



Production of Polyurethane Elastomers from *Ximenia americana* L (Wild Olive) Seed Oil and Diisocyanates

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ABSTRACT: Seed oils readily undergo derivatization by alcoholysis to yield biodegradable polyols and *Ximenia americana* plant from the family of Olacaceae has oily seeds. Hence, the objective of this paper is to assess the production of polyurethane elastomers from *Ximenia americana* L (Wild Olive) Seed Oil with diisocyanates, namely, hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI) and 4,4'-methylene diphenyl diisocyanate (MDI) respectively using standard procedure and characterized by Fourier-Transform Infrared Spectroscopy (FTIR), Instron Tensile Testing Machine and Thermogravimetric Analyzer (TGA). The tensile strength and tensile modulus for HDI-based polyurethane elastomers, 5.83 ± 0.15 and 3.95 ± 0.07 MPa respectively are higher than the corresponding ones for TDI- and MDI-based polymers. This is consistent with the highest crosslink density (γ) of 5.05×10^{-3} for HDI-based polymer with corresponding average molecular weight between crosslinks (M_c) of $197.87 \text{ g mol}^{-1}$. The polyurethane elastomers are stable up to $250\text{-}265^\circ\text{C}$ with order of stability: HDPU-1.50 > MDPU-1.50 > TDP-1.50. The results showed that diol from *Ximenia americana* seed oil is effective for production of polyurethane elastomers with properties which are comparable to ones of the non-oil-based polymers.

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Polyurethane is a versatile polymer with varied applications in materials which include foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibres, etc Miao *et al.*, (2010). It is a high tonnage polymer with production level at 14 metric tons in 2006, representing the 6th most widely used polymer. Polyurethane is the product of a reaction between a polyol (diol, oligomeric, or polymeric, hydroxyl-terminated) with an organic diisocyanate (aliphatic, aromatic or cycloaliphatic). These materials are derived from petroleum sources. But sustainable development of the environment demands increasing use of materials from bio-sources, many of which are biodegradable. Seed oils are biodegradable having functional groups which lend

them readily to derivatization reactions. They are abundant, largely non-toxic, both of which properties stand them in good stead as raw materials for polymer production. Derivatization of various vegetable oils (peanut, corn, soybean and linseed) for production of polyols via epoxidation and subsequent ring-opening reactions has been reported Garrison, (2013). An alternative method for polyol production via the alcoholysis of vegetable oils has also been reported. Radojčić, *et al.*, (2013). In both cases, polyurethanes have been produced based on the polyols and characterized. Specifically, JEFFADA™B650 is a brand name for a bio-based polyol commercialized by HUNSTMAN Company in 2010 for production of polyurethane rigid foams, sprays, coatings, adhesives,

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mastics and elastomers. The polyol was synthesized by the reaction of epoxidized soybean oil having 2 to 6 epoxide groups per molecule with an alcohol Miao *et al.*, (2010). The properties of polyurethanes from seed oil derivatives depend on a number of factors which include type, composition and distribution of fatty acid residues in the constituent triglycerides. Thus, the intrinsic properties of vegetable oils, as pertaining to fatty acid constituents can have profound influence on the ultimate properties of polyurethanes based on them Fazal-Ur-Rahman, (2010). *Ximenia americana* (Linn) plant is shrubby, grows wild and is of the family Olacaceae. Eromosele and Eromosele, (2002). It is a tropical plant which grows in the savannah part of Nigeria to an average height of about 5 meters. The fruit is a reddish brown plum which is edible and contains an oily seed kernel.

The objective of this study is to assess the production of polyurethane elastomers from *Ximenia americana* L (Wild Olive) Seed Oil by reactions with diisocyanates, namely, hexamethylene diisocyanate (HDI), toluene diisocyanate (TDI) and 4,4'-methylene diphenyl diisocyanate (MDI).

MATERIAL AND METHODS

Collection and preparation of Ximenia americana seeds: The seeds of *Ximenia americana* were collected in Yola, Adamawa State, Nigeria. The seeds were shelled by cracking to remove the kernel. The kernel were washed with water, sun-dried for two weeks (14 days) and milled into paste with a previously cleaned blender (Binatone, Japan, model BLG-400). The paste was then packed in polyethylene bag and stored in a refrigerator prior to oil extraction process.

Extraction of Ximenia americana seed oil: Oil was extracted from the paste with petroleum ether (40-60 °C) using a soxhlet extractor (Eromosele and Eromosele, 2002). 100 g of ground *Ximenia americana* seeds were packed in a soxhlet thimble and 500 ml solvent (petroleum ether) was poured into the 1000 ml soxhlet round bottom distillation flask. A condenser was connected to the top of the extractor. The heating mantle was switched on (set at 50 °C) and heat was supplied to the distillation flask. Vaporized solvent were generated and condensed as hot liquid solvent in the packed thimble. This process continued for 3 hours and resulted in the extraction of the oil through various siphoning of oil plus solvent into the distillation flask. The mixture of oil and solvent was separated by the use of rotary evaporator.

