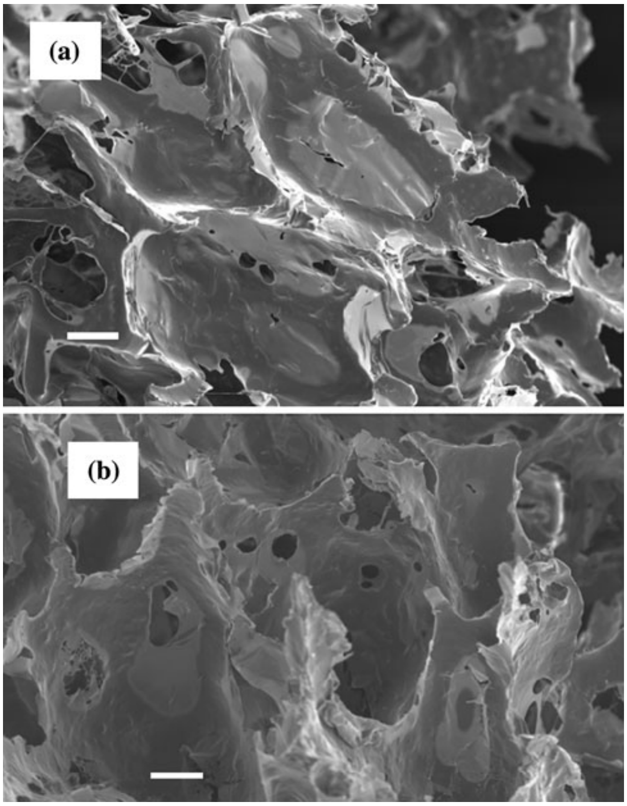


Fig. 3 Scanning micrographs of PU foams derived from ML polyol. MDI/TDI ratio: **a** 80/20, **b** 90/10. *Scale bar* indicates 100 μm

Thermal properties

Figure 6 shows representative TG and DTG curves of PU foams derived from ML prepared using MDI/TDI mixtures at NCO/OH ratio = 1.05. The mass of PU foams decreases in two steps, as shown in the TG and DTG curves of Fig. 6. The low side decomposition (T_{d1}) is in a temperature range from 270 to 280 °C. The high temperature side decomposition (T_{d2}) is observed in a temperature range from 370 to 375 °C regardless of MDI content. DTG curves in Fig. 6 indicate that the peak height of T_{d2} is higher than that of DT_{d1}. Figure 7a shows the relationship between T_{d1}, T_{d2}, and MDI content and Figure 7b shows mass residue at 450, 500, and 550 °C and MDI content.

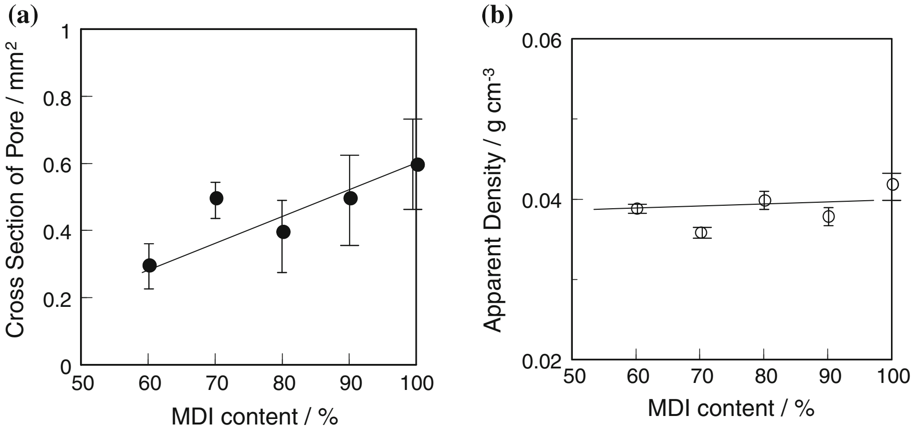


Fig. 4 **a** Relationship between cross-section of pore of PU foam and MDI content. **b** Relationship between apparent density and MDI content

