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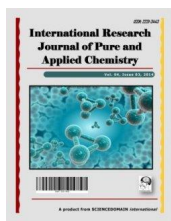


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Development of Poly (Ester Amide-Urethanes) from De-saturated *Thevetia peruviana* Seed Oil-FAMES

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Authors' contributions

Authors carried out the scientific investigations of this work. Author TOS designed the study and prepared the first draft. Author SK managed data evaluation. Author RN assessed data reports. Authors BA and BVSKR respectively prepared FAMES and ran GC-FID. Authors OO and ETA managed literature searches and editing of script. Author KVSNR supervised the entire bench work. All authors read and approved the final script.

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ABSTRACT

This study present the synthesis of eco-friendly poly(ester amide-urethane) coating from *Thevetia peruviana* seed oil (TPSO). FT-IR, ¹H NMR and ¹³C NMR spectral analyses were used in confirming the structure of compounds. Physico-chemical properties of desaturated N,N'-bis (2-hydroxyethyl) *Thevetia peruviana* seed oil fatty amide (DHETA), poly(ester amide) (PESA) and poly(ester amide urethanes) (PESAU), as well as chemical resistance, antibacterial studies and thermal analysis of PESAU were also examined.

Aims: To evaluate the thermal stability and antibacterial activities of PESAU.

Study Design: Extraction of seed oil from the air-dried seedlings of *Thevetia peruviana* seeds and preparation of polyol through urea fractionation. Followed by urethane synthesis using 4,4'-

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diisocyanatodicyclohexylmethane (H₁₂MDI).

Result: The 46.4 g ICI/100g Iodine value (I.V.) of the amide (DHETA) base polyol was reduced to 10.5 g ICI/100 g value for the urethane (PESAU). The zero percent value for PESAU hydroxyl value (H.V.) is an indication of complete reaction of the hydroxyl functional groups on PESA with H₁₂MDI. Spectroscopic examinations carried out confirm the formation of synthesized compounds.

Conclusion: The synthesized urethane (PESAU) shows excellent inhibitive activities against tested organisms.

Keywords: *Thevetia peruviana*; poly(esteramide); antibacterial; thermal analysis; urea fractionation.

1. INTRODUCTION

Over the years, the petroleum based chemicals have been used for the development of many industrial products like organic coatings, foams, elastomers, fibres, adhesives etc. However, due to the limited availability and non biodegradability of petroleum resources, it is essential to replace them with materials derived from renewable resources [1-3]. For this reason, many research groups all over the world focused on the use of renewable resources like starch, cellulose, protein, natural rubber, and plant seed oils [3-6] for the development of many industrial products like lubricants, diluents, soaps, composite materials, plasticizers, biodiesel, surface coatings [6-8].

In general, plant seed oils are composed of triglyceride molecules containing different and varying percentages of saturated and unsaturated fatty acids [9]. However, chemical modifications such as aminolysis [10], epoxidation [11,12], hydroformylation [13], ozonolysis [14] and urethanation [15,16] can be performed on the triglyceride oil to tune the physico-chemical properties of the seed oils. Unsaturated fatty acids chain provides functional sites for epoxidation, hydroformylation and ozonolysis modification. However, the contrary are for saturated fatty acids that are dangling chains acting as internal plasticizer that causes the lowering of glass transition temperature of polymer networks [15,16]. The influence of saturated fatty acids in polymer matrix was discussed by Zlatanić et al. [15] and Dušek et al. [15]. They both observed drawback such as poor flow properties at low temperatures as a result of high composition of saturated fatty acids in the bio-diesel produced from triglycerides containing high percentages of saturated fatty acids. This leads to the product crystallizing and clogging of the fuel lines and engine filters. This is due to the fact that the triglycerides tend to have poor flow properties at low temperatures as a result of high composition of saturated fatty acids [17].

Similarly, the preparation of resins from triglycerides containing high percentages of saturated fatty acid such as *Thevetia peruviana* seed oil (TPSO) will induce unnecessary coagulation of the resin system and attaining an irreversible state known as gel point [3]. Apparently, useful modification of the fatty acid profile in the triglyceride chains will checkmate this deficiency as well as provide unsaturated sites for subsequent modifications in such triglycerides.

In view of this, this paper present the synthesis of air drying poly(esteramide-urethane) resin from de-saturated fatty acid methyl esters (FAMES) of *Thevetia peruviana* seed oil, commonly known as Yellow Oleanda [a tropical ornamental shrub] having about 68.8% unsaturated and 30.9% saturated fatty acids [18] via urea fractionation method. This method (urea fractionation) optimizes the percentage functionality of the double bond in TPSO by physisorption of the saturated fatty acids [19]. The physico-chemical characterization of the optimized unsaturated FAMES such as hydroxyl value, iodine value, saponification value, refractive index, inherent viscosity were carried out using standard methods. Through condensation reaction, the N,N'- bis(2-hydroxyethyl) *Thevetia peruviana* fatty amide (DHETA) were prepared from the FAMES, and consequently reacted with isophthalic acid in order to form poly (ester amide) (PESA). The latter was made to undergo urethanation with H₁₂MDI. The structural elucidation of the moisture cured poly(esteramide-urethane) coating was based on FTIR, ¹H NMR and ¹³C NMR spectroscopic analyses. The coatings film was evaluated for its antibacterial activity and thermal stability properties using TGA and DSC.

2. EXPERIMENTAL DETAILS

The FTIR, ¹H NMR and ¹³C NMR were used to characterize the chemical structure of DHETA, PESA, and PESAU. FTIR spectra of the resin were taken over KBr on Perkin Elmer spectrum

100 spectrometer (PerkinElmer Inc. USA) by scanning 8 times. ^1H NMR and ^{13}C NMR were respectively recorded on Varian VXR-Unity 200 MHz spectrometer and Bruker UXNMR 400 MHz spectrometer by using CDCl_3 and DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. The thermal stability of the hybrid resins and curing behaviour were studied by thermogravimetric analysis (Perkin Elmer TGA 7, TA Instrument, and USA) and Differential scanning calorimetry (Perkin Elmer TA DSC Q100 USA) at a constant heating rate of $10^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Elcometer was used in taking the thickness of the coatings on metal steel panels.

