



Surface Modification of Areca Fibre by Benzoyl Peroxide and Mechanical Behaviour of Areca-Epoxy Composites

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Abstract

Natural fibre composites are playing great role in current life scenario where the focus is more on replacing synthetic fibre composites with natural fibre composites. In this current study, investigation was done on tensile and flexural behaviour of benzoyl peroxide treated areca sheath fibre epoxy composites. The surface modification of the fibre was confirmed by FTIR analysis. Treatment concentration was the major criteria which effects mechanical properties of the composites. At 4% concentration tensile strength and flexural strength was found to be maximum which was reported as 37.05 N/mm² and 235.5 N/mm² respectively which gradually decreased with increasing concentration of benzoyl peroxide. SEM analysis proved that at lesser concentration, the bonding between fibre and resin was effective which reduced as the concentration of benzoyl peroxide increased. This results in ineffective stress transfer between reinforcing material and the matrix which was the reason for failure of composites manufactured at higher treatment concentration.



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Sem Analysis;
Tensile Strength.

Introduction

Fibre reinforced polymer composites play a major role in wide variety of applications like aircraft, sport equipment, marine applications, automobile industries because of its higher mechanical properties and hence they serve as a promising material in the field of composite.^{1, 2} But with respect to environmental concern, synthetic fibre composites creates a negative vibe because of

its adverse properties like non-renewability, high cost and its hazardous nature. As a result of this, researchers began to think about natural fibre composites because of its advantages like easy availability, less density, renewability and eco-friendly nature,^{3, 4} The major drawback associated with natural fibre composite is its hydrophilic nature and its inability to interconnect with hydrophobic resin. Many researchers have investigated chemically

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modifying fibre surface and finding their compatibility with different resins and to study effect of these chemical treatments on different properties of natural fibre composites.⁵ Different possible chemical treatments identified are alkali treatment, potassium permanganate, acetylation, benzylation, stearic acid, peroxide, sodium chlorite treatment on different fibres like areca husk fibre, sisal, abaca, hemp, bagasse, flax,⁶ where the treatment improves the surface morphology, surface becomes rougher and hence, the interfacial bonding improves interaction between fibre and resin and the mechanical property of composite is improved. In the current study, more focus is on peroxide treatment and their effect on composite property. The peroxide treatment is carried out using benzoyl peroxide or dicumyl peroxide and impact of treatment on composite properties were studied by few of the researchers which are documented as follows. Augustine *et al* in year 1997, analysed effect of peroxide treatment on electric property of the sisal fibre reinforced LDPE composite. Studies revealed that peroxides undergo free radical mechanism which effectively helps in bonding between fibre and resin thereby improving the dielectric property of fibre composites.⁷ Elena *et al* in year 2014 studied crosslink density, swelling behavior and water uptake behavior on benzoyl peroxide treated hemp and rubber composites. The treatment revealed positive results in the tests conducted.⁸ Taslima *et al* in year 2017 studied the mechanical behavior of benzoyl peroxide treated teak sawdust reinforced HDPE composites. The investigation revealed that tensile strength and impact strength of treated composites were high in comparison with untreated teak sawdust HDPE composites. And the water uptake behavior of untreated composites was more compared to treated composites.⁹ Joseph *et al* in year 1996 carried out chemical treatments on sisal fibres and studied mechanical property of sisal LDPE composites. Chemical grafting increased the roughness of fibre surface as proved in SEM analysis and mechanical properties of fibre composites increased.¹⁰ Sapieha *et al* in year 1990 investigated effect of benzoyl peroxide and dicumyl peroxide on bleached hardwood pulp-LLDPE composites. The free radical mechanism involved in the study was depicted and the study revealed that chemical modification improved mechanical property of the composites and effect is high when the concentration of peroxide is lesser.¹¹ Wang *et al* in year 2007 investigated

