

Development of a Rigid Polyurethane Foam from Palm Oil

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ABSTRACT: The reactions between polymeric diphenyl methane diisocyanate (polymeric MDI) and conventional polyols to produce foamed polyurethane products are well documented and published. Current polyurethane foams are predominantly produced from these reactions whereby the polyol components are usually obtained from petrochemical processes. This article describes a new development in polyurethane foam technology whereby a renewable source of polyol derived from refined-bleached-deodorized (RBD) palm oil is used to produce polyurethane foams. Using very basic foam formulation, rigid polyurethane foams were produced with carbon dioxide as the blowing agent generated from the reaction between excess polymeric MDI with water. The foams produced from this derivatized RBD palm oil have densities in excess of 200 kg/m³ and with compression strengths greater than 1 MPa. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 509–515, 1998

Key words: palm oil; polyurethane foams; rigid foams; renewable polyols

INTRODUCTION

Since the invention of polyurethanes by Professor Otto Bayer in 1937, the utilization of polyurethanes is ubiquitous. These polymers have found applications in a wide range of products, from thermal insulation to medical implants. Polyurethanes are block copolymers containing blocks of low-molecular-weight polyesters or polyethers covalently bonded by a urethane group, (—NHCO—O—).¹

These polymers are synthesized by reacting three basic components consisting of polyisocyanate; polyhydroxyl-containing polymer (i.e., polyester or polyether polyols); and a chain extender, which is usually low-molecular-weight diols or di-

amines (i.e., 1,4-butanediol or 1,4-dibutylamine). Currently, there is a very wide range of polyisocyanates, polyols, and chain extenders commercially available and this has led to almost unlimited formulation possibilities for polyurethane materials. Because of the inherent versatility in polyurethane syntheses, the properties of this class of polymers can be easily engineered to suit their application environments.

One of the most important commercial polyurethane products is the foam. Polyurethane foams are commonly classified as either flexible, semi-rigid, or rigid, depending on their mechanical performances and core densities. The applications of these foams are highly dependent on the cellular structure of the resulting foam.

In the case of polyurethane foam production, in addition to the usual basic components of polymeric diphenyl methane diisocyanate (MDI), polyol and chain extender, blowing agent, and surfactants are commonly employed to regulate

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the morphology of the cellular structures. Currently, the majority of the polyols, including polyether and polyester polyols, for polyurethane manufacture are derived from petrochemical refining of crude oil and coals, both of which are rapidly diminishing natural resources. There is pressing need, therefore, to find an alternative source of polyols for polyurethane syntheses. One such viable naturally occurring and renewable resource is the plant.

The use of renewable sources, such as castor oil, to produce polyurethanes is not new. Castor oil is used to produce polyurethane adhesives and coatings for which good adhesion property and high-temperature stability are prerequisites. However, castor oil is expensive compared with other vegetable oils, such as palm oil and coconut oil. Palm oil is of particular importance in the Asia Pacific region because it is grown in the region with Malaysia and Indonesia among the major producers. In addition, palm trees have the highest yield of 3.8 tons per hectare per year of vegetable oil in comparison with other sources, such as coconuts and castor and, hence, offers economic advantage of lower costs.²

Palm Oil

Palm oil is a triacylglycerol, which is fat and oil produced by the palm trees. Triacylglycerols that are liquids at room temperature are generally termed oils, whereas those that are solids are known as fats. The properties and compositions of palm oil are well documented and reported elsewhere.^{3,4,5} In this project, refined-bleached-deodorized (RBD) palm oil was chemically derivatized using proprietary chemical formulation and process developed at the Nanyang Technological University (NTU) to produce an alternative polyol to conventional ones suitable for synthesizing polyurethane foams. This technology is not restricted to palm oil but is also applicable to the majority of the vegetable-based oils, which are largely triacylglycerol.

METHODOLOGY

The following two distinct processes are described in this article: (1) derivatization reaction of RBD palm oil, and (2) the production of polyurethane

