



## Physical characterization of natural lignocellulosic single areca fiber

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### Abstract

In the recent decades, natural lignocellulosic fibers are used as reinforcements in the fabrication of polymer composites which are considered as most promising materials in structural applications due to its superior properties, eco-friendly nature and economic advantages. The main drawback of usage of these natural fibers as reinforcement for composites is their low degradation temperatures around 200 °C, which make them inadequate for processing temperatures above 200 °C. Hence, the aim of this research work is to improve thermal stability of natural lignocellulosic areca fibers by various chemical treatments and to assess the influence of chemical treatments on the crystallinity of areca fibers. So, in this study, areca fibers were subjected to chemical treatments such as NaOH, KMnO<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>COCl, H<sub>2</sub>C=CHCOOH and CH<sub>3</sub>CO-O-OC-CH<sub>3</sub> to improve its thermal stability. Thermal stability and crystallinity of untreated and chemically treated areca fibers were characterized by TGA-DTG and XRD studies respectively. The results from TGA-DTG data have shown improved thermal stability for chemically treated areca fibers and the results from XRD analysis indicated the little decrease in percentage crystallinity and crystallinity index for the chemically treated areca fibers. The SEM micrographs confirmed the chemical modification and its influence on the morphological aspects of areca fibers.

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**Keywords:** areca fibers; chemical treatments; TGA-DTG analysis; XRD analysis; SEM image analysis.

### 1. Introduction

At present, natural lignocellulosic fibers are gaining tremendous progressive importance as renewable, light weight, strong, environmentally acceptable and biodegradable reinforcement material for the fabrication of polymeric composite materials because of rapid depletion of fossil fuel reserves due to continuous consumption of the world's consumed chemicals, fuels and energy. Now research is focussed

on more effective utilization of these renewable energy sources as they do not contribute to the amount of CO<sub>2</sub>. Further, these natural fiber reinforced polymer composites possess better chemical resistance, electrical resistance, good thermal, acoustic insulating properties and high resistance to fracture. This result has stimulated the use of hard natural lignocellulosic fibers as an attractive alternative to synthetic fibers [1-2].

At present, automobile industry is currently shifting to "green" outlook, as consumers are looking for environmentally friendly vehicles. Bio-fiber reinforced polymer composites have been embraced by European car makers for door panels, seat backs, headliners, package trays, dashboards and trunk liners.

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Currently, fiber composites have found their way into the ship building industry also. Polymer composite materials are playing a significant role in current and future aerospace components. Reduced airframe weight by polymer composites enables better fuel economy and hence lowers the operating costs. Hence, natural fiber reinforced polymer composites are gaining progressive significance. So, by selecting appropriate combination of matrix and reinforcement, it is possible to tailor the properties of natural fiber reinforced polymer composites for suitable structural applications [3-4].

But the main constraint in using natural fibers as reinforcing materials in the preparation of polymer composites is incompatibility between the natural fibers and polymeric resin because of the hydrophilic nature of natural fibers which in turn leading to poor wettability with polymeric matrix. And the next most important setback here is the low thermal stability of these natural fibers. That is majority of natural fibers as a function of cellulose and lignin has low degradation temperatures around 200 °C and makes them inadequate for processing temperatures above 200 °C [5]. In general, natural fibers are having different chemical composition of cellulose, hemicelluloses, lignin and pectin and so their flammability varies from fiber to fiber. Higher cellulose content results in higher flammability while higher lignin content results in greater char formation with lower degradation temperature [6-8]. Hence, the cellulose and lignin content present in these natural fibers decides the thermal stability of natural fibers and the thermal stability of natural fiber reinforced polymer composites.

These defects can be remedied by chemical modification of natural fibers as this chemical treatment can increase the interfacial adhesion between the fibers and matrix, improves surface roughness and decrease the water absorption of fibers. Further, it is explained in detail about various chemical treatments that are carried out on natural fibers and its effects on improving the properties of natural fibers and natural fiber reinforced polymer composites [9]. And also, chemical modification of natural fibers can strongly influence the thermal properties of both natural fibers and natural fiber reinforced polymer composites [10]. So, it is very important to promote surface modification of natural fibers [11] with various chemical treatments to decrease hydrophilicity and to improve the thermal stability of natural fibers.

Areca fiber has a greater potential in the polymer composite field since the areca fibers are possessing superior properties such as light weight, strong and high strength-to-weight ratio. Further areca fibers are

biodegradable, non-toxic and eco-friendly and have low maintenance cost. Areca fiber is a better acoustic material compared to wood based plywood or particle boards. So, areca fiber reinforced polymer composite materials would be a promising material with moderate life for packaging and other structural applications. The areca husk is a hard fibrous material covering the endosperm and constitutes about 60-80% of the total weight and volume of the areca fruit. The husk fiber is composed of cellulose with varying proportions of hemicelluloses (35–64.8%) and lignin (13.0–26.0%), pectin and protopectin [12-14].

No literature is available on the thermal stability and crystallinity of areca fibers. Hence, the aim of this research work is to improve the thermal stability of natural areca fibers by various chemical treatments and to assess the influence of these chemical treatments on the crystallinity of areca fibers. So that the chemically modified areca fibers with improved thermal stability can be effectively used as reinforcement in the fabrication of polymer composites which would have its applications in light weight materials industries.

In this research work, areca fibers were subjected to chemical treatments such as sodium hydroxide, potassium permanganate, benzoyl chloride, acrylic acid and acetic anhydride to decrease its hydrophilicity, to improve surface roughness and hence finally to improve its thermal stability. Thermal stability and crystallinity of untreated and chemically treated areca fibers was characterized by TGA-DTG and XRD studies respectively. TGA and DTG data have shown improved thermal stability for chemically treated areca fibers and XRD analysis results indicated the little decrease in percentage crystallinity and crystallinity index for chemically treated areca fibers. These results are correlating with other naturally occurring fiber materials. SEM image analysis of areca fibers was done to confirm the chemical modification and its influence on morphology of areca fibers.

## 2. Materials and methods

### 2.1. Materials

Areca empty fruits were obtained from Madhu Farm House, Nilogal, Davangere, Karnataka, India. The analytical grade reagents were purchased from Qualigens Company and used as received.

### 2.2. Fiber Extraction

The dried areca empty fruits were soaked in de-ionized water for about five days. This process is

called retting; allowing the fiber to be removed from the fruit easily and then the fibers were removed from the fruit and separated with a comb and dried in the room temperature. Then the fibers were combed in a carding frame to further separate the fibers into an individual state. Then a sieve was used to remove broken fibers and impurities. The resulting fibers were treated in the condition (temperature 30 °C, RH 70%) for 72 h before the chemical treatment [14,15].

### *2.3. Alkali treatment of areca fibers*

Areca fibers were soaked in a stainless steel vessel containing 6% NaOH solution at room temperature (30-32 °C) for 1h. The alkali treated areca fibers were immersed in distilled water for 24 h to remove the residual NaOH. Final washing was done with distilled water containing little amount of acetic acid. Fibers were dehydrated in an oven at 70 °C for a period of 3 h [12,16-18].

