

SYNTHESIS AND CHARACTERIZATION OF NOVEL *PLUKENETIA CONOPHORA* SEED OIL-STYRENE-DIVINYLBENZENE THERMOSETTING COPOLYMER

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ABSTRACT

Vegetable oils are perfect alternatives for petrochemicals. During this study the cationic copolymerization of conjugated and unconjugated *Plukenetia conophora E.* seed oil with styrene and divinylbenzene was carried out in the presence of boron trifluoride etherate as catalyst. Polymers starting from soft rubbers to strong and rigid plastic were formed in quantitative yield. Nuclear magnetic resonance spectroscopy (¹HNMR) was employed in monitoring the functionalization process. The polymers were soxhlet-extracted using methylene chloride as refluxing solvents and also the extracts were studied using ¹HNMR in order to understand the microstructure of the materials. About 71 – 96 wt% of insoluble substances were retained after extraction of bulk polymers. Result of spectroscopic analysis indicated that all the aromatic monomers were incorporated within the cross-linked polymer networks. Thermogravimetric analysis (TGA) indicated that these copolymers were thermally stable below 150°C. The maximum temperature (T_{max}) of the TGA derivative curves of polymers prepared from unconjugated *Plukenetia conophora* (320°C) and conjugated *Plukenetia conophora* (330°C) which was determined as a corresponding derivative weight loss curve only varied slightly. The tensile mechanical properties of the conjugated *Plukenetia conophora* polymer showed a significant decrease in the tensile modulus (ε_t) from 304.25Mpa to 240.40Mpa and yield stress (σ_b) from 6.85Mpa to 2.52Mpa. There was a rise in the elongation at break (ε_b) from 2.77Mpa to (20.26Mpa) showing the impact of conjugation on the polymer which resulted in an increased ductility of the resulting polymer compared to polymers prepared from the unconjugated *Plukenetia conophora*. This result revealed that both *Plukenetia conophora* and its conjugated derivative are good candidate for preparation of thermosetting polymers which may find application in industries and serve as alternative to polymers made from fossil fuel.

Keywords: *Plukenetia conophora*, styrene, divinylbenzene, conjugation, copolymerization

INTRODUCTION

The application of vegetable oil as raw material for monomers and polymers is of great interest to scientists as it can be used in partial or total replacement for petrochemical products. Vegetable oil in this regard has served variety of objectives from environmental challenges to reduction in the use of fossil fuels, reduced volume of waste and reduction in ozone layer depletion. The presence of reactive groups (double bond, hydroxyl etc.) in

triglyceride make it easy to attach appropriate functional groups through chemical modification. The availability, sustainability, versatility in structure and properties and comparative low cost of plant oil give it the advantage of serving as a potential alternative to petroleum products (Meier *et al.*, 2007; de and Meier, 2011). The change from fossil feed stock to renewable resources can considerably contribute to a sustainable development in the future.

Furthermore, the environmental friendliness of products obtained from plant oils are primarily derived from the fact that chemists take advantage of the synthetic potential of nature by slightly modifying the triglyceride, thereby retaining the naturally occurring chemical structure, which makes the derived compounds biocompatible and biodegradable (Bornscheuer, 2006). Some oils like sunflower, linseed, soybean, and rubber seed have been employed in the preparation of different polymers from alkyds (Akintayo and Bayer 2002), polyesteramides, (Lam *et al.*, 2004), polyepoxides (John *et al.*, 2002), or polyurethanes (Ahmad *et al.*, 2003 ; Alam *et al.*, 2004). Due to the quest for environmental sustainability, there have been an increasing demand for replacing petroleum derived raw materials with renewable materials in the production of polymers by scientists. (Belgacem and Gandini, 2011).

