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# X-RAY DIFFRACTION AND THERMO GRAVIMETRIC ANALYSIS OF SURFACE MODIFIED ARECA SHEATH FIBRE EPOXY COMPOSITES

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**Abstract** Focus of the current study is to shed more light on thermal behaviour of composites made up of areca sheath fibres. The XRD analysis revealed that crystallinity index and crystallinity percentage increased with different treatments, as it leads to better interaction of fibre and resin. The crystallinity percentage of alkali treated fibre and benzoyl peroxide treated fibre increased by 5.87 and 8.44% respectively compared to untreated fibre. This was further evident in thermal studies which proved better thermal stability in benzoyl peroxide treated fibre composite.

**Keywords:** areca sheath fibre, thermal studies, X-ray diffraction, composites

## 1. INTRODUCTION

Natural fibres are worthy substitutes for synthetic fibres as reinforcing agents in polymer composites as they have an advantage of being natural, renewable, easily biodegradable and are available at a low cost [1-3]. This has been the reason for the increased interest to use natural fibres in polymer composites and is evident in the recent times with a substantial increase in the number of publications which was about 200 publications in the year 1999 and is increased to 3959 publications in the year as sourced from Science-Direct. However, one major shortcoming with the natural fibres is its hydrophilicity due to presence of polar hydroxyl groups in its structure which attracts water molecule and as an effect results in the improper bonding with the polymeric resins in a matrix [4]. Therefore various chemical treatments are undertaken on the natural fibres in order to reduce the fibre's hydrophilic nature and so as to increase the better bonding between the fibres and the resin.

Areca palm trees are cultivated in a large scale in southern part of India, Sri-Lanka and in South-east Asia [5], as the Areca Catechu nut is consumed as a mouth freshener in huge numbers. Areca husk fibres, leaf fibres and the sheath fibres which are the byproducts are usually thrown away or burnt as firewood for processing areca nuts. Areca sheaths are sometimes used as disposable cutlery in some parts of the world. Thus, a huge potential can be unlocked by using the areca fibres as possible alternatives to more popular natural fibres such as Jute [6], Kenaf [7] or Sisal fibres [8]. Recently the interest of using Areca fibres is growing and various studies are done to assess the mechanical properties of the same [9-13].

Understanding the thermal behavior of the fibres is an important criterion for the fabrication of the NFPCs, which can have a say on the choice of compatible processing steps that can be envisaged beforehand in the manufacture of composites. Thermal studies, hence act as a guiding hand in deciding the allowed temperature range for processing and so as not to cause the deterioration/degradation of the fibres which otherwise can result in the reduced mechanical strengths. Further, XRD studies indicate the crystallinity in the fibres and directly correlate with the superior mechanical strengths. Literature survey has indicated that not much work is carried out on the thermal and XRD studies of the composites made of Areca fibre-epoxy resin except a few [14-17]. Reported work on Areca Sheath fibres is still rare [18-19], hence this work of thermal and XRD studies was undertaken to shed the light on the same.

## 2. MATERIALS & METHODOLOGY

### 2.1. Areca Sheath Fibre

Leaf with sheath from areca tree was collected as shown in Fig 1. and sheath was separated. The sheath was dipped in water for 5 h duration of time. Then the fibres were extracted from the sheath by manual hand pulling method. It was again washed with water to remove dust and dirt deposit. Fibres were then oven dried at 70°C for 15 h for complete removal of traces of water if any. Further, fibres were cut having length approximately 10-12 mm. These were considered as untreated fibre and was mixed with epoxy resin for composite fabrication.

### 2.2. Alkali and Benzoyl Peroxide Treatment of Fibres

The untreated fibres were subjected to 1% alkali solution for half an hour. After treatment process, fibres were washed with distilled water repeatedly to remove the traces of NaOH present on it. Fibres were then air dried and further dried in oven at 70℃ for 15 h. These are termed as alkali treated fibre. The alkali pretreated fibres were taken and subjected to 4% benzoyl peroxide solution for 30 min. Benzoyl peroxide solution was prepared by dissolving appropriate amount of salt in acetone. Fibres were then air dried for 24 h and are now known as benzoyl peroxide treated fibres. Treatment of fibres with 1% NaOH results in replacing –OH group present in the cellulose of fibres by –ONa functional group (Fig. 2). Hence, hydrophilic fibres behaves as hydrophobic in nature so that it can effectively bind with epoxy resin. Similarly, when alkali pretreated fibres are treated with benzoyl peroxide, the –ONa group is replaced by benzoyl peroxide group as shown in Fig. 3 [20].