In vitro antimicrobial activity of the polymers was studied and tested against Gram-positive organisms viz. *Bacillus subtilis* (MTCC 441), *Staphylococcus aureus* (MTCC 96) and Gram-negative organisms viz. *Escherichia coli* (MTCC 443), and *klebsiella pneumoniae* (MTCC 618) by Agar diffusion Method [20]. The ready-made Nutrient Agar was suspended in distilled water (1000 mL) and heated to boiling until it dissolved completely; the medium and Petri dishes were autoclaved at pressure of 15 lb/in^2 for 20 min. The medium was poured into sterile Petri dishes under aseptic conditions in a laminar air flow chamber. When the medium in the plates solidified, 0.5 mL (approx. 10^6 CFU/mL) of culture of test organism was inoculated and uniformly spread over the agar surface with a sterile L-shaped rod. Embedded polymer samples with 2×2 cm (approx) samples were washed with double distilled water and placed on the medium and incubated at 37°C (bacteria) for 24 h. Uncoated polymers were used as Controls. The antibacterial activity was performed based on the formation of inhibition zone loss of growth of organism beneath and surroundings of the films placed on agar medium. Three replicates were maintained for each treatment. MTCC is the Microbial Type Culture Collection in IMTECH (CSIR LAB) Chandigarh, India.

Silicon carbide papers of varying grades were used for the preparation of mild steel strips; which were washed with water, ethanol and acetone. The degreased metal strips were dried under vacuum for 3 h. The pristine and hybrid coatings were prepared by brush application of 60 wt % of resin in xylene on the mild strips. For chemical resistance test in water, acid (5 wt % HCl), alkali (5 wt % NaOH) taking in 3 in. diameter porcelain dishes standard sizes of mild strips of $30 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$ were used. The

salt spray tests were carried out in a salt mist chamber following ASTM B 177-94 standard. A 3.5 wt % NaCl solution was atomized by compressed air in the chamber containing the specimen [3].

Gas Chromatographic Analysis: The fatty acid composition (FAMEs) was analyzed using an Agilent 6890 N series gas chromatography equipped with FID detector on a split injector. A fused silica capillary column (DB-225, $30 \text{ m} \times 0.32 \text{ m i.d.}$, J & W Scientifics, USA) was used with the injector and detector temperature maintained at 230°C and 250°C , respectively. The oven temperature was programmed at 160°C for 2 min and finally increased to 230°C at 4°C/min . The flow rate of the carrier gas, nitrogen was maintained at 1.5 ml/min. The area percentages were recorded with a standard Chemstation Data System [21].

Iodine value determination: 8 g of iodine trichloride (ICl_3) was dissolved in 450 ml acetic acid (solution 1). In the same vein, 9 g of iodine was dissolved in a 450 ml acetic acid by heating (solution 2). Gradually, solution 2 was added to solution 1 until the colour changed to reddish brown. Then 50 ml of solution 2 was added to solution 1. The solution was gently heated to 100°C for 20 mins. and allowed to cool down [22]. Depending on the expected iodine value, sample weight (0.2-1.0 g) was weighed accurately in an Erlenmeyer flask. 15 ml of carbon tetrachloride was added from the top of the flask, the flask was swirled so as to ensure dissolution of the sample. 25 ml of Wij's solution was dispensed into the flask containing the sample with the use of a pipette. The flask was swirled so as to ensure intimate mixing of content. Swirling was done for 30 mins. The flask was then stored in a dark area for the required reaction time at a temperature of $25 \pm 5^\circ\text{C}$. The flask was removed from the dark area and treated with 20 ml of 20% KI solution, followed by 100 ml distilled water. The mixture in the flask was titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, solution under constant and vigorous shaking. Titration was continued until the yellow colour almost disappeared. 2 mL of starch indicator solution was added and titration continued until the blue colouration just disappeared [22].

Hydroxyl value determination: The acetylating mixture was prepared by adding 1 part of acetic anhydride and 7 parts of pyridine together. Both compounds were freshly prepared [22,23]. An accurate weight of about 0.5-2.0 g of resin was

transferred into a 250 ml round bottom (R.B) flask. 5 ml of acetylating mixture was added to the weighed resin in the flask. Water condenser/reflux condenser was connected to the quick fit mouth of the flask and refluxed for about 60 mins over a water bath. The flask content was allowed to cool down. Upon cooling down 10 ml of distilled water was added through the top of the condenser. The content was gently warmed for 5-10 mins on a water bath. The flask was again allowed to cool to room temperature under a tap and the condenser was rinsed with n-butanol into the flask. After rinsing the condenser with n-butanol, it was removed and the content in the R.B flask was titrated against alcoholic KOH using phenolphthalein as indicator. Blank titration under same conditions was also carried out. Acid value of the polyol/polymer was determined as well as discussed earlier [22,24].

2.1 Synthesis of De-saturated N,N'-bis (2-hydroxyethyl) *Thevetia peruviana* Seed Oil Fatty Amide (DHETA)

Step 1: The fatty acid methylesters (FAMES) of *Thevetia peruviana* seed oil was prepared by refluxing the oil (10 g) samples at 80°C for 3-4 hours together with 100 ml of 2% sulphuric acid in methanol (The progress of the reaction was monitored by micro TLC technique using hexane and ethyl acetate (9:1 vol/vol solvent system). At the end of reaction, the esters were extracted into ethyl acetate, washed free of mineral acid and passed over anhydrous sodium sulphate. The ethyl acetate extracts was further concentrated using a rotary evaporator.

Step 2: Urea fractionation of FAMES: The urea fractionation was done according to a reference procedure [25]. FAMES (10 g) obtained from Step 1 were dissolved in 100 ml of methanol to which urea (20 g) was added. The mixture was heated (~60°C) until all the urea has dissolved. The contents were cooled to 20°C with slow stirring over a period of 5-6 h. The urea adduct was filtered and adduct was washed twice with 25 ml portions of methanol saturated with urea. The methanol solution was poured into 1% hydrochloric acid (50 ml) and the organic phase was extracted with diethyl ether (2 × 100 ml). The ether extract was washed with water (2 × 50 ml), dried over anhydrous sodium sulphate and concentrated over rotary evaporator to get FAMES rich in unsaturated fatty acids.

