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Biobased Polyurethane from Palm Kernel Oil-Based Polyol

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1. Introduction

Polyurethanes are block copolymers containing segments of low molecular weight polyester or polyether bonded to a urethane group (-NHCO-O). Traditionally, these polymers are prepared by reacting three basic materials; polyisocyanates, hydroxyl-containing polymers (polyester or polyether polyol) and chain extender, normally low molecular weight diol or diamine (such as 1, 4-butanediol or 1, 4-dibutylamine).

Polyols are generally manufactured by one or two possible chemical routes, namely alkoxylation and esterification. Alkoxylation, by far is the most common route, involves the reaction between a hydroxyl or an amine-containing initiator (such as sucrose, glycerol) and either propylene- or ethylene oxide. A molecular weight of up to 6000 can be obtained by extending the polymer chain with the addition of alkylene oxide. This product is suitable for more flexible polyurethanes in cushioning and elastomeric applications. The alkylene oxide used in this process is derived from mineral oil via the petroleum industry. Propylene for instance, is derived from the petroleum cracking process and is then converted to propylene oxide before being further converted to polyol by reaction with an amine or hydroxyl-containing initiator such as glycerol.

At present, most polyols used in polyurethane industry are petroleum-based where crude oil and coal are used as starting raw materials. However, these materials have been escalating in price and rate of depletion is high as well as required high technology processing system. This necessitates a look at utilizing plants that can serve as alternative feed stocks of monomers for the polymer industry. Moreover, with increasing annual consumption of polyurethane, its industrial waste is a serious matter. In Europe and the United States of America for instance, government regulations encouraged recycling of materials to avoid excessive usage of landfill area. However, with thermosetting behavior of polyurethane the recycling activity is difficult and limited. The best alternative is

biodegradation. Biodegradable polymers have widely been used in pharmaceutical industry such as suture usage, wound-dressings, surgical implants and medicine delivering system. But there are still some usage limitations either due to high production cost or its low performance. This performance can be achieved by chemical and physical modification of these materials through combination of biodegradable and non-biodegradable materials.

Polyurethane based on polyester has been known to be more biodegradable than from polyether. Utilization of renewable resources to replace petrochemicals in polyurethane industry has attracted attention of many technologists. Most of these renewable resources are forest products. Palmeri oil, vernonia oil, castor oil and cardanol oil (extracted from the cashew nut shell) have been used to synthesize polyurethane polyols with multiple functionality to replace the petrochemical-based polyols (Pourjavadi et al. 1998 and Bhunia et al. 1998). Castor oil has long been used in the polyurethane industry. Relatively, it is stable to hydrolysis due to its long fatty acid chain but sensitive to oxidation due to the present of unsaturated fatty acid. Commercially, it can only be used in the coating and adhesive industries.

Polyester polyols are generally consisted of adipic acid, phthalic anhydride, dimer acid (dimerized linoleic acid), monomeric glycol and triol. It has low acid number (normally 1-4 mg KOH/g) and low moisture content (less than 0.1%). These properties are not easily achieved unless a high-technology processing method is applied. Due to these industrials requirements, polyester polyols are usually supplied at higher price compared to polyether polyols. Polyether polyols on the other hand, are commercially produced from catalytic reaction of alkylene oxide i.e. propylene oxide or ethylene oxide to di- or polyfunctional alcohol. Its functionality is four and above and is useful in the production of rigid foam. It can also be produced with the presence of di- or polyfunctional amine i.e. diethanolamine when high reactivity is required (such as laminated continuous panel production). Important properties specified in polyurethane industry for polyols are as summarized in Table 1.

Classification	Flexible foam / Elastomer	Rigid / Structural foam
Molecular Weight	1,000 to 6,500	400 to 1,200
Hydroxyl value, mgKOH/g	28 to 160	250 to 1,000
Functionality	2.0 to 3.0	3.0 to 8.0

Table 1. Technical requirements for polyols used in polyurethane industry (Wood 1990).

The lower the equivalent weight of polyol is, the higher the rigidity of the polyurethane. These contributed to higher compressive strength, modulus, thermal stability and dimensional stability polyurethanes. If the equivalent weight is excessively low, the resulting polymer becomes more friable and required more isocyanate especially for the production of rigid polyurethane foam (Berlin and Zhitinkina 1982).

Natural occurring oils and fats are water-insoluble substances originated from vegetable, land or marine animal known as triglycerides. A triglyceride is the reaction product of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water

and one molecule of a triglyceride. The molecular weight of the glycerol portion (C_3H_5) of a triglyceride molecule is 41. The combined molecular weight of the fatty acid radicals ($RCOO-$) varies. Natural oils can undergo a number of chemical reactions such as hydrolysis, esterification, interesterification, saponification, hydrogenation, alkoxylation, halogenation, hydroxylation, Diels-Alder reaction and reaction with formaldehydes. Polyester is a high molecular weight chemical with ester group $-O-C=O-$ as repeating unit. It is achieved by polycondensation and esterification of carboxylic acid with hydroxyl-containing compounds.

Lauric oil or better known as lauric acid is the main source of fatty acids. The only lauric oils available to the world market are coconut oil and palm kernel oil. The oil palm is a monocotyledon belonging to the *Elaeis Guiness* species. Palm kernel oil (PKO) is obtained from the kernel part of the oil palm fruit. The percentage of unsaturated fatty acids is much lower compared to palm oil as shown in Table 2. PKO consist of 80 percent saturated fatty acid and 10% of each polyunsaturated and unsaturated fatty acid. Palm oil on the other hand, consist of 53% saturated fatty acid, 10% polyunsaturated and 37% unsaturated fatty acids. The higher the unsaturated fatty acid contents the unstable it is when exposed to heat. The reactivity increases substantially if the double bond are conjugated (separated by one single bond) or methylene-interrupted (separated by a $-CH_2$ unit). PKO contains only traces of carotene.

Vegetable Oil	Saturated Fatty Acid, %							Unsaturated Fatty Acid, %					
								Enoic				Dienoic	Trienoic
Carbon Chain	C8	C10	C12	C14	C16	C18	>C18	<C16	C16	C18	>C18	C18	C18
Palm Oil				1-6	32-47	1-6				40-52		2-11	
Palm Kernel Oil	2-4	3-7	45-52	14-19	6-9	1-3	1-2		0-1	10-18		1-2	

Table 2. Fatty acid contents in palm oil and palm kernel oil (Khairiah Haji Badri 2002).

Two major reactions occurred during polymerization of polyurethane. First, the reaction of isocyanate with water yields a disubstituted urea and generates carbon dioxide. This is called the blowing reaction because the carbon dioxide is acting as an auxiliary-blowing agent. The second reaction is between the polyfunctional alcohol (polyol) and the isocyanate (Fig. 1).

