

Graft Copolymerization of Acrylonitrile onto Allylated Pineapple Leaf (*Ananas Comosus*) Fibre by Ceric Ion – N-Butyl Acetate Redox System

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Abstract

Graft copolymerization of acrylonitrile onto allylation pineapple (*Ananas comosus*) fiber by ceric ion-butyl acetate redox pair was investigated in aqueous media. The degree of substitution of the fiber was 2.39 mole which suggests that at least two of the hydroxyl groups of anhydroglucose units of the fiber were substituted. The graft yield increased initially and then decreased with an increase in ceric ion concentration at the range of $4.17 - 20.80 \times 10^{-3}M$. The initial increase arises from increased redox interaction of the ceric ion with the fiber but the decrease in the graft yield suggested the involvement of the ceric ion in the termination of grafted polymer. Fourier Transform Infra-red spectroscopy showed the existence of allylation of the fiber at 1642.58 cm^{-1} and 1157.54 cm^{-1} characteristics for $-C=C-$ and $-C-O-C-$ stretching vibration. Further, the band at 2238.4 cm^{-1} characteristics for $-CN$ stretching vibration confirmed the formation of the graft copolymer.

Keywords: Graft copolymerization, Fibre, anhydroglucose, allylation, acrylonitrile, Pineapple leaf fiber; (*Ananas comosus*), holocellulose.

1.0.0 INTRODUCTION

1.1.0 POLYMER

A polymer is a large molecule or macromolecule composed of many repeated subunits. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life (Kalia et al., 2009). Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function.

1.2.0 CELLULOSIC FIBRE

Cellulose ($C_6H_{10}O_5$)_n is a long chain polymeric polysaccharide carbohydrate of beta-glucose. A cellulose molecule may be from several hundred to over 10,000 glucose units long. It forms the primary structural component of green plants. The primary cell wall of green plants is made primarily of cellulose.

Cellulose is similar in form to complex carbohydrates like starch and glycogen. These polysaccharides are also made from multiple subunits of glucose. The difference between cellulose and other complex carbohydrate molecules is how the glucose molecules are linked together. By condensation, cellulose monomers (β -glucose) are linked together through β 1 – 4 glycosidic bonds. This is in contrast to the α 1 – 4 glycosidic bonds present in other carbohydrates like starch. In addition, cellulose is a straight chain polymer, and each cellulose molecule is long and rod-like. This differs from starch, which is a coiled molecule. The result of these differences in structure is that, compared to starch and other carbohydrates, cellulose cannot be broken down into its glucose subunits by any enzymes produced by animals.

Cellulose is the major constituent of paper, further processing can be performed to make cellophane and rayon, and recently Modal, a textile derived from beechwood cellulose. Viscose is a very important fiber made out of cellulose and has been used for textiles since the beginning of the 20th century.

1.2.1 CHEMICAL COMPOSITION OF NATURAL FIBRES

The major constituents of natural fibers are cellulose, hemicellulose, lignin, pectin, and ash (Robin et al., 2007). The percentage of each component varies for each different type of fiber, however, generally, are presents around 60-80% cellulose, 5-20% lignin, 20% moisture, besides hemicellulose, and a small percent of residual chemical components. The amount of these components affect directly the properties of the fibre since the hemicellulose is responsible for the moisture absorption, bio-, and thermal degradation whereas lignin ensures thermal stability but is responsible for UV degradation (Xue et al., 2007)

1.2.2 WEAKNESSES OF CELLULOSIC FIBRE

The major weakness of cellulosic fibre includes the following;

- Lower strength properties, particularly its impact strength.
- Variable quality, depending on unpredictable influences such as weather.
- Moisture absorption causes swelling of the fibers.
- They restricted the maximum processing temperature.
- Lower durability
- Poor fire resistance

1.2.3 CELLULOSE MODIFICATION

Chemical modification of cellulose is generally achieved through derivatization such as esterification, etherification, oxidation, cross-linking, and grafting of cellulose (Mohanty et al., 2000). Chemical modification of cellulose by graft copolymerization has generated interest among researchers because few commoner molecules change a number of characteristics of the original natural polymer significantly. Thus new areas of application might be opened for the modified cellulose-type material. Being a polymer itself, cellulose can be copolymerized only with a block or grafting procedure. The block copolymerization of cellulose essentially modifies its physical structure and therefore cannot be used.