effect of peroxide treatment on flax fibre reinforced LDPE, HDPE and LDPE-HDPE mix composites. Investigation revealed that the chemical modification leads to superior physical and mechanical property of the composite.¹² Izwana *et al* in year 2020 studied the effect of benzoyl treatment on SPF. The treatment duration was different where in composites showed good thermal properties after treatment and 15 min soaking time revealed better mechanical properties for the same.¹³ In year 2019, Vijay *et al* investigated on effect of benzylation on mechanical properties of *Impomeapescaprae* fibre reinforced epoxy composites where benzylation resulted in better properties of the composites manufactured.¹⁴ The literature reveals that there was an attempt made by scientists where different combinations of peroxide treated fibres were used and composites were fabricated using LDPE and HDPE to study the changes in the property of the composites. But the peroxide treated epoxy composite study was rare. As a result of this, in the current study; areca sheath fibres were used, treated with benzoyl peroxide solutions at different concentrations. This was fabricated with epoxy resin and the composites were manufactured to analyse their mechanical properties.

Materials and Methodology

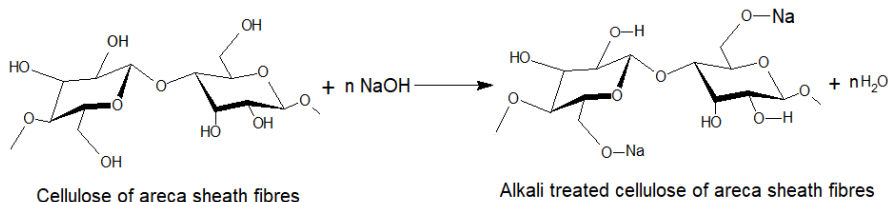
Surface Modification by Benzoyl Peroxide Treatment

Areca sheath fibres were initially washed with double distilled water to eliminate dust from the surface.^{15,16} Fibres were dried in an oven at 70°C for 15 h to remove moisture content. Fibres were next treated with 1% NaOH solution for one hour. The fibres were repeatedly washed with double distilled water to get rid of alkali solution on the surface and then it was washed with concentrated HCl for complete removal of alkali from fibre surface. Final washing was done with distilled water to ensure complete removal of traces of acid from surface of fibres after which they were dried in an oven for complete elimination of water at 70°C for 15 h. These are specified as alkali pre-treated fibres. The reaction sequence is shown in Scheme 1.

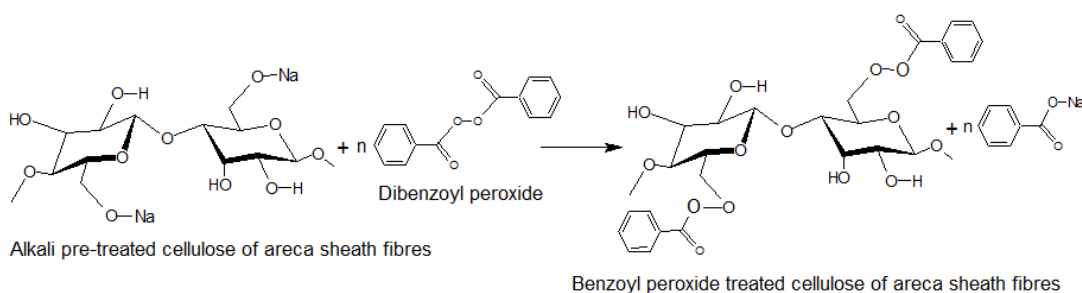
Further, surface modification is carried out by benzoyl peroxide treatment. Benzoyl peroxide solution is prepared at different concentrations like 4%, 5%, 6%, 7% and 8% in acetone. The pre-treated fibres are then dipped in these respective benzoyl

peroxide solutions for 30 min duration. Further, fibres were air dried for 24 h. These dried fibres were cut with the fibre length range of 10 mm to 20 mm and used for composite fabrication. Similar treatment was carried out by Vijay *et al* in year 2013 where the

effect of 5% benzoyl peroxide was studied on sisal fibre at different duration like 30 min and 45 min to analyse the crystallinity index and thermal studies.¹⁷ The reaction between alkali treated cellulose and benzoyl peroxide is as shown in Scheme 2.¹⁸



Scheme 1: Reaction between cellulose of fibres and NaOH



Scheme 2: Reaction between cellulose of fibres and Benzoyl peroxide

Spectral Analysis

FTIR spectroscopy, BRUKER ALPHA FT-IR Spectrometer: ATR mode was used to investigate different chemical bonding existing in raw and chemically modified fibres. The fibres of approximately 10 mm length were taken in the sample holder and FTIR spectra of samples were evaluated in a range between 500 cm^{-1} and 4000 cm^{-1} .