Step 3: Synthesis of desaturated N,N'-bis (2-hydroxyethyl) *Thevetia peruviana* seed oil fatty

amide (DHETA); The preparation of DHETA from desaturated fatty acid methyl esters of the oil was carried out in a four necked round bottom Pyrex flask containing diethanolamine and *Thevetia peruviana* seed oil fatty amide, fitted with mechanical stirrer, condenser, and thermometer. The flask was submerged in an oil bath. With a molar ratio of 6:1 diethanolamine to oil in the presence of 2% sodium methoxide, the mixture in the four necked round bottomed flask was reacted at 115°C while stirring. The progress of the reaction was monitored by thin layer chromatography (TLC). At the completion of the reaction, the reaction mixture was allowed to cool and it was dissolved in diethyl ether in a separating funnel. The ethereal layer was washed with 5% aqueous hydrochloric acid. The ether layer was separated and washed with water and later dried over anhydrous sodium sulphate. Rotary evaporator was used in concentrating the ether layer [3,26].

2.2 Synthesis of *Thevetia peruviana* Poly (Ester Amide) (PESA)

PESA was synthesized by reacting DHETA (0.06 mol) with isophthalic acid (0.03 mol) and 30 ml xylene as solvent in a four neck round bottom flask connected to a Dean stark, thermometer, mechanical stirrer and a nitrogen inlet tube. The reaction mixture was refluxed at 145-150°C until the theoretical amount of water was collected and the reaction was monitored by the determination of acid value at regular intervals [27]. At the end of the reaction the product (PESA) was taken out of the four neck round bottom flask and xylene (solvent) was withdrawn from the compound using rotary evaporator under reduced pressure.

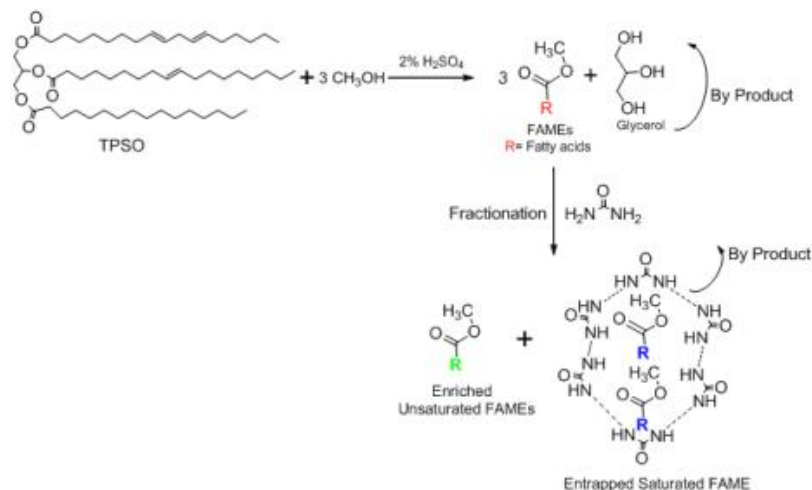
2.3 Synthesis of Poly (Ester Amide-Urethane) from FAMES Polyol (PESAU)

The synthesis of PESAU was done using a one-shot technique (single stage process). To a three necked round bottom flask fitted with nitrogen gas inlet, thermometer, dropping funnel and a magnetic stirrer [28]. 3 ml of 4-methyl pentan-2-one and 2.38 ml of H₁₂MDI was added. 7.165 g of PESA dissolved in minimum amount of solvent was then added to the round bottomed flask. The reaction mixture was continually stirred under nitrogen environment. The progress of the reaction was monitored by TLC and also by determining the hydroxyl value at regular interval [3,29].

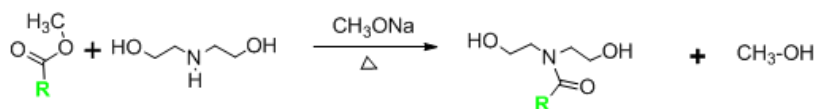
3. RESULTS AND DISCUSSION

The reaction mechanisms for the synthesis of enriched unsaturated FAMES, DHETA, PESA

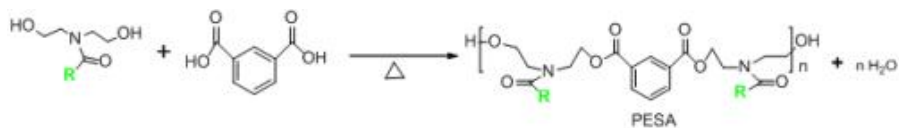
and PESAU resins from *Thevetia peruviana* seed oil are presented in Schemes 1-4 below.



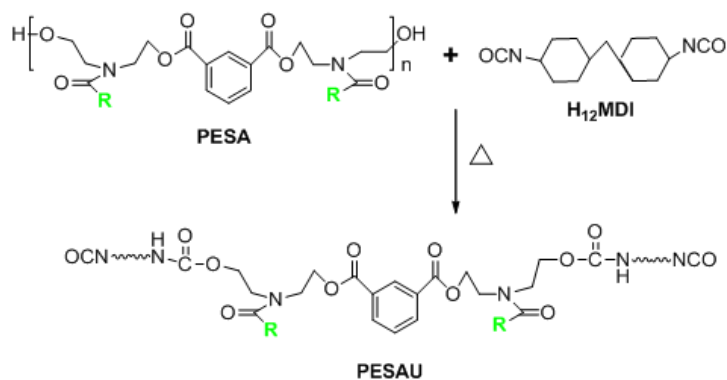
Scheme 1. Reaction paths towards the preparation of enriched double bond FAMES



Scheme 2. Synthesis of N,N'-bis(2-hydroxyethyl) *Thevetia peruviana* oil fatty amide from desaturated fatty acid methyl esters (DHETA)



Scheme 3. Synthesis of polyesteramide from DHETA



Scheme 4. Synthesis of polyesteramide-urethane

Preparation of enriched unsaturated FAMES from TPSO is given in Scheme 1. FAMES prepared from *Thevetia peruviana* seed oil (TPSO) were reacted with diethanolamine in the presence of sodium methoxide as catalyst to form DHETA [Scheme 2]. The FAMES poly (ester amide) (PESA) was synthesized by the combination of DHETA and isophthalic acid [Scheme 3]. Subsequently, PESA was synthesized by reacting PESA with H₁₂MDI [Scheme 4].

3.1 Gas Chromatographic Analysis of Desaturated TPSO FAMES

The gas chromatographic analysis results of TPSO FAMES and desaturated TPSO FAMES respectively are presented in Table 1. The result confirms that urea forms an inclusion complex (physical sorption) with the saturated fatty acids in TPSO FAMES. There was a complete entrapment of myristic (14:0), arachidic (20:0), and erucic (22:1) acids present in TPSO FAMES (Scheme 1 and Table 1). The 22.3% composition of palmitic acid (16:0) in TPSO FAMES dropped to 9.99% composition in desaturated TPSO FAMES. Likewise, stearic acid (18:0) percentage composition dropped from 7.1 in TPSO FAMES to 1.3 in desaturated TPSO FAMES. However, there was approximately 13.0 and 7.5 enrichment in the percentage compositions of oleic (18:1) and linoleic (18:2) {unsaturated} acids respectively.