Figure 1. Addition polymerization of polyurethane

It generates a urethane linkage and this is referred to as the gelation reaction. The isocyanate reacts slowly with alcohols, water and the unstable amino products without the present of catalyst. However, for most commercial requirements the acceleration of these reactions is required.

One characteristic of amorphous polymeric systems is the glass transition temperature, T_g that defines the point where the polymer undergoes a change from glassy to rubbery behavior. Considerable attention has been devoted over the last several years to these studies: synthesis of polyurethane polyol from PKO and the production of oil palm empty fruit bunch fiber-filled PU composites (Badri et al. 1999, 2000^a, 2000^b, 2001; Khairiah Haji Badri 2002; Badri et al. 2004^a, 2004^b; Badri et al. 2005; Badri & Mat Amin 2006; Badri et al. 2006^a, 2006^b; Mat Amin et al. 2007, Norzali et al. 2011^a, 2011^b; Liow et al.; Wong & Badri 2010, Badri & Redhwan 2010;). These include intensive evaluation on the chemical, mechanical, thermal and environmental stress on the synthesized polyol and PU foam by looking at various scopes:

- Synthesis of the palm kernel oil-based polyol from refined, bleached and deodorized (RBD) palm kernel oil via esterification and polycondensation.
- Preparation of the polyurethane foam from the RBD PKO-based polyol and evaluation of its chemical, mechanical and thermal decomposition and glass transition temperature of the foam.

2. Vegetable oil-based polyurethane polyol

Several reports have been published in producing polyurethane from vegetable oils and some of them have even been patented (Arnold 1983, Chittolini 1999 & Austin et al. 2000). Focus was given to utilization of mixture of vegetable oils in the polyurethane system and not as raw materials to produce the polyurethane. Vegetable oils that are frequently used are soybean oil, safflower oil, corn oil, sunflower seed oil, linseed oil, oiticica, coconut oil, palm oil, cotton seed oil, perilla oil, olive oil, rape seed oil and nuts oil. Researches carried out using these oils were focusing on full usage of materials found abundance in certain area such as production of polyurethane foam from mixture of starch and triol polycaprolactone (Alfani et al. 1998) and mixture of starch, soybean oil and water (*Fantesk*) (Cunningham et al. 1997). Polyurethane products based on vegetable oils like nuts oil, soybean oil, corn oil, safflower oil, olive oil, canola oil and castor oil (Nayak et al. 1997, Bhunia et al. 1998, Mohapatra et al. 1998, Javni et al. 1999) exhibited high thermal stability. In Malaysia, the Malaysian Palm Oil Board (MPOB) has taken the initiative to produce polyol from the epoxidation and alcoholysis of palm oil (Ahmad et al. 1995, Siwayanan et al. 1999). An early finding has indicated that when natural oils or fats are epoxidized, they react with polyhydric alcohols to produce polyols. A study by Guthrie and Tait (2000) has successfully produced an ultraviolet (UV) curable coating from epoxidized and unprocessed palm oil, and epoxidised palm olein.

These researches however, are pointing to one direction that is synthesizing polyester. Polyester may be defined as heterochain macromolecules containing repeating ester groups (-

COO-) in the main chain of their skeletal structures. Most useful routes to polyester synthesis of carboxylic acids are step growth or direct polyesterification (condensation polymerization) and ring opening polymerization of lactones. The former is suitable for synthesis of aliphatic polyester where it utilizes primary and secondary glycols where the primary hydroxyl groups being esterified more readily. The removal of liberated water from the process is carried out by stirring and percolation of inert gas such as nitrogen, N₂. If a volatile monomer is used (i.e. glycol), an excess amount with respect to dicarboxylic acid (10 %w/w) should be added to compensate for losses caused by evaporation at high temperature. Side reactions may occur usually at 150°C and above which leads to changes in polymer structure and reduces molecular weight distribution of the polyester (Jedlinski 1992).

Esterification is one of many substitution reactions of carboxylic acids and their derivatives that involve tetrahedral addition intermediates. The extension of mechanism of carbonyl addition is as shown below. The best leaving group is the weakest base. In addition, reaction of ester with hydroxylamine (:NH₂OH) gives N-hydroxyamides (known as hydroxamic acids). This is the point where it is vital to add some reactivities to the existing polyester by addition of the amide group to form polyesteramide (Loudon 1988).

Polyurethanes are possible to decompose by prolonged contact with water, diluted acids or moist heat (causes swelling and slow hydrolysis, particularly in some ester-type polyurethanes), chlorine bleach solutions (may cause yellowing and decomposition) and prolonged exposure to light (discoloration of derivatives of aromatic isocyanates) (Roff et al. 1971). The dimensional stability of foams is a time-dependent property that receives considerable attention. Disregarding cold aging at -15±2°C, humid aging (70± 2°C at 95±5% relative humidity) is usually a prime property. Humid aging requirements (specifications) are determined by the end use of the foam. A foam that has expanded and the shrunk is considered, as a first approximation, to be caused by the effect of plasticization by heat and moisture that would allow the stresses built into the foam at the gel to relax, which will then allow the foam to return to a lower energy state. For urethane foams specifically, high thermal stability results in excellent dimensional stability over a large temperature range.

3. Green material and technology

The RBD palm kernel oil (viscosity of 65 cps, specific gravity of 0.99 g/ml, and moisture content of 0.02%) was obtained from Lee Oilmill Sdn Bhd, Kapar, Klang, Malaysia and was used as received without further purification. Polyhydric compounds consisted of dietanolamine, DEA (purity of 99.8%, hydroxyl value of 1057 mg KOH/g and functionality

of 2, with viscosity of 236 cps and moisture content of 0.05%) and ethylene glycol, MEG (hydroxyl value of 1122 mg KOH/g) were supplied by Cosmopolyurethane (M) Sdn Bhd, Pelabuhan Klang, Malaysia with the inclusion of potassium acetate which was manufactured by Merck (M) Sdn Bhd, Shah Alam Malaysia. Chemicals used for the preparation of polyurethane foam were crude MDI (2,4-diphenylmethane diisocyanate), tetramethylhexanediamine (TMHDA) and pentamethyldiethyltriamine (PMDETA) (Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia) and silicon surfactant (Tegostab B8408, Th. Goldschmidt, Singapore). The blowing (foaming) agent used was tap water.

DEA, MEG and potassium acetate were mixed homogeneously with a ratio of 90:7:3 to form the polyhydric compound. A mixture of this polyhydric compound with RBD PKO at stoichiometric ratio was continuously stirred in a 2-L glass reactor and was reacted separately at three different temperature ranges: 165-175°C, 175-185°C and 185-195°C, each for 30 minutes. The nitrogen gas was flushed into the system throughout the process. The reflux flask was connected to a condenser and a vacuum pump to withdraw the water and excess of reagent from the system. The progress of the reaction was monitored by sampling at intervals. The samples collected were then analyzed. At the end of the reaction, the polyol produced was kept in a sealed cap glass jar for further analysis. 140 g of crude MDI was poured into 100 g mixture of resin (Table 3 and Appendix A).

