Synthesis and Characterization and Performance Evaluation of Poly (Ester Amide) Urethane Derived From *Thevetia Nerrifolia* Seed Oil From Nigeria

B. A. Ikyenge, I. G. Agbidye, and S. S. Igirah

Department of Chemistry, Benue State University, P. M. B. 102119, Makurdi, Nigeria

donbkyenge@gmail.com

Abstract

Thevetia nerrifolia seed oil was extracted from the seed-bearing oil using hot extraction method involving the use of Soxhlet apparatus. The oil was characterized for physicochemical properties which include; specific gravity, refractive index, acid value, iodine value, and saponification value respectively. N,N-bis (2-hydroxyl ethyl) Fatty amide was obtained from the oil by reacting the oil with diethanol amine at 120^{o}C, which was then reacted with phthalic anhydride at 140-150^{o}C to give poly (ester amide). The poly (ester amide) was modified by reacting with 2, 4-diisocyanate under N_2 atmosphere at 120^{o}C to give poly (ester amide) urethane. Physicochemical characterization was carried out on both fatty amides, the unmodified and modified poly (ester amide). The film properties and chemical resistance were carried out on both the unmodified and urethane modified poly (ester amide). FTIR and TGA analysis were also carried out on the unmodified and the modified poly (ester amide). Findings revealed that the oil is semi-drying; suitable for surface coatings and that the performances of the poly (ester amide) were enhanced in terms of chemical resistance, film properties and thermal stability upon modification with diisocyanate.

Keywords: *Thevetia Nerrifolia*, Urethane, Fatty Amides, Poly Ester Amide

1.0 INTRODUCTION

Poly (ester amide), (PEAs) are new class of polymers that shows good degradability of polyesters as well as high thermal stability, high modulus and high tensile strength of polyamide in combination [1]. They have attracted considerable interest in surface coating research because they are produced from renewable resources as a result of depleting petroleum resources and ecological challenges [2, 3].

These biodegradable polymers are useful for various biomedical applications due to the fact that they possessed both the ester and amide bonds in their chemical backbone that enable biogradability as well as good thermal and mechanical properties. They also are known to exhibits good biocompatibility and cell-material interactions [4, 5].

The hydrolysable bonds in the chemical structures of poly (ester amide) are responsible for hydrolytic and enzymatic degradation in a wide range of biological environment, resulting in the release of non-toxic building blocks including amino acids, diols, and dicarboxylic acids. It has been shown by structure-property relationship that by rational design of the backbone, the polymer's chemical functionality, degree of crystallinity and biodegradability, solubility, thermal and mechanical properties can be readily tailored [6, 7].

These functionalized polymers are of great importance for biomedical applications since they are able to link different kinds of drugs or modulate cellular function and induce tissue ingrowth [8, 9]. PEAs are also used in other varieties of applications such as agricultural films, disposable bags, drug carriers, and matrix resins for biomedical materials, etc [10]. As a result of the advantages of poly (ester amide) in various applications, this work seeks to synthesize and introduce into the skeleton backbone, urethane linkages to enhance the performances of poly (ester mide).

2.0 MATERIALS AND METHODS

2.1 Extraction and Characterization of *Thevetia nerrifolia* Seed Oils

Thevetia nerrifolia seeds were collected from Makurdi Local Government area of Benue State. The seed were sun dried and then oven-dried at 45°C to constant weight and ground with porcelain mortar and piston to coarse particle size and stored in plastic containers for analysis. The oil was extracted with petroleum ether (40-80°C) using Soxhlet extractor for four hours [11]. The specific gravity, refractive index, acid value, iodine value, and saponification value were determined using the method described by Pearson [12].

2.2. Synthesis of N.N-bis (2- Hydroxyl Ethyl) *Thevetia nerrifolia* oil Fatty Amide (HETFA)

This was done by heating Diethanolamine (0.32 mole), sodium methoxide (0.007 mole) and *Thevetia nerrifolia* seed oil (0.1 mole) in a four-necked flask fitted with electrical stirrer, thermometer, dropping funnel and a condenser. This reaction was monitored by TLC, for 1 hour at 120°C [13].

