SYNTHESIS OF RIGID POLYURETHANE FOAM USING POLYOLS FROM FRACTIONATED LOCALLY SOURCED VEGETABLE OIL

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Abstract: The palm and groundnut oil used for this study were bleached, fractionated and subjected to conventional method of synthesizing polyol from vegetable oil. The synthesized polyols were used for production of rigid polyurethane (RPU) foams through reaction with 2,4–diphenyl methylene diisocyanate (MDI) using two-shot method. The density, water absorptivity and compressive strength of the vegetable oil based RPU foams were better than those of the petrochemical based RPU foam. These results indicate that bio-based polyols have good potential for replacement of petroleum based polyols in synthesis of RPU foam as precursor in chemical and allied industries.

Keywords: Compressive strength, density, polyols, rigid polyurethane, vegetable oil

Introduction

Polyurethanes (PU) are any type of polymer containing a urethane linkage. The urethanes bond is formed by reacting isocyanates with compound containing active hydrogen, such as diols, that contain hydroxyl-groups (Pechar *et al*., 2006). Since there are many compounds containing active hydrogen and many different diisocyanate, the number of PU that can be synthesized is also large. The specific properties of the PU can be tailored to a specific need by combining the appropriate compounds (Dworakowska *et al*., 2014). PUs come in so many forms and can have a wide variety of properties; it is also used in many different applications, such as rigid or flexible foams, and as coating or adhesive material (Jabar *et al*., 2017a). Rigid polyurethanes (RPU) are used in insulation and floatation applications (Chian and Gan, 1998).

Biodegradable polymer foams are investigated not only because of the increasing waste and environmental problems from traditional polymer foams, but also because of the unpredictable price of petroleum products that are used in manufacturing the polymer foams (Tu *et al*., 2007). Replacing petrochemical based raw materials with bio based raw materials used in the synthesis of polyurethane foam will be a major milestone in Nigeria PU foam industry (Jabar *et al*., 2017a). Several research works have been published on synthesis of polyols from vegetable oil. Some of the researchers that have done this are. Meier *et al*. (2007) in plant oil renewable resources as green alternatives in polymer science. Prociak, (2008) in heat-insulating properties of rigid PU foams synthesized with use of vegetable oil-based polyols. Jabar *et al*. (2015) in Chemical modification of *Jatropha curcas* and *Thevetia peruviana* oil as starting materials for chemical industry. Preparation of PU foam from triglycerides containing mixture of saturated and unsaturated fatty acid may induce unnecessary coagulation of the resin system and attaining an irreversible state known as gel point (Siyanbola *et al*., 2013).

Modification of the fatty acid profile in the triglyceride chains may checkmate this deficiency by providing enough unsaturated sites for subsequent modifications (such as epoxidation and hydroxylation) in such triglycerides. As a result of this limitation, this paper presents the synthesis of RPU foam from fractionated vegetable oil, where saturated fatty acids are eliminated from the extracted oil in order to optimize the percentage functionality of the double bond in vegetable oil by physisorption of the saturated fatty acids (Siyanbola *et al.*, 2015).

The major focus in this research work is to investigate the possibility of converting fractionated vegetable oil into polyol and subsequent production of rigid polyurethane foams from the synthesized vegetable oil based polyol.

Materials and Methods

Materials

Palm and groundnut oil were obtained from Oja-Oba market Akure, Ondo State, Nigeria. Reagents used were AnalaR grade and obtained from Pascal scientific limited, Akure and Department of Chemistry, Federal University of Technology, Akure, Ondo State, Nigeria.

Methodology

Bleaching

Activated earth (6.8 g) was weighed into a 500 ml beaker containing vegetable oil (200 ml). The mixture was heated at 100^{o}C for 15 min with continuous stirring; the slurry was then filtered into a conical flask (Okolo and Adejumo, 2014).

Fractionation

Vegetable oil (150 ml) was measured into a 500 ml beaker, heated for about 5 min at 70^{o}C and allowed to cool down for 90 min in a cooling container to 5^{o}C according to Norizzah *et al*. (2014). The fractionated oil was centrifuged at 2500 rpm for 10 min. The liquid fractionated vegetable oil was separated using separating funnel.