### *2.4. Potassium permanganate treatment of areca fibers*

Areca fibers, pre-treated with 6% NaOH were immersed in 0.5% KMnO<sub>4</sub> in acetone solution for 30 min. The treated areca fibers were then decanted and dried in air [12,16,19].

### *2.5. Benzoyl chloride treatment of areca fibers*

During benzoylation treatment, 6% NaOH pre-treatment was used to activate the hydroxyl groups of the fibers. This alkali pre-treated areca fibers were then soaked in 6% NaOH and agitated with benzoyl chloride for 15 min. The treated areca fibers were soaked in ethanol solution for 1 h to remove benzoyl chloride that adhered to the fiber surface. Then the treated areca fibers were washed thoroughly using distilled water and dried in air [12,20,21].

### *2.6. Acrylic acid treatment of areca fibers*

6% NaOH treated areca fibers were immersed in 5% acrylic acid solution at 50 °C for a period of 1 h and then treated areca fibers were washed thoroughly using distilled water and dried in air [1,12,22].

### *2.7. Acetic anhydride treatment of areca fibers*

The areca fibers were placed in a round bottom flask containing acetylating solution. Acetylating solution consists of 250 ml toluene and 125 ml acetic anhydride and a small amount of catalyst perchloric

acid (60%). The process temperature of acetylation was 60 °C and duration was 3 h. After modification, the fibers were washed periodically with distilled water until acid free. Finally, acetylated areca fibers were air dried in air [12,23,24].

All the untreated and various chemically treated areca fibers were cured in an oven and then conditioned under the environment of relative humidity of 70% and temperature, 30 °C for 24h.

### *2.8. Thermal stability of areca fibers*

The thermal stabilities of untreated and various chemically treated areca fibers were measured by using a STA 409 PL Luxx instrument operating at a temperature range of RT (room temperature) to 500 °C at a heating rate of 10 °C/min under a nitrogen atmosphere using TGA-DTG sample carrier and TGA-DTG alumina crucible.

### *2.9. X-ray diffraction studies of areca fibers*

X-ray diffraction studies of untreated and all chemically treated areca fibers in powder form were performed under ambient condition on X-Ray Diffractometer using Cu-K $\alpha$  radiation ( $k = 1.5405 \text{ \AA}$ ) run at 40 KV and 30 mA using Ni filter on rotation between 3° to 60° at 2 – Theta – Scale.

### *2.10. SEM image analysis of areca fibers*

The SEM images of untreated and all chemically treated areca fibers were taken by using JEOL JSM-T330A scanning electron microscope at the accelerating voltage of 20 KV to characterize the morphological investigations of areca fibers. Surfaces of the fiber samples were sputter-coated with gold prior to their observation.

## **3. Results and discussion**

### *3.1. Chemical treatments of areca fibers*

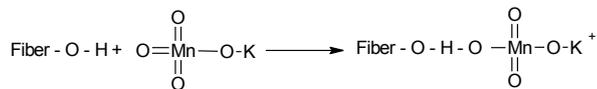
Natural areca fibers are amenable to chemical modification due to the presence of hydroxyl groups. Due to chemical treatments, more reactive groups are exposed on the areca fiber surface, hydrophilic hydroxyl groups are reduced and the fibers moisture resistance property is increased. Areca fiber surface became more uniform due to the elimination of micro voids. Further, there is improvement in surface characteristics of areca fibers such as wetting, adhesion and porosity. And also, the thermal stability of areca fibers is improved [25-28].

### 3.1.1. Alkali treatment of areca fibers



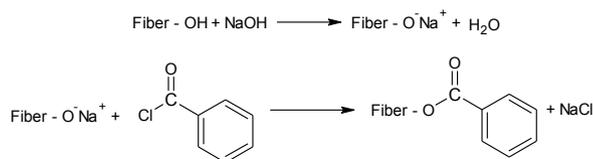
Fiber-cell-O-Na groups are formed between the cellulose molecular chains due to the alkali treatment of areca fibers and there is increase in the amount of amorphous cellulose at the expense of crystalline cellulose. The effect of alkali on cellulose fiber is a swelling reaction and there is a change in the surface topography of the areca fibers. Hydrogen bonding present in the network structure is removed and new reactive hydrogen bonds are formed between the cellular molecular chains and the natural crystalline structure of the cellulose relaxes and this provides more access to penetration of chemicals. As a result, hydrophilic hydroxyl groups are reduced, fibers moisture resistance property is increased and thermal stability is improved [9,12,16-18,29-30].

### 3.1.2. Potassium permanganate treatment of areca fibers



Cellulose manganate is formed when highly reactive permanganate ions ( $\text{Mn}^{3+}$ ) reacts with cellulose hydroxyl groups. Permanganate ions react with the lignin constituents and carve the areca fiber surface and as a result, areca fiber surface becomes physically rough. This reduces hydrophilic nature of areca fibers and improves thermal stability of treated areca fibers when compared with that of untreated areca fibers. [12,19,31].

### 3.1.3. Benzoyl chloride treatment of areca fibers



When benzoyl chloride reacts with alkali pre-treated areca fibers, an ester linkage is formed. Hence, there is reduction in hydrophilicity of treated areca fibers. Also, the treated areca fiber surface became physically rough. Benzoylation treatment also enhances thermal stability of the fibers [9,12,20,21,28].

### 3.1.4. Acrylic acid treatment of areca fibers



During acrylation treatment, an ester linkage is formed with the areca fiber by the carboxylic acids present in acrylic acid. Acrylic acid provides more access of reactive cellulose macro radicals to the polymerization medium by reacting with the cellulosic hydroxyl groups of the fiber. Moisture absorption of areca fibers is reduced due to the replacement of hydrophilic hydroxyl groups by hydrophobic ester groups and thermal stability is increased [1,12,22].

### 3.1.5. Acetic anhydride treatment of areca fibers



This chemical reaction renders the areca fiber surface to become more hydrophobic due to the replacement of hydrophilic hydroxyl groups by hydrophobic acetyl groups and also it causes plasticization of cellulosic fibers. As a result, thermal stability of acetylated areca fibers is improved [12,23,24].

## 3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) measures the amount and rate of change in the mass of a sample as a function of temperature/time in a controlled atmosphere. Thermal stabilities of materials are measured by using TGA. Maximum decomposition rates for weight losses of components present in natural fibers are shown by DTG curve [32].

TGA - DTG is specifically useful for the study of polymeric materials including thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints. TGA - DTG measurements provide valuable information that can be used to select materials for certain end-use applications.

