Formation and Characterization of Chain-Extended Polyurethanes Elastomers from One-Step Hydroxylated *Ximenia americana L* (Wild Olive) Seed Oil and Diisocyanates

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Abstract*:* Vegetable oils readily undergo functionalization to produce monomers suitable for step-growth polymerization. Accordingly, this study aimed to evaluate the characteristics of hydroxylated *X. americana* seed oil and its right for purpose in separate condensation polymerizations with isophrone diisocyanate (IPDI) and 4, 4'-methylene diphenyl diisocyanate (MDI) as diisocyanate contents, ethylene diamine (EA) and ethylene glycol (EG) as chain-extenders for preparation of chain-extended polyurethanes at isocyanate index of 1.30 using the prepolymer method. The hydroxyl number (253.12±3.22 mgKOH/g) and functionality (12.21±0.54) for hydroxylated *X. americana* seed oil are within range for polyols technically required for rigid polyurethane materials. The tensile and flexural properties for the chain-extended polyurethanes in the order IPPU-1.30-EA>MDPU-1.30-EA>IPPU-1.30-EG>MDPU-1.30-EG, is in reverse order for their elongations and consistent with glass transition temperature (144-161^{0}C), polymer volume fraction (0.555-1.443), molecular weight between crosslinks (826-2874 gmol^{-1}) and crosslinked density (2.96x10^{-3}-7.01x10^{-3}). The MDI- based extended *X. americana* polyurethanes, showed greater thermal stability, while the extended aliphatic polyurethanes were less polydispersed. In conclusion, this study showed that hydroxylated *X. americana* seed oil is a suitable monomer for polyurethane production with properties comparable to those for synthetic step-growth polyurethanes.

Keywords: Chain-extenders; Copolymerization; Diisocyanates; Hydroxylated; Isocyanate index; Seed oil; Step-growth; *Ximenia americana*

Introduction

Polyurethane is a step-growth polymer prepared from hydroxyl and isocyanate-terminated molecules with vast material applications among other things, as alkyd resins, foams, elastomers, adhesives, composites and fibres, (Samuel *et al.*, 2023). Conventional method for preparation of this condensation polymer involves polyols and diisocyanates derived from petrochemicals (Bakare *et al.*, 2008). However, with the fast-depleting non-renewable petroleum resource and its contribution to carbon footprint with consequential contamination of the environment, it's imperative to explore the potential implicit in biomass to replace in part or completely these petro-derived monomers in the polyurethane industry (Oladapo *et al.,* 2013). Renewable resource notably; polysaccharides, protein and vegetable oil have been used as starting materials for the production of a plethora of polymer materials (Sharma and Kundu, 2006). Nevertheless, vegetable oil an agro-based resource, stands out from the trio and has gained more prominence as starting material for preparation of polyurethane, because of the following: plant-based oils are biodegradable and endowed with functional groups on the triglyceride molecule which lend themselves readily to derivatization reactions to import polymerizable moieties, they are plentiful and largely non-toxic (Samuel *et al.*, 2023). Properties absolutely necessary for the utilization of a reactive polyester polyol derived from vegetable oil are the characteristics of the oil with respect to; extent of oil content, composition and distribution of saturated and unsaturated fatty acid residues in the constituent triglycerides (Gonzalez-Paz *et al.*, 2011). Accordingly, the basic and essential properties of vegetable oils, with respect to fatty acid constituents can have profound influence on the ultimate properties of polyurethanes based on them (Fazal-Ur-Rahman, 2010).

Polyurethane materials are composed of short alternating polydispersed blocks of soft segment formed from polyester or polyether-polyols and hard segment with molecular rigidity are based on diisocyanates and low molecular weight chain extenders (Xiao-Dong *et al.*, 2009). The high degree of thermodynamic immiscibility between the rigid polar and malleable polyol components, accounts for polyurethanes exhibiting micro-structural phase separation (Yakushin *et al.*, 2014), and present chain-extended and crosslinked polyurethanes with an architectural orientation with the rigid domain dispersed in the matrix of soft segment (Swapan, 2018). These two phased morphological arrangements is greatly determined by diisocyanate and polyol-types, stochiometric ratio of monomers, type of chain extender, polymerization temperature and mode of polymer preparation (Bakare *et al.*, 2008). Traditionally, polyols from the alcohoylysis of the ester groups in *X. americana* seed oil by glycerol (a trihydric alcohol) and epoxidation followed by oxirane-ring opening has received remarkable attention as candidate for many applications; foam, adhesives, lubricant, and composites (Okoye *et al.*, 2021). However, these processes present with the following demerits: loss of fatty acid acyl chains, multi-step and energy intensive. In addition, the derived polyol (α or β- monoglyceride) via alcoholysis, at best, have only two hydroxyl groups per triglyceride molecule, low hydroxyl number and functionality, with diglyceride and residual triglyceride molecules (Samuel *et al.*, 2024). The presence of these esters with dangling pendant acyl chains, constitute steric burden and results to an imbalance in the physico-mechanical, physico-chemical and thermo-physical properties of the polyurethane material

(Engels *et al.*, 2013), occasioned by dispersed distribution of urethane groups on the isotactic polymer chain.

Ximenia americana plant is a semi-scandent bush-forming shrub of the family Olacaceae and native to tropical Africa (Storr, 1995). The flowering and fruiting of *X. americana* is not determined by climatic condition, the fruits are pleasant to eat and also used for making juice, jams and jellies. *X. americana* plant is known locally as; Tsada in Hausa, Chabbuli in Fulani, Anomadze in Tiv and Igo in Yoruba (Oladapo *et al.*, 2013). The seed oil of *X. americana* is replete with polyunsaturated fatty acids, non-edible due to the presence of erucic acid and rarely used for any commercial purpose, relative to soybean, linseed, palm, cotton, groundnut oils (Eromosele and Eromosele, 2002). Vinyl groups are known to react with alkaline potassium permanganate solution to import nucleophilic hydroxyl moieties, which also connote a qualitative confirmatory assay for unsaturated organic molecules (Nair *et al.,* 2018). Recently, for the first time, polyurethane was produced from one-step hydroxylated rubber seed oil as polyol and methylene diphenyl diisocyanate (Justine *et al.,* 2020). However, this novel chemical route has never been exploited to transform *X. americana* seed oil into a hydroxyl-terminated molecule and broaden the polyurethane raw material base. Therefore, this study aims to prepare a reactive polyester polyol from one-step hydroxylation of *X. americana* seed oil, characterized the modified oil and evaluate the properties of chain-extended polyurethanes from its copolymerization reactions with different diisocyanates and chain-extenders in toluene at 1.30 isocyanate index.

