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ANNEXURE – 13

UTILIZATION CERTIFICATE

Program Name: CISEE

Project Title: "Physicochemical & Mechanical Characterisation of Natural Areca Fibre Reinforced Polymer Composite Materials"

Sl. No.	Details	Amount
1	Previous year Balance (Opening Balance (OB),If any)	6,988.27
2	Grants Received (chq no: 522752 chq dt: 19/06/2017)	10,00,000.00
3	Management Contribution	4,50,000.00
4	Bank Interest (If any)	57,108.00
5a	Bank Charges towards NEFT	14.75
5b	Bank Charges for account keeping	2,529.50
5c	Bank Charges towards WDL TFR	9,576.00
6	Total Available Grants (1+2+3+4-5)	15,01,976.02
7	Actual Grants Utilized (Statement of Expenditure Enclosed)	15,01,976.32
8	Unspent Balance (6-7)	0.0

Certified that **Rs.10,00,000.00** (Ten lakhs only) of grant–in-aid under **CISEE Program** was released by Karnataka Science and Technology Promotion Society (KSTePS) in favour of The Principal, Alva's Institute of Engineering & Technology, vide letter No. KSTePS/VGST/03/GRD-183/CISEE/17-18/67 as stated above during the year 2017-18. The above grant was sanctioned towards **Project Title, "Physicochemical & Mechanical Characterisation of Natural Areca Fibre Reinforced Polymer Composite Materials**". The management of the grantee institution, Alva's Education Foundation, Moodbidri, has also sanctioned an amount of **Rs. 4,50,000.00** (Four lakhs fifty thousand only) through vide letter No. AEF/FO/AIET/2017-18/43 dated 10/05/2017 for the above said project. Out of sanctioned grants, a sum of **Rs. 15,01,976.32** (Fifteen lakhs one thousand nine hundred seventy six thirty two paisa only) has been utilized for the purpose of which it was sanctioned and **Rs.0.0** remained unutilized at end of the financial year 2017-18. Expenditure incurred for the purpose for which the grant was sanctioned is verified with the vouchers produced before me.

Certified that I have satisfied myself that the conditions on which the grant-in-aid was sanctioned have been fulfilled and that I have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Signature and Address of the Project Coordinator

Dr. BASAVARAJU B.
Professor, Department of Chemistry
Alva's Institute of Engineering & Technology
MIJAR - 574225 D.K., Karnataka

Signature of the Head of Institution and Seal

PRINCIPAL
Alva's Institute of Engg. & Technology,
Mijar, MOODBIDRI - 574 225, D.K

M.NO. 207835

UMESHA RAO M
Chartered Accountant
FRN: 09191S
M.NO: 207835

Statement of Expenditure for the Project Title "Physicochemical & Mechanical Characterisation of Natural Areca Fibre Reinforced Polymer Composite Materials"

Sl. No.	Particulars	Total Expenses (Rs.)
1	Total Grants Received (Including Opening Balance & Bank Interest)	15,01,976.02
	➢ **Expenditure Break Up(Each Item wise as approved and sanctioned of Non Recurring and Recurring Equipment's)**	
	Non Recurring (NRE)	
NR1		
NR2	Wear and Friction Monitor	9,75,000.00
NR3	3-Point Bend Jig & Load Cells for Universal Testing Machine	3,83,921.32
NR4	Moisture Balance	89,680.00
A	Oven Toaster Grill	10,766.00
	Total of Non Recurring Expenditure	14,59,367.32
	Recurring (RE)	
RE1		
RE2	Chemicals	4885.00
RE3	Contingency	13143.50
RE4	Electrical, Electronics & Mechanical spare parts	23777.00
B	Maintenance & Repair of Equipment	803.50
2	**Total of Recurring Expenditure**	42609.00
3	Total Expenditure (A+B)	15,01,976.32
	Unspent Balance (1-2)	0.0

Kind of checks exercised:

1. Vouching
2. Bank Reconciliation
3. Supporting Bills

CERTIFICATE

Certified that we have verified the disbursement of Rs. 15,01,976.32 (Fifteen lakhs one thousand nine hundred seventy-six thirty-two paisa) towards the Project, "Physicochemical & Mechanical Characterisation of Natural Areca Fibre Reinforced Polymer Composite Materials" as mentioned above.

We have exercised the verification of vouchers and supporting documents to see that the money was actually utilized for the purpose for which it was sanctioned.

Place: Moodbidri
Date: 24/11/2018

M.NO. 207835

UMESHA RAO M
Chartered Accountant
FRN: 09191S
M.NO:207835

Signature and Address of the Project Coordinator

Dr. BASAVARAJU B.
Professor, Department of Chemistry
Alva's Institute of Engineering & Technology
MIJAR - 574225 D.K., Karnataka

Signature of the Head of Institution and Seal

PRINCIPAL
Alva's Institute of Engg. & Technology,
Mijar, MOODBIDRI - 574 225, D.K

GRD No. ☐

VISION GROUP ON SCIENCE AND TECHNOLOGY
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PART – C

FINAL PROGRESS REPORT
of
CISEE Programme

"PHYSICOCHEMICAL & MECHANICAL CHARACTERISATION OF NATURAL ARECA FIBRE REINFORCED POLYMER COMPOSITE MATERIALS"

Submitted by

Dr. BASAVARAJU BENNEHALLI
PROFESSOR, DEPARTMENT OF ENGINEERING CHEMISTRY
ALVA'S INSTITUTE OF ENGINEERING & TECHNOLOGY
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1

OVERVIEW OF POLYMER COMPOSITES REINFORCED WITH NATURAL FIBRES

1.1 INTRODUCTION

Environmental hazards of non biodegradable products,exhaustion of petroleum assets and climate changealong with increment in ecological rules have aroused theneed for the researchers to develop newclass of environmental friendly greener materials with superior properties. A more viable solution would be the use of natural fibre based materials as a substitute for petroleum products. Because the development of these bio-based resources helps in the production of light weight, strong, eco-friendly and cost effective products with diverse applications. At present,extensive research is going on the highly developed polymer composites fortified with natural fibres. About polymer matrix, natural fibres, studies on effect of surface modifications on composites fortified with natural fibres, natural areca fibres and the aim of the present research have been given in detail.

1.2 SCOPE OF RESEARCH

In the technological development, material modernizations are playing a major role. The novel class of advanced materials is characterized by its properties which are superior than from which it is obtained and hence make them to be used for diverse applications. The expanded specialized developments, distinguishing proof of new applications and government interest in new ways for fibre extraction and handling are prompting to the projections of continued growth in the development of utilization of natural fibres in polymer composites. At present, polymer composites fortified with natural fibres are considered as most promising materials in structural applications especially in automobile industry due to its superior properties, environmental friendly nature and economic advantages.

1.3 COMPOSITES

Composites are defined as a multiphase material comprising of dissimilar segments and giving a combination of properties and diversity of applications which are not obtainable with metals, ceramics or polymer alone. In composites, one of the components, usually the reinforcement has superior mechanical properties and has a definite interface between the matrix and reinforcement.In material science, the composite is defined as a material consisting of matrix as a binder which is a continuous phase and fibrous or non fibrous filler as reinforcement which is a discontinuous phase.

Matrix present in the polymer composites supports the reinforcement and helps the reinforcement to stay in proper position and orientation. Ductility is more and hardness is less for the polymeric resin and this resin is responsible for the toughness of composites.

Reinforcement is harder than matrixand it is embedded into the matrix. Reinforcement is the load carrying material and it strengthens the composites by imparting its properties into the matrix.

Hence, composites possess the properties such as high specific strength, durability and design flexibility, high fatigue resistance and light weight. Even though composites are light in weight they arecompetent of bearing severe loading conditions and hence these composites are extensively used in marine applications, automotive and transport industry, construction industry and in manufacturing aerospace components like wings, tail, fuselage panels and propellers [1-3]. Composites are also used in making boat hulls and decks, bicycle frames, racing car bodies, baseball bats and fishing rods.Hence, by selecting appropriate combination of matrix and reinforcement, it is conceivable to adapt the properties of composites suitable for specific structural utilization.

1.4 CLASSIFICATION OF COMPOSITES

The classification of composites can be done based on matrix material as metal, ceramicand polymer matrix composites [4]. It is very simple to manufacture the polymer matrix composites than the other two because polymer processing does not requirehigh temperature andpressure and the types of equipments needed for composite fabricationsare simple. Polymer matrix composites are further classified into thermoplastic, thermoplastic elastomeric and thermoset polymer composites. Based on the shape ofreinforcement, the composite classification can be made as particulate composites,fibrous composites and laminate composites.

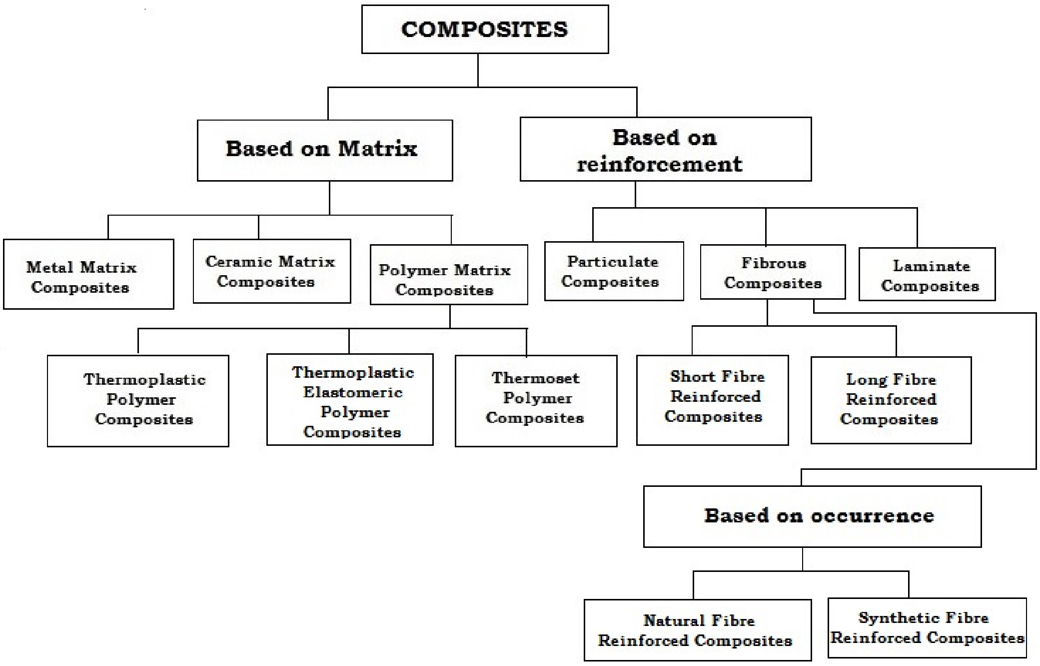


Fig: 1.1 Classification of composites

Fibrous composites arefurther subdivided into short fibre (discontinuous)reinforcedand long fibre(continuous) reinforcedpolymer composites. Depending on the occurrence of fibres, again fibrous composites can be classified into natural fibre reinforced composites and synthetic fibre reinforced composites.

1.5 NATURAL FIBRE REINFORCED POLYMER COMPOSITES

Natural fibre reinforced polymer composites comprise of natural fibresof great quality and modulus embedded into a polymeric resinhaving dissimilar interfaces amongthem.Presently, research is centered on greater effective usage of renewable vitality sources, similar to biomass as these renewable energy sources are not releasing the carbon dioxide into the environment.And also, the measure of carbon dioxide discharged into the environment by burning is balanced by the measure of carbon dioxide devoured by plants during the process of photosynthesis. Further, manmadefibreslike glass, carbon, boron and Kevlarthat are being utilized as reinforcing materials for the fibre-reinforced plastics are highly expensive in their use and are not biodegradable and eco-friendly.Consequently, the utilization of natural filaments for specialized composite applications has as of late been the subject of serious examination in the world by the scientists and technologists. They reported that these naturalfibre fortified polymer composites have enhanced electrical and chemical resistance, predominant thermal, acoustic protecting properties and high imperviousness to break. This outcome has likewise revitalized the utilization of hard natural lignocellulosic strands as an appealing distinct option for engineered filaments.

At present, automobile industry is currently shifting to“green” outlook, as consumers are looking for environmentally friendly vehicles.Polymer composites fortified with natural fibres have been grasped by European automobile industry.Currently, fibre composites have found their way into ship building industry also.Polymer composite materials are assuming a noteworthy part in the present and future aviation segments. Lessened airframe weight by composites empowers better efficiency and subsequently brings down the working expense. Henceforth, natural fibre strengthened polymer composites are gaining progressive significance.

1.6 LITERATURE SURVEY OF STUDIES ON THE POLYMER COMPOSITES REINFORCED WITH NATURAL FIBRES

The possibility of using bio-fibres as reinforcement in polymer based composites has been examined by a several researchers [5-9].

Amplenumber of researches was carried out on various types of natural fibresto take in the impact of these fibres on the characterization of polymer composite materials [10-13]. Pothana et al. reported the optimum percentages of banana fibre as 40 wt. % [14]. Luo and Netravali have studied the mechanical properties of pineapple fibrebased polymer composites [15]. Pavithran et al. studied the ruptureenergies of various natural fibrebased polyester composites [16]. Karmaker and Schneider studied the mechanical properties of jute and kenaf fibre reinforced PP composites [17]. Gowda et al.reported in their study that jute - polyester composites have shown improved strengththan wood reinforced composites [18]. Okubo et al.discussed the mechanical properties of bamboo - PP composites [19]. Studies have been conducted on Natural Rubber based composites [20-21]. Sisal and short pineapple fibres have been used for the reinforcement of NR and low density polyethylene [22-30]. Chakraborty et al.studied theproperties of jute - carboxylated nitrile rubber composites [31]. Bledzki and Gassan reviewed the studies on composites reinforced with cellulosic fibres [32]. This literature study revealed that still a lot of research is needed in the field of natural fibres and natural fibrereinforced polymer compositesto improve their properties.

1.7 POLYMER MATRIX

1.7.1 Thermoplastic Matrix

The structure of thermoplastic polymermatrixmay beone dimensional or two dimensional. At room temperature, they exist in a solid state and theydo not create a cross linked network structure. The basic monomericmoleculespresent in theseresins are bound by a very weak Vander Wall's forces.So,a simple force can break them very easily. Henceforth, thermoplastic resins have the capacity to liquefy upon heating and turns into a solid upon cooling to room temperature.

Thermoplastic resins offer wide range of advantages because they can be repetitively heated and re-shaped. Thermoplastic resinsgivehigh toughness and increased moisture resistance behaviour. The processing time of thermoplastic resins is shorter and they have unlimited shelf-life and better recyclability. The thermoplastic matrix material used in this research work is Polypropylene.

1.7.2 Thermoplastic Elastomeric Matrix

Thermoplastic elastomers like rubbers are materials that combine the easyprocessing ability of thermoplastics and the elastic behaviour of rubbers. Natural rubber gives numerous uses like inexpensiveness, small hysteresis,high versatility, fabulous element properties and weariness resistance[33].The thermoplastic elastomeric matrix material used in this research work is Natural Rubber.

1.7.3 Thermoset Matrix

The low molecular weight thermoset matrixwhich ispresent in liquid or semi-solid state is changed into a firm inflexible solid through cross linking by a curing reaction. After curing, a strongly bound cross linked structure is produced for thermoset matrix and hence it cannot be recycled. So, in the composite fabrication technology, reinforcement of fibres should be done prior to the curing of thermoset matrix.

Generally, thermoset resins containlow rupturestiffness and are brittle at room temperature. At the same time, owingto its network structure, theypossessgood resistance to chemicals and also have good thermal, dimensional and creep properties. The thermoset resin materials used in this research work areEpoxy resin and Urea Formaldehyde resin.

1.8 NATURAL FIBRES

Naturalfibre is characterized by its adaptability, fineness and good aspect ratio [34]. Agro-waste fibres can be referred to as lignocellulosic and they possessappropriate superior propertiessuitable to be used as fibre reinforcementforpolymer composites [5]. For the polymer which is not having sufficient toughness in the non-fortified structure, the stiffness and strength can be expanded by natural fibre reinforcement [35]. Short fibre reinforced polymer composites gives numerous favourable circumstances like simplicity of manufacture, lower fabrication expense and chance of making complex designed articles over ceaseless fibre support [36].

1.8.1 Advantages of Natural Fibres as Reinforcement for Polymer Composites

- Scientific information of structure and properties of natural fibres are promptly accessible.
- The specific gravities of natural fibres are 1.25-1.50 g/cc which is lower than that of glass. This low specific gravity of natural fibre gives higher strength-to-weight ratio for reinforcing plastics. This is having more advantages particularly in parts intended for twisting firmness.
- Natural fibres can be used to reinforce biodegradable polymers since these natural fibres themselves are biodegradable.
- Natural fibres are lighter than inorganic reinforcements and can lead to advantages such as fuel savings when their composites are used in transportation applications.
- Producible with low investment at low cost andhence makes the material an interesting product for low-wage countries.
- Natural fibres have good thermal and acoustic insulating properties.
- Thermal recycling of these natural fibre reinforcements is possible but glass causes problems in combustion furnaces.
- Natural fibres are nontoxic, eco-friendly, biodegradable and sustainable and hence they made the final product light weight and further they provide waste management solutions.

1.8.2 Disadvantages of Natural Fibres as Reinforcement for Polymer Composites

- Quality of natural fibres cannot be maintained equally andit depends on unpredictable influences such as weather.

- Moisture absorption property of natural fibre causes swelling of fibres.
- Restricted maximum processing temperature for fabrication of natural fibre reinforced polymer composites.
- They have lower durability andnatural fibre treatments can improve this considerably.
- Natural fibres have poor fire resistance.
- Cost of natural fibres can change by crop results or farming governmental issues.

1.8.3 Benefits of Natural Fibres as Reinforcement for Polymer Composites

- Substantial scale creation and utilization of completely biodegradable composites will decrease the destructive impacts of plastic squanders into the earth.
- The natural fibre fortified polymer composites are recyclable and finally composted in the soil towards the end-of-life.
- The advancement of biocomposites from bounteous and renewable natural assets gives a key distinct option for the exhausting petroleum.
- Various agro-waste bio-strands already begun their way into the parts of automobiles.

Hence, natural fibres are gaining progressive importance as renewable, light weight, strong, environmentally acceptable and biodegradable reinforcement material for composite preparation.

1.8.4Classification of Natural Fibres

The classification of natural fibres is shown in Fig: 1.2. They are bast, leaf, seed, fruit and stalk fibres [37].

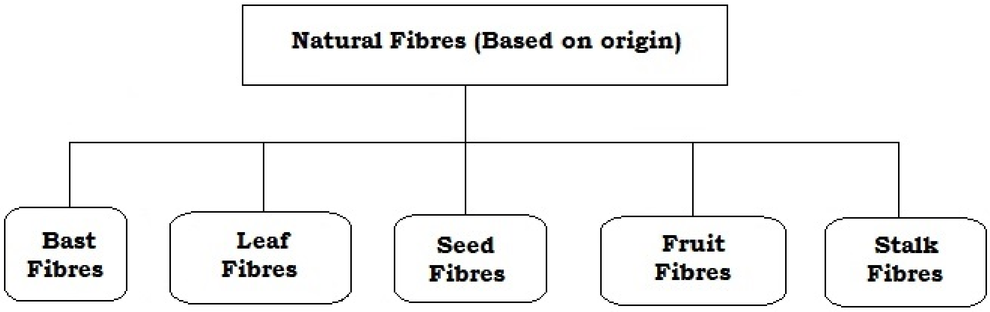


Fig: 1.2 Classification of natural fibres

The bast fibres consist of a wood center encompassed by a stem. Inside of the stem there are various fibre packages, each containing individual fibre cells. Hemp, jute and ramie are some examples for bast strands. By nature,the leaf strands are coarser than the bast filaments. Sisal, manila, curaua, palm and banana are examples for leaf fibres. Cotton and kapok are examples of seed fibres. Cotton is the most widely recognized seed fibre. Examples of fruit fibres are areca and coir. Areca and coir arefibres of areca fruit husk and coconut shell respectively.These fibres are thick and coarse however strong fibre.Bamboo, wheat, rice, grass and barley are examples for stalk fibres.

1.8.5 Chemical Composition of Natural Fibres

Cellulose, hemicelluloses, lignin, pectin and waxesare the fundamental significant principle components present in any natural filaments. The major constituent present in natural fibres is cellulose and it is a linear polymer and it consists of D-anhydro glucose ($C_6H_{11}O_5$) repeating units with three hydroxyl groups per unit and is attachedthrough1,4-β-D-glycosidic linkages at C_1 and C_4 position [32, 38]. Cellulose is crystalline andFig: 1.3 shows the crystal structure of cellulose.

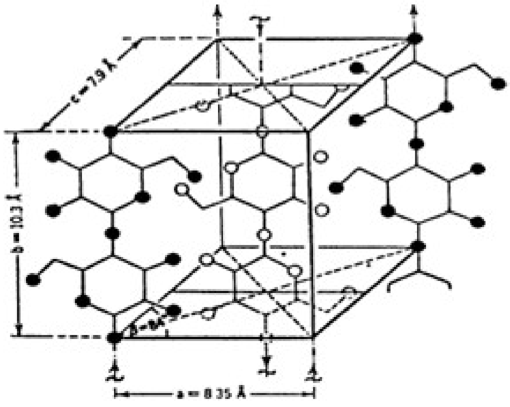


Fig: 1.3 Crystal structure of cellulose

Cellulose plays a key role in providing strength, stiffness and structural stability.So, if higher is the cellulose content higher will be the fibre strength. The fibre stiffness is determined by microfibrillar angle. Micro fibrillar angle is the angle between the micro fibrils and the fibre axis. Cellulose is having good resistance for oxidizing reagents and alkalibut hydrolyzed by acid to form sugars which are water soluble. Fig: 1.4 shows its molecular structure.

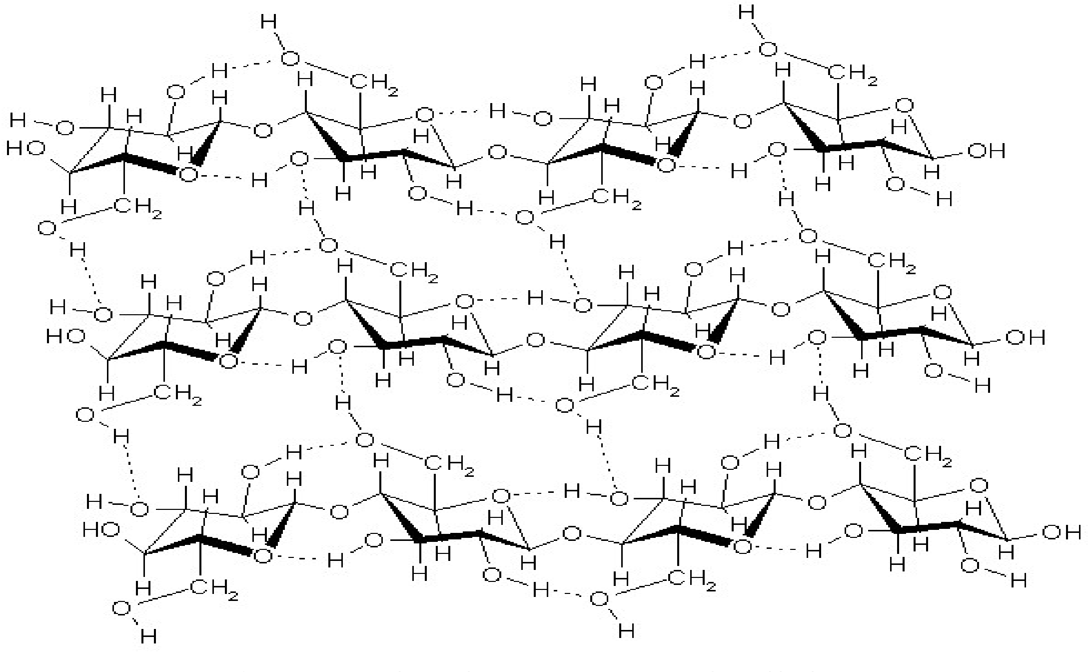


Fig: 1.4Molecular structure of cellulose

The molecular structure of cellulose is similar for different plant based natural fibres but the degree of polymerization and cell geometry is different and due to this, different properties are observed for different fibres [32].

Chemical structures of hemicelluloses, lignin and pectin are shown in Fig:1.5. Hemicelluloses are amorphous, branched polymers whose molecular weight is less than that of cellulose. Hemicelluloses consist of bunch of polysaccharides comprising a mixture of sugar units with 5-carbon and 6-carbon rings.Hemicelluloses show dissimilarity with cellulose molecules in 3 differentways. First of all, hemicelluloses contain various dissimilarsugar units but cellulose consists of 1,4-β-D-glucopyranose units. Next, they are amorphous in nature due to the significant presence of branched polymers with pendant side groups while cellulose is linear in nature. At last, degree of polymerization value of hemicelluloses which is around 50-300 is 10-100 times lower than that of cellulose. Hemicelluloses form a protective matrix for cellulose micro fibrils. Hemicelluloses enlarge in water, soluble in base and effortlessly hydrolyzed by acids[34, 39-40].