The thermal degradation behaviour of untreated (AR1), alkali treated (AR2), potassium permanganate treated (AR3), benzoyl chloride treated (AR4), acrylic acid treated (AR5) and acetic anhydride treated (AR6) areca fibers are shown in Figure 1. The derivative thermo gravimetric curve of untreated (AR1), alkali treated (AR2), potassium permanganate treated (AR3), benzoyl chloride treated (AR4), acrylic acid treated (AR5) and acetic anhydride treated (AR6) areca fibers are shown in Figure 2. The thermal stability of untreated (AR1), alkali treated (AR2), potassium permanganate treated (AR3), benzoyl

chloride treated (AR4), acrylic acid treated (AR5) and acetic anhydride treated (AR6) areca fibers are analysed by using TGA curves and DTG curves and

the results are presented in Table 1 and Table 2 respectively.

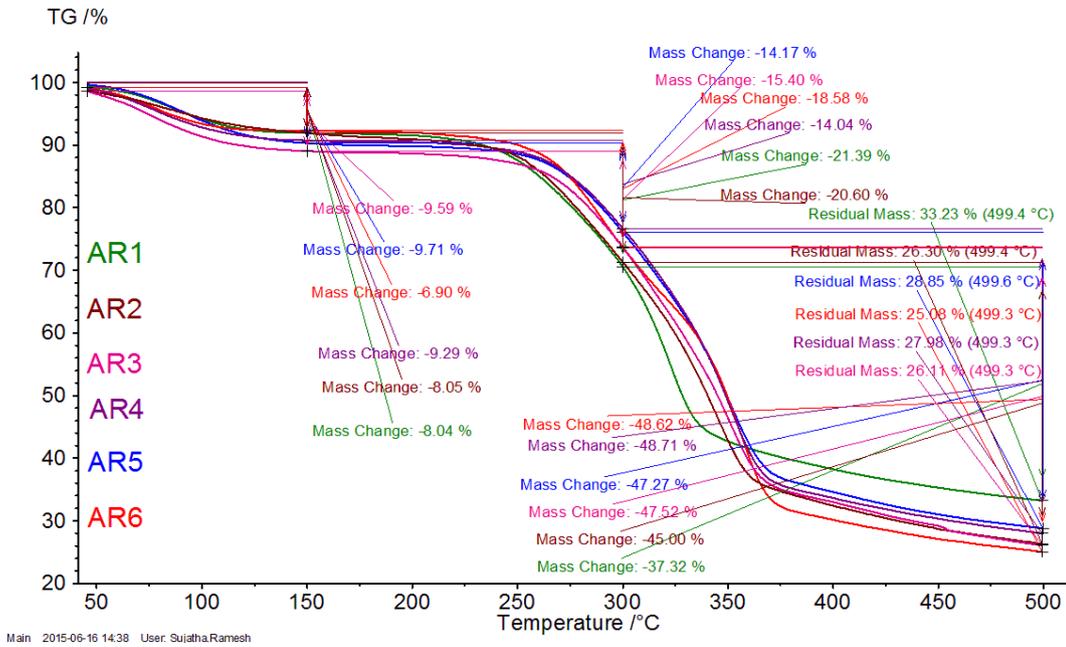


Fig. 1. TGA of untreated and chemically treated areca fibers. AR1: Untreated; AR2: Alkali treated; AR3: Potassium permanganate treated; AR4: Benzoyl chloride treated; AR5: Acrylic acid treated; AR6: Acetic anhydride treated.

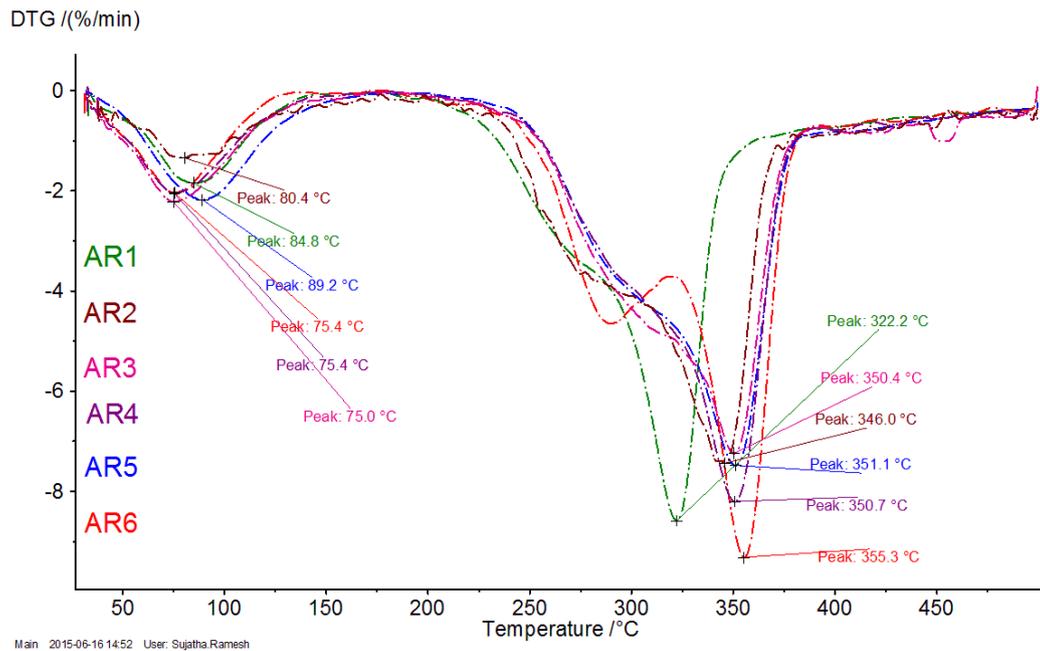


Fig. 2. DTG of untreated and chemically treated areca fibers. AR1: Untreated; AR2: Alkali treated; AR3: Potassium permanganate treated; AR4: Benzoyl chloride treated; AR5: Acrylic acid treated; AR6: Acetic anhydride treated.

Table 1. TGA results of untreated and chemically treated areca fibers.

Areca Fibers	1 <sup>st</sup> stage degradation in TGA curve		2 <sup>nd</sup> stage degradation in TGA curve		Decomposition temperature, °C in TGA curve at		Weight loss of areca fibers, % in TGA curve at			Residual mass % at 500 °C
	Temperature range	Weight loss	Temperature range	Weight loss	25% weight loss	50% weight loss	150 °C	300 °C	500 °C	
	T <sub>1</sub> °C	%	T <sub>2</sub> °C	%						
Untreated (AR1)	241.5 to 297.0	17.13	297.0 to 353.0	29.54	289.5	328.5	8.04	21.39	37.32	33.23
NaOH treated (AR2)	250.8 to 306.0	19.16	306.0 to 384.0	35.00	291.0	340.0	8.05	20.60	45.00	26.30
KMnO <sub>4</sub> treated (AR3)	259.0 to 332.5	28.47	332.5 to 382.5	23.21	297.0	345.0	9.59	15.40	47.52	26.11
Benzoyl chloride treated (AR4)	257.0 to 319.5	19.95	319.5 to 371.0	32.00	304.0	349.0	9.29	14.04	48.71	27.98
Acrylic acid treated (AR5)	252.0 to 309.5	16.27	309.5 to 380.0	35.83	302.5	349.5	9.71	14.17	47.27	28.85
Acetic anhydride treated (AR6)	251.0 to 320.0	24.11	320.0 to 369.0	32.00	297.0	349.5	6.90	18.58	48.62	25.08

Table 2. DTG results of untreated and chemically treated areca fibers.