Composite Fabrication

Areca sheath fibres treated with benzoyl peroxide solutions are used to manufacture fibre reinforced epoxy composites. Composites were fabricated using Compression molding unit (Santec) at 55% fibre loading. The curing time used was 24 h under pressure at 40 bar and in the lab temperature was 15 days. Further, composites were cut according to ASTM standards for mechanical characterization.

Tensile and Flexural Strength Analysis

Composites manufactured were cut according to ASTM standards; ASTM D638-03¹⁹ and ASTM-D790²⁰ for tensile strength and flexural strength analysis

respectively. Testing was carried out in Universal testing machine (Mecmesin Multi Test 2.5-xt). The test was conducted at lab temperature of $35\pm 2^\circ\text{C}$.

Field Emission Scanning Electron Microscopy

Benzoyl peroxide treated areca sheath epoxy composites were subjected to FESEM analysis so as to understand the changes in the surface morphology where the surface is scanned by the electrons according to Zig-Zag pattern. The instrument used for analysis was CARL ZEISS SIGMA (03-81). The samples were subjected to gold sputtering before the analysis.

Results and Discussion

FTIR Analysis

FTIR spectrum of UT (untreated fibre) is shown in Figure 1. The absorption peak of untreated areca sheath fibres at 3646.63 cm^{-1} indicates the free $\nu(\text{OH})$ of cellulose. Absorption peaks at 3483.56 cm^{-1} , 3369.55 cm^{-1} and 3339.08 cm^{-1} referred to hydrogen bonded $\nu(\text{OH})$ of alcoholic group of cellulose. Figure 2 represents the FTIR spectrum of benzoyl

peroxide treated fibre. Absence of absorption peak at 1820.28 cm^{-1} confirms elimination of hemicellulose and lignin. During the chemical reaction of alkali treated fibres with benzoyl peroxide, there is formation of new carbonyl group with cellulose of fibres. This new carbonyl group absorption at

1753.64 cm^{-1} and 1722.26 cm^{-1} confirmed the chemical modification. The detailed IR peak range for different functional groups present in areca fibre is given in our previous work.²¹ The current result is in accordance with the same.