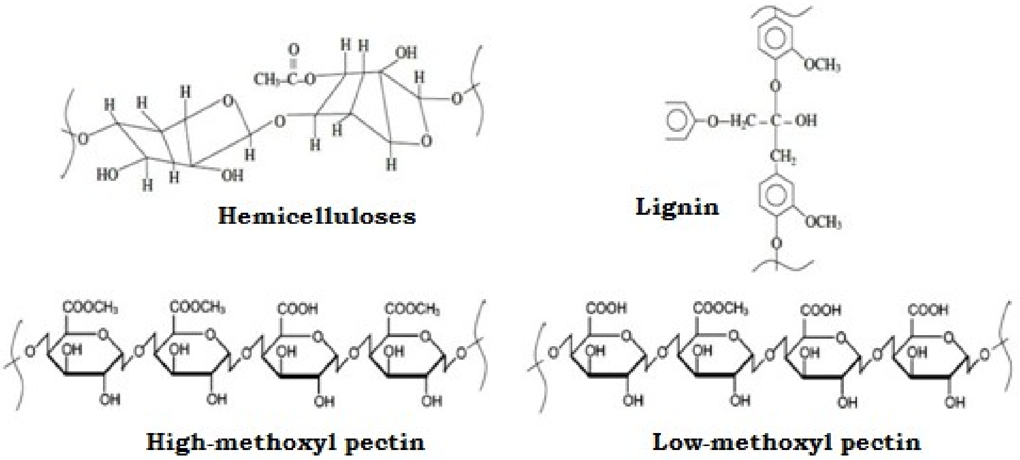


Fig: 1.5 Chemical structures of hemicelluloses, lignin and pectin

Lignin is amorphous, complex polymer.It has both aliphatic and aromatic constituents. By nature, lignin is hydrophobic.It gives rigidity to the plants. Lignincontainsfive-OH groups and five $-OCH_3$ groups per building unit.Furthermore, it contains carbonyl groups. Lignin can't be separated to monomeric units. They are absolutely insoluble in many solvents.$T_g$value of thermoplastic lignin is 90 ^{o}C and it melts at 170 °C [41]. Lignin readily dissolves in warm bases and can undergo oxidation easily. It is condensable with phenol but it will not undergo hydrolysis by acids [42-43].

Pectin is a complex hetero polysaccharide. The branches present in the pectin are cross linked with arabinose sugars and calcium ions. The flexibility to the plants is given by pectin. The cementing agent that binds cellulosic micro fibrils together are pectin along with lignin and hemicelluloses. The last part of the fibres is made by waxes and they comprise alcohols of various types[39].

The physical properties and chemical composition of natural fibresare the most imperativevariables that focus the general properties of natural fibres[5].The microfibrillar angledecides the firmness of the filaments. Plant filaments are more bendable if the micro fibrils have a coiled orientation to the fibre axis. On the off chance that the micro fibrils are situated parallel to the fibre axis, then the strands will be unbending, rigid and have high elasticity [44-45].

1.8.6Moisture Absorption Characteristics of Natural Fibres

In general, natural lignocellulosic fibres are hygroscopic and they ingest or discharge dampness relying upon the ecological conditions. The significant restrictions of utilizing natural lignocellulosic fibres as a part of sturdy polymer composite uses are their extreme dampness ingestion and weak dimensional strength (swelling)[46]. Bulging of natural fibres can prompt micro-cracking of composites and deprivation of composite properties. The hygroscopic nature of natural fibres can be reduced by surface modification of natural fibres which involves the replacement of few of the cell wall-OH groups with chemical moieties [47]. So, chemical treatments of natural fibres are very vital in polymer composite fabrication.

1.8.7 Thermal Stability of Natural Fibres

Most of the natural filaments having cellulose and lignin constituents possess low degradation temperatures (around 200 °C) and make them inadequate for processing temperatures above 200 °C [48]. Thermal properties of natural fibre filaments can be improved by chemical modification.

1.8.8Natural Fibre – Polymer Matrix Interface

The quality and strength of natural fibre fortified polymer composite materials are controlled by the interface between the polymer matrix and the fortifying natural fibres [49-50].The interface impacts are observed as kind of bonding and are frequently interpreted with reference to surface structure of the reinforced materials. The imperative surface components are wettability, presence of polar groups and roughness of the material to be bonded [51]. Interface cracks initiates composite damage and hence change the composite properties [52].

Hence, the bond potency among the reinforcing natural fibres and the surrounding polymeric resin is of crucial important for many polymer composite properties. So, in order to improve the fibre-matrix interfacial bonding, chemical modifications of natural fibres are necessary to make the fibre surface clean and physically rough [53].

1.8.9 Chemical Treatment of Natural Fibres

The presence of hydroxyl groups in the constituents of natural fibresmake them easy totake part inthe chemical treatments.Due to the presence of hydrogen bonding, the reactivity of natural fibres towards the polymericresin is decreased.Surfacemodifications of natural fibres may stimulate these hydroxyl groups or add new chemical groups that canefficientlyimprove the interfacial bonding of fibres with the polymeric resin. That means efficient coupling with the polymeric matrix can be obtained by different surfacemodificationswhich expose greater number of chemical moieties on the surface of the natural fibres.

Chemical modification improves surface propertiesfor example, wetting, attachment and surface strain or porosity of natural strands.Chemical treatments reduce fiber'slength dispersion and increase its aspect ratio. At the same time polarity and density of fibres is reduced and consequently it increases fibre cost. As a result, natural fibre reinforced thermoplastic, thermoplastic elastomeric and thermoset polymer composites with enhancedthermal and mechanical properties can be accomplished [48, 54-56].

1.9 LITERATURE SURVEY OF STUDIES ON THE INFLUENCE OF CHEMICAL MODIFICATIONS ON COMPOSITE PROPERTIES

A number ofresearchers have carried out a lot of research work on the properties of natural fibre-reinforced polymer composites.Joseph et al. reportedthat the tensile strength was improved for chemically modifiednatural fibre basedpolymer composites [30].Improvements in composite propertieswere reported by Joseph et al. forsisal-polyethylene composites due to chemical treatments [57].Mohan et al. explainedthatsodium hydroxide treated jute fibre reinforced composites showed improvementsgreater than 40% for tensile properties [58].Sreekala et al. reported thatpolymer composites strengthened with oil palm fibres withstood tensile properties to a greater strain level when the fibres werechemically modifiedbyisocyanante, silane, acrylation and peroxidetreatments and by latex coating. This was due to the changes in chemical structure and the bond ability of treated fibres[59]. Weyenberg et al. reported that mechanical properties of flax fibre reinforced polymer composites showed improvement when subjected to various chemical treatments [60].6% increase on rigidity and 33% increase on dampness resistance propertieswere reported for benzoylated flax fibre reinforced LDPE composites [61]. Acrylic acid treatedHDPE composites reinforced with flax fibres indicatedmore prominent rigidity properties [62]. Epoxy-phenolic resin composites fortified with acrylated jute fibre showed increment in flexural and tensile strength values by 13.9% and 42.2% in that order [63]. Kushwaha et al. have explained the properties of bamboo fibre reinforced compositeswhenthe fibre was subjected to various chemical modifications [64-66].The mechanism of chemical modification of various types of natural fibres has been explained by Maya JacobJohn et al. [43].Paul et al. reported that surface modifications of banana fibres improved the mechanical properties of banana–polypropylene composites [67].Effects of mercerization and acetylation on sisal-rubber composites were studied by Martins and Jokes[68].Flexural properties of epoxy composites reinforced with bamboo fibres enhancedup to 30% fibre weight and there after they showeddecreased values. Chemical treatments increased flexural strength because of removal of external fibre surface, increment in cellulose content and interfacial attachment[69]. Research was carried out on the surface characterization and water uptake behaviour of modified sisal and coir fibres[70].Scanning electron microscopic study of chemically modified coir fibres was done[71].FTIR spectra were used to characterize the properties of raw and surface modifiedcoir fibres[72]. Flexural and impact properties of maleic anhydride graftedpolypropylene composites reinforced with abaca fibres were increased up-to 50% weight of abaca fibres [73]. Several researchers showed that augmented flexural and impact properties with enhancementin fibre loading and with chemical modifications[74 – 78].

1.10 LITERATURE REVIEW

The most of present and past studies includes studies on many different kinds of non-wood plant materialsbut only very less attention has been made on areca fibres.

Amongst all natural fibre strengthening materials areca seems, by all accounts, to be a maturing fibre, in light of the fact that it is inexpensive and copiously accessible. Areca fibre has a greater prospective in the polymer composite field since the areca fibres possess superior properties like light weight, strong and high strength-to-weight ratio. And also,areca fibres are biodegradable, non-toxic and eco-friendly and have low maintenance cost. Areca fibre is a better acoustic material.

Karnataka is India's biggest areca plantmanufacturing state which has a share amount of around 50% of areca productions in the nation.In Dakshina Kannada, areca is one of the major crops and is cultivated in 27,600 hectares with an annual production of about 40,000 tones.Hence, enormous quantity of unmanaged areca husk is available for further processing. Presently, these cellulosic substances are being used as firewood. Furthermore, a lot of unused husks which are left in the estate cause terrible scent and other rot related issues [79].

Areca *catechu* Linnaeusshell is a rigidfibrous material.It covers the endosperm and comprises around sixty to eighty percentage of the aggregate weight and quantity of the areca organic product. Areca husk fibre is made out of cellulose with differing extents of 35% to 65% of hemicelluloses and 13.0% to 26.0% of lignin, pectin and protopectin [80-81].The mechanical properties of polymer composites fortified with areca fibres were studied only by a few scientists and they reported that areca composites have excellent resistance to moisture absorption when contrasted to wood fortifiedcomposite boards. Areca composites can likewise be utilized for making quality products like thick sheets, feathery pads, non-woven fabrics and thermal insulators [82-87].

Thus to utilizetheseareca fibres as reinforcement, itneeds a complete thoroughlearning on physical properties, chemical properties and mechanical properties of areca fibres and also on the areca fibre reinforced polymer composite properties.

1.11 AIM OF THE PRESENT RESEARCH WORK

The aim of this current research work is: To study the overall properties of areca fibres; To carry out various chemical treatments on areca fibres to modify the surface properties so that effective interfacial bonding between areca fibres and the polymer matrix will occur; To study FTIR, TGA-DTG, XRD and SEM for untreated and all chemically treated areca fibres to identify changes in chemical components, to observe enhancement in thermal stability for chemically treated areca fibresin correlation toraw areca filaments, to analyze crystallinity changes for chemically treated areca filamentsand to observe the changes in surface topography for all chemically treated areca fibres respectively; To study water absorption behaviour of untreated and all chemically treated areca fibres; To fabricate untreated and chemically treated areca fibre reinforced thermoplastic, thermoplastic elastomeric and thermoset polymer composites with different fibre loadings; To determine the tensile, flexural and impact strength of all fabricated areca fibre reinforced thermoplastic, thermoplastic elastomeric and thermoset polymer composites. Then, finally to assess the influence of surfacemodifications and the impact of fibre loadings on tensile, flexural and impact properties of all fabricated areca fibre reinforced polypropylene, areca fibre reinforced natural rubber, areca fibre reinforced epoxy and areca fibre reinforced urea formaldehyde polymer composites.

CHAPTER 2

CHARACTERIZATION OF NATURAL ARECA FIBRES

2.1 INTRODUCTION

In this chapter, overview of areca fibres, materials used and methods adopted in the present investigation and physical, chemical and mechanical properties of areca fibres have been discussed. Surface modification of areca fibres carried out by alkali treatment, potassium permanganate treatment, benzoyl chloride treatment, acrylic acid treatment and acetic anhydride treatment has been explained. FTIR spectral analysis of untreated and all chemically treated areca fibresisexplained in detail. Thermal stability of untreated and all chemically treated areca fibresis characterized by TGA–DTG studies. The crystallinity and morphological investigations of untreated and all chemically treated areca fibresare analyzed by XRD studies and SEM studies respectively. Water absorption studies of untreated and all chemically treated areca fibres have been discussed.

2.2 OVERVIEW OF NATURAL ARECA FIBRES

Areca plant is a slim, single-trunked palm that can develop to thirty meter height (100ft). Areca is a kind of around fifty types of palms in the Arecaceae family, found in muggy tropical backwards from China and India, over the Malay Archipelago, to the Solomon Islands. It is grown from East Africa and the Arabian Peninsula crosswise over tropical Asia and Indonesia to the focal Pacific and New Guinea. Betel nut is specified in Sanskrit under the name guvaka, and in Chinese writings dating from 150 BCE it was referred to as pinlang. Utilization of areca nut is regularly socially ritualized and business interest for the areca nuts is expanding as this customary supply decreases. This effectively developed palm has the capability for being a beneficial harvest for agriculturists and lawn nursery workers.

Plate2.1 Areca Catechu LinnaeusSingle-Trunked Palm

2.2.1 Botanical Description of Areca

- **Preferred scientific name:** *Areca catechu* Linnaeus
- **Family:** Arecaceae (Palmae), palm family
- **Subfamily:** Arecoideae
- **Non-preferred scientific names** (synonyms): *Areca catechu* Burman, *Areca faufel* Gaertner, *Areca hortensis,* Loureiro, *Areca himalayana* H. Wendland, *Areca nigra* H.

Plate2.2Areca nut (Betel Nut) – fruit

Plate 2.3(a) Areca nut surrounded by areca husk (b) Areca fibres

2.2.2 Advantages of Areca Nut

- Areca nut helps to inhibit the growth of bacteria on the teeth.
- It is eaten after meals in south Asia.
- It is one of the most popular Indian commercial goods.

2.2.3 Disadvantages of Areca Nut

- Heavy intake of betel nut causes serious health problems including permanent discoloration of the teeth, oral leucoplakia, sub mucous fibrosis and squamous cell carcinoma.

2.2.4 Applications of Areca Nut

- Areca nuts are used medicinally in the treatment of intestinal worms.
- Areca nut is used as an aromatic and astringent.
- The leaves of areca plant are used to make disposable plates.
- Areca nut increases the flow of saliva, lessens perspiration and sweetens the breath. It is also used to strengthen gums.
- Areca nut is widely used for chewing. The chewing of areca nuts causes mild stimulation and a feeling of well-being.

2.3MATERIALS AND METHODS

2.3.1 Areca Fibre

Areca empty fruits were collected from Madhu Farm House, Nilogal, Davangere, Karnataka, India.

2.3.2 Chemicals and Reagents

The analytical gradechemicals such as sodium hydroxide, glacial acetic acid, potassium permanganate, acetone, benzoyl chloride, ethanol, acrylic acid, toluene, acetic anhydride, perchloric acid, sulphuric acid and sodium chloride that were used in this present study were utilized as obtained. These chemicalswere bought from Qualigens Company.

2.3.3 Areca FibreExtraction

The areca empty fruits that were in dried condition wereimmersed in the de-ionized water for a period of5 days. This procedure is called retting; permitting the fibre to be extracted from the empty fruit effectively. The areca strands were extracted from the areca empty fruits and were isolated by using a comb. The existing impurities and the broken fibres were removed by using a sieve. Then,the areca fibres were kept at a temperature of 30 ^{o}C and at a relative humidity of 70% for a period of 72 h prior to their chemical treatments [88-89].

2.4 PHYSICAL PROPERTIES OF ARECA FIBRES

2.4.1 Size Distribution of Areca Fibres

Fibre size is a very important parameter in natural fibre reinforced polymer composite technology. Because natural fibres with high cellulose content, high aspect ratio i.e. length to diameter ratio and low microfibrillar angle i.e. the angle between fibre axis and the micro fibrils, possess superior mechanical properties [90].

In this study, the determination of areca fibre dimensions wascarried outby taking 2000 areca fibres.Areca fibre dimensions were obtained via optical microscopy (Olympus SZ-PT).

2.4.1.1 Length Distribution of Areca Fibres

Each areca fibre length was determined with help of scale having accurateness of 1 mm at 30 °C. Here, areca fibre length was considered asa distance between one ending of the fibre to another ending of fibre and during this measurement, the areca fibre was extended andwas not stretched out.In this study, it was revealed that 26 mm was the length of the smallest areca fibre and 54 mm was the length of the longest areca fibre. Based on their length, groups were made in such a way that each succeeding group was greater than 3 mm length by the earlier group and total of 10 groups were made for the test[91].

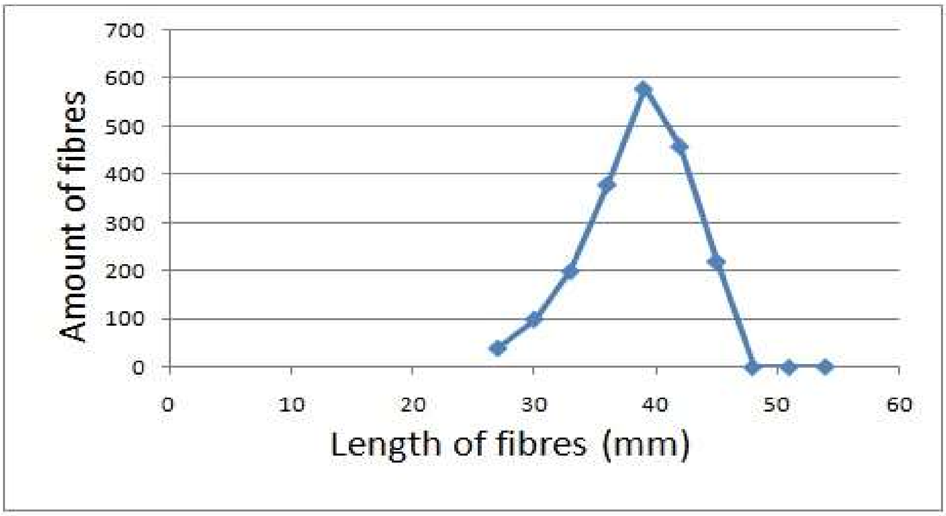


Fig:2.1 Areca fibres - length allocation in terms of amount of fibres

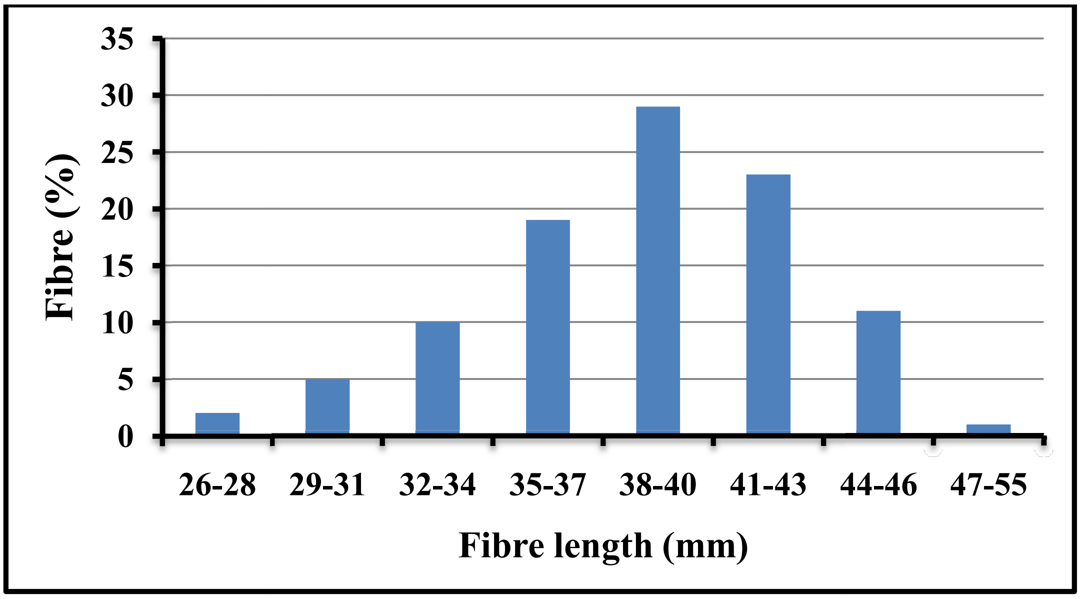


Fig:2.2 Areca fibres - length allocation in terms of % of fibres

26 mm to 28 mm was the length range of first group and 53 mm to 55 mm was the length range of last group. X-axis indicates theaveragelengthof everygroup. Fig:2.1 and Fig: 2.2show the areca fiber'slength distribution and from this, it can be observed that the greatest number of areca fibres belongs to the group of 39 mm. Maximum numbers of areca fibres were found to be in the range of shortest and average length, 26-43 mm and it was calculated as 88 %. Thelongestareca filaments (44-54 mm) took only a very little part [92].

2.4.1.2 Weight Distribution of Areca Fibres

Electronic balance with accurateness of 0.1 mg was used in the measurement of overall weight of areca fibrespresent in every group. 9.4410 g was found to be the overall weight of two thousand areca fibres. Fig: 2.3 indicate the weight % of every group involved in the study.

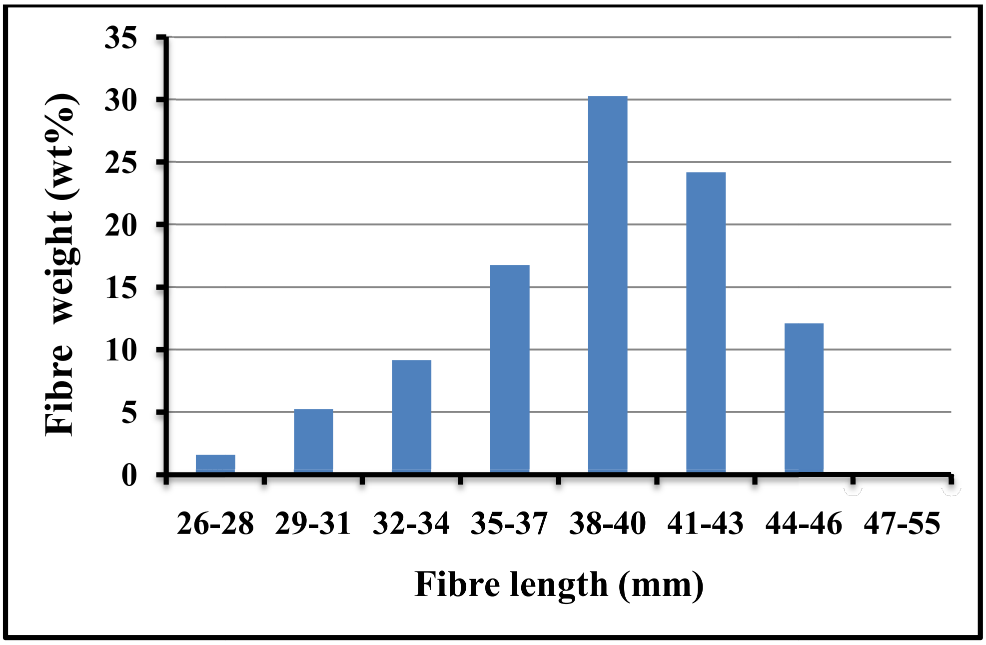


Fig:2.3 Weight distributionof Areca fibre

It was noticed that the greater weight was distributed in fibres with the medium length, 35-43 mm. The weight of fibres with lengths of 35-43 mm accounted for 71.90%of the total measurement [92].

2.4.1.3 Fineness Distributionof Areca Fibres

Areca fibres exhibit a variety of cross sectional shapes and also they vary in section along their length and vary from fibre to fibre. So, it is necessaryto calculate the fineness of fibre and at the same time it will be comparatively easy tocalculate the diameter of the fibres.Tex is a measure for the linear mass densityand is defined as the mass in grams per 1000 meters. The fineness (Tex) value of the areca fibre was calculated by using total length and weight in each group. Theresults are summarized in Fig:2.4.

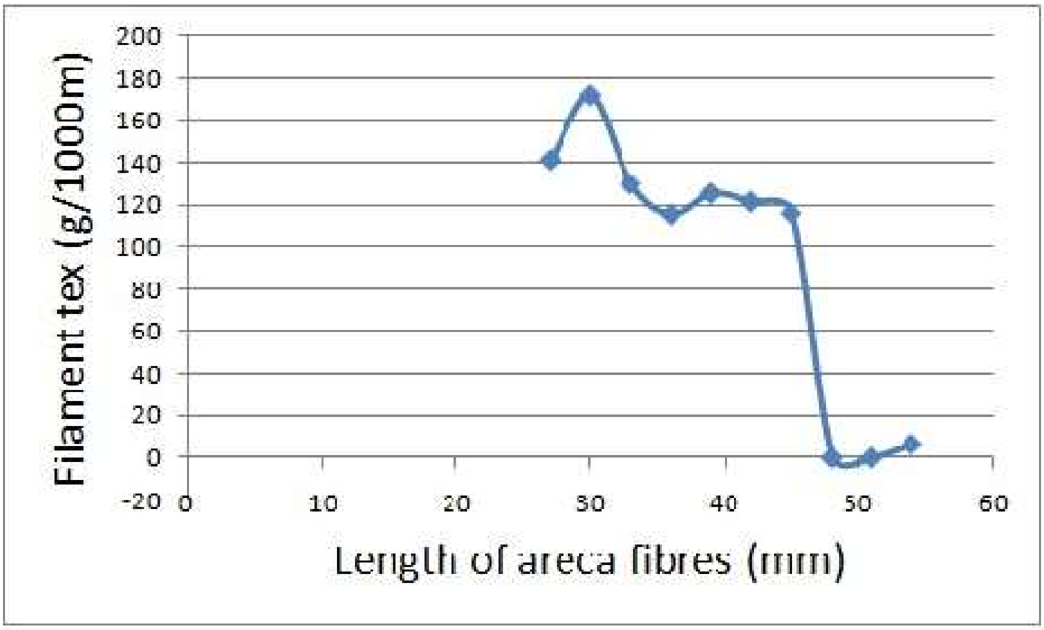


Fig:2.4 Areca fibre fineness curve

It was observed that the fineness of areca fibres of length 35-43 mm were somewhere around 120 tex, for those in the length range from 29-31 mm, the fineness raises to about 180 tex. The average fineness of the areca fibres involved in this investigation was 131.52 Tex [92].