3.2 FTIR and NMR Spectra Analysis

3.2.1 N,N'- bis (2-hydroxyethyl) *Thevetia peruviana* oil fatty amide from desaturated fatty acid methyl esters (DHETA)

In the first stage, the formation of the desaturated FAME was confirmed by the presence of characteristic peaks corresponding to C=O group stretching of ester linkage around 1740 cm⁻¹ and =C-H stretching and bending of alkene groups around 1500 cm⁻¹ and 700 cm⁻¹. The FT-IR spectrum was given in Fig. 1(a); while, the overlay FTIR spectra of DHETA and PESA is presented in Fig. 1(b). DHETA reveals a characteristic absorption band for -OH at 3468 cm⁻¹. Asymmetric and symmetric methylene (CH₂) stretching bands appear at 2923 cm⁻¹ and 2853 cm⁻¹ respectively. The amide C=O stretching vibration band appears at 1744 cm⁻¹, the band at 1235 cm⁻¹ is ascribable to amide C-N stretching vibrations and the double bond of fatty acid is observed at 1646 cm⁻¹. The characteristic bands of alkane C-H and alkene C-H bending

shows vibrations at 1463 cm⁻¹ and 721 cm⁻¹ respectively.

Fig. 2 represent the ¹H NMR spectra of DHETA. The terminal aliphatic group protons resonant at δ = 0.88 ppm and the alpha methylene protons to the terminal aliphatic group is observed at δ = 1.31 ppm (-CH₂-CH₃), δ = 1.29 ppm represent the methylene protons of the fatty acid chain but the carbon double bond protons on the fatty acid chain (-CH=CH-) is seen at δ = 5.31 ppm. The alpha methylene protons to the carbon double bond (-CH₂-CH=CH-CH₂-) is observed at δ = 2.01 ppm, the alpha and beta methylene protons to the amide carbonyl group are observed at δ = 2.32 ppm and δ = 1.53 ppm respectively. The proton of hydroxyl groups (-OH) appears at δ = 3.79 ppm while the alpha and beta methylene groups to the hydroxyl functional group are respectively due to δ = 3.61 ppm and δ = 3.39 ppm. The ¹³C NMR spectra of DHETA (Fig. 3) reveals characteristic peaks of terminal carbon of the methylene group (-CH₃) of the fatty acid chain at δ = 14.01 ppm and the olefin carbon (-CH=CH-) at δ = 129.84 ppm. The alpha carbon to the terminal methylene group on the fatty acid chain resonate at δ = 22.51 ppm. Most importantly, the appearance of the amide carbonyl peak at δ = 172.45 ppm confirms the formation of DHETA from desaturated FAMES.

3.2.2 *Thevetia peruviana* poly(ester amide) (PESA)

The FT-IR spectrum of PESA (Fig. 1) prepared from desaturated FAMES of *Thevetia peruviana* confirms the formation of the poly(ester amide). The strong broad stretching band of the -OH functional group is observed at 3405 cm⁻¹ and the characteristic stretching peaks of CH₂ symmetric and asymmetric is seen at 2854 cm⁻¹ and 2924 cm⁻¹ respectively. Band at 1636 cm⁻¹ represents the stretching vibration of C=O of amide while 1738 cm⁻¹ stands for strong stretching peak of ester carbonyl functional group (C=O). The C-N medium stretching vibration peak is observed at 1072.00 cm⁻¹ and the CH₂ bending is at 1462 cm⁻¹. C-O stretching vibration peak of ester is noticed at 1173 cm⁻¹ also the absorption band at 722 cm⁻¹ is due to the presence of C-H vibration in the isophthalic acid ring [30,31].

The proton NMR of PESA in Fig. 4 gives a characteristic peak of terminal methyl protons (-CH₃) and its alpha methylene group at 0.89 ppm and 1.32 ppm respectively. The appearance of methylene protons (-CH₂-) peak at δ = 4.51

ppm linked with -O- of the isophthalic acid confirms the formation of the poly (ester amide) in the reaction Scheme 3 of DHETA and isophthalic acid. The -CH2- attached to nitrogen resonate at $\delta = 3.78$ ppm and the multiplet peaks at $\delta = 3.62$ ppm may be attributed to -CH2- attached to -OH group. The internal fatty acid

methylene protons is observed at $\delta = 1.29$ ppm also, the fatty acid double bond protons and its alpha methylene protons are seen at $\delta = 5.35$ ppm and $\delta = 2.03$ ppm respectively. The aromatic ring proton peaks appear at $\delta = 7.56$ -8.61 ppm.

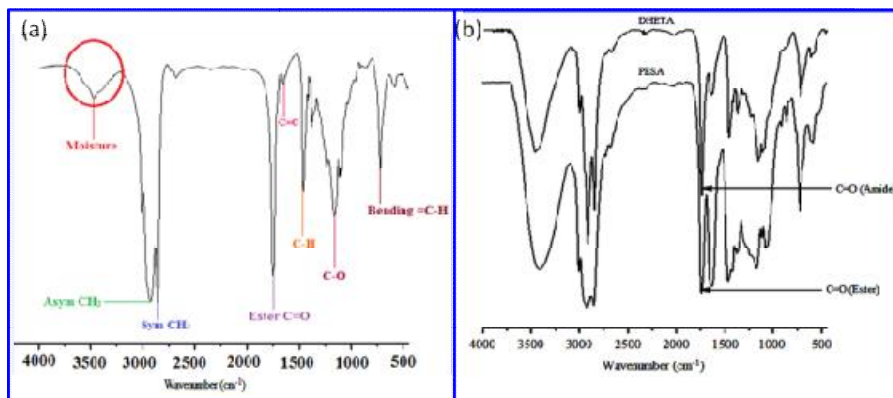


Fig. 1. Overlay FTIR spectra of (a) FAMEs, (b) DHETA and PESA

Table 1. GC analysis of TPSO Fame and desaturated TPSO Fame

Fatty acids	TPSO FAME(s) % composition	Desaturated TPSO FAME(s) % composition
Myristic acid	0.1	-
Palmitic acid	22.3	9.99
Palmitoleic acid	0.5	0.2
Margaric acid	0.1	-
Stearic acid	7.1	1.3
Oleic acid	48.2	61.2
Linoleic acid	19	27.3
Arachidic acid	1.3	-
Erucic acid	0.6	-