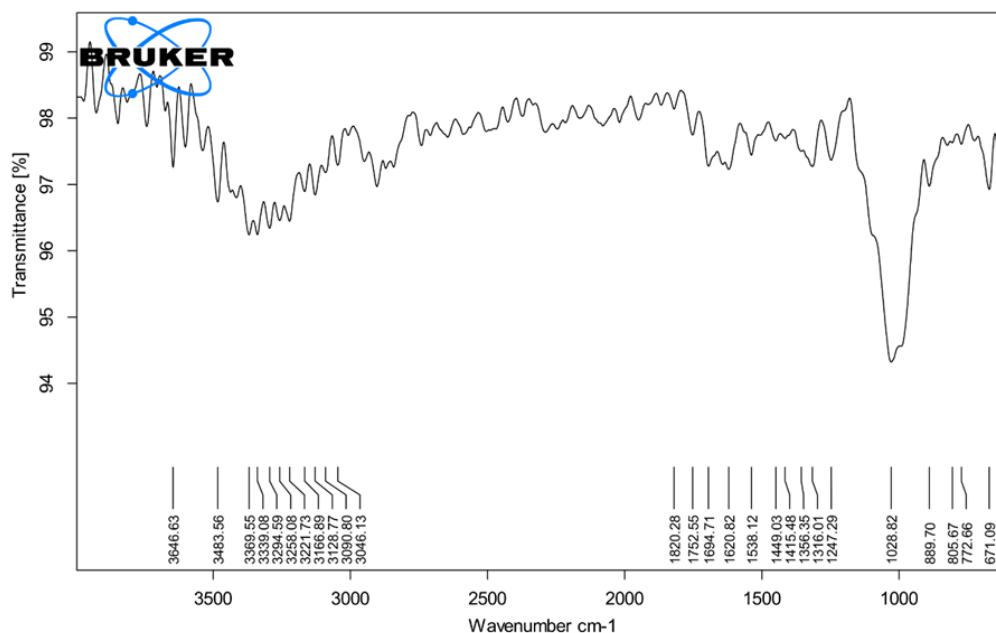


Fig. 1: IR spectra of untreated areca sheath fibre

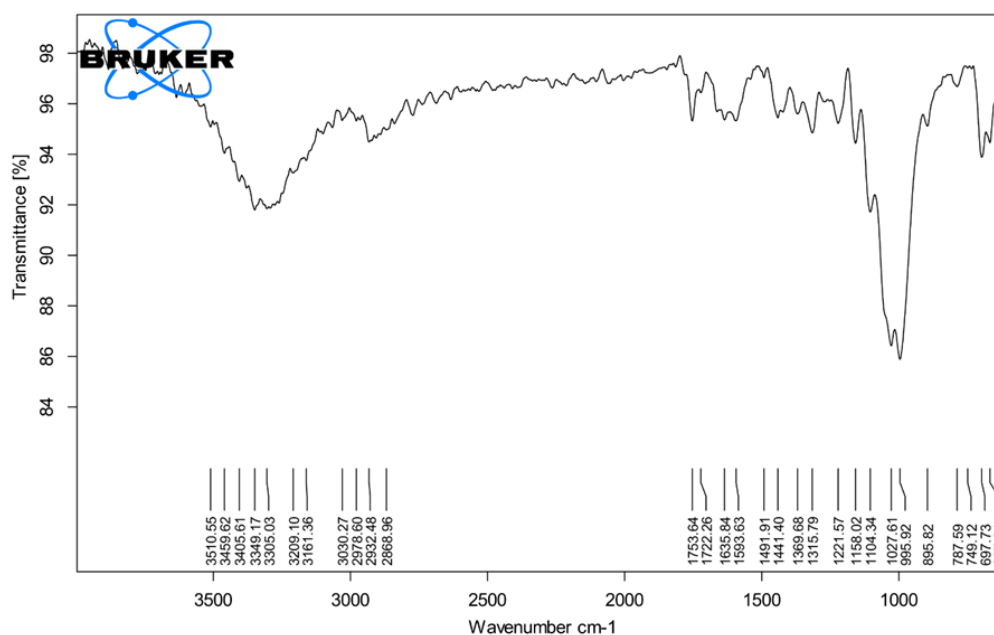


Fig. 2: IR spectra of benzoyl peroxide treated areca sheath fibre

Tensile Strength Analysis

Benzoyl peroxide treatment was carried out on areca sheath fibre at different concentrations like 4%, 5%, 6%, 7% and 8%. Tensile strength analysis was carried out for untreated fibre composite and benzoyl peroxide treated fibre epoxy composite to analyse the effect of benzoyl peroxide concentration on the tensile strength. The specimens were cut with dimensions having length, width and thickness of 165 mm x 19 mm x 3 mm respectively. It was revealed that at 4% concentration, the tensile strength was high which was found to be 37.05 N/mm². the concentration increases from 4% to 5%, tensile strength decreased to 32.07 N/mm²; which further decreased to 25.6 N/mm² at 6% concentration. At 7% and 8% concentration, tensile strength was recorded

as 26.6 N/mm² and 27.9 N/mm² respectively which is higher compared to 5% and 6% but lesser than 4% treated fibre composite. This indicates that as treatment concentration increases, tensile strength of composite decreases. Also, the tensile strength for untreated fibre composite was found to be 22.06 N/mm² which is less compared to benzoyl peroxide treated composite. As the treatment is carried out, the surface morphology is changed because of which effective interaction between fibre and resin was observed. Hence, there is improvement in the tensile strength of the composite. The tensile strength of untreated composite (UC) and the treated composites along with the standard deviation is shown in the Figure 3.