Preparation of Ximenia americana diol: *Ximenia americana* seed oil and glycerol; molar ratio of 1:3 were poured into a 500 ml three-neck reaction round

bottom flask equipped with a stirrer, a thermometer and nitrogen inlet tube. The mixture was stirred (300 rpm) and heated on a thermostatic heating mantle to a temperature of 200°C for 45 minutes. At this point, calcium hydroxide (0.1 wt % of the oil) was added as catalyst and the temperature raised to 230°C and maintained at this temperature for 3 h, after which an aliquot was withdrawn from the reaction mixture and tested for its solubility in methanol. After, cooling the reaction mixture it was dissolved with diethyl ether and washed first with 0.1 M HCl solution and then with distilled water to remove the catalyst and the residual glycerol. The ethereal layer was then dried over sodium sulphate for 24 h. The residual solvent was removed with the aid of a rotary evaporator.

Determination of gel time: The required equivalent weight of *Ximenia americana* seed oil diol as shown in table 1 was weighed into a 250 ml three-neck round bottom flask, 0.001 wt % of dibutyltindilaurate compared to the weight of diol (Sobhan *et al.*, 2002) was put into the flask. The flask was fitted with a stirrer, nitrogen gas inlet, and thermometer and reflux condenser. The set-up was mounted on a thermostatic heating mantle (Stuart, Germany). The magnetic stirrer was set at 300 rpm for each experimental run as the temperature varied between (40-80 °C). The addition of diisocyanate (HDI, TDI and MDI) from a calibrated syringe (HDI and TDI) or addition of MDI flakes was taken as the start time (measured from a stop-watch). The viscosity of the polymerization increases with time. The time at which the stirring bar became stationary, owing to high viscosity of the polyurethane resin was recorded as the gel time.

Preparation of polyurethane elastomers: A calculated quantity of diisocyanate as presented in Table 1 was added into a three-necked round bottom- reaction flask equipped with a stirrer, thermometer, reflux condenser and a nitrogen inlet mounted on a thermostatic heating mantle (Staurt Germany). A known quantity of *Ximenia americana* diol previously dried for 48h in a desiccator (containing silica gel) was added with 0.001 wt % of dibutyltindilaurate compared to the weight of polyol Sobhan *et al.*, (2002). The reaction was maintained at 30°C with continuous stirring (300 rpm) for 2h under nitrogen atmosphere to give a polyurethane prepolymer as a viscous liquid. The prepolymer was poured into a tightly covered Teflon mold to keep out moisture Bakare *et al.*, (2008), and allowed to cure at ambient temperature for 7h and at 80°C for 12h. The polymer sheets were latter removed from the mold and post-cured at an elevated temperature (for 6h at 110°C). The sheets were stored at ambient temperature for one month (30 days), during which period, secondary chemical reaction had

been completed and the microstructure fully established.

Table 1: Molar Equivalent formulation for Polyurethane Elastomers from *Ximenia Americana* diol and different diisocyanate.

Sample code	Diol	Component (equivalent in mole) Diisocyanate			
		HDI	TDI	MDI	r=[NCO]/[OH]
HDPUI.02	0.050	0.051	-	-	1.02
HDPUI.50	0.050	0.075	-	-	1.50
TDPUI.02	0.050	-	0.051	-	1.02
TDPUI.50	0.050	-	0.075	-	1.50
MDPUI.02	0.050	-	-	0.051	1.02
MDPUI.50	0.050	-	-	0.075	1.50

Determination of mechanical properties of polyurethane elastomers: Cured polyurethane elastomers were kept in a desiccator (containing silica gel) for 48h. Tensile properties were determined from stress-strain curves, with an Instron Tensile Test Machine (Model M500-25KN), at a strain rate of 10mm/min using rectangular specimens (dimensions: 50mm × 25mm × 2mm) at room temperature (25 ± 2°C). Readings for three samples from each network was used for the study. The values reported are the mean and standard deviation respectively.

Determination of density of polyurethane elastomers: The densities of polyurethane films were determined by floatation method (Gopalakrishnan and Fernando, 2011). Elastomeric films of size 50mm × 25mm × 2mm were cut-out from the cast sheets from each network. The dry weight of six specimens from each network was obtained using an analytical weight balance (LIBROR EB-330H SHIMADZU). 50 ml of distilled water was measured into six 100 ml measuring cylinders. The polymer sheets were introduced into each cylinder; the cylinders were gently spiked for the films to attain buoyancy (Barton, 1991). On attainment of equilibrium the volume of water displaced by the film from each cylinder was measured from the graduated mark on the surface of the cylinder. Density of films from each network was calculated as outlined in equation 1;

$$Density = \frac{\sum W_p/n}{\sum V_d/n} \quad 1$$

Where, $\sum W_p/n$ = summation of polyurethane films weights over n trials (n = 6); $\sum V_d/n$ = summation of volume of water displaced over n trials (n = 6)

Determination of network properties by swelling experiment: The network properties of polyurethane samples were determined by gravimetric technique (Gopalakrishnan and Fernando, 2011). Polyurethane

films (50mm × 25mm × 2mm) after taking their dry weight were placed in four different solvents: toluene (aromatic solvent), dimethylacetamide (nitrogenous solvent), acetone (ketone) and ethanol (alcohol) in a standard test-tube stopped with aluminum foil, supported on a rack and maintained at room temperature (30 ± 2°C). The films were taken out at regular intervals (24h) and solvent adhering to the surface was wiped off with cotton wool, weighed immediately and replaced in the solvent. This procedure was carried-out for three samples from each network. The time taken for wiping out the solvent from film surface and weighing was kept to a minimum in order to minimize error due to solvent evaporation. The data from swelling studies carried-out in dimethylacetamide was used to evaluate the network parameters of the polyurethane films, owing to the fact that dimethylacetamide presents the maximum equilibrium swelling coefficient for all polyurethane samples.

