Production of a High-Functionality RBD Palm Kernel Oil-Based Polyester Polyol

K. H. BADRI, S. H. AHMAD, S. ZAKARIA

Material Science Programme, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor

ABSTRACT: A diol-based refined, bleached, and deodorized (RBD) palm kernel oil polyol was prepared. It was found that the polyurethane foam produced only gives a good compressive strength property at a 45 kg/m^3 molded density. The combination of sorbitol into the polyol system resulted in a better dimensional stability and improved thermal conductivity as well as enhanced compressive strength. These were obtained by increasing the functionality of the polyol (functionality of 4.5) through introduction of a high molecular weight and branching polyhidric compound. Direct polycondensation and transesterification methods were used for the syntheses. The hydroxyl value, TLC, and FTIR were used to study the completion of the reaction. A comparative study of the mechanical properties and morphological behavior was carried out with a diol-based polyol. From the water-blown molded foam (zero ODP) with a density of about 44.2 kg/m^3 and a closed-cell content of 93%, a compressive strength of 222 kPa and a dimensional stability of 0.09, 0.10, and 0.12% at the length, width, and thickness of the foam, respectively, conditioned at $-15°C$ for 24 h, were obtained. The thermal conductivity improved to an initial value of 0.00198 W/mK, tested at 0°C. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 384–389, 2001

Key words: high-functionality polyester; sorbitol; dimensional stability; compressive strength; zero ODP

INTRODUCTION

Polyurethane is a versatile class of polymers due mainly to their rapid and easy processing and to some excellent chemical and physical properties which can be tailored to suit a wide range of applications including elastomers, fibers, foams, surface coatings, and adhesive products. The mechanical properties and morphological structure of polyurethane depend mainly on the polyol structure, molar mass, and its functionality and, to a lesser extent, on the nature of the polyisocya-nates. The stoichiometric ratios of isocyanate-to-hydroxyl groups, the amount of the chain extender used, and the processing method also have significant effects on the polyurethane properties.

Higher functionality polyols, although derived from non-oil-based polyhydric compounds such as sorbitol and sucrose, tend to form stiff and brittle polyurethane and are used mainly in rigid foam production.[1] In the first phase, refined, bleached, and deodorized (RBD) palm kernel oil (PKO) was reacted with glycol to obtain a diol-based RBD palm kernel oil-based polyol (DBPKO).[2,3] However, the dimensional stability and thermal conductivity at lower density (lower than 38 kg/m^3 of the core density) is not suitable for an insulator in the refrigeration application. Gast et al.,[4] Khoe et

al.,[5] Motawie et al.[6] also synthesized some amides for coating purposes. The present study, however, varied the functionality of the RBD PKO-based polyol with a long chain or higher hydroxyl value compounds by using sorbitol powder (functionality of 8.0).[1] This is the rule of thumb in synthesizing high functionality polyol based on the following equation[7]:

Functionality

$$= \frac{\begin{array}{c}\text{hydroxyl value of the polyol}\\ \times \text{ molecular weight of the polyol}\end{array}}{56,100} \quad (1)$$

The higher the hydroxyl value, the higher the functionality is and the better the mechanical properties required for a rigid foam would be. The decrease in the equivalent weight of polyol (increase in the molecular weight) increases the rigidity of the polyurethane and its compressive strength, modulus, thermal stability, and dimensional stability.[8]

In the present study, the PKO was derivatized using the previous new development in polyurethane technology by combining it with alkanolamine under a basic condition. The methods used in the process involved polycondensation and polyesterification,[9] where a low reaction temperature and a short reaction time as well as a high percentage of yield are offered.[10]

EXPERIMENTAL

Materials

RBD PKO (Lee Oilmill, Klang, Malaysia) was used without further purification. Its characteristic values such as the hydroxyl value, acid number, and typical properties such as viscosity, specific gravity, and water content were noted for the consistency of the results. Diethanolamine (DEA), potassium octanoate (P46), ethylene glycol (MEG), and the sorbitol powder were of industrial grades. The crude isocyanate was obtained from Cosmopolyurethane (Port Klang, Malaysia) with a NCO content of 31%.

