

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

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ABSTRACT: In the previous article, a diol-based RBD palm kernel polyol was prepared. It has been found that the polyurethane foam produced is only giving a good compressive strength property at 45 kg/m³ molded density. The combination of sorbitol into the polyol system resulted in a better dimensional stability and improved thermal conductivity as well as enhanced the compressive strength. These were obtained by increasing the functionality of the polyol (functionality of 4.5) through introduction of high molecular weight and branching polyhydric compound. Direct polycondensation and transesterification methods were used for the syntheses. The hydroxyl value, TLC, and the FTIR were determined to study the completion of the reaction. A comparative study of the mechanical properties and morphological behavior was carried out with the diol-based polyol. From the water-blown molded foam (zero ozone depletion potential ODP) with density of about 44.2 kg/m³ and closed-cell content of 93%, it resulted in a compressive strength of 222 kPa, dimensional stability of 0.09, 0.10, and 0.12% at the length, width, and thickness of the foam, respectively, conditioning at -15°C for 24 h. The thermal conductivity improved to an initial value of 0.00198 W/mK, tested at 10°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 827–832, 2001

Keywords: 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 that can be tailored to suit a wide range of application including elastomers, fibers, foams, surface coatings, and adhesive products. The mechanical properties and morphological structure of polyurethane depend mainly on polyol structure, molar mass, and its functionality, and to a lesser extent on the nature of the polyisocyanates. The stoichiometric ratios of isocyanate to hydroxyl

groups, the amount of chain extender used and processing method also have significant effects on the polyurethane properties.

Higher functionality polyols, although derived from nonoil-based polyhydric compounds such as sorbitol and sucrose, tend to form stiff and brittle polyurethane and are used mainly in the rigid foam production.¹ In the first phase, the refined, bleached, and deodorized palm kernel oil (RBD PKO) was reacted with glycol to get a diol-based RBD PKO polyesteramide (DBPKO).^{2,3} However, the dimensional stability and thermal conductivity at lower density (lower than 38 kg/m³ of core density) is not suitable for insulator in the refrigeration application. Gast et al., Khoe et al., and Motawie et al. have also synthesized some amides for coating purposes.^{4–6} The present study, how-

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ever, varies the functionality of the RBD PKO polyesteramide with 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 equation⁷:

Functionality

$$= \frac{\text{hydroxyl value of the polyol} \times \text{molecular weight of the polyol}}{56100} \quad (1)$$

The higher the hydroxyl value, the higher the functionality, and the better the mechanical properties required for rigid foam. The decrease in the equivalent weight of polyol (increase in the molecular weight) increases the rigidity of the polyurethane, 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 with alkanolamine under basic conditions. Methods used in the process involved polycondensation and polyesterification⁹ where low reaction temperature and short reaction time as well as high percentage of yield are offered.

EXPERIMENTAL

Materials

The RBD PKO (Lee Oilmill, Klang, Malaysia) was used without further purification. Its characteristic values such as hydroxyl value, acid number, and typical properties such as viscosity, specific gravity, and water content were noted for consistency of result. 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).

Sorbitol-Based RBD PKO Polyesteramide (SBPKO) Synthesis

To prepare the polyesteramides, the first step involved forming 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 catalyst to prepare the site for the urethane linkage formation. The PKO, together with the anhydrous sorbitol mix-

ture and P46 as the catalyst, as well as MEG as the emulsifier, were reacted at a ratio of 75 : 25 to obtain the highest possible functionality value as possible, without affecting the flowability of the whole polyurethane system later. The liquid sorbitan mixture was used at 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 $205 \pm 5^\circ\text{C}$ for 15–30 min, with nitrogen flow of 40 mL/min/L of mixture, into the system throughout the process. The heating rate was set to $2.5^\circ\text{C}/\text{min}$. The reflux flask was connected to a condenser and the vacuum pump to withdraw the water and excess of glycols 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 polyesteramide produced was kept in a sealed cap glass container for analysis.