Materials and Methods

Materials

Hydroxylated *X. americana* seed oil derived from *Ximenia americana* seeds purchased from a local market in Kanya, Danko-Wasagu Local Government Area of Kebbi State, was used as polyol, isophrone diisocyanate (IPDI), methylene diphenyl diisocyanate (MDI), ethylene diamine (EA), ethylene glycol (EG) and other chemicals, reagents and materials used for this study were procured from Sigma-Aldrich and used as supplied. Distilled water used was prepared in the Central Research Laboratory of the Federal University of Agriculture, Zuru where this study was domiciled.

Methods

Pretreatment of Ximenia americana seeds

The seeds were cracked to obtain the kernel, which were washed under running tap water, sun-dried, milled to paste with a food blender. The paste was packed in plastic container and stored in a refrigerator prior to oil extraction.

Extraction of Ximenia americana seed oil

Ximenia americana oil was extracted from the paste using a soxhlet extractor as described by (Samuel *et al.*, 2024) with slight modification. 100 g of paste was packed in a soxhlet thimble and 500 ml petroleum ether was poured into the 1 L soxhlet round bottom distillation flask. A condenser was connected to the top of the extractor. The heating mantle was set at 60 ºC and heat was supplied to the distillation flask, to vaporize petroleum ether, which later condensed in the packed thimble as a mixture with *X. americana* oil. After a 6 h exhaustive extraction process, *X. americana* oil was separated from the solvent in a rotary evaporator (RE-100D).

Hydroxylation of X. americana seed oil

X. americana seed oil was degummed (Samuel *et al.,* 2024). The method as described by (Nair *et al.*, 2018) was used with slight modification for the hydroxylation reaction. 100 g of degummed *X. americana* seed oil was weighed into 500 ml three- neck reaction round bottom flask containing 10 ml 0.1 M NaOH (to saponify free fatty acid and produced soap molecule insitu). The flask was then fitted with a thermometer, a stirrer and dry nitrogen gas inlet tube, homogenized (100 rpm for 30 minutes) under nitrogen purged at 5 mL/min and heated on a thermostatic heating mantle to a temperature of 50ºC for 1 h with continuous stirring (100 rpm) under nitrogen. The neutralized oil was then cooled to ambient temperature and equilibrated in an ice-bath, to attained 4º C. The hydroxylating reagent ; prepared by adding 50 ml 5.0×10^{-3} M $KMnO_4$ to 5ml 1.0×10^{-4} M NaOH in a 250 ml volumetric flask containing 20 ml distilled water, was then added slowly over a period of 30 minutes to 100 g neutralized *X. americana* oil with the temperature of the reaction mixture maintained at 4º C. After the addition, the reaction flask was stirred (200 rpm) for 2 h (to allow for transport of the oxidant across the micelle) (Justine *et al.*, 2020). The hydroxylated oil was extracted twice with ethyl acetate; and the solvent (ethyl acetate), separated with a vacuum pump. The crude product was purified by warming (60^0 C) with activated charcoal and the purified hydroxylated *X. americana* seed oil (polyol) dried over silica gel for 72 h.

Characterization of X. americana seed and hydroxylated oils

The oils were characterized for the following; hydroxyl number, acid value, functionality, iodine value and specific viscosity. All determination was done in triplicate and the values reported are the mean and standard deviation.

Measurement of hydroxyl number and functionality for X. americana seed and hydroxylated oils

The hydroxyl number was determined as outlined (ASTM D4274-88). 2.0 g of oil sample was weighed into a 250 ml glass-stopped Erlenmeyer flask. 5 ml maleic anhydride was added to the flask, the flask was thoroughly but gently swirled for 10 minutes. 5 ml maleic anhydride was measured into an empty flask (for the blank determination). The flasks were placed on a steam bath, under reflux condensers and heated for 1 h. 10 ml distilled water was added to each flask, to hydrolyze excess maleic anhydride. The flasks were then cooled to room temperature and three drops of phenolphthalein indicator added to each flask and titrated with 0.5 N ethanolic potassium hydroxide solution to a faint pink endpoint. The hydroxyl number and functionality of the oils were evaluated as follows;

$$Hydroxyl\ number\ = \frac{[(B-S)\ x\ N\ x\ 56.1]}{W} \qquad (i)$$

$$Functionality = \frac{[OH\ number\ x\ W]}{56.100} \qquad (ii)$$

B = volume of KOH solution required for blank; S = volume of KOH solution required for titration of the maleiated sample W = weight of sample used for maleiation N = normality of the ethanolic KOH solution.

Measurement of iodine value for X. americana seed and hydroxylated oils

Iodine value of the oil samples were measured according to (AOAC 1992). 10 ml 15% KOH was added to 2.0 g of oil sample contained in a 250 ml volumetric flask. 30 ml Dam's reagent mixture that was stationed initially for 30 minutes in a cupboard was also added. The resulting solution was titrated with 0.12 M Sodium Thiosulfate. Titration was also carried out for the blank. The iodine value (IV) was evaluated;

$$Iodine\ value = \frac{[(B-V)\ x\ M\ Sodium\ Thiosulfate\ x\ (0.3\ x\ 12.69)\ ]}{W} \quad \text{(iii)}$$

B is the volume of blank titre; V is the volume of sample titre, M is the molarity of Sodium Thiosulfate and W is the weight of oil sample.