Composition	Part by weight, pbw
RBD PKO Polyol	100
Tegostab B8408	2
TMHDA	0.3
PMDETA	0.15
Water	4.5
Total pbw	106.95
Ratio of 100 parts to MDI	100:140

Table 3. Formulation of palm-based polyurethane foam system.

The mixture was agitated vigorously using a standard propeller at a speed of 200 rpm for 10 seconds at 20°C (Fig. 2).

Figure 2. Polymerization of the palm-based polyurethane

The reaction time: cream time (CT), fiber/gel time (FT), tack-free time (TFT) and rise time (RT) was noted (Appendix B). The free-rise density (FRD) was calculated using equation (1).

$$\text{Free - rise density, FRD (kg / m}^3\text{)} = \frac{(\text{mass of foam and cup} - \text{mass of cup}), \text{ kg}}{\text{capacity of cup, m}^3} \quad (1)$$

The mixture was poured into a waxed mold, covered and screwed tight. The foam was demolded after 10 minutes. The molded density was determined using equation (2). The molded foam was conditioned for 16 hours at $23 \pm 2^\circ\text{C}$ before further characterization of the polyurethane foam.

$$\text{Molded density, MD (kg/m}^3\text{)} = \frac{\text{mass of molded foam, kg}}{\text{volume of molded foam, m}^3} \quad (2)$$

Fourier Transform Infrared analysis of the RBD PKO polyol and palm-based PU was carried out on the Perkin Elmer Spectrum V-2000 spectrometer by Diamond Attenuation Total Reflectance (DATR) method. The samples collected during the intervals were scanned between 4000 and 600 cm^{-1} wavenumbers. For the former, two selected peaks (designated as peaks A and B) were used to monitor the progress of the reaction (derivatization).

Chromatography analyses were carried out on the former by thin layer chromatography followed by gas chromatography. A sample of 1 pph (part per hundred) by dilution in methanol was dropped on the silica plate with minimal diameter of about 0.5 mm and was applied 2 cm from the edge of the silica plate. The plate was removed once it traversed $2/3$ of the length of the plate (normal length of a silica plate is 20 cm). The plate was placed in a chamber containing iodine crystals (iodine reacts with organic compounds to yield dark stain) after the methanol has all evaporated. The molecular weight was determined using gas chromatography coupled with mass spectrometer, GC-MS model Bruker 200 MHz with splitless inlet and HP5 (polar) column with flow rates of $1.0 \mu\text{l/min}$. The oven was programmed to a temperature range of 100 to 280°C at 6°C/min .

Standard method ASTM D4274-88 (Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols) was used to determine the hydroxyl value of the polyol. The value calculated would be able to verify the FTIR peak ratio method for completion of derivatization process. The water content of the polyol was determined using the Karl Fischer Titrator model Metrohm KFT 701 series (ASTM D4672-00(2006) e1: Standard Test Methods for Polyurethane Raw Materials: Determination of Water Content of Polyols) while the viscosity of the polyol was determined using the Brookfield digital viscometer model DV-I (ASTM D4878-88: Standard Test Methods for Polyurethane Raw Materials- Determination of Viscosity of Polyols). The viscosity of the polyol is important in determining the flowability of the polyurethane resin in the foaming process where it is advantageous in the material consumption. The specific gravity was determined following ASTM D4669-07: Standard Test Method for Polyurethane Raw Materials: Determination of Specific Gravity of Polyols. Other physical characterizations were determination of cloud point, pH and solubility of polyol in methanol, benzene, acetone, ether and water.

The PU foams were characterized for their apparent molded and core densities, compression strength, dimensional stability and water absorption following standard method BS4370: Part 1:1988 (1996) Methods 1 to 5: Methods of test for rigid cellular materials. Foam samples were cut using into cubes of 100 mm × 100 mm × 100 mm in dimensions. A replicate of five specimens were used and carefully weighed using an analytical balance. The dimensions were measured following BS4370: Part 1:1988 (1996): Method 2. The apparent molded density was determined by using a simple mathematical equation, mass (kg)/volume (m³). The core density is determined by the same method but using skinless foam. The compressive strength test was carried out on a Universal Testing Machine Model Testometric Micro 350 following BS4370: Part 1:1988 (1996): Method 3 at 23 ± 2°C. The specimens were cut into cubes of 50 mm × 50 mm × 50 mm in dimensions. The foam rise direction was marked and a crosshead speed of 50 mm/min was applied. The compression stress at 10% deflection, compression stress at 5% strain and compression modulus was noted. For the dimensional stability test, the specimens were cut into dimensions of 100 mm × 100 mm × 25 mm. The specimens were then put into a controlled temperature-humidity chamber each at -15 ± 2°C and 70 ± 2°C, 95 ± 5% relative humidity for 24 hours. Method 5A of BS4370: Part 1:1988 (1996) standard was followed. The specimens were remeasured and percentage of change in dimensions was calculated. These are then converted to percentage in volume change. The water sorption was carried out using method in Annex D BS6586: Part 1:1993. The specimens were cut into dimension of 50 mm × 50 mm × 50 mm.

The thermal decomposition of the polyurethane foam was measured using a thermogravimetric analyzer model Shimadzu TGA-50 with temperature ranging from room temperature to 600°C at heating rate of 10°C/min under nitrogen gas atmosphere. Samples were placed in alumina pan holders at a mass ranging from 5 to 15mg. The thermal property of the foam was determined using a Perkin Elmer Model DSC-7 differential scanning calorimeter interfaced to the Model 1020 Controller. The samples were analyzed from room temperature to 200°C at a heating rate of 10°C/min. Standard aluminum pans were used to analyze 10 mg samples under nitrogen gas atmosphere. The insulation value (k-factor or λ -value) of the polyurethane foam was determined using the Thermal Conductivity Analyzer model Anacon at testing temperature for cold plate at 25°C and hot plate at 35°C. The thickness of the specimens was 20-30 mm and method 7 of BS4370: Part 2: 1993 standard was followed.

The RBD PKO consists of triglycerides that when undergoes esterification form by products such as glycerol and other possible polyester network (Loudon 1988) as shown in Scheme 1 and Scheme 2. During the reaction, the acetate ion forms an intermediate, the carboxylic acids. These acids attack the lone pair in nitrogen atom in diethanolamine, DEA and formed the probable structure of the esteramide with hydroxyl terminal (Scheme 2)

R₁, R₂ and R₃ generally are represented by R and it is very common to have lauric-lauric-oleic composition of fatty acid in the carbon chains (Scheme 2).