Areca Fibers	Decomposition temperature, °C in DTG curve at	
	First Peak	Second Peak
Untreated (AR1)	84.8	322.2
NaOH treated (AR2)	80.4	346.0
KMnO <sub>4</sub> treated (AR3)	75.0	350.4
Benzoyl chloride treated (AR4)	75.4	350.7
Acrylic acid treated (AR5)	89.2	351.1
Acetic anhydride treated (AR6)	75.4	355.3

### 3.2.1. Thermal analysis of untreated areca fibers

In accordance with other studies on natural lignocellulosic fibers [33–36], the TGA curve of untreated areca fibers (AR1 in Figure 1) shows three weight loss steps and their decomposition occurs in two main stages.

The initial weight loss, 10.94% observed around RT (room temperature) to 241.5 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the fibers. Above this temperature, it can be observed that the thermal

stability is gradually decreasing and the degradation of natural areca fibers occurs.

The first stage degradation temperature, T<sub>1</sub> around 241.5 °C to 297.0 °C is associated to the thermal depolymerisation of hemicelluloses, pectin, cleavage of glycosidic linkages of cellulose and lignin and the weight loss in this temperature range is 17.13% and the second stage degradation temperature, T<sub>2</sub> around 297.0 °C to 353.0 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the fiber and the weight loss in this temperature range is 29.54% [36]. The weight loss, 9.16% observed after 353.0 °C up to 500 °C is due to the degradation of lignin. Generally, the decomposition of lignin, owing to its complex structure containing aromatic rings with various branches [37], occurs slowly within the whole temperature range around 241.5 °C to 500 °C [38]. The decomposition temperature corresponding to 25% and 50% weight loss of untreated areca fibers are 289.5 °C and 328.5 °C respectively. Thermally degraded mass change percentage of untreated areca fibers at 150 °C, 300 °C and 500 °C are 8.04%, 21.39% and 37.32% respectively. In an inert atmosphere, the final products of degradation of natural lignocellulosic areca fibers consist of carbonaceous residues and possible un-degraded fillers and it has been observed a residual weight percentage of 33.23% at 499.4 °C [39].

These results are confirmed by DTG curve of untreated areca fibers (AR1 in Figure 2) wherein the maximum decomposition rates for weight losses are

shown. The small first peak at 84.8 °C corresponds to evaporation of moisture from the untreated areca fibers and the second peak observed at 322.2 °C confirms the maximum decomposition rates for weight losses of cellulose present in the untreated areca fibers [32, 40].

### 3.2.2. Thermal analysis of alkali treated areca fibers

Similarly, the TGA curve of alkali treated areca fibers (AR2 in Figure 1) shows three weight loss steps and their decomposition occurs in two main stages.

The initial weight loss, 11.99% observed around RT to 250.8 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the fibers. Above this temperature, the thermal stability is gradually decreasing and the degradation of alkali treated areca fibers occurs.

The first stage degradation temperature,  $T_1$  around 250.8 °C to 306.0 °C is associated to the thermal depolymerisation of hemicelluloses, pectin, cleavage of glycosidic linkages of cellulose and lignin and the weight loss in this temperature range is 19.16% and the second stage degradation temperature,  $T_2$  around 306.0 °C to 384.0 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the fiber and weight loss in this stage is 35%. The weight loss, 7.55% observed after 384.0 °C up to 500 °C is due to the degradation of lignin. But the decomposition of lignin occurs slowly within the whole temperature range around 250.8 °C to 500 °C. The decomposition temperature corresponding to 25% and 50% weight loss of alkali treated areca fibers are 291.0 °C and 340.0 °C respectively. Thermally degraded mass change percentage of alkali treated areca fibers at 150 °C, 300 °C and 500 °C are 8.05%, 20.60% and 45.00% respectively. In an inert atmosphere, the final products of degradation of alkali treated areca fibers consist of carbonaceous residues with weight percentage of 26.30% at 499.4 °C.

These results are confirmed by DTG curve of alkali treated areca fibers (AR2 in Figure 2). The small first peak at 80.4 °C represents the evaporation of water from the alkali treated areca fibres and the second peak at 346.0 °C confirms the maximum decomposition rates for weight losses of cellulose present in the alkali treated areca fibers.

Alkali treatment of areca fibers reduced the certain portion of lignin, pectin, wax and oil covering materials and it mainly reduced hemicelluloses to a considerable amount. Thus it leads to the formation of lignin-cellulose complex and made the product more stable than the native one [9,12,18,29-30]. As a result, in TGA, decomposition temperature corresponding to first stage as well as the second stage degradation of

alkali treated areca fiber is increased, the residual mass percentage left after degradation is decreased and there is increase in decomposition temperatures corresponding to 25% and 50% weight loss of the alkali treated areca fibers when compared with that of untreated areca fibers. And also, the thermally degraded mass change percentage of alkali treated areca fibers at 300 °C is lower and at 500 °C is higher than that of untreated areca fibers. Further, the main second peak decomposition temperature of alkali treated areca fibers in DTG curve was higher than that of untreated areca fibers. These results confirmed the improved thermal stability for alkali treated areca fibers.

### 3.2.3. Thermal analysis of potassium permanganate treated areca fibers

The TGA curve of  $\text{KMnO}_4$  treated areca fibers (AR3 in Figure 1) also shows three weight loss steps and their decomposition occurs in two main stages.

The initial weight loss, 13.97% observed around RT to 259.0 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the permanganate treated areca fibers. Above this temperature, the thermal stability is gradually decreasing and the degradation of permanganate treated areca fibers occurs.

The first stage degradation temperature,  $T_1$  around 259.0 °C to 332.5 °C is associated to the thermal depolymerisation of hemicelluloses, pectin, cleavage of glycosidic linkages of cellulose and lignin and the weight loss in this temperature range is 28.47% and the second stage degradation temperature,  $T_2$  around 332.5 °C to 382.5 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the permanganate treated areca fibers and weight loss corresponding to this temperature range is 23.21%. The weight loss, 8.24% observed after 382.5 °C up to 500 °C is due to the degradation of lignin. The decomposition of lignin occurs slowly within the whole temperature range around 259.0 °C to 500 °C. The decomposition temperature corresponding to 25% and 50% weight loss of permanganate treated areca fibers are 297.0 °C and 345.0 °C respectively. Thermally degraded mass change percentage of  $\text{KMnO}_4$  treated areca fibers at 150 °C, 300 °C and 500 °C are 9.59%, 15.40% and 47.52% respectively. In an inert atmosphere, the final products of degradation of permanganate treated lignocellulosic areca fibers consist of carbonaceous residual weight percentage of 26.11% at 499.3 °C.