Determination of acid value for X. americana seed and hydroxylated oils

A mixture of 25 ml diethyl ether with 25 ml of ethanol and 1ml 1% phenolphthalein solution contained in a 250 ml volumetric flask was carefully neutralized with 0.1 M KOH (blank titration), A 0.1 M KOH solution was used to titrate 2.0 g of the solvent homogenized oil sample (25 ml diethyl ether + 25 ml ethanol + 1ml 1% phenolphthalein + 2.0 g), with constant agitation until the content of the flask turned pink. The acid value (AV) was evaluated;

$$Acid\ value = \frac{[(B-V)\ x\ N\ x\ 56.1\ ]}{W} \quad \text{(iv)}$$

B is the volume of KOH for blank titre, V is the volume of KOH for sample titre, N (Normality) of KOH solution and W is the weight of oil sample.

Measurement of viscosity of X. americana seed and hydroxylated oils

The viscosities of the oil samples were determined with an Ostwald viscometer. The viscometer was rinsed with acetone and then dried in an aspirator. 5.0 g of oil was dissolved in 95 ml methanol, homogenized (50 rpm for 10 minutes) and fed into the upper bulb of the viscometer, and the capillary flow time of the solution from the upper to lower bulb was recorded with a stop clock. The efflux time for equal volume of 5 % sucrose solution was also determined.

$$Viscosity = \frac{t_2 - t_1}{t_1} \quad \text{(v)}$$

Where t_1 = flow time for sucrose solution, t_2 = flow time for oil sample

Preparation of X. americana chain-extended polyurethanes

The prepolymer method (Samuel, 2019) was used for the preparation, with isophrone diisocyanate (IPDI) and 4, 4'-methylene diphenyl diisocyanate (MDI) as diisocyanate contents, ethylene diamine and ethylene glycol as chain-extenders. A calculated quantity of diisocyanate equivalent to the isocyanate index as shown in table 1 was injected into the flask from a calibrated syringe (for IPDI) or was weighed into the flask in the case of MDI flakes. The three-necked round bottom- reaction flask was equipped with a stirrer, thermometer, reflux condenser and a nitrogen inlet and mounted on a thermostatic heating mantle (Staurt Germany). A known quantity of hydroxylated *X. americana* oil previously dried for 72 h was added with 10 ml toluene and 0.002 wt % of dibutyltindilaurate compared to the weight of modified oil (Sobhan *et al.*, 2002). The reaction was maintained at 30°C with continuous stirring (200 rpm) for 3 h under nitrogen purged at 10 mL/min. to obtain a yellow viscous gel (isocyanate-terminated prepolymer resin). The required quantity of chain extender (Table 1) was added, stirred at 300 rpm for 45 minutes, aliquots of the chain-extended polymer resins were withdrawn for Gel Permeation Chromatography (GPC) to determine number and weight-average molecular weights distributions and the residual viscous polymer poured into a Teflon mold and conditioned (allowed to cure) at ambient temperature and humidity for 168 h (7 days) during which period, secondary chemical reaction occurs to fully establish the polymer microstructure. IPPU-1.30-EA, IPPU-1.30-EG, MDPU-1.30-EA and MDPU-1.30-EG represent; Isophrone polyurethane at 1.30 isocyanate index extended with ethylene diamine, Isophrone polyurethane at 1.30 isocyanate index extended with ethylene glycol, 4, 4'-methylene diphenyl polyurethane at 1.30 isocyanate index extended with ethylene diamine, and 4, 4'-methylene diphenyl polyurethane at 1.30 isocyanate index extended with ethylene glycol respectively.

Table 1: Recipes for Formation of *X. americana* chain-extended polyurethanes

Polymer sample	IPDI (g)	MDI (g)	POLYOL (g)	EA (g)	EG (g)	r = [NCO]/[OH]
IPPU-1.30-EA	9.80	-	11.56	2.24	-	1.30
IPPU-1.30-EG	9.80	-	11.56	-	3.11	1.30
MDPU-1.30-EA	-	14.52	11.56	2.84	-	1.30
MDPU-1.30-EG	-	14.52	11.56	-	4.02	1.30

Characterization of X. americana chain-extended polyurethanes

The chain-extended polymers were characterized for their average molecular weights, physico-mechanical and thermo-physical properties.

Determination of mechanical properties of X. americana chain-extended polyurethanes

The tensile properties of the polymers were determined from stress-strain curves, with an Instron Tensile Test Machine (Model M500-25KN), at a strain rate of 10mm min^{-1} using rectangular samples (dimensions: 25mm × 15mm × 1mm) at room temperature (25± 2°C). Flexural properties were measured using Instron Machine (Model 1190) according to ASTM D-790, using the same specimen dimension and a cross head speed of 2 mm/min and a gauge length span of 40 mm. All readings were taken in triplicates. The values reported are the mean and standard deviation respectively.

Measurement of network properties of X. americana chain-extended polyurethanes

The network properties of polyurethane samples were determined by gravimetric technique as polymer samples were swelled in different solvents. Polyurethane sheets (25mm×15mm×1mm) after taking their dry weight and densities (Samuel *et al.*, 2023) were placed in two different solvents: Ethyl acetate and Distilled water in a standard test-tube stopped with aluminum foil, supported on a rack and maintained at room temperature (30 ±2°C). The sheets were taken out at regular intervals (24 h) and solvent adhering to the surface was wiped off with cotton wool, weighed immediately and replaced in the solvent. This measurement was evaluated for three samples from each polyurethane-type. The swelling data from Ethyl acetate was used to determine the network parameters (equilibrium degree of swelling, volume fraction of the polymer, average molecular weight between crosslinks and crosslink density). The equilibrium degree of swelling (Q) and volume fraction of the polymer were calculated (Bakare *et al.,* 2008);

$$Q = \frac{W_p / d_p + W_s / d_s}{W_p / d_p} \qquad \text{(vi)}$$

$$V_p = Q^{-1} \qquad \text{(vii)}$$

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

The average molecular weight between crosslinks (M_c) and crosslink density (γ) were determined (Gopalakrishnan and Fernando, 2011);

$$M_c = \frac{\cup_s\, d_p \left(V_p^{1/3} - V_p / 2 \right)}{In\left(1 - V_p\right) + V_p + xV_p^2} \qquad \text{(viii)}$$