Scheme 1. Probable reaction mechanism between the RBD PKO and the hydroxyl-containing compound

Scheme 2. Conversion of RBD PKO to the esteramide (RBD PKO-based polyol)

RBD PKO reacts with the polyhydroxyl compound in an alkaline medium (contributed by the potassium acetate). The alkalinity of the system ensured that the RBD PKO is fully reacted. The selection on polyhydroxyl compound being used is the critical part where it should offer highest hydroxyl value and functionality polyol possible to fully converting the RBD PKO into polyol (highest yield). Methods used in this study involved polycondensation and esterification where these are the only routes that offered low reaction temperature and short reaction time. It produced polyol (compound with functional group –OH) at high yield (almost 100%), low moisture content and no toxic vapor. The esteramide or PKO-based polyol is a monoester with OH terminal.

4. Properties of the PKO-based polyol

The derivatised RBD PKO-based polyol is a golden yellow liquid with a cloud point of 13°C. It has very low moisture content of 0.09% and low viscosity of 374 cps and specific gravity of 0.992 g/cm³ at room temperature. Low water content and liquid nature of the polyol are advantageous in formulating the polyurethane system especially when processing of end product is concerned. Less viscous polyol offers less viscous polyol resin which leads to system with good flowability. The viscosity increases as the degree of polycondensation and branching increases (Wood 1990). The physical properties of the PKO-based polyol are summarized in details in Table 4. It is important to note that raw RBD PKO solidified at room temperature with cloud point of about 23–24°C whilst the derivatized polyol solidified only at 13°C (cloud point). Polyol heating system is not required here as what is being used by other studies (Parthiban et al. 1999 and Ahmad et al. 1995).

Parameters	Result
State at 25°C	Liquid
Color	Golden yellow
Odor	Odorless
Density at 25°C, g/cm ³	0.992
Solubility	Alcohol, Ketone, Ether, Alkane, Water
Cloud Point, °C	13
Viscosity at 25°C, cps	374
pH	9-10
Moisture content at 25°C, %	0.09

Table 4. Physical properties of the derivatised RBD PKO-based polyol.

4.1. Chemical analysis

a. Fourier Transform Infrared Spectroscopy (FTIR)

The RBD PKO, a chain of fatty acid with carboxylic acid group displays intense C=O stretching bands of acids absorb at 1711 cm⁻¹ as shown in Fig. 3 (a). The C-H stretches at 2932 and 2855 cm⁻¹. Two bands arising from C-O stretching and O-H bending appear in the spectra of RBD PKO near 1320-1210 and 1440-1395 cm⁻¹ respectively. Both of these bands involve some interactions between C-O stretching and in-plane C-O-H bending. The C-O-H bending band near 1440-1395 cm⁻¹ is of moderate intensity and occurs in the same region as the CH₂ scissoring vibration of the CH₂ group adjacent to the carbonyl (Silverstein et al. 1991).

The FTIR spectrum of the derivatized RBD PKO was obtained from samples taken at 175-180°C (Fig. 3(b)) during the esterification process. The spectrum was evaluated at peak 3351 cm⁻¹ (designated as peak A) and 1622 cm⁻¹ (designated as peak B). Peak A and B, which are the hydroxyl (-OH) and carbamate (O=C=N-) peaks respectively (assigned by IR Mentor Pro Classes, Sadtler Division Bio-Rad Laboratories 1990 and Silverstein et al. 1991). These peaks do not appear in the spectra of the raw RBD PKO (Fig. 3(a)). A vague trace of the hydroxyl peak was observed when PKO is mixed with the hydroxyl compound. Further increase in the reaction temperature and reaction time changed the percentage of transmittance for both peaks A and B significantly. It also indicated a formation of ester cleavage at 1710 cm⁻¹. The sharp absorption bands in the region of 1750-1700 cm⁻¹ are characteristic of carbonyl group of ester (C=O) stretching vibrations (Silverstein et al. 1991).

Transmittance ratio of both peaks, the OH and the carbamate peaks (% transmittance of peak A divided by the % transmittance of peak B) was plotted as in Fig. 4. It was used to

identify the progress of the derivatization process (Chian and Gan 1998). Fig. 4 also showed that the hydroxyl value (OHV) reached to a constant at 350-370 mg KOH/g sample at intervals of 175-180°C for 15-30 minutes of reaction time. The FTIR spectrum and hydroxyl value (OHV) curves both demonstrated that 175-180°C at 15-30 minutes as optimum temperature and reaction time respectively. Both methods are advantageous in the identification of optimum processing parameters assuming that Beer's Law is applicable here. However, OHV determination method is slow and time-consuming. Therefore, FTIR method is more preferable in determining the completion of reaction for the RBD PKO-based polyol (Chian and Gan 1998).

Figure 3. FTIR spectra of (a) the raw RBD PKO and (b) the palm-based esteramide

Note:

25 refers to derivatized RBD PKO at ambient temperature, 25°C

140 refers to derivatized RBD PKO at 140°C

160 refers to derivatized RBD PKO at 160°C

180/0 refers to derivatized RBD PKO at starting of 180°C

180/15 refers to derivatized RBD PKO at 180°C for 15 minutes

180/30 refers to derivatized RBD PKO at 180°C for 30 minutes

185/0 refers to derivatized RBD PKO at starting of 185°C

185/15 refers to derivatized RBD PKO at 185°C for 15 minutes

185/30 refers to derivatized RBD PKO at 185°C for 30 minutes

Figure 4. Curve of ratio of OH peak to the C-N peak and the OHV curve of the blend at intervals

b. Thin Layer Chromatography

The thin layer chromatography (TLC) test on the desired products obtained at intervals of reaction time at 175-180°C (0, 15 and 30 minutes) indicated a clear qualitative separation. These separations were compared to TLC carried out on individual ingredients: The RBD PKO, diethanolamine (DEA), the catalyst-potassium acetate in monoethylene glycol and standard lauric acid (Athawale et al. 2000). There were three separation peaks, identify as the PKO, DEA and small trace of the catalyst up to 175-180°C at 0 minute. At 175-180°C for 15 minutes, only two separation peaks were observed and finally at 175-180°C for 30 minutes, only one separation peak was observed (Fig. 5). The result is parallel to the gas chromatography (GC) peaks of the final product, the RBD PKO-based polyol (Fig. 6)).

c. Gas Chromatography-Mass Spectrometry (GC-MS)

The samples collected at intervals ranging from 165-170°C, 170-175°C, 175-180°C and 180-185°C were also evaluated for its purity using gas chromatography, GC coupled with mass spectrometry, GC-MS. Fig. 6 is the GC of the RBD PKO-based polyol reacted at 175-180°C for 15-30 minutes. The signal at retention time of 31.92 min is the desired product, the RBD PKO-based polyol (98.24%) while signals at retention time of 13.37 (0.08%), 16.36 (0.92%) and 27.91 (0.27%) representing small percentage traces of MEG, glycerol (by-

product of esterification) and DEA (C:\ DATABASE\WILEY275.L). Others (0.49%) are traces of oligomeric polyester components from C₁₄ and C₁₈ chains. The GC-MS scan of the RBD PKO-based polyol showed an estimated molecular weight of 477. Molecular weight obtained at 165-170 and 170-175°C of reaction temperature was 296 and 355 respectively. Thus, molecular weight obtained at 175-180°C is considered to be the most desirable molecular weight for this study. The functionality of the RBD PKO-based polyol derived from this molecular weight and the determined hydroxyl value (OHV of 350 to 370 mg KOH/g) is 2.98 to 3.15 calculated using the mathematical equation in equation 3.