These results are confirmed by DTG curve of permanganate treated areca fibers (AR3 in Figure 2). The small first peak at 75.0 °C represents the evaporation of water from the permanganate treated

areca fibres and the second peak at 350.4 °C confirms the maximum decomposition rates for weight losses of cellulose present in the  $\text{KMnO}_4$  treated areca fibers. In potassium permanganate treatment, permanganate ions react with lignin constituents and carve the areca fiber surface and reduced the certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials [12,19,31]. As a result, in TGA, the decomposition temperature corresponding to first stage as well as the second stage degradation of permanganate treated areca fiber is increased, the residual mass percentage left after degradation is decreased and there is increase in decomposition temperatures corresponding to 25% and 50% weight loss of the  $\text{KMnO}_4$  treated areca fibers when compared with that of untreated areca fibers. And also, the thermally degraded mass change percentage of permanganate treated areca fibers at 300 °C is lower and at 500 °C is higher than that of untreated areca fibers. Further, the main second peak decomposition temperature of potassium permanganate treated areca fibers in DTG curve was higher than that of untreated areca fibers. These results confirmed the improved thermal stability for  $\text{KMnO}_4$  treated areca fibers.

#### 3.2.4. Thermal analysis of benzoyl chloride treated areca fibers

The TGA curve of benzoyl chloride treated areca fibers (AR4 in Figure 1) also shows three weight loss steps and their decomposition occurs in two main stages similar to that of untreated areca fibers.

The initial weight loss, 11.80% observed around RT to 257.0 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the benzoylated areca fibers. Above this temperature, it can be seen that the thermal stability is gradually decreasing and the degradation of benzoyl chloride treated areca fibers occurs.

The first stage degradation temperature,  $T_1$  around 257.0 °C to 319.5 °C is associated to the thermal depolymerisation of hemicelluloses, pectin, cleavage of glycosidic linkages of cellulose and lignin and the weight loss in this stage is 19.95% and the second stage degradation temperature,  $T_2$  around 319.5 °C to 371.0 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the treated fiber and weight loss in this temperature range is 32.00%. The weight loss, 8.27% observed after 371.0 °C up to 500 °C is due to the degradation of lignin. The decomposition of lignin, owing to its complex structure containing aromatic rings with various branches, occurs slowly within the whole temperature range around 257.0 °C to 500 °C. The decomposition temperature

corresponding to 25% and 50% weight loss of benzoyl chloride treated areca fibers are 304.0 °C and 349.0 °C respectively. Thermally degraded mass change percentage of benzoyl chloride treated areca fibers at 150 °C, 300 °C and 500 °C are 9.29%, 14.04% and 48.71% respectively. In an inert atmosphere, the final products of degradation of benzoylated areca fibers consist of carbonaceous residual weight percentage of 27.98% at 499.3 °C.

These results are confirmed by DTG curve of benzoyl chloride treated areca fibers (AR4 in Figure 2). The small first peak at 75.4 °C represents the evaporation of water from the benzoylated areca fibres and the second peak at 350.7 °C confirms the maximum decomposition rates for weight losses of cellulose present in the benzoyl chloride treated areca fibers.

In benzoyl chloride treatment, alkali pre-treatment which was used to activate the hydroxyl groups of the areca fibers reduced the certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials from the fibers. Then benzoyl chloride forms an ester linkage to the alkali pre-treated areca fibers and a rough surface is produced [9,12,20,21,28]. Due to this, in TGA, decomposition temperature corresponding to first stage as well as the second stage degradation of benzoyl chloride treated areca fibers is increased and the residual mass percentage left after degradation is decreased and there is increase in decomposition temperatures corresponding to 25% and 50% weight loss of the benzoyl chloride treated areca fibers when compared with that of untreated areca fibers. And also, the thermally degraded mass change percentage of benzoyl chloride treated areca fibers at 300 °C is lower and at 500 °C is higher than that of untreated areca fibers. Further, the main second peak decomposition temperature in DTG curve of benzoyl chloride treated areca fibers was higher than that of untreated areca fibers. These results confirmed the improved thermal stability for benzoyl chloride treated areca fibers.

#### 3.2.5. Thermal analysis of acrylic acid treated areca fibers

According to other studies on lignocellulosic fibers, the TGA curve of acrylic acid treated areca fibers (AR5 in Figure 1) shows three weight loss steps and their decomposition occurs in two main stages.

The initial weight loss, 11.58% observed between RT and 252.0 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the acrylic acid treated areca fibers. Above this temperature, it can be observed that the thermal

stability is gradually decreasing and the degradation of acrylic acid treated areca fibers occurs.

The first stage degradation temperature,  $T_1$  around 252.0 °C to 309.5 °C is associated to the thermal depolymerisation of hemicelluloses, pectin, cleavage of glycosidic linkages of cellulose and lignin and the weight loss is 16.27% and the second stage degradation temperature,  $T_2$  around 309.5 °C to 380.0 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the acrylic acid treated fibers and the weight loss is 35.83%. The weight loss, 7.47% observed after 380.0 °C up to 500 °C is due to the decomposition of lignin. The decomposition of lignin occurs slowly within the whole temperature range around 252.0 °C to 500 °C. The decomposition temperature corresponding to 25% and 50% weight loss of acrylic acid treated areca fibers are 302.5 °C and 349.5 °C respectively. Thermally degraded mass change percentage of acrylic acid treated areca fibers at 150 °C, 300 °C and 500 °C are 9.71%, 14.17% and 47.27% respectively. In an inert atmosphere, the final products of degradation of acrylic acid treated areca fibers consist of carbonaceous residual weight percentage of 28.85% at 499.6 °C.

These results are confirmed by DTG curve of acrylic acid treated areca fibers (AR5 in Figure 2). The small first peak at 89.2 °C represents the evaporation of water from the acrylated areca fibres and the second peak at 351.1 °C confirms the maximum decomposition rates for weight losses of cellulose present in the acrylic acid treated areca fibers.

In this chemical treatment, the carboxylic acid present in acrylic acid forms ester linkages with the cellulose hydroxyl groups. Acrylic acid treatment removes most of the hemicelluloses and lignin and destroys cellulose structures and produces large number of pits on the fiber surface [1,12,22]. So, in TGA, the decomposition temperature corresponding to first stage degradation as well as the second stage degradation of acrylic acid treated areca fiber is increased and the residual mass percentage left after degradation is decreased and there is increase in decomposition temperature corresponding to 25% and 50% weight loss of the acrylic acid treated areca fibers when compared with that of untreated areca fibers. And also, the thermally degraded mass change percentage of acrylated areca fibers at 300 °C is lower and at 500 °C is higher than that of untreated areca fibers. Further, the main second peak decomposition temperature in DTG curve of acrylic acid treated areca fibers was higher than that of untreated areca fibers. Hence, acrylic acid treatment resulted in improved thermal stability for the treated areca fibers.

### 3.2.6. Thermal analysis of acetic anhydride treated areca fibers

The TGA curve of acetic anhydride treated areca fibers (AR6 in Figure 1) shows three weight loss steps and their decomposition occurs in two main stages like that of untreated areca fibers.