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

Where, V_p = volume fraction of polyurethane sheet swelled to equilibrium, ν_s = molar volume of the solvent, d_p = density of polyurethane film, M_c = average molecular weight between crosslinks, χ = polyurethane – solvent interaction parameter which was evaluated;

$$x = \frac{\beta + \cup_s \left(\delta_s - \delta_p \right)^2}{RT} \qquad \text{(x)}$$

Where, δ_s = Solubility parameter of solvent, δ_p = Solubility parameter of polyurethane, R = molar gas constant (8.314 J mol^{-1} K^{-1}), T = Absolute temperature, ν_s = Molar volume of solvent, β = Lattice constant which is taken as 0.34 for good solvent

Thermal analysis of X. americana chain-extended polyurethanes

The thermal stability of *X. americana* chain-extended polyurethanes were studied with PerkinElmer TGA-50, single flow meter Thermal Analyzer. 200mg of polymer sample was heated from 30°C to 950°C at an incremental rate of 10^oCmin^{-1}, under nitrogen atmosphere purged at 10 mL/min. The glass-transition temperatures (T_g) of the polymers were measured with a Heat-flux Shimadzu Differential Scanning Calorimetry (DSC-60 plus Japan). 5 mg of polyurethane sample in a sealed pan was heated at a rate of 5^0Cmin^{-1} from -140 to 600^0C

Determination of Average Molecular Weights of X. americana polyurethanes

The number average molecular and weight average molecular weights of *X. americana* chain-extended polyurethanes were investigated by Gel Permeation Chromatography (Shimadzu Shim-Pack GPC- 805) with a refractive index indicator (RID-20A), a column (CTO-40C), force air circulation column temperature and Sus piping (ID. 0.3 mm x 600 mm). Determinations were done at 35^0C with Tetrahydrofuran (THF) as eluent at a flow rate of 10 $mLmin^{-1}$. Polystyrene standard with molecular weight range $3.0x10^3$ to $4.5x10^5$ were used for calibration of the system.

Results and Discussion

Physicochemical characteristics of X. americana seed and hydroxylated oils

The hydroxyl number, functionality, viscosity, acid value and iodine value for XO (*Ximenia americana* seed oil) and HXO (Hydroxylated *Ximenia americana* seed oil) are represented in table 2.

Table 2: Physicochemical properties of hydroxylated *X. americana* seed oil and its precursor

Parameter	**OH Number (mgKOH/g)**	**Functionality**	**Viscosity (cP)**	**Acid value (mgKOH/g)**	**Iodine value (g I_2/100g)**
XO	0.00	0.00	899.97±2.44	16.11±1.01	151.98±3.13
HXO	253.12±3.22	12.21±0.54	922.85±1.05	1.82±0.06	41.98 ±0.43

X. americana seed oil (XO) Hydroxylated *X. americana* seed oil (HXO)

The remarkable decreases in acid and iodine values for the hydroxylated *X. americana* oil, relative to *X. americana* seed oil, suggest significant formation of soap molecule in-situ, occasioned by saponification of *X. americana* seed oil free fatty acid by NaOH during the neutralization process and substantial conversion of vinyl groups on the fatty acyl chain of *X. americana* seed oil to epoxy (oxirane) and hydroxyl groups even though nominal for the former group respectively. The higher viscosity and hydroxyl number recorded for the hydroxylated oil compared to its precursor, could be attributed to the oxidative stability of the preponderant vinyl groups on *X. americana* seed oil triglyceride molecule (a drying oil), thanks to the cumulative content of 92.72% polyunsaturated fatty acids largely accrued from oleic, linoleic and linolenic acids, which provided allylic ($-CH=CHCH_2-$) and diallylic ($-CH=CHCH_2CH=CH-$) centres (Eromosele and Eromosele,

2002) and the soap molecule in-situ act as dispersing agent (Justine *et al.,* 2020). All these resulted in improved molecular interaction between the hydroxylating reagent and *X. americana* triglycerides molecules, with consequential proliferation of secondary hydroxyl groups on the triglyceride chain. As expected intra-molecular hydrogen bonds between vicinal hydroxyl moieties in the hydroxylated oil will be more acute resulting in greater restricted molecular chain mobility (Cermark and Ishell, 2006), consistent with improved viscosity and higher hydroxyl functionality as evidenced in table 1. The viscosity for hydroxylated *X. americana* oil are lower compared to 987 cP for hydroxylated groundnut oil and 1128 cP for hydroxylated palm oil (Jaber *et al.*, 2018), the higher viscosities for the latter modified oils could be attributed to intra-molecular drag offered by the preponderance long chain saturated fatty acid (palmitic and stearic) in these oils occasioned by increased internal resistance of flow (Samuel, 2019). The values for hydroxyl number and functionality recorded for hydroxylated *X. americana* oil is within range (250-1000 mgKOH g^{-1}) and (3-15) respectively, technically required for polyols suitable for rigid polyurethanes materials (Zhang *et al.*, 2007), but higher than 230 mgKOH/g and 10 reported for one-step hydroxylation of rubber seed oil (Justine *et al.,* 2020).

Mechanical properties of X. americana chain-extended polyurethanes

Mechanical properties of polymers are parameters used in material science to elucidate the molecular mobility of components in the polymer mass. Table 3 shows the Tensile strength (TS), Tensile modulus (TM), Elongation at break (EB), Flexural strength (FS) and Flexural modulus (FM) of the chain-extended *X. americana* polyurethanes.