The equilibrium degree of swelling (Q) and volume fraction of the polymer for each network was calculated using the equations 2;

$$Q = \frac{W_p/d_p + W_s/d_s}{W_p/d_p} \quad 2$$

$$V_p = Q^{-1} \quad 3$$

Where, d_p = polyurethane film density; W_p = dry weight of polyurethane film; W_s = weight of solvent sorbed by the polyurethane film; d_s = solvent density; V_p = volume fraction of polyurethane film, swelled to equilibrium; Q = equilibrium degree of swelling

The average molecular weight between crosslinks (M_c) and crosslink density (γ) were determined using Flory-Rehner equations;

$$M_c = \frac{v_s d_p \left(V_p^{1/3} - V_p/2 \right)}{\ln(1 - V_p) + V_p + \chi V_p^2} \quad 4$$

$$\gamma = d_p (M_c)^{-1}$$

Where; V_p = volume fraction of polyurethane film swelled to equilibrium; v_s = molar volume of the solvent; d_p = density of polyurethane film; M_c = average molecular weight between two crosslinks; χ = polyurethane – solvent interaction parameter which was calculated using;

$$x = \frac{\beta + v_s (\delta_s - \delta_p)^2}{RT} \quad 5$$

Where, δ_s = Solubility parameter of solvent; δ_p = Solubility parameter of polyurethane; R = molar gas constant; T = Absolute temperature; v_s = Molar volume of solvent; β = Lattice constant which is taken as 0.34 for good solvent.

FT-IR spectroscopy: The structural components of *Ximenia americana* seed oil and its derivatives were studied with a Bruker fourier transform infrared spectrophotometer (Model 12028429). For each study, the sample was mixed with KBr cells and the spectrum was recorded, scanned in the range, 3500 to 500 cm^{-1} .

Thermal analysis of *Ximenia polyurethanes*: The thermal stability of *Ximenia americana* polyurethanes were studied with a Perkin Elmer Thermal Analyzer. For each study the sample was heated under nitrogen atmosphere from 30°C at an incremental rate of 10°C/min up to 950°C.

RESULTS AND DISCUSSION

The FTIR spectrum for *Ximenia americana* seed oil is presented in Figure 1. The peak at 722 cm^{-1} represents the bending frequency of saturated (C-C) carbon atom, while the stretching frequency at 1160 cm^{-1} shows the presence of carbonyl (C=O) in the ester group of fatty acid. The bending frequency of unsaturated alkene occurred at 1462 cm^{-1} . The peak at 1744 cm^{-1} indicates the presence of ester (C=O-O) group. The stretching at 2852 cm^{-1} and 2922 cm^{-1} show the presence of CH_2 and CH_3 moieties. The weak peak at 3008 cm^{-1} is for unconjugated unsaturation in *Ximenia americana* seed oil. The main peaks in the FTIR for *Ximenia*

americana seed oil are similar to the ones for rubber seed oil Bakare *et al.*, (2008) and linseed oil Xuecheng *et al.*, (1999). Figure 2 shows the FTIR spectrum for *Ximenia americana* diol. The spectrum shows a broad adsorption band at 3449 cm^{-1} , a stretching vibration which indicates the presence of hydroxyl (OH) group. This confirms the presence of a diol from the alcoholysis process. The peak at 1742 cm^{-1} indicates the presence of ester (C=O-O) group on the pendant fatty acid chain of monoglyceride and diglyceride molecules. Figure 3 is FTIR spectrum for *Ximenia americana* diol-based polyurethane prepolymer. The spectrum show a prominent band at 2262 cm^{-1} and disappearance of the broad band at 3449 cm^{-1} , indicating utilization of the hydroxyl groups of the diol for urethane formation (Dave and Hasmukh, 2017). The band at 2262 cm^{-1} is attributed to isocyanate (-NCO) group and indicates an NCO- terminated prepolymer. The band at 3325 cm^{-1} is the stretching vibration for urethane (-NH-C=O-O) group. The stretching vibrations at 1572 cm^{-1} and 1617 cm^{-1} (Dave and Hasmukh, 2017), are for deformation of amide I and amide II respectively.

Figure 4 is the spectrum for polyurethane film obtained from *Ximenia americana* diol. The stretching vibration at 3335 cm^{-1} shows the presence of urethane linkage. The stretching at 3009 cm^{-1} represents unconjugated unsaturation on the pendant fatty acid chain. The band at 1416 cm^{-1} shows olefinic C-H bonding vibration from the pendant fatty acid, while the band at 1623 cm^{-1} represents conjugated $\text{C}=\text{C}$ -bond of the fatty acid. The disappearance of the prominent peak at 2262 cm^{-1} and appearance of vibrations from 1623 to 1693 cm^{-1} shows the interaction of isocyanate-terminated prepolymer with the urethane linkage to form the N-H group in the allophanate crosslinks Bakare *et al.*, (2008) and Yakushin *et al.*, (2014).