Analysis of the Polyol

FTIR analyses were carried out on the Perkin-Elmer Paragon 500 Spectrometer. The samples collected during the intervals were scanned between 4000 and 400 cm^{-1} wave numbers. A drop of each sample was spread into thin layer on the ZnSe plate. Two selected peaks (designated as peaks A and B) were used to monitor the progress of the reaction by means of 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 by the Mark-Houwink equation.¹⁵

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 polyesteramide to verify the FTIR peak ratio method for completion of derivatization reaction. It would also be very important for 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.

The water content of the polyesteramide was determined using the Karl Fischer Titrator 702,

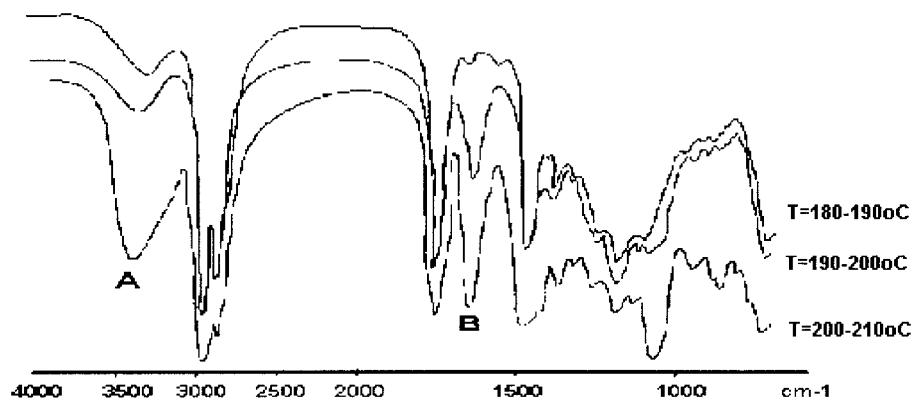


Figure 1 Differences in FTIR spectrum at peaks A and B at various reaction temperatures at $t = 65$ min.

while the viscosity of the polyesteramide was determined using the Brookfield digital viscometer. The pH of the polyesteramide was also determined using the universal pH paper. The cloud point was determined by immersing the polyesteramide in a beaker into the ice bath, stirred vigorously until it reached the cloudy state, where the temperature was noted.

Polyurethane Synthesis

One hundred twenty grams of crude MDI (Cosmonate M-200, Cosmopolyurethane, Port Klang, Malaysia) was poured into 100 g of the mixture of the SBPKO (sample taken from the polyesteramide production that have optimum parameters) with additives (surfactant, catalyst, and water) and were mixed thoroughly using a standard propeller with speed of 3500 rpm for 10 s. This is considered to be a zero ODP system where water was used as blowing agent in replacement of chlorofluorocarbon. The mixture was then poured into a waxed mold, covered, and screwed tight. The foam was demolded after 10 min. It was then conditioning for 16 h at $23 \pm 2^\circ\text{C}$ 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 will follow the standard method BS 4370: Part 1: 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 $100 \times 100 \times 100$ mm in dimensions. 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 $50 \times 50 \times 50$ mm dimensions. The foam rise directions were marked and a crosshead head speed of 10 mm/

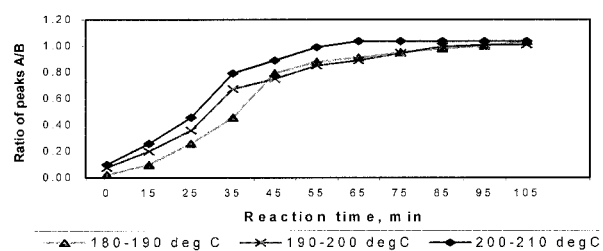


Figure 2 Reaction profile of derivatization of SBPKO from FTIR spectrum at $T = 180\text{--}190^\circ\text{C}$, $T = 190\text{--}200^\circ\text{C}$ and $T = 200\text{--}210^\circ\text{C}$.