The African walnut, *Plukenetia conophora* (*Tetracarpidium conophorum*) called “*Awusa*”, “*Asala*” in Yoruba, “*Ukpa*” in Igbo, Nigeria and “*Kaso*”, “*Ngak*” in Cameroon is one of the top non-timber yielding plant species in the tropical lowland rainforest of southwestern Nigeria (Amusa and Jimoh, 2012). It is a perennial plant belonging to the family *Euphorbiaceae* in the order *Malpighiales*. It is widely cultivated for its nuts, which are cooked and consumed as snack. The seed can be grounded into a powder and used with flour in baking cakes. It is contained in a pod which may be one shelled nut (single), two shelled nut (double) and three shelled nut, the nut is whitish upon cracking from the shell. There is always a bitter taste upon drinking water immediately after eating the nuts. This might be attributed to the presence of chemical substances like alkaloids (Oke, 1995; Ayodele, 2003).

The leaves of Walnut are used for the treatment of infectious disease and also the presence of tocopherol within the leaf supports its use in southern Nigeria ethno drugs as a male fertility agent (Ajaiyeoba and Fadare, 2006). The leaves are

edible and usually eaten up with rice. The leaves are also used historically for curing headache and also the contemporary fresh leaves are used for curing snakebites (Zhou *et al.*, 2018). The oil is fast drying and has been employed in the formulation of wood varnish, stand oil, vulcanized oil for rubber and leather substitute (Awodoyin *et al.*, 2000; Jiofack *et al.*, 2013).

The seed yields 48-60% oil with a flavor resembling linseed oil. The oil has been reported to be extremely unsaturated and consist of linolenic (70.1%), oleic (11.7%), stearic (0.6%) and palmitic (0.8%) acids (Akintayo and Bayer, 2002). It is therefore a very high unsaturated oil with high content of linolenic acid compared to soybean oil that has been popularly studied for lubricating substance applications (Akintayo and Bayer, 2002). The very high saponification and iodine values of *Plukenetia conophora* (PKCO) recommends its utilisation in alkyd resin, shoe polish, and shampoo production (Akintayo and Bayer, 2002). Edem *et al.* (2009) have reported proximate analysis of the seed to be crude fat (6.21%), moisture content (48.70%), crude protein (35.22%), crude fibre (3.34%), ash content (2.03%) and carbohydrate content (53.2%). Considering the percentage of the crude fat, it is very low which may be due to the condition for the proximate. Okpero (2001) reported on the methods of processing the *Plukenetia conophora* nuts.

Moreover, PKCO which consists of 98.0% unsaturated fatty acids made up of mainly 70.1% of linolenic acid, has been reported to belong to the drying oil group and might be a substitute for linseed oil (Akintayo and Bayer, 2002). It was reported that *Adenopus breviflorus* and *Plukenetia conophora* possess high oil content, indicating that processing of its oil for industrial or edible purposes would be economical. *Plukenetia conophora* has low moisture content which implies good shelf life characteristics (Akintayo and Bayer, 2002). With the increased interest in the exploitation of less-common seed oils, several studies have been carried out on *Plukenetia*

conophora and based on the Nigerian government initiative to promote industrialization following its natural resources, this research focuses on the synthesis of polymers from both modified and unmodified PKCO through cationic copolymerization with styrene and divinylbenzene initiated by boron trifluoride etherate as catalyst.

MATERIALS AND METHODS

Materials

Walnut seeds were obtained from Erekesan market, Ado Ekiti, Nigeria. Chlorobis(cyclooctene) rhodium(I) $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$, ethanol ($\text{C}_2\text{H}_5\text{OH}$), Tin(II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), Tris(*o*-tolyl) phosphine ($\text{P} - \text{CH}_3\text{C}_6\text{H}_4)_3\text{P}$, pH paper, boron trifluoride etherate (BF_3E), styrene (C_8H_8), divinyl benzene ($\text{C}_{10}\text{H}_{10}$), toluene ($\text{C}_6\text{H}_5\text{CH}_3$), tetramethyl ammonium hydroxide ($\text{C}_4\text{H}_{13}\text{NO}$), hydrogen peroxide (H_2O_2), magnesium sulphate (MgSO_4), sodium bicarbonate (NaHCO_3), and methylene chloride (CH_2Cl_2), were all purchased from Sigma-Aldrich and used as received.