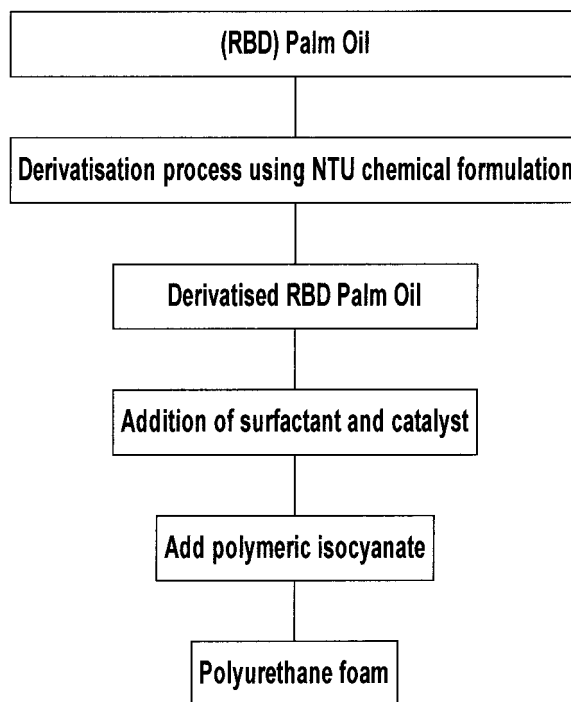


Figure 1 Flow diagram of NTU polyurethane foam process using RBD palm oil.

foam. Figure 1 shows the schematic flow of the overall process from palm oil to polyurethane foam.

Derivatization Process

The derivatization process was carried out in a custom-designed 17-L-size stainless steel reactor fitted with a combined air and water condenser system to enable refluxing of the reaction mixture at elevated temperature. The progress of the derivatization reaction was monitored by removing samples of the reaction mixture at regular intervals for hydroxyl number and Fourier transform infrared spectroscopy (FTIR) analyses. The reaction is deemed complete when the hydroxyl number or the ratio of areas under two specially selected FTIR peaks of the reaction mixture remained constant.

After the reaction, the derivatized RBD palm oil is stored in a polypropylene carboy until needed for further experiments and foam preparation.

FTIR Analysis

FTIR analyses were carried out on the Perkin-Elmer FTIR System 2000. A drop of the sample

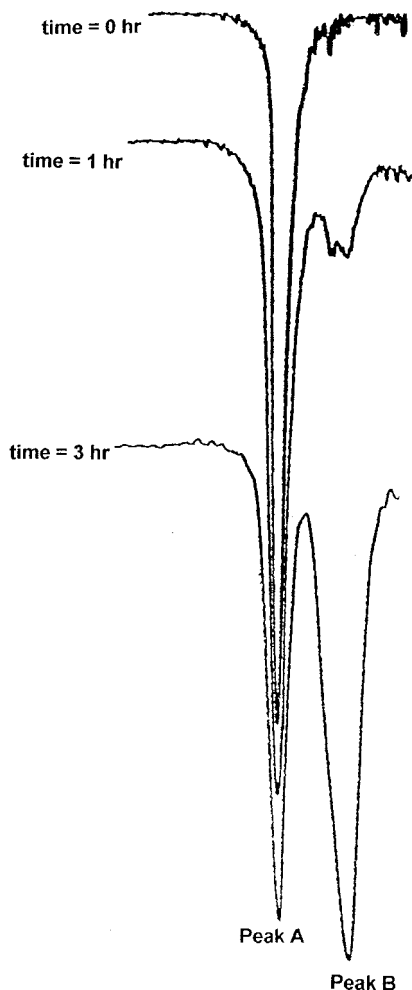


Figure 2 Changes in the areas under FTIR peaks A and B with derivatization reaction time.

was sandwiched between two sodium chloride plates (without any spacer) and secured using a cell holder. Samples were scanned between 4000 and 400 cm^{-1} wave numbers. Two specially selected FTIR peaks (designated as peaks A and B), unique to the reactants, and the derivatized product were used for purpose of monitoring the reaction progress. Figure 2 shows the two peaks used for monitoring the derivatization process. FTIR spectrum of underivatized RBD palm oil does not have a transmittance peak B. The wavenumbers are not shown in Figure 2 for reasons of impending patent application. The ratio of the areas under these two peaks are calculated and plotted against the derivatization reaction time.

Acid Value Determination

Approximately 2 g of the derivatized RBD palm oil was accurately weighed into a 500-mL conical

flask containing 75 mL of freshly distilled pyridine and 75 mL of distilled water. 0.5 mL of phenolphthalein indicator was then added to the mixture. The mixture was agitated and titrated against 0.1N aqueous NaOH standard solution to a pink end point.

The procedure was repeated without the derivatized RBD palm oil for the blank titration. The acid value was determined using the following equation:

$$\text{Acid value} = \frac{[A - B]}{w} \times N \times 56.1$$

where A is volume of standard NaOH solution used for palm oil sample, B is volume of standard NaOH solution used for blank sample, N is Normality of the standard NaOH solution, and w is weight of derivatized RBD palm oil used. The acid value is required for correcting the total hydroxyl value of the derivatized RBD palm oil.