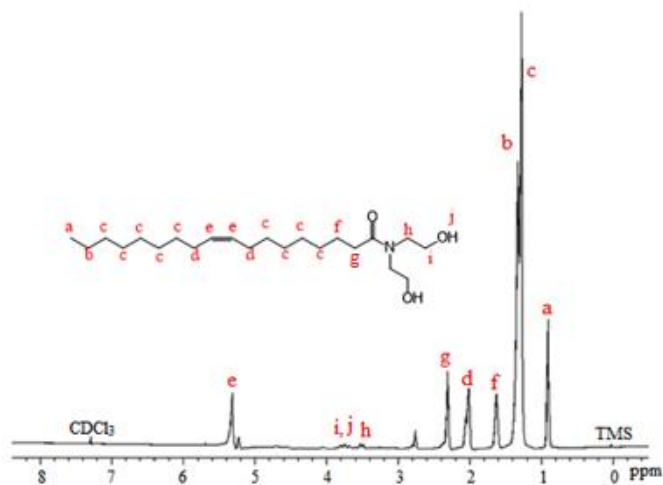


Fig. 2. ¹H NMR spectrum of DHETA (here the chemical structure represented only for oleic acid based product)

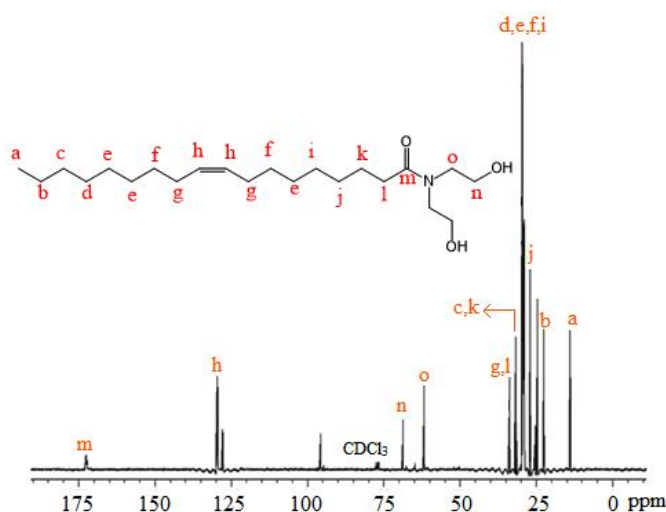


Fig. 3. ^{13}C NMR spectrum of DHETA (here the chemical structure represented only for oleic acid based product)

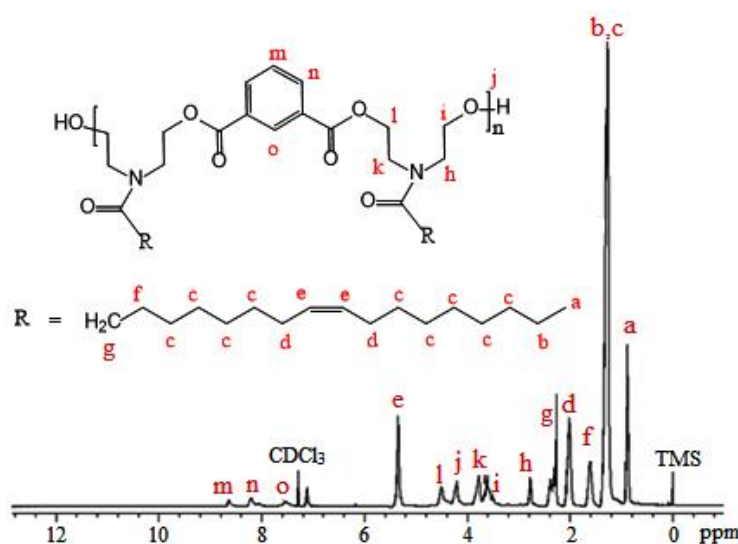


Fig. 4. ^1H NMR spectrum of PESA (here the chemical structure represented only for oleic acid based product)

The structural formation of PESA is further confirmed by ^{13}C NMR spectroscopy (Fig. 5) as presented below. The methyl ($\text{H}_3\text{C}-$) terminal carbon shows peak at $\delta = 14.08$ ppm and the carbon to carbon double bond ($-\text{HC}=\text{CH}-$) on the fatty acid chain resonate at $\delta = 129.69$ ppm. Also, its alpha methylene group is seen at $\delta = 33.69$ ppm. The internal methylene group on the fatty acid chain appears at $\delta = 30.14-22.66$ ppm whereas, the amide carbonyl functional group is observed at $\delta = 61.53$ ppm. The isophthalic aromatic carbon resonates at $\delta = 127.83$ ppm, $\delta = 129.87$ ppm, $\delta = 130.25$ ppm and 125.97 ppm.

3.2.3 Spectroscopic evaluation of poly(esteramide-urethane) (PESAU)

In the FT-IR spectra of PESAU (Fig. 6), characteristic bands for $-\text{NH}$ stretching vibration of urethane groups ($\nu\text{-NH}$) is observed at 3436 cm^{-1} , the carbonyl stretching vibration ($\nu\text{C}=\text{O}$) of the amide resonate at 1625 cm^{-1} while the urethane carbonyl is seen at 1746 cm^{-1} . The amide and distinct urethane C-N stretching bands are observed at 1432 cm^{-1} and 1242 cm^{-1} respectively.

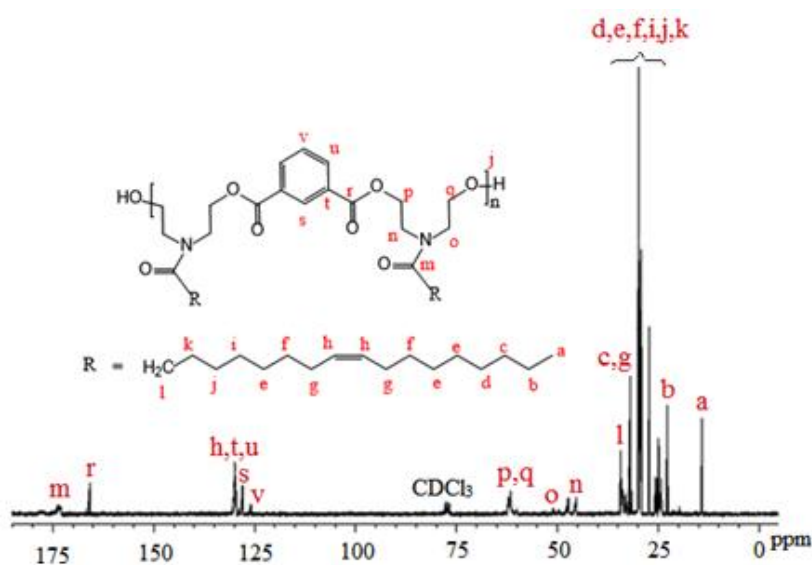


Fig. 5. ¹³C NMR spectrum of PESA (here the chemical structure represented only for oleic acid based product)