Methods

Extraction of oil from Walnut

Walnut seed pods that floated on water were regarded as bad and were subsequently removed by hand picking. The good ones were washed with water, cracked open to remove the nuts, air dried and later milled using Christy mill. The samples were oven dried at 103°C and were extracted by Soxhlet method using *n*-hexane. Solvent was removed over rotary evaporator. The crude oil was

refined by agitating with 18 M NaOH (1:30 g/g of alkali: oil) for 15 min. The resultant mixture was heated to $75\text{--}80^\circ\text{C}$ to break the soap stock and the neutral oil separated by centrifugation.

Isomerization of *Plukenetia conophora* oil

To 30.8 g (100 mmol) of PKCO in 200 ml ethanol were added 71.5 mg (5mol %) of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$, 120.5 mg (20mol %) of $(\text{P} - \text{CH}_3\text{C}_6\text{H}_4)_3\text{P}$, and 180.5 mg (40 mol %) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The system was flushed with nitrogen gas while stirring was carried out for 24h at 60°C . The solvent was removed over rotary evaporator and the product purified by chromatography on a silica gel column to obtain the conjugated *Plukenetia conophora* oil (CPKCO) (Andjelkovic *et al.*, 2006).

Cationic copolymerization

Varying amount of the styrene and divinylbenzene (DVB) were added to the desired amount of *Plukenetia conophora* seed oil in a flask with a magnetic stirring bar followed by the addition of an appropriate amount of a modified initiator which was generally required to produce homogenous resins and polymers. The modified initiator was prepared by mixing PKCO ethyl ester with BF_3E . The reaction mixture was then injected into a Teflon mold and cured as follows: 60°C for 10 min 80°C for 20 min and 110°C for 24 h (Olufunke *et al.*, 2015). Table 1 shows the series of polymers prepared using different percentage composition but only two polymers (C and E) were characterized.

Table 1: Percentage composition of resin

Sample	Oil	Styrene (ST)	DVB	Catalyst (BF_3E)	Total
A	10% (0.20g)	55% (1.09g)	28% (0.55g)	8% (0.16g)	2g
B	20% (0.40g)	48% (0.96g)	24% (0.48g)	8% (0.16g)	2g
C	30% (0.60g)	42% (0.83g)	22% (0.41g)	8% (0.16g)	2g
D	45% (0.90g)	32% (0.64g)	15% (0.30g)	8% (0.16g)	2g
E	30% (0.60g)	42% (0.83g)	22% (0.41g)	8% (0.16g)	2g

A-PKCO10-ST55-DVB28- BF_3E , B- PKCO20-ST48-DVB24- BF_3E , C- PKCO30-ST42-DVB22- BF_3E , D- PKCO45-ST35-DVB15- BF_3E and E- CPKCO30-ST42-DVB22- BF_3E

Soxhlet extraction of the bulk polymer

In this work, the following nomenclatures were adopted for the polymer samples obtained: extraction was carried out on all the polymers but only two were characterized. Polymer sample prepared from 30 wt % PKCO, 42 wt % ST, and 22wt % DVB and 8wt% BF₃E8 is designated as PKCO30-ST42-DVB22- Bf₃E8, while a polymer sample prepared from 30 wt % CPKCO, 42 wt % ST, and 22wt % DVB and 8wt% Bf₃E8 is designated as CPKCO30-ST42-DVB22- Bf₃E8. Bulk polymer samples C (PKCO30-ST42-DVB22- Bf₃E8) and E (CPKCO30-ST42-DVB22- Bf₃E8) of known weight were extracted with refluxing methylene chloride over a period of 24h in a soxhlet extraction. The resulting solution was concentrated by rotary evaporator and subsequently vacuum dry. The soluble substances were characterized by ¹HNMR spectroscopy.

¹HNMR spectroscopic characterization

All the ¹HNMR spectra were recorded quantitatively using Bruker Avance – 400 (Bruker instruments, Inc Karlsruhe, Germany). Sample solutions were prepared in CDCl₃, 15% v/v concentration. Proton NMR spectra were obtained from 16 co-added FIDs. The gated decoupling pulse sequence was used to give digital resolution of 2Hz / point. The following parameters were engaged on the gated decoupling pulse sequence: number of scans, 512; acquisition time, 1.3665; pulse width, 10.3Ns; free induction decay was transformed and zero filled to 300k.

