

Industrial Precursors from Agricultural Wastes

¹Olakunle A. Akinsanoye, ²Mopelola A. Omotoso and ³Olugbenga A. Falode

¹Department of Chemical Sciences, Faculty of Science, Dominican University, Ibadan, Nigeria.

²Department of Chemistry, University of Ibadan, Ibadan, Nigeria.

³Department of Petroleum Engineering, University of Ibadan, Ibadan, Nigeria.

Corresponding e-mail: alexolakunle024@gmail.com

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Abstract

Potential copolymers as industrial precursors were developed from *Carica papaya* seeds oil. *Carica papaya* fruits were collected in Ibadan, Nigeria. Seed oils of this fruit were extracted using n-hexane and concentrated. Phenolated *carica-papaya* biopolymer(PCPB) was prepared by polymerizing the oil with phenol through cationic polymerization method. Polyacrylamide(PAA) and Polyacrylonitrile(PAN) were prepared through free radical polymerization technique. The copolymers were prepared by polymerizing PCPB, PAA and PAN to produce PCPB-PAA and PCPB-PAN. They were characterized using FTIR for functional groups modifications, ¹H-NMR for changes in chemical environments and Viscometry techniques for mean molecular weight determination. The oil yield is 32.22%. Iodine value(gI₂/100g) is 99.55±0.38 and 61.98±0.06 for oil and PCPB respectively. FTIR band shifts at 1552.75cm⁻¹ confirm C=C stretch of aromatics in PCPB. PAA formation was confirmed with C=O stretch at 1680.00cm⁻¹. Peak at 2250cm⁻¹ confirm C≡N of PAN. Peak at 3474.24cm⁻¹ confirm N-H stretching vibration of amides that suggest polyester-amide copolymer. C-N bond occurred at 2034.28cm⁻¹ to establish PCPB-PAN copolymer. The ¹H-NMR spectra showed peaks at δppm, δ8.11ppm(s, 2H) to confirm aromatics in PCPB. δppm at 7.18 confirmed peptide protons in PAA. δ 7.18(s, 1H) and 6.86(s, 3H) suggest that PAA was grafted to PCPB backbone. δ4.89ppm(q, J = 8.8 Hz, 1H) suggests the presence of substituted nitrile in PCPB-PAN. Both FTIR and ¹H-NMR results confirmed formation of new copolymers. The mean molecular weight(g/mol) for PCPB, PCPB-PAA and PCPB-PAN are 7.482x10⁹, 1.062x10¹² and 1.135x 10¹² respectively to affirm the grafting processes.

The results suggest that ecologically friendly industrial precursors are feasible from Agricultural wastes.

Keywords: Copolymers, Industrial, Agricultural wastes, polymerization, *Carica Papaya*

Introduction

Agricultural activities all over the world generate wastes that are underutilised or not in use at all. In most countries in Africa, these wastes are consistently discarded as there are less available proven technologies to find purposes for them (Nikesh and Prakash 2015; Srikanth et al., 2022). Some of the wastes includes seeds of fruits, peels, rice bran, fruits shells, nuts of fruits like cashew, palm fruit and coconuts and the list is endless. Many of them are allowed to decompose and germinate and others litter the environments(Montero et al., 2011). Among these endless waste seed is *Carica papaya* seeds. *Carica papaya* fruit is widely produced and consumed on the African continent. This is because most of the countries in Africa operate agro-based economies. Nigeria in particular, Agriculture has been a stable component of the life of people in the various savannahs. *Carica papaya* is an annual crop which means its available every year. It will also be available all through the year round if it is well preserved (Malacridai et al., 2011). The seeds from this fruits are often discarded after the flesh has been consumed since they have limited use. Researchers have however shown that the seed is rich in viable functional groups like esters, vinyl group, carbonyl group, fatty acid group, fatty alcohol and ether groups. These seeds can then be modified under suitable chemical/unit process to obtain viable chemical precursors.

The feedstock used in the various industries like the petrochemicals, pharmaceuticals, textile, polymer industries and a host of others have gotten their starting materials majorly from petroleum sources(Askarian et al., 2018). These petroleum sources have been found to be finite and hence at a certain time and counts, it may not be available to man anymore. Besides, relying heavily on petroleum has resulted into some environmental nuisances. Plastics from ethane and propene monomers are not biodegradable. They can occupy the land fill sites for years and then lead to alteration in the food chain which can contribute to food scarcity and astronomical prices. One of the problems facing the earth today is the end use of the plastics that have been produced(Gupta and Kashani 2021). Several propositions have been made such as recycling, incineration and sustainable processes with each creating new set of problems. Incineration releases toxic chemicals to the environment like CO and SO₂ (Poudyal and Adhikari, 2021). Recycling releases harmful chemicals such as HCl and H₂S and the sustainable process implies postponing the evil day for a foreseeable future. Relying on petrol for fuel has contributed heavily to the release of excess CO₂ into the environment which had led to sporadic increase in the temperature of the earth(Nair and Vishnudas, 2024). Excess heat can also lead to the denaturation of proteins in the body that can lead to various



degree of sicknesses and major life damages such as infertility, undue death, weakness of the flora and fauna antibodies and blue blood syndrome. Oil spillage, water pollution and poisoning are other problems associated with regions where oil rigs exist. Aquatic species are facing difficulty in breathing, migration and extinction and quality of water available to homo-sapiens in these regions are low and uneconomical. Wrong government policies and allied by the oil industries contribute further issues around these parts of the countries. Nations in Africa always experiences militancy, bunker, pipe line vandalization (Thomas 2018).

These problems and similar factors had prepared the chemical industries to think of alternatives to crude oil for feed stock production (Jittin et al., 2021; Afolabi et al., 2020). Among the array of other things such as coal, ammoniacal liquors, bitumen, biomass and others considered, the biomass wastes offers viable alternative. Biomass are all from agricultural sources. To avoid creating problems of sporadic increase in food prices, the non-edible underutilised biomass have been the most viable agricultural wastes that can moderately satisfy the requirement of man in his technological growth and desires without affecting the ecosystem. Among these non-edible underutilised biomass is *carica papaya* seed oil.

Carica papaya L. is grown all over the world and is available to the tune of 100 million metric tons, all over the world annually. Its central cavity contains large quantities of seeds that comprise averagely 15% of the wet weight. *Carica papaya* L. seeds have been used for decades in parts of Asia and South America as a vermifugal agent, folk medicine due to its abortive properties, to enhance good menstrual flow in women and to adulterate black pepper. The availability of the seeds shows that it can be depended upon. The oil yield from literatures shows the oil to be in the range of 30-45% depending on the region to suggest commercial viability. The oil has also been confirmed to be rich in oleic acid up to 70%. This makes the oil to be a viable candidate for addition polymerization reaction (Elahi et al., 2020).

Despite the plethora of literature works on this *carica papaya* L. seed oil. There are sparse literary submissions on its viability as source for producing feedstock for chemical industries. This research therefore probe into the possible use of *Carica papaya* seed oils for production of suitable industrial precursors for chemical industries with the focus on mitigating the problems associated with those from petroleum sources (Blesson et al., 2023; Omotoso and Akinsanoye, 2017). The precursors and materials form them are expected to be biodegradable and photodegradable. The research will also contribute immensely to the available agricultural starting materials for producing environmental friendly industrial chemicals' precursors.