The initial weight loss, 10.04% observed between RT and 251.0 °C is attributed to the vaporization of the moisture and decomposition of volatile extractives from the acetylated areca fibers. Above this temperature, the thermal stability is gradually decreasing and the degradation of acetylated areca fibers occurs.

The first stage degradation temperature,  $T_1$  around 251.0 °C to 320.0 °C is associated to the thermal depolymerisation of hemicelluloses, pectin and cleavage of glycosidic linkages of cellulose and the weight loss is 24.11% and the second stage degradation temperature,  $T_2$  around 320.0 °C to 369.0 °C corresponds to the degradation of  $\alpha$ -cellulose and lignin present in the treated areca fibers and the weight loss is 32%. The weight loss, 8.78% observed after 369.0 °C up to 500 °C is due to the degradation of lignin. The decomposition of lignin occurs slowly within the whole temperature range around 251.0 °C to 500 °C. The decomposition temperature corresponding to 25% and 50% weight loss of acetylated areca fibers are 297.0 °C and 349.5 °C respectively. Thermally degraded mass change percentage of acetic anhydride treated areca fibers at 150 °C, 300 °C and 500 °C are 6.90%, 18.58% and 48.62% respectively. In an inert atmosphere, the final products of degradation of acetylated areca fibers consist of carbonaceous residual weight percentage of 25.08% at 499.3 °C.

These results are confirmed by DTG curve of acetic anhydride treated areca fibers (AR6 in Figure 2). The small first peak at 75.4 °C corresponds to the evaporation of water from the acetylated areca fibres and the second peak at 355.3 °C confirms the maximum decomposition rates for weight losses of cellulose present in the acetic anhydride treated areca fibers.

Upon acetylation treatment, the wax and cuticle present in the surface is removed by the interaction with acetyl groups and the fiber surface becomes smoother and also it causes plasticization of cellulosic fibers. The fibrillation is also found to arise as the binding materials are removed and some micro-pores appeared in the acetylated areca fibers [12,23,24]. As a result, in TGA, decomposition temperature corresponding to first stage as well as the second stage degradation of acetylated areca fibers is increased and the residual mass percentage left after degradation is

decreased and there is increase in decomposition temperature corresponding to 25% and 50% weight loss of the acetylated areca fibers when compared with that of untreated areca fibers. And also, the thermally degraded mass change percentage of acetylated areca fibers at 300 °C is lower and at 500 °C is higher than that of untreated areca fibers. Further, the main second peak decomposition temperature in DTG curve of acetylated areca fibers was higher than that of untreated areca fibers. Hence acetic anhydride treatment resulted in improved thermal stability for the treated areca fibers.

Decomposition temperatures for selected natural fibers are shown in Table 3. The TGA results of untreated and chemically treated areca fibers from Table 1 revealed that the untreated, alkali treated, potassium permanganate treated, benzoyl chloride treated, acrylic acid treated and acetic anhydride treated areca fibers are stable until around 241.5 °C, 250.8 °C, 259.0 °C, 257.0 °C, 252.0 °C and 251.0 °C respectively. The DTG results of untreated and chemically treated areca fibers from Table 2 revealed that the temperature of maximum decomposition for untreated, alkali treated, potassium permanganate treated, benzoyl chloride treated, acrylic acid treated and acetic anhydride treated areca fibers are 322.2 °C, 346.0 °C, 350.4 °C, 350.7 °C, 351.1 °C and 355.3 °C respectively. In conclusion, it is important to note that, this is in good agreement with the decomposition temperature values of many vegetable fibers as shown in Table 3 which is reported in literature [41–44] for selected natural fibers.

Table 3. Decomposition temperatures for selected natural fibers.

Natural fiber	Temperature of initial decomposition	Temperature of maximum decomposition
	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)
Jute	205	283
Okra	220	359
Hemp	250	390
Curaua	230	335
Kenaf	219	284

### 3.3. X-ray diffraction analysis of areca fibers

The influence of chemical treatment on the crystallinity of areca fibers is analyzed as follows: The counter reading of peak intensity at 22° is said to represent the crystalline material and the peak intensity at 18 ° corresponds to the amorphous

material in cellulose [45, 46]. Percentage crystallinity (%Cr) [47] and crystallinity index (C.I.) [48, 49] of untreated and all chemically treated areca fibers is calculated by using the given formula (1) and (2) where  $I_{22}$  and  $I_{18}$  are the crystalline and amorphous intensities at 2-Theta-Scale close to 22° and 18° respectively.

$$\%Cr = \frac{I_{22}}{(I_{22} + I_{18})} \times 100 \quad \text{----- (1)}$$

$$C.I. = \frac{(I_{22} - I_{18})}{I_{22}} \quad \text{----- (2)}$$

The effect of chemical modification of natural lignocellulosic materials on their crystallinity has been investigated by various researchers [50]. The reagent first react with the chain ends on the surface of crystallites, as it cannot diffuse into the crystalline region, resulting in the opening of some of the hydrogen-bonded cellulose chains. As a result, slight disturbance of cellulose chain arrangement may occur. A poor crystallinity index in case of chemically treated fibers means poor order of cellulose crystal to the fiber axis during chemical treatments [51]. Several researchers reported that chemical treatments reduced the proportion of crystalline material present in plant fibers [52].

X-ray diffraction patterns of untreated (Figure 3), alkali treated (Figure 4), permanganate treated (Figure 5), benzoyl chloride treated (Figure 6), acrylic acid treated (Figure 7) and acetic anhydride treated (Figure 8) areca fibers are shown below.

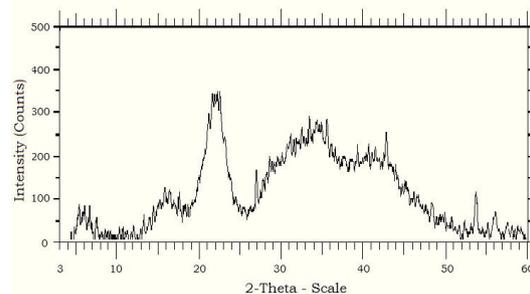


Fig.3. XRD patterns of untreated areca fibers.

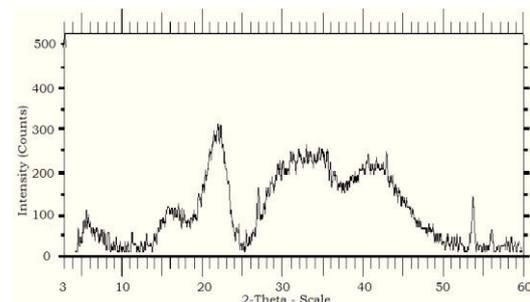


Fig. 4. XRD patterns of alkali treated areca fibers.

Table 4 shows the XRD analysis results of untreated and all chemically treated areca fibers. The little decrease in crystallinity obtained for alkali treated areca fibers is due to swelling of areca fibers and partial removal of cementing materials from the areca fibers which in-turn resulted in a slight disturbance of cellulose chain arrangement [53,54].

