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GRAFT COPOLYMERIZATION OF ACRYLONITRILE ON ALLYLATED PINEAPPLE (*ANANASCOMOSUS*) FIBRE USING REDOX PAIR OF POTASSIUM PERMANGANATE AND N-BUTYLACETATE

ABORODE TAOFEEK O[*], OGUNDELE OLUSOLA D[*],
THOMPSON SAMUEL O[*], HAMZAT YETUNDE A[*]

ABSTRACT

The graft copolymerization of acrylonitrile onto allylated pineapple (*Ananascomosus*) fibre by potassium permanganate, n-butylacetate as redox pair in aqueous media was investigated. Potassium permanganate, n-butylacetate redox pair was effective for the initiation of graft copolymerization of acrylonitrile onto cellulose and its ally derivative.The effect of permanganate on grafting of acrylonitrile onto modified and unmodified fibre was also examined. The graft yield was significantly higher for the unmodified fibre giving values of up to 290% compared to 130% for the allyl derivative at 12.5 x 10^{-3}M of $KMnO_4$. Resonance stabilization of the allyl radical and consequent reduction in its reactivity for graft reaction accounted for the difference in grant yield. At permanganate concentration greater than 12.5 x 10^{-3}M, the graft yield for the unmodified fibre decreased with increase in $KMnO_4$. This was associated with the termination of the graft reaction by manganite ion.The IR spectra of the unmodified, allylated and grafted pineapple (*Ananascomosus*) fibre were recorded. The absorption band of value 3419.83 cm^{-1} confirmed the presence of unbounded hydroxyl groups of anhydrous unit of the unmodified fibre. The absorption band of -C=C-, -C-O-C- and -C-H bending at values of 1642.58 cm^{-1}, 1157 cm^{-1} and 898.01 cm^{-1} respectively which confirmed the presence of allylic moiety in the allylated pineapple (*Ananascomosus*) fibre. The absorption bands of -C=C-, -C-O-C-, =C-H, and C=N at values of 1634.28 cm^{-1}, 1160.74 cm^{-1}, 896.79 cm^{-1} and 2346.40 cm^{-1} respectively confirmed the grafting of acrylonitrile onto pineapple (*Ananascomosus*) fibre.

INTRODUCTION

It is believed that source of petroleum based products are limited and uncertain. So an alternative with cheap sustainable and easily available raw material is required. The countries growing plant and fruit are not for only agricultural purpose but also to generate raw materials for industries.

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[*] Federal University of Agriculture, Abeoruta, Nigeria.
Correspondence E-mail Id: editor@eurekajournals.com

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Recently polymer composites containing cellulosic fibres are under focus in literature as well as industries [1]. Natural fibers are mainly composed of cellulose, lignin and hemicelluloses components. Due to these components, natural fibers are also named as cellulosic or lignocellulosic fibers. According to their origin, these natural fibres were classified. They are grouped into *leaf:* date palm, sisal, banana; *seed*: cotton; *bast*: flax, hemp, jute; *fruit:* coir, oil palm [2]. Among these various natural fibers the flax, bamboo, sisal, hemp, jute, and wood fibres are of particular interest [3]. Cellulose occurs in the form of fibres in a wide variety of growing plants. It takes the largest portion of cell walls in trees/plants. Cellulose is a long chain polymer consisting of about 3000-4000 glucose units [4]. The chains of cellulose or cellulose molecules are formed from glucose anhydride units linked together by glucosidic bonds. The chemical structure of cellulose from different plant source is the same consisting of the same anhydroglucose units. However, cellulose from different plant sources often varies in molecular weights, degree of molecular orientation and morphological structures [5].

Crystalline micro fibrils are made up of cellulose chains which are surrounded by a non-cellulosic matrix. Various treatments such as the successive chemical and mechanical treatments were used to extract high purified micro fibrillated cellulose from the cell. Bleaching agents such as the sodium chlorite or hydrogen peroxide is added mainly to the lignocellulosic fibers to degrade lignin content and the reagent sodium hydroxide is used to solubilize pectin and hemicelluloses. Mechanical treatments such as homogenization lead to homogeneous suspensions of micro fibrils. Since the cellulosic fibers are are cheap, renewable, low in density, and better processing flexibility, it became so popular [6]. Farmers harvest around 35milliontonsof natural fibers in each year from a wide range of plants and animals. Among many natural fibers, pineapple (*Ananascomosus*) is of particular interest. Pineapple (*Ananascomosus*) is perennial herbaceous plant with 1-2mfor height and width belongs to family Bromeliaceae [7]. It is cultivated in coastal and tropical regions, mainly for its fruits purpose and is continuously increasing its production. It is a short stem with dark green color. First sprout of leaf looks decorative; later it converts into 3 ft. long, 2 to 3 inch wide sword shaped and numerous spirally arranged fibrous leaves edges as well as curved towards the cross section to maintain the stiffness of the leaf [8].