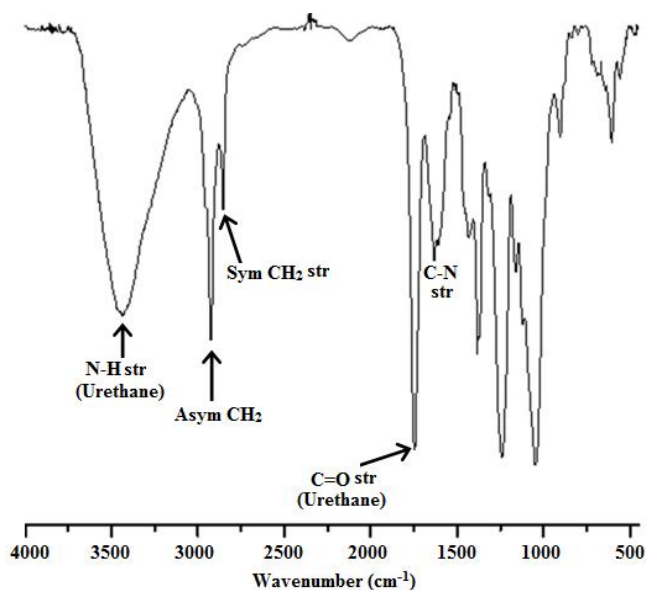


Fig. 6. FTIR spectrum of PESAU

The pathway towards the synthesis of poly(esteramide-urethane) is described in Scheme 4. The reaction was followed using ¹H NMR spectra shown in Fig. 7. The formation of urethane linkages is confirmed by the resonances of hydrogen bonded -OOCNH- at $\delta = 8.05$ ppm along with amide methylene protons (-CH₂-) attached to -OCO- which resonates at $\delta = 4.51$ ppm. The dicyclohexyl protons are observed at $\delta = 3.54, 1.76, 1.52, 1.60, 1.25,$

$1.36, 1.97, 1.62, 3.52$ ppm. Also the methylene protons (-CH₂-) in between the two cyclohexyl ring of H₁₂MDI is observed at $\delta = 1.21$ ppm. The terminal methyl protons of the fatty acid chain are seen at $\delta = 5.35$ ppm, while the resonance at $\delta = 2.13$ ppm originates from the alpha methylene protons to the methyl hydrogen of carbon bearing double bond on the fatty acid chain. The isophthalic acid ring protons appear at $\delta = 8.21$ ppm, $\delta = 8.26$ ppm, and $\delta = 7.56$ ppm.

The reassertion of the poly(ester amide-urethane) (PESAU) prepared from desaturated fatty acid methyl esters of *Thevetia peruviana* seed oil is presented in its ^{13}C NMR (Fig. 8). Spectra signals at $\delta = 22.49\text{-}34.82$ ppm represent various methylene carbon ($-\text{CH}_2-$) on the fatty acid chain as well as that of the dicyclohexyl ring of the isocyanate (H_{12}MDI). The terminal methyl carbon ($-\text{CH}_3$) of the fatty acid chain resonates at $\delta = 13.91$ ppm while the olefin carbon is observed at $\delta = 129.87$ ppm. The amide carbon linkage of the urethane ($-\text{OOC}-\text{NH}$) which

also stands as a principal signal for urethane formation and the carbon of the amide carbonyl functional group linking the fatty acid chain appeared at $\delta = 155.47$ ppm and $\delta = 173.01$ ppm respectively. $\delta = 60.82$ ppm represent the methylene carbon attached to the oxygen linking the urethane group ($-\text{CH}_2-\text{OOC}-$) whereas, resonance at $\delta = 61.91$ ppm is indicative of the methylene carbon connecting with oxygen of isophthalic acid ring ($-\text{CH}_2-\text{OOC}-\text{Ar}-$). Isophthalic acid ring carbons appears at $\delta = 129.31$, 133.62 , 134.17 and 127.83 ppm.