Thermogravimetric analysis (TGA)

Thermogravimeter, Q5000 IR (TA Instruments, New Castle, DE, USA) was used to measure the weight loss of polymers in air (20ml/min). Samples were heated from 30°C to 800°C at a heating rate of 20°C /mm.

Mechanical test

The compressive mechanical tests were conducted according to DIN EN ISO 527 specification using a Zwick Universal Testing Machine (Zwick GmbH and Co, KG, Ulm, Germany) at a cross head speed of 2 mm/min. The tensile modulus (Et), tensile stress (σ_m), yield or failure stress (σ_b) and elongation at break (ε_b) were obtained from the tensile tests.

RESULTS AND DISCUSSION

Calculation of double bond equivalent per mole of PKCO

Based on the fatty acid composition of the PKCO earlier reported by Akintayo and Bayer (2002) and using the formular:

$$\text{Mole of double bonds/mole of Triglyceride} = \frac{\sum \text{mole of double bond}}{\frac{100\text{g}}{\sum \text{mole of fatty acid}}} * 3$$

as reported by Olufunke *et al.* (2015), the PKCO oil is calculated to have 7.67 carbon-carbon double bonds per triglyceride as presented in Table 2. This value is much higher than that in corn oil 4.2 (Li *et al.*, 2003) and 4.5 C=C bonds in soybean oil (Li and Larock, 2001) which have successfully been used to prepare thermosetting polymers. This clearly indicates that *Plukenetia conophora* would be a good candidate for synthesizing polymers. This result therefore places PKCO in good light as materials that have the potential to provide functionally equivalent, renewable and environmentally friendly replacement for the fossil-based raw materials as the oil can be readily modified to match the different end use requirements of many industrial products. The renewability, sustainability, availability, cost-effectiveness, non-toxicity and biodegradability of vegetable oil-based chemical products are major driving forces for the shift to plant oils from fossil sources.

Table 2: Fatty acid composition, moles of double bond and fatty acid per 100g of oil for *Plukenetia conophora*

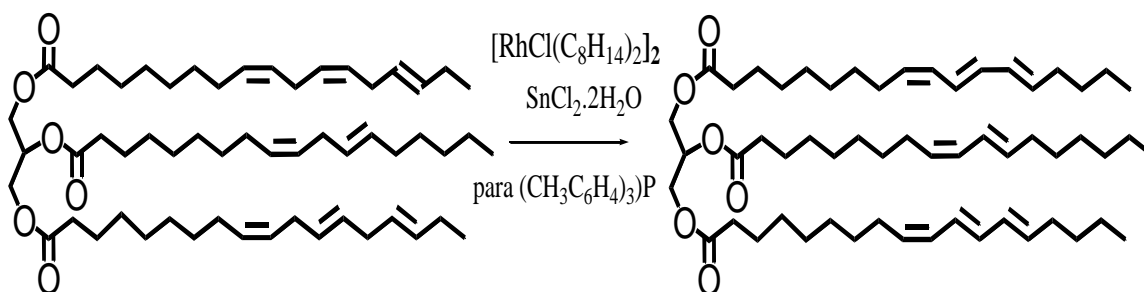
	% Fatty acid ^a	Molar mass (g/mole)	Number of double bonds	Moles of double bond/100g	Moles of fatty acid/100g oil solution
Oleic	11.70	282.4614	1	0.0414	0.0414
Linoleic	17.05	280.4500	2	0.1216	0.0608
Linolenic	70.10	278.4500	3	0.7553	0.2518
Stearic	0.60	284.4800	0	0	0.5010
Palmitic	0.80	256.4200	0	0	0.0031
Σ				0.9183	0.3592

Spectroscopic characterization

¹HNMR results

The results of the ¹HNMR of the ordinary PKCO and conjugated PKCO are represented in Figures 2 and 3 respectively. The peaks at 0.7-0.9 ppm correspond to the terminal methyl groups of the linolenic acid. The huge peak at δ1.1-1.3 ppm arises from the methylene groups usually surrounded by single bonded carbon atoms (-CH₂-). The peaks at 1.95- 1.99 ppm indicate the presence of -CH₂C=. Peaks in the region 2.2-2.3 ppm and 2.6-2.8 ppm signify the presence of methylene groups next to carboxyl (-CH₂COO-) and methylene groups surrounded by carbon atoms