$$\text{Functionality} = M_w \times \text{OHV} / 56100 \quad (3)$$

Note: M_w is the estimated molecular weight of the RBD PKO-based polyol obtained from GC-MS which is 477 OHV is the hydroxyl value of the RBD PKO-based polyol obtained using ASTM D4274-88 method, which is about 350-370 mg KOH/g sample

Note:

PEA	RBD PKO-based polyol
DEA	diethanolamine
MEG	monoethylene glycol
STD	standard lauric acid
180/0	derivatised RBD PKO at starting of 180°C
180/15	derivatised RBD PKO at 180°C for 15 minutes
180/30	derivatised RBD PKO at of 180°C for 30 minutes

Figure 5. The thin layer chromatography of the ingredients

This range of functionality is suitable for rigid foam application (Wood 1990).

Both FTIR (IR Mentor Pro 1990) and GC-MS approaches (Wiley MS-database) could be used to estimate the most probable molecular structure of the RBD PKO-based polyol at 175-180°C/30 minutes (optimum temperature and reaction time) as 2-hydroxy-undecanoamide as in Scheme 2 (library search on Wiley MS-database giving 98% quality match). There is no intention of purification of the synthesized RBD PKO-based polyol as all these hydroxyl-containing compounds would react with crude MDI.

Figure 6. GC chromatogram of the RBD PKO-based polyol obtained at 175-180°C for 30 minutes.

4.2. Thermal testing

The thermogram of the resulted RBD PKO-based polyol is as shown in Figure 7. Thermally, it is stable up to 167.6°C and undergoes two stages decomposition at 167.6 to 406.3°C with total weight loss of 99.41%. The initial 3.34% weight loss is contributed to the moisture content and other volatile impurities in the RBD PKO-based polyol (Oertel 1993). The initial decomposition is contributed by the degradation of RBD PKO-based polyol and traces of glycerol supported by the DTA curve which representing the softening temperature at 385°C. Charred residue was obtained after testing.

Figure 7. TGA thermogram of the RBD PKO-based polyol obtained at 175-180°C for 30 minutes

5. Properties of the PKO-based polyurethane foam

5.1. Physical properties

The PKO-based polyurethane foam (PUF) produced is a light yellow solid with skin thickness of about 1.5 mm. It is a stiff/rigid but brittle solid at 43-44 kg/m³ molded density and core density of 38-39 kg/m³ with average void size of 0.10-0.15 mm (Fig. 8).

Figure 8. Scanning electron micrograph of the PUF at 250× magnification

5.2. FTIR analysis

The PUF is analysed by FTIR spectroscopy which showed the absence of the free OH groups and indicates a complete conversion of both –OH groups of the PEA to the urethane moiety (NH-C(O)-O). Typical FTIR spectrum of the PU is as shown in Fig. 9. The characteristic –NH stretching vibration of the –NH₂– (amide) is located at 3405 cm⁻¹, overlapping with the OH peak as a broad band. Bands at 2932 and 2894 cm⁻¹ are the synchronous reflection of asymmetric and symmetric of CH₂ bridges, from the linkage of the urethane with the PEA. Bands at 1650 cm⁻¹ is the overlapping of –N=C=O (urethane) and ester linkage of the PEA. Obviously, bands 1550, 1650 and 3350 cm⁻¹ indicate complete conversion to urethane moiety (Silverstein et al. 1991).

Figure 9. FTIR spectrum of the RBD PKO polyurethane foam

5.3. Thermal properties

The thermal instability of a PU may be defined as the ease by which heat produces changes in the chemical structure of the polymer network. These may involve simple bond-rupturing dissociation or reaction reversals and provide more volatile components, or they may result in extensive pyrolysis and fragmentation of the polymer. This characteristic provides a measure of fire hazard in that a more thermally stable polymer is less likely to ignite and contribute to a conflagration than a less stable one (Burgess, Jr. & Hilado 1973). Thermodynamic parameters such as decomposition temperatures, percentage of weight loss, melting temperature, T_m and glass transition temperature, T_g were determined by thermal analyses of the PU.

TGA thermogram of the PU is as shown in Fig. 10. Presence of three degradation stages implying the presence of three thermal degradation temperatures. It was thermally stable at 191.9°C, a common stability temperature for PU (Hepburn 1991). The initial weight loss of about 41.24% commences at 191.9 to 396.9°C. T_{max} from the DTA curve occurred at 275°C attributed by carbon dioxide trapped in the sample. Degradation started at 396.3 to 498.4°C, which was initially a fast process. The total weight loss up to 500°C is 74%. This second stage of degradation rationalized the urethane linkage reported by Hepburn (1991).

Figure 10. TGA thermogram of the RBD PKO PU foam

There is no indication of melting and crystallization temperatures curves in the DSC thermogram of the PU foam. Therefore, this polymer could be identified as an amorphous polymer (Badri et al. 2000). The glass transition temperature is 39.74°C, a regular glass transition temperature for thermosetting polymers, with heat capacity of 33.0 J/g. Since the heat of evaporation of water is 2300J/g, moisture content of the PU was detected to be 1.43%.

However, the initial thermal conductivity of PU foam is found to be 0.0244 W/m-K. This is expected since it is a water-blown PU system where water has poor properties i.e. boiling point and k-factor compared to its industrial counterpart, chlorofluorocarbon, CFC (Crawford & Escarsega 2000). Low thermal conductivity is normally contributed by the low boiling point of the blowing agent such as CFC and finer cell structure of the foam (Hardings 1965, Frisch 1985, Hepburn 1991). However, another fact to be remembered is that water is a chemical blowing agent compared to CFC, a physical blowing agent. Water is capable of interfering in the polymerization of polyurethane by producing by-product such as urea and large amount of carbon dioxide when being used in larger quantity. Functionality of polyols also plays an important role in producing good insulated material (Wood 1990, Hass and Uhlig 1985).

5.4. Mechanical properties

The mechanical properties of the foam produced from the derivatized RBD PKO show comparable results (Table 5) to the British Standard requirement (practiced by industry such as building construction industry). It is expected for water-blown PU foam to have lower compressive stress at 5% strain and the compression due to irregular formation of cellular structure. This decreased the strength upon higher percentage of strain. Table 5 showed the summary of the mechanical properties of the PU foam.