Methodology

Materials

The materials employed for this research work include Pawpaw seeds (*Carica papaya*), phenol, acrylamide, acrylonitrile, toluene, perchloric acid, distilled water, hydroquinone, Fenton's reagent (Hydrogen peroxide+ Ferric ammonium sulphate in 1:1), ethanol.

Methods

Sample collection and sampling methods

Pawpaw seed sample preparation

Pawpaw seeds were obtained largely from Ibadan in Oyo state, Nigeria. The seeds were obtained from the fruits by mechanical means. The seed samples were dried and the moisture contents were determined. The seeds (dark brown) were grounded with a blender and were prepared for extraction.

Extraction and phenolation of oil

The oil was extracted from the seeds using hot extraction technique and concentrated. Physicochemical parameters were determined. The extracted oil was phenolated with phenol through grafting technique. This was done by mixing melted phenol and the triglyceride in ratio 1:3 using a batch reactor in the presence of nitrogen gas to provide inert environment. The mixture was thoroughly homogenised for few minutes. The reaction mixture (1% of the combination) was combined with perchloric acid (HClO_4) as catalyst. They were allowed to proceed for six hours at 90°C in an inert atmosphere created by utilizing nitrogen gas. After the reaction materials were polymerized for six hours, they became dark-brown. The reaction products were observed to have grown very viscous after four hours of polymerization. The final product was a dark-brown viscous liquid. The process was stopped after six hours. They were allowed for 20 minutes to cool. To ensure that the unreacted phenol, unreacted triglycerides, and acid catalysts were eliminated, powdered $\text{Ca}(\text{OH})_2$ was added to the reaction mass. To get rid of any remaining impurities, ethanol was used to wash the finished product. The resultant phenolated product was dried for 48 hours on sodium sulfate. The product obtained were stored in tightly fitting containers until Analysis. $^1\text{H-NMR}$, FTIR and iodine value were used in the analysis. The products were used as starting materials for the copolymers.



Percentage Oil yield determination

The oil yield was determined from the relationship.

$$\text{Percentage oil yield} = \frac{A-B}{W} \times 100$$

Where:

A = weight of flask + oil

B = weight of flask only

W = weight of sample

Determination of Physiochemical parameters:

The iodine value, free fatty acid, saponification value and peroxide value were determined using standard techniques.

Iodine value measurement.

0.1g of the sample was weighed into 200ml flask. Solution is effected by adding 5ml of carbon tetrachloride, dried over calcium chloride, 10ml of the Wij's solution was added from a dry pipette, the flask is closed with a stopper and allowed to stand for few minutes. 5ml of 10% KI solution and 50 ml of water was added to the content. Titration was conducted with 0.1N sodium thiosulphate solution using 10 drops of 1% starch solution as indicator. A blank test, omitting the sample was simultaneously performed. Similar test was carried out for the PCPB. The iodine value was calculated using the formula:

$$\text{Iodine value} = \frac{(x-y) \times 1.269}{w}$$

where x = ml of thiosulphate solution required by the blank, y = ml of thiosulphate solution required in the test. w = weight of sample. The factor 1.269 is for an accurate 0.1N solution of sodium thiosulphate (AOAC, 1984).

Saponification value measurement

The saponification value was determined by taking 1.0 g of the oil sample in a conical flask to which was added 15 mL 1 N KOH and 10 mL of distilled water and heated under a reserved condenser for 40 min to ensure that the sample was fully dissolved. After this sample was cooled, phenolphthalein was added and titrated with 0.5 M of HCl until a pink endpoint was reached. A blank was determined with the same time conditions (Zahir et al., 2014).

Peroxide value measurement

1.0g of oil sample was dissolved in acetic acid then chloroform and saturated KI mixture were added. The iodine liberated from KI by the oxidative action of peroxides present in the oil was determined by titration with standard sodium thiosulphate using starch solution as the indicator. Titration was also performed for blanks (AOAC, 1984, Zahir et al., 2014).

$$\text{PV (meq/kg oil)} = (S-B) \times W \times N.$$

Where B is the volume of sodium thiosulphate used for blank, W is the weight of sample, S is the volume of sodium thiosulphate consumed by the sample oil and N is the normality of standard sodium thiosulphate.

Free fatty acids determination

The acid value was determined using the method described by Ronald (1991). Equal volumes of diethyl ether and ethanol were mixed together and 1ml of 1% phenolphthalein indicator solution was added and then neutralized with 0.1M potassium hydroxide solution. The oil was dissolved in the neutralized solvent mixture and titrated with 0.1M potassium hydroxide solution with constant shaking until a pink colour which persists for 15seconds is obtained.

$$\text{Acid value} = \frac{\text{Titre value (ml)} \times 5.61}{\text{Weight of sample used (g)}}$$

Preparation of copolymers from phenolated vegetable oils.**Homopolymerization of acrylamide and acrylonitrile.****Preparation of polyacrylamide(PAA)**

1.5 litres of 30% wt./vol. acrylamide in water was transferred into a three necked batch reactor, 30ml of 0.05M NaNO₃ solution was added. The mixture was thoroughly stirred for few minutes under nitrogen gas. Fe²⁺-H₂O₂ (Fenton's reagent) was added as initiator and this was stirred for 5 minutes. Nitrogen gas was bubbled through for sometimes. The reaction continued for the next four hours. After the desired reaction time, the reaction was terminated by adding 0.2 g hydroquinone powder and the contents were stirred for another some minutes before being stopped. The homopolymer was cleaned with ethanol to remove unreacted acrylamide, remnants of NaNO₃ solution and the catalyst. The product was allowed to dry for half a day over sodium sulphate to ensure the total



removal of the moisture content. It was kept in a cool dry place until the period of further application and analysis. The product was analysed with FTIR and ¹H-NMR.

Homopolymerization of acrylonitrile

100g of acrylonitrile was added to 200mL of distilled water in a 3-necked batch reactor equipped with a mechanical stirrer and gas inlet. Then 1.5g of Fenton's reagent (H₂O₂-Fe²⁺) was added to the acrylonitrile solution. The mixture reacted at 90°C for 3 h. Then, the precipitates were collected by filtration, washed with acetone, and dried under vacuum at room temperature, yielding Polyacrylacrylonitrile.

Copolymerization reactions.

The copolymerization reaction of PCPB with polyacrylamide and Polyacrylonitrile was performed using the same method in a 1 L isothermal three-necked batch reactor, equipped with an overhead stirrer and a temperature regulator to allow the control of the reaction temperature. The catalysts employed are Fenton's reagents (Hydrogen peroxide + Ferric ammonium sulphate in 1:1). The copolymerization reactions were carried out using a hybrid of the methods described by Witono in 2012 and Nur Azmyra et al., 2014.