Table 3: Mechanical properties of *X. americana* chain-extended polyurethanes

Polymer sample	T.S (MPa)	T.M (MPa)	E.B (%)	F.S (MPa)	F.M (GPa)
IPPU-1.30-EA	74.81±1.33	2.35±0.11	38.39±1.78	46.28±2.06	1.12±0.07
IPPU-1.30-EG	60.99±2.21	1.83±0.05	54.14±2.46	34.79±1.43	0.62±0.03
MDPU-1.30-EA	66.93±1.78	2.16±0.14	46.92±2.07	41.66±1.64	0.81±0.04
MDPU-1.30-EG	52.86±1.89	1.24±0.09	59.47±1.93	30.45±1.23	0.43±0.02

The ethylene diamine extended polyurethanes exhibited superior tensile and flexural properties compared to those extended by ethylene glycol irrespective of diisocyanate-type. The ethylene glycol extended polymers presents as a better extensible elastomer, evidenced by their elongation at break. The higher tensile and flexural properties for the amine extended polymers could be attributed to the concentration of more urea, biuret and polyurea molecules in these polymers accrued during the preparation and conditioning of these polymers. Moreover, the stronger Hydrogen-bonds by these nitrogenous molecules, with –NH- groups, in the urethane linkages (Bakare *et al.,* 2008), provided crosslinks, which contributed immensely to the rigidity of these polymers, on application of mechanical load, these molecules act in concert with crosslinked allophanate groups and the whole fatty acid acyl chain contained in the rigid polar hard and flexible polyol components (Yakushin *et al.,* 2014), to hold-up stress to a greater proportion with reduced material elasticity,. In contrast, the lower tensile and flexural properties recorded for the alcohol extended *X. americana* polyurethanes, suggest the isotactic polymer chain is more endowed with flexible allophanates and low molecular crosslinks. Apparently, the mechanical properties of these chain-extended *X. americana* polyurethanes, indicates that the amine-extended polymers are rigid and highly crosslinked whereas, the alcohol-extended *X. americana* polyurethanes are very stretchy with low crosslinks. Generally, the highest tensile and flexural properties for the amine extended polymers, even though lower elongation for IPPU-1.30-EA relative to MDPU-1.30-EA could be attributed to the symmetrical aliphatic monomers in the former to readily crystallized and condensed into a polymer mass. While in contrast, the relative reactivities of the isocyanate moieties in MDI (Zlatanić *et al.*, 2004), resulted in formations of carbodiimide and isocyanurate, the presence of these asymmetrical heterocyclic oligomers within the polymer (Samuel, 2019), distorted the regular distributions of the constituent repeat units and crosslinks thereby, increases its free volume with a consequential reduced rigidity and enhanced flexibility. Besides, the distinctive characteristics by these oligomers to the structural orientations is more acute in MDPU-1.30-EG as evidenced by its lowest values for tensile properties, with a corresponding highest elongation at break. The elongation at break for this study (38.39±1.78-59.47±1.93%) is higher than (2.878-42.226%) recorded for polyurethane elastomers from rubber seed oil monoglyceride and diisocyanates (Bakare *et al.*, 2008). The greater elasticity for the former could be ascribed to greater internal plasticization of the whole fatty acyl chains in the hydroxylated oil relative to a single pendant acyl chain in rubber seed oil monoester in the latter polyurethanes. The tensile strength (52.86±1.89-74.81±1.33 MPa) for this study is higher than (14.80-56.30 MPa) for other polyurethanes based on hydroxylated vegetable oil (Zlatanić *et al.,* 2004) and (3.95-41.27 MPa) for polyurethanes from one-step hydroxylation of rubber seed oil (Justine *et al.*, 2020). The higher tensile strength for the condensation polymers in this study, comparatively to those highlighted, could be reconciled by the understanding that polyol with higher hydroxyl number and functionality produces highly crosslinked polymers with enhanced tensile properties.

Network properties of X. americana chain-extended polyurethanes

The network parameters are shown in table 4, while figures 1 and 2 represent the swelling behavior of the chain-extended polymers in ethyl acetate and distilled water respectively.

Table 4: Network properties of *X. americana* chain-extended polyurethanes

Polyurethane	Polymer volume fraction (V_p)	M_c (gmol^{-1})	$\gamma \times 10^3$
IPPU-1.30-EA	1.443	861	7.01
IPPU-1.30-EG	1.216	826	6.42
MDPU-1.30-EA	0.616	2874	3.54
MDPU-1.30-EG	0.555	2659	2.96

The network properties of the polymers indicate the chain-extended aliphatic polyurethanes are more endowed with stereorugalar crosslinks even though grater for IPPU-1.30-EA, thereby making these condensation polymers more infusible compared to the chain-extended cyclo-aliphatic polyurethanes as affirmed by their crosslink densities (γ). This suggests oligomerization in MDI-based reactions occasioned by the relative reactivities of isocyanates moieties (Zlatanić *et al.,* 2004) resulted in amorphous polymers with dispersed crosslinks within the polymer chain, lower polymer volume fraction and higher molecular weight between crosslinks. The higher polymer volume fraction and low molecular weight between crosslinks as shown by the aliphatic polyurethanes, implies the participating symmetrical monomers readily crystallizes in to a polymer mass with little void and low molecular weight congregants within their crosslinks.