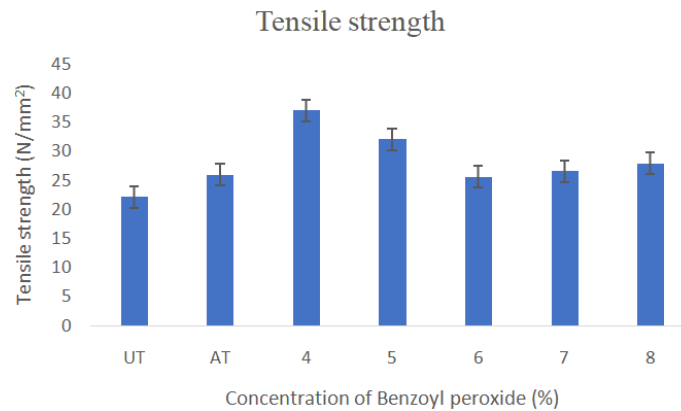


Fig. 3: Tensile strength of composites v/s concentration of Benzoyl peroxide

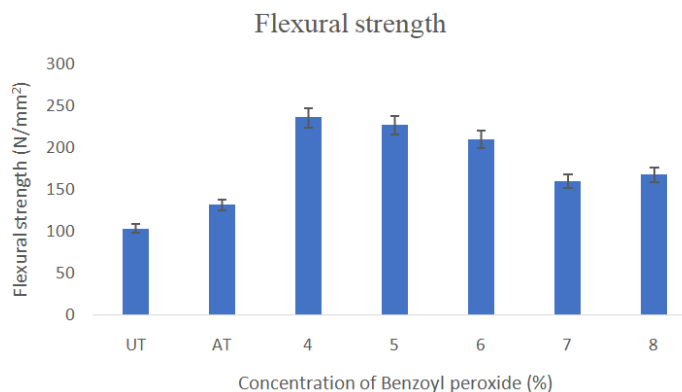


Fig. 4: Flexural strength of composites v/s concentration of Benzoyl peroxide

Flexural Strength Analysis

The flexural strength determination was carried out for all samples which were cut according to ASTM

standards with length 150 mm, width 25 mm and thickness 3 mm. When the fibres were subjected to benzoyl peroxide treatment; the flexural strength

increased from 131.25 N/mm² to 235.5 N/mm². This indicates that, benzoyl peroxide treatment results in changing surface morphology of fibre as a result of which bonding between fibre and resin improves which thereby enhances flexural strength of composite materials. Flexural strength for untreated fibre composite (UC) and benzoyl peroxide treated composites are shown in the Figure 4. At lower

concentration of benzoyl peroxide, the strength will be high and as the concentration increases, it was observed that fibres become supersaturated with chemical, resulting in fibre agglomeration. The bonding between fibre and the resin becomes weak and the composite breakdown takes place. Hence, the flexural strength decreases with increasing concentration of benzoyl peroxide.

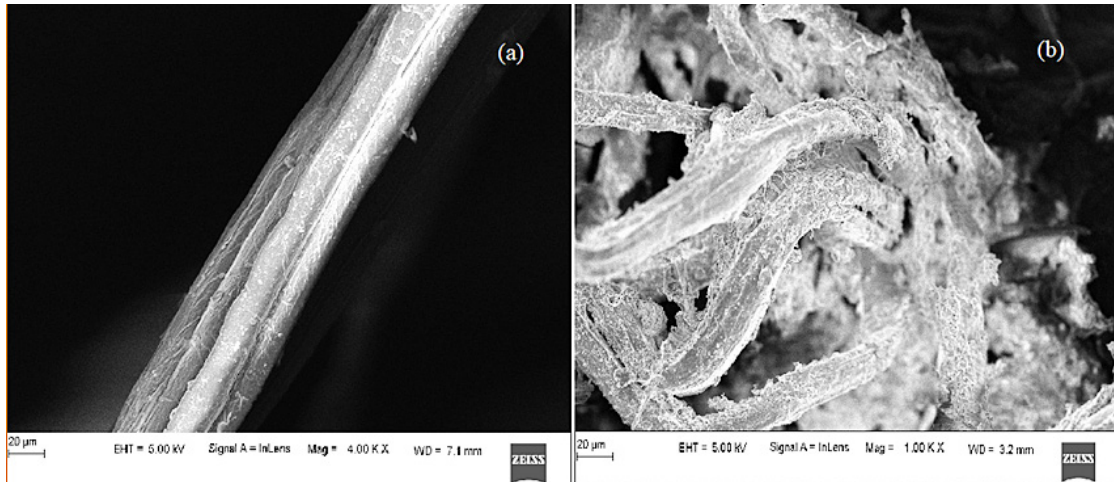


Fig. 5: (a): SEM image of Untreated fibre and 5(b): Benzoyl peroxide treated fibre in composite