The dimensional stability which is described in percentage of volume change indicated changes of -0.090% and 0.012% at $-15\pm 2^\circ\text{C}$ and $70\pm 2^\circ\text{C}$ at $95\pm 5\%$ relative humidity for 24 hours respectively. A very minimum shrinkage and expansion problem was observed on the foam prepared from this palm oil-based polyurethane polyol in a water-borne system. Identical resin formulation was used using petroleum-based polyol to substitute the palm-based polyol. Major shrinkage and expansion problems were observed. Shrinkage and expansion problems are normally used as indicators of how good the foam is as an insulator. The mechanical properties could be enhanced by using low or high pressure dispersing machines (Oertel 1993). Better mechanical properties could also be achieved by introducing filler in the PU system (Rozman et al. 2001^a, 2001^b, 2000, 1998).

5.5. Rheological and kinetic properties

The PU system is polymerized kinetically using tetramethylhexadamine, TMHDA as a gel/blow catalyst and pentamethyldiethylenetetramine, PMDETA as a blow catalyst. The addition of both catalysts is very minimum (0.05-0.10 pbw) in achieving an optimum kinetic reaction time (Tamano et al. 1996) especially when reactive RBD PKO-based polyol (Scheme 2) is used in the formulation. The cream time, gelling/fiber time, tack-free time and rise time (Appendix B) were 23, 71, 105 and 156 seconds respectively at 20°C . The PUF is demolded after 10 minutes of mixing with skin thickness of about 1.5 mm. It has a flow index of 1.050 cm/g, a moderate flowability PU system (Colvin 1995). This is assumed to be helpful in reducing the consumption of raw materials, especially the RBD PKO-based polyol.

5.6. Resistance to environmental stress

The chemical resistance of the PU with normal closed-cell structures of rigid urethane foam prepared from the crude MDI and RBD PKO-based polyol is carried out to investigate the limitation of the interactions with surroundings to the surface layer in order to produce a chemically and physically stable material. Effects produced by chemical agents depend both on the chemicals and on the permeability of cell membranes. Solubility of the chemical in the foam affects both permeability and swelling. Results obtained are not representative of other temperatures, concentrations or exposure times.

Parameter	Method	Standard	Results
*Apparent molded density, kg/m ³	BS 4370:Part 1:1988 (Method 2)	Min 38	43.6 ±0.85
*Apparent density (core), kg/m ³	BS 4370:Part 1:1988 (Method 2)	Min 35	38.9 ±0.53
*Compressive strength to foam rise at 10% deflection, kPa	BS 4370:Part 1:1988 (Method 3)	Min 180	185.7 ±8.22
*Compressive stress at 5% strain, kPa	BS 4370:Part 2: 1993 (Method 6)	Min 140	105.4 ±2.41
Compressive modulus, N/m ²	BS 4370: Part 1: 1988 (Appendix A)	Not available	8.52 ±0.46
*Dimensional stability,%	BS 4370: Part 1: 1988 (Method 5B)		
	At -15 ±2°C for 24h	Maximum 1.0	Length: -0.151 ±0.03 Width: -0.433 ±0.03 Thickness: 1.373 ±0.06
	At 70 ±2°C, 95 ±5% r.h. for 24h	Maximum 3.0	Length: 0.359 ±0.25 Width: 0.017 ±0.04 Thickness: 1.654 ±0.09
*Apparent water absorption,%	BS 6586: Part 1: 1993 (Annex D)	Maximum 6.5	2.25 ±0.89
Shore A Hardness	ASTM D 2240	Not Available	29.0 ±1.4

Note: * Physical property requirements following BS6586: Part 1: 1993 industrial standard.

Table 5. The mechanical properties of the PU foam synthesized from the RBD PKO-based polyol.

Fig. 11 illustrates the compressive strength at 10% deflection and 5% strain as well as its compression modulus upon exposure to stress. All resistivity test medium being used result

in a major increment in the strength at 10% deflection. Readings of above 0.20MPa (compared to the control foam) with maximum compressive strength are observed in benzene at about 0.34MPa, followed by PUF at ambient temperature (0.30MPa), freeze-thaw condition (0.26MPa), 10% NaOH (0.25MPa), saltwater (0.20MPa) and finally 10% HNO_3 (0.19MPa). The same trend is observed in compressive strength at 5% strain where the maximum value is encountered at freeze-thaw condition followed by at ambient temperature, 10% NaOH and finally benzene. The compression modulus reaches as high as 11.0MPa and others are in the range of 8.0 to 9.0MPa.

Figure 11. Effect of various environmental stresses on the compressive strength and compression modulus of the RBD PKO-based PU foam

Practically, the absorption of chemicals into the foam results in swelling of the cell faces, which apparently increases the compressive strength. Weathering conditions (ambient and freeze-thaw) however are very much dependence on the diffusion rate of carbon dioxide being replaced by the air which causes expansion of the foam and increases the compressive strength (Wood 1990). The foams are found to be unaffected by the test medium basically due to the mixture of organic components (RBD PKO-based polyol and MDI). Rigid PU foam is stable in the present of most solvents such as found in binders and sealers (Oertel 1993).

Physically, the foam becomes spongy with the formation of waxy material on the surface of the foam, as a result of prolonged exposure to benzene as an aromatic hydrocarbon. It is important to note that ester-based polyurethanes are easily attacked by hot aqueous alkali or moderately concentrated mineral acids, swollen by aromatic hydrocarbons and decomposed by prolonged contact with water, diluted acids and moist heat (causes swelling and slow hydrolysis) (Roff et al 1971).

The compression modulus of the PUF ranges from 7.8 to 10.8MPa. the compression modulus for the control PUF is at 8.5MPa which is lower compared to the modulus in 10% HNO_3 ,

10%NaOH, under freeze-thaw condition, and in saltwater but higher if compared to the modulus of the rest of the resistivity test.

Rigid PU prepared has high resistivity to the action of most organic solvents and are seriously degraded only by strong acid, oxidizing agent and corrosive chemicals. Only stronger polar solvents, which significantly swelled the polymer, led to shrinkage of the foam structure. Evaporation of the solvent normally returns the polymer to its original state (Oertel 1993).

6. Conclusion

Several advantages are foreseen from this study. Some important advantages are being identified through this method of polyol production. Firstly, it is attractive and economical. RBD PKO-based polyol is a naturally formed macromolecules found in Malaysia. It is extremely plentiful, easy to process and refine, capable of being cultivated with minimum capital investment and suitable for conversion to quality polyols using an inexpensive reaction process. Secondly is the simplicity of the process, which requires only a few reactors for producing the polyol as well as formulating the resin. Commercially, the process acquires only a few personnel to produce consistently good quality polyols. Thirdly, compare to the manufacturing of the petrochemical-based polyols, the process is relatively safe, where it involves the usage of hazardous chemicals. Generally, it is non-toxic and of low volatility.

Two major environmental advantages can be realized. Firstly, the source of oil is truly renewable, where it does not lead to permanent depletion of resources which has a limited global availability. Secondly, the amount of energy required to convert the natural oils to polyol is considerably less than using the conventional process. The foam made from this RBD PKO-based polyol is low in density, light in color, high in strength but low in water sorption. The produced RBD PKO-based polyurethane foam in this study also has other advantages as tabulated in Table 6.