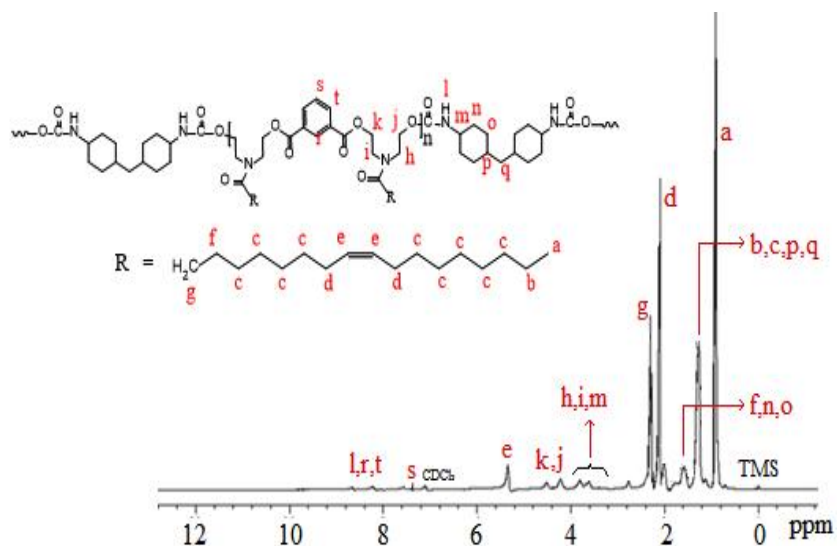


Fig. 7. ^1H NMR spectrum of PESAU

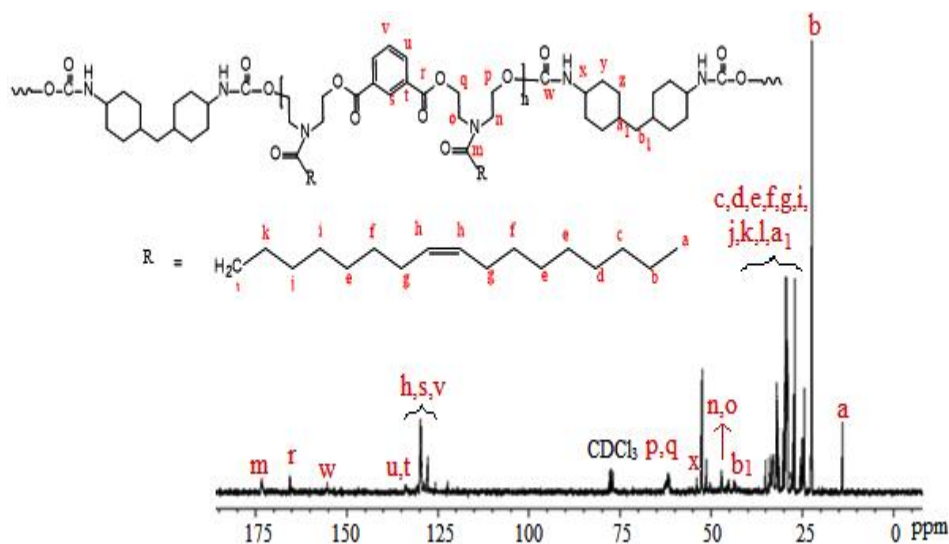


Fig. 8. ^{13}C NMR spectrum of PESAU

3.3 Physico-chemical Characteristics

The primary essence of desaturating TPSO FAMES through urea fractionation method is to concentrate polyunsaturated fatty amide. The increase in iodine value from 74.9 for TPSO to 98.7 gI₂/100 g [3] in desaturated FAMES confirms the product formed in reaction Scheme 1. By this modification desaturated TPSO FAMES can now be regarded as semi-drying material (since the iodine value is greater than 90) which is suitable for coating purposes. The viscosity of the desaturated FAMES is 7.58 cSt lower than that of TPSO, also corroborating that percentage unsaturation increase in the desaturated TPSO FAMES. The physico-chemical characterizations data of the various resins prepared from desaturated TPSO FAMES is presented in Table 2. The order of decreasing values of iodine and hydroxyl is DHETA > PESA > PESAU. These declines in the iodine and hydroxyl values is associated with decrease in the composition of unsaturated functional group in the compound as DHETA react with isophthalic acid to form PESA and subsequently PESAU by the combination of PESA with H₁₂MDI. This will eventually culminate in increase in the molar mass of the polymer thereby reducing the said characteristics. On the other hand, the specific gravity, inherent viscosity and refractive index show increase in values as the polymer weight increases along side with increase in cross link density of the polymeric resins from DHETA to PESA and finally to PESAU.

The solubility tendencies of the resins in various solvents such as carbon tetrachloride, diethyl ether, petroleum ether, toluene, MIBK, xylene, ethanol, acetone, methanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and chloroform. DHETA, PESA and PESAU show 90-100 wt% solubility in MIBK, DMF, DMSO, chloroform, toluene, carbon tetrachloride and xylene. The observed high solubility behaviour can be attributed to the presence of long fatty acid hydrocarbon chains in the resins. Between 15-40 wt% is observed in the other solvents (that is ethanol, methanol and acetone).

3.4 Film Properties of Resins

The films were cast after adding cobalt and zirconium driers and dibutyl tin dilaurate catalyst to the PESAU solution. It was observed that PESAU film became dry to touch in about 45 minutes after casting on the panels, but became entirely tack free in 8 h. This development leads to chain entanglement in the system and

subsequently create an environment whereby free unreacted isocyanate groups chemically react with moisture forming urea linkages or the already formed urethane group, thereby leading to the formation of allophanate [32].

The PESA and its urethane modified samples (PESAU) were coated on mild steel strips (that had been polished with various grades of silicon carbide papers, washed with water and degreased with alcohol and carbon tetrachloride and having 30 mm × 10 mm × 1 mm as its standard dimension) and used for chemical resistance test in water, 2% NaOH, 2% HCl, Xylene. The strips were kept in vertical position for drying. The results presented in Table 3 show that PESA is non-drying. As a result of this, the chemical resistance of PESA resin coated on steel panels cannot be examined, but with the coupling of PESA with H12MDI in ratio 1:2, the resulting PESAU with two terminal –NCO groups enabled cross linking activities within the polymer matrix of the coated film which then showed adherence to the substrate panels as well as useful chemical resistance against water, xylene and 2% HCl.

3.5 Thermal Analysis of PESAU Film

Fig. 9 shows the graphical results of TGA analysis and its derivatives. The thermogram (TGA) of PESAU shows three stage degradation steps at n, o and p while its derivative of TGA curve brings out four distinct degradation processes b, c, d and e. The initial 3.05% of weight loses at 126.49°C corresponding to position “a” on the DTG represent evaporation of entrapped solvent and moisture. The first degradation step positioned at “b” corresponds to 7.28% weight loss at 220.99°C, the second degradation step at “c” has 40.82% weight loss at 300.59°C, the third degradation step at position “d” occurred with 79.27% weight loss at 408.73°C and the fourth degradation step positioned at “e” has 91.25% weight loss at 490.99°C. Janvi et al., 2000 have also observed the first, second, third and fourth degradation steps in the TGA thermogram of polyurethanes from polyols derived from safflower, soybean, corn, olive, sunflower, peanut, canola, and castor oil as representative degradation of urethane bonds, ester and amide functional groups and hydrocarbon chains respectively [33] It may be said that the four degradation steps highlighted in the thermograms of PESAU above (TGA and DTG) also corresponded to degradation of urethane, ester, amide, and hydrocarbon bonds and confirms PESAU formation.

The curing and degree of curing of the resin were also observed on the differential scanning calorimetry (DSC). The DSC thermogram is presented in Fig. 10. Curing of PESAU starts at 46.17°C and stretches up to 73.46°C. An endothermic peak centering on position “S” was observed at 62.94°C, though the TGA thermogram did not show any weight loss at this temperature. However, a broad exotherm is also seen from 158.19°C to 196.57°C and centering on position “T”. The exotherm is probably attributed to the decomposition of the resin.