Sorbitol-based RBD PKO Polyol (SBPKO) Synthesis

To prepare the polyesteramides, the first step involved forming an anhydrous sorbitol mixture (liquid sorbitan mixture) from sorbitol powder and DEA with a mixing ratio of 70 : 30. DEA is used as a polymerization agent and as a catalyst for urethane linkage formation. The PKO together with the anhydrous sorbitol mixture and P46 as the catalyst as well as MEG as the emulsifier were reacted at ratio of 75 : 25 to obtain the highest possible functionality value without affecting the flowability of the whole polyurethane system later. The liquid sorbitan mixture used was 10% in weight excess with respect to the fatty acid in PKO to compensate for the losses caused by evaporation at high temperature.[9] The reaction was carried out in laboratory scale. The mixture was continuously stirred in a 2-L glass reactor and was maintained at three different temperatures: 185 ± 5, 195 ± 5, and $205 \pm 5°C$ for 15–30 min, with a nitrogen flow of 40 mL min^{-1} L^{-1} of the mixture, into the system throughout the process. The heating rate was set to 2.5°C/min. The reflux flask was connected to a condenser and a vacuum pump to withdraw the water and the excess of glycol from the system. The progress of the reaction was monitored by sampling at intervals. The samples were then analyzed. At the end of the reaction, the polyol produced was kept in a sealed cap glass container for analysis.

Analysis of the Polyol

FTIR analyses were carried out on a Perkin–Elmer Paragon 500 spectrometer. The samples collected during the intervals were scanned between 4000 and 400 cm^{-1} wavenumbers. A drop of each sample was spread into a thin layer on a ZnSe plate. Two selected peaks (designated as peaks A and B) were used to monitor the progress of the reaction using the ratio of transmittance readings for both peaks. The molecular weight was determined by the Ostwald method of viscometric determination[11–14] using methanol as the solvent at 25°C. This method utilized both the Huggins and Kraemer equations and determination of the molecular weight was by the Mark–Houwink equation.[15]

The standard method, ASTM D4274-88 (Standard Test Method for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyol), was used to determine the hydroxyl values of the polyol to verify the FTIR peak ratio method for completion of the derivatization reaction. It would also be very important for the calculation of the isocyanate index in determining the amount of isocyanate required to start the foaming reaction and also for the determination of the functionality of the polyol.
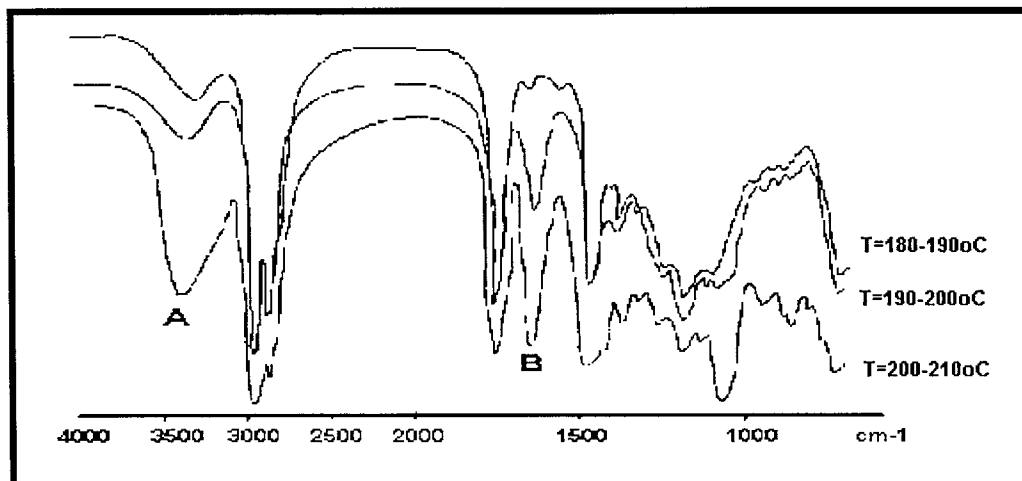
Figure 1 Differences in FTIR spectrum at peaks A and B at various reaction temperatures at $t = 65$ min.