Property	Rating	Consequence	Benefit
Thermal Insulation	Highest	Thinnest Section	Space
Rigidity	High	Added Strength	Structural
Adhesion	High	No glue-line	Manufacturing
Dimensional Stability	High	Non-sag, non-heave	Maintenance
Density	Low	Lightweight	Handling
Water Vapor Transmission	Low	Less Condensation	Construction

Table 6. The advantages of producing RBD PKO-based polyurethane.

The PUF meets the British Standard requirements in any medium of the tested environmental stress test. This ester-type polyurethanes are easily attacked by prolonged contact with water, diluted acids and moist heat (causes swelling and slow hydrolysis) and swollen by aromatic hydrocarbons. These rigid PUs either the PUF, are resistant to the

action of most organic solvents and are seriously degraded only by strong acids, oxidizing agents and corrosive chemicals. Only polar solvents, which significantly swell the polymer, lead to shrinkage of the foam structure. Evaporation of the solvent normally returns the polymer to its original state.

In terms of application, these composites are most suitable in structures where stiffness and dimensional stability are of prime importance but is only a secondary choice to areas where structural strength is more vital than the component rigidity.

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7. References

- Ahmad, S., Siwayanan, P. & Wiese, D. 1995. Porim and INTERMED Sdn.Bhd. Malaysian Patent Application Number. PI9502302. Filling Date: 7 August, 1995.
- Alfani, R., Iannace, S. & Nicolais, L. 1998. Synthesis and Characterization of Starch Based Polyurethane Foams. *J. Appl. Polym. Sci.* 68 (5) : 739-745
- Apukhtina, N.P. 1973. Methods for Increasing the Thermal Stability of Polyurethanes: Soviet Urethane Technology, Ed. Schiller, A.M. pp. 198-210. Connecticut: Technomic Publishing Co., Inc.
- Arnold, J.M. 1983. *Vegetable Oil Extended Polyurethane System*. US 4375521
- Athawale, V.D., Rathi, S.C. & Bhabe, M.D. 2000. Novel Method For Separating Fatty Ester From Partial Glycerides in Biocatalytic Transesterification Of Oils, *Separation and Purification Technology*, 18:3:209-215.
- Austin, P.E., Derderian, E.J. & Kayser, R.A. 2000. Hydrosilation in High Boiling Natural Vegetable Oils. US 6071977.

- Norzali N.R.A., Badri, K.H. & Nawawi, M.Z. 2011^a. Loading Effect of Aluminum Hydroxide onto the Mechanical, Thermal Conductivity, Acoustical and Burning Properties of the Palm-based Polyurethane Composites, *Sains Malaysiana* 40(7): 737-742
- Norzali N.R.A., Badri, K.H. & Nawawi, M.Z. 2011^b. The Effect Of Aluminium Hydroxide Loading On The Burning Property of The Palm-Based Polyurethane Hybrid Composite, *Sains Malaysiana* 40(4):385–390.
- Liow, C.H., Badri, K.H. & Ahmad, S.H. 2011. Mechanical and Thermal Properties of Palm-Based Polyurethane Composites Filled With Fe₃O₄, PANI and PANI/Fe₃O₄, *Sains Malaysiana* 40(4): 379–384.
- Wong, C. S. & Badri, K.H. 2010. Sifat Terma Dan Kerintangan Api Poliuretana Berasaskan Minyak Isirung Sawit Dan Minyak Kacang Soya, *Sains Malaysiana*, 39 (5): 775-784.
- Badri, K.H. & Redhwan, A. M. 2010. The effect of phosphite loading on the mechanical, thermal and fire properties of palm-based polyurethane, *Sains Malaysiana*, 39 (5): 769-774.
- Mat Amin, K. A., Badri, K.H. & Othman, Z. 2007. Oil Palm-Based Hybrid Biocomposites with Kaolinite. *Journal of Applied Polymer Science* 105:2488-2496.
- Badri, K.H., Ujar, A. H., Othman, Z. & Sahaldin, F. H. 2006^a. Shear Strength of Wood-to-Wood Adhesive Based on Palm Kernel Oil, *Journal of Applied Polymer Sciences*, 100(3): 1750-1759
- Badri, K.H., Mat Amin, K. A., Khalid, N. K., Othman, Z. & Abdul Manaf, K. 2006^b. Effect Of Filler-To-Matrix Ratio On The Mechanical Strength Of Palm-Based Biocomposite Board, *Polymer International*, 55: 190-195
- Badri, K.H. & Mat Amin, K. A. 2006^c. Oil Palm-Based Biocomposites. *Journal of Oil Palm Research*, (Special Issue-April 2006):103-113
- Badri, K.H., Othman, Z. & Mohd Razali, I. 2005. Mechanical properties of polyurethane composites from oil palm resources. *Iranian Polymer Journal*, 14 (5): 987-993
- Badri, K.H., Othman, Z. & Ahmad, S.H. 2004^a. Rigid Polyurethane Foams From Oil Palm Resources, *Journal Of Materials Science*. 39(16-17):5541-5542
- Badri, K.H., Shahaldin, F. H. & Othman, Z. 2004^b. Indigenous Coating Material From Palm Oil-Based Polyamide. *J. Mater. Sci. Letters*, 39 (13):4331-4333.
- Khairiah Haji Badri. 2002. Preparation and Charaterization of Polyurethane Foam from RBD Palm Kernel Oil-Based Polyurethane Polyol and Oil Palm Empty Fruit Bunch Fiber As Filler. *Proceeding of National Science Fellowship (NSF) Workshop*, pp 114-120.
- Badri, K.H., Ahmad, S.H & Zakaria, S. 2000^a. Development of Zero ODP Rigid Polyurethane Foam From RBD Palm Kernel Oil: *J. Mater. Sci. Letters*, 19: 1355-1356.
- Badri, K.H, Ahmad, S.H. & Zakaria, S. 2000^b. Thermal, Crystallinity and Morphological Studies on the Filled RBD Palm Kernel Oil Polyurethane Foam: *Nuclear Science Journal of Malaysia*, 18 (2): 57-62.
- Badri, K.H., Ahmad, S.H. & Zakaria, S. 2001^a. Production of a High-Functionality RBD Palm Kernel Oil-Based Polyester Polyol. *J. Appl. Polym. Sci.*, 81 (2): 384-389.
- Benli, S., Yilmazer, U., Pekel, F. & Ozkar, S. 1998. Effect of Fillers on Thermal and Mechanical Properties of Polyurethane Elastomer, *J. Appl. Polym. Sci.* 68: 1057-1065.