### 2.3. Composite Fabrication

Areca sheath fibre before and after respective treatments were cut into length size of approximately 10 mm - 12 mm. It was mixed with epoxy resin at the fibre:resin proportion of 55:45 [9]. The composite was manufactured by random mixing method using the compression moulding unit (Santec) at 40 bar atmospheric pressure for 24 h and curing was done at lab temperature for 15 days.

### 2.4. X-Ray Diffraction Analysis

X-Ray Diffractogram (Bruker D8 Advance) was used to analyze supermolecular structure of cellulose present in fibres. Sample was taken in powdered form and experiment was performed under room temperature using Cu-Kα radiation (1.54439 Å), run at 40 KV and 40 mA using Ni-filter on rotation between 3° to 60° at 2–Theta – Scale at 0.020° step size.

### 2.5. Thermo Gravimetric Analysis

Thermo gravimetric analysis was performed to analyze thermal behaviour of fibres, before and after treatment. Approximately 10 mg of the sample was considered for the analysis in between the temperature range of 40℃ to 700℃ with the heating rate of 10℃ per minute. Nitrogen was used as the purging gas for analysis.

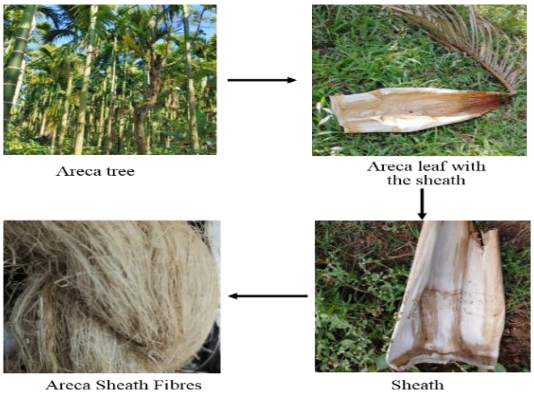

Fig. 1. Areca sheath fibre

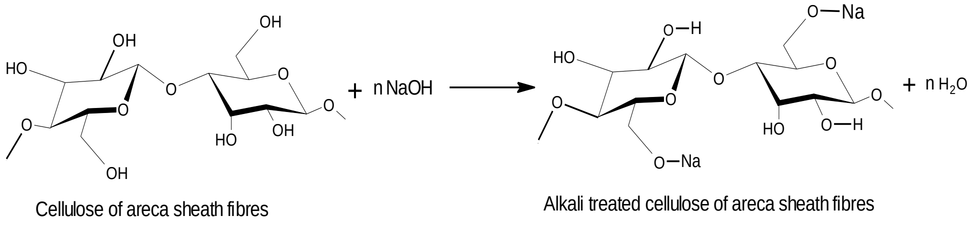

Fig. 2. Reaction of cellulose of fibres with NaOH

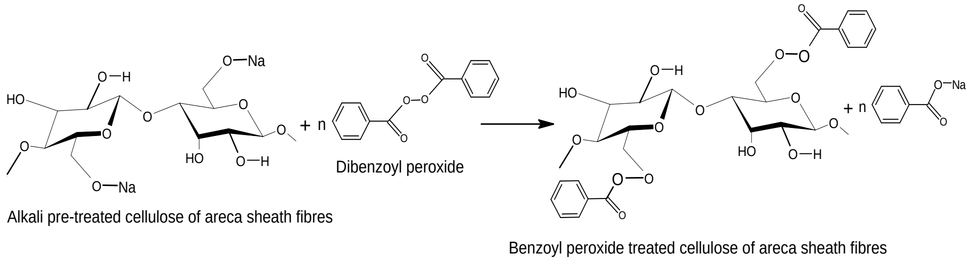

Fig. 3. Reaction of cellulose of fibres with Benzoyl peroxide

## 3. RESULT AND ANALYSIS

### 3.1. X-Ray Diffraction analysis

The X-Ray diffractogram of areca sheath fibres before and after treatment is shown in Fig. 4. The $2\theta$ pertaining to 18° indicates peak corresponding to amorphous material present in fibre and peak shown at 22° attributes to crystalline material present in fibre. Percentage crystallinity and crystallinity index is recorded in Table 1. Crystallinity percentage of untreated/raw areca fibre is reported as 79.80. The crystallinity percentage of sisal fibre is reported to be 71.7% [21] and that of jute fibre is 71% [22] which is lesser compared to the areca sheath fibre. Literature reveals that the greater crystallinity results in improvising mechanical properties of composites manufactured.

Treatment of areca sheath fibres with 1% NaOH and 4% Bezoyl peroxide improved percentage crystallinity and crystallinity index of fibre. The I22 for untreated fibre which was initially at 14213.0, increased to 19072.0 and 22939.0 for alkali treated and benzoyl peroxide treated fibre respectively. The fibres after alkali treatment showed 5.55% increment in the crystallinity percentage and the peroxide