PCPB was loaded into the reactor and mixed with a known volume of distilled water. The mixture was thoroughly stirred for some minutes under nitrogen gas environment. This was followed by the addition of predetermined amount of homopolymerized polyacrylamide to give specific ratios. The mixture was stirred for 5 minutes and was heated under nitrogen gas atmosphere at 70°C for 25 minutes. The temperature was reduced to 60°C for the first two and increase to 80°C for the last 4. Each of the reaction continued for 5 or 6 hours. The reaction was ceased by adding 2 ml of 0.1 M hydroquinone and the contents were stirred for another 10 minutes before opening the reactor to collect the samples. The copolymerized phenol and vegetable oils and the various homopolymers were separated from the unreacted homopolymer by washing a representative sample of 30 g from the reaction contents with 40ml of acetone for several times until homopolymer could not be detected in the supernatant. The product obtained was dried and then transferred into separate labelled containers for analysis and applications.

Analytical techniques

The oil, PCPB and the synthesized copolymer precursors were analysed using a ¹H-NMR techniques. The NMR analysis were carried out using Agilent - 400 MHz, temperature of 31°C and CDCl₃ as solvent, FTIR was used to monitor the change in functional groups. This was done by using Perkin Elmer FTIR system spectrum BX. Viscometry was used to monitor the change in molecular weights. Details of results are in the next chapter.

Results and Discussion

Table 1: Physicochemical analysis of oil

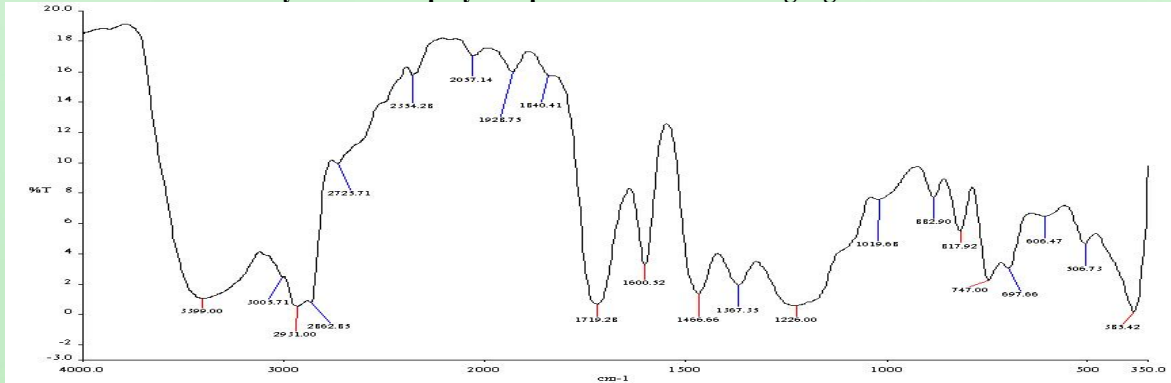
Samples	Oil yield (%)	Iodine value of oils (gI ₂ /100g)	Iodine value of PCPB(gI ₂ /100g)	Peroxide value (meq/kg)	Saponification value (mgKOH/g)	Free fatty acids (%)
<i>Carica papaya</i> oil	32.22	99.55±0.38	61.98±0.06	10.56±0.51	186.39±0.42	7.56±0.07

Mean value ±standard deviation (n=3).

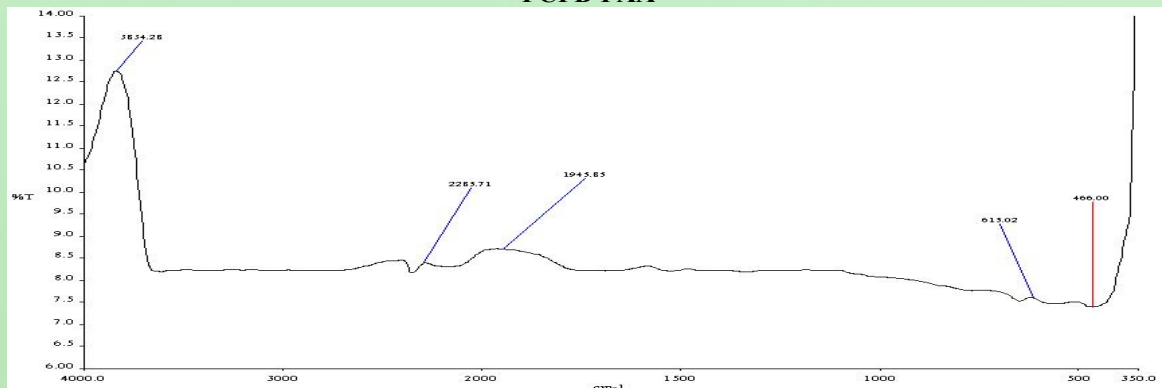
The oil yield for this sample is 32.22%. This suggests that the oil quantity is of commercial viability for the production of oleo chemicals. It is also in the range of values reported for most oil employed for polymerization processes such as Neem seed oil, soya bean oil, rape seed oil and lots more. The oil showed an iodine value of 99.55±0.38(gI₂/100g) to suggest it's a semi drying oil. This feature shows that the oil is rich in unsaturation. Literature works on the oil confirmed it to be rich in oleic acid. This level of unsaturation suggests that the oil has potential features of been deployed into chain growth polymerization techniques, be it cationic, anionic or free radical. The PCPB showed a lesser iodine value(Table 1) to suggest that grafting of phenol to the oil(triglyceride) backbone occurred at the vinyl groups present in the oil moiety. This led to a reduction in the number of vinyl groups within the *Carica papaya* oil sample (Oladiji et al., 2010). Peroxide value is an indicator of oil's rancidity. Values lower than 10 ml/kg does not show rancidity but values around 30 to 40 ml/kg suggest that the oil may be rancid. PCPB showed a value of 10.56±0.51 meq/kg to suggest that it is extremely low in rancidity or less oxidized. A non-rancid oil gives information about its stability, the high stability of this seed oil shows that it has the potential to be modified into suitable product(s) of interest. Saponification value of the oil (Table 1) is the range coated in literatures for seed oil. The saponification value of the oil suggests that oil is rich in unsaturated fatty acids. This also complement the iodine value result and affirm the suitability of the oil for chain growth polymerization processes. The free fatty acid gives information about oil quality, a low value of free fatty acid suggests better oil and complement the peroxide value result for the sample. The oil's free fatty 7.56±0.07% to show that its of good quality and stability. The physicochemical analysis outcome suggests that the seed oil sample which is an Agricultural wastes has viable features that can convert it to useful starting material in the chemical industries. This will inevitably create a market for this agricultural waste and similar others with minimal impairment to the environment.