2.4.1.4 Density of Areca Fibres

The densitytest of areca fibre was conducted in accordance with ASTM D-792 method using a Sartorius analytical balance and the density of areca fibre was found to be 1.095g/cm^3 [92].

2.4.1.5 Diameter Distribution of Areca Fibres

The diameter of areca fibres was calculated by using the following equation (2.1) where D is the diameter of areca fibre in mm and ρ is the density of areca fibresin g/cm^3.

$$\mathbf{D} = \sqrt{\frac{\boldsymbol{Tex}}{\mathbf{1000}\ \boldsymbol{x}\ \boldsymbol{\rho}\ \boldsymbol{x}\ \mathbf{0.7855}}} - - - - - - - - \quad (2.1)$$

Thediameter of the fibre groups with length32-43 mm was found to be falling in therange of 0.37-0.384 mm and hence the fibres of the above said group was considered in finding out the average diameter in connection with analyzing thetensile strength of areca fibres.

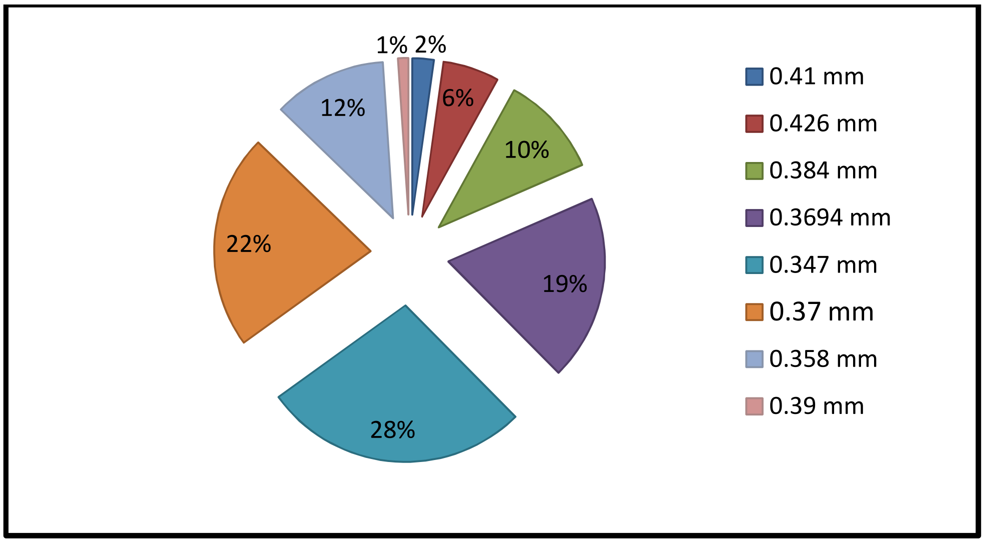


Fig: 2.5 Diameter distributionof Areca fibre

Diameter distribution of areca fibres is presented in Fig: 2.5. From this Fig: 2.5, the average diameter of untreated areca fibres was found to be 0.347 mm and the study revealed that the short areca fibres usually have higher diameter.

Based on the results of Fig:2.1, Fig:2.2, Fig: 2.3, Fig: 2.4 and Fig:2.5, areca fibres can be approximated as cylindrical shape with an average length of 39 mm, with an average diameter of 0.347 mm and giving aspect ratio, L/D of 112.39 [93-95].

2.5CHEMICAL PROPERTIES OF ARECA FIBRES

2.5.1 Chemical Composition of Areca Fibres

The chemical composition and properties of natural lignocellulosic fibres varies from fibre to fibre and even for the same fibre also based on the harvesting conditions. Even though natural lignocellulosic fibreshavedifferent chemical composition, they have very similar properties such as thermo plasticity, moisture sorption, flammability and degradation by acids, bases and ultra-violet (UV) radiation. All of these characteristics will result in the specific end use of natural lignocellulosic fibres in polymer composite fabrication. The chemical composition of areca fibres was determined according to the following procedures.

2.5.1.1 ExtractableContent

5 g of Air dried areca fibre was placed in a Soxhlet extraction unit. A mixture of ethanol and toluene was used as a solvent and the extraction process was continued for a period of 5 h. After extraction, the sample was rinsed with ethanol and hot water and dried up to constant weight at the temperature of 60 °C. The extractable were calculated as a percentage of the oven dried test sample [95-97].

2.5.1.2 Lignin Content

2 g of extracted sample was placed in a flask and 15 mL of 72% sulphuric acid was added. The mixture was stirred frequently for 3 h at 25 °C and 200 mL of distilled water was added to the mixture. Then the mixture was boiled for about 2 h and cooled. After 24 h, the lignin was transferred to the crucible and washed with hot water repeatedly until becoming acid free. The collected lignin was dried at 105 °C and cooled down in desiccators and weighed. The drying and weighing were repeated until constant weight was obtained [95-97].

2.5.1.3 Holocellulose Content

3 g of Air dried areca fibres were weighed and placed in an Erlenmeyer flask and then 160 mL of distilled water, 0.5 mL of glacial acetic acid and 1.5 g of sodium chloride were added successively. The flask was placed in a water bath and heated up to 75 °C for an hour and then an additional of 0.5 mL of glacial acetic acid and 1.5 g of sodium chloride were added. The additions of acetic acid and sodium chloride were repeated two times hourly. The flask was placed in an ice bath and cooled down to below 10 °C. The holocellulose was filtered and washed with acetone, ethanol and water respectively. Then, the sample was dried in an oven at 105 °C before weighing [95-97].

2.5.1.4 α-Cellulose Content

2 g of Holocellulose was placed in a beaker and 10 mL of 17.5% sodium hydroxide solution was added. The areca fibres were stirred up by glass rod so that they could be soaked with sodium hydroxide solution vigorously. Then the sodium hydroxide solution was added to

the mixture periodically (once in every five minutes) for half an hour and the mixture temperature was kept at 20 ^{o}C. About 33 mL of distilled water was added in the beaker andkept it for an hour. The holocellulose residue was filtered and transferred to the crucible and washed with 100 mL of 8.3% sodium hydroxide, 200 mL of distilled water, 15 mL of 10% acetic acid and with water, successively. The crucible with α-cellulose was dried and weighed [95-97].

2.5.1.5 Hemicelluloses Content

Thehemicelluloses content of areca fibres was determined by calculating the difference between holocellulose and α-cellulose [95-97].The chemical composition of the major components of areca fibres is listed in the Table 2.1.

Table 2.1 Chemical composition (wt %) of Areca fibres

Reference	Cellulose	Hemi-celluloses	Lignin	Moisture content	Ash content
Experimental	55.82	34.28	6.82	1.80	1.28
Ramachandra et al. [81]	35-64.8	29-33.1	13-26	--	1.1-2.1
Yusriaha et al.[98]	53.20	32.98	7.20	--	1.05

Hence, areca fibres composed of 55.82% cellulose, 34.28% hemicelluloses, 6.82% lignin, 1.80% moisture content and 1.28% ash content [95] and the experimental value of cellulose content in the areca fibres is in agreement with the previous studies [81, 98].

2.5.2 Surface Modification of Areca Fibres by Chemical Treatments

The hydroxyl groups present in the natural fibres may be involved in hydrogen boding within the cellulose molecules. For reinforcement of naturalfibres in polymer composites, several problems arise along the interface owing to the presence of these hydrophilic hydroxyl groups on the fibre surface because this hydrophilic nature hinders efficient reaction with the polymeric matrix.The chemical structure of cellulose of natural fibre is presented in Fig: 2.6.

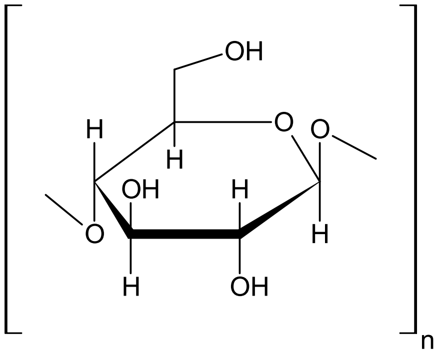


Fig: 2.6 Chemical structure of cellulose

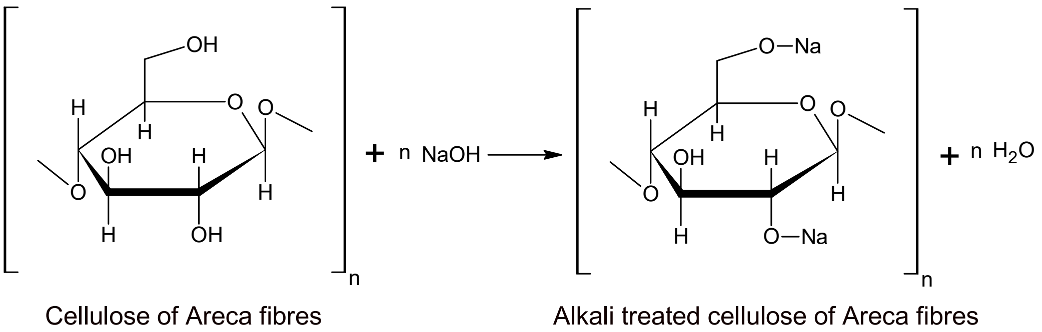
In addition to this, pectin and waxy substances cover the reactive functional groups of the fibre and act as a barrier for interlocking with the polymer matrix. And also,flammability of natural fibres varies from fibre to fibre because each natural fibre is having different chemical composition of cellulose, hemicelluloses, lignin and pectin. Higher cellulose content results in higher flammability while higher lignin content results in greater char formation with lower degradation temperature [99-101]. Hence the cellulose and lignin content present in natural fibres decides the properties of natural fibres as well as natural fibre reinforced polymer composites. Further, low degradation temperature (around 200 °C) value of majority of natural fibres makes them inadequate for processing temperature above200 °C [48]. The irregularities of the fibre surface also play a vital role in the mechanical interlocking at the interface. These defects can be remedied by surface modification of natural fibresthrough various chemical treatments.Hence, surface modifications of natural fibres by various chemical treatments are very important in the field of technical utilization of natural fibre reinforced polymer composites in various engineering applications.

Naturalareca fibres are amenable to chemical modification due to the presence of hydroxyl groups. Chemical treatments expose more reactive groups on the fibre surface and facilitate well-organized coupling with the polymer matrix. Thermal stability of areca fibres can be improved. The interfacial properties can be improved by giving appropriate modifications to the components, which give rise to changes in physical and chemical interactions at the interface.

Hence, in this study, areca fibres were subjected to different chemical treatments such as alkali treatment, potassium permanganate treatment, benzoyl chloride treatment, acrylic acid treatment and acetic anhydride treatment to optimize effective interfacial bonding between areca fibres and polymeric matrix so thatareca fibre reinforced thermoplastic, thermoplastic elastomeric and thermoset polymer composites with enhanced properties can be obtained[43, 54-56].

2.5.2.1 Alkali Treatment of Areca Fibres

Areca fibres were soaked in a stainless steel vessel containing 2%, 4%, 6%, 8% and 10% NaOH solution respectively at the room temperature (30-32 °C) for 1h. The alkali treated areca fibres were immersed in distilled water for 24 h to remove the residual NaOH. Final washing was done with distilled water containing little amount of 2% acetic acid. Then, the treated areca fibres were washed again in running water to remove the last traces of acid sticking on to it, so that the pH of the fibres was approximately 7. Fibres were dehydrated in an oven at 70 °C for 3 hto obtain alkalitreated areca fibres.

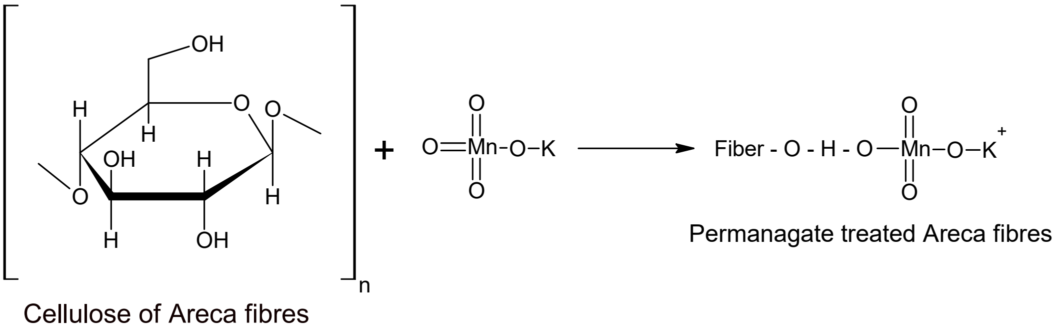


Scheme 2.1 Reaction between areca fibres and sodium hydroxide

The effect of alkali on cellulose fibre is a swelling reaction. 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 cellulose relaxes.This provides more access of penetration of chemicals. Cellulose micro-molecules are separated at larger distances in the amorphous region and the corresponding spaces are filled by water molecules. Now, alkali sensitive hydroxyl groups present among the molecules are broken which in-turn react with water molecules and move out from the areca fibre structure. Fibre–cell–O–Nagroups are formed between the cellulose molecular chains by the remaining reactive molecules. Due to this, hydrophilic hydroxyl groups are reduced and moisture resistance property of areca fibres is increased.
It also takes out certain portion of hemicelluloses, lignin, adhesive pectin, waxy epidermal tissue and oil covering materials. As a result, fibre surface became clean and there is a change in the surface topography of areca fibres.In other words, fibre surface became more uniform due to the elimination of micro voids and stress transfer capacity between the ultimate cells improves. In addition to this, it reducesareca fibre diameter and thereby increasesits aspect ratio, which in-turn results in better areca fibre-polymer matrix interfacial adhesion. If the alkali concentration is higher than the optimum condition excess delignification of fibre takes place and results in weakness or damage to the fibre[34, 40, 61, 92, 95, 102-107].

2.5.2.2 Potassium Permanganate Treatment of Areca Fibres

Areca fibres, pre-treated with 6% alkali were immersed in 0.5% $KMnO_4$ in acetone solution for 30 min. Potassium permanganate treated fibres were then decanted and dried in air.

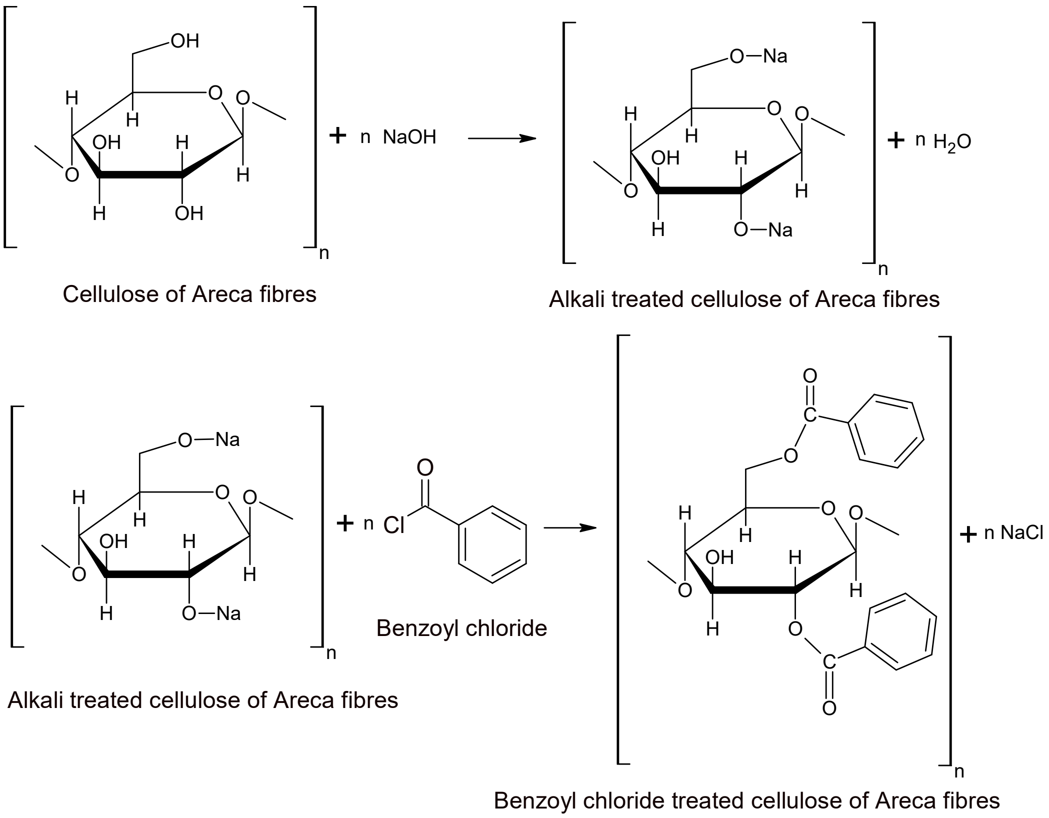


Scheme 2.2 Reaction between areca fibres and KMnO4

Extractable materials such as lignin, waxes and oil covering materials are removed and more reactive hydroxyl groups are exposed on the areca fibre surface during alkali pre-treatment. Potassium permanganate reacts with alkali pre-treated areca fibres in acetone solution and produces highly reactive permanganate ions (Mn^{3+}). Then, this highly reactive permanganate ions (Mn^{3+}) reacts with cellulose hydroxyl groups and forms cellulose-manganate complex. Permanganate ions also reacts with the lignin constituents (hydrophilic –OH groups) and carve the arecafibre surface. As a result, areca fibre surface becamephysically rough. This reduces hydrophilic nature of the areca fibres and improves chemical interlocking at the interface and provides better adhesion with the polymeric resin. Higher concentrations of $KMnO_4$ (more than 1%) causes excess delignification (removal of cementing materials) within the cellulose structure and degrade the fibre properties. [34, 40, 67, 92, 95, 102-103, 108-110].

2.5.2.3 Benzoyl Chloride Treatment of Areca Fibres

During benzoylation treatment, 6% alkali pre-treatment was used to activate the hydroxyl groups of areca fibres. This alkali pre-treated areca fibres were soaked in 6% NaOH and agitated with benzoyl chloride for 15 min. The treated areca fibres were then immersed in ethanol solution for 1 h to remove benzoyl chloride that adhered to the fibre surface. Finally, benzoylated areca fibres were washed thoroughly using distilled water and dried in air.

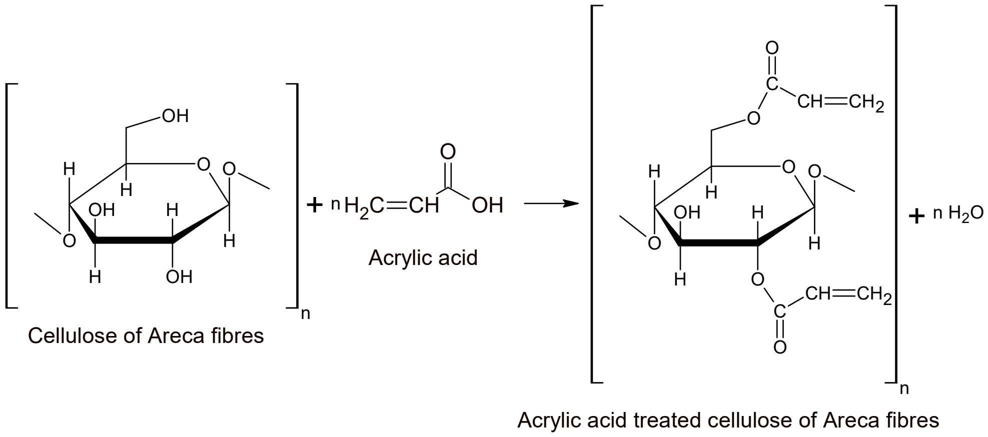


Scheme 2.3 Reaction between areca fibres and benzoyl chloride

The alkali pre-treatment which is used during benzoyl chloride treatment removes extractable materials such as lignin, waxes and oil covering materials and exposes more reactive groups on the areca fibre surface. Benzoyl chloride reacts with this alkali pre-treated areca fibres and forms ester linkage and benzoyl groups are attached on to the cellulose backbone of areca fibres. Due to the introduction of hydrophobic groups on the areca fibre surface, moisture resistance property of areca fibres is increased andcompatibilityof areca fibres with polymer matrix is improved. It also improves thermal stability of areca fibres. The treated areca fibre surface became physically rough. Hence, benzoylation treatment improved chemical interlocking at the interface and provided effective fibre surface area for good adhesion with the polymer matrix [34, 40, 57, 61, 95, 102-103, 105, 111].

2.5.2.4 Acrylic Acid Treatment of Areca Fibres

6% alkali pre-treated areca fibres were immersed in 5% acrylic acid solution at 50 °C for a period of 1 h and then treated areca fibres were washed thoroughly using distilled water and dried in an oven for 24 h at the temperature of 70 °C.

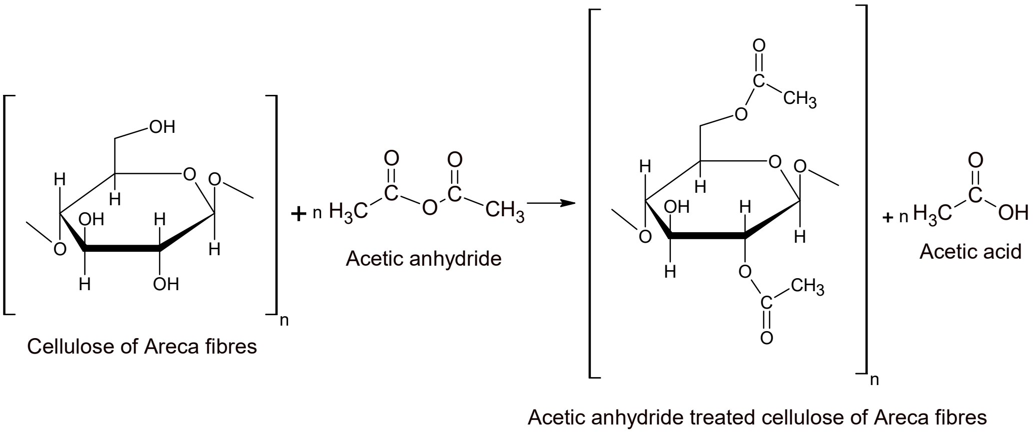


Scheme 2.4 Reaction between areca fibres and acrylic acid

Extractable materials such as lignin, waxes and oil covering materials are removed and more reactive hydroxyl groups (-OH groups) are exposed on the areca fibre surface when areca fibres are pre-treated with alkali. Acrylic acid provides more access of reactive cellulose macro radicals to the polymerization medium by reacting with cellulosic hydroxyl groups of the fibre. An ester linkage is formed with the areca fibres by the carboxylic acids present in acrylic acid. It removed most of the hemicelluloses and lignin and destroyed the cellulose structure. As a result, large number of pits is formed on the treated areca fibre surface. Moisture absorption of areca fibres is reduced due to the replacement of hydrophilic hydroxyl groups by hydrophobic ester groups and the effective fibre surface area for good adhesion with the matrix is increased [34, 40, 95, 102-103, 112-113].

2.5.2.5 Acetic Anhydride Treatment of Areca Fibres

The areca fibres were placed in a round bottom flask containing acetylating solution. Acetylating solution consists of toluene and acetic anhydride in 2:1 ratio and a very small amount of 0.052%perchloric acidcatalyst. The process temperature of acetylation was60 °Cand duration was 3 h. After chemical modification, the treated areca fibres were washed periodically with distilled water until acid free. Finally acetylated areca fibres were dried in air.



Scheme 2.5 Reaction between areca fibres and acetic anhydride

Chemical modification of areca fibres takes place in acetylation treatment, as the acetic anhydride substitutes the cell wall hydroxyl groups with acetyl groups. This chemical reaction renders the areca fibre surface to become more hydrophobic due to the replacement of hydrophilic hydroxyl groups by hydrophobic acetyl groups and further causes plasticization of cellulosic areca fibres. By the interaction with acetyl group, the wax and cuticle present in the fibre surface is removed and surface becomes smoother. As the binding materials are removed, the fibrillation is found to arouse and some micro-pores appeared in the acetylated areca fibres[40, 95, 102-103, 112-113].

All the untreated, alkali treated, potassium permanganate treated, benzoyl chloride treated, acrylic acid treated and acetic anhydride treated areca fibres were cured in an oven and then conditioned under the environment of relative humidity of 70% and temperature, 30 °C for 24h.

2.6 MECHANICAL PROPERTIES OF ARECA FIBRES

2.6.1 Tensile Strength of Areca Fibres

The method, ASTM D3822-01 was applied to determine the tensile strength of areca fibres. The testing was performed using the model 2.5 X*t* single fibre strength tester (Mecmesin, UK) with the sample gauge length and crosshead speed of 15 mm and 5 mm/min, respectively.To minimize the influence of fibre length variation, 10 samples from eachgroup ranging from 32-43 mm were subjected to test the tensile strength.Afterthe measurement, average tensile strength is reported by omitting the extremevalues, if any.