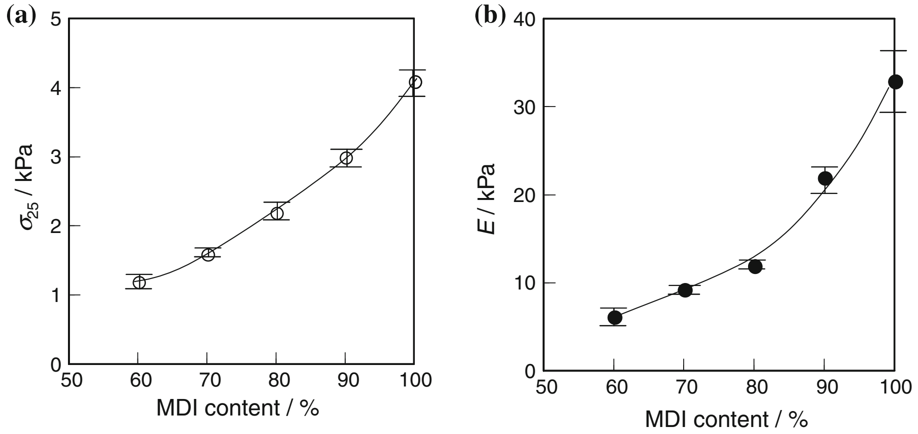


Fig. 5 **a** Relationship between compression strength at 25% strain (σ_{25}) and MDI content (%) in MDI/TDI mixtures. **b** Relationship between compression modulus (E) and MDI content (%) in MDI/TDI mixtures

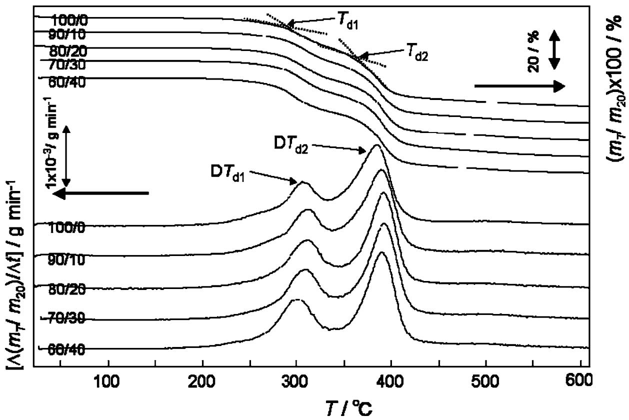


Fig. 6 TG and DTG curves of PU foams derived from ML prepared using MDI/TDI mixtures at NCO/OH ratio = 1.05. Heating rate = 20 °C min^{-1}

Thermal decomposition behavior of mono- and disaccharides has been investigated mainly by TG and TG-Fourier transformed infrared spectrometry (FT–IR) [17]. Gas evolution of monosaccharide and oligosaccharides in dry state starts immediately after melting at around 200 °C. It is appropriate that T_{d1} and the peak temperature of derivative curves are observed at the same temperature regardless of MD/TDI ratio, since the amount of saccharide component is the same. The value of T_{d1} is higher than that of pure mono- and disaccharides and suggests that the hydroxyl group of saccharides is blocked. Accordingly, the first step thermal decomposition of PU foams derived from ML is attributed to decomposition of saccharide component of PU. At the same time, it is known that dissociation of urethane linkage occurs at the temperature range where the first step decomposition is observed. The second step thermal decomposition is attributed to the decomposition of oxyethylene group and also isocyanurate reaction, which is caused by the ring formation of (NCO–R–NCO) trimers. The temperature range of the decomposition can be calculated from peak width of DTG curves. The peak width of the first step decomposition maintained a constant value regardless of MDI content. In contrast, that of the second step decomposition increased with increasing MDI content. The above facts also suggest that the 2nd step decomposition is attributed to isocyanurate reaction. As shown in Fig. 7b, the mass residue increases slightly with increasing MDI content. These facts also indicate that MDI has a