treatment resulted in 7.78% improvement in the percentage crystallinity value when compared to raw fibres. The treatment of the fibre with alkali and benzoyl peroxide resulted in removal of lignin, wax, hemicellulose and amorphous cellulose responsible for amorphous behavior of fibre. The cellulose present in the fibre material will be poorly organized in untreated fibres because of which the crystallinity percentage will be lesser and the treatment of fibre with alkali and peroxide leads to the orderly arrangement of the cellulose, removing amorphous material present in the cellulose and causing higher crystallinity index and crystallinity percentage. This result goes in hand with Anand *et al.* in year 2017 who reported similar result with hemp fibre reinforced epoxy composite showing enhanced crystallinity in the composites manufactured with fibres after alkali and peroxide treatment [23].

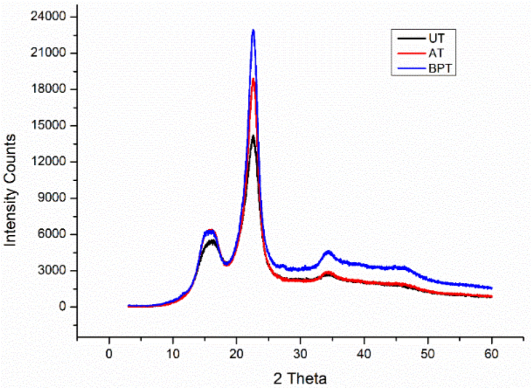

Fig. 4. X-ray diffractograms of UT, AT and BPT fibres

The crystallinity index of untreated fibre was recorded to be 0.74. Alkali and benzoyl peroxide treatment reported 0.81 and 0.84 crystallinity index respectively. Increasing stiffness and rigidity of the fibre owes to the better crystallinity of the fibre after treatment. Similar results were obtained by Sundarraj *et al.* in year 2018 which confirmed the removal of amorphous material on fibre surface owing to the better crystallinity index and crystallinity percentage of the jackfruit peel [24].

Tab. 1. XRD intensity peaks of untreated and chemically modified fibres

| Sample | 2Θ | I22 | 2Θ | I18 | % Crystallinity | Crystallinity index |
|---|---|---|---|---|---|---|
| Untreated fibre | 22.63 | 14213.0 | 18.502 | 3597.0 | 79.80 | 0.74 |
| Alkali treated fibre | 23.06 | 19072.0 | 18.523 | 3499.0 | 84.49 | 0.81 |
| Benzoyl peroxide treated fibre | 22.59 | 22939.0 | 18.482 | 3567.0 | 86.54 | 0.84 |

### 3.2. Thermo Gravimetric Analysis

The TGA curve for untreated fibre epoxy composite (UTFEC), alkali treated fibre epoxy composite (ATFEC) and benzoyl peroxide treated fibre epoxy composite (BPTFEC) is shown in Fig. 5. As observed in Fig. 5, the thermal stability of UTFEC is comparatively lesser than ATFEC and BPTFEC. Thermal degradation is observed in 2 stages for natural fibre polymer composites. The first stage degradation between 200°C to 300°C is because of degradation of hemicelluloses present in the fibre and second stage degradation is between 300°C to 500°C which is because of degradation of lignin and cellulose material present in fibre of the composite.