(=CCH₂C=) respectively. The peaks at 3.6 ppm arise from CH₂OCO of glycerol. The peaks at 5.2-5.3 ppm arise from hydrogens on double bonded carbon atoms -CH=. The presence or absence of series of peaks in the range 5.7 to 6.5 ppm showed the existence or absence of conjugation respectively. The non-conjugated vinylic protons in ordinary PKCO gave its vinyl peaks at about 5.30 ppm (Figure 2). The ¹HNMR spectra of the isomerized PKCO presented in Figure 3 shows similar peaks in many respect to that of the non-conjugated oil. However, the peaks for the conjugated vinylic protons appeared as three sets of peaks shifted down field to 5.60 – 6.4 ppm. These observations corroborate those of Larock *et al.* (2001). The mechanism for the isomerization of oil is shown in Figure 1.

**Figure 1: Mechanism for the isomerization of oil**

Molecular structure of microstructures of resulting thermosetting polymers from PKCO and CPKCO

Different polymeric materials ranging from soft rubbers to tough and rigid plastics were obtained from the cationic polymerization of PKCO and CPKCO with styrene and divinylbenzene and the yields were found to be quantitative. The different polymers were soxhlet extracted using methylene chloride as refluxing solvents and the extractables were studied using ^1H NMR in order to understand the structure of the materials. Generally, about 71 – 96wt% of insoluble substances were retained after extraction of bulk polymers.

Figures 4 and 5 present the ^1H NMR of extractables from PKCO30 – ST42 – DVB22 – $\text{Bf}_3\text{E8}$ and CPKCO30 – ST42 – DVB22 – $\text{Bf}_3\text{E8}$ while Figure 6 presents the ^1H NMR of the pure boron trifluoride etherate catalyst. It is observed that the extracted soluble substances are composed of catalytic initiator fragment (≈ 4.2 ppm), triglyceride protons (4.2 – 4.5 ppm) of the oil and weak vinylic protons peaks at 5.2 – 5.5 ppm indicating that the extracted oil are much less unsaturated than the PKCO originally used. The absence of peaks in the region 6.4 – 7.5 ppm in the spectra in Figures 4 and 5 indicate that all of the aromatic monomers were incorporated in the cross-linked polymer networks.

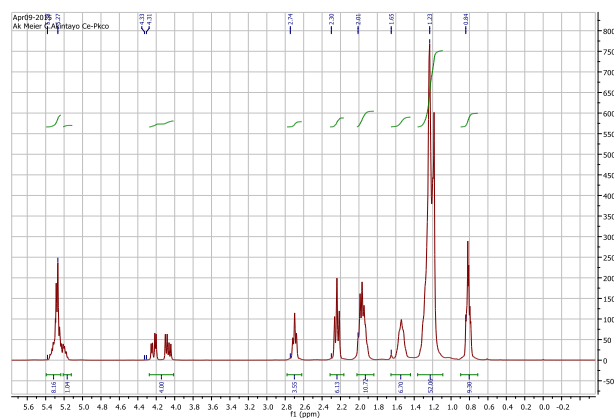


Figure 2: Proton nuclear magnetic resonance spectra of *Plukenetia conophora* seed oil

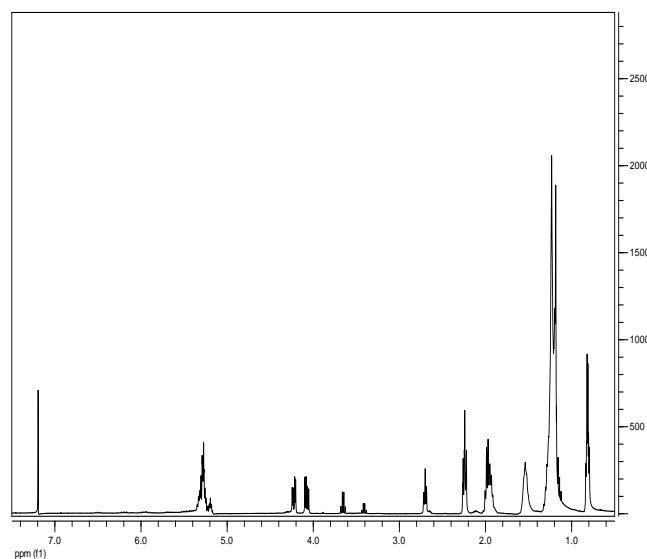


Figure 3: Proton nuclear magnetic resonance (CDCl_3) of conjugated *Plukenetia conophora* seed oil (CPKCO)