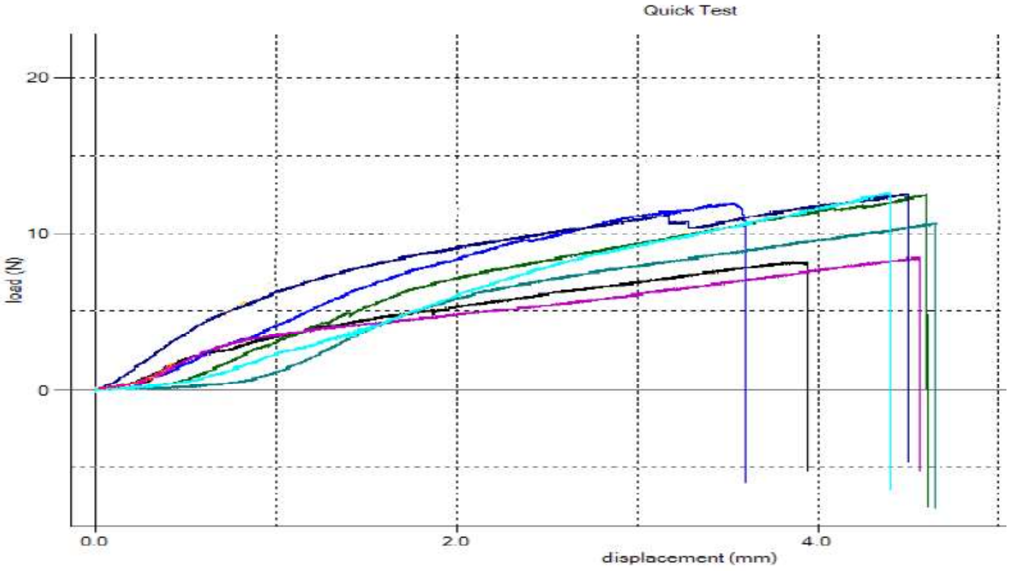


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Fig:2.7 Tensile behaviour of natural Areca fibres of length 39 mm

According to this method, ASTM D3822-01,the tensile strength of fibreswasfound to be 116.93N/mm^2[92]. The loaddisplacementcurve for raw areca fibreswas shown in Fig:2.7.The averageload and displacement was found to be 11.25 N and4.5 mm respectively.

Similarly, tensile strength of 2%, 4%, 6%, 8% and 10% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated, 5% acrylic acid treated and acetylated areca fibres has also been determined according to ASTMD3822-01 standard procedures [92] and the values are given in the following Table 2.2.

It has been observed that the tensile strength of areca fibreswas decreased withincreased NaOHconcentration andthis may be due to the fact that the denser alkali solutionprovided more sodium ions and hydroxyl ions to react with the substances present on the fibre surface causing greater amounts of lignin, pectin, fatty acid and celluloseto ooze out. This implies that the alkali treatment removes most of the fat, lignin, pectin and oil covering the external surface of the fibre cell wall which in-turn improves the fibre adhesive quality in combination with the polymer matrix. Alkalitreatment eliminates the micro voids and makes the fibre surface to become more uniformand thus increases the stress transfer capacity between the ultimate cells [114]. The least tensile strength noticed for 10% NaOH treated areca fibres indicates the degradation of arecafibre on treatment with denser alkali. Severealkali treatment induces larger fibrillation which in-turn reduces the fibre efficiency in the composite strengthening.

Thetensile strength of all chemically treated areca fibreswas found to be lower than that of raw areca fibres. This implied that the chemical treatment removed most of the fat, ligninand pectin covering the external surface of the fibre cell walland this in-turn improves the fibre adhesive quality in combination with polymer matrix [114].

Table 2.2 Tensile strength values of Areca fibres

Areca fibres	**Tensile Strength (N/mm^2)**
Untreated	116.93
2% alkali treated	109.33
4% alkali treated	102.43
6% alkali treated	100.13
8% alkali treated	97.82
10% alkali treated	89.77
0.5% permanganate treated	108.02
Benzoyl chloride treated	110.34
5% Acrylic acid treated	112.42
Acetic anhydride treated	108.68

2.7 FTIR SPECTRAL STUDIES OF ARECA FIBRES

FTIR spectroscopy, model Perkin Elmer System 2000 was used to analyze the possible chemical bonding existing in the untreated and all chemically treated areca fibres. 1 mg of powdered areca fibre samples were mixed with 100 mg of KBr powder. The powder mixtures were then pressed into transparent thin pellets. FTIR spectra of each sample were analyzed in a range between 500 cm^{-1} and 4000 cm^{-1}.

FTIR peaks position of areca fibres and their characteristic Infrared absorption frequencies for untreated and all chemically treated areca fibres are given in Table 2.3.

Table 2.3 FTIR peaksposition of Areca Fibres

Characteristic absorption frequencies forAreca fibres	
Frequency Range, cm^{-1}	**Compound type**
600 - 500	C-OH bending.
700 - 800	Lignin components
800 - 900	β-glycosidic linkages between the monosaccharide
1000 - 1300	Alcohols, Ethers
1060 - 1040	C-O stretching vibrations of polysaccharides
1100-1600	Hemicelluloses
1200 - 900	Polysaccharides (C-O-C, C-O)
1280 - 1200	C-O stretching vibration of ester linkage of acetyl group in hemicelluloses and pectin components
1370 - 1320	Bending vibration of C-H and C-O groups of aromatic rings in polysaccharides
1377.86	Alcohol group of cellulose
1480 -1400	CH_2 symmetric bending in cellulose
1500 - 1540	Lignin and lignocelluloses (Aromatic skeletal)
1600 - 1400	Aromatic rings (C=C stretching)
1620 – 1680	Alkenes
1680 – 1760	Aldehydes, Ketones, Carboxylic acids, Esters
1700	Carbonyl group
1727.65	Carbonyl C=O stretching vibration of ester and ether crosslink's between cellulose and lignin or cellulose and hemicelluloses.
2650 – 2880	Aldehydes
2920 - 2850	Methylene (C-H stretch)
2960 - 2830	C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses
3419.18	Hydroxyl group and H_2 bonded OH stretching.
3600 – 3650	Monomeric alcohols and phenols
3850 – 3300	H_2 bonded O-H stretching vibration of cellulose

The FTIR spectra of untreated and all chemically treated areca fibre shows absorption bands characteristic of chemical groups of lignocellulosic fibre components such as cellulose, hemicelluloses, lignin and pectin. These components chieflyconsist of alkenes, aromatic groups and various oxygen containing functional groups (ester, ketone and alcohol) [115-116].

2.7.1 Spectral Analysis of Untreated Areca Fibre

The FTIR spectrum of untreated areca fibre is presented in Fig: 2.8.

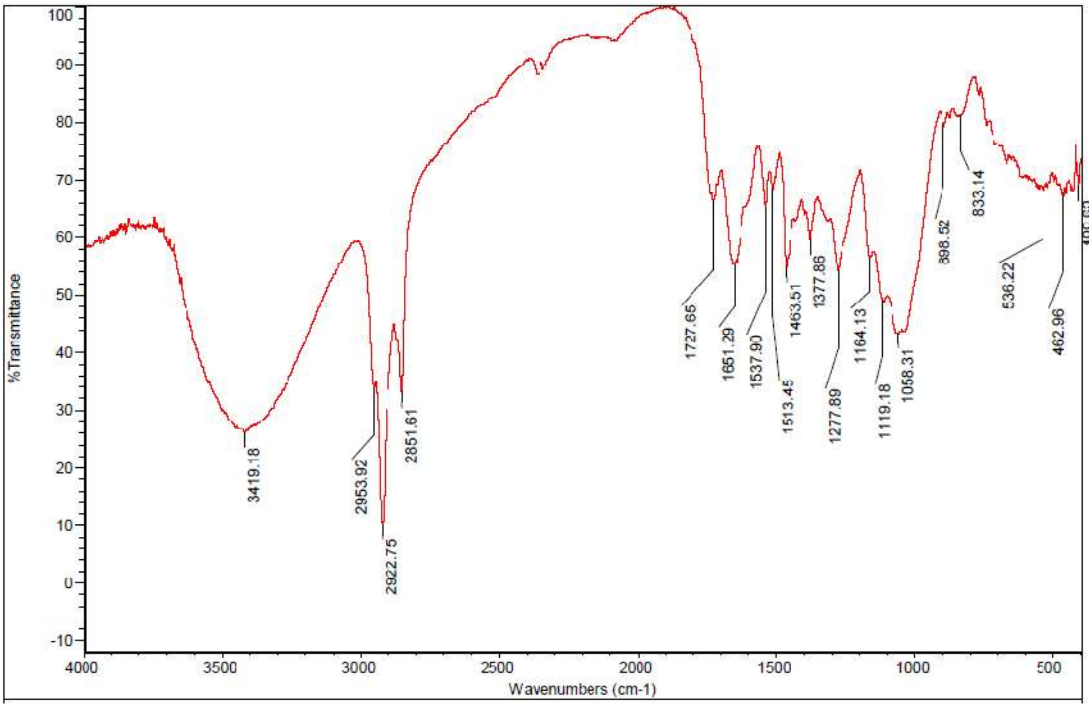


Fig:2.8 FTIR spectrum of untreated Areca fibre

The absorption band in the region of 3850 to 3300 cm^{-1} corresponds to the hydrogen bonded O-H stretching vibration of cellulose. The spectrum of untreated areca fibres are dominated by the peak at 3419.18 cm^{-1}and indicatesthe hydroxyl group and hydrogen bonded -OH stretching vibration of cellulose.

The absorption peaks at 2953.92 cm^{-1}, 2922.75 cm^{-1} and 2851.61 cm^{-1} are the characteristic bands responsible for C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses components.

The peak at 1727.65 cm^{-1} is referred to carbonyl C=O stretching vibration of ester and ether crosslink's between cellulose and lignin or cellulose and hemicelluloses. The small peak at 1651.29 cm^{-1} may be due to the presence of alkenes in the fibres. The two small peaks at 1537.90 cm^{-1} and 1513.45 cm^{-1} are attributed to C=C stretching of aromatic ring of lignin and lignocelluloses. The absorbance at 1463.51 cm^{-1} is associated to the CH_2 symmetric bending in cellulose.

The peak at 1377.86 cm^{-1} is referred to alcoholic group of cellulose. The peak at 1277.89 cm^{-1} corresponds to C-O stretching vibration of ester linkage of acetyl group in hemicelluloses and pectin components. The absorption peaks at 1164.13 cm^{-1} and 1119.18 cm^{-1} are due to anti-symmetrical deformation of C-O-C band of polysaccharides in hemicelluloses. The absorption peak at 1058.31 cm^{-1} is due to C-O stretching vibration of polysaccharides in cellulose.

The peaks observed at 898.52 cm^{-1} and 833.14 cm^{-1} are due to the presence of β-glycosidic linkages between the monosaccharide. Further, the absorbance at 536.22 cm^{-1} corresponds to the C-OH bending in cellulose of untreated areca fibres [40, 92, 107, 117 – 124].

2.7.2 Spectral Analysis of Alkali Treated Areca Fibre

The FTIR spectrum of 6% alkali treated areca fibre is presented inFig:2.9.

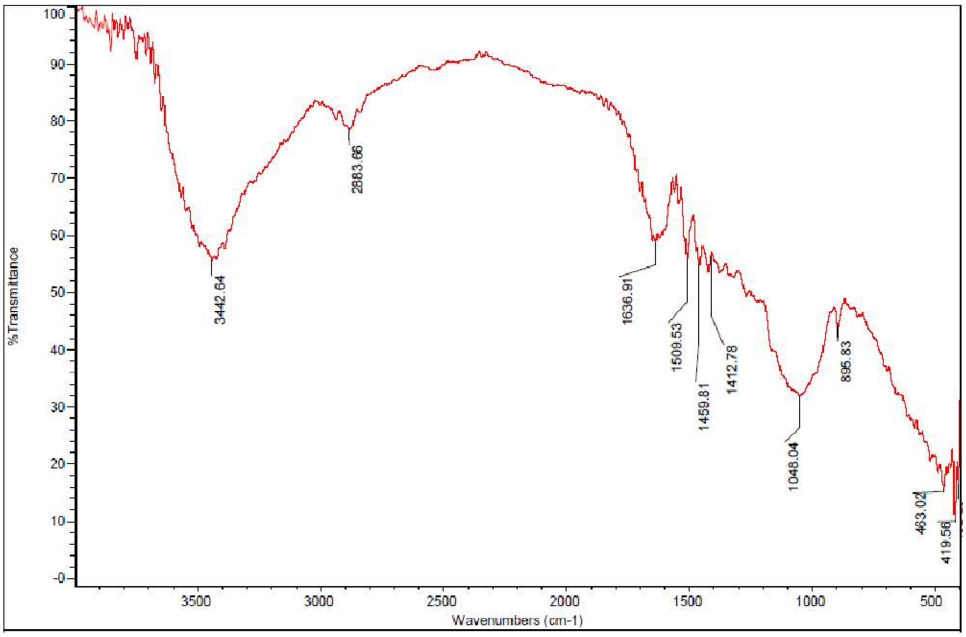


Fig:2.9 FTIR spectrum of alkali treated Areca fibre

A reduction in the broadening of the peak ranging from 3850 cm^{-1} to 3300 cm^{-1} due to hydroxyl group and hydrogen bonded -OH stretching vibration of cellulose which is observed at 3442.64 cm^{-1} in the treated areca fibre confirmed the chemical modification of areca fibres by alkali treatment.

The absorption at 2883.66 cm^{-1} is referred to the characteristic band for the C-H stretching vibration from CH and CH_2 in both celluloseand hemicelluloses components. After alkali treatment, hydrolysis occurs and breaks down the ester bond or ether bond, resulting in the absence of 1727.65 cm^{-1} peak in alkali treated areca fibres and this further confirmed the chemical modification.

The little peak at 1636.91cm^{-1} may be due to the presence of alkenes in the fibres. The peak at 1509.53 cm^{-1} is due to C=C stretching of aromatic ring of lignin and lignocelluloses. The little absorbance peaks at 1459.81 cm^{-1} and 1412.78 $cm^{-1}$are associated to the CH_2 symmetric bending in cellulose.

Alkali treatment of areca fibres resulted in the formation of Fibre–cell–O–Na groups between the cellulose molecular chains and hence there is absence of peak due to the alcoholic group of cellulose at 1377.86 cm^{-1} in the alkali treated areca fibres.

The peaks observed between 1100-1600 cm^{-1} in the untreated areca fibre shows the presence of hemicelluloses, lignin and pectin and the reduced intensity of these peaks in alkali treated areca fibre indicates the slight removal of hemicelluloses, lignin, pectin, wax and oil covering materials from the fibre.The absorption peak at 1048.04cm^{-1} is due to C-O stretching vibration of polysaccharides in cellulose.

The peak observed at 895.83 cm^{-1} is attributed to the presence of β-glycosidic linkage between the monosaccharide. Further, the absence of peak due toC-OH bending in cellulose at 536.22 cm^{-1} in the treated areca fibres confirmed the chemical modification of areca fibresby NaOH [40, 92, 107, 117 – 124].

2.7.3 Spectral Analysis of Potassium Permanganate Treated Areca Fibre

The FTIR spectrum of 0.5% potassium permanganate treated areca fibre is presented in Fig: 2.10.

A small peak at 3457.06 cm^{-1} in the potassium permanganate treated areca fibre is due to hydroxyl group and hydrogen bonded O-H stretching vibration of cellulose. The absorption peaks observed at 2937.57 cm^{-1}, 2884.91 cm^{-1} and 2831.33 cm^{-1} are the characteristic bands responsible for the C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses components.

After alkali pre-treatment and $KMnO_4$ treatment, hydrolysis occurs and breaks down the ester bond or ether bond resulting in the absence of 1727.65 cm^{-1} peak in the treated areca fibres and this in-turn confirmed the chemical modification of areca fibres by $KMnO_4$.

The little peak observed at 1661.30 cm^{-1} may be due to the presence of alkenes in the fibres. The absorbance at 1605.45 cm^{-1} is due to the presence of hemicelluloses in the treated fibre. The little peak at 1513.14 cm^{-1} is attributed to C=C stretching of aromatic ring of lignin and lignocelluloses. The absorbance at 1426.42 cm^{-1} is due to CH_2 symmetric bending in cellulose.

During permanganate treatment, highly reactive permanganate ions (Mn^{3+}) react with cellulose hydroxyl groups and forms cellulose manganate and hence there is absence of peak due to alcoholic group of cellulose at 1377.86 cm^{-1} in the treated areca fibres.

The absorption at 1272.81 cm^{-1} corresponds to C-O stretching vibration of ester linkage of acetyl group in hemicelluloses and pectin components. The peaks at 1172.30 cm^{-1} and 1127.36 cm^{-1} are due to anti-symmetrical deformation of C-O-C bands of polysaccharides in hemicelluloses.

The peaks observed between 1100-1600 cm^{-1} shows the presence of hemicelluloses, lignin and pectin in the untreated areca fibres and the reduced intensity of these peaks in $KMnO_4$ treated areca fibres indicates the slight removal of hemicelluloses, lignin, pectin, wax and oil covering materials from the areca fibres.

The absorption peak at 1043.68 cm^{-1} is due to C-O stretching vibration of polysaccharides in cellulose. The peak at 895.40 cm^{-1} is due to the presence of β-glycosidic linkages between the monosaccharide. Further, the absence of peak due to C-OH bending in cellulose at 536.22 cm^{-1} in the treated areca fibres confirmed the chemical modification by $KmnO_4$ [40, 92, 107, 117 – 124].

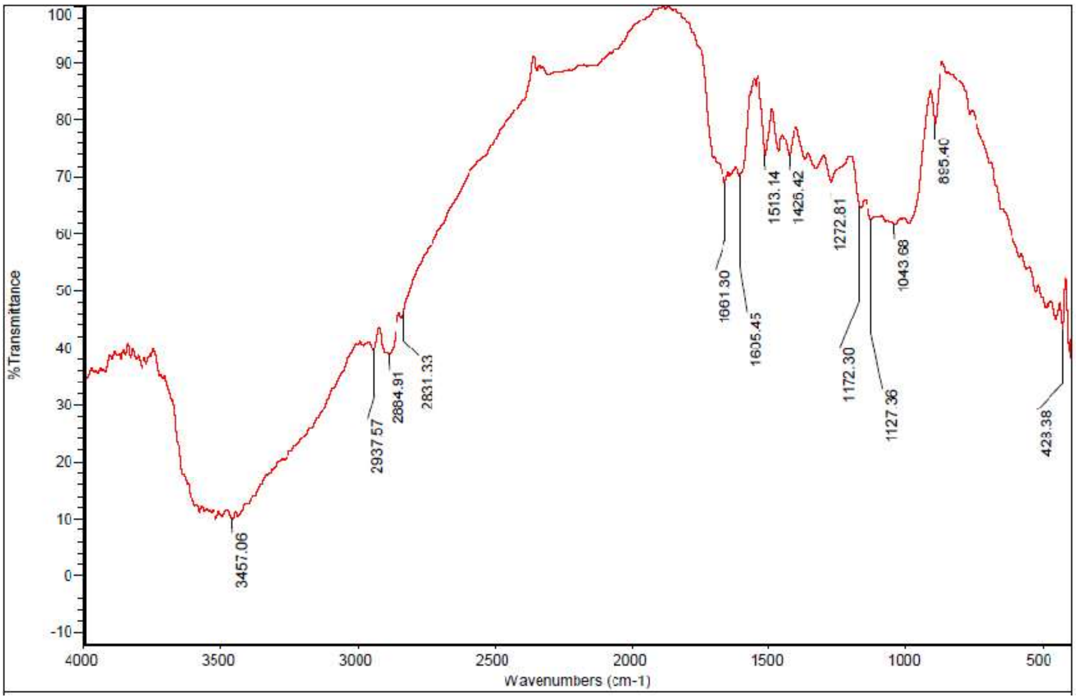


Fig:2.10 FTIR spectrum of permanganate treated Areca fibre

2.7.4 Spectral Analysis of Benzoyl Chloride Treated Areca Fibre

The FTIR spectrum of benzoyl chloride treated areca fibre is presented in Fig: 2.11.

A reduction in the broadening of the peak ranging from 3850 cm^{-1} to 3300 cm^{-1} due to hydroxyl group and hydrogen bonded O-H stretching vibration of cellulose which is observed at 3833.30 cm^{-1} and 3627.72 cm^{-1} in the treated areca fibres confirmed chemical modification of areca fibres by benzoyl chloride treatment.

The absorption observed at 2953.92 cm^{-1}, 2879.35 cm^{-1} and 2830.00 cm^{-1} are the characteristic bands responsible for the C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses components.

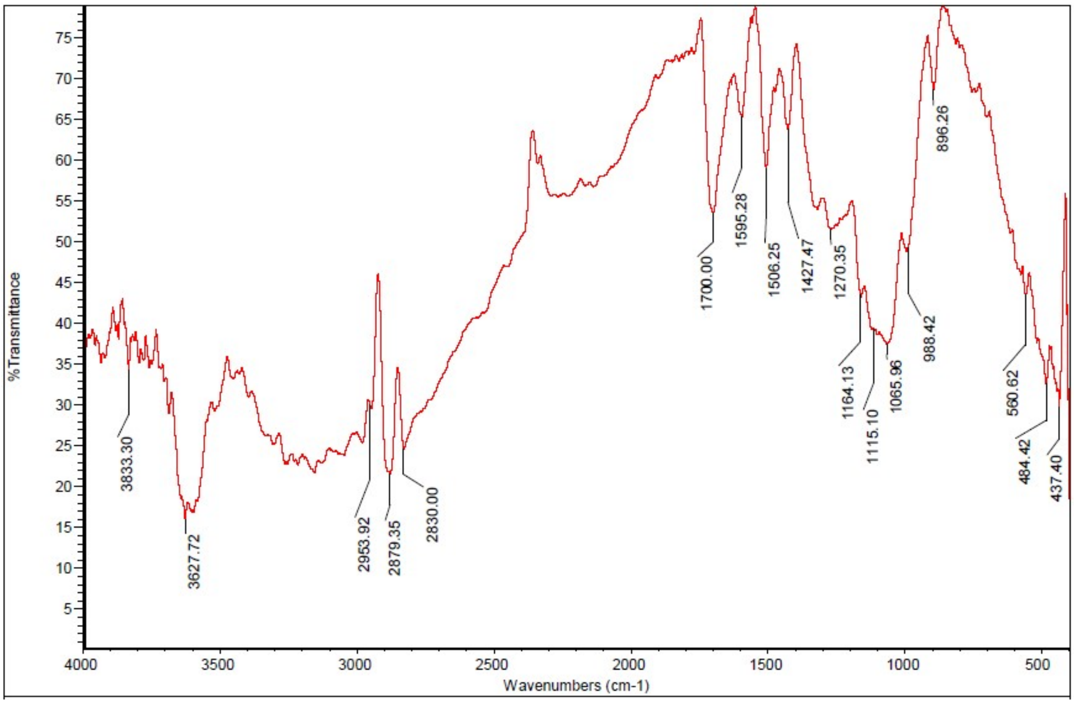


Fig:2.11 FTIR spectrum of benzoyl chloride treated Areca fibre

Alkali pre-treatment which is used to activate the hydroxyl groups of the areca fibres during benzoylation treatment breaks down the ester bond or ether bond, resulting in the absence of 1727.65 cm^{-1} peak in the benzoyl chloride treated areca fibres.

And also, during the chemical reaction of alkali pre-treated areca fibres with benzoyl chloride, there is a formation a new ester linkage between benzoyl chloride and the areca fibres occurs. The carbonyl group absorption at 1700 cm^{-1} confirmed the introduction of ester linkage in the benzoyl chloride treated areca fibres. Further, the absorbance at 1595.28 cm^{-1} which is due to C=C stretching of an introduced aromatic ring by benzoyl chloride in the treated areca fibres confirmed the chemical modification. The peak at 1506.25 cm^{-1} is attributed to the C=C stretching of aromatic ring of lignin and lignocelluloses.

There is absence of peak due to alcoholic group of cellulose at 1377.86 cm^{-1} in the treated areca fibres and this confirmed chemical modification of areca fibres by benzoyl chloride treatment.

The peak observed at 1270.35 cm^{-1} corresponds to C-O stretching vibration of ester linkage of acetyl group in hemicelluloses and pectin components. The absorption peaks at 1164.13 cm^{-1} and 1115.00 cm^{-1} are due to the anti-symmetrical deformation of C-O-C band of polysaccharides in hemicelluloses. The absorption peaks observed at 1065.96 cm^{-1} and 988.42 cm^{-1} are due to C-O stretching vibration and side group vibration of polysaccharides in hemicelluloses.

The peak observed at 896.26 cm^{-1} is attributed to the presence of β-glycosidic linkages between the monosaccharide. The very little absorbance at 560.62 cm^{-1} corresponds to the C-OH bending in cellulose of benzoylated areca fibres [40, 107, 117 – 124].

2.7.5 Spectral Analysis of Acrylic Acid Treated Areca Fibre

The FTIR spectrum of 5% acrylic acid treated areca fibre is presented in Fig:2.12.