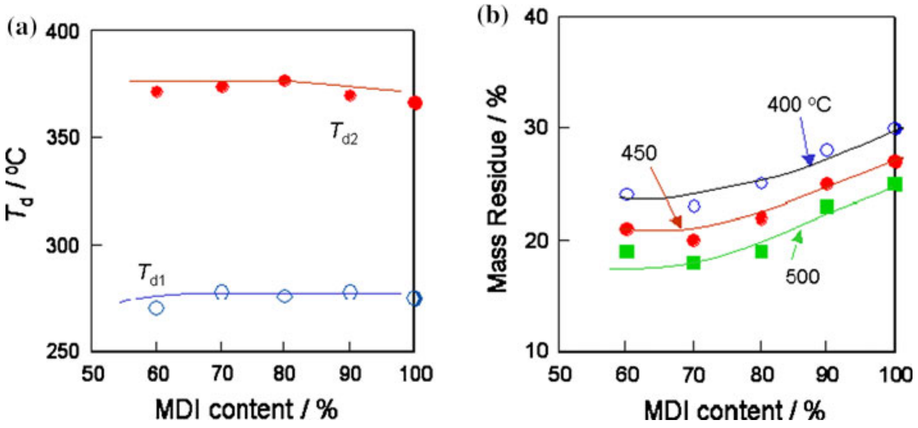


Fig. 7 **a** Relationships between T_d and MDI content of PU foams derived from ML polyol. **b** Relationships between mass residue at 450, 500, and 550 °C and MDI content of PU foams derived from ML polyol

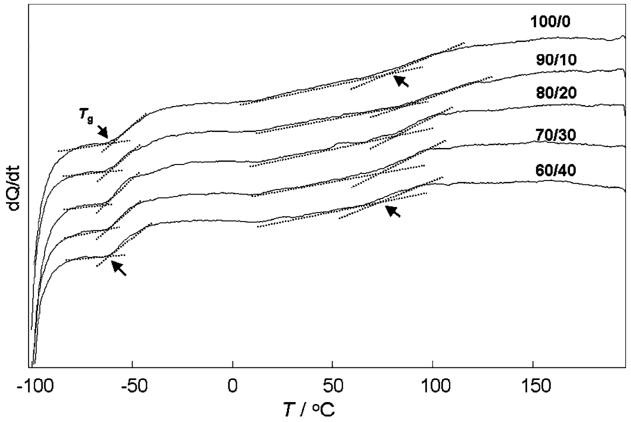


Fig. 8 Stacked DSC heating curves of PU foams derived from ML polyol. *Numerals* show MDI/TDI ratio. *Arrows* indicate glass transition temperature

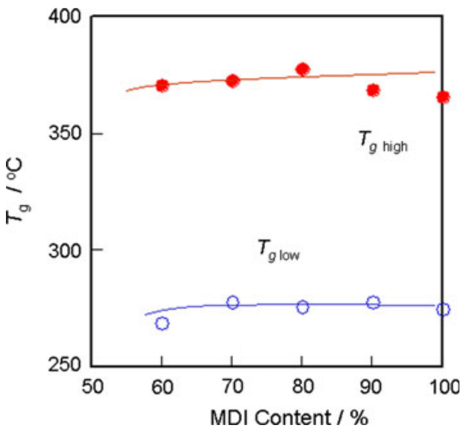


Fig. 9 Relationships between glass transition temperatures (T_{glow}, T_{ghigh}) of PU foams derived from ML polyol and MDI content

larger mass than TDI which suggests that mass of trimers generated by isocyanurate reaction is larger than that of TDI.