1.2.4 GRAFT POLYMERS

They are segmented copolymers with a linear backbone of one composite and randomly distributed branches of another composite (Rahmat et al., 2007). The labeled “graft polymer” shows how grafted chains of species B are covalently bonded to polymer species A. Although the side chains are structurally distinct from the main chain, the individual grafted chains may be homopolymers or copolymers. Graft polymers have been synthesized for many decades and are especially used as impact-resistant materials, thermoplastic elastomers, compatibilizers, or emulsifiers for the preparation of stable blends or alloys (Feng et al., 2011).

1.2.5 PROPERTIES OF GRAFT COPOLYMER

By grafting polymers onto polymer backbones, the final grafted copolymers gain new properties from their parent polymers. Specifically, cellulose graft copolymers have various different applications that are dependent on the structure of the polymer grafted onto the cellulose (Kalia and Sabaa, 2013). Some of the new properties that cellulose gains from different monomers grafted onto it include: Absorption of water, Improved elasticity, Hydrophilic/Hydrophobic character, Ion-exchange, Dye adsorption capabilities, and Heat resistance, Thermosensitivity, pH sensitivity, Antibacterial effect.

1.3 GENERAL OBJECTIVE

To determine the grafting characteristics for the graft copolymerization of acrylonitrile onto modified and unmodified pineapple fibre by ceric ion-butyl acetate redox pair.

1.4 SPECIFIC OBJECTIVE

To modify pineapple fibre by allylation.

To determine the degree of substitution

To determine the effect of ceric ion on the graft yield.

1.5 JUSTIFICATION

Cellulose fiber is one of the most demanded materials in the world today, due to its wide application. These cellulose fibers have some weaknesses which are of major concern and these have prompted researchers to look for a way of overcoming such weaknesses.

In this study, graft copolymerization of acrylonitrile onto pineapple leaf fiber was carried out to improve some of the weaknesses of this fiber such as impact strength, water solubility e.t.c. Thus new areas of application might be opened for the modified cellulose-type material.

2.0.0 MATERIALS AND METHOD

2.1.0 DISTILLATION OF ACRYLONITRILE MONOMER

5 % NaOH solution was added to the monomer in a separating funnel and the mixture was shaken for 20 – 30 minutes. The aqueous layer was decanted and the monomer was washed with a 5 % NaCl solution. This was carried out to remove the stabilizer, usually hydroquinone, from the monomer. The monomer was dried over anhydrous calcium chloride and then fractionally distilled.

2.2.0 SAMPLING AND SAMPLE TREATMENT

Pineapple leaf fiber (*Ananas comosus*) was obtained at the Fadama farm of the Federal University of Agriculture Abeokuta.

Preparation of Holocellulose Ceaserweed Fibre:

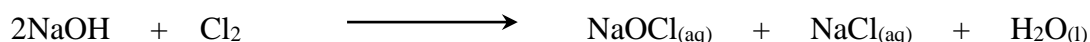
The fiber from pineapple leaf was air-dried, and beaten in a mortar to a fine pulp. The fiber was then refluxed in butanol for one hour to remove waxes and resinous materials. The fiber was then boiled in 10 % sodium sulfite for eight hours in an open pan with continuous stirring. The resultant holocellulose was thoroughly washed with water and air-dried.

Bleaching of Holocellulose:

Bleaching of the holocellulose was done with sodium hypochlorite bleaching agent which was produced in the lab.

Chlorine gas was generated by reacting 20 g potassium permanganate crystal with excess concentrated hydrochloric acid. The generated chlorine gas was then passed into 100 ml of chilled 2 M sodium hydroxide solution to yield sodium hypochlorite solution. The latter was then mixed with half of its volume of 0.5 M nitric acid. The holocellulose was then steeped in the bleaching agent and heated for 15 minutes. The bleached holocellulose was filtered and washed with distilled water to neutral pH and then air-dried.