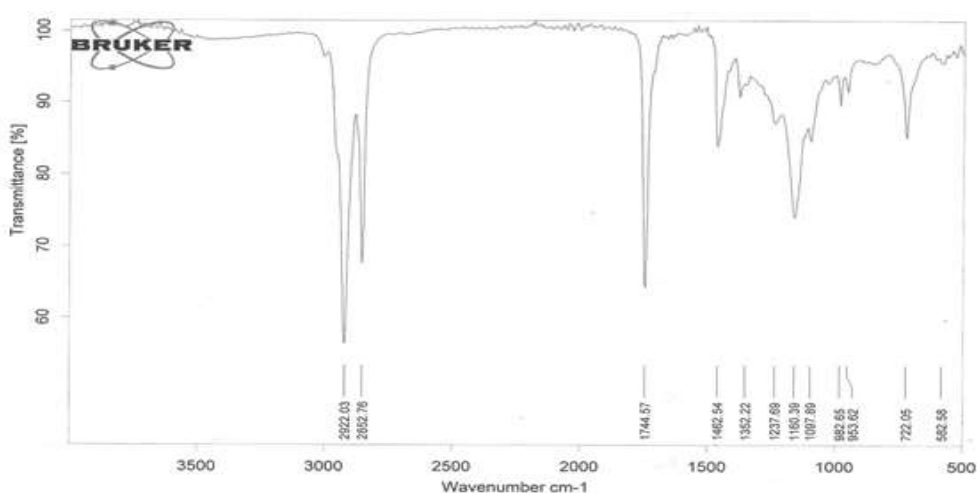


Fig 1: FTIR spectrum of *Ximenia americana* seed oil

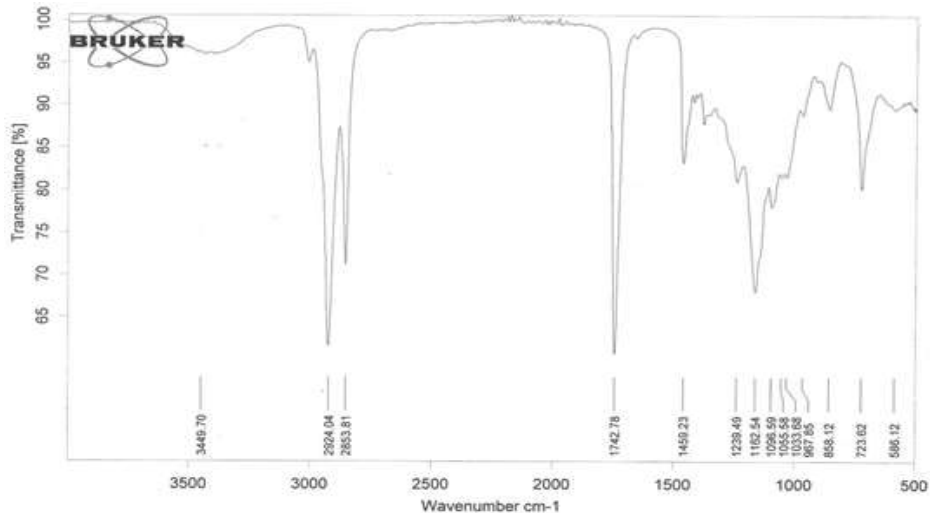


Fig 2: FTIR spectrum of *Ximenia americana* diol

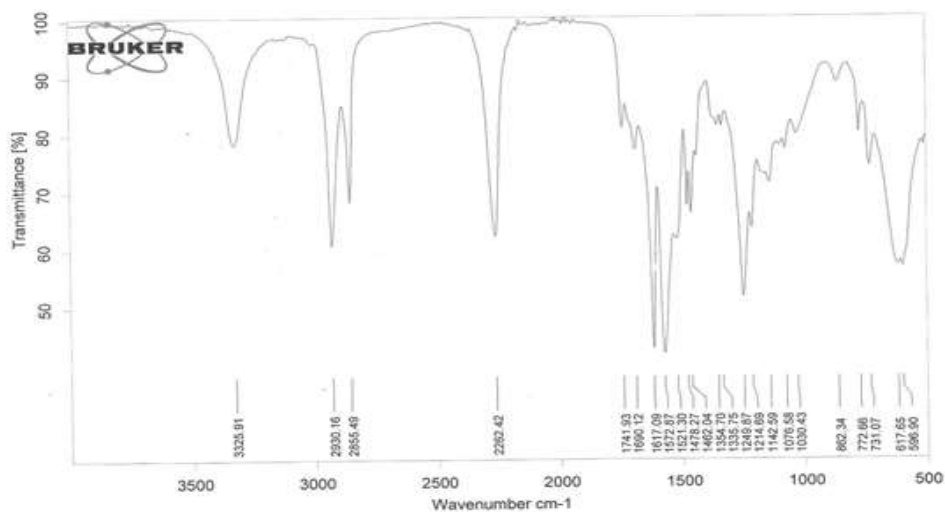


Fig 3: FTIR spectrum of *Ximenia americana* based polyurethane prepolymer

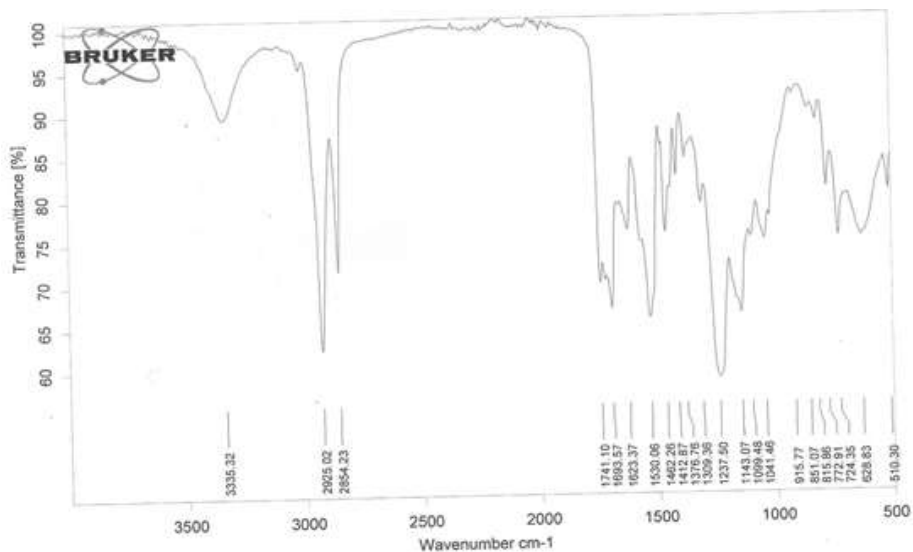


Fig 4: FTIR spectrum of *Ximenia americana* based polyurethane film

Time-Temperature gelation plots in Figures 5 and 6 for polyurethanes showed decrease in gelation time with increase in temperature characterized by temperatures of which there is rapid reduction in gelation time followed by steady decrease. The gelation time, irrespective of the isocyanate index and diisocyanate type, decreases with increase in reaction temperature. However, the decrease in gel time with increasing temperature was more pronounced for MDPU.

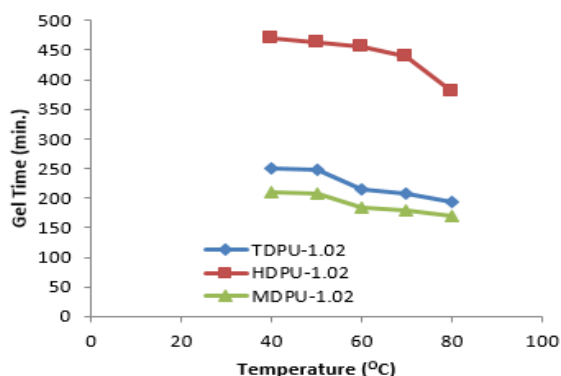


Fig 5: Time-temperature gelation for polymerization of *Ximenia americana* diol and different diisocyanate at isocyanate index of 1.02.

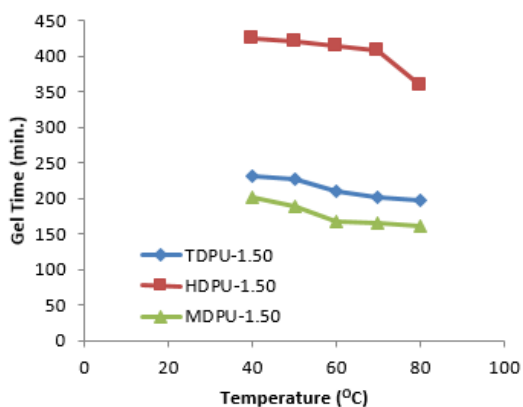


Fig 6: Time-temperature gelation for polymerization of *Ximenia americana* diol and different diisocyanate at isocyanate index of 1.50.

This suggests a more profound trimerization of methylene diphenyl diisocyanate into a heterocyclic isocyanurate ring, polyclotrimers of isocyanurate ring and formation of carbodimide Li *et al.*, (2001) and Sharma and Kundu (2006), as temperature increases. This is consistent with the relatively more reactive substituted isocyanate groups on the phenyl rings Randall and Lee (2003), making the reaction medium more viscous as temperature increases. At 80°C the gel time for MDPU-1.50 is 18 and 55% shorter than the corresponding values for TDPU-1.50 and HDPU-1.50 respectively. The time-

temperature for onset of crosslinking reaction is lower for the aromatic polyurethanes, compared to the corresponding values for aliphatic polyurethane. Specifically, for MDPU-1.50 and HDPU-1.50, the values are 188 min./50°C and 408 min./70°C respectively. These results affirm the previous reports on studies on rubber seed oil polyurethane Bakare *et al.*, (2008).