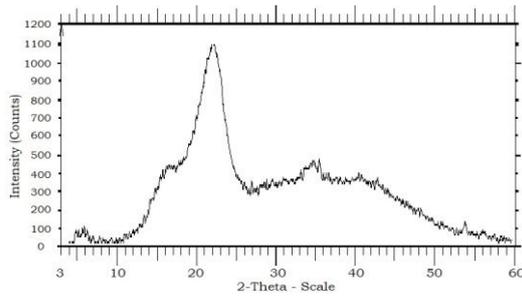


Fig. 5. XRD patterns of permanganate treated areca fibers.

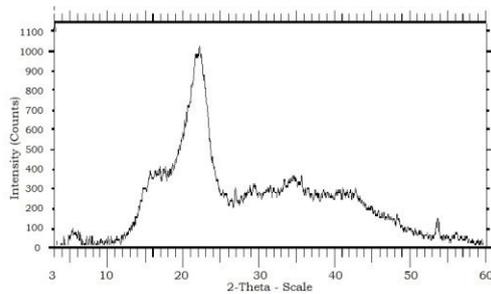


Fig. 6. XRD patterns of benzoylated areca fibers.

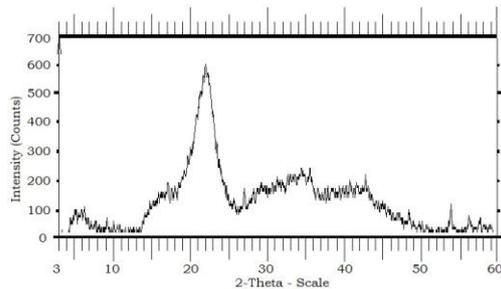


Fig. 7. XRD patterns of acrylic acid treated areca fibers.

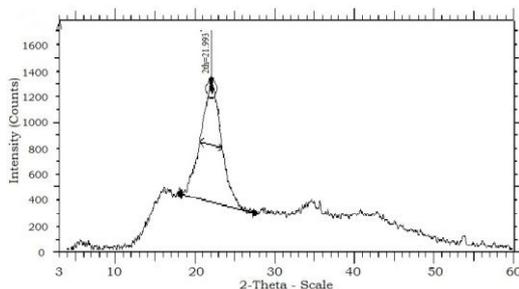


Fig. 8. XRD patterns of acetylated areca fibers.

Table 4. XRD analysis results of untreated and chemically treated areca fibers.

Areca fibers	Crystalline Intensity $I_{22}$ (at 2 $\theta$ Scale)	Amorphous Intensity $I_{18}$ (at 2 $\theta$ Scale)	%Cr	C.I.
Untreated	335	79.1	80.90	0.76
Alkali treated	302	74.5	80.21	0.75
Potassium permanganate treated	1106	449	71.13	0.59
Benzoyl chloride treated	1016	367	73.46	0.64
Acrylic acid treated	585	162	78.31	0.72
Acetic anhydride treated	1269	485	72.35	0.62

The decrease in crystallinity observed after  $KMnO_4$  treatment is due to the fact that cellulose molecular chains in a micro fibril loss their crystalline structure partly due to the partial removal of cementing materials such as hemicelluloses, lignin, pectin, waxy materials and other impurities.

The decrease in crystallinity observed for benzoylated areca fibers is due to the partial removal of cementing materials, impurities and as well as the introduction of bulky  $C_6H_5CO-$  groups into cellulose molecular chains in a micro fibril which would destroy the orderly packing of cellulose chains by reducing its molecular regularity to a certain extent.

The observed decrease in crystallinity in case of acrylated areca fibers is due to the fact that acrylic acid treatment removes most of the hemicelluloses, lignin and destroys cellulose structure which in turn resulted in decrease in orderly packing of cellulose chains to a certain extent.

In case of acetylated areca fibers, the wax and cuticle present in the fiber surface is removed by the interaction with acetyl group. Broadening in  $2\theta = 21.993^\circ$  peak is also observed. Further, acetic anhydride substitute the cell wall hydroxyl groups with bulky acetyl groups and causes plasticization of cellulosic areca fibers and destroyed the orderly packing of cellulose chains to a certain extent and thereby decreased percentage crystallinity and crystallinity index of acetylated areca fibers.

Table 5 shows the tensile strength values of untreated and all chemically treated areca fibers [16].

The tensile strength values of any natural lignocellulosic fibers are based on the crystallinity

present in those natural lignocellulosic fibers. If crystallinity decreases then the tensile strength of natural fibers also decreases accordingly [55]. Surface modification of natural lignocellulosic areca fibers resulted in little decrease of percentage crystallinity and crystallinity index values as indicated in Table 4. In conclusion, it is observed that this little decrease in crystallinity is in agreement with the little decrease in tensile strength values as given in Table 5 for chemically treated areca fibers.

Table 5. Tensile strength values of untreated and chemically treated areca fibers.

Areca fibers	Tensile Strength, N/mm <sup>2</sup>
Untreated	116.93
6% alkali treated	100.13
0.5% potassium permanganate treated	108.02
Benzoyl chloride treated	110.34
5% Acrylic acid treated	112.42
Acetic anhydride treated	108.68

### 3.4. SEM image analysis of areca fibers

The influence of chemical treatments on the morphology of areca fibers is analyzed by Scanning Electron Microscope (SEM) images.

#### 3.4.1. SEM image analysis of untreated areca fibers

The SEM image of untreated areca fibers is shown in Figure 9.

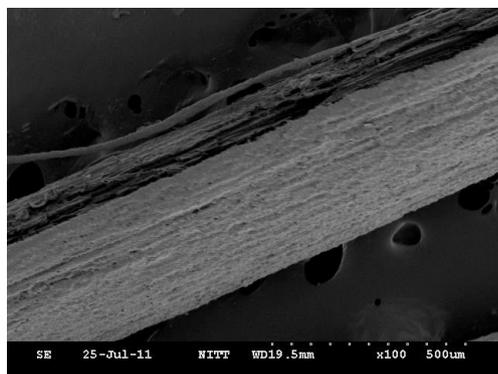


Fig. 9. SEM image of untreated areca fibers.

It shows a network structure where the fibrils are bound together by hemicelluloses and lignin. It clearly shows the presence of longitudinally oriented unit cells with almost parallel orientations. The intracellular gap is filled up by the adhesives, lignin

and fatty substances and these hold the unit cells firmly in the untreated areca fibers [12,16,17].

#### 3.4.2. SEM image analysis of alkali treated areca fibers

The SEM image of alkali treated areca fibers is shown in Figure 10.

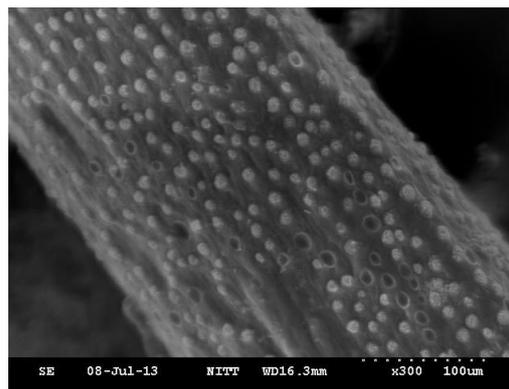


Fig. 10. SEM image of alkali treated areca fibers.