Reaction to the production of bleaching agent can be represented as follows:

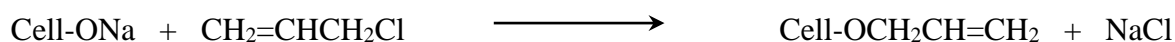


2.3.0 CHEMICAL MODIFICATION OF CELLULOSIC FIBRE BY ALLYLATION

7 g of bleached holocellulose was reacted with 150 ml of 20 wt-% aqueous sodium hydroxide solution at 0 °C for 20 minutes. The fiber was then filtered and air dried.

The fiber was refluxed for 3 hours with 50 wt-% of allylchloride in 80 ml of petroleum ether. The resultant allylcellulose was then washed several times with the ether to remove excess allylchloride and air-dried.

Reaction to the allylation of pineapple fiber can be represented as follows:



2.3.1 DETERMINATION OF ALLYL MOIETY IN THE FIBRE

The amount of allyl moiety in the fiber was determined by reacting 0.5 g of the allylfibre with 25 ml of 0.1 M iodine solution for an hour followed by back titration with 0.05 M thiosulphate solution. The titration was repeated three times using starch solution as an indicator. Blank titration was also carried out by titrating the iodine solution against the thiosulphate solution.

The allyl content of the fiber was calculated from the equation below;

$$\dot{N} = (V_o - V_t) \times M_t \times 162$$

$$W_s \times 127$$

Where

N = the number of moles of allyl moiety per anhydroglucose unit (AGU) of the fiber

V_o and V_t = the blank and sample titers respectively

M_t = the molarity of the thiosulphate solution

W_s = the weight of the allyl fiber.

2.3.2 GRAFT COPOLYMERIZATION REACTION

0.1 g of allylated fiber was immersed in a measured quantity of distilled water at room temperature. A measured quantity of nitric acid, glacial acetic, butyl acetate, and ceric ammonium nitrate was introduced into the reaction vessel (conical flask), such that the total volume of the reaction medium was 30 ml.

A pre-oxidation time (POT) (i.e time for butyl acetate and ceric ammonium nitrate redox pair initiator to react with allylated fiber) of 10 minutes was allowed, before the introduction of the measured quantity of acrylonitrile. The reaction was allowed to proceed for a given period of time before it was terminated by the addition of 50 ml of distilled water.

The product was filtered with a Buchner funnel through a sintered glass of known weight. The ungrafted homopolymer was removed with N,N-dimethylformamide (DMF). The grafted copolymer was dried in an oven at 40 °C to a constant weight.

The total weight obtained minus the weight of sintered glass gave the weight of the graft copolymer W_2 .

The percentage graft yield was calculated from;

$$\% \text{ graft yield} = \frac{(W_2 - W_1) \times 100}{W_1}$$

Where;

W_1 = weight of grafted fiber in gram

W_2 = weight of fiber in gram

3.0.0 RESULTS AND DISCUSSION

3.1.0 RESULT

3.1.1 DEGREE OF SUBSTITUTION OF ALLYLATED PINEAPPLE FIBRE

Table 1: Results for blank and sample titration

READING	1ST TITRE (cm ³)	2ND TITRE (cm ³)	3RD TITRE (cm ³)
Blank	46.90	46.70	46.80
Sample	28.00	28.10	28.00

Allylated derivatives of pineapple (*Ananascomosus*) fiber had a degree of substitution of 2.39mole as shown in table 1 above indicating that trihydroxy groups of the anhydrous glucose units were all substituted.

Table 2: Effect of ceric ion on the graft yield of modified and unmodified pineapple fiber.

Concentration of ceric ion $\times 10^{-3}$ M	% graft yield of allylated fibre	% graft yield of unmodified fibre
4.17	20	30
8.33	130	120
12.50	60	230
16.70	40	130
20.80	30	110

$[H^+] = 0.49$ M; $[AcOH] = 0.57$ M; Fibre = 0.1g; $[BuAc] = 8.33 \times 10^{-3}$ M; POT = 10 min; $[AN] = 0.25$ M; Temp. = 30 °C; Time = 3 hrs