Table 2 gives the detail information of temperature ranges and maximum degradation temperature recorded of different samples. The initial degradation of the composite below 100°C is attributed to moisture content present in the composite which is clearly observed in Fig. 5. This is referred to as pre-degradation stage which occurs from 50°C to 100°C which is also quoted by Siakeng *et al.* in year 2018 [25]. The first stage degradation is noted between temperature range of 202.38°C and 344.4°C for UTFEC. Whereas, the treatment of fibre with alkali and benzoyl peroxide improves thermal stability of the composite and hence, shift in the degradation curve is observed and it is recorded between 208.17°C to 366.18°C and 216.17°C to 373.96°C respectively. This is because after treatment, the fibre removes certain amount of hemicelluloses, pectin and amorphous cellulose material present in the fibre. Also treatment of fibre results in effective interaction of the fibre with the resin thereby improving the thermal stability of the composites manufactured. Similar results are obtained by different researchers that the chemical treatment of fibre improved the thermal stability of the composites [26-28]. The degradation of the fibre composite takes place at higher temperature which is 492.88°C for benzoyl peroxide treated fibre composite whereas the degradation temperature decreases in case of untreated (431.30°C) and alkali treated composite (484.65°C). The second stage of degradation occurs because of cellulose and lignin present in fibres. Degradation from 300°C to 350°C is because of cellulose. Lignin is generally the hardest component present in the cell wall which will be highly stable and hence the degradation takes place at the higher temperature range of 350°C to 500°C. Similar result is observed by Chin *et al.* in year 2020 for bamboo reinforced polymer composite showing degradation of the composites at 199°C - 379°C and 364°C to 499°C for hemicelluloses, celluloses and lignin respectively [27]. Residual weight percentage is observed to be increasing after treatment. UTFEC showed it to be 1.0042%, after alkali treatment residual weight percentage increased to 1.00929% and 3.403% for BPTFEC.

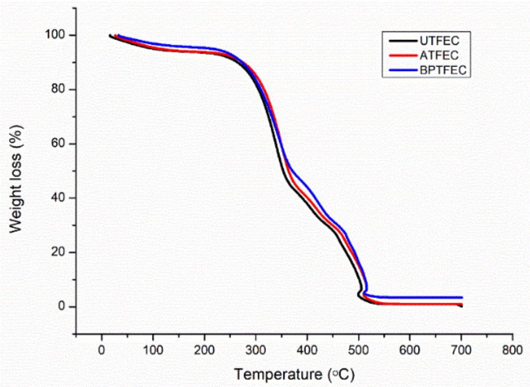

Fig. 5. TGA curve of UTFEC, ATFEC & BPTFEC

Tab. 2. TGA Curve analysis showing 1st stage and 2nd stage degradation range of different samples

| Specimen | 1st stage degradation in TGA curve | 2nd stage degradation in TGA curve | Maximum degradation temperature, °C |
|---|---|---|---|
| | Temperature range, °C | Temperature range, °C | |
| UTFEC | 202.38 to 344.45 | 344.45 to 513.06 | 431.30 |
| ATFEC | 208.17 to 366.18 | 366.18 to 515.69 | 484.65 |
| BPTFEC | 216.17 to 373.96 | 373.96 to 520.45 | 492.88 |

Table 3 and Table 4 indicates the weight loss of the composites at various temperatures. As represented in table 3, weight loss of the composite decreases after treatment. Similar trend is observed at 200°C, 300°C and 650°C temperature. Treatment results in removal of non-cellulosic material and results in the formation of lignin-cellulose complex. Hence, the composite becomes comparatively more stable after treatment which gives better thermal stability to the material [27]. The temperature at which decomposition of the composites occurs at 25, 50 and 75% of weight loss of the composite recorded in Table 4 shows better temperature stability of the composites after alkali and benzoyl peroxide treatment. Similar results are reported by Alessandra *et al.* in year 2017 for Buriti and Ramie fibre reinforced polyester composites reported lesser weight loss after treatment [29].