Table I Properties of Polyesteramides DBPKO and SBPKO from RBD PKO

Parameter	DBPKO	SBPKO
State @ 25°C	Liquid	Liquid
Color	Golden yellow	Brown
Odor	Odorless	Odorless
Specific gravity @ 25°C, g/mL	0.992	0.985
Cloud point, °C	13	13
Viscosity @ 25°C, cps	374	1135
pH	9–10	10–11
Moisture content before drying	0.09	0.09
Moisture content after drying	0.08	0.09
OH value, mg KOH/g sample	350–370	450–470
Molecular weight	460–480	480–500
Functionality	2.8–3.0	4.0–4.5

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°C and +70°C at 95 ± 5% r.h. 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 method 7A of BS 4370:

Part 2: 1993, where guarded hot plate apparatus was used as shown in Figure 1. 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 of 25 × 25 × 40 mm, and should be free from voids, blemishes, or skins. The samples are placed in a chamber, as shown in Figure 2. 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

$$= \frac{10^5 \times V_c}{\text{Length} \times \text{width} \times \text{thickness of the specimen}} \quad (2)$$

Water Absorption Determination

The foam samples were cut into dimension of 50 × 50 × 50 mm and test was carried out using method in Annex D BS4370: Part 1: 1988.

RESULT AND DISCUSSION

Observation

Synthesized SBPKO

The PKO changed from a cloudy pale yellow solid (at 24–25°C) before derivatization to a brown liq-

Table II Mechanical Properties of Both the DBPKO and SBPKO

Parameter	Panel Standard Specification	DBPKO	SBPKO
Apparent density (moulded)	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 @ −15°C for 24 h	≤1% linear change	Length: −0.55 Width: −0.50 Thickness: −0.34	Length: −0.09 Width: −0.10 Thickness: −0.12
@ 70°C and 95% r.h. for 24 hours	≤3% linear change	Length: +0.13 Width: +0.33 Thickness: +1.03	Length: +0.08 Width: +0.08 Thickness: +0.54
Thermal conductivity (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