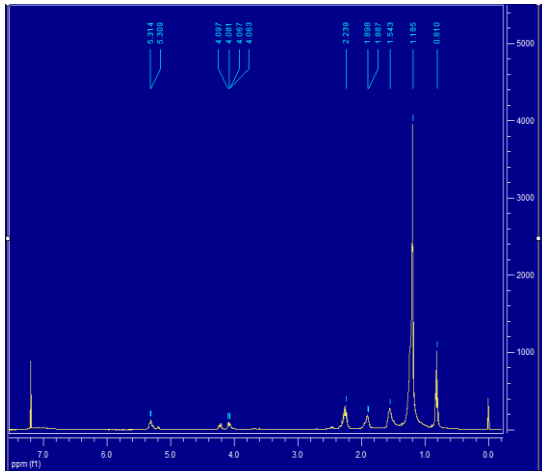


Figure 4: Proton NMR of soluble materials from PKCO30 –ST42 –DVB22 –Bf3E8

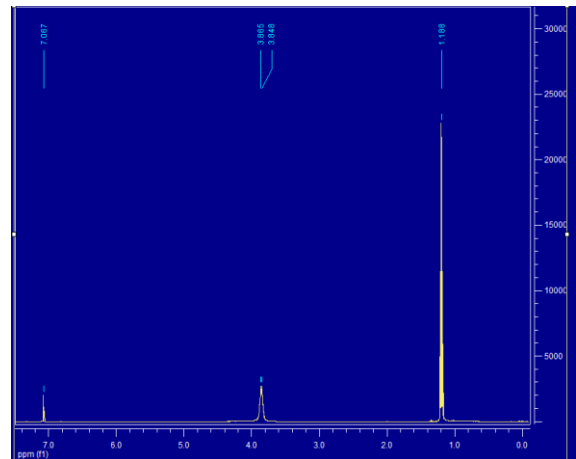


Figure 6: Proton NMR of pure Boron Tri Fluoride etherat

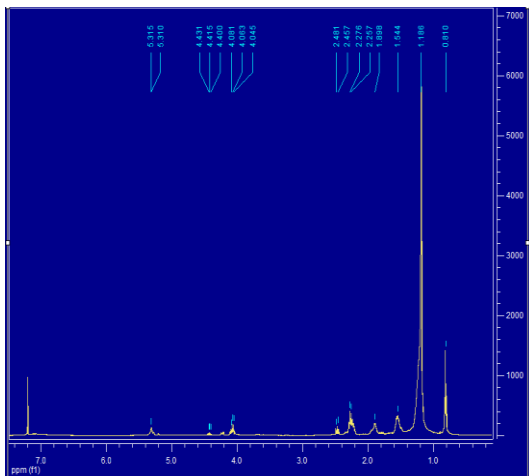


Figure 5: Proton NMR of soluble materials from CPKCO30 –ST42 –DVB22 –BF3E8

Table 3 shows that increase in percentage oil leads to decrease in the yield of cross-linked polymer whereas an increase in divinyl benzene (DVB) content, yielded an increase of the cross-linked polymer indicating DVB as an effective cross-

linker. Table 3 further revealed that using the conjugated *Plukenetia conophora* oil (CPKCO) rather than the PKCO led to increased yield of the cross-linked polymer. Hard, ductile and plastic polymers could be obtained with percentage oil at 30%. Increasing the percentage oil to 45% yielded soft cross-linked polymers.