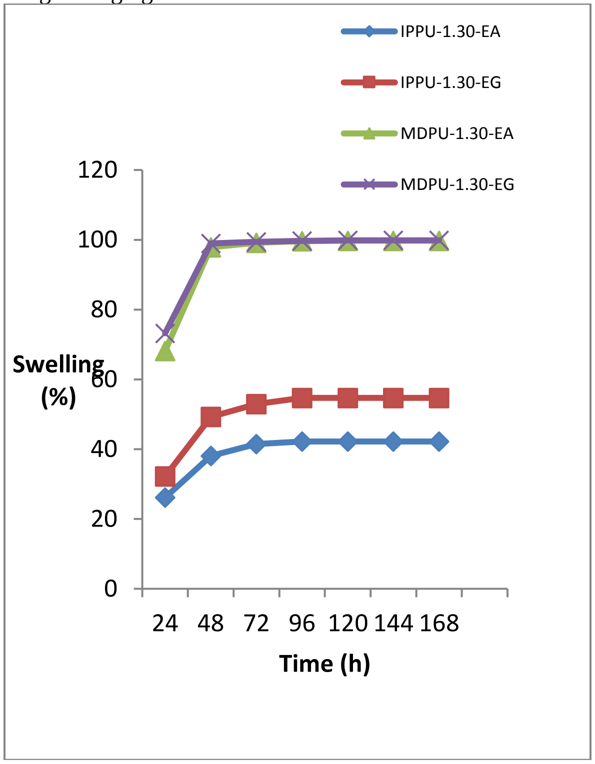

Figure 1: Swelling behavior of *X. americana* chain-extended polyurethanes in ethyl acetate

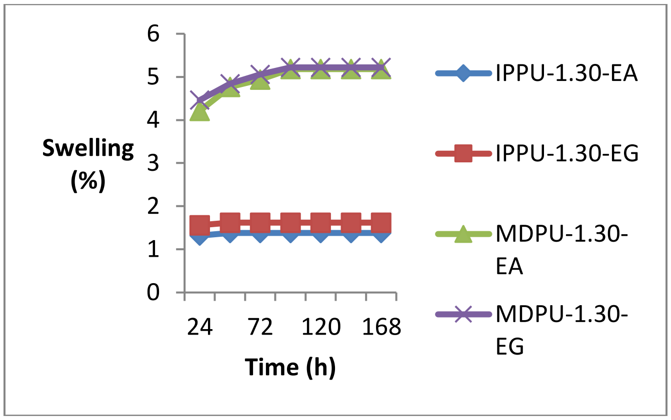

Figure 2: Swelling behavior of *X. americana* chain-extended polyurethanes in distilled water

The polymers swell incrementally with time, as elucidated in figures 1 and 2. The extended polyurethanes swells better in ethyl acetate to a maximum of 42.20% and 54.70 % for IPPU-1.30-EA and IPPU-1.30-EG respectively after 96 h and 99.73% and 99.84 % respectively for MDPU-1.30-EA and MDPU-1.30-EG after 5 days. Apparently, ethyl acetate with Hildebrand solubility parameter (δ) of 9.1(cal/cm^3)$^{1/2}$, presents as a good solvent for *X. americana* chain-extended polymers and could be ascribed to the closeness of the solubility parameter for ethyl acetate to 11.3 (cal/cm^3)$^{1/2}$ for polyurethane (Barton, 1991). The closeness of the solubility parameter of this aprotic solvent to that for polyurethane, increases osmotic pressure and consequent impregnation of the polyurethane chains by ethyl acetate due to readily convection transport of its molecules (Samuel *et al.,* 2023), consistent with the hydrophobic character of the chain-extended polymers. However, the elevated sorption of water by the cyclo-aliphatic polyurethanes as evidenced in figure 2 corroborate their amorphous morphologies, presumably, from a cocktail of isotactic, atactic and syndiotactic polyurethane chains orientations in their matrices facilitated more interplay of water molecules with the occluded isocyanate moieties in these polymers as evidenced by sol formation on their surfaces. The convoluted swelling behavioral pattern as demonstrated by the MDI-based extended polyurethanes, in both solvents, indicates the molecular similarity of their hard segments (Petrović *et al.*, 2008). Besides, the marginal increase in sorption of distilled water by the chain-extended aliphatic polyurethanes, during the whole period suggests their crystallo-hydrophobic characters and absence of water hydrolysable isocyanate moieties in the matrices of these polymers.

Thermal properties of X. americana chain-extended polyurethanes

The thermal properties of *X. americana* chain-extended polyurethanes as determined from the differential thermal analysis and thermogravimetric thermograms are shown in table 5.

Table 5: Thermal properties of *X. americana* chain-extended polyurethanes

Parameter	Polyurethane sample			
	IPPU-1.30-EA	IPPU-1.30-EG	MDPU-1.30-EA	MDPU-1.30-EG
First peak (^{0}C)	162	158	340	169
Second peak (^{0}C)	390	382	480	410
T_1 (^{0}C)	258	256	262	260
$T_{10\%}$ (^{0}C)	261	258	273	268
$T_{50\%}$ (^{0}C)	431	427	466	454
T_{max} (^{0}C)	491	482	512	508
Char (g) at 600 (^{0}C)	14.6	11.7	20.2	17.4
T_g (^{0}C)	161	147	157	144

The First and Second peaks-temperatures, T_1 (onset degradation temperature), $T_{10\%}$ (degradation temperatures at 10%), $T_{50\%}$ (degradation temperatures at 50%), T_{max} (maximum temperature of degradation), char weight at 600^{o}C and T_g (glass transition temperature) were derived from their thermograms. The higher first and second peaks temperatures for MDI-based *X. americana* extended polyurethanes, suggest the heterocyclic-ring oligomers enhances the thermal stabilities of these polymers (Petrović *et al.,* 2008). Besides, bond braking at the methylene bridge of the aromatic rings in MDI, produces phenylisocyanates, aniline, and 4-methyl aniline (Shlensky *et al.,* 1991). Fragmentation and degradation of these secondary products in the MDI-polyurethanes is associated with more thermal energy.