One of the effective techniques which were used to improve the inherent properties of natural fiber was the graft copolymerization. In the graft copolymerization process the branched copolymer was formed by covalently attaching the side chain grafts to the main chain of the polymer backbone. The grafting phenomenon introduces a large number of functional groups and structures onto the fiber surface [9]. Depending on the chemical structure of the monomer grafted onto cellulose, graft copolymers gain new properties such as hydrophilic and hydrophobic character, improved elasticity, water absorption, ion-exchange capability and heat resistance. These copolymers are finding applications for water treatment for textile industry, for reclaiming ions of precious metals, and for personal care products such as diapers etc. [10].

Grafting of lignocellulose material such as jute, pineapple leaf, wheat straw, kenaf, and coir, have been done successfully using differ different types of initiator such as ceric ion, potassium permanganate, and potassium monopersulfate. Chemical modification of cellulose to yield cellulosic derivations such as allylation, carboxymethylation and ethylation, thiolationetc can result in profound change in reaction of cellulose in graft copolymeization reaction [11]. For this study, it is intended to graft acrylonitrile onto allyl-cellulose derived from pineapple fibre using permanganate and butyl acetate as redox initiator in aqueous medium in order to establish the grafting characteristics under varying conditions. Pineapple (*Ananascomosus*) plant possesses blast fibres that are cellulosic. The morphological features of the fibre have not been reported and commercial utilization of the fibres in the textile industries is limited. However, in some applications it is used as a substitute for jute fibres.

MATERIALS AND METHODS

COLLECTION AND PREPARATION OF MATERIALS

Pineapple (*Ananascomosus*) fibrewas obtained from Federal University of Agriculture Abeokuta's farm. All reagent and solvent that were used are of analytical grade.

Figure 2.1.Pineapple (*Ananascomosus*)fibre

PREPARATION OF HOLOCELLULOSE FROM CELLULOSIC FIBRE

The pineapple (*Ananascomosus*) cellulosic fibre was air dried and beaten to a fibre pulp. The fibre was refluxed in 200 mL methanol for one hour to remove waxes and resinous materials. The refluxed fibre was boiled in 300 mL 10% sodium sulphite for 8 hours in an open pan with continuous stirring and wash with water and air dried.

BLEACHING OF HOLOCELLULOSE

Chlorine gas was generated by reacting 20g of $KMnO_4$ crystal with excess concentrated hydrochloric acid and passed into 100 mL of chilled 2M NaOH solution to yield Sodium hypochlorite. The sodium hypochlorite was then mixed with 50ml of 0.5M HNO_3. The holocellulose was then immersed in the bleaching agent and heated until it just started to boil. It was then removed from the heater and stirred continuously until the holocellulose appeared white [12]. The bleached holocellulose was then removed and washed with distilled water to neutral pH. Afterwards, it was air dried.

$2KMnO_4 + 16HCl \rightarrow 2MnCl2_{(aq)} + 2KCl_{(aq)} + 8H_2O_{(l)} + 5C_{(l)}$

$2NaOH_{(l)} + Cl_{2(g)} \rightarrow NaCl_{(aq)} + NaClO_{(aq)} + H_2O_{(l)}$

ALLYLATION OF PINEAPPLE (*ANANASCOMOSUS*) FIBRE

7g of the fibre was reacted with 150 mL of 20 weight percent of aqeous sodium hydroxide solution at 0^oC for 20 minutes. After the completion of the reaction, the fibre was filtered and air dried. The fibre was then refluxed for three hours with 50 % v/v solution of allylchloride in 80 mL of ether. After refluxing, the fibre was filtered, rinsed with ether several times to remove excess allyl chloride and air dried [12].

DETERMINATION OF ALLYLCHLORIDE-MOEITY CONTENT

0.5g of the modified fibre was reacted with 25 mL of 0.1M iodine solution for an hour. The unreacted iodine was back titrated with 0.05 thiosulphate solution. The titration was carried out in duplicate. Color changed from brick red to blue black initially and finally to colorless [13]. Equation for the reaction