Hydroxyl Number Determination

The hydroxyl values were determined in accordance with the ASTM D4274-88 Method (Standard Test Method for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols). It was also used as a means of verifying the validity of using FTIR peak ratio method for monitoring the progress of the derivatization reaction.

Water Content Determination

The water contents of the derivatized RBD palm oil were determined using a Mitsubishi (CA-06 Moisture-meter) automatic Karl Fisher titrator. The residual water content of polyols is an important parameter in polyurethane foam formula-

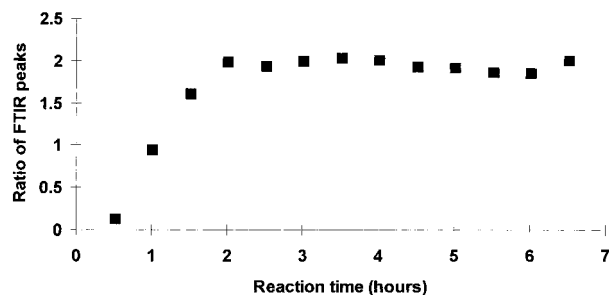


Figure 3 Reaction profile of RBD palm oil (FTIR peak ratio method).

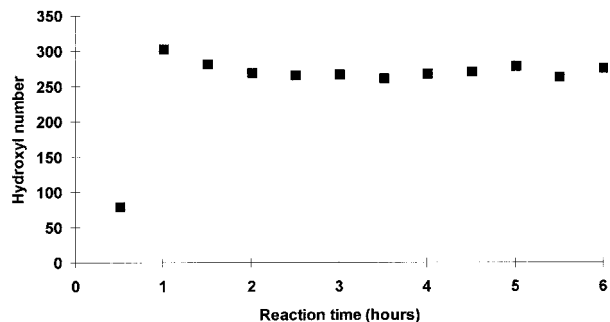


Figure 4 Plot of hydroxyl number of derivatized RBD palm oil against reaction time.

tion because of its reactivity with isocyanate groups to produce gaseous carbon dioxide, which is largely responsible for the blowing process. The amount of carbon dioxide evolved during foaming determines the final density of the foam.

Viscosity Measurement

The viscosity of the derivatized RBD palm oil at 25°C was determined using the Brookfield digital viscometer (Model DV-3) fitted with a small sample adaptor.

Foam Production Process

The isocyanate value for the foam formulation was maintained at 105, and the surfactant (silicone oil) and catalyst (*n*-dibutyl-tin-dilaurate, BDH Chemicals, U.K.) concentrations used were 1 and 0.5% (based on the weight of the derivatized RBD palm oil), respectively. The residual water content of the derivatized RBD palm oil was found to be consistent at approximately 0.4% and no additional water was added to the formulation.

Derivatized RBD palm oil, catalyst, and surfactant were first mixed in a 800-mL polypropylene beaker using a high-speed overhead mixer (2000 rpm) fitted with a shearing rotor for approximately 60 s. The appropriate amount of polymeric MDI (Voramate R-288 crude MDI, Dow Chemicals) was then added to the mixer and stirring continued for a further 30 s. Stirring was then stopped and the mixture was moved away from the stirrer and rotor to allow for creaming and rising of the foam to take place.

After removing the foam from the beaker, the sample was allowed to postcure in an air oven at 60°C for 3 days before further tests.

Foam Characterization

Foams were characterized for their densities, compression strengths, and glass transition (T_g) temperatures. Scanning electron micrographs of the foams were also taken for structural investigations.

Densities

Foam samples were cut using a bench saw into cubes of 30 cm in dimensions. Samples from the top, middle, and bottom sections of the foam were noted. Quintuplicate samples of the foam were carefully weighed using an analytical balance and the exact dimensions were measured using a digital vernier caliper. Foam density was determined using the usual density equation, that is, mass/volume.

Compression Strength

Compression strength evaluation was carried out on an Instron 4206 Universal Tensile Tester. The samples were cut using the same procedure described above, but, in addition, the foam rise directions were noted. Quintuplicate cuboid samples of the foam were used to determine their compression strengths. A test was carried out in accordance with ASTM D1621-73 Procedure A method (Standard Test Method for Compressive Properties of Rigid Cellular Plastics). A Crosshead speed was set at 2.5 mm/min and the load was applied until the foam was compressed to approximately 15% of its original thickness.