Similarly, thermogravimetric degradations at all temperatures and weight of char polymer residues at 600^0 C, presents the polyurethanes with MDPU-1.30-EA>MDPU-1.30-EG>IPPU-1.30-EA>IPPU-1.30-EG order of thermal stabilities. This suggest, the competing reactions leading to evolution of carbon dioxide, amine and olefins (Bakare *et al.,* 2008) will occur at lower temperature in IPDI-based polyurethanes relative to MDI-based *X. americana* chain-extended polyurethanes due to the low volatile character of methylenediphenyldiisocyanate in the latter compared to isophrone diisocyanate in the former (Shlensky *et al.,* 1991). Furthermore, the higher glass transition temperature shown by the amine extended polymers irrespective of diisocyanate-type could be attributed to the higher thermal stress required for the scission of the preponderant tough and rigid polyurea linkages in these polymers consistent with mechanical studies (table 3). In addition, the higher thermal stability for MDPU-1.30-EA, relative to IPPU-1.30-EA with the highest crosslinked density as evidenced by swelling studies indicates the overriding contributory effect of heterocyclic-ring oligomers on the thermal stabilities of these polymers. Overall, the results showed that the thermal properties of the chain-extended polyurethanes prepared with hydroxylated *X. americana* seed oil are slightly higher than those reported for rubber seed oil monoester (Bakare *et al.,* 2008) and hydroxylated rubber seed oil (Justine *et al.,* 2020) and different diisocyanates without chain extenders.

Average molecular weights properties of X. americana chain-extended polyurethanes

The number and weight-average molecular distribution and polydispersity index of *X. americana* extended polyurethanes are represented in table 6.

Table 6: Molecular weights distribution of *X. americana* chain-extended polyurethanes

Polymer	Average molecular weights		
	Number average molecular weight M_n (g/mol)	Weight average molecular weight M_w (g/mol)	Polydispersity index M_w/M_n
IPPU-1.30-EA	3444.258	4822.551	1.40
IPPU-1.30-EG	3688.655	7045.332	1.91
MDPU-1.30-EA	7478.967	20193.212	2.70
MDPU-1.30-EG	7501.409	24004.509	3.20

The low polydispersity indices for the aliphatic polyurethanes suggests, the primary isocyanate moieties in isophrone diisocyanate and secondary hydroxyl groups on the acyl chain hydroxylated *X. americana* seed oil, easily lend themselves to copolymerization and production of preponderance step-growth polymer chains with narrow molecular weight distributions and higher degree of polymerization. In contrast, the MDI-based *X. americana* extended polyurethanes showed kinetic chains with broader molecular weights distributions as evidenced by their higher polydispersity indices. This implies the cyclization and polycyclotrimerization of MDI (Zlatanić *et al.,* 2004), resulted in proliferation of *X. americana* extended polyurethanes oligomers with lower degree of polymerization. Moreover, the presences of oxazolidone a five-membered ring, acid anhydride and amide fragments from the competing side reactions, occasioned by epoxy residues on *X. americana* triglyceride chain and residual free fatty acid in hydroxylated *X. americana* oil with diisocyanates (Kadurina *et al.,* 1991), interfere strerically with the step-growth polymerizations, which is expected to be more acute in the MDI-based reactions. Evidently, from table 6 irrespective of diisocyanate-type, the amine extended condensation polymers are less polydispersed compared to their alcohol extended counterparts. This suggest the higher reactivity of the basic and nucleophilic primary NH_2 group relative to OH, with terminal isocyanate moieties on the prepolymer resin (El-Hamshary, 2012), produces more monomodal isostatic polymer chain with higher degree of polymerization in the amine extended polymers. The polydispersity index (1.40-1.91) for the extended aliphatic polyurethanes, comparable to 2.0 for step-growth polymers (Yigit *et al.,* 2019), indicates IPPU-1.30-EA and IPPU-1.30-EG are composed of more homogenous covalently linked urethane repeat units, whose chain length distributions is multimodal. Generally, the polydispersity indices (1.40-3.20) for the extended *X. americana* polyurethanes shows broader molecular weights relative to (1.2-2.2) for polyurethanes from rubber seed oil monoester and diisocyanates without chain-extenders (Bakare *et al.,* 2008), the lower polydispersity indices for the latter could be ascribed to the more reactive primary hydroxyl groups in the bi-functional α-monoglyceride from glycerolysis of rubber seed oil, participated in a more coordinated step-growth polymer formation compared to lower reactive secondary hydroxyl groups distributed on the triglyceride acyl chains of hydroxylated *X. americana* oil.

Conclusion

The polyester hydroxyl-terminated molecule derived from one-step hydroxylation of *X. americana* seed oil was effective as a base material in the production of chain-extended polyurethanes. The amine extended polyurethanes showed better tensile and flexural properties whereas; the alcohol-extended elastomers were more extensible. The extended aliphatic polyurethanes were more crosslinked consistent with their lower swelling character. The extended cyclo-aliphatic polyurethanes demonstrated superior thermal stability and were more polydispersed. The material properties exhibited by these condensation polymers, stand *X. americana* seed oil in good stead as a renewable resource with auspicious potentials for the production of biodegradable and specialty urethane-linked polymers.

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Declaration of Conflict of Interest

The authors declare no conflict of interest

References

AOAC 1992. Official methods of analysis (17th edition). Washington, DC: *Association of Official Analytical Chemists.* pp. 102-103

ASTM D 4274-88. 1990. Standard Test Methods for Testing Polyurethane Raw Materials: Determination of Hydroxyl Numbers of Polyols. *American System Testing and Materials International Philadelphia.* pp. 76

ASTM D-790 2003. Standard Test Method for Tensile, Elongation and Flexural Properties of Polymers. *American System Testing and Materials International* United State. pp. 65-67

Bakare IO, Pavithran C, Okieimen FE & Pillai CKS 2008. Synthesis and characterization of rubber-seed-oil-based polyurethanes. *J. Appl. Polym. Sci*., 109: 3292–3301.

Barton AFM 1991. Handbook of Solubility Parameters and Other Cohension Parameters. 2nd Edition CRC Press Taylor & Francis Group, pp. 98-100.

Cermark SC & Ishell T 2003. Synthesis and physical properties of ester-based functional fluids. *Ind. Crops Prod.*, 18: 183-196.

El-Hamshary H 2012. Improved graft Copolymerization of some modified cellulose Polymers with vinyl monomers using Dibenzoyl Peroxide as Initiator. *J. Macromol. Sci.: Part A*, 49(7): 554-561.