FTIR Analysis of the copolymer precursors and starting Agricultural Wastes

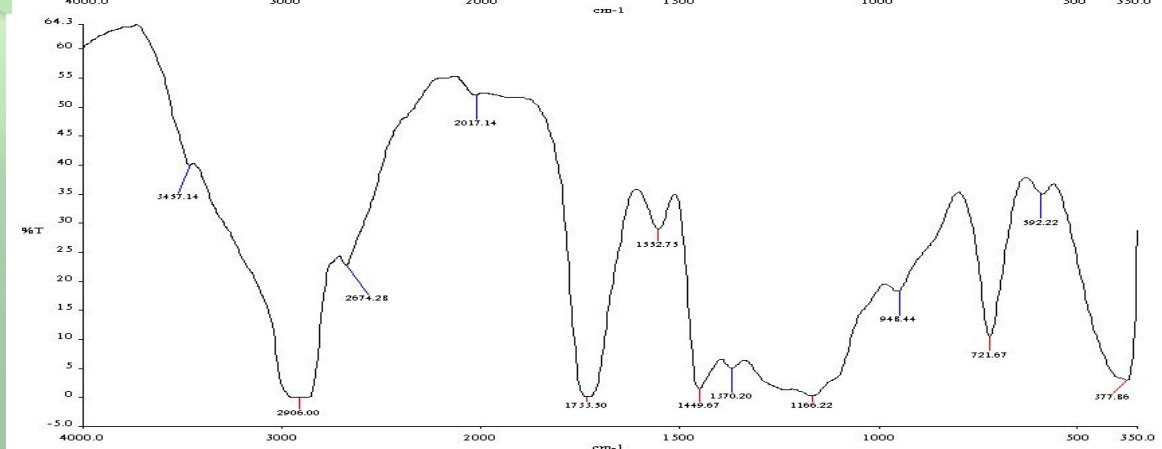
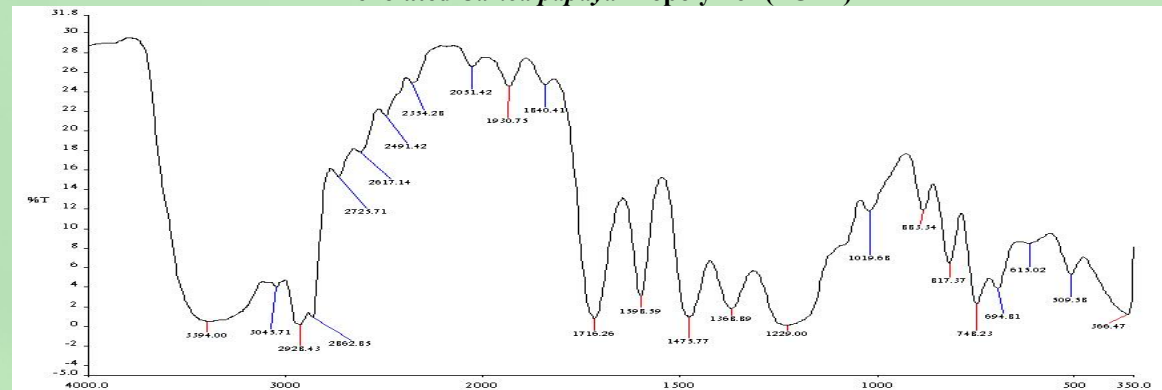


PCPB-PAA



Polyacrylamide (PAA)

Phenolated *Carica papaya* Biopolymer (PCPB)



Carica papaya oil

Figure 1: FTIR spectra of the copolymer precursors and starting Agricultural Wastes



The spectrum of *carica papaya* oil (Figure 1) showed a carbonyl group of an ester at 1733.50 cm^{-1} , C-O band at 1166.22 cm^{-1} and a C-H band at 2906.00 cm^{-1} . This bands confirmed this oil to be a fatty esters. This establishes the literature reports that triglycerides are majorly esters. The peaks at 1449.67 cm^{-1} , 948.44 cm^{-1} and 721.62 cm^{-1} confirm C-C stress and C-H bend of aromatics and vinyl groups in the triglyceride moiety. This shows that the crude sample contain some phenolic. The peak at 1552.75 cm^{-1} serves as evidence that the oil is rich in substituted alkene. This complements the result of the physiochemical parameters for the sample. This peak affirms that the oil can undergo addition polymerisation processes. The presence of ester and vinyl functional groups in this agricultural waste carica papaya seed oil show that it can be a viable feedstock in producing useful industrial chemicals precursors (Takahashi et al., 2008). The carbonyl group in the fatty ester is an evidence that the products from this feedstock will be biodegradable and photodegradable.

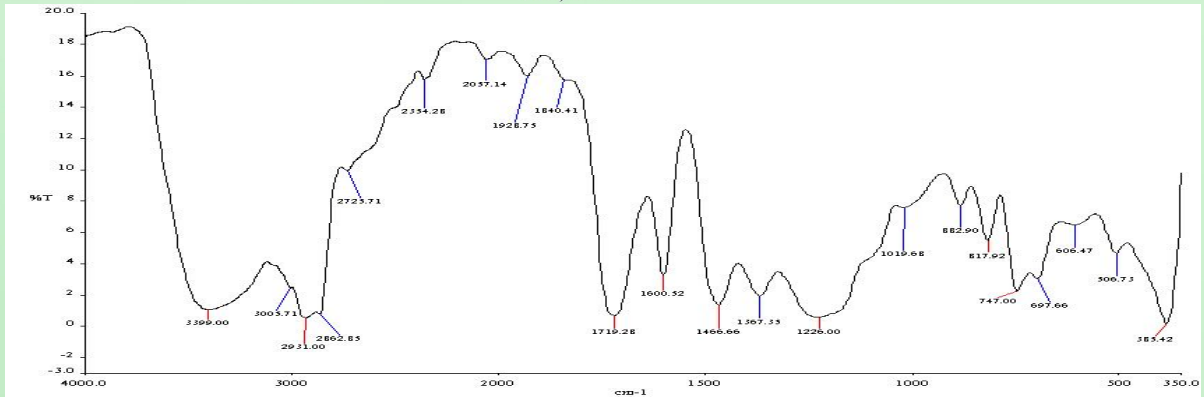
Polymerising phenol and the *Carica papaya* oil produced Phenol *Carica papaya* biopolymer (PCPB). The spectrum is presented in Figure 1. Strong C=O stretch of ester was found at 1716.26 cm^{-1} , C-O stretch was confirmed at 1229.00 cm^{-1} and 1019.68 cm^{-1} . These peaks confirmed the existence of the triglyceride in the new material. This shows that grafting did not occur at the ester/triglyceride group since there is no hydrolysis. C-C stretch band of aromatics was confirmed at 1475.77 cm^{-1} and C=C. Stretching vibrations of arene occurred at 1552.75 cm^{-1} to show that the new material contains phenolic. The starting material also show the presence of phenolics but the number of C-H bending vibration in PCPB outweighs those in the oil to confirm grafting (Figure 1). The oil shows two C-H bending vibrations at 948.44 cm^{-1} and 721.62 cm^{-1} while the PCPB showed 4 distinct C-H bending vibrations of aromatic at 883.34 cm^{-1} , 817.37 cm^{-1} , 748.23 cm^{-1} and 694.81 cm^{-1} to affirm the grafting process. O-H stretch of phenolic was similarly affirmed at 3394.00 cm^{-1} . The grafted oil showed additional reactive groups through the phenolic/arene on its backbone and hence may be deployed as biodegradable alternatives alkenes in the production of materials such as bio-plastics, bio-polyvinyl chlorides and other bio-polymeric materials.