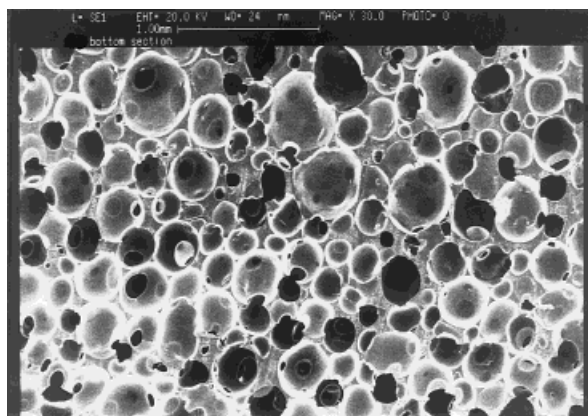


Figure 5 SEM micrograph of the bottom section of the foam.

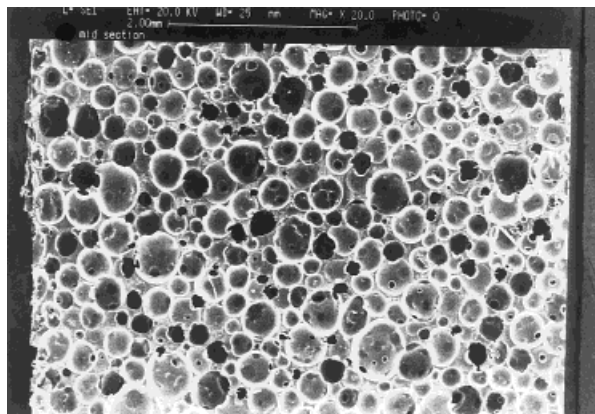


Figure 6 SEM micrograph of the midsection of the foam.

Glass Transition Temperature

The glass transition temperatures of the foams were determined using the Perkin–Elmer DSC-7 differential scanning calorimeter (DSC). The samples were heated from 25 to 150°C at a constant heating rate of 10°C/min.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) observations were carried out using Joel JSM-5310 scanning electron microscope.

RESULTS AND DISCUSSION

Observations

Derivatized RBD Palm Oil

The RBD palm oil changes from a golden yellow liquid before derivatization to a clear, dark, brownish liquid after reaction with a viscosity of approximately 1300 cps at 25°C.

Foams

The foams produced were found to be very rigid and lightweight. There is a dense integral skin at the top surface of the foam, which is hard and has low porosity. In contrast, cut foam shows a uniformly distributed, highly porous cellular cross section beneath the skin layer. The cut foam surface has low friability unlike the skin layer, which is nonfriable.

Derivatization Reaction Profile (FTIR and Hydroxyl Number)

Figure 2 shows the changes in the areas under FTIR peaks A and B with the derivatization reaction time. As the reaction progresses, the area under FTIR peak B increases with time until the ratio of the areas under peaks A and B reached a constant value.

The derivatization reaction profiles of the RBD palm oil using both the hydroxyl number and FTIR peak ratio methods are shown in Figures 3 and 4. Both reaction profiles showed a plateau value at approximately 2 h of derivatization reaction time. No further significant changes are observed after 2 h, which clearly indicated that the derivatization reaction of the RBD palm oil is completed.

The similarity in both profiles shown in Figures 3 and 4 demonstrates good agreement between both methods in determining the end point of the derivatization reaction process. Although the hydroxyl number method provides an absolute measure of the reaction process, it is, however, very tedious and time-consuming. The FTIR peak ratio method, on the other hand, is convenient and rapid, and since the reaction profile obtained is shown and has similar end point as the hydroxyl number determination method, its use in this study is therefore justified.

Acid Value

The acid value of the derivatized RBD palm oil was found to be approximately 12.70 mg KOH/g.

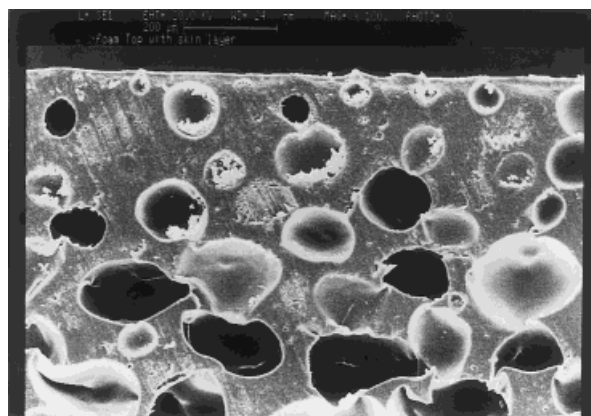


Figure 7 SEM micrograph of the integral skin layer of the foam.