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2Na$

The number of moles of allychloride moiety per anhydroglucose unit was calculated using the formula:

$$N = \frac{(Vo-Vs)Mx162}{Wt\ x\ 127} \qquad \textbf{Equation 1}$$

Where N = Number of moles of allylchloride moiety per anhydroglucose unit

Vo = Volume of the blank

Vs = Volume of the sample

Wt = Weight of the sample

M = Molarity of the thiosulphate

METHOD OF GRAFT CO-POLYMERIZATION REACTION

Measured quantities of distilled water, concentrated HNO_3, glacial acetic acid, butylacetate, potassium permanganate, and 0.1g of the fibre were introduced into the reaction vessel such that the total volume of the reaction medium was made up to 30mL.A peroxidation time of 10 minutes was allowed before introducing a measured quantity of the acrylonitrile monomer. The reaction was allowed to proceed for a period of three hours before it was terminated by diluting to infinite dilution with distilled water. The grafted polymer was filtered dry with the aid of a vacuum pump. The fibre was completely immersed in N,N-dimethylformamideto remove homopolymer and it was later filtered off. Distilled water was added and filtered to remove residual N,N-dimethylformamide. The grafted fibre was dried in an oven at $40^{O}C$ overnight and reweighed [14]. The percentage yield was calculated using:

$$Percentage\ yield = \frac{W1-Wo}{Wo} x100 \qquad \textbf{Equation 2}$$

Where Wo = the weight of the fibre (g)

W_1= weight of grafted fibre (g)

RESULTS AND DISCUSSIONS

ALLYLATION OF PINEAPPLE FIBRE

The allylation of the fibre gave value of 2.39 moles of allyl moiety per anhydroglucose unit which suggests that virtually all the hydroxyl groups of the anhydroglucose were substituted i.ethe allyl hydrogen is intrinsically labile and is thus susceptible to oxidation by hydrogen abstraction to radical species i.e

$R\text{-}O\text{-}CH_2\text{-}CH{=}CH_2 + Mn^{+4} \rightarrow ROCH\text{-}CH{=}CH_2 + Mn^{+3} + H$

The allyl radical species can stabilize itself by resonance i.e $ROCH\text{-}CH{=}CH_2$ to $ROCH{=}CH\text{-}CH_2$ resulting in lowering of its reactivity towards a vinyl monomer for the graft copolymerization reaction. Thus, the overall lower graft yield is consistent with this expectation.

EFFECT OF KMNO$_4$ CONCENTRATION ON GRAFT YIELD

Table 3.1 shows the effect of $KMnO_4$concentration on grafting of acrylonitrile onto pineapple fibre (*Ananascomosus*) and on the allyl modified form. Acrylonitrile was grafted on both polymers but yield is significantly higher for the unmodified fibre. The unmodified fibre yield ranges from 50 % to 260 % and it was noticed that the percentage yield increased with increase in concentration of $KMnO_4$.The yield onallyl modified form ranges from 100 % to 180 % and the same trend of increment in percentage yield as concentration of$KMnO_4$ increases was noticed. This variation is in accordance with the research earlier reported by [15]. The increment in the percentage yield asconcentrationincreases wasdue to increase in the active free radicals on the cellulose backbone at which the monomer can be grafted. These active free radicals in the presence ofmonomer generatemore number of graft copolymers.

Table 3.1.Effect of $KMnO_4$Concentration on graft yield of unmodified and allylatedfibre

Concentration (10^{-3}M)	% yield of unmodified fibre	% yield of allylatedfibre
4.17	130	100
8.33	130	110
12.5	290	130
16.7	50	150
20.8	260	180

IRCHARACTERIZATION

The IR spectra of the unmodified,allylated and grafted pineapple (*Ananascomosus*) fibrewere recorded. Figure 3.1 shows the IR spectra of unmodified pineapple (*Ananascomosus*) fibre, the absorption band of value 3419.83 cm^{-1} confirmed the presence of unbounded hydroxyl groups of anhydrous unit of the unmodified fibre. Figure 3.2 shows the IR spectra of allylated pineapple (*Ananascomosus*) fibre. It shows the absorption band of -C=C-, -C-O-C- and -C-H bending at values of 1642.58cm^{-1}, 1157cm^{-1} and 898.01cm^{-1} respectively. This ultimately confirmed the presence of allylic moiety in the allylated pineapple (*Ananascomosus*) fibre. Figure 3.3 shows the IR spectra ofgrafted pineapple (*Ananascomosus*) fibre. It shows the absorption bands of -C=C-, -C-O-C-, =C-H, and C=N at values of 1634.28cm^{-1}, 1160.74cm^{-1}, 896.79cm^{-1} and 2346.40cm^{-1} respectively. This ultimately confirmed the grafting of acrylonitrile onto pineapple (*Ananascomosus*) fibre, showing evidence of graft copolymerization reaction.