The water content of the polyol was determined using a Karl Fischer Titrator 702, while the viscosity of the polyol was determined using a Brookfield digital viscometer. The pH of the polyol was also determined using a universal pH paper. The cloud point was determined by immersing the polyol in a beaker into an ice bath and stirring vigorously until it reached the cloudy state, where the temperature was noted.

Polyurethane Synthesis

Crude MDI (Cosmonate M-200, Cosmopolyurethane, Port Klang, Malaysia), 120 g, was poured into 100 g of the mixture of the SBPKO (sample taken from the polyol production that had opti-

mum parameters) with additives (surfactant, catalyst, and water) and were mixed thoroughly using a standard propeller with a speed of 3500 rpm for 10 s. The mixture was then poured into a waxed mold, covered, and screwed tight. The foam was demolded after 10 min. It was then conditioned for 16 h at $23 \pm 2°C$ before the characterization process of the polyurethane foam.

Foam Characterization

Foams were characterized for their apparent densities, compressive strength, dimensional stability, thermal conductivity, closed-cell content, and water absorption. All the characterization tests followed the standard method BS 4370: Part 1:
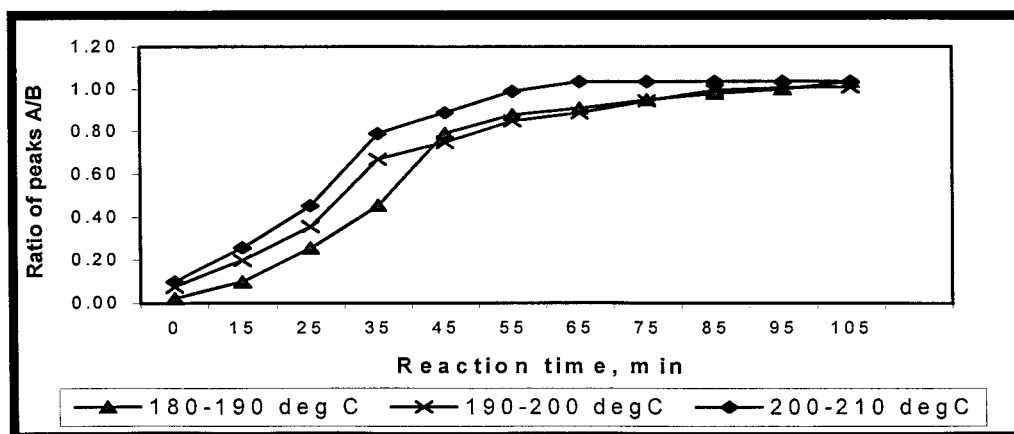

Figure 2 Reaction profile of derivatization of SBPKO from the FTIR spectrum at $T = 180–190°C$, $T = 190–200°C$, and $T = 200–210°C$.

Table I Mechanical Properties of Both DBPKO and SBPKO

Parameter	Panel Standard Specification	DBPKO	SBPKO
Apparent density (molded)	40–45 kg/m^3	44.9	44.2
Apparent density (core)	38–40 kg/m^3	39.0	38.5
Compressive strength	More than 180 kPa	196.8	222.2
Dimensional stability at			
$\quad$ −15°C for 24 h	≤1% linear change	Length: −0.55	Length: −0.09
		Width: −0.50	Width: −0.10
		Thickness: −0.34	Thickness: −0.12
$\quad$ 70°C and 95% RH for 24 h	≤3% linear change	Length: +0.13	Length: +0.08
		Width: +0.33	Width: +0.08
		Thickness: +1.03	Thickness: +0.54
Thermal conductivity			
$\quad$ (initial)	<0.0023 W/mK	0.00244	0.00198
Closed-cell content (%)	≥90%	86	93
Apparent water absorption	Maximum 6.5%	2.25	4.21

1988 and BS 4370: Part 3: 1993 (Rigid Polyurethane Foam Produced by the Press-injection Method). The cell structures were observed using light micrographs and comparisons were made with DBPKO.