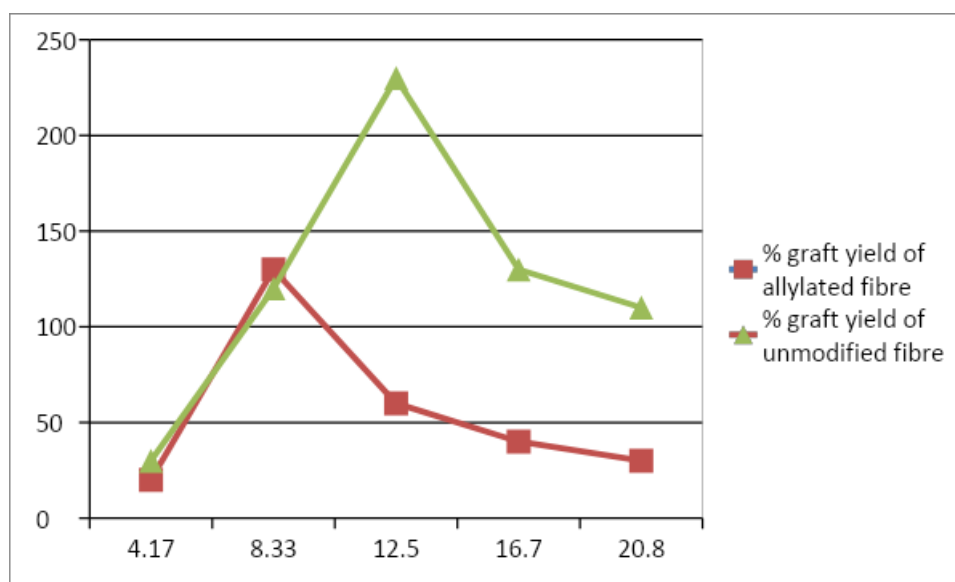


Fig 1: shows the graphical representation of the effect of ceric ion on graft yield of both the modified and unmodified fiber

3.2.0 DISCUSSION

3.2.1 EFFECT OF CERIC ION ON GRAFT YIELD

Table 2 and Figure 1 above show the effect of ceric ion on grafting of acrylonitrile onto modified and unmodified pineapple fiber.

Graft yield increased initially and decreased in the concentration range of $4.17 - 20.80 \times 10^{-3}$ M. Graft yield increased initially with an increase in ceric ion concentration in the range of $4.17 - 12.5 \times 10^{-3}$ for grafting of acrylonitrile onto unmodified pineapple fiber in the presence of butyl acetate. The initial increase arises from the increased redox interaction of ceric ion and allylated fiber. Beyond 12.5×10^{-3}

Meric ion concentration, termination of grafted polyacrylonitrile by ceric ion may occur resulting in a lowering of graft yield.

It is to be noted that grafting of acrylonitrile onto allylated fiber showed a much lower yield compared to the unmodified but followed the same trend as the ceric ion concentration is increased in the range $4.17 - 20.8 \times 10^{-3}$ M. The reduction in graft yield at a high concentration of Ce^{+4} ion may be due to the termination of the graft reaction by the ceric ion.

The overall lower graft yield observed for the allylated fiber compared to the unmodified fiber may be ascribed to a lower reactivity of the allylated radical species formed for the graft copolymerization reaction. The lower reactivity was added to resonance stabilization of the allylated radical species.

This variation is in accordance with the research earlier reported by (Mohamed et al., 2009). The increment in the percentage yield as concentration increases was due to an increase in the active free radicals on the cellulose backbone at which the monomer can be grafted. These active free radicals in the presence of monomer generate more a number of graft copolymers.

3.2.2 CHARACTERIZATION OF UNMODIFIED, MODIFIED, AND GRAFTED PINEAPPLE FIBRE USING FT-IR

The infrared spectrum of the unmodified pineapple fiber is shown in figure 2 below. Figure 2 shows the absorption band of value 3419.83cm^{-1} which confirmed the presence of unbounded hydroxyl groups of anhydroglucose unit (AGU).