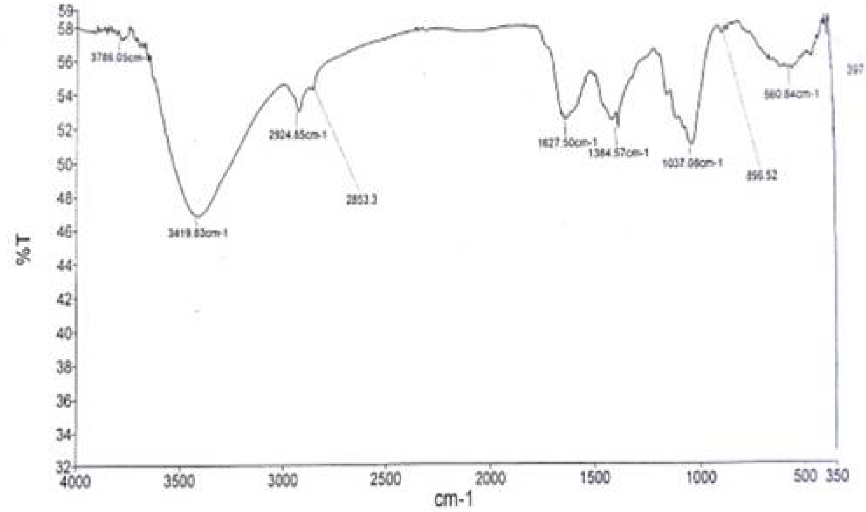

Figure 3.1.The IR spectra analysis of the unmodified pineapple (*Ananascomosus*) fibre

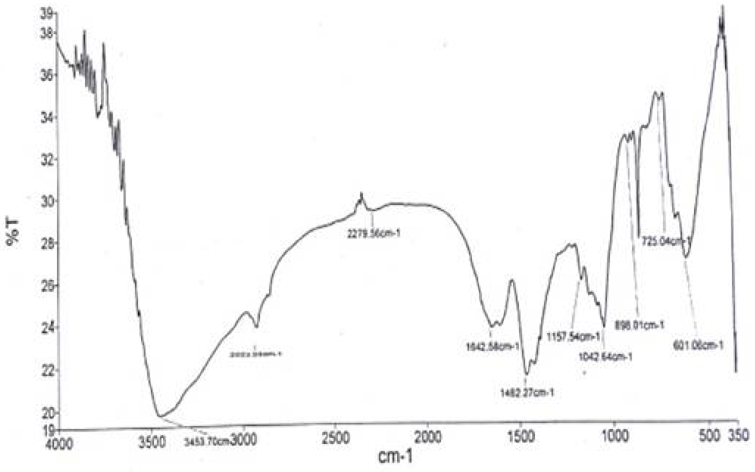

Figure 3.2.IR Spectrum of allylated pineapple (*Ananascomosus*) fibre

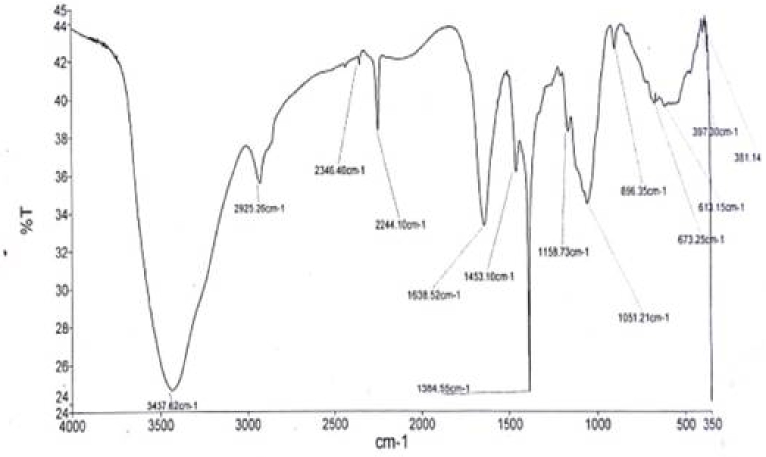

Figure 3.3.IR Spectrum of grafted pineapple (*Ananascomosus*) fibre

CONCLUSION

Chemical modification of pineapple (*Ananascomosus*) fibre by allylation gave a degree of substitution of 2.39 moles suggesting that two of the hydroxyl groups of anhydroglusoce units were substituted by allyl functions. Graft yield generally increased with increase in concentration of permanganate in the range from 4.17 x 10^{-3}M to 20.8 x 10^{-3}M giving values up to 260% for the unmodified fibre. For the allyl modified fibre, graft yields also increased with increase in permanganate concentration with values which are overall much lower by a factor of up to two compared to the ones for the unmodified. The lower yield for the allylfibre is attributed to resonance stabilization of the allylfibre making it less reactive for graft reactions [16].

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