The mechanical properties (tensile strength, tensile modulus and elongation at break) of polyurethane elastomers from *Ximenia americana* diol and different diisocyanate at varying isocyanate index are presented in Table 2 below. Tensile strength and tensile modulus are highest for HDPU at 1.02 and 1.50 isocyanate index. On the other hand, elongation at break is highest for MDPU at both isocyanate indices. The latter is unexpected in light of the presence of two phenyl rings of MDI in the polymer chain which result in higher stiffness. However, the oligomerization of MDI in the polyurethane into isocyanurate rings and concomitant lengthening of crosslink points results in lowering of crosslink density, in higher average molecular weight between crosslinks and the associated high free volume within the polymer matrix. All these confer an unhindered motion on MDPU molecular chain resulting in enhanced flexibility Chattopadhyay and Webster (2009); Radojčić *et al.*, (2013). Enhanced flexibility of the later is consistent with observed lower tensile strength and tensile modulus of the polymer. The tensile modulus and elongation at break, 3.95 ± 0.07 MPa and 37.56 ± 1.09 % respectively for HDPU-1.50 are comparable to the corresponding values, 5.15 MPa and 42.226 % for rubber seed oil-based polyurethane Bakare *et al.*, (2008). Furthermore, results from studies of polyurethane elastomers based on poly (butadiene-acrylonitrile) copolymer diol and two different diisocyanate, namely, HDI and MDI, showed values for Young's modulus of 1.96 and 2.20 MPa respectively (Eromosele, 1981) which are comparable to the ones obtained from *Ximenia* diol-based polyurethane elastomers. For polyurethane elastomers synthesized from TDI, hydroxyl-terminated polybutadiene and 1,2-ethane diol as chain extender at isocyanate index of 1.3, the values for modulus and tensile strength, 0.51 and 1.08 MPa respectively Fazal-Ur-Rahman (2010) are much lower than the corresponding ones for *Ximenia* TDI-based elastomers at 1.50 isocyanate index and in the absence of chain extender i.e, 3.46 and 5.29 MPa. The effect of chain extender is apparent in the much higher value of elongation at break for the polybutadiene-based polyurethane elastomers. i.e, 311 compared to 2.62 % for *Ximenia* polyurethane. The symmetrical nature of HDPU lends it readily to crystallization and attendant strength accounting for

the highest tensile strength and modulus observed for the polymer. However, the tensile strength at both isocyanate indices are much lower compared to the value (56.7 MPa) for polyurethane from castor oil fatty amide and hexamethylene diisocyanate Yakushin *et al.*, (2014), but are higher than 0.80 to 1.40 MPa reported for castor-based polyol Hablot *et al.*, (2008). The latter is explained as arising from the lower hydroxyl number of castor oil-based polyol and a functionality of 2.7 Hablot *et al.*, (2008) compared to a much higher value (189.3 mg KOH/g) for *Ximenia* diol. High levels of covalent crosslinks are associated with high hydroxyl number and functionality of diol resulting in enhanced tensile properties of the polyurethane Prashantha *et al.*, (2001) In the case of fatty amide polyol from castor oil, the main contributory factor to the higher tensile strength are; the presence of a stronger intermolecular interaction in poly (urethane amide) due to the hydrogen bonding in the -NH groups and the fatty acids residues forming long pendant chains in poly (urethane amide), are linked directly to the rigid amide group.

Table 2: Mechanical Properties of Polyurethane elastomers from *Ximenia americana* seed oil.

Polyurethane Sample	Tensile Strength (MPa)	Elongation @ break (%)	Tensile Modulus (MPa)
HDPU-1.02	2.62 ± 0.09	16.75 ± 0.07	1.65 ± 0.05
TDPU-1.02	2.18 ± 0.13	1.06 ± 0.11	1.51 ± 0.12
MDPU-1.02	1.32 ± 0.19	18.39 ± 0.26	0.94 ± 0.16
HDPU-1.50	5.83 ± 0.15	37.56 ± 1.09	3.95 ± 0.07
TDPU-1.50	5.29 ± 0.26	2.62 ± 0.35	3.46 ± 0.22
MDPU-1.50	3.99 ± 0.34	48.53 ± 2.06	2.41 ± 0.28

The flaking and dissolution characteristics for polyurethanes at 1.02 isocyanate index in different solvents are shown in Table 3. MDPU-1.02 showed total dissolution in all the solvents albeit at varying times with minimum time in dimethylacetamide and acetone. HDPU-1.02 and TDPU-1.02 showed total dissolution in dimethylacetamide. Apparently, dimethylacetamide is a good solvent for the polyurethanes having solubility parameter (δ) of 11.3

(cal/cm³)^{1/2} Barton, (1991). The solubilities in dimethylacetamide and in toluene by the polyurethanes at 1.02 isocyanate index suggest absence of covalent crosslinks in the polymers. The swelling ratios for the polyurethanes at isocyanate index of 1.50 suggest that they are crosslinked. This is because crosslinked, polymers are infusible and can only swell in an appropriate solvent. The equilibrium swelling in such appropriate solvent can be used to determine the degree of crosslinking and average molecular weight between crosslinks Kwok *et al.*, (2004) Table 4 shows the derived parameters from swelling studies, carried-out in dimethylacetamide i.e, density, equilibrium swelling, volume fraction of polymer, average molecular weight between crosslinks and crosslink density. The crosslink densities for the polymer are in the order HDPU-1.50 > TDPU-1.50 > MDPU-1.50 consistent in reverse order, with the average molecular weight of polymers between two crosslinks, i.e, MDPU-1.50 > TDPU-1.50 > HDPU-1.50. The latter is expected judging from the sizes of the structural repeat units of the polyurethanes:

Thermal characteristics of the polyurethanes were determined from the onset degradation temperature (T_1), temperatures at 10% ($T_{10\%}$) and temperature at 50% weight loss ($T_{50\%}$); maximum temperature of degradation (T_{max}) and residual weight of sample at 500°C. this are shown in Table 5. From the degradation temperatures, it is evident that the order of stability of the polyurethanes is HDPU-1.50 > MDPU-1.50 > TDPU-1.50. the highest stability of HDPU-1.50 is consistent with its highest crosslink density as established in swelling studies. Furthermore, the results suggest more effective crosslinks in HDPU-1.50 arising from allophanates, urea, and biuret, crosslinks in addition to hydrogen bonds between the aliphatic polyurethane chains resulting in a tougher network polymer. The higher stability of MDPU-1.50 relative to TDPU-1.50 may be attributed to a preponderance of isocyanurate, uretdione and carbodiimide within the MDPU-1.50 polymer.

Table 3: Flaking and dissolution times for polyurethane samples in different solvents

Solvent	Polyurethane sample		
	HDPU-1.02	TDPU-1.02	MDPU-1.02
	Time(h)		
Dimethylacetamide	7.42 (D)	7.00 (D)	6.58(D)
Toluene	9.83 (F)	9.25 (F/D)	8.75 (D)
Acetone	8.25 (F/D)	7.17 (F/D)	6.58(D)
Ethanol	12.42(F)	11.00 (F)	9.50(D)

D- Dissolve; F- Flakes; F/D- Flakes and Dissolve.

Table 4: Network parameters of polyurethane samples in dimethylacetamide

Polyurethane sample	Density (gcm ⁻³)	Swelling degree (Q)	Volume fraction (V _p)	M _c (gmol ⁻¹)	$\gamma \times 10^3$
HDPU-1.50	1.31 ± 0.02	1.08 ± 0.16	0.926	197.87	5.05
TDPU-1.50	1.28 ± 0.20	2.42 ± 0.20	0.413	1062.55	0.94
MDPU-1.50	1.24 ± 0.06	3.16 ± 0.30	0.316	1816.75	0.55