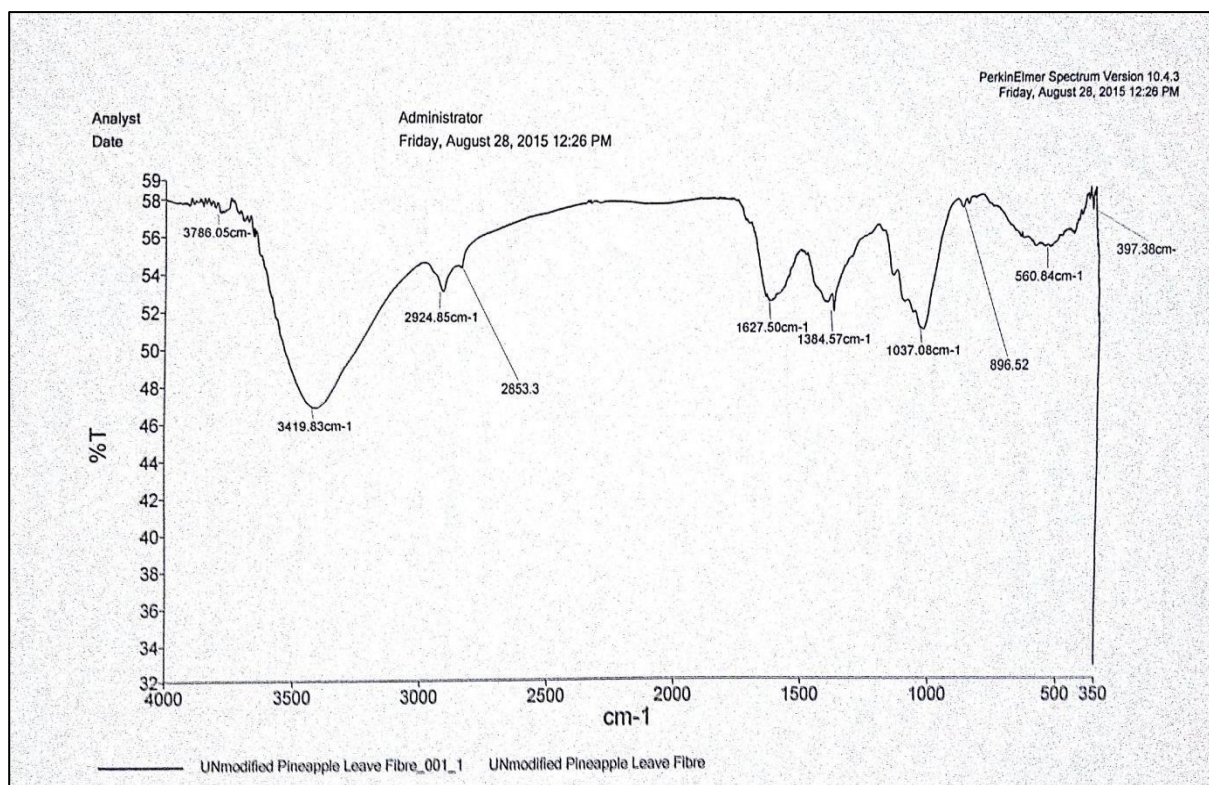


Fig 2: IR spectrum of unmodified pineapple fiber

The infrared spectrum of the allylated pineapple fiber is shown in figure 3 below. Figure 3 shows the absorption bands of $-C=C-$ and $-C-O-C-$ at values of 1642.58 cm^{-1} and 1157.54 cm^{-1} respectively. An additional peak was also observed at the value of 898.01 cm^{-1} which corresponds to the allylic $=C-H$ bending. This ultimately confirmed the presence of allylic moiety in the modified pineapple fiber.