In this research, it was deployed to the production of copolymer by grafting PAA unto its backbone. The spectrum of the polyacrylamide that was synthesized showed C=O vibrational stretch at 1680.00 cm^{-1} . C-N stretch band peak occurred at 2285.71 cm^{-1} . C-H bend of alkenes was found around 615.02 cm^{-1} to show that the PAA homopolymer is unsaturated. PCPB-PAA is the grafted copolymer material from the agricultural waste. The spectrum showed the presence of C=O stretch of esters at 1711.21 cm^{-1} , C-O stretch occurred at 1025.38 cm^{-1} and C-H stretch appearing as a doublet occurred at 2927.57 cm^{-1} and 2862.85 cm^{-1} . These peaks similarly establishes that the ester and triglyceride moiety is still present in the new copolymer material. The spectrum also showed invaluable bands at 2354.28 cm^{-1} and 3472.24 cm^{-1} to suggest that C-N stretch and N-H stretch are present in the new material. These bands are commonly found in amides and are absent in the starting material. They are evidences that the polyacrylamide was grafted to the PCPB backbone. The bands occurring at 1600.46 cm^{-1} , 1465.18 cm^{-1} are due to C=C stretch of aromatics and C-C stretch of aromatics. They confirm that the phenolic group is still present in the new copolymer. C-H bend of aromatics were also found within the finger print region at 948.44 cm^{-1} , 885.75 cm^{-1} , 819.30 cm^{-1} and 697.36 cm^{-1} to affirm this observation. The multiple reactive groups in the copolymer makes it a good starting precursor for various industrial chemical synthesis. This material can therefore be a substitute to styrene, propene, but-1, 3 diene and lots more in industrial processes as a precursor (Srikanth et al., 2022). Exploring the *Carica papaya* oil also yielded another copolymer with the IR details presented in Figure 2.

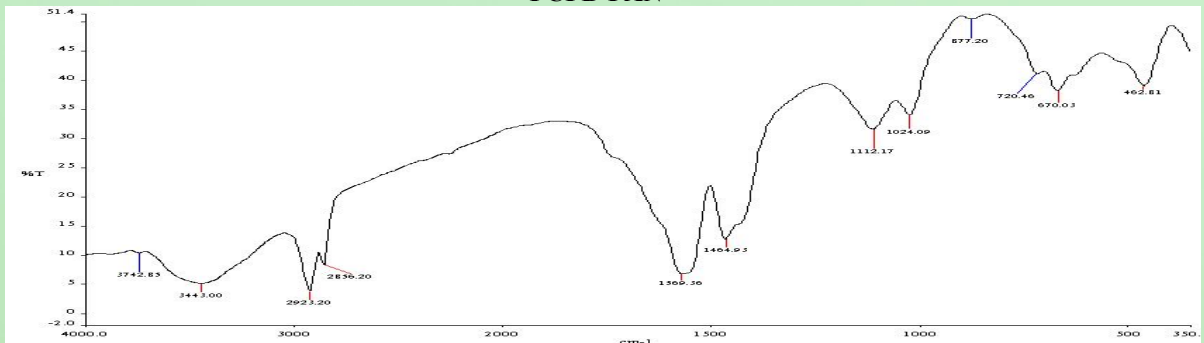
The *carica papaya* and phenol *carica papaya* biopolymer (PCPB) have been earlier discussed in Figure 1. Polyacrylonitrile was employed as the second grafting parameter to the PCPB. The spectrum is presented in Figure 2. The spectrum confirms PAN bands at 1569.36 cm^{-1} and 1464.93 cm^{-1} stretching vibration. This occurred due to high crosslinking and ladder-like structure within the PAN homopolymer moiety. Methylene group vibration occurred at 2923.20 cm^{-1} and 2856.20 cm^{-1} . They are attributed to the loss of hydrogen atoms as part of the hydrogenation process. Copolymerizing the PCPB and PAN produces PCPB-PAA. The spectrum is presented in Figure 2. The spectrum showed similar features as found in the triglyceride with C=O stretch occurring at 1719.28 cm^{-1} and C-O band vibration found at 1226.00 cm^{-1} and 1019.68 cm^{-1} . C=C stretch of alkenes/arene occurred at 1600.52 cm^{-1} to affirm unsaturation within the newly synthesized PCPB-PAA material. It shows that the grafting process occurred within the vinyl moiety. The C=C bending vibrations were found at 882.92 cm^{-1} , 817.92 cm^{-1} , 747.00 cm^{-1} , 697.66 cm^{-1} , 606.47 cm^{-1} and 506.73 cm^{-1} as additional factors suggesting the vinyl and aromatic groups in the new copolymer. The evidence of the cross-linked polyacrylonitrile in the new material was found at 1466.66 cm^{-1} and 1387.35 cm^{-1} . This affirm that the Polyacrylonitrile was grafted to the PCPB backbone. $^1\text{H-NMR}$ was further used to confirm this.

Figure 3 shows the various chemical environments in the carica papaya oil and the industrial precursors from it. The spectrum of carica papaya oil showed five different chemical environments $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.47 (s, 0H), 2.44 (s, 1H), 2.14 (s, 1H), 1.41 (s, 7H), 1.01 (s, 1H). The peak at δ 5.47ppm is for vinyl protons within the oil sample. It is similarly confirmed by the FTIR result for the sample. Substituted carbonyl peaks were found at δ 2.44ppm and δ 2.14ppm as evidences for ester functional group within the oil moiety. Substituted saturated protons common to triglycerides occurred at δ 1.41ppm and δ 1.01ppm as singlet. The presence of vinyl protons in the oil affirm its ability to undergo addition polymerization.