3.6 Antibacterial Study

The formation of inhibition zone, which deprive the growth of bacterial in the surrounding and beneath the PESAU film placed on Luria bertani

agar medium was used in assessing the bacterial activity of the synthesized resin. The results are presented in Table 4, bacterial inhibition was observed on *E. coli*, *S. aureus* and *K. pneumonia* media. However, no zone of inhibition was observed around *B. subtilis*. The enriched unsaturated fatty acid methyl esters were developed from *Thevetia peruviana* seed oil using urea fractionation method. The FAMES was successfully used in preparing desaturated N,N'-bis (2-hydroxyethyl) *Thevetia peruviana* seed oil fatty amide (DHETA), poly (ester amide-urethane) (PESA) and subsequently PESAU. The air drying resin films (PESAU) showed antibacterial activities on all tested media except *B. subtilis*. The observed chemical resistance of the resin may be attributed to the effective curing of PESAU on its substrate.

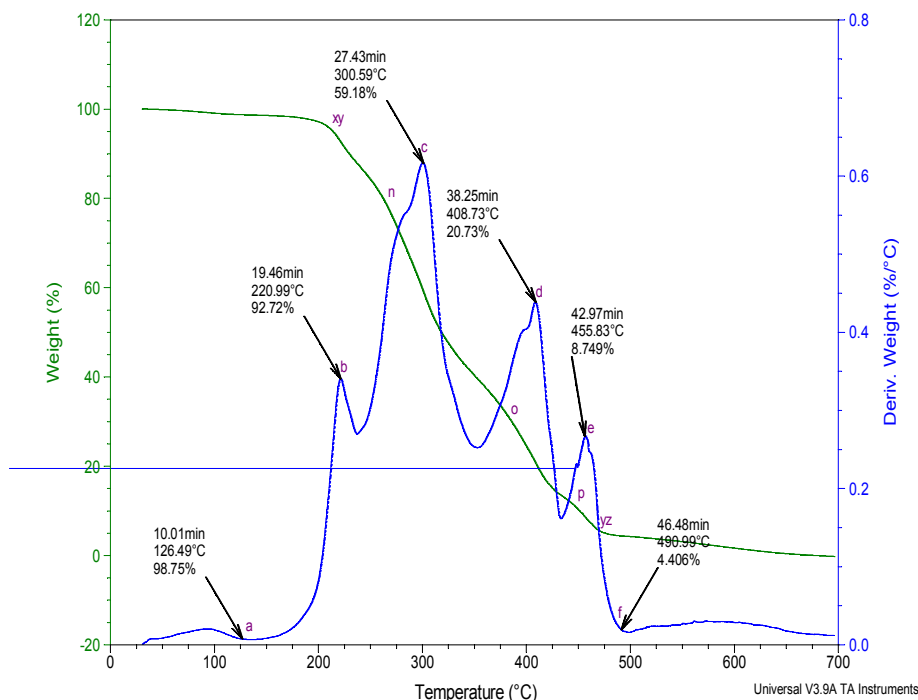


Fig. 9. Overlay profiles of TGA and DTG thermograms of PESAU

Table 2. Physico-chemical characterizations of DHETA, PESA and PESAU

Resin code	Iodine value (gI ₂ /100g)	Specific gravity (g/ml)	Inherent viscosity (dl/dg)	Refractive index	Hydroxyl value %
DHETA	46.4	0.908	-	1.58	12.1
PESA	25.3	0.993	0.698	1.58	9.7
PESAU	10.5	1.064	0.743	1.60	0

Table 3. Chemical resistance of resins

Resins	Hard drying time ^a	Water (10 days)	Xylene	2 % HCl	2% NaOH	Salt spray test (2 weeks)
PESA	Non-drying	-	-	-	-	-
PESAU	18 hours	A	A	A	B	C

^A unaffected, ^B slightly loss of gloss, ^C loss of gloss and blistering, ^a ambient cured

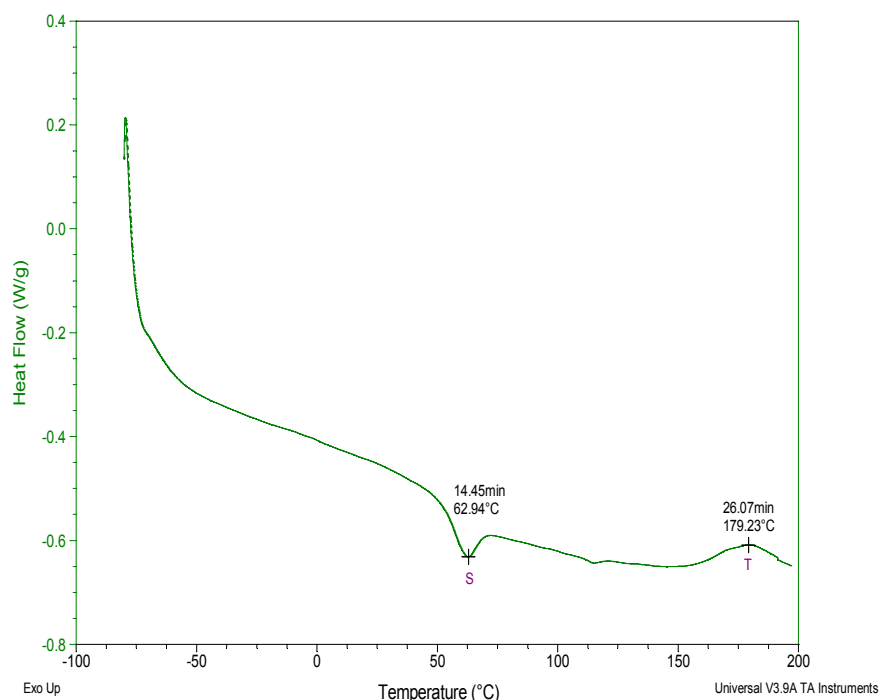


Fig. 10. DSC thermogram of PESAU

Table 4. Antibacterial activity of PESAU

Sample	<i>E. coli</i>	<i>S. aureus</i>	<i>B. subtilis</i>	<i>K. pneumoniae</i>
PESAU	+	+	-	+

⁺ indicates showing of antibacterial activity of the film, ⁻ indicates without antibacterial activity

4. CONCLUSION

The enriched unsaturated fatty acid methyl esters were developed from TPSO using urea fractionation method. The FAMES were successfully used in preparing desaturated N,N'-bis (2-hydroxyethyl) *Thevetia peruviana* seed oil fatty amide (DHETA), poly (ester amide-urethane) (PESA) and subsequently PESAU. The air drying resin (PESAU) showed antibacterial activities on all tested media except *B. subtilis*. The observed chemical resistance of the resin may be attributed to the effective curing of PESAU on its substrate.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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