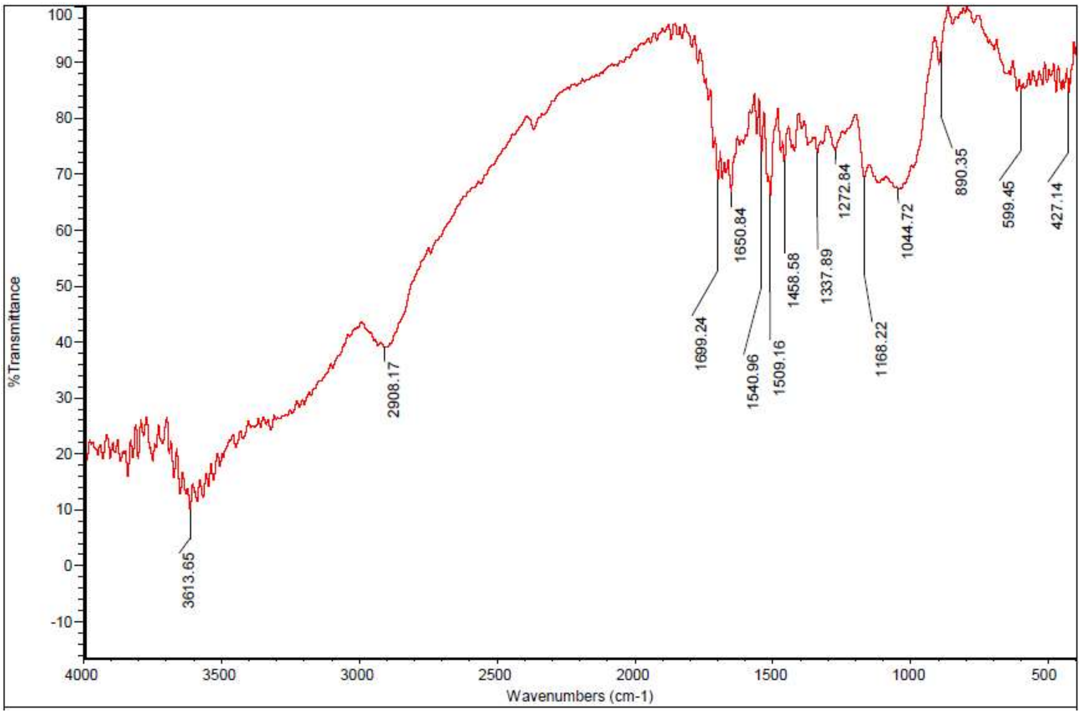


Fig:2.12 FTIR spectrum of acrylic acid treatedAreca fibre

A reduction in the broadening of the peak ranging from 3850 cm^{-1} to 3300 cm^{-1} due to hydroxyl group and hydrogen bonded O-H stretching vibration of cellulose which is observed at 3613.65 cm^{-1} confirmed chemical modification of fibres by acrylic acid treatment.

The absorption observed at 2908.17 cm^{-1} is the characteristic band responsible for the C-H stretching vibration from CH and CH_2 in both cellulose and hemicelluloses components.

Alkali pre-treatment which is used to activate the hydroxyl groups of areca fibres during acrylic acid treatment breaks down the ester bond or ether bond resulting in the absence of 1727.65 cm^{-1} peak in the treated areca fibres.

But during chemical reaction of alkali pre-treated areca fibres with acrylic acid, carboxylic acids present in acrylic acid form new ester linkages with the cellulose -OH groups of areca fibres. The carbonyl group absorption at 1699.24 cm^{-1} confirmed the introduction of ester linkage in the acrylated areca fibres. Further, the peak at 1650.84cm^{-1} shows the presence of alkenes that is introduced by acrylic acid to the treated areca fibre and this confirmed chemical modification.

The peaks at 1540.96 cm^{-1} and 1509.16 cm^{-1} are attributed to C=C stretching of aromatic ring of lignin and lignocelluloses. The peak at 1458.58 cm^{-1} is due to CH_2 symmetric bending in cellulose.

Further, the absence of peak due to alcoholic group of cellulose at 1377.86 cm^{-1} in the treated areca fibres confirmed chemical modification of areca fibres by acrylic acid.

The absorbance at 1337.89 cm^{-1} indicates the bending vibration of C-H and C-O groups of aromatic rings in polysaccharides. The peak observed at 1272.84 cm^{-1} corresponds to C-O stretching vibration of ester linkage of acetyl group in hemicelluloses and pectin components. The absorption peak observed at 1168.22 cm^{-1} is due to anti-symmetrical deformation of C-O-C band of polysaccharides in hemicelluloses. The absorption peak at 1044.72 cm^{-1} is due to C-O stretching vibration of polysaccharides in cellulose.

The little peak observed at 890.36 cm^{-1} is due to the presence of β-glycosidic linkages between the monosaccharide. Further, the very little absorbance at 599.45 cm^{-1} corresponds to the C-OH bending in cellulose of acrylic acid treated areca fibres [40, 107, 117 – 124].

2.7.6 Spectral Analysis of Acetic Anhydride Treated Areca Fibre

The FTIR spectrum of acetic anhydride treated areca fibre in presence of catalystperchloric acid is presented in Fig:2.13.

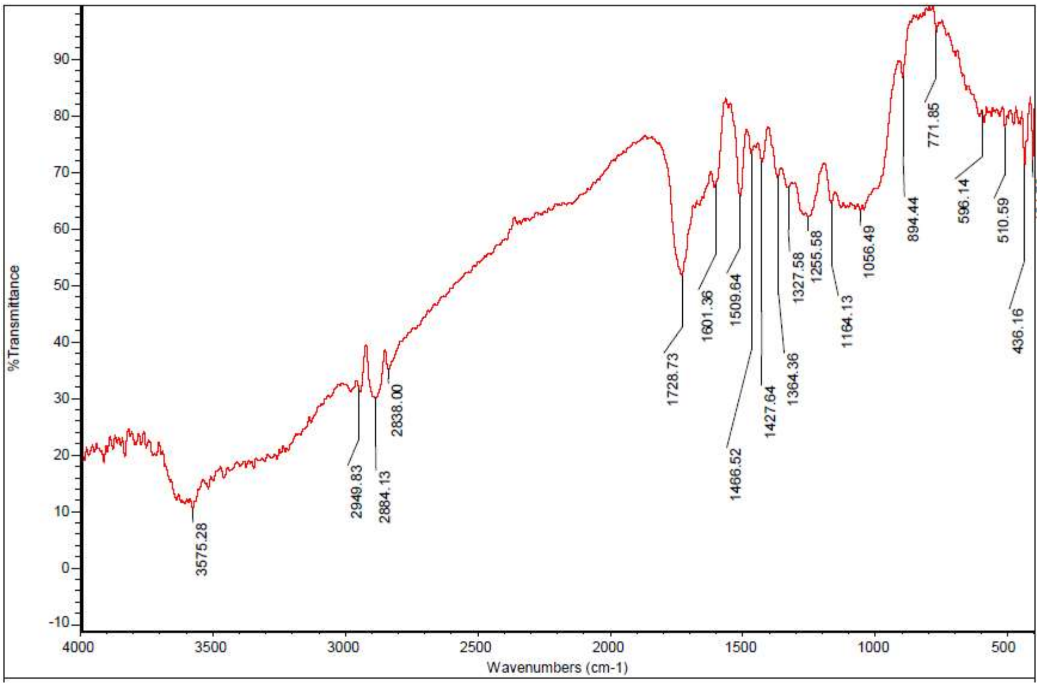


Fig:2.13 FTIR spectrum of acetic anhydride treated Areca fibre

A reduction in the broadening of the peak ranging from 3850 cm^{-1} to 3300 cm^{-1} due to hydroxyl group and hydrogen bonded O-H stretching vibration of cellulose which is observed at 3575.28 cm^{-1} confirmed chemical modification.

The absorption observed at 2949.83 cm^{-1}, 2884.13 cm^{-1}, 2838.00 cm^{-1} are the characteristic bands responsible for the C-H stretching vibration from CH and CH_2 in cellulose and hemicelluloses components.

Comparison of spectra of untreated areca fibres and the acetylated areca fibres showed that there is appearance of new absorption peak upon acetylation. The peak observed at 1728.73 cm^{-1} is attributed to C=O stretching vibration of carbonyl groups and it confirmed the formation of new acetyl groups in the cellulose. This observed peak is due to an esterification reaction which is resulteddue to the stretching vibration of C=O groups of ester linkages. The absorption in this region is attributed to both the C=O groups in acid and ester groups attached to the treated areca fibres.

If the $-COCH_3$ groupis in the form of acetic acid, then the stretching of C=O should have appeared lower than 1720 cm^{-1} in the case of diacids and in about 1760 cm^{-1} in case of mono acids. The absence of peak in the region of 1840 cm^{-1} to 1790 cm^{-1} of the spectrum of acetylated areca fibreindicates that acetylated product is free of un-reactive acetic anhydride. Absence of the peak at 1700 cm^{-1} for a carboxylic acid in the spectra of acetylated areca sample also denotes that the acetylated product is free of the acetic acid by-product.

The absorbance at 1601.36 cm^{-1} is due to the presence of hemicelluloses in the treated areca fibres. The peak at 1509.64 cm^{-1} is due to C=C stretching of aromatic ring of lignin and lignocelluloses. The absorbance at 1466.52 cm^{-1} and 1427.64 cm^{-1} are owing to CH_2 symmetric bending in cellulose.

Further, there is absence of peak due to the alcoholic group of cellulose at 1377.86 cm^{-1} in the acetylated areca fibres and thisalso confirmed chemical modification of areca fibres.

The peaks observed at 1364.36 cm^{-1} and 1327.58 cm^{-1} indicates the bending vibration of C-H and C-O groups of aromatic rings in polysaccharides. The emergence of new peak at 1255.58 cm^{-1}which corresponds to C-O stretching vibration of ester linkage of acetyl groups further confirmed that an esterification reaction is occurred.

The absorption peak at 1164.13 cm^{-1} is due to anti-symmetrical deformation of C-O-C band of polysaccharides in hemicelluloses. The absorption peak at 1056.49 cm^{-1} is due to C-O stretching vibration of polysaccharides in cellulose.

The peak observed at 894.44 cm^{-1} is attributed to the presence of β-glycosidic linkages between the monosaccharide. The peak observed at 771.85 cm^{-1} shows the presence of lignin in the treated areca fibres. Further, the very little absorbance at 596.14 cm^{-1} and 510.59 cm^{-1}

corresponds to the C-OH bending in cellulose of acetic anhydride treated areca fibres [40, 107, 117 – 125].

2.8 THERMAL STUDIES OF ARECA FIBRES BY TGA-DTG

The thermal stabilities of untreated and all chemically treated areca fibre were measured by using 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 nitrogen atmosphere using TGA-DTG sample carrier and TGA-DTG alumina crucible.

Thermal analysis is a highly important and very useful method to characterize any materials such as lignocellulosic fibres and thermoplastic or thermosetting polymer matrix.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.TGA measurements are usedto study the thermal stabilities of polymeric materials. Maximum decomposition rates for weight losses of components present in the natural fibres are shown by DTG curves [126-127].

The thermal degradation behaviour of untreated (AR1), 6% alkali treated (AR2), 0.5% permanganate treated (AR3), benzoylated (AR4), 5% acrylated (AR5) and acetylated (AR6) areca fibres are shown below.

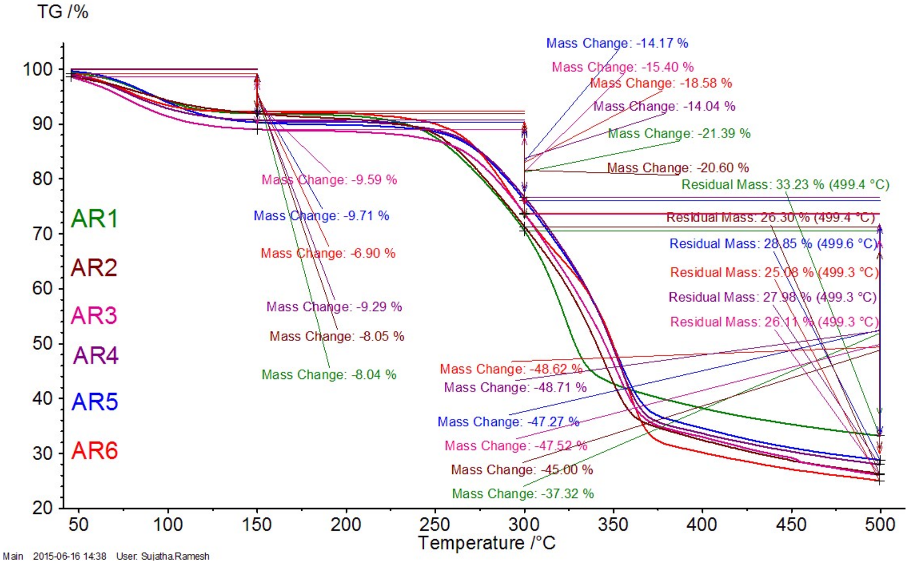


Fig:2.14 TGA curves of Areca fibres

AR1: Untreated; AR2: Alkali treated; AR3: Potassium permanganate treated; AR4: Benzoylated; AR5: Acrylated; AR6: Acetylated

The Derivative Thermogram curve of untreated (AR1), 6% alkali treated (AR2), 0.5% potassium permanganate treated (AR3), benzoyl chloride treated (AR4), 5% acrylic acid treated (AR5) and acetic anhydride treated (AR6) areca fibres are shown in Fig: 2.15.

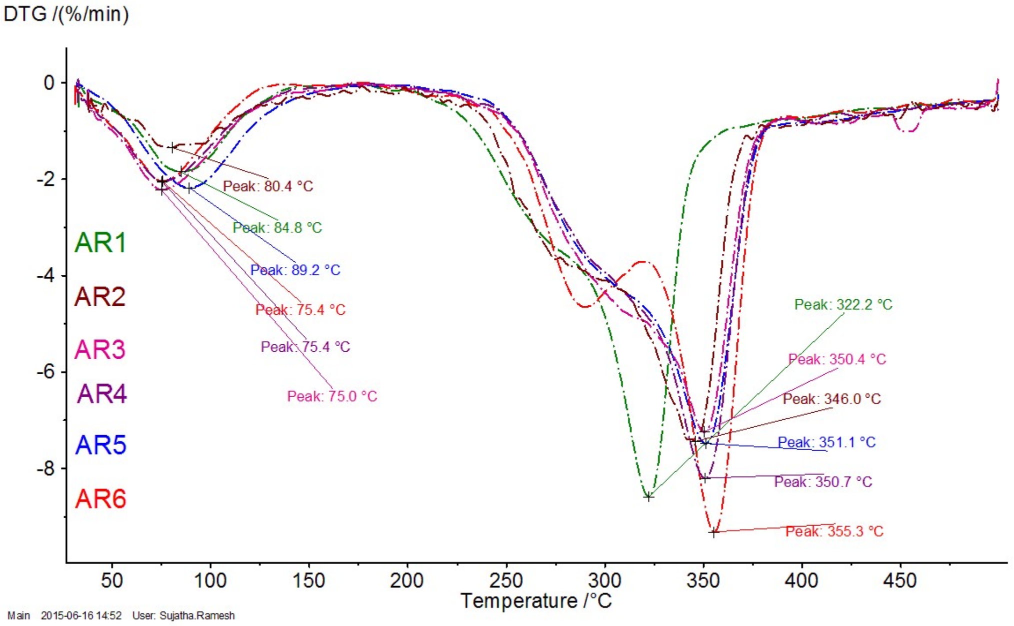


Fig:2.15 DTGcurves of Areca fibres

AR1: Untreated; AR2: Alkali treated; AR3: Potassium permanganate treated; AR4: Benzoylated; AR5: Acrylated; AR6: Acetylated

The thermal stability of untreated(AR1), 6% alkali treated (AR2), 0.5% permanganate treated (AR3), benzoylated (AR4), 5% acrylated (AR5) and acetylated (AR6) areca fibres are analyzed by using TGA curves and the results are presented in Table 2.4 and Table 2.5.

The thermal stability of untreated(AR1), 6% alkali treated (AR2), 0.5% permanganate treated (AR3), benzoylated (AR4), 5% acrylated (AR5) and acetylated (AR6) areca fibres are analyzed by using DTG curves and the corresponding results are presented in Table 2.6.

Table 2.4 TGA results of first stage and second stage degradation temperature of Areca fibres

Areca Fibres	1st stage degradation in TGA curve		2nd stage degradation in TGA curve	
	Temperature range T_1 °C	Weight loss %	Temperature range T_2 °C	Weight loss %
Untreated (AR1)	241.5 to 297.0	17.13	297.0 to 353.0	29.54
6% NaOH treated (AR2)	250.8 to 306.0	19.16	306.0 to 384.0	35.00
0.5% $KMnO_4$ treated (AR3)	259.0 to 332.5	28.47	332.5 to 382.5	23.21
Benzoyl chloride treated (AR4)	257.0 to 319.5	19.95	319.5 to 371.0	32.00
5% Acrylic acid treated (AR5)	252.0 to 309.5	16.27	309.5 to 380.0	35.83
Acetic anhydride treated (AR6)	251.0 to 320.0	24.11	320.0 to 369.0	32.00

Table 2.5 TGA results of decomposition temperature and weight loss percentage of Areca fibres

Areca Fibres	Decomposition temperature, °C in TGA curve at		Weight loss of areca fibres, % in TGA curve at			Residual mass % at 500 °C
	25% weight loss	50% weight loss	150 °C	300 °C	500 °C	
Untreated (AR1)	289.5	328.5	8.04	21.39	37.32	33.23
NaOH treated (AR2)	291.0	340.0	8.05	20.60	45.00	26.30
$KMnO_4$ treated (AR3)	297.0	345.0	9.59	15.40	47.52	26.11
Benzoylated (AR4)	304.0	349.0	9.29	14.04	48.71	27.98
Acrylated (AR5)	302.5	349.5	9.71	14.17	47.27	28.85
Acetylated (AR6)	297.0	349.5	6.90	18.58	48.62	25.08

Table 2.6 DTG results of Areca fibres

Areca Fibres	Decomposition temperature, °C in DTG curve at	
	First Peak	Second Peak
Untreated (AR1)	84.8	322.2
6% NaOH treated (AR2)	80.4	346.0
0.5% $KMnO_4$ treated (AR3)	75.0	350.4
Benzoyl chloride treated (AR4)	75.4	350.7
5% Acrylic acid treated (AR5)	89.2	351.1
Acetic anhydride treated (AR6)	75.4	355.3

2.8.1 Thermal Analysis of Untreated Areca Fibres

In accordance with other studies on natural lignocellulosic fibres [120, 128-130], the TGA curve of untreated areca fibres (AR1 in Fig: 2.14) shows three weight loss steps and their decomposition occurs in two main stages.

The initial weight loss, 10.94% observed aroundRT (room temperature) to 241.5 °C is attributed to the vaporization of moisture and decomposition of volatile extractives from the fibres. Above this temperature, it can be observed that thethermal stability is gradually decreasing and the degradation of natural areca fibres occurs.

The first stage degradation temperature, T_1 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_2 around 297.0 °C to 353.0 °C corresponds to the degradation of α-cellulose and lignin present in the areca fibres and the weight loss in this temperature range is 29.54% [130].

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 [131], occurs gradually within the whole temperature range around 241.5 °C to 500 °C [119].

The decomposition temperature corresponding to 25% and 50% weight loss of untreated areca fibres are 289.5 °C and 328.5 °C respectively. Thermally degraded mass change percentage of untreated areca fibres 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 fibres 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 [132].

These results are confirmed by DTG curve of untreated areca fibres (AR1 in Fig: 2.15) 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 fibres and the second peak observed at 322.2 °C confirms the maximum decomposition rates for weight losses of cellulose present in the untreated areca fibres [116, 133].

2.8.2 Thermal Analysis of Alkali Treated Areca Fibres

Similarly, the TGA curve of 6% alkali treated areca fibres (AR2 in Fig: 2.14) 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 moisture and decomposition of volatile extractivesfrom the alkali treated areca fibres. Above this temperature, the thermal stability is gradually decreasing and the degradation of alkali treated areca fibres 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 α-cellulose and lignin present in the fibre 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 fibres are 291.0 °C and 340.0 °C respectively. Thermally degraded mass change percentage of alkali treated areca fibres 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 fibre consist of carbonaceous residues with weight percentage of 26.30% at 499.4 °C [119, 130-132].

These results are confirmed by DTG curve of 6% alkali treated areca fibres (AR2 in Fig: 2.15). The small first peak observed at 80.4 °C represents the evaporation of water from the treated areca fibres and the second peak observed at 346.0 °C confirms the maximum decomposition rates for weight losses of cellulose present in the alkali treated areca fibres [116, 133].

Alkali treatment of areca fibres 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 [34, 40, 61, 92, 95, 102-107].

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

2.8.3 Thermal Analysis of Permanganate Treated Areca Fibres

The TGA curve of 0.5% $KMnO_4$ treated areca fibres (AR3 in Fig: 2.14) also shows three weight loss steps and their decomposition occurs in two main stages.

Theinitial weight loss, 13.97% observed around RT to 259.0 ^oC is attributed to the vaporization of moisture and decomposition of volatile extractives from the permanganate treated areca fibres.Above this temperature, the thermal stability is gradually decreasing and the degradation of permanganate treated areca fibres occurs.

The first stage degradation temperature, T_1 around 259.0 ^oC to 332.5 ^oC 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 ^oC to 382.5 ^oC corresponds to the degradation of α-cellulose and lignin present in the permanganate treated areca fibres and the weight loss corresponding to this temperature range is 23.21%. The weight loss, 8.24% observed after 382.5 ^oC up to 500 ^oC is due to the degradation of lignin. The decomposition of lignin occurs slowly within the whole temperature range around 259.0 ^oC to 500 ^oC.

The decomposition temperature corresponding to 25% and 50% weight loss of permanganate treated areca fibres are 297.0 ^oC and 345.0 ^oC respectively. Thermally degraded mass change percentage of $KMnO_4$ treated areca fibres at 150 ^oC, 300 ^oC and 500 ^oC are 9.59%, 15.40% and 47.52% respectively.

In an inert atmosphere, the final products of degradation of potassium permanganate treated lignocellulosic areca fibres consist of carbonaceous residual weight percentage of 26.11% at 499.3 ^oC [119, 130-132].

These results are confirmed by DTG curve of 0.5% potassium permanganate treated areca fibres (AR3 in Fig: 2.15). 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 $KMnO_4$ treated areca fibres [116, 133].

In potassium permanganate treatment, cellulose-manganate is formed by the reaction of areca fibres with highly reactive permanganate ions and this imparts greater strength to the treated areca fibres. Permanganate ions also reacts with lignin constituents and carve the areca fibre surface and reduced the certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials [34, 40, 67, 92, 95, 102-103, 108-110].

As a result, in TGA, the decomposition temperature corresponding to firststage as well as the second stage degradation of permanganate treated areca fibres is increased, the residual mass percentage left after the degradation is decreased and there is increase in decomposition temperature corresponding to 25% and 50% weight loss of the $KMnO_4$ treated areca fibres when compared with that of untreated areca fibres. And also, the thermally degraded mass change percentage of permanganate treated areca fibres at 300 °C is lower and at 500 °C is higher than that of untreated areca fibres. Further, the main second peak decomposition temperature of potassium permanganate treated areca fibres in DTG curve is higher than that of untreated areca fibres. These results confirmed the improved thermal stability for $KMnO_4$ treated areca fibres.

2.8.4 Thermal Analysis of Benzoyl Chloride Treated Areca Fibres

The TGA curve of benzoyl chloride treated areca fibres (AR4 in Fig: 2.14) also shows three weight loss steps and their decomposition occurs in two main stages similar to that of untreated areca fibres.

The initial weight loss, 11.80% observed around RT to 257.0 °C is attributed to the vaporization of moisture and decomposition of volatile extractives from the benzoylated areca fibres. Above this temperature, it can be seen that the thermal stability is gradually decreasing and the degradation of benzoylated areca fibres 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 α-cellulose and lignin present in the treated areca fibres 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 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 benzoylated areca fibres are304.0 °C and 349.0 °C respectively. Thermally degraded mass change percentage of benzoyl chloride treated areca fibres 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 fibres consist of carbonaceous residual weight percentage of 27.98% at 499.3 °C [119, 130-132].

These results are confirmed by DTG curve of benzoyl chloride treated areca fibres (AR4 in Fig: 2.15). 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 fibres [116, 133].

In benzoyl chloride treatment, alkali pre-treatment which was used to activate the hydroxyl groups of the areca fibres reduced the certain portion of hemicelluloses, lignin, pectin, wax and oil covering materials from the fibres. During the chemical reaction of alkali pre-treated areca fibres with benzoyl chloride, there is a formation of new ester linkage between benzoyl chloride and areca fibres and benzoyl groups are attached on to the cellulose backbone and a rough surface is produced [34, 40, 57, 61, 95, 102-103, 105, 111].

Due to this, in TGA, decomposition temperature corresponding to first stage as well as the second stage degradation of benzoyl chloride treated areca fibres is increased and the residual mass percentage left after the degradation is decreased and there is increase in decomposition temperatures corresponding to 25% and 50% weight loss of the benzoyl chloride treated areca fibres when compared with that of untreated areca fibres. And also, the thermally degraded mass change percentage of benzoyl chloride treated areca fibres at 300 ^{o}C is lower and at 500 ^{o}C is higher than that of untreated areca fibres. Further, the main second peak decomposition temperature in DTG curve of benzoyl chloride treated areca fibres is higher than that of untreated areca fibres. These results confirmed the improved thermal stability for benzoyl chloride treated areca fibres.