Epoxidation and hydroxylation reaction

Epoxidation and hydroxylation reaction of palm and groundnut oil were carried out as described in previous study (Jabar *et al*., 2015).

Physicochemical properties of the vegetable oil

The physicochemical properties of the unmodified and chemically modified vegetable oil were determined as described in the previous study Jabar *et al*. (2015).

Synthesis of the rigid polyurethane foams (RPU)

Polyurethane (PU) foams were synthesized by 2-shot method at room temperature as described by Jabar *et al*. (2017a) with a slight modification. The modification read thus; The resin (mixture of polyol and additives) was reacted with stoichiometric amount of 2,4–diphenyl methylene diisocyanate (MDI as part B) at ratio 1.5:1 (resin to MDI), stirred manually for 10 s in a disposable container as described by Jabar *et al*. (2017a). The mixture was then poured into a cardboard open mould with dimensional size (100 × 120 × 70 mm) and allowed to rise freely. The formulations used for petroleum based, palm oil and groundnut oil based PU foams are given in Table 1. The stages undergone before RPU foam finally formed are development of cream colour from whitish colour mixture, formation gel, gel rise freely to full height and finally becomes a tack free mould of foam. The foam was then cured for 25 min. The foams were later conditioned at room temperature (about 28^{o}C) for two weeks before finally characterized (Jabar *et al*., 2017a).

Table 1: Polyurethane foam production recipe

Reagents (php)	Petroleum based PU	Bio/Petroleum based PU	
	PBRPU	PORPU	GORPU
Petroleum based polyol	100	50	50
Bio based polyol	-	50	50
Distilled water	3	3	3
Silicone oil	4	4	4
Triethylenediamine	0.45	0.45	0.45
Dibutyl-tin dilaurate	0.15	0.15	0.15
MDI	66.7	66.7	66.7

PU: Polyurethane foam; PBRPU: Petroleum based PU; POP: Palm oil based polyol; GOP: Groundnut oil based polyol

Core density

The densities of the PBP, POP and GOP based RPU foams were measured according to ASTM D 1621-08. Total of three samples from each of the foam specimens with dimensional size 30 × 30 × 30 mm (length × breadth × thickness) were cut from RPU foam at room temperature. The exact dimension of the foam samples was measured as described in previous study (Jabar *et al*., 2017b).

Water absorption measurement

Water absorption test was carried out according to ASTM D 570. Each of the RPU foam specimens with dimensional size 30 × 30 × 30 mm (length × breadth × thickness) was weighed before 24 h of soaking in distilled water and the final weight of foam sample was taken after the sample has been withdrawn from distilled water and dried with tissue paper as described by Vashist and Kaushal (2013). Water absorption was calculated using Eq. 1.

$$\text{Water absorption} = \frac{W_1}{W_2} \text{ X } 100\% \qquad (1)$$

Where: W_1 = Weight of initial foam sample; W_2 = Weight of wet foam sample

Compressive strength of the rigid polyurethane foam

Compressive strength of the RPU foams was determined using instron universal testing machine (model 3369) according to ASTM D 1621-04. The sizes of the specimen samples were 30 × 30 × 30 mm (width × length × thickness) and crosshead speed was 25 mm/min at load of 2000 N until the thickness reduced to 90% of its original thickness as described by Jabar *et al*. (2017b). The compressive stress was recorded as average of the three replicates of each of the specimen samples.

Results and Discussion

Physicochemical properties of palm and groundnut oil

The physicochemical properties of refined palm and groundnut oil are presented in Table 2. It shows that palm and groundnut oil can serve both edible and industrial purposes according to Ibeto *et al*. (2012). The low percentage moisture content of the refined oil indicates the storage ability and quality of the oils (Jabar *et al*., 2015). Palm oil has reddish yellow colour while groundnut oil has light yellow and sweet odour like most vegetable oils. These observations are in agreement with those made by Rudrappa (2016). The values of specific gravity and viscosity may be attributed to the different fatty-acid composition and different degree of saturation (Jabar *et al*., 2015). Analysis of the unsaturated bond content indicates that palm and groundnut oil are a convenient raw material for the synthesis of the polyols (Pawlik and Prociak, 2012).