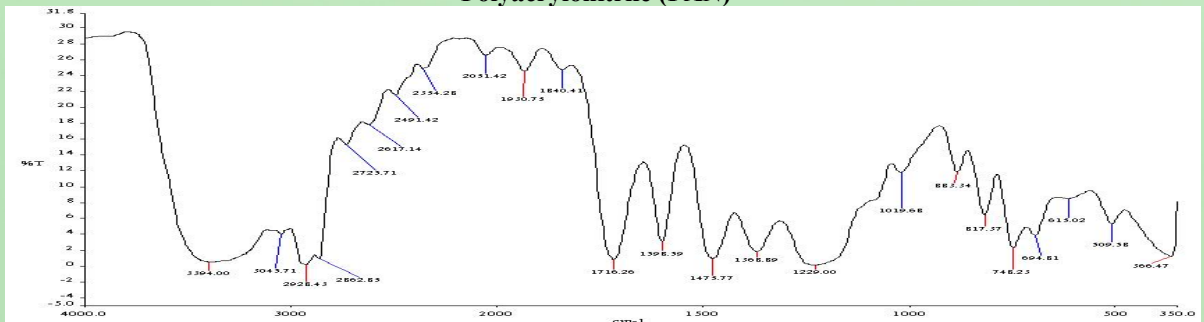




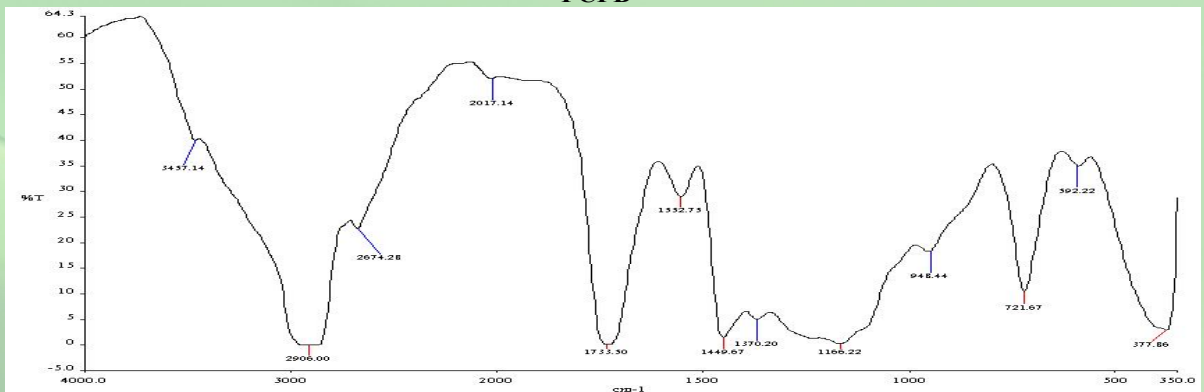
PCPB-PAN



Polyacrylonitrile (PAN)

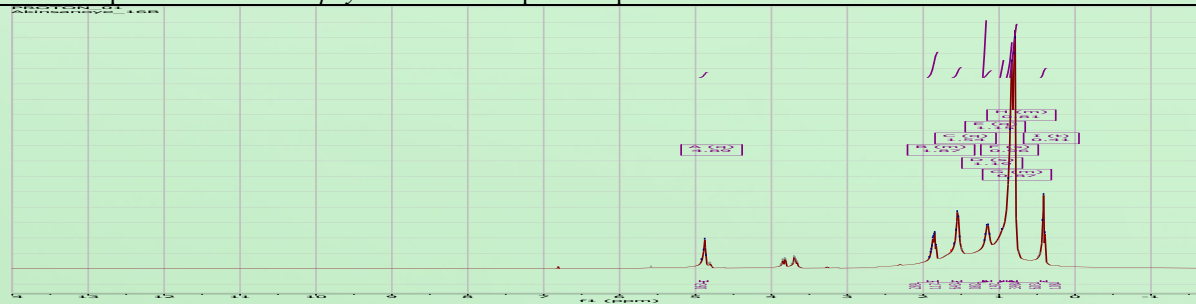
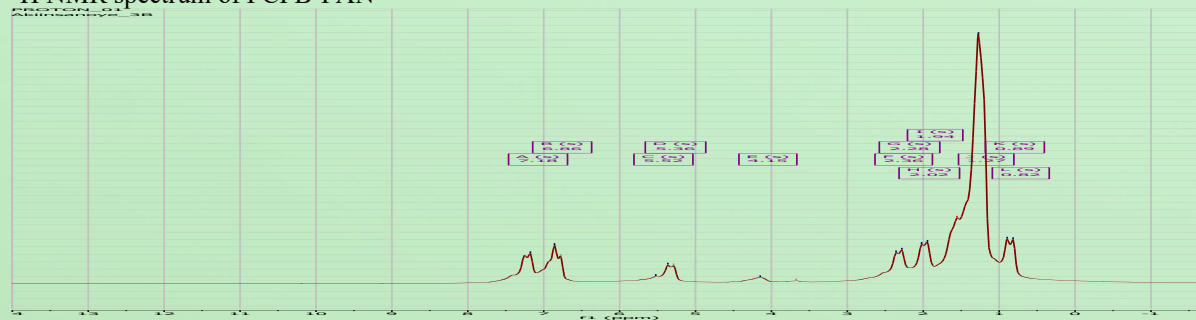
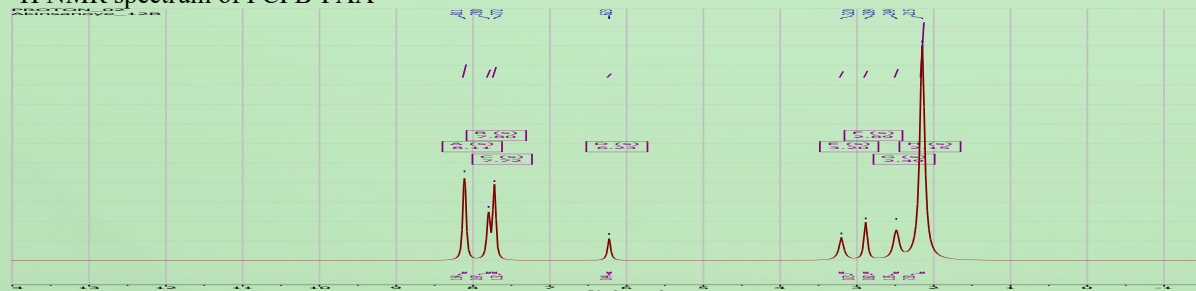


PCPB



Carica papaya waste seed oil



¹H NMR spectra of *Carica Papaya* oil and some possible precursors

¹H NMR spectrum of PCPB-PAN

¹H NMR spectrum of PCPB-PAA

¹H-NMR spectra of Phenol *Carica Papaya* Biopolymer (PCPB)

¹H-NMR spectra of *Carica Papaya* oil

Figure 3: ¹H NMR spectra of *Carica papaya* oil and some possible precursors

Copolymerizing phenol and the carica papaya oil produced the PCPB. The spectrum is also presented in Figure 3. It shows that the new chemical environments different from those in the oil has been introduced which resulted from the introduction of the phenolic group to the oil's backbone. The chemical environments from the spectrum are highlighted as ¹H NMR of Phenol *Carica Papaya* Biopolymer (PCPB) (400 MHz, cdcl₃) δ 8.11 (s, 2H), 7.80 (s, 1H), 7.72 (s, 1H), 6.23 (s, 0H), 3.20 (s, 1H), 2.89 (s, 1H), 2.49 (s, 1H), 2.15 (s, 7H). The peaks at δ, 8.11ppm, δ, 7.80ppm, δ, 7.72ppm and are evidences of substituted protons in the new material. These peaks were absent in the CPO. They therefore affirm that the grafting process occurred. This result was confirmed by the FTIR details for the sample. δ,6.23ppm is also an evidence that the new product is still unsaturated. The higher downfield absorption confirms the effect of the phenolic group on the unsaturated component of the oil. Integrating Polyacrylamide to the PCPB backbone produces PCPB-PAA. The spectrum also is presented in Figure 3 and labelled. It shows several distinct chemical environments form the starting materials. ¹H NMR PCPB-PAA (400 MHz, cdcl₃) δ 7.18 (s, 1H), 6.86 (s, 3H), 5.52 (s, 1H), 5.36 (s, 1H), 4.15 (s, 1H), 2.36 (s, 2H), 2.28 (s, 1H), 2.02 (s, 2H), 1.94 (s, 1H), 1.27 (s, 23H), 0.89 (s, 2H), 0.82 (s, 1H). Peaks at δ 7.18ppm, δ 5.52ppm and δ , 5.36ppm