Measurement of the Apparent Densities

Foam samples were cut using a handsaw into cubes of 100 × 100 × 100 mm in dimension. Three samples were used and were carefully weighed using an analytical balance. The dimensions were measured following BS4370: Part 1: 1988 Method 1B, using a digital vernier caliper. Foam density was calculated following BS4370: Part 1: 1988 Method 2, using the equation mass (kg)/volume (m^3).

Compressive Strength

The compressive strength test was carried out on a Lloyd universal tensile tester following BS4370: Part 1: 1988 Method 3. The foam samples were cut into cubes of 50 × 50 × 50 mm dimension. The foam rise directions were marked and a crosshead head speed of 10 mm/min was applied. The foam was compressed to 10% of its original thickness.

Dimensional Stability Measurement

The foam samples were cut into dimensions of 100 × 100 × 2.5 mm. The length, width, and thickness were measured using the vernier caliper. The representative foam samples were put into a controlled temperature and humidity chamber each at −15 and +70°C at 95 ± 5% RH for 24 h. Method 5A of BS4370: Part 1: 1988 was followed.

Thermal Conductivity

The foam samples were cut into blocks of 305 × 305 × 30 mm, following the method 7A of BS 4370: Part 2: 1993, where a guarded hot-plate apparatus was used. The temperature difference between the hot and cold plates should be at least 15°C. Samples were tested at 0 and 10°C.

Closed-cell Content Determination

The foam samples were cut into rectangular sections of 25 × 25 × 40 mm and should have been free from voids, blemishes, or skins. The samples were placed in a chamber. The difference of the flask distance between the two measurement chambers is taken as the volume of air displaced by the specimen, V_c, from the specified calibration graph following method 10 of BS 4370: Part 2: 1993. This is then divided by the volume of the specimen as shown in eq. (2):

Apparent volume percentage of closed cell

$$= \frac{10^5 \times V_c}{\text{length} \times \text{width} \times \text{thickness of the specimen}}$$

(2)

Water-absorption Determination

The foam samples were cut into dimensions of 50 × 50 × 50 mm and the test was carried out using the method in Annex D BS4370: Part 1: 1988.
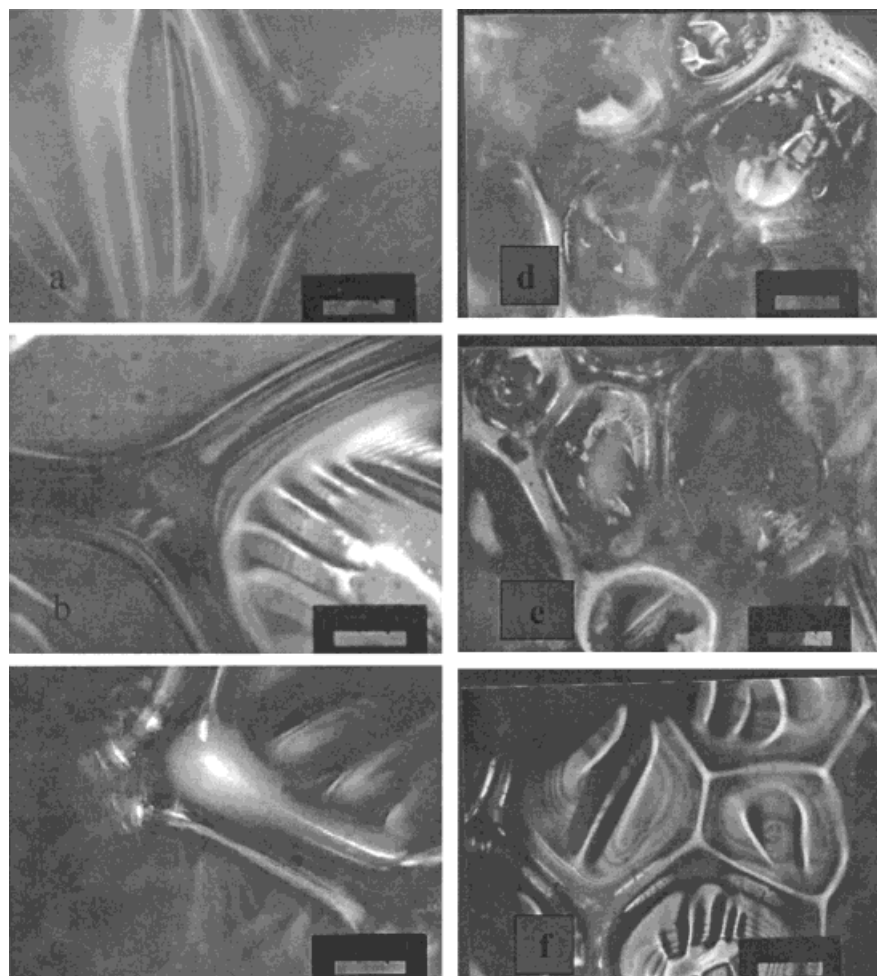
Figure 3 Light micrographs of the cell structures of [(a) bottom, (b) side, (c) top] DBPKO and [(d) bottom, (e) side, (f) top] SBPKO at magnification of 200× at core density of 38 kg/m^3.