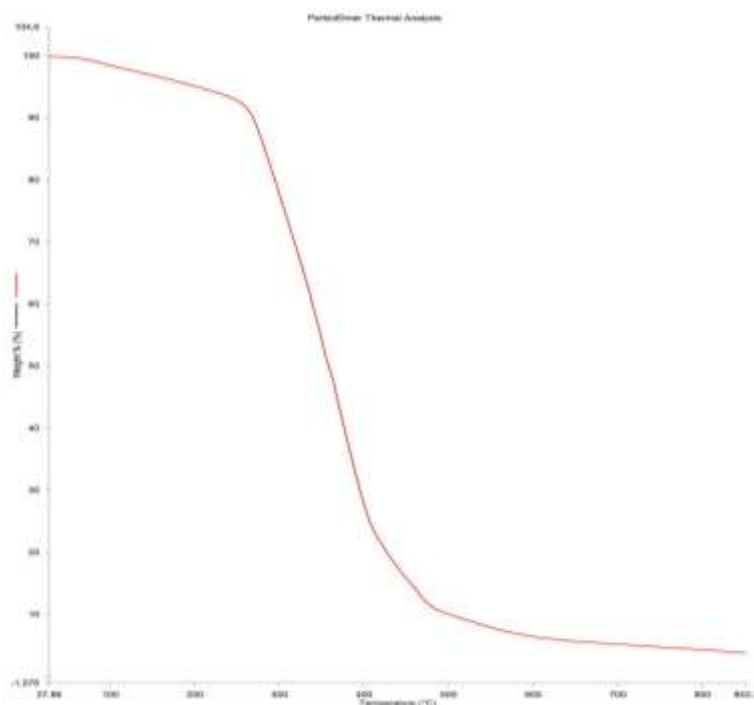


Fig 7: Thermogram for TDPU-1.50 Polyurethane

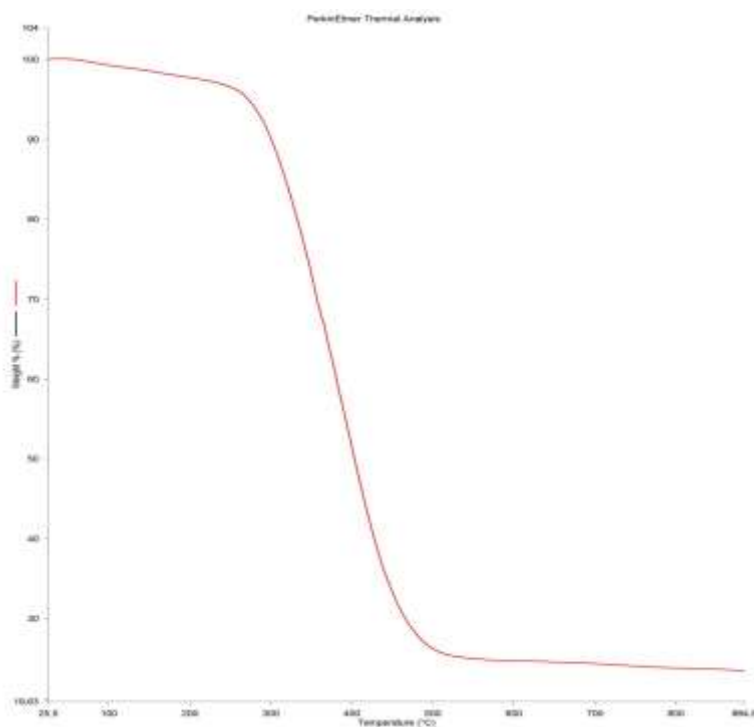


Fig 8: Thermogram for MDPU-1.50 Polyurethane

Table 5: Thermogravimetric data for *Ximenia americana* polyurethanes

Polyurethane Sample	T ₁ (°C)	T _{10%} (°C)	T _{50%} (°C)	T _{max} (°C)	Residual weight at 500° C (%)
TDPU-1.50	250	280	380	492	12.40
MDPU-1.50	260	310	420	495	18.60
HDPU-1.50	265	325	440	510	29.80

The presence of these oligomers in the polyurethane network could enhance its thermal stability Petrović *et al.*, (2008). In addition, methylenediphenyldiisocyanate is less volatile than toluene diisocyanate Shlensky *et al.*, (1991), in which case, the competing reactions leading to evolution of carbon dioxide and amine will occur at lower temperature in TDPU-1.50.

Bond scission is believed to occur at the methylene group between the aromatic rings in the methylenediphenyldiisocyanate, resulting in the possible evolution of phenylisocyanates, aniline, and 4-methyl aniline Shlensky *et al.*, (1991). The fragmentation of these secondary products to simpler molecules in MDPU-1.50 polymer network is associated with more thermal energy.

The maximum decomposition temperature, in the range 492-510°C, may be attributed to decomposition of *Ximenia americana* diol pendant fatty acid. The temperatures at maximum decomposition for *Ximenia americana*-based polyurethanes, are close to values (490-499°C) reported for rubber seed oil polyurethanes Bakare *et al.*, (2008), but are higher than the ones (418-434°C) reported for castor oil polyurethanes Hablot *et al.*, (2008). The chars at 500°C degradation temperature for the polyurethanes corroborate the relative stabilities of the polymers at preceding temperatures, HDPU-1.50 having the highest char residue of 29.80%. Overall, the results show that the polyurethanes prepared without chain extenders are stable up to 250-265°C. For TDPU-1.50, T₁ of 250°C is slightly higher than the range reported for polyurethane obtained from TDI, and Hydroxyl-terminated polybutadiene extended by various aliphatic alkane diol i.e., 215-239°C (Fazal-Ur-Rahman 2010).

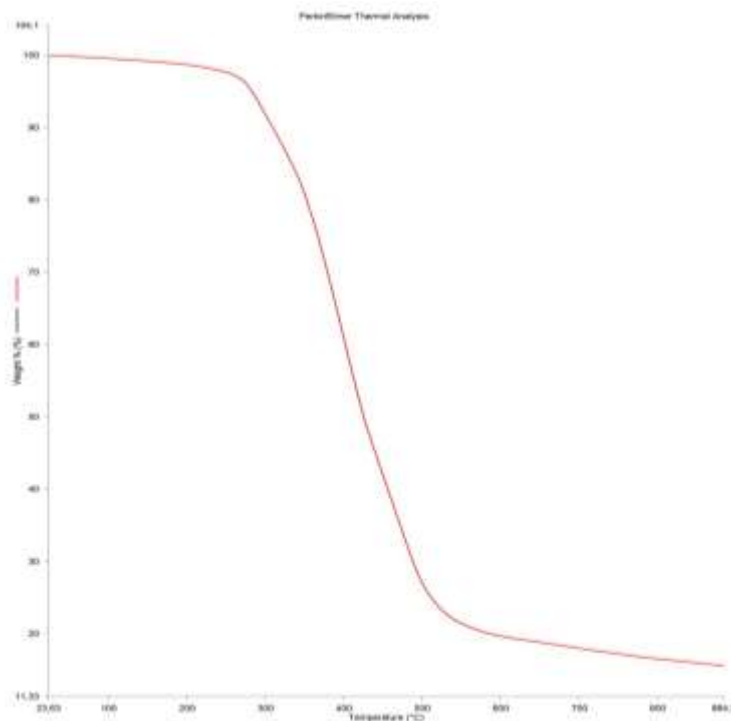


Fig 9: Thermogram for HDPU-1.50 Polyurethane

Conclusion: Polyurethane elastomers based on *Ximenia americana* diol (monoglyceride) and different diisocyanates, namely, hexamethylene diisocyanate, toluene diisocyanate and 4,4'-methylene diphenyl diisocyanate have been produced and characterized. Glycerolysis of *Ximenia americana* seed oil produced monoglyceride (diol), amongst others things. It can be concluded that *Ximenia americana* seed oil shows potentials as a renewable resource for the polyurethane industry.

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