occurred due to the formation of substituted amide and occur as singlet in the spectrum. Peak at δ , 6.86ppm are evidences of highly substituted phenolic group in the new polymeric material. It affirms the presence of PCPB in the new material. The peak at δ , 4.15ppm is an evidence of phenolic protons. It further confirms the grafting process. Carbonyl peaks showing the presence of the ester and triglyceride group moiety in the new polymeric material were affirmed with peaks at δ 2.36ppm, δ 2.28ppm and δ 2.02ppm. Substituted allylic protons occurred at δ , 1.94ppm. They serve as new reactive centre in the new material. Several authors have confirmed that allylic centres are reactive points in vinyl compounds. Substituted saturated protons were found at δ , 1.27ppm. The large values of the singlet emanates from the hydrogenation occurring at vinyl groups and aromatic groups during the cationic polymerization processes. Other saturated protons in the spectrum are δ , 0.82ppm and δ ,0.89ppm. They are further evidences for the further hydrogenation processes. Another copolymer from the PCPB was termed PCPB-PAN. It was formed by copolymerizing with PCPB and Polyacrylonitrile (PAN). The spectrum is also presented in Figure 3. The various chemical environments from the spectrum is ¹H NMR for PCPB-PAN (400 MHz, cdcl₃) δ 4.89 (q, J = 8.8 Hz, 1H), 1.94 – 1.81 (m, 3H), 1.54 (q, J = 6.5 Hz, 1H), 1.19 (s, 6H), 1.15 (q, J = 7.4 Hz, 1H), 0.96 (s, 2H), 0.90 – 0.83 (m, 4H), 0.86 – 0.76 (m, 6H), 0.41 (t, J = 6.6 Hz, 1H).

The peak at δ 4.89ppm is an evidence for the nitrile formation in the new copolymer. There are no aromatic protons in the spectrum to suggest that the phenolic group in the starting material and vinyl moiety that reacted with the polyacrylonitrile have been hydrogenated during the free radical reaction process. This may have resulted from the ability of the Fenton's reagent (catalyst) deployed in the reaction to form categories of intermediates and resonances which had initialized series of reaction while the polymerization was been carried out and had led to the final product observed. Peaks at δ 1.94 – 1.81 (m, 3H) range confirm allylic protons in the new material. The high level of saturation occurring at δ ppm 1.19ppm, δ 1.15ppm, 0.96ppm, δ 0.90 – 0.83ppm (m, 4H), δ ,0.86 – 0.76 (m, 6H), 0.41 (t, J = 6.6 Hz, 1H) affirm that phenolic group and vinyl group had been heavily hydrogenated. The result from copolymerizing PAN and PCPB differ greatly from that observed in PAA and PCPB. The drastic observations may have resulted from the triple bonds associated with nitriles and its ease of hydrolysis with acids. The two copolymers spectra analysis affirm that polymerizing carica papaya can be depended upon in producing useful industrial precursors. The new materials shows promising functional groups like amide, arenes, vinyl groups, nitrile, esters and alcohols that can be exploited as precursors for petrochemical companies in polymer production, oil and gas industries in producing oil field chemicals (Falah et al., 2020). The viability of these precursors is in the renewability and availability. They can therefore become long term alternative to fossil fuel in keeping the chemical industries on track with minimal environmental and ecological details.

Mean molecular weight determination

Table 2:Viscometry analysis results of synthesised Carica papaya oil biomaterials

Biomaterial	Mean Molecular weights (g/mol.)	Copolymers	Average Molecular weights(g/mol.)
PCPB	7.482 x10 ⁹	PCPB-PAA	1.062 x 10 ¹²
		PCPB-PAN	1.558 x 10 ¹²

Keys:

Phenol *Carica papaya* biopolymer (PCPB)

Phenol *Carica papaya* biopolymer-polyacrylamide (PCPB-PAA)

Phenol *Carica papaya* biopolymer-polyacrylonitrile (PCPB-PAN),

The above molecular weights were determined from Mark-Hauwink Sakurada techniques through the calculations of the flow rates and various viscosities like specific viscosities, intrinsic viscosities', reduced viscosity and inherent viscosity. The results of the viscometry technique are in tandem with the FTIR and ¹H-NMR for all the biomaterials considered. The mean molecular weight of the copolymers are greater than the starting PCPB to show that the grafting between PCPB and PAA occurred (Table 2). This was confirmed for the PCPB-PAN. The results affirmed that through various polymerization techniques, seed oils which are agricultural wastes can be used to generate using materials similar to those from petroleum industries and as alternative biodegradable feedstock source. The results showed that there is no part of the Agricultural material that is a waste. The copolymers and phenolated material from the seed oil have the potential to become viable industrial precursors through the right unit operations and unit processes.

Conclusion

The feasibility of producing industrial precursors from seed oils was examined using carica papaya seed as sampled study. The first phase of the research after sample collection and preparation was to extract oil from the carica papaya seeds. The next phase was the determination of the physicochemical properties of the oil extracted oil. The oil contains high iodine value to make it semi drying oil. Saponification value was similarly high and in the expected trend. Free fatty acid value of the oil is in the standard range to affirm no rancidity or oxidation. The third phase was to polymerized the oil with phenol to yield the phenolated intermediate which was identified as



Phenolated *Carica papaya* biopolymer(PCPB. Homopolymers of acrylamide and acrylonitrile were prepared and characterized using FTIR.

The PCPB and polyacrylamide were copolymerized using free radical polymerization method to obtain the corresponding copolymer termed PCPB-PAA. Similarly PCPB and the synthesized PAN were copolymerized to yield the copolymer termed PCPB-PAN. They were all characterized using FTIR to determine the functional groups. ¹H-NMR was used to determine the various chemical environments. Viscometry technique was used to measure the flow rates while Mark-Houwink Sakurada relation was used to estimate the average molecular weights. The new copolymers showed characteristics features of ester, amide, nitrile, alcohols, arenes and vinyl to establish that they possess enough active sites that can make them viable industrial precursors and compete favourably with their counterparts from finite sources like crude oil, coal and shale oil. This research therefore creates environmentally friendly ways of converting agricultural wastes into useful starting materials for the chemical industries. This will increase the economic value of these wastes and ensures that they have improved value chain to the farmers, regions and countries where they are found in large amount such as Nigeria. They will therefore improve the nation's GDP. They are also environmentally friend and photodegradable. Hence they will contribute in mitigating the unpleasant effects of green house gases. This serves as a major route to the sustainability of the green chemistry policies and sustainable development goals (SDGs).

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Authors' individual contribution:

Dr. Olakunle Alex Akinsanoye was involved in the experimental design, carrying out the experiment, analysis of results, financing and manuscript design.

Professor Olugbenga A. Falode was involved in the composition, result analysis, financing and proof reading of the manuscript.