2.3 Synthesis of *Thevetia nerrifolia* Poly (ester amide) (TNPEA)

This was synthesized by heating Hydroxyl Ethyl ***Thevetia nerrifolia*** amide with pthalic acid in equal molar ratio using xylene as a solvent, in a four-necked flask fitted with Dean and Stark trap, thermometer and mechanical stirrer at 140-150°C until the theoretical amount of water was collected in Dean-Stark trap and the reaction was monitored by TLC and the determination of acid value at regular intervals [14].

2.4 Synthesis of Poly (ester amide) Urethane (TNPEAU)

TNPEA dissolved in xylene was placed in a four-necked round bottom flask fitted with Dean-stark trap, thermometer, and mechanical stirrer. The toluene-2, 4 diisocyanate (TDI) (3 wt %) was added and stir continuously under N_2 atmostphere at 120^0C. The reaction was monitored by TLC as well as hydroxyl value determination at regular intervals of time [13].

2.5 Physicochemical characterization of HETFA, TNPEA and TNPEAU

The physicochemical properties of the fatty amide, poly (ester amide) and poly (ester amide) urethane were determined using ASTM standards [15-18].

2.6 FTIR Spectroscopy

FTIR spectra were obtained with a Smimadzu FTIR-8400s. Spectra were collected in the region of 4000-500 cm^{-1} with a spectral resolution of 0.1 cm^{-1}.

2.7 Thermo-gravimetric analysis (TGA)

Decomposition characteristics of the samples were determined with a PerkinElmer Thermal analyzer. About 5 mg of each sample was placed in the pan and heated from 50 to 650°C at the heating rate of 10°C/min under a nitrogen atmosphere.

3.0 Results and Discussion

The physicochemical properties of *Thevetia nerrifolia* are shown from Table 1. From Table 1, the oil yield was found to be 47.52. The yield is good and shows that the oil has potential in surface coating and in the manufacture of oleo chemicals.

The saponification value of the oil was found to be 184.78. Saponification value indicates the average molecular weight of the oil [12]. A high saponfication value indicates that the oil contained a higher proportion of low molecular weight fatty acids.

The acid value was found to be 3.16. Acid value of oil measures the extent to which the glycerides had been decomposed by lipase action. The decomposition is usually accelerated by heat and light. The acids that are usually formed include free fatty acids, acid phosphate, and amino acids. Free fatty acids are formed at a faster rate than the other acids [19].

The iodine value of 112.10 indicated that the oil is semi-drying, which means that there are high levels of poly unsaturated fatty acids [20].

The refractive index 1.466 and the specific gravity of 0.92 conform to the values given by literatures to other vegetable oils.

Table 1: Physicochemical Properties of *Thevetia nerrifolia* **Seed Oil**

Parameters	**Value**
Oil yield (%)	47.53 ± 0.20
Specific Gravity(g/cm^3)	0.92 ± 0.05
Refractive index	1.47 ± 0.02
Acid value (mg/KOH/g)	3.16 ± 0.28
Iodine value(Wij's)	112.10 ± 0.03
Saponification value (mg/g)	184.78 ± 0.43

The physicochemical characterization of the poly (ester amide) and poly (ester amide) urethane are shown from Table 2. The physicochemical properties in Table 2 in comparison to the extracted *Thevetia nerrifolia* seed oils established that; the Iodine value decreases because more bonds are open for reactions as the reagents were added, causing the unsaturation to decrease. The saponification value decreases due to increase in molecular weight occasioned by TDI addition. Acid value of the TNPEA tends to increase due to the addition of pthalic acid. The refractive index of TNPEAU was not dictated due to higher viscosity [13].

Table 2: Physicochemical properties of TNPEA and TNPEAU

Characteristic	**TNPEA**	**TNPEAU**
Acid value (mg/KOH/g)	8.84	7.62
Iodine(Wij's)	27.50	12.05
Saponification value(mg/KOH/g)	122.72	119.72
Refractive index	1.58	-
Specific gravity(g/cm^3)	0.95	0.99

TNPEA - *Thevetia nerrifolia* poly (ester amide)

TNPEAU -*Thevetia nerrifolia* poly (ester amide) urethane

The chemical resistance and film properties of the unmodified and urethane modified poly (ester amide) are shown from Table 3. The urethane modified poly (ester amide) was not affected by water. Water is a common enemy to most materials of construction. The absorption of water by films can lead to loss of components from the films and subsequent deterioration [21]. The poor alkali resistance of both the unmodified and the urethane modified poly (ester amide)s may be explained on the basis that they consists of ester groups, which are known to be susceptible to hydrolysis by alkali [22]. Both samples performed satisfactorily in 0.1M H_2SO_4.

