

SYNTHESIS AND CHARACTERIZATION OF POLY ESTER AMIDE URETHANE DERIVED FROM *JATHROPHA CURCAS* SEED OIL FROM NIGERIA

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### Abstract

Poly ester amides are synthetic polymers that combine the thermal and mechanical properties of polyamides as well as biocompatibility and biodegradability of polyesters and hence are used in many fields. Their modification with polyisocyanates in surface coating formulations improved their performances due to unusual capacity of the polymer chains to align themselves to give maximum hydrogen bonding. In this research, *Jathropha curcas* seed oil was extracted from the seed bearing oil using hot extraction method involving the use of Soxhlet apparatus. Physicochemical properties of the oil viz; specific gravity, refractive index, acid, iodine, and saponification values were determined. N,N-bis (2-hydroxyl ethyl) fatty amide was obtained from the oil by reacting the oil with diethanol amine at 120°C, followed by reaction with phthalic anhydride at 140-150°C to give poly ester amide. The poly ester amide was modified by reacting with 2, 4-diisocyanate under N<sub>2</sub> atmosphere at 120°C, in which the diisocyanate groups reacted with the hydroxyl groups of the poly ester amide to form the urethane moieties, thus resulting to poly ester amide urethane. Physicochemical characterization, Fourier transform infrared spectroscopy and thermo-gravimetric analysis were carried out on both the unmodified and modified poly ester amide. Findings revealed that *Jathropha curcas* seed oil is semi-drying; suitable for the synthesis of oleo chemicals and that the performances of the poly ester amide was enhanced in terms of drying times and thermal stability upon modification with toluene-2, 4- diisocyanate.

**Keywords:** *Jathropha curcas*, Fatty polyamide, poly ester amide, urethane.

### 1. INTRODUCTION

Research has been keen on developing materials from renewable resources as a result of the depleting petroleum resources and ecological challenges. Thus poly ester amide has attracted great interest since they can be produced from renewable resources [1]. Poly ester amide (PEAs) are synthetic materials that combined the unique properties of biodegradability of polyesters and the excellent mechanical properties of polyamides and are known to exhibit good mechanical and thermal behaviours [2, 3]. Their rigidity is due to the double bond character of the amide coupled with the extensive hydrogen bonding which influences the ordering of the PEAs that promote the mechanical and thermal stability.

These synthetic biodegradable polymers also serves as alternative to the non-degradable materials used in biomedical applications. 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 in growth [4, 5]. PEAs are also used in other varieties of applications such as agricultural films, disposable bags, surface coatings and matrix resins for biomedical materials etc [6].

A considerable body of literature refers to the preparation of PEAs with different architectures, which could lead to amorphous, semi-crystalline and elastomeric materials. Furthermore, published data shows that a variety of monomers can be employed and that  $\alpha$  amino acid,

carbohydrate or oligo (ethylene glycol) units can be easily incorporated. In this way, it is easy to get a wide range of final properties [3]. Since the 1990s, research on poly ester amide has mainly focused on the preparation of functionalized polymers. Strategies are based on the incorporation of amine, hydroxyl and carboxyl pendant groups, or even on the incorporation of carbon-carbon double bonds in either the chain backbone or the pendant group [7]. It is in relation to established works on poly ester amide that this work seeks to synthesize poly ester amide from *Jathropa curcas* seed oil, a non-edible vegetable oil to conserve food security and incorporate urethane linkages in the polymer to improve its performances in terms of; adhesion, abrasion resistance, flexibility, durability, hardness, thixotropy etc occasioned by extensive hydrogen bonding due to urethane modification, for surface coating applications.

## 2. MATERIALS AND METHODS

### 2.1 Extraction and Characterization of *Jathropa curcas* Seed Oils

*Jathropa curcas* seeds were collected from Makurdi Local Government area of Benue State. The seeds were sun dried and 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 [8]. The specific gravity, refractive index, acid, iodine and saponification values were determined using the method described by Pearson [9].

### 2.2 Synthesis of (HEJCA)- Hydroxyl Ethyl *Jatropa curcas* Amide

This was done by heating Diethanolamine (0.32 mole), sodium methoxide (0.007 mole) and *Jathropa curcas* 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 [10].