RESULTS AND DISCUSSION

Observation: Synthesized SBPKO

The PKO changed from a cloudy pale yellow solid (at 24–25°C) before derivatization to a brown liquid after the reaction. It has a viscosity of 1313.3 cps and a specific gravity of 1.114 g/mL at 25°C. The moisture content was 0.09% and had a pH value of about 10–11. The cloud point was observed at 12–13°C. The hydroxyl number calculated was approximately in the range of 450–470 mg KOH/g sample. The molecular weight was calculated at the range of 480–500. Using both values, the hydroxyl number and the molecular weight, the functionality was 4.0–4.5 using eq. (1).

Figure 1 shows the two peaks used for monitoring the derivatization process. Peak B does not appear in the FTIR spectrum of underivatized RBD PKO. The ratio of the percentage transmittance of these two peaks are calculated and plotted against the derivatization reaction temperatures and three different reaction temperatures: 180–190°C, 190–200°C, and 200–210°C.

The ratio of the two peaks at A and B increases until it reached a constant value (Fig. 2). However, it was found that the optimum temperature and reaction time for a cost-effective method was 200–210°C acquired at 65 min of reaction time. Since determination using the hydroxyl value is tedious and time-consuming, it is justified and convenient to choose just the FTIR method.[2,3] The purity of the synthesized polyol was checked by thin-layer chromatography (TLC). Two peaks of separation were observed on the silica plate at

both 180–190°C and 190–200°C at a reaction time of 65 min. However, polyol from 200 to 210°C at the reaction time of 65 min shows a single peak, confirming the FTIR method of determining the completion of the reaction.

Polyurethane Foam Synthesis

Comparisons were made on the mechanical properties of both the DBPKO and SBPKO. The results are shown in Table I.

The compressive strength was found to be higher for SBPKO (222.2 kPa) compared to DBPKO (196.8 kPa), contributed by overpacking in the cell structures of the foam (Fig. 3). This effect also contributed to better thermal conductivity for a water-blown system of SBPKO (0.00198 W/mK compared to 0.00244 W/mK), although the water absorption became worse (4.21% for SBPKO compared to 2.25% for DBPKO) as the strut's size for SBPKO became smaller. The narrow strut expected in the SBPKO lowered the rate of carbon dioxide, CO_2, gas diffused out to the air diffused into the closed cells and also increased the entrapment of water. The closed-cell contents therefore were expected to be higher: 93% in SBPKO compared to 86% in DBPKO.

CONCLUSIONS

A high-functionality polyurethane polyol can be synthesized from RBD PKO by a reaction with sorbitol. Its branching structure and the OH-terminal offer a functionality of 4.5, an advantage for various applications in the rigid foam area. Apart from offering a cost-effective raw material from PKO and sorbitol, this process also offers a simple route to high-functionality polyurethane polyol production, as well as improved properties of the rigid foam products.

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