The urethane modified poly (ester amide) showed excellent adhesion as opposed to the unmodified. According to Nigerian Industrial Standard NIS 268: 1989, gloss paint should not exhibit more that 50% removal of the dry film. Thus the unmodified and the modified showed good adhesion since none gave a removal of up to 50% as recommended by the NIS standard. The pencil hardness from lead pencils graded from 5B to 6H showed that the urethane modified poly (ester amide) has the highest pencil hardness. The increase in hardness could be attributed to enhanced network structures occasioned by the modification [23]. The drying times of the poly (ester amide) was longer than that for poly (ester amide) urethane because the –NH groups of urethane linkages form hydrogen bonds both with the mild steel and with the carbonyl oxygen atoms of the polymer itself [14].

Table 3: Chemical Resistance and Film properties of TNPEA and TNPEAU

Media	**TNPEA**	**TNPEAU**
Distilled water	2	1
Acid(0.1 H_2SO_4)	1	1
Brine (5% w/w NaCl)	2	2
Alkali (0.1 NaOH)	2	2
	FILM PROPERTIES	
Adhesion(%)	3B (5-15)	5B (0)
Hardness	2H	5H
Drying times(Minutes)	48	31

1 = No effect 2 = whitening of film

The FTIR spectrum of *Thevetia nerrifolia* poly (ester amide) Fig. 1, showed the presence of a strong broad stretching band of the –OH functional group at 3394.83 cm^{-1}, asymmetric and symmetric CH_2 stretching peak at 2931.9 cm^{-1} and 2862.46 cm^{-1} respectively. The stretching band at 1728.28 cm^{-1} for the carbonyl of ester in addition to a band at 1581.68 $cm^{-1}$of the amide confirm the formation of ester linkage. The band at 1273.06 cm^{-1} is ascribable to the amide C-N. The characteristic bands of alkane C-H and alkene C-H bending shows the vibration at 1458.23 cm^{-1} and 732.97 cm^{-1}.

Figure 2 is the FTIR spectrum of the *Thevetia nerrifolia* poly (ester amide) urethane. It showed similar peaks observed in the unmodified poly (ester amide). In addition N-H deformation mode, this appears at 1550.82 cm^{-1}. The band due to carbonyls of ester appears at 1728.28 cm^{-1} whereas carbonyl of amide appears at 1620.26 cm^{-1} as a result of the TDI modification.