### 2.3 Synthesis of *Jatropa Curcas* Polyester amide (JCPEA)

This was synthesized by heating hydroxyl ethyl *Jatropa curcas* amide with phthalic 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 [11].

### 2.4 Synthesis of Poly (esteramide) Urethane (JCPEAU)

JCPEA 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<sub>2</sub> atmosphere at 120°C. The reaction was monitored by TLC as well as hydroxyl value determination at regular intervals of time [10].

### 2.5 Physicochemical characterization of HEJCA, JCPEA and JCPEAU

The physicochemical properties of the fatty amide, poly ester amide, poly ester amide urethane and the drying times were determined using ASTM standards [12-16].

### 2.6 FTIR Spectroscopy

FTIR spectra were obtained with a Smimadzu FTIR-8400s. Spectra were collected in the region of 4000-500 cm<sup>-1</sup> with a spectral resolution of 0.1 cm<sup>-1</sup>.

### 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. Results and Discussion

The physicochemical properties of *Jathropa curcas* oil are shown in Table 1. From Table 1, the oil yield was 48.83. The yield is appreciable and shows that it has potential in surface coating and in the manufacture of oleo chemicals.

The saponification value of the oil was 196.35. Saponification value indicates the average molecular weight of the oil [9]. A high saponification value indicates that the oil contained higher proportion of low molecular weight fatty acids.

Acid value was 5.66. 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 [17].

The iodine value of 106.08 indicated that the oil is semi-drying which shows that there are high levels of poly unsaturated fatty acids [18]. The

refractive index 1.466 and the specific gravity of 0.909 conform to the values given by literatures to other vegetable oils.

**Table 1: Physicochemical Properties of *Jathropa curcas* Seed Oil**

Parameters	Value
Oil yield (%)	48.83 ± 0.26
Specific Gravity	0.909 ± 0.03
Refractive index	1.466 ± 0.02
Acid Value (mg KOH/g)	5.66 ± 0.28
Iodine Value (Wij's)	106.08 ± 0.03
Saponification Value (mg/g)	196.35 ± 0.45

The physicochemical characterization of the fatty polyamide, poly ester amide and poly ester amide urethane are shown in Table 2. The physicochemical parameters in Table 2 in comparison to the extracted *Jathropa curcas* seed oil established that; the Iodine value decreases because more bonds are open for reactions as the reagents were added, causing the unsaturation as well as the drying times to decrease. The saponification value decreases due to increase in molecular weight occasioned by

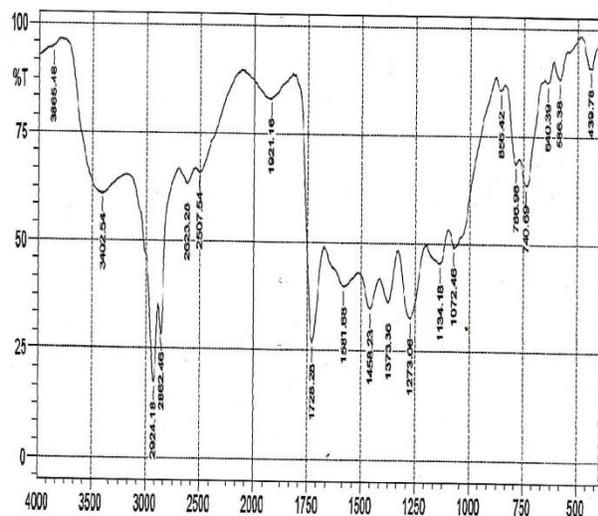
toluene-2, 4-diisocyanate addition. Acid value of the JCPEA tends to increase due to the addition of phthalic acid. The refractive indices of HEPEA and JCPEA were not dictated due to higher viscosity. The drying times of the poly ester amide was longer than that for poly ester amide urethane because the -NH groups of urethane linkages form hydrogen bonds both with the mild steel and with the carbonyl oxygen atoms of the polymer itself [11].