2.8.5 Thermal Analysis of Acrylic Acid Treated Areca Fibres

According to other studies on lignocellulosic fibres, the TGA curve of 5% acrylic acid treated areca fibres (AR5 in Fig: 2.14) 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 ^{o}C is attributed to the vaporization of moisture and decomposition of volatile extractives from the acrylic acid treated areca fibres. Above this temperature, it can be observed that the thermal stability is gradually decreasing and the degradation of acrylic acid treated areca fibres occurs.

The first stage degradation temperature, T_1 around 252.0 ^{o}C to 309.5 ^{o}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 ^{o}C to 380.0 ^{o}C corresponds to the degradation of α-cellulose and lignin present in the acrylic acid treated areca fibres 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 fibres are 302.5 °C and 349.5 °C respectively. Thermally degraded mass change percentage of acrylic acid treated areca fibres 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 fibres consist of carbonaceous residual weight percentage of 28.85% at 499.6 °C [119, 130-132].

These results are confirmed by DTG curve of 5% acrylic acid treated areca fibres (AR5 in Fig: 2.15). The small first peak observed at 89.2 °C represents the evaporation of water from the acrylic acid areca fibres and the second peak observed at 351.1 °C confirms the maximum decomposition rates for weight losses of cellulose present in the acrylic acid treated areca fibres [116, 133].

In this chemical treatment, the carboxylic acid present in acrylic acid forms ester linkages with the cellulose hydroxyl groups and this ester groups are introduced into the polymer backbone of the chemically treated areca fibres. Acrylic acid treatment removed most of the hemicelluloses and lignin and produced large number of pits on the acrylated areca fibre surface [34, 40, 95, 102-103, 112-113].

So, in TGA, the decomposition temperature corresponding to first stage degradation as well as the second stage degradation of acrylic acid treated areca fibres is increased and the residual mass percentage left after the degradation is decreased and there is increase in decomposition temperature corresponding to 25% and 50% weight loss of the acrylic acidtreatedareca fibres when compared with that of untreated areca fibres. And also, the thermally degraded mass change percentage of acrylated areca fibres at 300 °C is lower and at 500 °C is higher than that of untreated areca fibres. Further, the main second peak decomposition temperature in DTG curve of acrylic acid treated areca fibres is higher than that of untreated areca fibres. Hence, acrylic acid treatment resulted in improved thermal stability for the treated areca fibres.

2.8.6 Thermal Analysis of Acetic Anhydride Treated Areca Fibres

The TGA curve of acetic anhydride treated areca fibres (AR6 in Fig: 2.14) shows three weight loss steps and their decomposition occurs in two main stages like that of untreated areca fibres.

The initial weight loss, 10.04% observed between RT and 251.0 °C is due to the vaporization of moisture and decomposition of volatile extractives from the acetylated areca fibres. Above this temperature, the thermal stability is slowly decreasing and the degradation of acetylated areca fibres 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 α-cellulose and lignin present in the acetic anhydride treated areca fibres 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 fibres are 297.0 °C and 349.5 °C respectively. Thermally degraded mass change percentage of acetic anhydride treated areca fibres 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 fibres consist of carbonaceous residual weight percentage of 25.08% at 499.3 ^{o}C [119, 130-132].

These results are confirmed by DTG curve of acetic anhydride treated areca fibres (AR6 in Fig: 2.15). The small first peak at 75.4 ^{o}C corresponds to the evaporation of water from the acetylated areca fibres and the second peak at 355.3 ^{o}C confirms the maximum decomposition rates for weight losses of cellulose present in the acetic anhydride treated areca fibres [116, 133].

Upon acetylation treatment, acetyl groups are attached on to the cellulose backbone of treated areca fibres through ester linkages. The wax and cuticle present in the surface is removed by the interaction with acetyl groups and the fibre surface becomes smoother and also it causes plasticization of cellulosic fibres. The fibrillation is also found to arise as the binding materials are removed and some micro-pores appeared in the acetylated areca fibres [40, 95, 102-103, 112-113].

As a result, in TGA, decomposition temperature corresponding to first stage as well as the second stage degradation of acetylated areca fibres is increased and the residual mass percentage left after the degradation is decreased and there is increase in decomposition temperature corresponding to 25% and 50% weight loss of the acetylated areca fibres when compared with that of untreated areca fibres. And also, the thermally degraded mass change percentage of acetylated areca fibres at 300 ^{o}C is lower and at 500 ^{o}C is higher than that of untreated areca fibres. Further, the main second peak decomposition temperature in DTG curve of acetylated areca fibres is higher than that of untreated areca fibres. Hence, this treatment resulted in improved thermal stability for acetylated areca fibres.

The TGA results of untreated and all chemically treated areca fibres revealed that the untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated, 5% acrylic acid treated and acetic anhydride treated areca fibres 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 all chemically treated areca fibres revealed that the temperature of maximum decomposition for untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated, 5% acrylic acid treated and acetic anhydride treated areca fibres are 322.2 °C, 346.0 °C 350.4 °C, 350.7 °C, 351.1 °C and 355.3 °C respectively.

Table 2.7 Decomposition temperatures for selected natural fibres

Natural fibre	Temperature of initial decomposition T_o (°C)	Temperature of maximum decomposition T_p (°C)
Jute	205	283
Okra	220	359
Hemp	250	390
Curaua	230	335
Kenaf	219	284

In conclusion, it is important to note that, this result is in good agreement with the decomposition temperature values of many vegetable fibres as shown in Table 2.7which is reported in literature [115, 134-136] for selected natural fibres.

2.9 X-RAY DIFFRACTION STUDIES OF ARECA FIBRES

X-ray diffraction studies of untreated and all chemically treated areca fibres in powdered form were performed under ambient condition on X-Ray Diffractometer using Cu-Kα radiation, run at 40 KV and 30 mA using Nickel filter on rotation between 3 ° to 60 ° at 2 – Theta – Scale to assess the crystallinity values of all areca fibres.

X-ray diffraction is an adaptable and non-destructive technique that gives detailed information about the crystallographic structure of the material. In X-Ray crystallography, a beam of X-rays strikes a crystal and diffracts into many precise directions and from the intensities of the diffracted beam, the crystallinity of the material can be assessed.

The influence of chemical treatments on the fibre crystallinity of areca fibres is analyzed as follows. The counter reading of peak intensity at 22° represents the crystalline material and the peak intensity at 18 ° corresponds to the amorphous material in cellulose [137-138]. Percentage crystallinity (%Cr) [139] and crystallinity index (C.I.) [140-141] of untreated and all chemically treated areca fibres is calculated by using the formula given in equation (2.2) and equation (2.3) respectively where I_{22} and I_{18} are the crystalline and amorphous intensities at 2–Theta–Scale close to 22° and 18° correspondingly.

$$\%Cr. = \frac{I_{22}}{(I_{22} + I_{18})} \; x \; 100 - - - - - - - - (2.2)$$

$$\mathrm{C.I.} = \frac{(I_{22} - I_{18})}{I_{22}} \; - - - - - - - - \; (2.3)$$

The effect of chemical modification of lignocellulosic materials on their crystallinity has been investigated by various researchers [142]. 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 fibres means poor order of cellulose crystal to the fibre axis during chemical treatments [143]. Several researchers reported that chemical treatments reduced theproportion of crystalline material present in the plant fibres [144].

2.9.1 Crystallinityof Untreated Areca Fibres

X-ray diffraction patterns of untreated areca fibres are shown in Fig: 2.16.

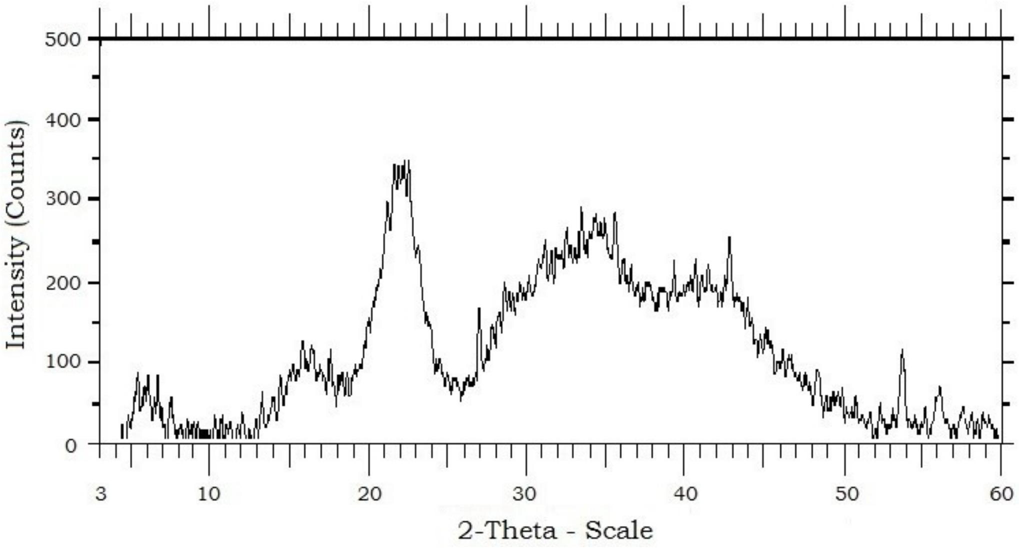


Fig: 2.16 XRD patterns of untreated Areca fibres

X-ray diffraction patterns of untreated areca fibres at 2θ scale gave peaks close to 22° and 18° with relative crystalline and amorphous intensities of 335 and 79.1 respectively. Percentage crystallinity (*%Cr*) and crystallinity index (*C.I.*) values of untreated areca fibres are calculated by the above said formula and are found to be 80.90 and 0.76 respectively.

2.9.2 Crystallinityof Alkali Treated Areca Fibres

X-ray diffraction patterns of 6% alkali treated areca fibres are shown in Fig: 2.17.

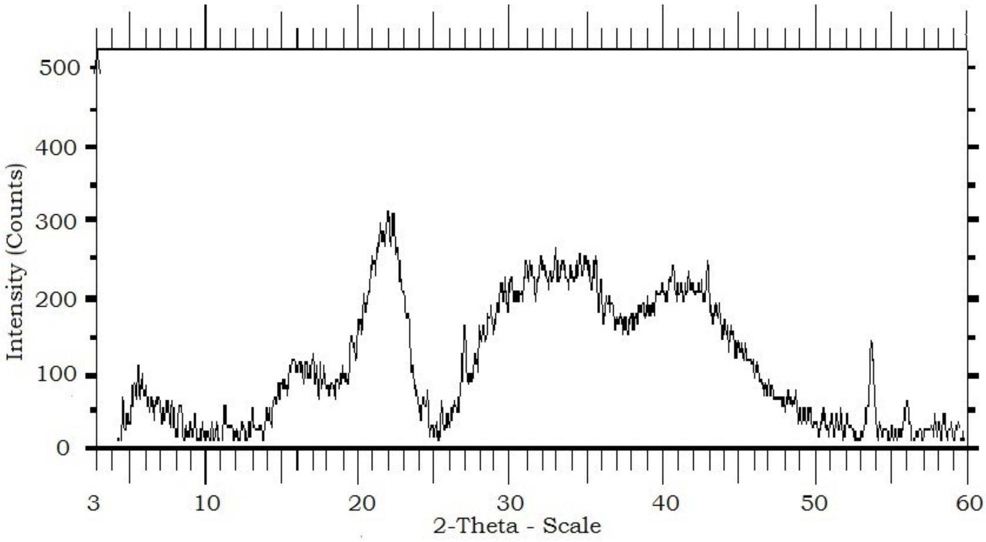


Fig:2.17XRD patterns of alkali treated Areca fibres

X-ray diffraction patterns of alkali treated areca fibres at 2θ scale gave peaks close to 22° and 18° with relative crystalline and amorphous intensities of 302 and 74.5 respectively. Percentage crystallinity (*%Cr*)and crystallinity index (*C.I.*)values of alkali treated areca fibres are calculated as 80.21 and 0.75 respectively andthese values are little less than that of untreated areca fibres.

This little decrease in crystallinity is due to the swelling of treated areca fibres and partialremoval of cementing materials from the areca fibres which in-turn resulted in a slight disturbance of cellulose chain arrangement [145-146].

2.9.3 Crystallinityof Potassium Permanganate Treated Areca Fibres

X-ray diffraction patterns of 0.5% potassium permanganate treated areca fibres are shown in Fig: 2.18.

X-ray diffraction patterns of $KMnO_4$ treated areca fibres at 2θ scale gave peaks close to 22° and 18° with relative crystalline and amorphous intensities of 1106 and 449 respectively. Percentage crystallinity (*%Cr*) and crystallinity index (*C.I.*) values of potassium permanganate treated areca fibres are determined as 71.13 and 0.59 respectively andthese values are less than that of untreated areca fibres.

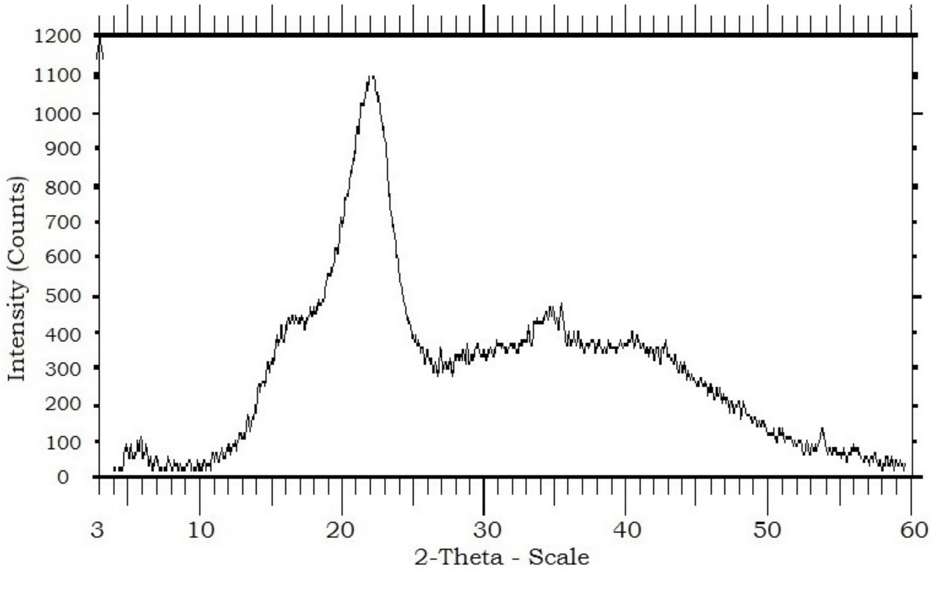


Fig:2.18 XRD patterns of permanganate treated Areca fibres

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

2.9.4 Crystallinityof Benzoyl Chloride Treated Areca Fibres

X-ray diffraction patterns of benzoyl chloride treated areca fibres are shown in Fig: 2.19.

X-Ray Diffraction patterns of benzoyl chloride treated areca fibres at 2θ scale gave peaks close to 22° and 18° with relative crystalline and amorphous intensities of 1016 and 367 respectively. Percentage crystallinity (*%Cr)* and crystallinity index (*C.I.*) values of benzoyl chloride treated areca fibres are calculated as 73.46 and 0.64 respectively andthese values are less than that of untreated areca fibres.

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

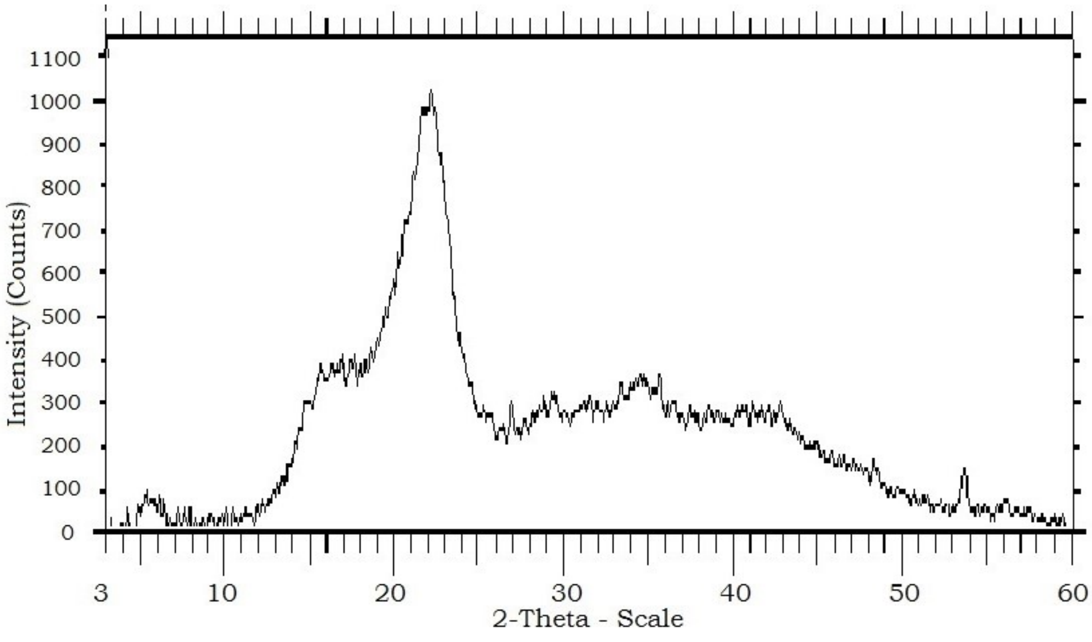


Fig:2.19 XRD patterns of benzoyl chloride treated Areca fibres

2.9.5 Crystallinityof Acrylic Acid Treated Areca Fibres

X-ray diffraction patterns of 5% acrylic acid treated areca fibres are shown in Fig: 2.20.

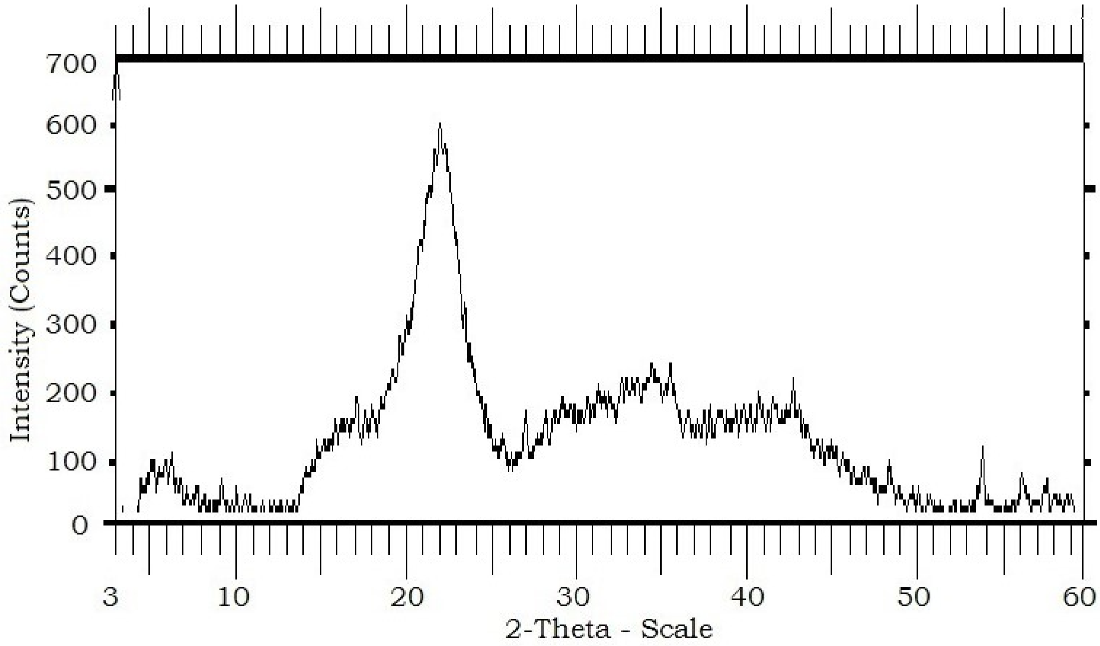


Fig:2.20 XRD patterns of acrylic acid treated Areca fibres

X-Ray Diffraction patterns of acrylic acid treated areca fibres at 2θ scale gave peaks close to 22° and 18° with relative crystalline and amorphous intensities of 585 and 162 respectively. Percentage crystallinity (*%Cr)* and crystallinity index (*C.I.*) values of acrylic acid treated areca fibres are found to be 78.31 and 0.72 respectively and these values are less than that of untreated areca fibres.

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

2.9.6 Crystallinityof Acetic Anhydride Treated Areca Fibres

X-ray diffraction patterns of acetic anhydride treated areca fibres are shown in Fig: 2.21.

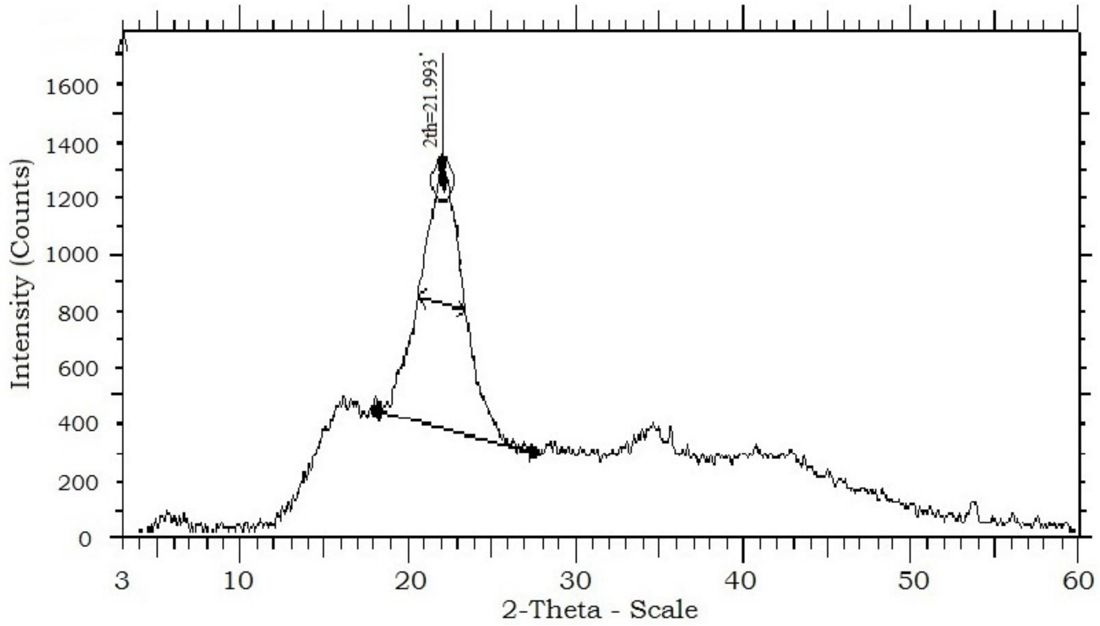


Fig:2.21 XRD patterns of acetic anhydride treated areca fibres

X-Ray Diffraction patterns of acetylated areca fibres at 2θ scale gave peaks close to 22^{o} and 18^{o} with relative crystalline and amorphous intensities of 1269 and 485 respectively. Broadening in 2θ = 21.993^{o} peak is also observed. Percentage crystallinity (*%Cr)* and crystallinity index (*C.I.*) values ofacetylated areca fibres are calculated as 72.35 and 0.62 respectively and are less than that of untreated fibres.

Here, the wax and cuticle present in the areca fibre surface is separated by the interaction with acetyl groups. Acetic anhydride substitute the cell wall hydroxyl groups with bulky acetyl groups and causes plasticization of cellulosic areca fibres.Thisin-turn destroyed the orderly packing of cellulose chains to a certain extent and thereby decreasedthe crystallinity of acetylatedareca fibres.

Table 2.8 shows the summarized XRD analysis results of untreated and all chemically treated areca fibres.

Table 2.8 XRD analysis results of Areca fibres

Areca fibre	Crystalline Intensity I_{22} (at 2θScale)	Amorphous Intensity I_{18} (at 2θ Scale)	*%Cr.*	*C.I.*
Untreated	335	79.1	80.90	0.76
6% Alkali treated	302	74.5	80.21	0.75
0.5% Potassium permanganate treated	1106	449	71.13	0.59
Benzoyl chloride treated	1016	367	73.46	0.64
5% Acrylic acid treated	585	162	78.31	0.72
Acetic anhydride treated	1269	485	72.35	0.62

The tensile strength values of any natural lignocellulosic fibres are based on the crystallinity present in the natural fibres. If crystallinity decreases then the tensile strength of natural fibres also decreases accordingly [147]. Table 2.2 shows the tensile strength values of untreated and all chemically treated areca fibres[92].

Surface modification of natural areca fibres resulted in little decrease of percentage crystallinity and crystallinity index values as shown in Table 2.8. This observed little decrease in crystallinity is in good agreement with the observed little decrease in tensile strength values as shown in Table 2.2 for all chemically treated areca fibres.

2.10 SEM IMAGE ANALYSIS OF ARECA FIBRES

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

2.10.1 SEM Image Analysis of Untreated Areca Fibre

The SEM image of untreated areca fibre is shown in Fig:2.22.