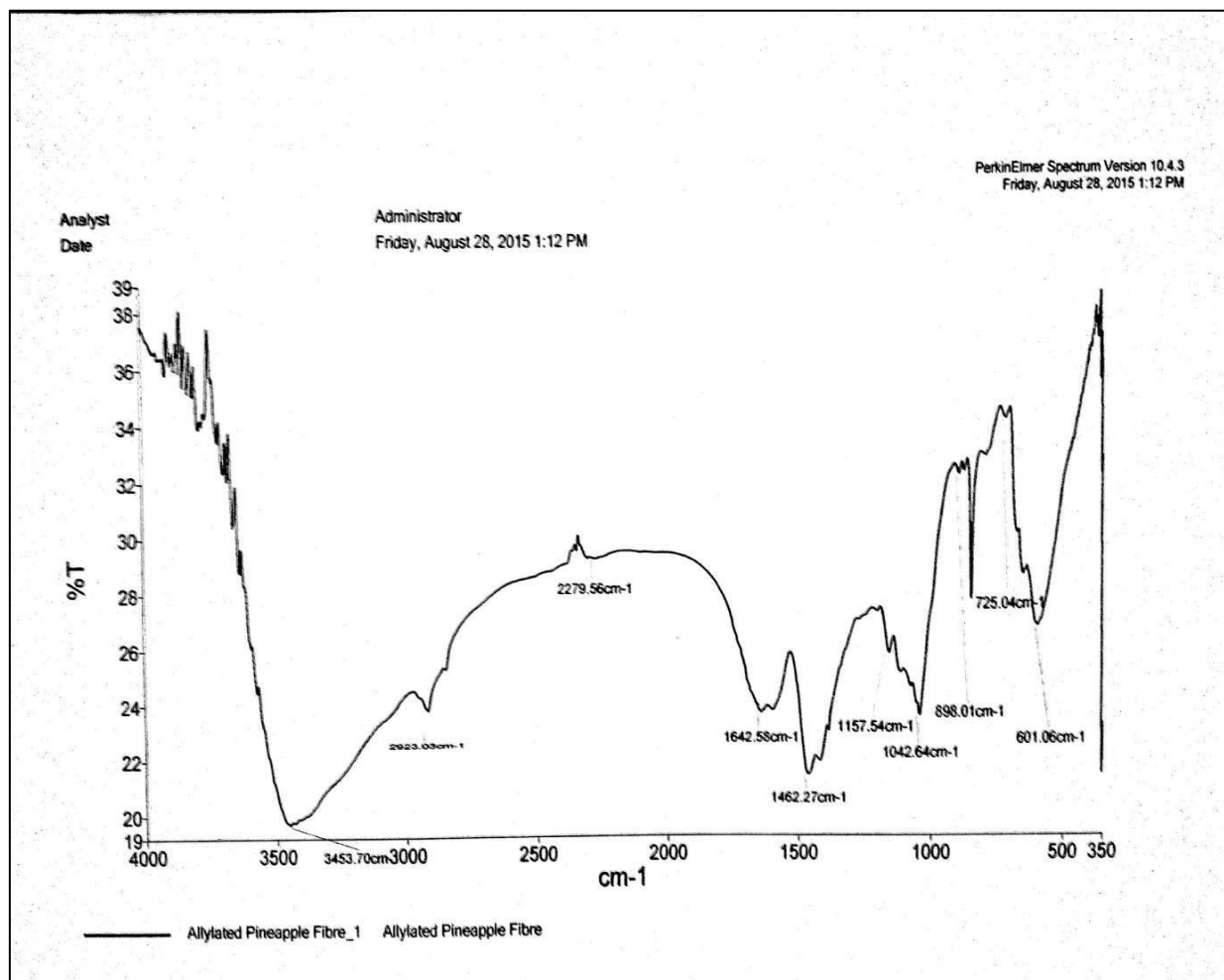


Fig 3: IR spectrum of allylated pineapple fiber

The infrared spectrum of the grafted allylated pineapple fiber is shown in figure 4 below. Figure 4 shows shifted absorption bands of $-C=C-$, $-C-O-C-$, and $=C-H$ bending at values of 1634.28 cm^{-1} , 1160.74 cm^{-1} , and 896.79 cm^{-1} respectively. An additional peak was observed at 2238.4 cm^{-1} . This peak is characteristic of the nitrile group ($-CN$) corresponding to acrylonitrile grafted onto allylated pineapple fiber. This ultimately shows that allylated pineapple fiber is being grafted with acrylonitrile monomer.