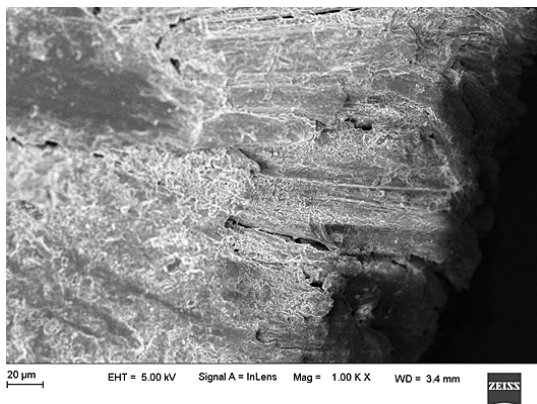


Fig. 6: SEM image of 4% benzoyl peroxide treated epoxy composite

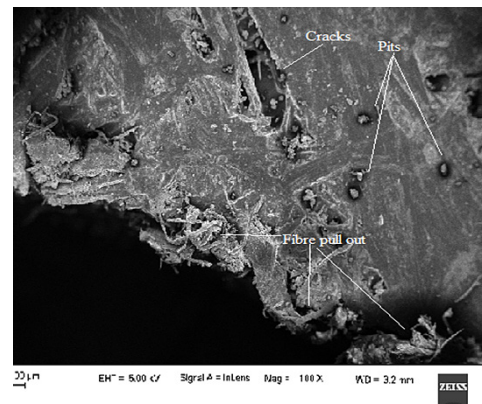


Fig. 7: SEM image of 6% Benzoyl peroxide treated composite

FESEM Analysis

SEM analysis was carried out to analyse surface morphology of untreated and benzoyl peroxide treated fibres. Figure 5(a) and 5(b) represents the topography of untreated and peroxide treated fibres respectively. Image reveals that untreated fibre surface is smooth because of deposition of wax and lignin. Surface treatment results in removal of

wax and other impurities from surface. As a result of this, surface becomes rough which increases surface area of fibre available for interaction with resin. Bonding between fibre and resin increases which improves the load withstanding capacity of the composites manufactured giving better mechanical property for the composite. Similar result was shown by Jothibasu *et al* in year 2018 which revealed that

surface treatment improves the mechanical property of jute composites where fibre pull-out is lesser compared to untreated areca sheath composites.¹⁶

SEM image of 4% treated fibre composite is shown in Figure 6. The image reveals that at this optimum concentration, fibre-matrix adhesion is stronger, stress transfer from fibre to resin takes place effectively; as a result of which the tensile property and flexural property of composite was high. Further, when SEM imaging was carried out for 7% benzoyl peroxide treated fibre composites as shown in Figure 7, the cracks in the resin surface was observed indicating poor wettability of fibres resulting in poor stress transfer during fracture. Pits were seen which was because of irregular distribution of fibre and resin. During the testing, fibre pull-out was clearly observed at higher concentration of benzoyl peroxide indicating higher concentration treatment leading to weakening the fibre strength which drastically reduces strength of composites manufactured.

Conclusion

Areca sheath fibre composites plays a prominent role in field of natural fibre polymer composites because of its properties like low density, ease of availability and its applications in constructing light weight material. The benzoyl peroxide treatment drastically improves tensile and flexural property of composites when compared to untreated

composites. The literature revealed, work carried with respect to different fibres which were modified with peroxide treatment and the composites manufactured using LDPE and HDPE resins. Hence, the attempt was made to study peroxide treated fibre fabrication with epoxy resin. The study revealed positive result where the drastic increase in mechanical property is observed where both tensile strength and flexural strength is found maximum at 4% treatment concentration. Tensile strength improved by 67% and flexural strength increased by 44%. SEM analysis reveals the effective bonding between fibre and the resin at 4% concentration and as concentration increases, the strength gradually decreases. This study proves that epoxy resin can be used in manufacture of benzoyl peroxide treated fibre composites which exhibits good result and thus, it can used in future application studies.

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Conflict of Interest

The authors have no conflicts of interest to disclose.

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