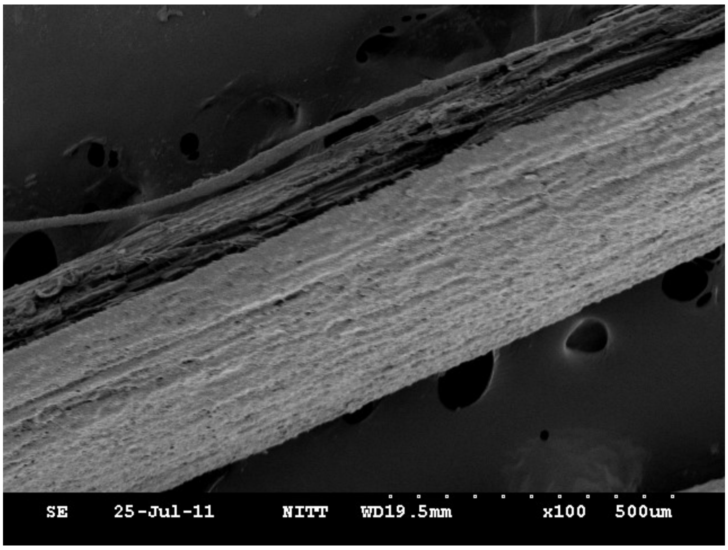


Fig: 2.22 SEM image of untreated Areca fibre

It clearly presents a network structure in which the fibrils are bound together by hemicelluloses and lignin. It also 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 theareca fibres[40, 92, 103].

2.10.2 SEM Image Analysis of Alkali Treated Areca Fibre

The SEM image of 6% alkali treated areca fibre is shown in Fig:2.23.

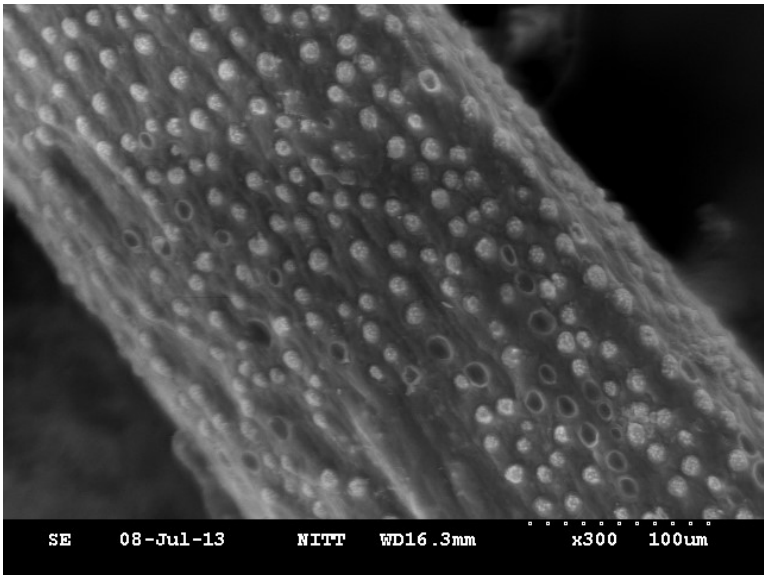


Fig: 2.23 SEM image of alkali treated Areca fibre

It clearly shows a large number of pinholes or pits on the fibre surface which are due to the removal of fatty deposits from the fibre. Alkali treatment of areca fibres removes waxy epidermal tissue, adhesive pectin and hemicelluloses. A comparison between the untreated and alkali treated areca fibres revealed topographical changes because of the removal of low molecular weight compounds resulting in the formation of a rough surface.This evidenced the chemical modification of areca fibres by NaOH. Further, this alkalitreatment resulted in effective fibre surface area available for good adhesion with the polymer matrix [40, 103-104].

2.10.3 SEM Image Analysis of Potassium Permanganate Treated Areca Fibre

SEM image of 0.5% potassium permanganate treated areca fibre is shown in Fig:2.24.

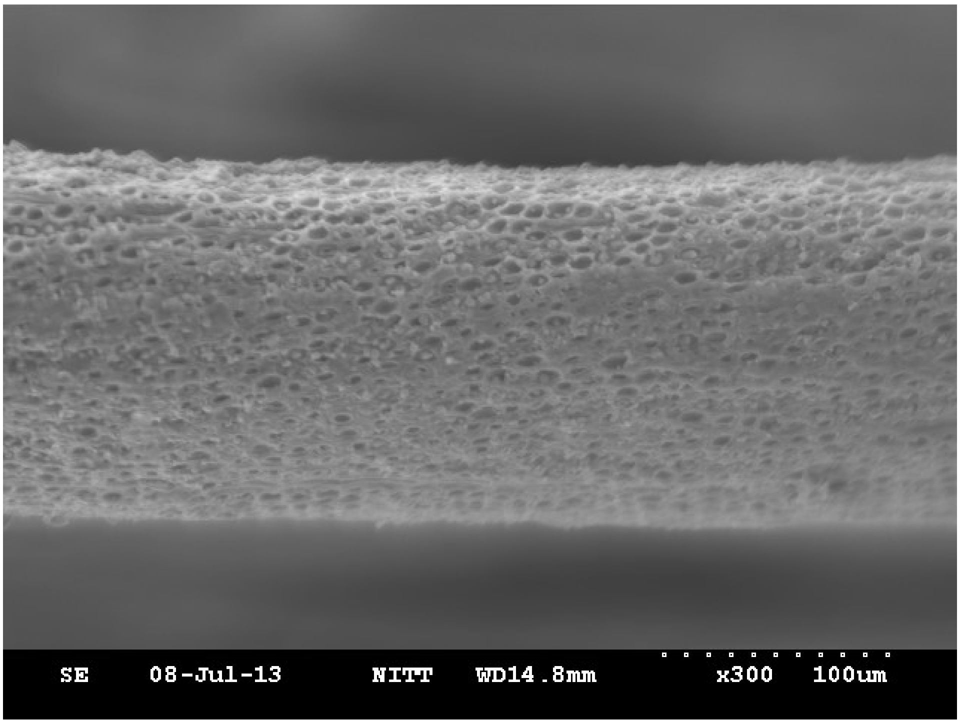


Fig: 2.24 SEM image of permanganate treated Areca fibre

Permanganate ions react with the lignin constituents(-OH groups) and carve the fibre surface. As a result of permanganate treatment, areca fibre surface became physically rough and thus provides effective fibre surface area for good adhesion with the matrix.This can be evidenced from the SEM micrograph. The topographical changes observed after the treatment evidenced the chemical modification of areca fibres by $KMnO_4$ [40, 92, 103, 109].

2.10.4 SEM Image Analysis of Benzoyl Chloride Treated Areca Fibre

The SEM image of benzoyl chloride treated areca fibre is shown in Fig:2.25.

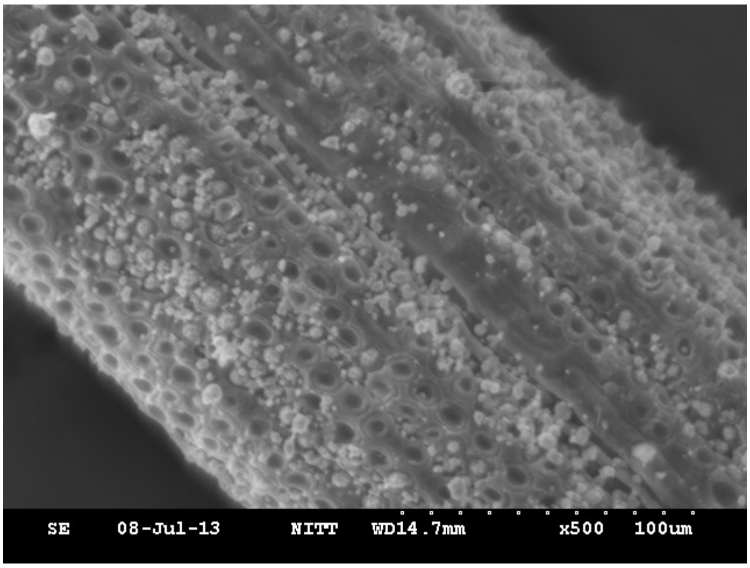


Fig: 2.25 SEM image of benzoylated Areca fibre

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 areca fibresurface by the reaction of benzoyl chloride. Hence, benzoyl chloride treatment provides effective fibre surface area for good adhesion with the polymer matrix. And also, the topographical changes observed after thebenzoylation treatment evidenced the chemical modification of areca fibres by benzoyl chloride [40, 103, 111].

2.10.5 SEM Image Analysis of Acrylic Acid Treated Areca Fibre

The SEM image of 5% acrylic acid treated areca fibre is shown in Fig:2.26.

It clearly shows a large number of pits on the areca fibre surface. Acrylic acid treatment removes most of the hemicelluloses, lignin and destroys the cellulose structure. There is replacement of hydrophilic hydroxyl groups by hydrophobic ester groups. Hence, this acrylic acid treatment increases effective fibre surface area available for good adhesion with the polymer matrix. The topographical changes observed after this acrylation treatment evidenced the chemical modification of areca fibres by acrylic acid [34, 40, 103].

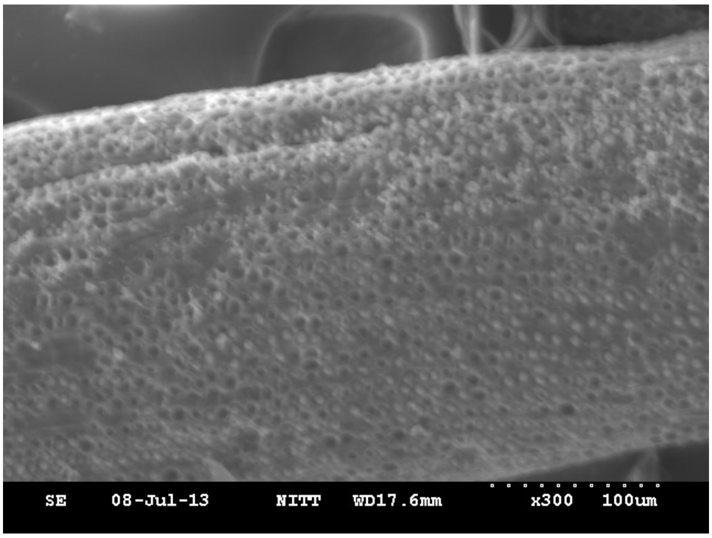


Fig: 2.26 SEM image of acrylated Areca fibre

2.10.6 SEM Image Analysis of Acetic Anhydride Treated Areca Fibre

The SEM image of acetylated areca fibre is shown in Fig:2.27.

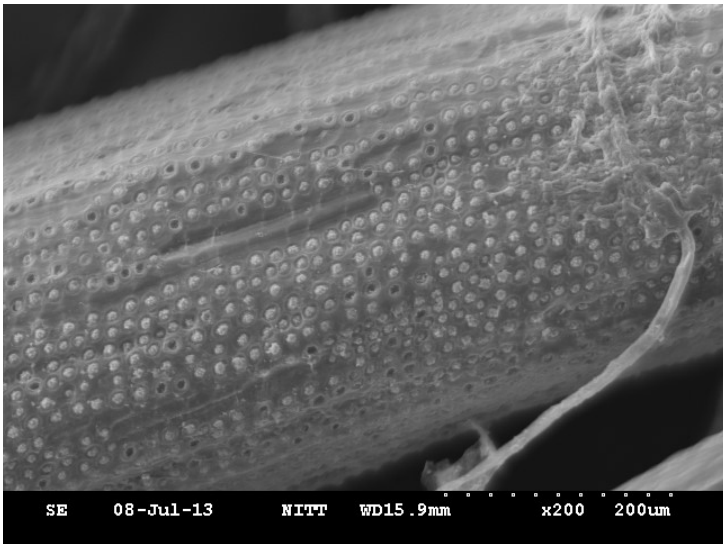


Fig: 2.27 SEM image of acetylated Areca fibre

Upon acetic anhydridetreatment, the wax and cuticle present in the areca fibre surface is removed by the interaction with acetyl groups. Further, acetylation of areca fibres causes plasticization of cellulosic fibres and the areca fibre surface became smoother. The fibrillation is also found to arise as the binding materials are removed and some micro-pores appeared in the acetic anhydride treated areca fibres. Surface topographical changes observed after acetylation treatment evidenced the chemical modification of areca fibres by acetic anhydride [40, 103, 112-113].

2.11WATER ABSORPTION STUDIES OF ARECA FIBRES

Natural Lignocellulosic fibres are three-dimensional, polymeric composites primarily made up of cellulose, hemicelluloses and lignin. In natural fibres, semi-crystalline cellulose is the main reinforcement material. The cellulose is held together by amorphous hemicelluloses and fibres are paved together in the plant by lignin which is generally known as plant cell adhesive.

The key constituent present in natural fibres that are chiefly responsible for moisture absorption is hemicelluloses. But, accessible cellulose, non crystalline cellulose, surface of crystalline cellulose and lignin also play most important roles in moisture absorption of natural fibres. Further, natural lignocellulosic fibres contain hydroxyl and other oxygen containing groups that attract moisture through hydrogen bonding. Moisture swells the cell wall and the natural fibre expands until the cell wall is saturated with water (fibre saturation point). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute further expansion [148].

In all natural lignocellulosic fibres, a hollow cavity called lumen exists in the unit cell of the fibres [148]. This hollow cavity generates more pathways for water to start diffusing into the natural fibres. By reducing the void content of the natural lignocellulosic fibres, this velocity of the diffusion process can be reduced and in turn water absorption of fibres can be reduced.Further, the hygroscopicity of the lignocellulosic materials can be reduced by replacing some of the hydroxyl groups on the cell wall polymers with bonded chemical groups [47].

The study of water absorption on untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated,5% acrylic acid treated and acetic anhydride treated areca fibres were carried out in distilled water. The untreated and all chemically treated areca fibre specimens were dried in hot air oven at 60 °C for 24 h and weighed in a balance accurate to 4 decimal places (± 0.1 mg). Humidity chambers (desiccators) were set up using distilled water. A bundle of untreated and all chemically treated areca fibres of 2 g was immersed in humidity chambers containing distilled water. After 24 h, each untreated and all chemically treated areca fibre bundle was taken out from the humidity chambers and the fibres were squeezed and dried in between the folds of filter paper. Then, the weight of untreated and all chemically treated areca fibres was taken and the percentage of water absorption was calculated by using equation (2.4).

$$\%\, of\ Water\ absorption\ = \frac{Final\ weight - Initial\ weight}{Initial\ weight} x100 - - - (2.4)$$

Then, again the fibre sample was soaked in humidity chambers containing distilled water and the same process was repeated after every 24 h up to 2400 h[149–151].

The maximum percentage of water absorption values of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated, 5% acrylic acid treated and acetic anhydride treated areca fibres are found out and the values are given in Table 2.9.

Table 2.9 Water absorption values of Areca fibres

Areca Fibres	Water absorption values (%)
Untreated	60
6% Alkali treated	47
0.5% Potassium permanganate treated	40
Benzoyl chloride treated	32
5% Acrylic acid treated	25
Acetic anhydride treated	29

The maximum percentage of water absorption values of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated, 5% acrylic acid treated and acetic anhydride treated areca fibres are pictorially represented in Fig: 2.28.

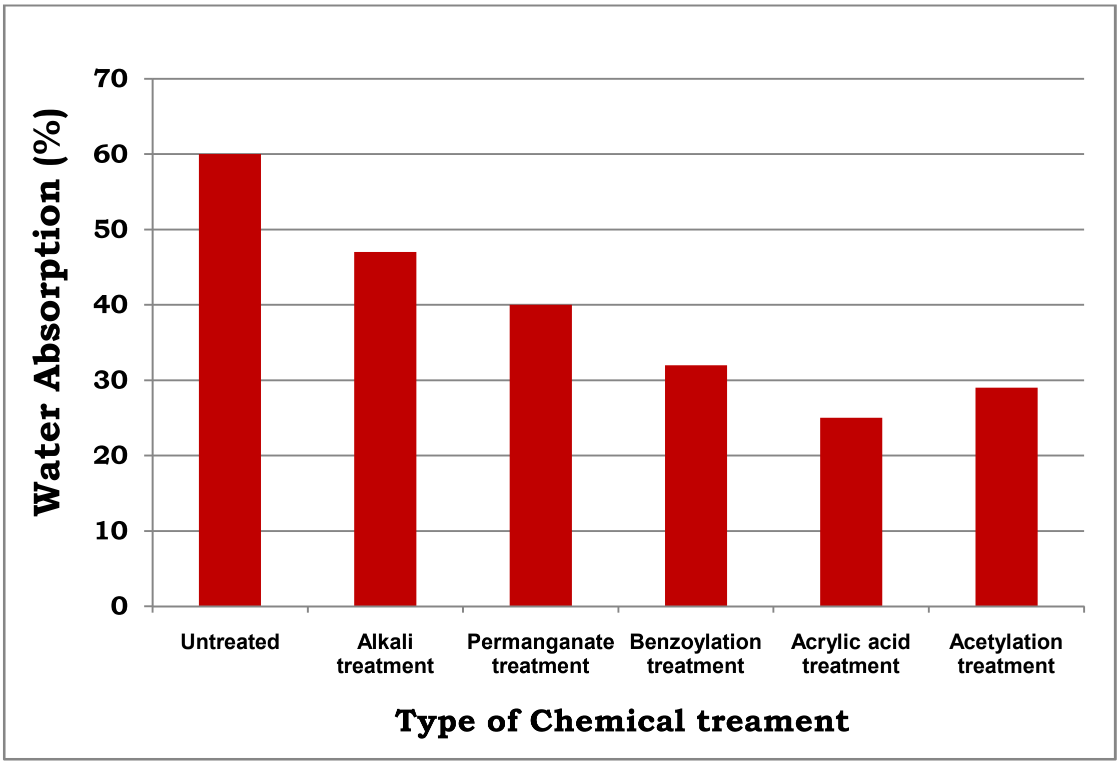


Fig: 2.28 Water absorption of Areca fibres

The percentage of maximum water absorption value of untreated areca fibres was found to be 60%.Decreased moisture absorption was observed for all chemically treated areca fibres. 6% Alkali treated areca fibres showed 21.67% decrease in moisture absorption values,0.5% potassium permanganate treated areca fibres showed 33.33% decrease in moisture absorption values,benzoyl chloride treated areca fibres showed 46.67% decrease in moisture absorption values,5% acrylic acid treated areca fibres showed 58.33% decrease in moisture absorption values and acetic anhydride treated areca fibres showed 51.67% decrease in moisture absorption values when compared with that of untreated areca fibresrespectively.

This decrease in moisture absorption is due to the slight removal of low molecular weight compounds such as waxy epidermal tissue, adhesive pectin, hemicelluloses and lignin components of areca fibres by various chemical treatments. Also, the replacement of hydrophilic hydroxyl groups by hydrophobic chemical groups by respective chemical treatments of areca fibres resulted in decrease of dissemination of water molecules into the chemically treated areca fibres. Further, chemical treatments destroyed the cellular structure of areca fibres and reduced the void content and this in turn reduced the moisture uptake of chemically treated areca fibres [89].Amongst all the chemical treatments carried out, acrylic acid treated areca fibres showed maximum reduction in moisture absorption values followed by acetic anhydride treatment, benzoyl chloride treatment, potassium permanganate treatment and alkali treatment.

2.12 CONCLUSION

Chemical treatments of natural fibres are very essential for increased adhesion between the hydrophilic fibres and the hydrophobic matrix and as a result of it, strong adhesion between the chemically treated fibres and polymeric matrix will occurswhich in turn improves the properties of prepared polymer composites. Here, in this research work, physical, chemical and mechanical properties of areca fibres have been studied. Surface modification of areca fibresweredone byNaOH, $KMnO_4$, C_6H_5COCl, $CH_2=CHCOOH$ and $CH_3COOCOCH_3$treatments. FTIR studies confirmed the chemical modification of areca fibres. TGA-DTGstudies evidenced the increase in thermal stability for all chemically treated areca fibres. XRD results of chemically treated areca fibres showed little less crystallinity than that of untreated areca fibres due to chemical reaction which would slightly alter the orderly packing of cellulose chains to a certain extent in the chemically treated areca fibres. Scanning Electron Microscope morphological investigations indicated the changes in surface topography for all chemically treated areca fibres when compared with that of untreated areca fibres.So the use of this surface modified areca fibres as reinforcement for polymer composites will definitely enhance the adhesion between theareca fibres and the polymeric resin and also helps in improving the properties of areca fibre reinforced polymer composites.The above characteristic studies confirmed that chemically treated areca fibres have wide scope in the field of polymer composites.

CHAPTER 3

CHARACTERIZATION OF ARECA FIBRE REINFORCED THERMOPLASTIC POLYMER COMPOSITES

3.1 INTRODUCTION

In this chapter, fabricationprocess of untreated,alkali treated, potassium permanganate treated, benzoyl chloride treated and acrylic acid treated areca fibre reinforced thermoplastic polypropylene composites with 30%, 40%, 50%, 60% and 70% fibre loadings have been discussed.The investigation of tensile strength, flexural strength and impact strength of untreated and all chemically treated areca fibre reinforced polypropylene composites under given fibre loadingsare done by following ASTM standard procedures.The effect of chemical treatments and the effect of fibre loadings on the properties of untreated and all chemically treated areca fibre reinforced polypropylene composites are studied.

3.2MATERIALS AND METHODS

3.2.1Thermoplastic Polymer Matrix

The thermoplastic polypropylene (PP) matrix in the form of homo-polymer pellets and polyvinyl alcohol mold releasing agent were obtained from Akolite Synthetic Resins, Mangalore.

3.2.2 Polypropylene Matrix.

Polypropylene is one of the most extensively used plastic both in developed and developing countries because of its inherent advantages with respect to economy, environmental (recycling behaviour) and technological needs (higher thermal stability) [152]. Therefore, the price of producing natural lignocellulosic polymeric composites is fairly low. So, these polypropylene composites have fascinated much attention and are becoming increasingly vital for the fabrication of large variety, inexpensive, light–weight, eco-friendly composites [153]. Hence, in this study, polypropylene is used as a matrix material for the fabrication of areca fibre reinforced thermoplastic polymer composites.

3.2.3 Properties of Polypropylene

Most commercial polypropylene is isotactic and crystallinitylies in between that of low-density polyethylene (LDPE) andhigh-density polyethylene (HDPE). The chemical structure of polypropylene in isotactic tacticity and syndiotactic tacticity is given in Fig: 3.1 and Fig: 3.2 respectively.

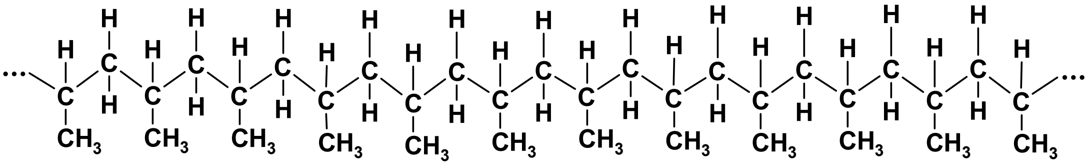


Fig: 3.1 Polypropylene in isotactic tacticity

In isotactic polypropylene, all the –CH3 groups are placed either above or below the plane of the carbon chain.

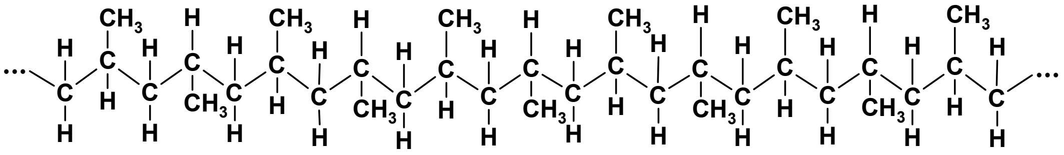


Fig: 3.2 Polypropylene in syndiotactic tacticity

In syndiotactic polypropylene, all the –CH3 groups are arranged alternatively above and below the plane of the carbon chain.

Polypropylene is rough and unusually resistant to acids, bases, solvents and many chemicals. In general, polypropylene is opaque and pigments can be used to add colour to polypropylene. Polypropylene has good fatigue resistance.The melting point range of commercial polypropylenein isotactic form is 160 to 166 °C whereas polypropylenein syndiotactic form with crystallinity of 30% has a melting point of 130 °C. The properties of polypropylene are given in the following Table 3.1.

Table 3.1Properties of Polypropylene

Properties	Polypropylene
Density (g/cm^3)	0.946
Tensile strength (N/mm^2)	25 – 38
Tensile modulus (N/mm^2)	1450 MPa
Elongation at break (%)	33.9
Young's modulus (GPa)	1.9 – 1.4
Strain at break (%)	300

3.2.4 Fabrication of Areca Fibre Reinforced Polypropylene Composites

The fabricationof untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced polypropylene composite process was done by compression molding technique.First, the areca fibres were weighed according to the required weight fraction needed and then they were dried in an oven at 70 °C for a period of 1 h to evaporate moisture. Sufficient amount of commercial polypropylene in the form of homo-polymer pellets were taken in a beaker and weighed. To prevent voids, water bubbles and poor fibre –matrix adhesion, the polypropylene was dried in an oven at about 100 °C for a period of 3 h [154]. Uniform mixing of the dried areca fibres and homo-polymer polypropylene pellets was done carefully. During the mixing of two ingredients, the weight fractions such as 30%, 40%, 50%, 60% and 70% of areca fibres was carefully controlled.

$$V_f = \frac{\frac{W_f}{\rho_f}}{\frac{W_f}{\rho_f} + \frac{W_m}{\rho_m}} \quad -------- \quad (3.1)$$

The equation (3.1) was used in the polymer composite fabrication where $W_f$is the weight of the areca fibre (g), W_m is the weight of polypropylene matrix (g), V_f *is* the areca fibre volume fraction (%), ρ_m is the density of polypropylene matrix (g/cm^3) and ρ_f is the density of areca fibres (g/cm^3).