Tab. 3. Weight loss of the samples at 200°C, 400°C and 600°C temperatures

| Temperature, °C | Weight loss of the composites, % | | |
|---|---|---|---|
| | UTFEC | ATFEC | BPTFEC |
| 200 | 6.39 | 6.26 | 4.72 |
| 300 | 18.20 | 14.87 | 16.77 |
| 650 | 98.99 | 98.99 | 96.59 |

Tab. 4. Degradation temperature at 25%, 50% and 75% weight loss

| Weight loss of the composites (%) | Temperature (˚C) | | |
|---|---|---|---|
| | UTFEC | ATFEC | BPTFEC |
| 25 | 16.08 | 26.54 | 20.74 |
| 50 | 53.21 | 63.67 | 71.14 |
| 75 | 61.63 | 72.09 | 78.38 |

The DTG curve is as shown in Fig. 6 for UTFEC, ATFEC and BPTFEC. The image displays 2 major peaks for all the samples which confirms the analysis with respect to TGA curve. The decomposition temperature with respect to the peak is shown in Table 5. The first peak corresponds to hemicellulose degradation which is at 317.67°C for untreated fibre composite whereas for alkali treated and benzoyl peroxide treated composite it is recorded as 346.53°C and 348.83°C respectively. The second small peak is observed at 373.45°C, 422.69°C and 426.29°C for untreated, alkali treated and benzoyl peroxide treated composites respectively. Further, the third peak is recorded at 431.30°C for untreated composites and at 484.65°C and 492.88°C for alkali treated and benzoyl peroxide treated composites respectively. The temperature range of 340°C to 520°C is responsible for degradation of cellulose and lignin present in fibre. This indicates that thermal stability of the composites is improved after both alkali treatment and benzoyl peroxide treatment.

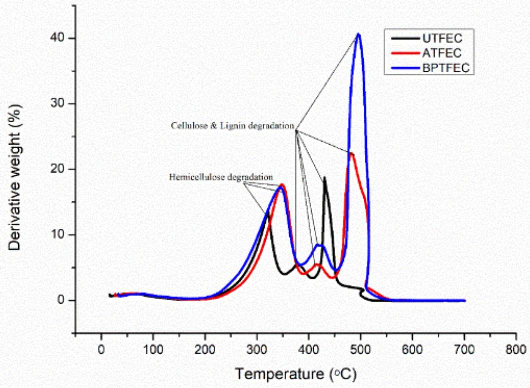

Fig. 6. DTG curve of UTFEC, ATFEC & BPTFEC

Tab. 5. Decomposition temperature in °C with respect to DTG curve

| Specimen | First Peak, °C | Second peak, °C |
|---|---|---|
| UTFEC | 317.67 | 431.30 |
| ATFEC | 346.53 | 484.65 |
| BPTFEC | 348.83 | 492.88 |

## 4. CONCLUSIONS

The empirical results carried on areca sheath fibre and its composite with respect to XRD and thermal studies respectively has led to following conclusions:

1. The crystallinity percentage of alkali treated fibre and benzoyl peroxide treated fibre increased by 5.87% and 8.44% respectively compared to untreated fibre.
2. Similarly crystallinity index of alkali treated fibre and benzoyl peroxide treated fibre was better compared to untreated fibre. This confirms the treatment on the fibre surface reduces the amorphous material in the fibre, increasing the effective interaction between fibre and resin.
3. Thermo-gravimetric studies have indicated that, the maximum degradation temperature of untreated fibre composite was 431.30°C and it increased to 484.65°C for alkali treated fibre composite. Further, it increased to 492.88°C for benzoyl peroxide treated fibre composite in hand with the result revealed in XRD studies.
4. This study shows that benzoyl peroxide treatment on sheath fibre is better suited for further scientific and commercial applications.

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