**Table 2: Physicochemical properties of HEJCA, JCPEA, JCPEAU**

Characteristic	HEJCA	JCPEA	JCPEAU
Specific gravity	0.920	0.930	0.930
Refractive index	-	-	1.502
Acid value (mg/KOH/g)	2.89	6.67	4.86
Saponification value (mg/g)	180.6	176.5	170.5
Iodine value (Wij's)	19.65	16.04	15.53
Drying times (min)	-	45	30

HEJCA- Hydroxyl Ethyl *Jatropa curcas* amide, JCPEA - *Jatropa Curcas* Poly (ester amide)  
JCPEAU- *Jatropa Curcas* Poly (ester amide) Urethane

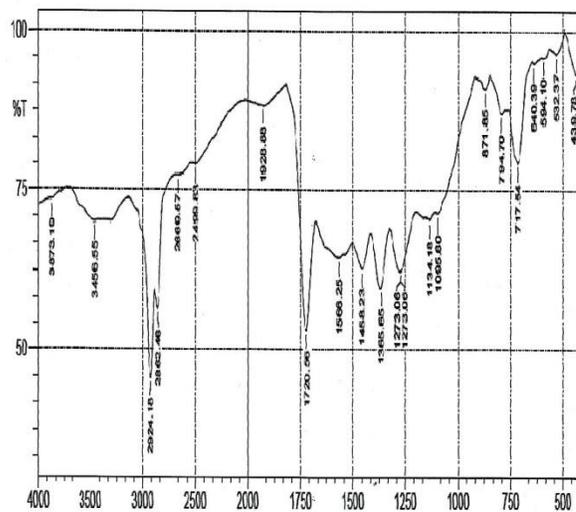
The FTIR spectra of the *Jathropa curcas* poly ester-amide in Fig. 1, shows the broad band of hydroxyl group at  $3402.54\text{ cm}^{-1}$ ,  $\text{CH}_2$  symmetric and asymmetric stretching vibrations at  $2924.18\text{ cm}^{-1}$  and  $2862.46\text{ cm}^{-1}$  respectively. The ester carbonyl vibration and the  $-\text{C}-\text{N}$  vibration of the amide at  $1728.28\text{ cm}^{-1}$  and  $1458.23\text{ cm}^{-1}$  respectively.



**Figure 1:** FTIR Spectrum of Poly ester amide from *Jathropa curcas* Seed Oil

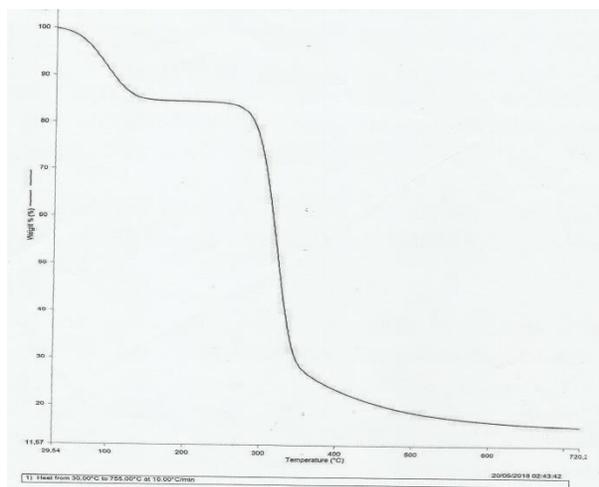
The thermo-gravimetric analysis thermo grams show the degradation steps for both the unmodified and urethane modified poly ester amide. The initial 15% weight loss at  $105^{\circ}\text{C}$  for the poly ester amide and 7% weight loss at  $170^{\circ}\text{C}$  for the poly ester amide urethane corresponds to entrapped solvent and moisture. The first step of degradation is associated with 27% weight loss at  $280^{\circ}\text{C}$  and 20% weight loss at  $330^{\circ}\text{C}$  corresponds to the decomposition of ester and amide. The faint second degradation with 90% weight loss at  $400^{\circ}\text{C}$  for poly ester amide and 78% weight loss at  $405^{\circ}\text{C}$  for the urethane modified poly ester amide corresponds to decomposition of fatty acid hydrocarbon chains. The drying times of the urethane

The FTIR spectrum of poly ester amide urethane in Fig. 2 shows showed similar peaks observed in the poly ester amide. In addition, carbonyl of urethane linkages and benzene ring occur at  $1720.56\text{ cm}^{-1}$  and  $717.54\text{ cm}^{-1}$  respectively and also N-H (deformation) occur at  $1566.25\text{ cm}^{-1}$  as a result of the toluene-2, 4- diisocyanate modification of the poly ester-amide.