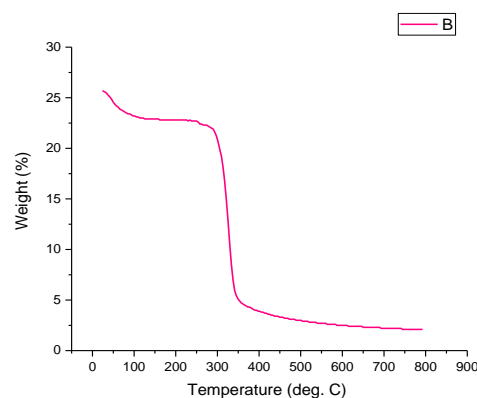
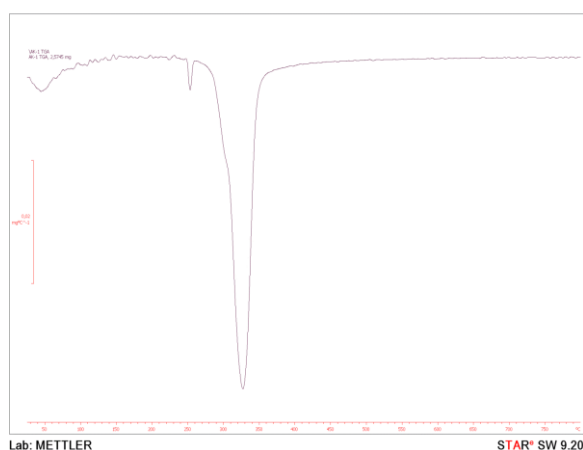
Table 3: Appearance and Soxhlet Extraction Results

Entry	Polymer	Product Appearance	Extraction (wt. %)	
			Insoluble	Soluble
A	PKCO10-ST55-DVB28- Bf ₃ E8	Hard, ductile, plastic	96.4	3.6
B	PKCO20-ST48-DVB24- Bf ₃ E8	Hard, ductile, plastic	95.9	4.1
C	PKCO30-ST42-DVB22- Bf ₃ E8	Hard, ductile, plastic	92.3	7.7
D	PKCO45-ST35-DVB15- Bf ₃ E8	Soft, ductile, plastic	72.4	27.6
E	CPKCO30-ST42-DVB22- Bf ₃ E8	Hard, ductile, plastic	96.6	3.4

Thermogravimetric Analysis (TGA)

TGA was used to study the thermal decomposition behaviour of the PKCO and CPKCO polymers. Figures 7a and 8a show the TGA thermograms of PKCO copolymer (PKCO30-ST42-DVB22-Bf₃E8) and of CPKCO copolymer (CPKCO30-ST42-DVB22-Bf₃E8) respectively while the TGA derivative curves are presented in Figures 7b and 8b respectively. According to literature, three different decomposition stages are usually observed (Li *et al.*, 2000 and Li *et al.*, 1999), but in this work only two decomposition stages were observed at 150 °C to 350 °C and 350 °C to 450°C. The first stage degradation appears to be primarily due to the evaporation and decomposition of unreacted oil and other soluble components in the bulk material; the second stage degradation appears to be as a result of the degradation and char formation of the cross-linked polymer. These results suggest that the first stage degradation, which relates to the unreacted free oil in the bulk material, plays a major role in determining the thermal stability of the materials and due to the little difference in the amount of the unreacted free oils in the bulk materials, the thermal stabilities of both PKCO and CPKCO polymers are very good and similar to one another. From the TGA derivative curves of PKCO and CPKCO, their Tmax which is determined as the corresponding derivatives weight loss curve only varied slightly (PKCO at 320 °C and CPKCO at 330 °C). This indicates that the PKCO and CPKCO copolymers

show similar thermal behavior and that they are thermally stable below 150°C.