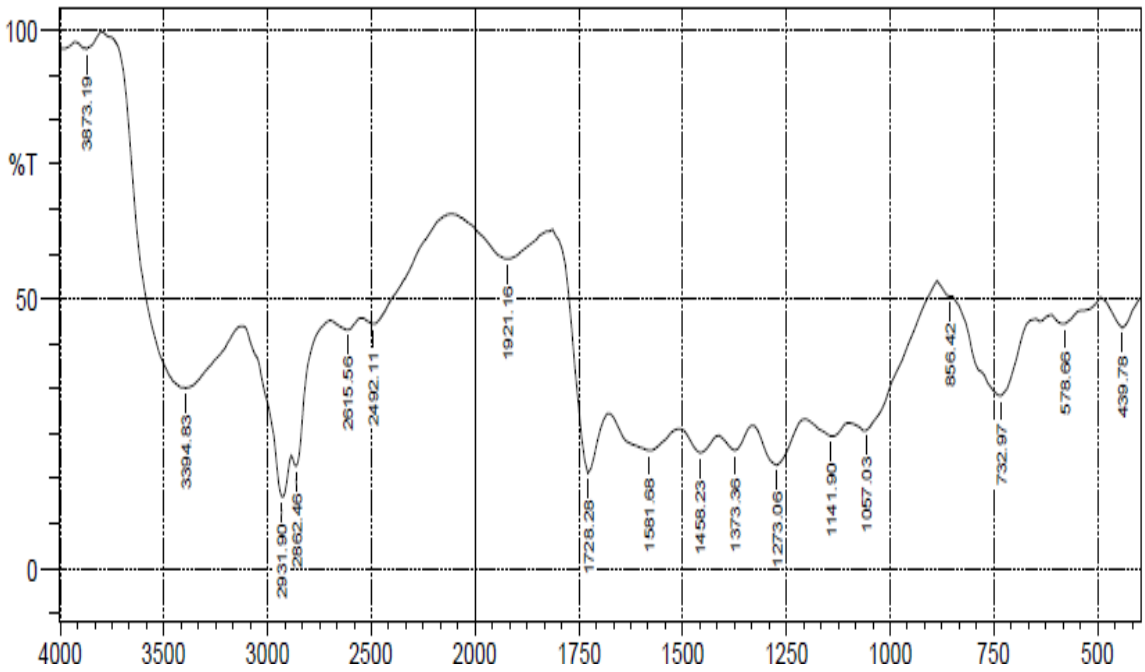

Figure 1: FTIR Spectrum of Poly (ester amide) from *Thevetia nerrifolia* Seed Oil

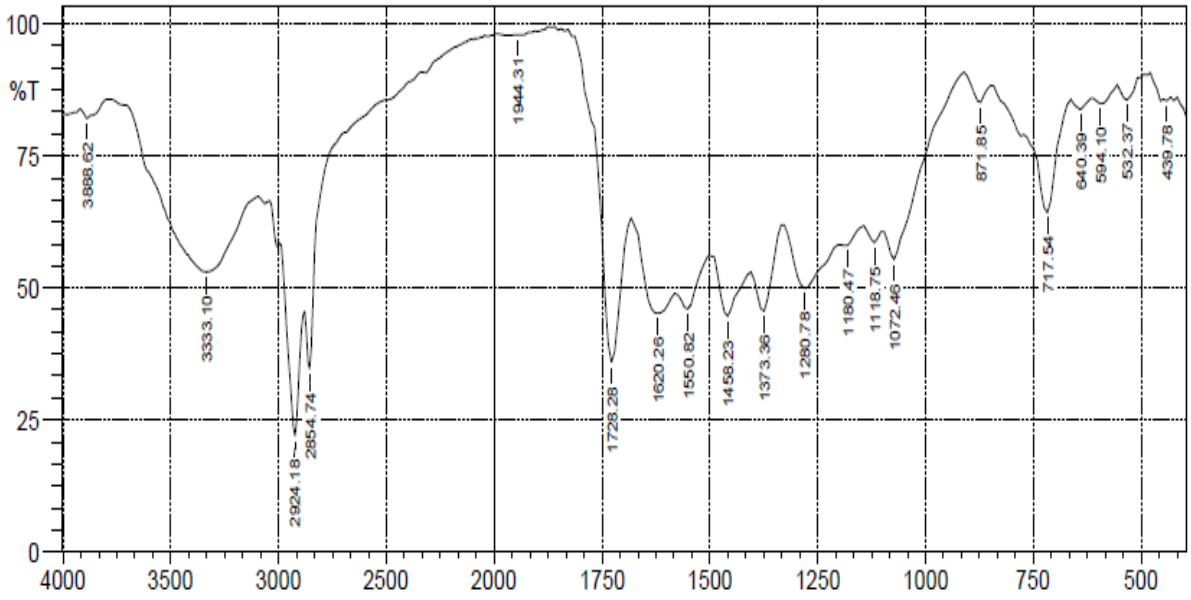

Figure 2: FTIR Spectrum of Poly (ester amide) Urethane from *Thevetia nerrifolia* Seed Oil

The TGA curves of unmodified and modified poly (ester amide) are shown Fig.3(a) and Fig. 4(a), while Fig.3(b) and Fig.4(b) represent the derivative of thermo-gravimetric analysis of both the unmodified and modified poly (ester amide), at a rate of 10°C/minute, studied under nitrogen atmosphere. TGA shows two degradation steps. The initial 11% weight loss at 170°C for the modified and 14% weight loss at 140°C for the unmodified correspond to entrapped solvent and moisture. The first step of degradation is associated with 19% wt loss at 315°C and 20% wt loss at 280°C, which corresponds to the decomposition of ester and amide. The faint second degradation with 80% wt loss at 410°C for modified and 89% wt loss at 390°C for unmodified which corresponds to decomposition of fatty acid hydrocarbon chain. This shows that the urethane modified poly (ester amide) display more thermal stability than the unmodified poly (ester amide).