Professor Mopelola Abeke Omotoso was involved in the conception of the work, financing and guide throughout the research.

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References

- Afolalu S.A., Samuel O.D., Ikumapayi O.M. (2020). Development and characterization of nano- flux welding powder from calcined coconut shell ash admixture with FeO particles. J Market Res 9(4):9232–9241. <https://doi.org/10.1016/j.jmrt.2020.06.067>
- Askarian M., Tao Z., Adam G., Samali B. (2018). Mechanical properties of ambient cured one-part hybrid OPC-geopolymer concrete. Constr Build Mater 186:330–337. <https://doi.org/10.1016/j.conbuildmat.2018.07.160>.
- Blesson S and Rao U.I. (2023). Agro-industrial-based wastes as supplementary cementitious or alkali-activated binder material: a comprehensive review. Innovative Infrastructure Solutions (2023) 8:125 <https://doi.org/10.1007/s41062-023-01096-8>.
- Elahi M.M.A., Hossain M.M., Karim M.R., Zain M.F.M., Shearer C. (2020). A review on alkali-activated binders: materials composition and fresh properties of concrete. Constr Build Mater 260:119788. <https://doi.org/10.1016/j.conbuildmat.2020.119788>.
- Falah M., Obenaus-Emler R., Kinnunen P., Illikainen M. (2020). Effects of activator properties and curing conditions on alkali activation of low-alumina mine tailings. Waste Biomass Valoriz11(9):5027–5039. <https://doi.org/10.1007/s12649-019-00781-z>.
- friendly Industrial Chemicals. Ponte Journal. 73(7) 237-258. doi: 10.21506/j.ponte.2017.7.49
- Gupta S., Kashani A (2021). Utilization of biochar from unwashed peanut shell in cementitious building materials – effect on early age properties and environmental benefits. Fuel Process Tech nol 218(April):106841. <https://doi.org/10.1016/j.fuproc.2021.106841>
- Jittin V., Rithuparna R, Bahurudeen A., Pachiappan B. (2021). Synergistic use of typical agricultural and industrial by-products for ternary cement: a pathway for locally available resource utilisation. J Clean Prod 279:123448. <https://doi.org/10.1016/j.jclepro.2020.123448>.
- Malacrida R., kimura I M and Jorge N. (2011). Characterization of a high oleic oil extracted from papaya (*Carica papaya* L.) seeds. Ciênc. Tecnol. Aliment., Campinas, 31(4): 929-934.
- Montero de Espinosa L. & Meier M. A. R. (2011). Plant oils: the perfect renewable resource for polymer science? Eur. Polym. J.;47:837–52.
- Nair D. G and Vishnudas S. (2014). Iaeme geopolymer binder from industrial wastes. International journal of Engineering Vol. 17(3) pp 219–225.
- Nikesh, B. S & Prakash A.M. (2015). Modified vegetable oil based additives as a future polymeric Material-Review. Open journal of Organic polymeric material. Pp 1-22.



- Oladiji, A.T., Idoko, A.S., Abodunrin, T.P. & Yakubu, M. T. 2010. Studies on the physiochemical properties and fatty acid composition of the oil from ripe plantain peel (*Musa paradisiaca*). Afr. Scientist: 11 (1): 73-78.
- Omotoso M.A and Akinsanoye O.A (2017). Grafting vegetable oils to develop environmental
- Peetu, P., Nirmal, A.J, Justin, K. George, A. B & Cherian. B. (2013). Development of Novel Polymer Composites," International Journal of Engineering and Innovative Technologies (IJEIT), vol. 3, Issue 2, August.
- Poudyal L, Adhikari K (2021) Environmental sustainability in cement industry: An integrated approach for green and economical cement production. Resour Environ Sustain 4(March):100024. <https://doi.org/10.1016/j.resenv.2021.100024>.
- Srikanth G., Fernando A, Selvaranjan K., Gamage J.C.P., Ekanayake L. (2022). Development of a plastering mortar using waste bagasse and rice husk ashes with sound mechanical and thermal properties. Case Stud Constr Mater 16(November):e00956. <https://doi.org/10.1016/j.cscm.2022.e00956>.
- Takahashi, T., Hirayama, K., Teramoto, N and Shibata, M. (2008). Bio-composites Composed of Epoxidized Soybean Oil Cured with Terpene-Based Acid Anhydride and Cellulose Fibers. Journal of Applied Polymer Science, 108, 1596-1602.
- Thomas B.S. (2018) Green concrete partially comprised of rice husk ash as a supplementary cementitious material – a comprehensive review. Renew Sustain Energy Rev 82(March):3913– 3923. <https://doi.org/10.1016/j.rser.2017.10.081>

Supplementary information for viscometry analysis

Flow rate, concentration and calculated viscosities for PCPB

Flow rates (s)	Concentrations (g/ml).	Relative Viscosity (t/t ₀)	Specific viscosity (η _r -1)	Reduced viscosity (η _{sp} /C)	Inherent viscosity lnη _r /C
46.0±0.14	-	-	-	-	-
93.4±0.11	4.44 x 10 ⁻⁴	2.03	1.03	2319.82	1609.17
146.3±0.13	8.88 x 10 ⁻⁴	3.18	2.18	2454.95	1302.79
200.0±0.00	13.3 x 10 ⁻⁴	4.35	3.35	2518.80	1105.40
261.0±0.14	17.8 x 10 ⁻⁴	5.67	4.67	2623.60	974.83
314.6±0.14	22.2 x 10 ⁻⁴	6.84	5.84	2630.63	866.12

Table 2. Flow rate, concentration and calculated viscosities for(PCPB-co- PAA)

Flow rates (s)	Concentrations (g/ml)	Relative Viscosity (t/t ₀)	Specific viscosity (η _r -1)	Reduced viscosity (η _{sp} /C)	Inherent viscosity lnη _r /C
57.0±0.41	-	-	-	-	-
123.0±0.41	4.44 x 10 ⁻⁴	2.16	1.16	2612.62	1734.45
214.0±1.55	8.88x 10 ⁻⁴	3.75	2.75	3094.84	1488.46
293.0±0.07	13.3x 10 ⁻⁴	5.14	4.14	3112.78	1230.87
345.0±0.07	17.8 x 10 ⁻⁴	7.10	6.10	3426.97	1101.18

ble 3. Flow rate, concentration and calculated viscosities for (PCPP-co-PAN)

Flow rates (s)	Concentrations (g/ml)	Relative Viscosity (t/t ₀)	Specific viscosity (η _r -1)	Reduced viscosity (η _{sp} /C)	Inherent viscosity lnη _r /C
21.0±0.02	-	-	-	-	-
35.1±2.16	2.50 x 10 ⁻⁴	1.67	0.67	2680.00	2051.29
49.6±1.55	5.00 x 10 ⁻⁴	2.63	1.36	2720.00	1717.30
65.0±1.55	7.50 x 10 ⁻⁴	3.10	2.10	2800.00	1508.54
82.3±1.55	1.00 x 10 ⁻⁴	3.92	2.92	2920.00	1366.09