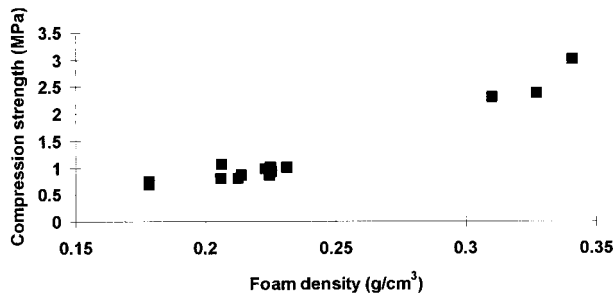


Figure 8 Plot of compression strength of foam in the direction perpendicular to foam rise versus foam density.

Hydroxyl Numbers

The corrected hydroxyl number of the derivatized RBD palm oil was found to be approximately 300 mg KOH/g.

Density

The density of water-blown foam is predominantly determined by the amount of residual water in the polyol component, and variations in the foam density between the bottom, middle, and top sections of the foam structure are not uncommon. However, it was found that there is insignificant differences in the density between the bottom and the midsection of the foam produced. This is further confirmed by the SEM micrographs, which show indistinguishable differences in the foam appearances and cellular structures. Figures 5 and 6 show the SEM micrographs of the bottom and mid-section of the foam. The foam density obtained is approximately 200 kg/m³.

The density of the foam layer close to the integral skin was significantly higher at approximately 300 kg/m³. The high density is attributed to the much lower porosity in the region at close proximity to the dense skin layer. Density measurements of the skin layer could not be determined because the thickness, approximately 600 μ m, was too thin for sampling. However, the density of the skin layer is expected to be the highest because of this layer relatively denser structure. Figure 7 shows the SEM micrograph of the integral skin layer.

Compression Strengths

Figures 8 and 9 show the relationship between the compression strength and the foam density. It was found that foams with densities in the range between 170 to 250 kg/m³ did not have any sig-

nificant effect on the compression strength (at 10% strain) of the foam. The average compression strength in this density range was approximately 1.5 MPa. However, as the foam density exceeds 300 kg/m³, a significant increase in the compression strength was observed, that is, up to 3.5 MPa was obtained.

The above observations were expected as the samples with higher densities were obtained from regions at close proximity to the integral skin layer. As the number of cellular structure decreases and tends towards a solid, the compression strength will correspondingly increases.

It was also observed that the compression strengths of the foam in the foam rise direction and in the traverse direction did not exhibit significant differences indicating isotropic behavior. This isotropic compression behavior is reflected in the shape of the cellular structure, which is predominantly spherical. The carbon dioxide blowing process during foam formation has not resulted in elongation effect on the cellular shape, which is not uncommon in polyurethane foams.

DSC

The glass transition (T_g) of the foam material was found to be approximately 50°C. However, the T_g of the foam is dependent on the overall formulation of the system, that is, the isocyanate index, addition of crosslinkers with large functionality, etc. It was found that as the isocyanate index increased to 1.20 the T_g of the foam increased to 80°C.⁶ This low T_g , therefore, limits the use of the foam to room temperature applications.

CONCLUSION

It is evident that palm oil provides a viable alternate source to the polyols in polyurethane syn-

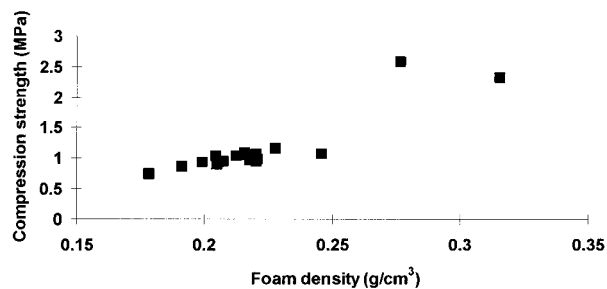


Figure 9 Plot of compression strength of foam in the foam rise direction versus foam density.

thesis. The proprietary process described here has shown to be suitable for derivatizing a relatively unreactive RBD palm oil into one that is suitable for reaction with polymeric MDI to form polyurethanes. Initial results obtained for the polyurethane foams derived from derivatized RBD palm oil showed useful and promising properties. The polyurethane foams obtained exhibited high compression strengths and densities and, in addition, these properties can be further controlled and manipulated through formulation. Further works are currently underway to evaluate the effect of formulation of the derivatized RBD palm oil on the properties of the polyurethane foams.

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