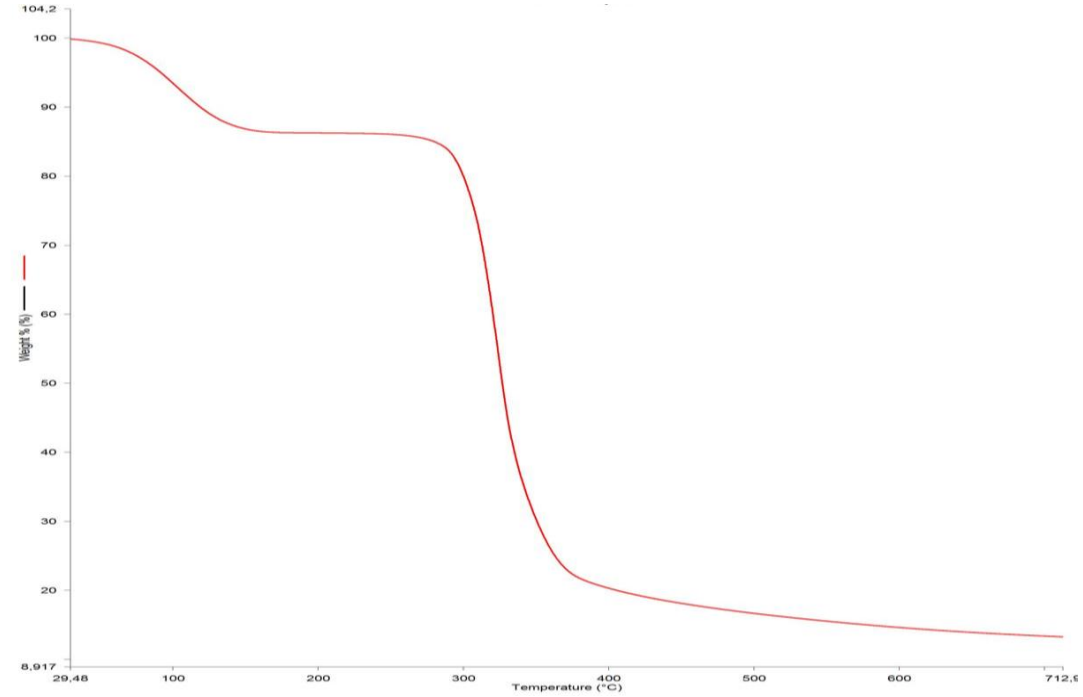

Figure 3(a): Thermo-gravimetric Analysis (TGA) Spectrum of Unmodified Poly (ester amide)