- Berlin, A.A. & Zhitinkina, A.K. 1982. Foam Based on Reactive Oligomers, Polyurethane Foams, pp. 51-111. London: Howard Publishing Inc.
- Bhunia, H.P., Jana, R.N., Basak A., Lenka, S. & Nando, G.B. 1998. Synthesis of Polyurethane From Cashew Nut Shell Liquid (CNSL), A Renewable Resource. *J. Appl. Polym. Sci.* 36 (3): 391-400.
- Burgess, Jr., P.E & Hilado, C.J. 1973. Thermal Decomposition and Flammability of Foams: *Plastic Foams* Part II. Ed. Frisch, K.C & Saunders, J.H. pp. 855-871. New York: Marcel Dekker, Inc.
- C:\Database\wiley275.1.1999. Library Search of Acquisition Method. University of Malaya.
- Chian, K.S. & Gan, L.H. 1998. Development of a Rigid Polyurethane Foam From Palm Oil. *J. Appl. Polym. Sci.*, 68 (3): 509-515
- Chittolini, C. 1999. *Polyurethane Foam-Mixing Isocyanate Component and Polyol Component Including Pentane and Dialkanolamine Derived from Vegetable Oil or Fat to Make Polyurethane Foam*. US 5859078
- Colvin, B.G. 1995. Low Cost Polyols From Natural Oils, *U'tech Asia '95*. 36: 1-10
- Crawford, D.M. & Escarsega, J.A. 2000. Dynamic Mechanical Analysis of Novel Polyurethane Coating for Military Applications. *Thermochimica Acta*, 357-358: 161-168
- Cunningham, R.L., Gordon, S.H., Felker, F.C. & Eskins, K. 1997. Jet-Cooked Starch Oil Composite in Polyurethane Foams. *J. Appl. Polym. Sci.* 64 (7): 1355-1361
- Frisch, K.C. 1985. Fundamental Chemistry and Catalysis of Polyurethanes, *Polyurethane Technology*, Ed. Bruins, P.F. pp. 12-17. New York: Interscience Publishers.
- Harding, R.H. 1965. Effect of Cell Geometry On PU Foam Performance, *J. Cell. Plastics*, 1: 224
- Hass, P.F. & Uhlig, K. 1985. Additive and Auxiliary Materials, *Polyurethane Handbook*, 2nd ed. Ed. Oertel, G. pp. 98. New York: Hanser Publisher.
- Hepburn, C. 1991. Polyurethane Elastomers. 2nd ed., pp. 441: Great Britain: Elsevier Science Publishers Ltd.
- IR Mentor Pro Classes. 1990. Bio-Rad Laboratories, Sadtler Division, PEIM: 6
- Javni, I., Petrovic, Z.S., Guo, A. & Fuller, R. 1999. Thermal Stability of Polyurethane-Based on Vegetable Oils. *Annu. Tech. Conf.-Soc. Plast. Eng.* 3: 3801-3805
- Jedlinski, Z.J. 1992. Polyester: Handbook of Polymer Synthesis Part A, Ed. Kricheldorf, H.R. pp. 645-648. London: McGraw-Hill.
- Loudon, G.M. 1988. Chemistry of Carboxylic Acids, *Organic Chemistry*. 2nd ed. pp. 816-817. London: Mc Graw Hill.
- Mohapatra, D.K., Das, D., Nayak, P.L. & Lenka, S. 1998. Polymers From Renewable Resources. XX. Synthesis, Structure And Thermal Properties Of Semi- Interpenetrating Polymer Networks Based On Cardanol-Formaldehyde Substituted Aromatic Compounds Copolymerized Resins And Castor Oil Polyurethanes. *J. Appl. Polym. Sci.* 70 (5): 837-842
- Nayak, P., Mishra, D.K., Parida, D., Sahoo, K.C., Nanda, M. Lenka, S. & Nayak, P.L. 1997. Polymers From Renewable Resources. IX. Interpenetrating Polymer Networks Based On Castor Oil Polyurethane Poly(hydroxyethylmetacrylate): Synthesis, Chemical, Thermal and Mechanical Properties. *J. Appl. Polym. Sci.* 63 (5): 671-679

- Oertel, G. 1993. *Polyurethane Handbook: Chemistry-Raw Material-Processing- Application- Properties*. Cincinnati: Hanser Gardner Publications, Inc.
- Parthiban, S., Ooi, T.L., Kassim Shaari, N.Z., Ahmad, S., Wiese, D. & Chua, M.C. 1999. Polyurethane From Palm-Based Polyols, *Palm Oil Technical Bulletin*, September-October 1999: 4-6
- Pourjavadi, A., Rezai, N. & Zohuriaan-M, M.J. 198. A Renewable Polyurethane: Synthesis and Characterization of the Interpenetrating Networks (IPNs) From Cardanol Oil. *J. Appl. Polym. Sci.*, 68: 173-183
- Roff, W.J., Scott, J.R. & Pacitti, J. 1971. *Fibres, Films, Plastics and Rubbers: A Handbook of Common Polymers*. Pp. 446-457. New York: Butterworth & Co. (Publishers) Ltd.
- Rozman, H.D. Tay, G.S., Kumar, R.N., Abusamah, A., Ismail. H. & Mohd Ishak, Z.A. 2001a. Polypropylene-Oil Palm Empty Fruit Bunch- Glass Fibre Hybrid Composites: A Preliminary Study on the Flexural and Tensile Properties. *European Polymer Journal*. 37 (6): 1283-1291.
- Rozman, H.D., Tay, G.S., Abubakar, A. & Kumar, R.N. 2001b. Tensile Properties of Oil Palm Empty Fruit Bunch- Polyurethane Composites. *European Polym. Journ.*, 37: 1759-1765
- Rozman, H.D., Lai, C.Y., Ismail, H. & Mohd Ishak, Z.A. 2000. The Effect Of Coupling Agents On the Mechanical And Physical Properties Of Oil Palm Empty Fruit Bunch- Polypropylene Composites. *Polym. Int.* 49 (11): 1273-1278
- Rozman, H.D., Kon. B.K., Abusamah, A., Kumar, R.N. & Mohd Ishak, Z.A. 1998. Rubberwood-High Density Polyethylene Composites: Effect of Filler Size and Coupling Agents on Mechanical Properties. *J. Appl. Polym. Sci.* 69: 1993-2004
- Silverstein, R.M., Bassler, G.C. & Morrill, T.C. 1991. *Spectrometric Identification of Organic Compounds*, 5th ed., New York: John Wiley & Sons, Inc
- Tamano, Y., Yoshimura, H., Ishida, M., Okuzono, S. & Lowe, D.W. 1996. The Characteristics and Role of tertiary Amine catalysts For Polyurethane Foams: Review of Tertiary Amine Catalysts "TEDA & TOYOCAT", *Conference Paper of UTECH '96*
- Wood, G. 1990. The Chemistry and Materials of PU Manufacture, *The ICI Polyurethane Book*, 2nd ed. Ed. Genge, R. & Sparrow, D. pp. 41-42. New York: John Wiley & Sons.

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