Table 2: Physicochemical properties of unmodified and chemically modified palm and groundnut oil

Properties	PO	GO	HPO	HGO
Colour	Reddish yellow	Light yellow	Yellow	Whitish yellow
Specific gravity	0.9140	0.9185	-	-
Refractive index	1.462	1.464	-	-
Viscosity mpa.s	57.65	46.58	1128	987
Moisture content (%)	0.21	0.11	0.12	0.08
Acid value (mg KOH/g)	3.71	1.43	1.82	2.1
FFA (mg KOH/g)	1.86	0.72	0.91	1.05
Iodine value (mg KOH/g)	53.5	58.8	18.45	14.89
Saponification value (mg KOH/g)	203.16	188.24	219.35	194.18

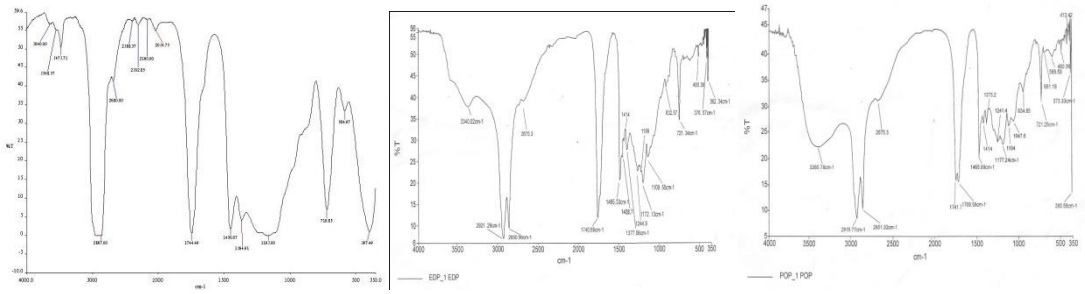
PO = Palm oil, GO = Groundnut oil, HPO = Hydroxylated palm oil, HGO = Hydroxylated groundnut oil

The acid values obtained showed that vegetable oils are good as starting material for industrial production according to the findings made by Abayeh *et al*. (2011), in quality characteristics of pumpkin seed oil. Increase in level of acid value and free fatty acid of the unmodified oil was caused by temperature of modification process greater than room temperature that might leads to formation of free fatty acid of lower molecular weight from glycerides (Adelaja, 2006).

The iodine values indicate that both palm and groundnut oil can be classified as non-drying oil (Ibeto *et al*., 2012). Saponification values implied that palm oil contains a greater number of saturated fatty acids than groundnut oil (Oluwaniyi and Dosumu, 2009). The iodine values reduced significantly while saponification increased after epoxidation and hydroxylation, this is in line with reports by Okieimen *et al*. (2005). The reduction in iodine values (Table 2) was one of the indications of successful epoxidation and hydroxylation of palm oil and groundnut oil according to Arniza *et al*. (2015).