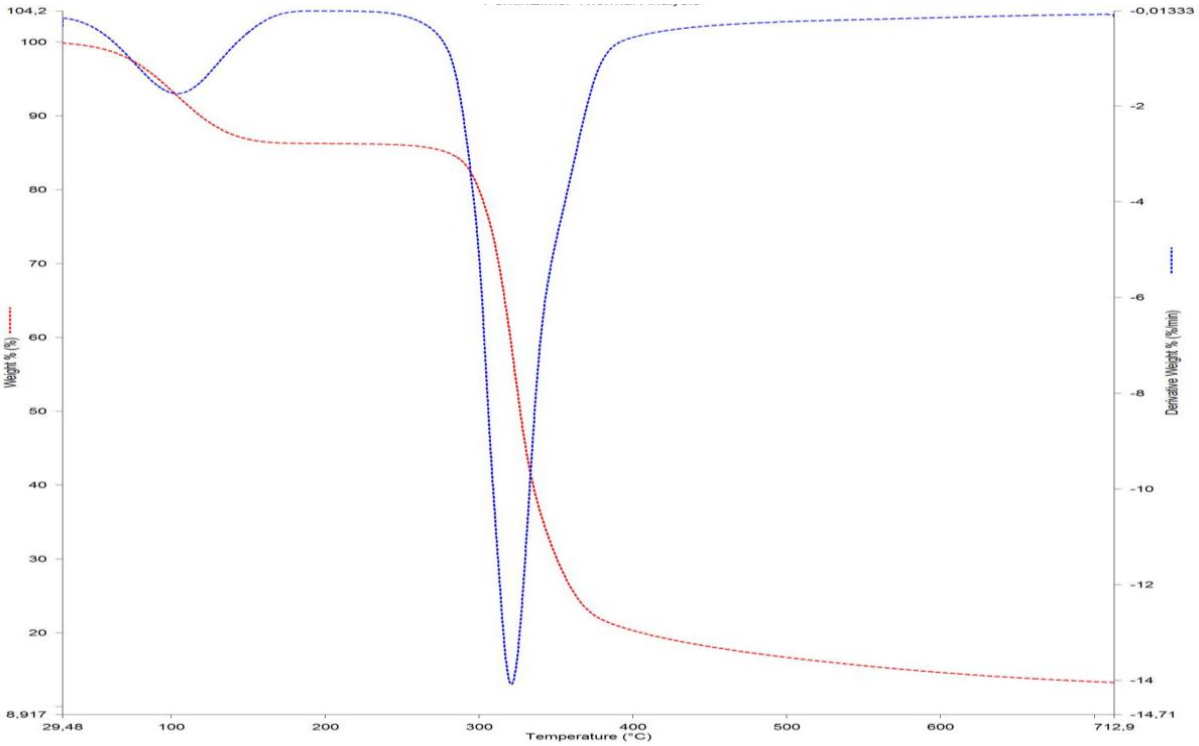

Figure 3(b): Derivative of (TGA) of Unmodified of Poly (ester amide)

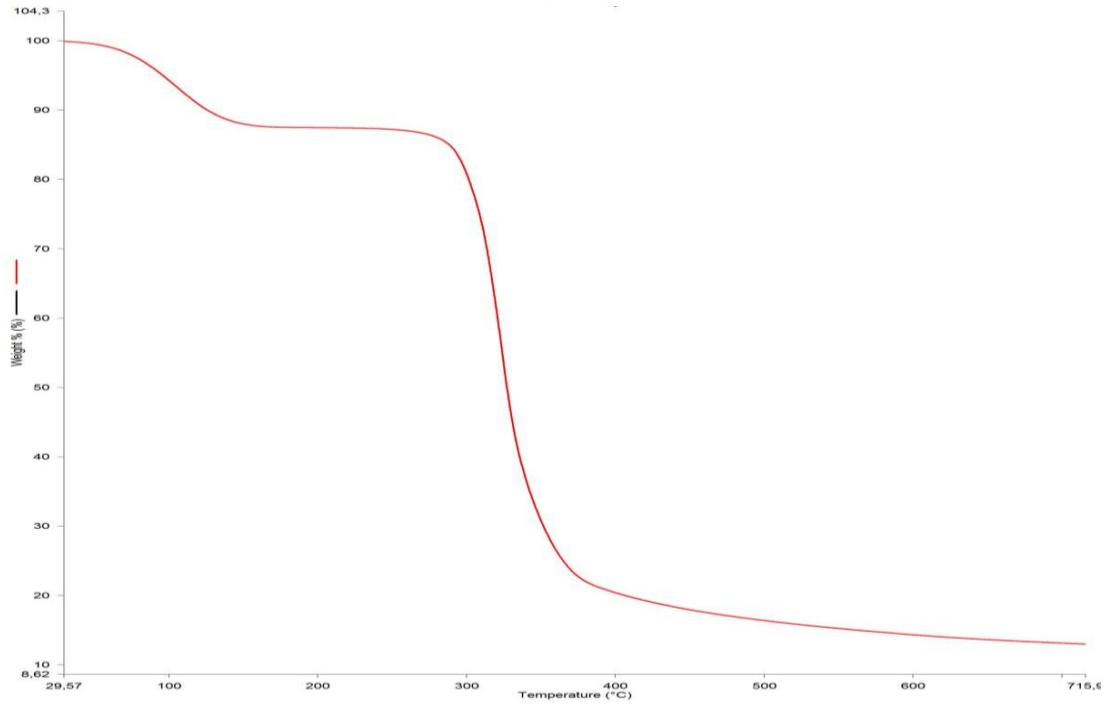

Figure 4(a): Thermo-gravimetric Analysis (TGA) Spectrum of Modified Poly (ester amide)