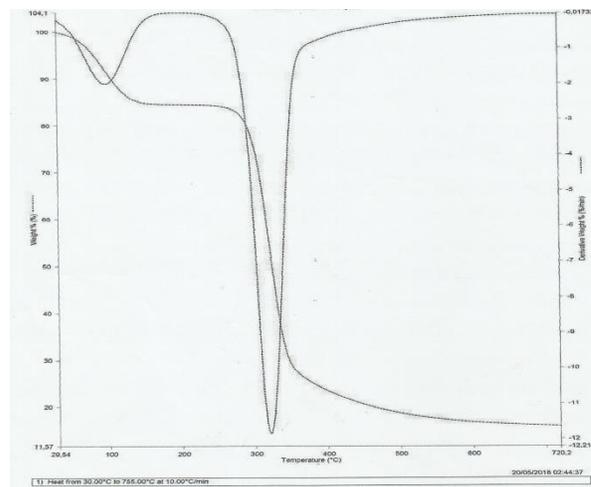


**Figure 2:** FTIR Spectrum of Poly ester amide Urethane from *Jathropa curcas* seed oil

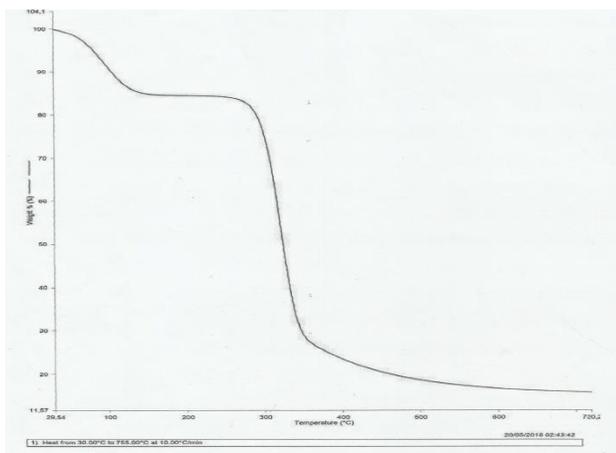
modified poly ester amide was shorter than that of the poly ester amide due to reduction in iodine value. Also the heat stability of the poly ester amide urethane was greater than that of the poly ester amide. This is an indication that modifying the poly ester amide with urethane enhanced its performances. The weight loss is indicated by the respective derivatives of the thermo-grams as shown in Fig. 4 and Fig. 6 for unmodified and modified poly ester amide. The first derivative peak temperature is the point of the greatest rate of change of the weight loss curve, the inflection point.



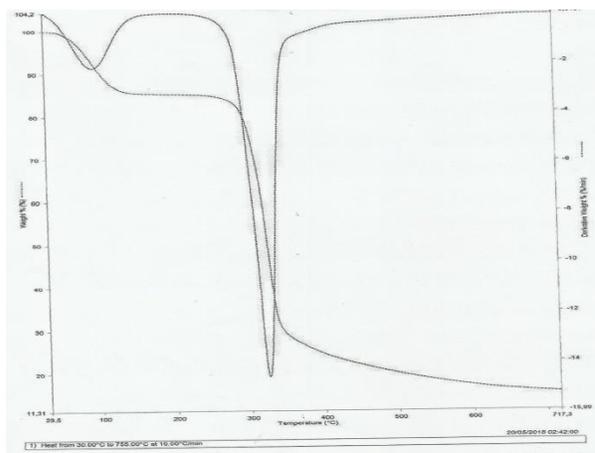
**Figure 3:** Thermo-gravimetric Analysis (TGA) Spectrum of Poly ester amide



**Figure 4:** Derivative of Thermo-gravimetric Analysis (TGA) Spectrum of Poly ester amide



**Figure 5:** Thermo-gravimetric Analysis (TGA) Spectrum of Poly ester amide urethane



**Figure 6:** Derivative of Thermo-gravimetric Analysis (TGA) Spectrum of Poly ester amide urethane

#### 4. Conclusion

he physicochemical properties of poly ester amide prepared from *Jathropa curcas* seed oil compared favourably with those prepared from other vegetable oils. Thus *Jathropa curcas* seed

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oil shows potency in the synthesis of poly ester amide. The results also indicated that modification of the poly (ester amide) with Toluene-2,4-diisocyanate enhances the performances in terms of drying times and thermal stability.

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