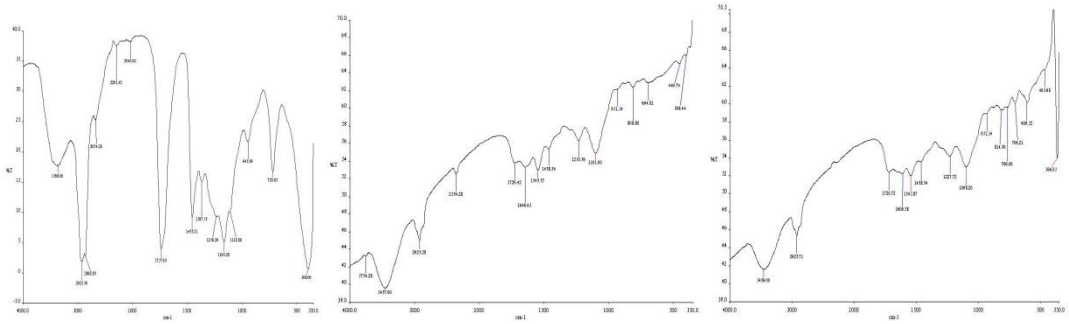
FTIR analysis

The FT-IR spectra of unmodified, epoxidized and hydroxylated palm oil are shown in Fig. 1 (spectra are of the same trend with those of groundnut oil). The replacement of peak of C=C at 308.00 in unmodified oil (Fig. 1A) with twin peak at 832.57 cm^{-1} in epoxidized oil (Fig. 1B) indicates that epoxidation was successful by converting the unsaturated double bonds (C=C) into epoxy group (C–O–C) Derawi and Salimon, (2010). The little broad peak appearing at 3340.02 cm^{-1} in epoxidized palm oil was an indication of hydrolytic cleavage of a portion of oxirane group to hydroxyl group (Fig. 1B). These observations agreed with findings made in the previous study (Jabar *et al*., 2015), in Chemical modification of *Jatropha curcas* and *Thevetia peruviana* oil as starting materials for chemical industry.



Unmodified palm oil (A) **Epoxidized palm oil(B)** **Hydroxylated palm oil (C)**

Fig. 1: FT-IR spectra of unmodified (A), epoxidized (B) and hydroxylated palm oil (C)



PBRPU (A) **PORPU (B)** **GORPU (C)**

Fig. 2: FT-IR spectra of PBRPU (A), PORPU (B) and GORPU (C)

The polyol synthesis is confirmed by the disappearance of the twin peak at 832 cm^{-1} and appearance of new broad peak at 3385.79 cm^{-1} (Fig. 1C) which indicates the opening of reactive oxirane group and its subsequent conversion into hydroxyl group in hydroxylation of epoxidized palm oil. This result agrees with report in the previous study (Jabar *et al*., 2015). The other peaks observed in unmodified and modified palm and groundnut oil polyols are: 1241.4, 1177.24 and 1211.33 (ester stretching), 1375.2 and 1369.1 (methyl groups, bending), 1465.89 and 1463.3 (alkanes, bending) and 1741.7 and 1725.11 (esters, aliphatic carbonyl stretching) cm^{-1} (Alam *et al*., 2008).

Characterization of the synthesized rigid polyurethane (RPU) foams

The FTIR spectrum of the petroleum based polyol and bio based RPU foams are shown in Fig. 2 A, B and C. The presence of amide (NH) peak was observed at 3368, 3457 and 3459 cm^{-1} for PBRPU, PORPU and GORPU, respectively (Su'ait *et al*., 2014), carbonyl group (C=O) was seen at 1737.65, 1726.42 and 1720.27 cm^{-1} and carbamate (CNH) peak was observed at 1646.63 and 1609.58 cm^{-1} in PORPU and GORPU confirming the formation of the urethane linkages in the PU according to findings made by Badri *et al*. (2010) in FTIR spectroscopy analysis of the palm-based polyurethane. The CH_2 anti-symmetric peaks were observed at 2923.50, 2925.28 and 2925.71 cm^{-1} for PBRPU, PORPU and GORPU, respectively.

The core densities of petroleum PBRPU, PORPU and GORPU foams are presented in Fig. 3. The density of PBRPU was the lowest. This observation might be as a result of moisture oven dried vegetable oil used in this study. This observation agreed with our previous study that showed how moisture in polyol enhances blowing reaction with isocyanate (Jabar *et al.*, 2017b).