**Figure 7a: TGA thermogram of cross-linked polymer, PKCO30 – ST42 – DVB22 – BF₃E8****Figure 7b: TGA derivative curve of PKCO30 – ST42 – DVB22 – BF₃E8**

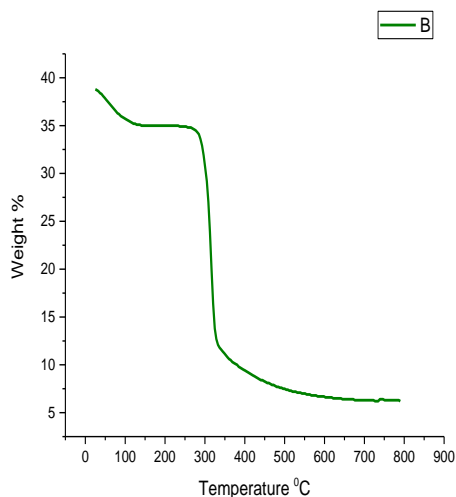


Figure 8a: TGA thermogram of cross-linked polymer, CPKCO30 – ST42 – DVB22 – BF₃E₈

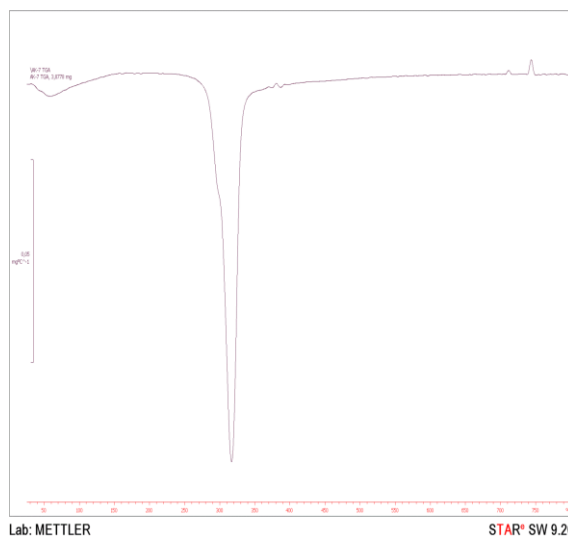


Figure 8b: TGA derivative curve of CPKCO30 – ST42 – DVB22 – BF₃E₈

Mechanical properties

The tensile mechanical properties of the PKCO and CPKCO polymers are presented in Table 4. The PKCO30-ST42-DVB22-Bf₃E₈ which contained significant amount of rigid aromatic co-monomer showed a tensile behavior of a plastic with tensile modulus (ϵ_t) 304.256 MPa and yield stress (σ_m) 6.85 MPa. There was an appreciable decrease in the tensile modulus (ϵ_t) of CPKCO45-ST32-DVB15-

Bf₃E₈ polymer from 304.256MPa to 240.40 MPa and yield stress (σ_b) from 6.85MPa to 2.52 MPa. Although, the elongation at break (ϵ_b) of CPKCO45-ST32-DVB15-Bf₃E₈ which is 20.26 MPa is far greater than that of the PKCO polymer showing the effect of conjugation on the polymer which resulted in an increase in the ductility of the resulting polymer.

Table 4: Tensile modulus, tensile stress, yield stress and elongation at break of the copolymerization of the ordinary PKCO and CPKCO with styrene and divinyl benzene initiated by boron trifluoride etherate

Polymer	σ_m Mpa	σ_b Mpa	ϵ_b Mpa	ϵ_t Mpa
PKCO30-ST42-DVB22-Bf3E8	6.85	6.85	2.77	304.25
CPKCO30-ST42-DVB22-Bf3E8	2.50	2.52	20.26	240.40

ϵ_t = Tensile Modulus; σ_m = Tensile Stress; σ_b = Yield Stress; ϵ_b = Elongation at break

CONCLUSION

Plukenetia conophora oil is a highly unsaturated oil having carbon-carbon double bond per triglyceride value of 7.67. A variety of polymeric materials ranging from soft rubbers to tough and

rigid plastics were obtained from the cationic polymerization of PKCO and CPKCO with styrene and divinyl benzene initiated by boron trifluoride etherate and the yields were found to be quantifiable. The results from the thermogravimetric analyses revealed that polymers

from both the PKCO and CPKCO exhibited three stages of degradation, and were thermally stable below 150°C. The elongation at break (ϵ_b) 20.26 Mpa of CPKCO polymer increased indicating the effect of conjugation on the polymer which resulted in an increase in the ductility of the resulting polymer. Generally, it has been observed from this study that both ordinary PKCO and conjugated PKCO have proven to be typical thermosetting materials which may find application in industries to replace the use of polymers from fossil fuel sources.

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