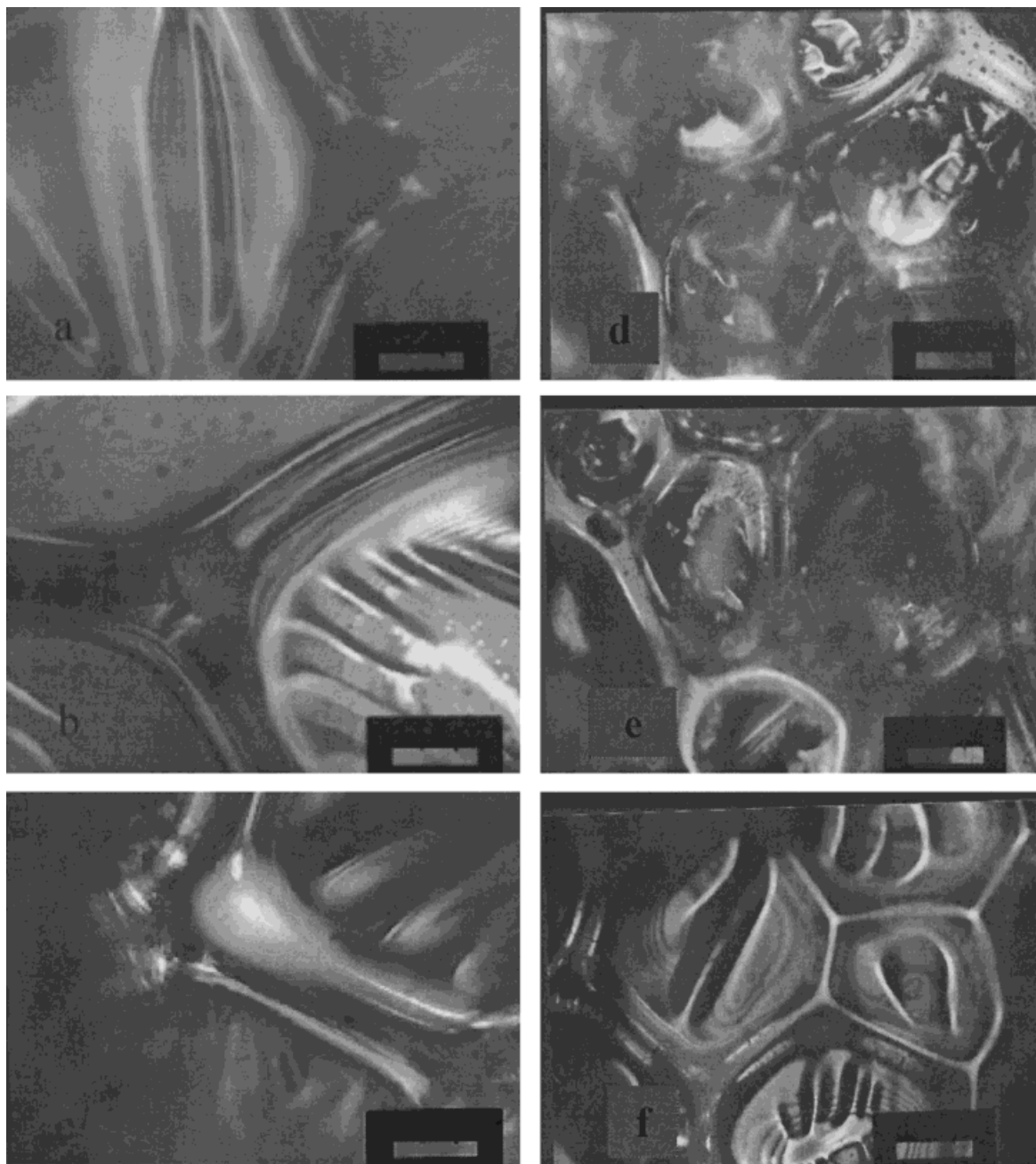


Figure 3 Light micrographs of the cell structures of DBPKO (a—bottom, b—side, c—top) and SBPKO (d—bottom, e—side, f—top) at magnification of $200\times$ at core density of 38 kg/m^3 .

uid after reaction. It has a viscosity of 1313.3 cps and specific gravity of 1.114 g/mL at 25°C . The moisture content was 0.09% and has a pH value of about $10\text{--}11$. The cloud point was observed at $12\text{--}13^\circ\text{C}$. The hydroxyl number calculated was approximately in the range of $450\text{--}470\text{ mg KOH/g sample}$. The molecular weight was calculated at the range of $480\text{--}500$. Using both values,

the hydroxyl number and the molecular weight, the functionality came out to be $4.0\text{--}4.5$ using equation (1). These values are summarized in Table I in comparison with the DBPKO.

Figure 1 show the two peaks used for the monitoring the derivatization process. Peak B does not appear in the FTIR spectrum of underivatized RBD palm kernel oil. 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, 190–200, and 200–210°C.

The ratio of two peaks at A and B increases until it reached a constant value (Fig. 2). However, it was found that optimum temperature and reaction time for a cost-effective method was 200–210°C acquired 65 min of reaction time. Because determination using the hydroxyl value is tedious and time-consuming; therefore, it is justified and convenient to choose just the FTIR method.^{2,3} The purity of the synthesized polyesteramide was checked by thin-layer chromatography (TLC). Two peaks of separation were observed on the silica plate at both 180–190 and 190–200°C at a reaction time of 65 min, indicating the presence of unreacted sorbitol. However, polyesteramide from 200–210°C at a reaction time of 65 min show a single peak, confirming the FTIR method of determining the completion of reaction.

Polyurethane Foam Synthesis

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

The compressive strength was found to be higher for SBPKO (222.2 kPa) compared to the DBPKO (196.8 kPa), contributed by the 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) though water absorption becoming 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, CO₂ gas diffused out to the air diffused into the closed cells and also increased the entrapment of water. The closed-cell contents, therefore, were, as expected, higher, 93% in SBPKO compared to 86% in DBPKO.

CONCLUSION

A high functionality polyurethane polyol can be synthesized from RBD PKO by reaction with sorbitol. The acid number has been successfully de-

creased up to 97.3% from the RBD PKO to the formation of the polyesteramide. The OH value increased from almost zero to a 450–470 mg KOH/g sample. 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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