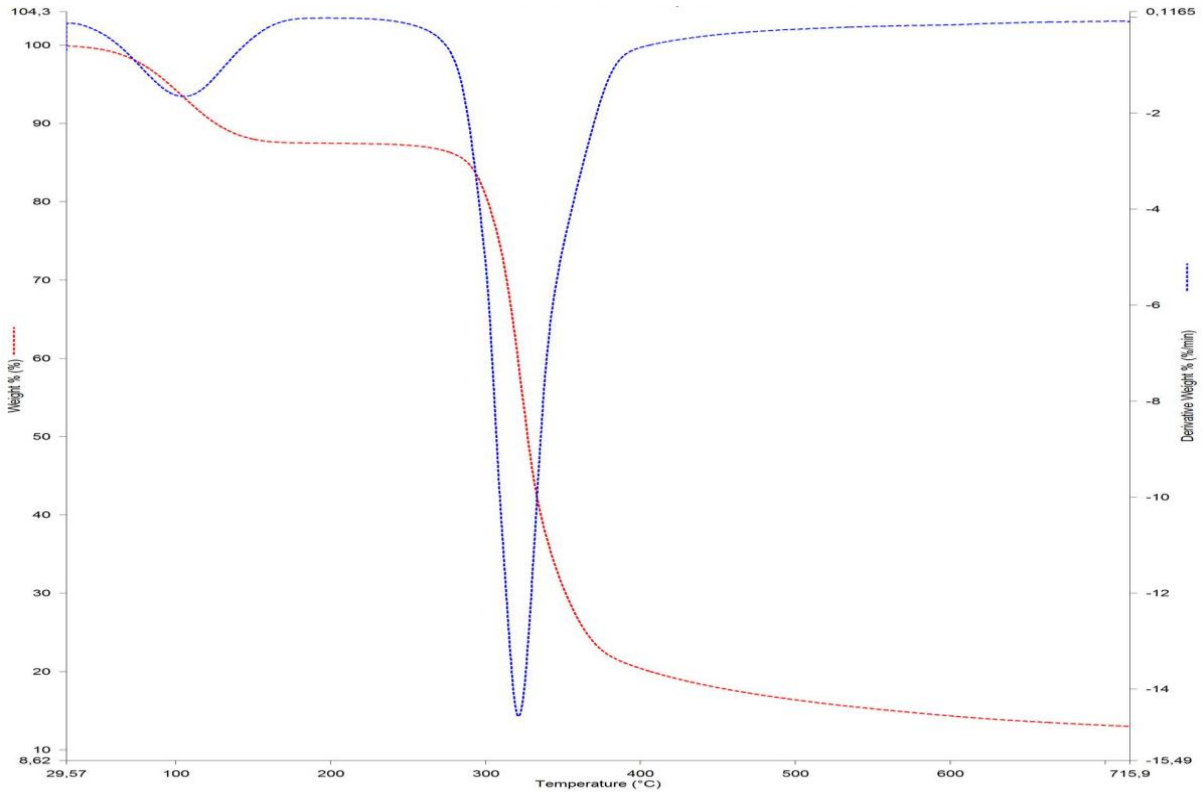

Figure 3(b): Derivative of (TGA) of Modified of Poly (ester amide)

4. Conclusion

The physicochemical properties of poly (ester amide) prepared from *Thevetia nerrifolia* seed oils compared favourably with those prepared from other vegetable oils. Thus *Thevetia nerrifolia* seed oils, non-edible oil shows potency in replacing the edible vegetable oils in the synthesis of poly (ester amide) and surface coatings, The results also indicated that modification of the poly (ester amide) with diisocyanate enhances the performances in terms of chemical resistance, film properties, and thermal stability, as the data on these parameter clearly suggested.

5. Acknowledgements

The authors wish to appreciate the Department of Chemistry, Benue State University for the financial support granted during this research work. We are equally grateful to the technical staff of the Chemistry Department of the University for their assistance during this research work.