It clearly shows a large number of pinholes or pits on the treated areca fiber surface, which are due to the removal of fatty deposits from the fiber. Alkali treatment of areca fibers removes waxy epidermal tissue, adhesive pectin and hemicelluloses. A comparison between the untreated and alkali treated areca fibers reveals topographical changes because of the removal of low molecular weight compounds resulting in the formation of a rough surface [12,18]. This SEM evidenced the chemical modification of areca fibers by NaOH.

#### 3.4.3. SEM image analysis of permanganate treated areca fibers

SEM image of potassium permanganate treated areca fibers is shown in Figure 11.

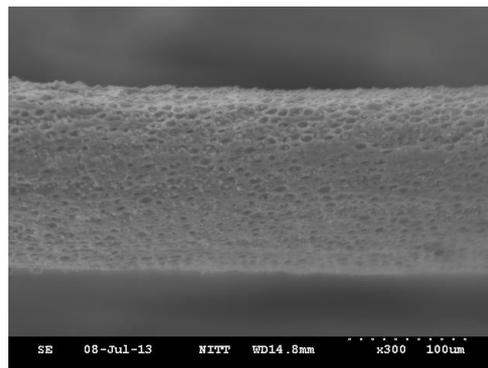


Fig. 11. SEM image of potassium permanganate treated areca fibers.

Permanganate ions react with the lignin constituents and carve the fiber surface. As a result of potassium permanganate treatment, areca fiber surface becomes physically rough and can be evidenced from the SEM micrograph. The topographical changes observed after permanganate treatment evidenced the chemical modification of areca fibers by  $\text{KMnO}_4$  [12,16,31].

#### 3.4.4. SEM image analysis of benzoyl chloride treated areca fibers

The SEM image of benzoyl chloride treated areca fibers is shown in Figure 12. It clearly shows a large number of pinholes and a rough surface. This is due to the removal of waxy epidermal tissue, adhesive pectin and hemicelluloses by alkali pre-treatment and further removal of fatty deposits from the fiber by the reaction of benzoyl chloride. The topographical changes observed after benzoyl chloride treatment evidenced the chemical modification of areca fibers by benzoyl chloride [12,28].

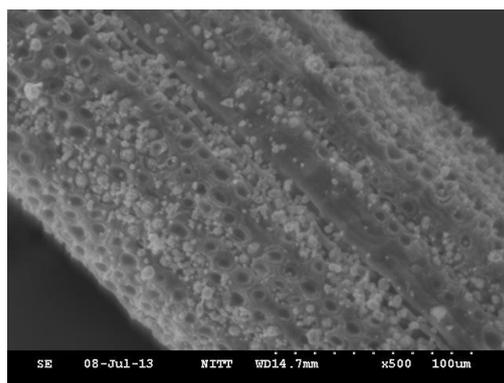


Fig. 12. SEM image of benzoyl chloride treated areca fibers.

#### 3.4.5. SEM image analysis of acrylic acid treated areca fibers

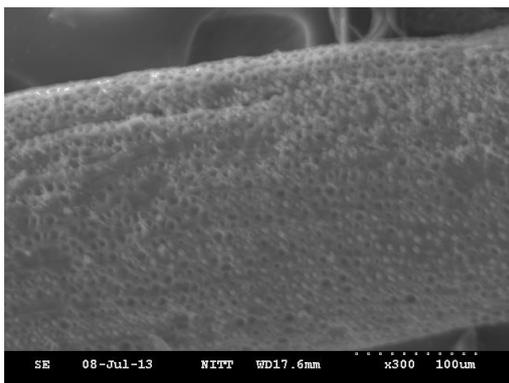


Fig. 13. SEM image of acrylic acid treated areca fibers.

The SEM image of acrylic acid treated areca fibers is shown in Figure 13. Acrylic acid treatment removed most of the hemicelluloses and lignin and destroyed the cellulose structure. As a result, large numbers of pits are observed on the surface of the fiber. The topographical changes observed after this acrylic acid treatment evidenced the chemical modification of areca fibers by acrylic acid [1,12,22].

#### 3.4.6. SEM image analysis of acetic anhydride treated areca fibers

The SEM image of acetylated areca fibers is shown in Figure 14. Upon acetylation treatment, the wax and cuticle present in the fiber surface is removed by the interaction with acetyl group. Further, acetylation of areca fibers caused plasticization of cellulosic fibers and the areca fiber surface becomes smoother. The fibrillation is also found to arise as the binding materials are removed and some micro-pores appeared in the acetylated fiber. [12,23,24]. Surface topographical changes observed after acetylation treatment evidenced the chemical modification of areca fibers by acetic anhydride.

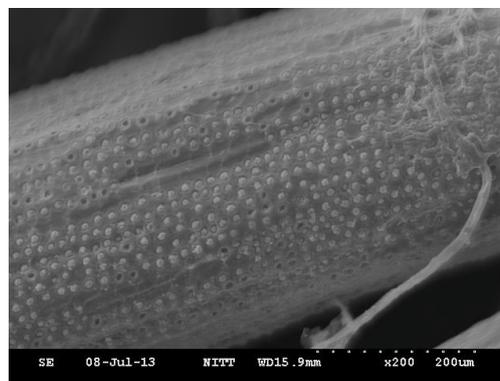


Fig. 14. SEM image of acetic anhydride treated areca fibers.

## 4. Conclusions

Chemical modification of natural lignocellulosic fibers would remove the impurities like pectin, fat and lignin present in the fibers. On the other hand, a rougher fiber surface may result after the chemical treatment due to the introduction of some reactive groups into the fibers. From this study, it is clearly concluded that chemical treatments of areca fibers are of greater importance in modifying the fiber surface, in reducing the hydrophilic nature of the fiber and in improving the thermal stability of areca fibers. Here, in this research work, areca fibers were subjected to chemical treatments such as alkali treatment, potassium permanganate treatment, benzoyl chloride

treatment, acrylic acid treatment and acetic anhydride treatment. TGA-DTG evidenced the increase in thermal stability for chemically treated areca fibers. XRD results of chemically treated areca fibers showed little less crystallinity than that of untreated areca fibers due to chemical reaction which would slightly alter the orderly packing of cellulose chains to a certain extent in the chemically treated areca fibers. These results are in accordance with other naturally occurring fiber materials. Scanning Electron Microscope morphological investigations indicated the changes in surface topography for chemically treated areca fibers when compared with that of untreated areca fibers. So the use of this surface modified areca fibers by various chemical treatments with improved thermal stability can be effectively used as reinforcement for fabrication of polymer composites. Hence, chemical treatments of areca fibers could benefit its application in lightweight materials industries and the above characteristic studies confirmed that chemically treated areca fibers can have wide scope in the field of polymer composites.

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