Figure 8 shows representative DSC heating curves of PU foams derived from ML. Two-step glass transitions are clearly observed as heat capacity difference of the baseline at around −55 °C (T_{glow}) and 75–85 °C (T_{ghigh}). Figure 9 shows relationships between T_g and MDI content in MDI/TDI blended mixture. T_{glow} was observed at around −55 °C, regardless of MDI content. Heat capacity difference at T_{glow} (ΔC_p) was 0.25–0.27 J g^{-1} K^{-1}, suggesting that a large number of molecular chains are associated with the relaxation when ΔC_p values of amorphous polymers at around −50 °C are 0.3 J g^{-1} K^{-1}. T_{glow} is attributable to the molecular motion of long oxyethylene chain of PPG 3000 which was introduced as a soft component in this PU foam. In contrast to ΔC_p values at T_{glow}, ΔC_p values at T_{ghigh} were in a range from 0.12 to 0.22 J g^{-1} K^{-1}. As reported previously, ΔC_p of amorphous linear polymers decreases with increasing T_g [24]. Accordingly, it is appropriate to consider that molecular enhancement observed at 75–85 °C is depressed by inter- and intramolecular cross-linking, i.e., the molecular motion is strongly restricted by urethane cross-linking, since the value is smaller than that of ordinary amorphous polymers. From DSC data, it can be said that the rigid glucopyranose rings in saccharides contribute to the main chain motion of PU.

In order to utilize PU foams for insulation materials, it is necessary to know the thermal conductivity of the sample. Figure 10 shows the relationship between thermal conductivity and MDI content. The temperature difference between the two plates that sandwiched the PU foam was 27.7 °C. The time required to reach equilibration was ca. 20 min. With increasing MDI content, thermal conductivity slightly decreased and reached a constant value of 0.035 J s^{-1} m^{-1} K^{-1}. When the above results were compared with commercial grade polystyrene foams, the value was almost the same. The data suggests that the thermal conductivity of PU foams derived from ML is similar or better than that of foams derived from petroleum. Accordingly, PU foams prepared in this study can be used as alternative materials to foams derived from petroleum.

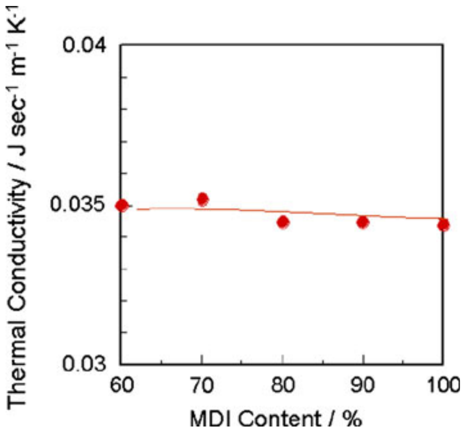


Fig. 10 Relationship between thermal conductivity and MDI content. Standard deviation of thermal conductivity is in a range from 1×10^{-4} to 4×10^{-4}

Conclusions

Molasses-based soft-type PU foams were prepared using two kinds of isocyanates, MDI and TDI, and polypropylene glycol with long molecular chain. The hydroxyl group in ML is used as the reaction site and soft-type PU foams were obtained at isocyanate (NCO)/hydroxyl group (OH) ratio 1.05. Thermal properties of PU foams were investigated by DSC and TG and thermal conductivity measurement. Two-step glass transition temperatures were observed regardless of kind of isocyanate. The low temperature side T_g (T_{glow}) was observed at −55 °C which is attributable to the molecular motion of long alkyl chain. The high temperature side T_g (T_{ghigh}) observed in a temperature range from 75 to 85 °C is caused by the molecular motion of ML polyol cross-linked via isocyanate. Thermal decomposition temperature (T_d) was observed in two steps, at ca. 270 and 380 °C. The low temperature side decomposition is attributed to the decomposition of ML and the high temperature side to cleavage of phenyl groups from isocyanate. Thermal conductivity of PU foams was in a range from 0.034 to 0.035 J s^{-1} m^{-1} K^{-1}. The above characteristic values of PU foams derived from ML are similar to or better than those derived from petroleum.

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