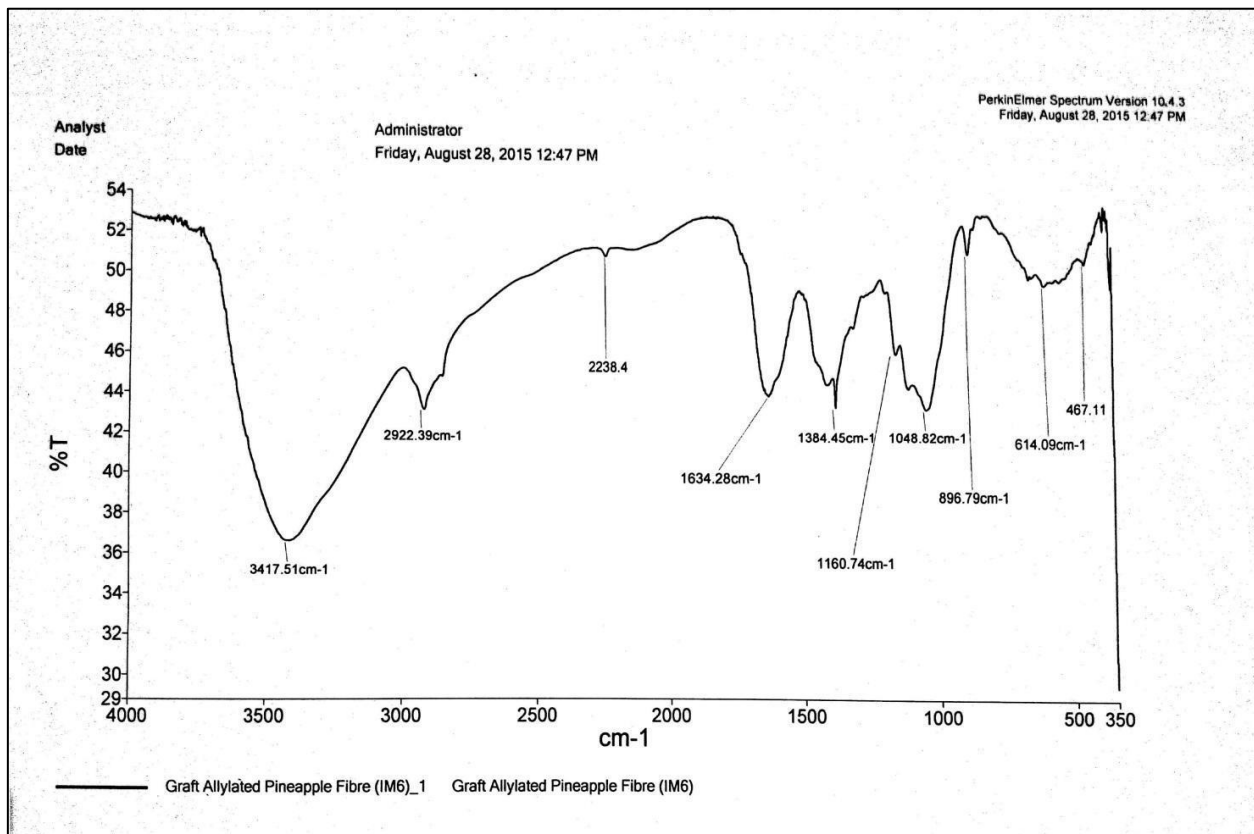


Fig 4: IR spectrum of grafted allylated pineapple fiber

4.0.0 CONCLUSION

Allylation of pineapple (*Ananascomosus*) fiber gave a value of 2.39mole for the degree of substitution and suggested that trihydroxy groups of the anhydrous glucose unit were all substituted.

The unmodified pineapple fiber gave a higher yield of graft copolymer at corresponding concentrations of ceric ion compared to the allylated derivative with a value of up to 230 %. The lower reactivity of the latter was adduced to resonance stabilization of the allylated radical species.

An increase in ceric ion concentration of up to 12.50×10^{-3} M increased the graft yield. Beyond this concentration of ceric ion, the graft yield decreased and suggest termination of the grafted polymer by ceric ion.

Consent to publish

All authors consented to the publication of this work. The authors all confirm the permission for publication for this research work.

Declaration of competing interest

The authors declare no known competing financial interests or no personal relationships that could have appeared to influence the work reported in this paper.

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Authors Contributions

Oluwafemi Ibukun Shittu: Methodology, Data curation, Writing- Original draft preparation. **Monsour Olawale Zakariyah:** Writing- Reviewing and Editing, Conceptualization, Methodology, Software Visualization, Investigation. **and Abdullahi Tunde Aborode:** Supervision. **OIS, MOZ, and ATA:** Software, Validation. **OIS, MOZ, and ATA:** Writing- Reviewing and Editing. All the authors read and approved the final version for submission.

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