Engels HW, Pirkl HG, Albers R, Albach R, Kraise J, Hoffmann A, Casselmann H & Dormish J 2013. Polyurethanes: Versatile Materials and Sustainable Problem solvers for Today's Challengers. *Angew Chemie.*, 52: 9422-9441.

Eromosele CO & Eromosele IC 2002. Fatty acid Compositions of Seed Oils of *Haematostaphis barteri* and *Ximenia americana*. *Bioresour. Technol.,* 80: 303-304.

Fazal-Ur-Rahman 2010. Synthesis and Characterization of Specialty Polyurethane Elastomers Unpublished Ph.D Thesis. University of Agriculture, Faisalad, Pakistan. pp. 214-220

Gonzalez-Paz RJ, Lluch G, Lligadas JC, Ronda M & Galia VC 2011. A Green Approach towards Oleic-and Undecylenic acid-derived Polyurethanes. *J. Polym. Sci. Part A:* 48: 2407-2416.

Gopalakrishna S & Fernando LT 2011. Bio-based Thermosetting Tough Polyurethanes. *Der Chemica Sinica*, 2 (5): 54-64.

Jabber JM, Fakinlede FK & Bello BE 2018. Synthesis of Rigid Polyurethane Foam using Polyols from Fractionated Locally Sourced Vegetable Oil. *FUW Trends Sci. Technol. J.*, 3 (2A): 384-388.

Justine G, Athul S & Reghunadhan-Nair CP 2020. One-step Hydroxylation of Rubber Seed Oil and Synthesis of Green Polyurethane Networks Thereof. *J. Polym. Res.,* 27: 191-201.

Kadurina TI, Prokopenko VA & Omelchenko SI 1991. Curing of Epoxy Oligomers by Isocyanates. *Polym.,* 33 (18): 3858-3864.

Okoye SI, Abubakar M & Ndagana SF 2021. Development of Polyurethane Foam using Biobased Polyol: Effect of *Ximenia americana* Seed Oil Polyol on some Properties of Polyurethane Foam. *FUW Trends Sci. Technol. J.,* 6 (2): 650-653.

Oladipo GO, Eromosele IC & Folarin OM 2013. Formation and Characterization of Paint Based on Alkyd Resin Derivative of *Ximenia americana* (Wild Olive) Seed Oil. *Environ. Nat. Res.,* 3 (3): 52-62.

Petrović ZS, Guo A, Javni I, Cvetković I & Hong DP 2008. Polyurethane Networks from Polyols obtained by Hydroformylation of Soybean Oil. *Polym.,* 57: 275–281.

Reghunadhan-Nair CP, Athul S & Justine G 2018. A Process for obtaining Polyols from Rubber Seed Oil by a One-step Hydroxylation, Crosslinkable Polymer Products Derived Thereof and Methods of Preparing Them. *Indian patent application No. 201841002976.*

Samuel AE 2019. Polyurethane Elastomers and Polyurethane-graft-Polystyrene Interpenetrating Polymer Network based on *Ximenia americana L* (Wild Olive) Seed oil Ph.D. Thesis, Federal University of Agriculture Abeokuta, Nigeria. pp. 165-171.

Samuel AE, Eromosele IC, Kamba SY & Samaila DS 2023. Production of Polyurethane Elastomers from *Ximenia americana L* (Wild Olive) Seed Oil and Diisocyanates. *J. Appl. Sci. Environ. Manage.,* 27 (11): 2581-2590.

Samuel AE, Samaila SD, Idris U & Hyeladzira YB 2024. Kinetics and Thermodynamic Studies of Polyurethane Formation based on *Ximenia americana L.* (Wild Olive) Seed Oil Monoglyceride and Different Diisocyanate. *J. Appl. Sci. Environ. Manage.,* 28 (10B), 3329-3338.

Sharma V & Kundu PP 2006. Addition Polymers from Natural Oils: A Review. *Prog. Polym. Sci.*, 31, 983-1008.

Shlensky OF, Aksenov LN & Shashkov AG 1991. Thermal Decomposition of Materials: Effect of Highly Intensive Heating. *Elsevier Amsterdam,* 8(20): 213-220.

Sobhan N, Sanjay S & Basudam A 2002. Catalytic Activity of DBTDL in Polyurethane Formation. *Indian J. Chem. Technol.*, 9: 330-333.

Storrs A E G 1995. Know your Trees. Some of the common Trees found in Zambia. Regional Soil Conservation Unit, Nairobi-Kenya 51: 59-62.

Swapan MA 2018. Polyurethanes from Vegetable Oils and Applications: A Review. *J. Polym. Res.*, 25, 184-202.

Xiao-Dong C, Nan-Qiao Z & Zhang H 2009. Preparation and Properties of Cast Polyurethane Elastomers with Molecularly Uniform Hard Segments based on 2, 4-toluene diisocyanate and 3, 5-dimethyl-thioltoluenediamine. *J. Biomed. Sci. Eng.,* 2: 245-253.

Yakushin V, Stirna U, Bikovens O, Misane M, Sevastyanova I & Vilsone D 2014. Synthesis and Characterization of Novel Polyurethanes Based on Vegetable oils Amide and Ester Polyols. *Mat. Sci.*, 20(3): 277-282.

Yigit Y, Kilislioglu A, Karakus S & Baydogan N 2019. Determination of the Intrinsic Viscosity and Molecular Weight of Poly (Methyl methacrylate) Blend. *J. Investiga. Eng. Technol*., 2(2): 34-39.

Zhang L, Jeon HK, Malsam J, Herrington R & Macosko CW 2007. Substituting Soybean Oil-based Polyol into Polyurethane Flexible Foams. *Polym.,* 48: 6656–6667.

Zlatanić A, Lava C, Zhang W & Petrović ZS 2004. Effect of Structure on Properties of Polyols and Polyurethanes based on different Vegetable Oils. *J. Polym. Sci.*, 42,809–819.