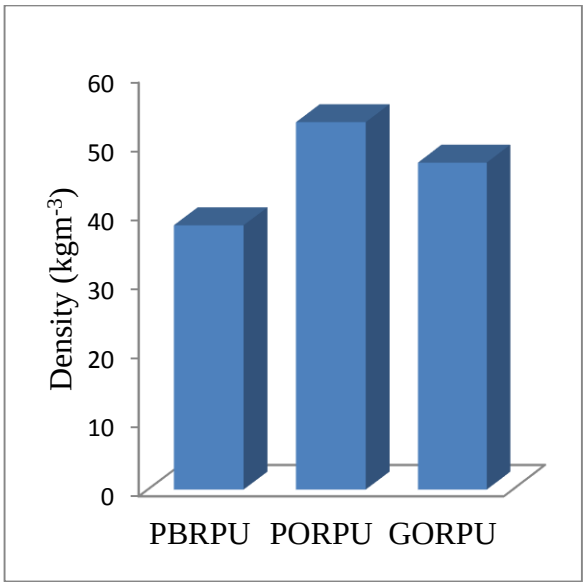


Fig. 3: Densities of PBRPU, PORPU and GORPU

Water absorptivity

Water absorptivity of foam is inversely related to foam core density. PBRPU foam has the highest water absorption capacity as seen in Fig. 4, followed by GORPU foam and PORPU foam has the lowest water absorption capacity. This observation agreed with Vashisht and Kaushal (2013). The higher porosity nature of the GORPU than PORPU also account for this observation according to our finding in previous study (Jabar *et al*., 2017b). Although, water absorptivity of all the RPU synthesized is less than industrial maximum allowed value of 1.5% according to Badri *et al*. (2010).

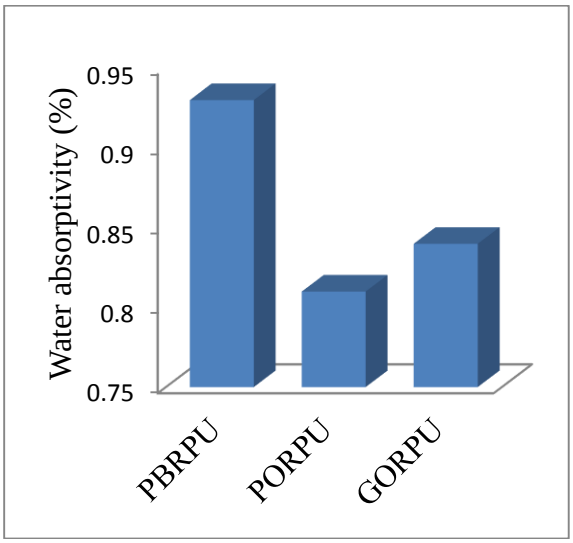


Fig. 4: Water absorptivity of PBRPU, PORPU and GORPU

Compressive strength

The result shows that vegetable oil based RPU (PORPU and GORPU) are of higher compressive strength compared to PBRPU (petroleum based); this might be due to wider pore size of PBPU (Fig. 5). This observation was supported by similar finding made by Saint-Michel *et al*. (2006) and Lee (2008). Although, all synthesized RPU are good enough for production of rigid PU foam since they formed PU foam with compressive strength greater than 100 kPa, which is the minimum recommended value of compressive strength for PU foam to be accepted as industrial standard rigid PU foam according to Seo *et al*. (2004).

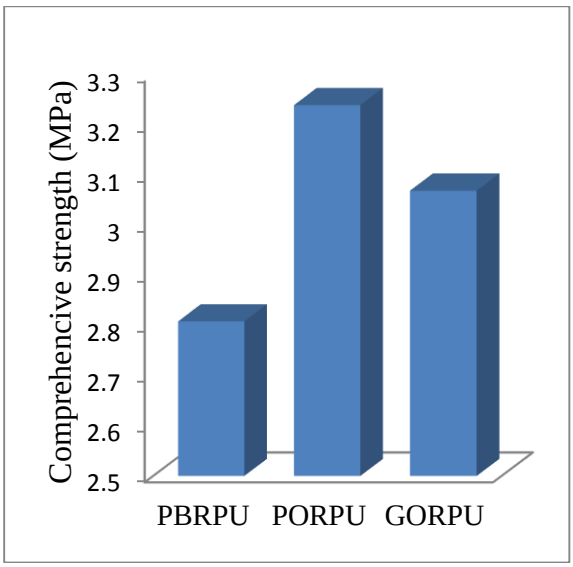


Fig. 5: Compressive strength of PBRPU, PORPU and GORPU

Conclusion

Synthesis of polyurethanes rigid foams using palm oil and groundnut oil derived polyols to partially replace petrochemical based polyol were successfully. The bio based polyols improved the density, water absorptivity and compressive strength of the synthesized RPU. The synthesized RPU could be useful in thermal insulation applications such as refrigerators, air conditioning, vacuum flask, insulated buildings as well as in flotation applications such as water and air craft where water absorption is not required.

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