References

1. S. Pramanik, K. Sagar, B. K. Konwar, and N. Karak (2012). Synthesis, characterization, and properties of a castor oil modified biodegradable poly (ester amide) resin. *Progress in Organic Coatings,* **75:** 569-578

2. S. Mallakpour and A. Zadehnazari (2011). Advances in synthetic optically active condensation polymers-A review. *Express Polymer Letters*, **5:** 142-181

3 M. Okada (2002). Chemical synthesis of biodegradable polymers, P*rogress in Polymer Science* **27:** 87-133

4 J. A. Horwitz, K. M. Shum, J. C. Bodle, M. X. Deng, C. C. Chu and C. A. Reinhart-King (2010) "Biological Performance of Biodegradable Amino acid-based poly (ester amide) s: Endothelial cell adhesion and inflammation in vitro" Journal *of Biomedical Material Research,* **95:** 371-380

5 D. K. Knight, E. R. Gillies and K. Mequanint (2011) "Strategies in Functional Poly (ester amide) Synthesis to Study Human Coronary Artery Smooth Muscle Cell Interactions" *Bio macro molecules* **12:** 2475-2487

6 R. Guo, C. C. Chu (2007) "Biodegradation of Unsaturated Poly (ester amide) s and their Hydro gels" *Biomaterials,* **28:** 3284-3294

7 R. Rodriguez-Galan, A. Franco, L. puiggali and J. Degradable (2011) "Poly (ester amide) s for Biomedical Application: Review", *Polymers,* **3:** 65-69

8 A. Akelah, A. Moet (1990). *Functionalized Polymers and Their Applications*; Chapman and Hall: London, UK, 67-84

9 A.S. Kulshrestha, A. Mahapatro (2008). Polymers for Biomedical Applications. *ACS Symp. Ser.* 977: 1-7.

10 S. Liu, C. Li, J. Zhao, Z. Zhang and W. Yang (2011). Synthesis and characterization of poly (ester-amides) having short nylon-6 segments in the main chains through poly-condensation and chain extension. *Polymer;* **52**: 6046-6055

11 N. Kaushik, K. Kumar, S. Kumar and S. Roy (2007). Genetic Variability and Divergence Studies in Seed Triats and Oil content of Jathropha curcas L. *Accessions Biomass and Bioenergy* 31: 497-502

12 D. Pearson (1991). The Chemical Analysis of Foods 11th Ed Church-hill

13 R. S. Mohammed, A. Manawwer, and M. A. Naser (2015). Development of Castor Oil Based Poly(urrthane-esteramide)/TiO Nan-composites as Anticorrosive and Antimicrobial Coatings. *Journal of Nano-materials***, 2(33):** 67-75

14 T. O. Siyanbola, K. Sasidhar, B. P. Anjaneyulu, B.V.S.K. Rao, N. Ramanuj, O. Olaofe, E.T. Akintayo and K. V. S. N. Raju (2013).. Anti-microbial and anti-corrosive poly (ester amide urethane) siloxane modified ZnO hybrid coatings: *RSC Advance*. 5**(59):** 47928-4794

15 ASTM D 1639-90 (1994). Standard Methods for Acid value of Organic Materials, In: Annual Book of American Society and Material Standard 6: 260-261

16 ASTM D 1541-60 (1979). Test for Iodine value of Drying Oils and their Derivatives, In: Annual Book of American Society and Material Standard 6: 260-261

17 ASTM D 1962-67 (1994). Test for Saponification value of Drying Oils, Fats and Polymerized Fatty Acids In: Annual Book of American Society and Material Standard 29: 259-61

18 ASTM D 1647-89 (1994) Resistance of Dried Film to Varnishes, Water and Alkalie Annual Book of American Society and Material Standard Philadelphia 6: 258-9

19 F.E.M. Booth and G.E Wickens (1998). Non-Timber uses of Selected and Zone Trees and Shrubs in Africa. FAO conservation Guide Rome 92-101

20 M. Baumer (1996). Food-producing Trees and Shrubs of West Africa *Serie-Etuides-et-Recherekes* Senegal 168-170: 252-260

21 C. M. Ewulonu, I. O. Igwe and G. N. Onyeagoro (2016) Performance of Local Clay-Titanium Dioxide Core-Shell Extender Pigments in Alkyd Paints. *Advances in Nanoparticles* **5**(1): 90-102

22 J. Mills and R. White (1979) Analysis of Paint Media. In: National Gallery Technical Bulletin, London: National Gallery **3:** 65-67

23 Mohammed Al-Shannag (2012) Energy Saving in Alkyd Resin and Aqueous-Emulsion Processes using a heat-integrated cycle. *Journal of the University of Chemical Technology and Metallurgy,* **47**(1): 31-36