Mold surface was cleaned thoroughly and the mold releasing agent polyvinyl alcohol was sprayed over the mold surface properly for the easy removal of the fabricated areca fibre reinforced polypropylene composites. The uniformly mixed areca fibres and polypropylene homo-polymer pellets were taken into the mold box having dimensions of 255 mm x 255 mm x 4 mm. Now, the mold box was placed in a hot pressing machine at a temperature of 170 ^{o}C and at a pressure of 40 KN for about 30 min. Then it was cooled slowly using water cooling system. Finally, the areca fibre reinforced polypropylene composite specimen was carefully discharged from the mold box after complete cooling.

3.2.5 Characterization of Areca Fibre Reinforced Polypropylene Composites

Tensile strength, flexural strength (3-point stating bending test) and impact strength of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced polypropylene composites were measured by following ASTM (American Standard for Testing Materials) standard procedures at a standard laboratory atmosphere of 30±2 ^{o}C and 65% relative humidity (RH 65%).At least 5 replicate specimens were tested and the results were presented as an average of tested specimens.

3.2.5.1 Tensile Strength Testing

Untreated and all chemically treated areca fibre reinforced polypropylene composite specimens prepared for the tensile strength test were cut and the measurement was carried out according to ASTM D638-10standard procedures using a Universal Testing Machine at a crosshead speed of 10 mm/min. The dimensions of areca fibre reinforced polypropylene composite specimens were165 mm x 19 mm x 4 mm. The specimen was loaded in the universal testing machine until the failure of the specimen occurred.

3.2.5.2 Flexural Strength Testing

Three – point static flexural tests of untreated and all chemically treated areca fibre reinforced polypropylene composites werecarried out according to ASTM D790-10standard proceduresusing a Universal Testing Machine at a crosshead speed of 10 mm/min.Specimens prepared for the flexural test were cut with help of zig saw and the specimen dimensions used were 79 mm x 10 mm x 4 mm.

$$\text{Flexural strength}, \sigma_f = \frac{3PL}{2\mathrm{bd}^2} - - - - - - - - \quad (3.2)$$

The flexural strength,was calculated from the measured load, according to the equation (3.2) given above where P = maximum applied load, L = length of support span (mm), b = width of specimen (mm) and d = thickness of specimen (mm).

3.2.5.3 Impact Strength Testing

Dynamic Charpy Impact test of the untreated and all chemically treated areca fibre reinforced polypropylene composite specimens were conducted on a notched composite specimens according to ASTM D6110-10standard procedures using a Universal Impact Testing Machine. The width and depth of each specimen was measured with a micrometer screw gauge to the nearest of 0.01 mm and the length was measured to the nearest of 0.1 mm with digital caliper.The dimension of the specimen used was127 mm x 12.8 mm x 4 mm.

3.3 RESULTS AND DISCUSSION

3.3.1 Tensile Strength of Areca - Polypropylene Composites

Tensile strength is defined as how good will the composite material reacts under a certain pressure of applied forces. That means the tensile strength is the force per unit area (N/mm^2 or MPa) required for breaking the composite material. Thistesting has been done until it complete failure or break. The objective of tensile strength test is to determine the strength ofbonding between the untreated, alkali treated, permanganate treated, benzoyl chloride treated and acrylic acid treated areca fibres and the thermoplastic polypropylene matrix.

The tensile strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced polypropylene composites under 40%, 50%, 60% and 70% fibre loadings are given in Table 3.2.

Table 3.2Tensilestrength values of Areca - PP composites

Areca fibre	**Tensile strength values in N/mm^2 at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	20.26	21.84	25.04	18.86
6% Alkali treated	22.46	22.84	28.04	20.32
0.5% Potassium permanganate treated	24.22	24.96	28.86	22.86
Benzoyl chloride treated	26.28	28.62	30.52	24.52
5% Acrylic acid treated	28.04	30.24	36.86	26.52

With respect tofibre content and chemical modifications of areca fibres, a great influence ontensile strength of areca fibre reinforced polypropylene composites wasobserved. The effect of chemical treatments on tensile strength of untreated and all chemically treated areca fibre reinforced polypropylene composites with 40%, 50%, 60% and 70%fibre loadings are represented in Fig:3.3.

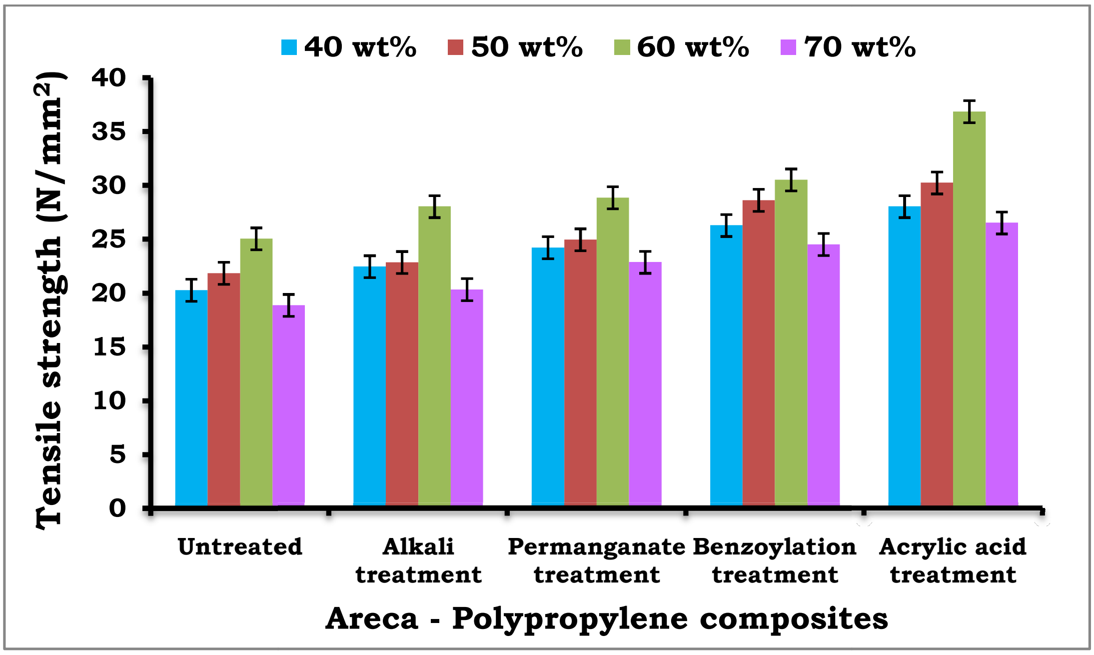


Fig:3.3 Tensile strength of Areca - Polypropylene composites with different fibre loadings

Irrespective of chemical treatment, all chemically treated areca fibre reinforced polypropylene composites showed higher tensile strength values than the untreated areca fibre reinforced polypropylene composites of respective fibre loadings. It was observed that areca fibre reinforced polypropylene composites with 60% fibre loading showed maximum tensile strength values when compared to areca fibre reinforced polypropylene composites with other fibre loadings.

The tensile strength of untreated areca fibre reinforced polypropylenecomposites with 60% fibre loading increased by 23.59% compared to 40% fibre loading, 14.65% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 24.68% when compared to 60% fibre loading.

The tensile strength of 6% sodium hydroxide treated arecafibrereinforced polypropylenecomposites with 60% fibre loading increased by 24.84% compared to 40% fibre loading, 22.77% compared to 50% fibre loading and for 70% fibre loading,it decreased by 27.53% when compared to 60% fibre loading.

The tensile strength of 0.5% potassium permanganate treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 19.16% compared to 40% fibre loading, 15.63% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 20.79% when compared to 60% fibre loading.

The tensile strength of benzoyl chloride treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 16.13% compared to 40% fibre loading, 6.64% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 19.66% when compared to 60% fibre loading.

The tensile strength of 5% acrylic acid treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 31.46% compared to 40% fibre loading, 21.89% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 28.05% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced polypropylene composites with 60% fibre loading showed 11.98%, 15.26%, 21.88% and 47.20% increase in tensile strength values respectively when compared to untreated areca fibre reinforced polypropylene composites with same 60% fibre loading.

3.3.2 Flexural Strength of Areca - Polypropylene Composites

Flexural strength is the ability of the material to resist deformation under load. Flexural strength plays a significant role in civil, mechanical, aerospace engineering and design.The flexural strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced polypropylene composites under 40%, 50%, 60% and 70% fibre loadings are given in Table 3.3.

Table 3.3 Flexural strength values of Areca - PP composites

Areca fibre	Flexural strength values in N/mm^2 at given fibre loadings (wt %)			
	40%	50%	60%	70%
Untreated	36.28	38.26	44.06	34.52
6% Alkali treated	38.04	40.28	46.86	38.02
0.5% Potassium permanganate treated	38.86	42.58	48.52	37.56
Benzoyl chloride treated	39.02	44.56	50.56	38.52
5% Acrylic acid treated	42.52	46.52	52.26	40.86

It wasindicated that the fibre content and the chemical modifications of areca fibressignificantly influenced the flexural strength of areca fibre reinforced polypropylene composites.The effect of chemical treatments on flexural strength of untreated and all chemically treated areca fibre reinforced polypropylene composites with 40%, 50%, 60% and 70%fibre loadings are shown in Fig:3.4.

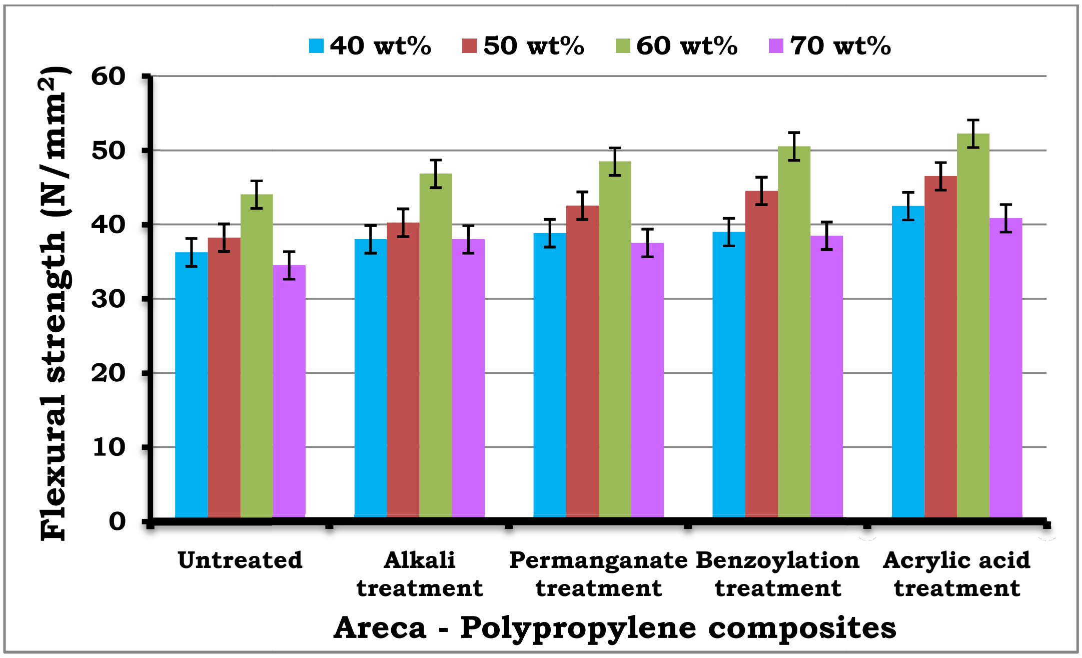


Fig: 3.4 Flexural strength of Areca - Polypropylene composites with different fibre loadings

Irrespective of chemical treatment, all chemically treated areca fibre reinforced polypropylene composites indicated higher flexural strength values than the untreated areca fibre reinforced polypropylene composites of respective fibre loadings. It wasclearly understood that areca fibre reinforced polypropylene composites with 60% fibre loading showed maximum flexural strength values when compared to areca fibre reinforced polypropylene composites with other fibre loadings.

The flexural strength of untreated areca fibre reinforcedpolypropylene composites with 60% fibre loading increased by 21.44% compared to 40% fibre loading, 15.16% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 21.65% when compared to 60% fibre loading.

The flexural strength of 6% alkali treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 23.18% compared to 40% fibre loading, 16.34% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 18.86%

when compared to 60% fibre loading.

The flexural strength of 0.5% potassium permanganate treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 24.86% compared to 40% fibre loading, 13.95% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 22.59% when compared to 60% fibre loading.

The flexural strength of benzoyl chloride treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 29.57% compared to 40% fibre loading, 13.46% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 23.81% when compared to 60% fibre loading.

The flexural strength of 5% acrylic acid treated areca fibre reinforced polypropylene composites with 60% fibre loading increased by 22.91% compared to 40% fibre loading, 12.34% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 21.81% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced polypropylene composites with 60% fibre loading showed 6.35%, 10.12%, 14.75% and 18.61% increase in flexural strength values respectively when compared to untreated areca fibre reinforced polypropylene composites with same 60% fibre loading.

3.3.3Impact Strength of Areca - Polypropylene Composites

Impact strength is defined as the capability of the material to withstand a suddenly applied load and is expressed in terms of energy absorbed. Impact strength is a very vital property of a material governing the life of a structure. For instance, the capacity of the aircraft to withstand the impact depends on the material'sstrength. Impact tests are used in studying the toughness of materials. Toughness is dependent upon temperature and the shape of the test specimen. Impact strength is determined by Charpy Impact test. The impact strength is calculated as the ratio of impact absorption to test specimen cross-section(J/mm^2).It is very important to identifyappropriatefibre loadings to get excellent impact properties [155].

Impact strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced polypropylene composites with 30%, 40%, 50%, 60% and 70% fibre loadings are given in Table 3.4.

Areca fibre content and the chemical modifications of areca fibresgreatly influenced the impact strength values of areca fibre reinforced polypropylene composites.

Irrespective of chemical treatment, all chemically treated areca fibre reinforced polypropylene composites showed higher impact strength values than the untreated areca fibre reinforced polypropylene composites of respective fibre loadings.

Table 3.4 Impact strength values of Areca - PP composites

Areca fibre	**Impact strength values in J/mm^{2}at given fibre loadings (wt %)**				
	30%	**40%**	**50%**	**60%**	**70%**
Untreated	32.56	34.68	36.82	28.86	22.86
6% Alkali treated	34.25	35.28	37.28	30.28	24.24
0.5% Potassium permanganate treated	34.86	36.82	38.28	32.52	25.64
Benzoyl chloride treated	35.28	37.02	39.82	34.24	27.24
5% Acrylic acid treated	36.86	38.28	40.24	36.82	28.82

The impact strength values of untreated and all chemically treated areca fibre reinforced polypropylene composites with 30%, 40%, 50%, 60% and 70% fibre loadings are shown in Fig: 3.5.

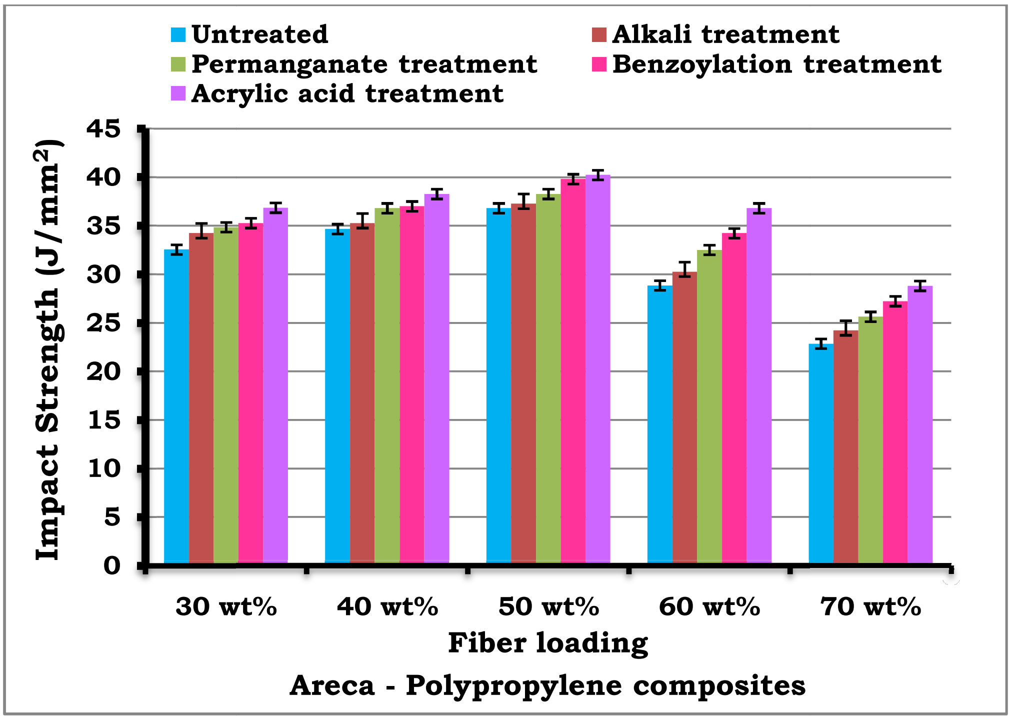


Fig: 3.5Impact strength of Areca - Polypropylene composites with different fibre loadings

In case of untreated areca fibre reinforced polypropylene composites, the impact strength of 50% fibre loading increased by 13.08% compared to 30% fibre loading, 6.17% compared to 40% fibre loading and for 60% and 70% fibre loadings, it decreased by 21.62% and 37.91% respectively when compared to 50% fibre loading.

In case of 6% alkali treated areca fibre reinforced polypropylene composites, the impact strength of 50% fibre loading increased by 8.84% compared to 30% fibre loading, 5.67% compared to 40% fibre loading and for 60% and 70% fibre loadings, it decreased by 18.78% and 34.98% respectively when compared to 50% fibre loading.

For 0.5% potassium permanganate treated areca - polypropylene composites, the impact strength of 50% fibre loading increased by 9.81% compared to 30% fibre loading, 3.97% compared to 50% fibre loading and for 60% and 70% fibre loadings, it decreased by 15.05% and 33.02% respectively when compared to 50% fibre loading.

In case of benzoyl chloride treated areca - polypropylene composites, the impact strength of 50% fibre loading increased by 12.87% compared to 30% fibre loading, 7.56% compared to 40% fibre loading and for 60% and 70% fibre loadings, it decreased by 14.01% and 31.59% respectively when compared to 50% fibre loading.

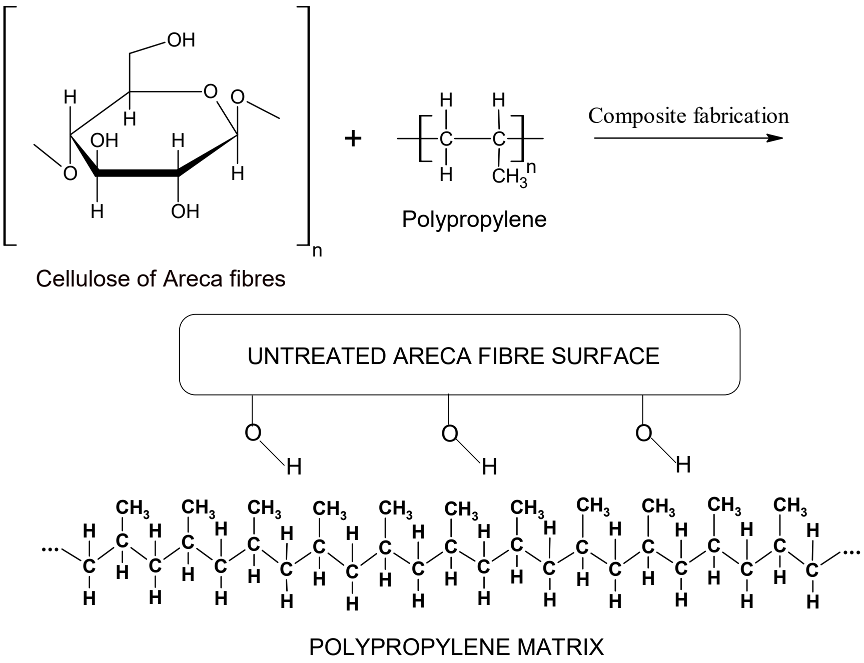
In case of 5% acrylic acid treated areca - polypropylene composites, the impact strengthof 50% fibre loading increased by 9.17% compared to 30% fibre loading, 5.12% compared to 40% fibre loading and for 60% and 70% fibre loadings, it decreased by 8.50% and 28.38% respectively when compared to 50% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca-polypropylene composites with 50% fibre loading showed 1.25%, 3.97%, 8.15% and 9.29% increase in impact strength values respectively when compared to untreated arecafibre reinforced polypropylene composites with same 50% fibre loading.

3.3.4 Effect of Chemical Treatments on Areca Fibre Reinforced Polypropylene Composite Properties

3.3.4.1 Untreated Areca – PolypropyleneComposites

The very much essential factor to achieve good fibre reinforcement is the existence of good interfacial bonding between the fibre and the polymeric matrix in the composites. Based on hypothetical model given by various researchers [124, 156], a possible hypothetical model of interface of untreated areca fibre – polypropylene matrix can be given as follows.

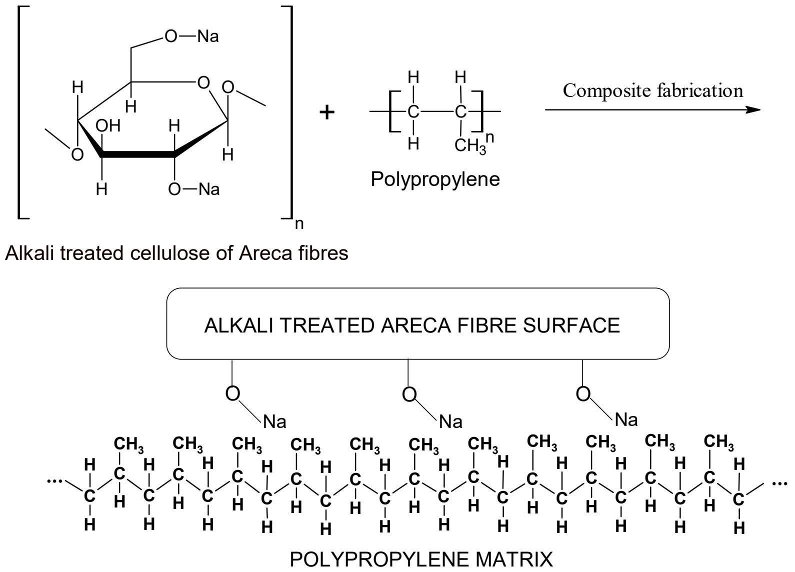


Scheme 3.1 Hypothetical model of interface between cellulose-OH of untreated Areca fibres with Polypropylene matrix

An interface is defined as a region where the reinforcing natural lignocellulosic fibres and the polymer matrix phase are chemically and/or mechanically combined or otherwise indistinct [49-50].Here, the untreated areca fibres are hydrophilic whereas the polypropylenematrix is hydrophobic and hence,there is incompatibility between the areca fibres and the polypropylene polymer matrix at the interface. So, the untreated areca -PP composites showed lower tensile strength, flexural strength and impact strength values when compared to all chemically treated areca -PP composites of respective fibre loadings.

3.3.4.2Alkali Treated Areca – PolypropyleneComposites

Based on hypothetical model given by various researchers [124, 156], a possible hypothetical model of interface of alkali treated areca fibre surface having reactive -ONa groups with the polypropylene matrix can be schematically represented as follows.

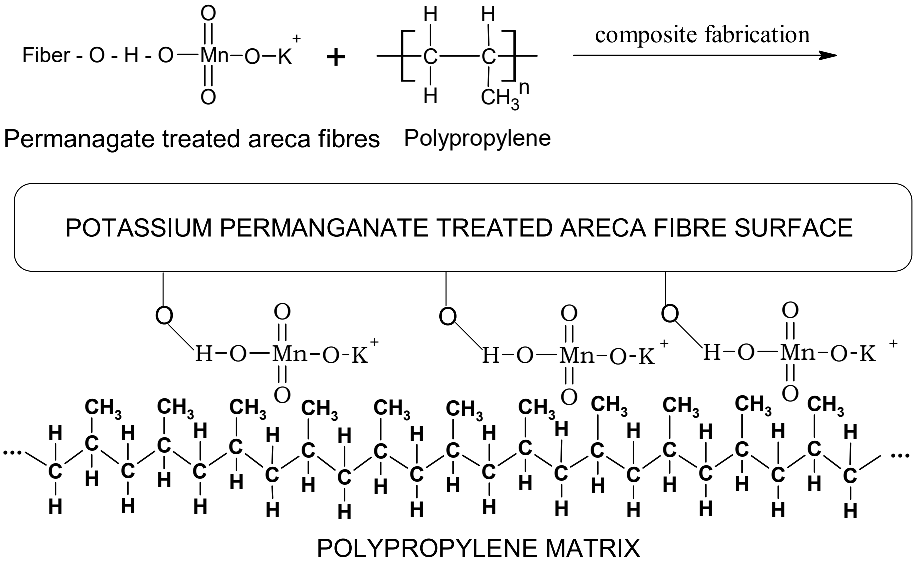


Scheme 3.2 Hypothetical model of interface of alkali treated Areca fibre - PP composites

Alkali treatment of areca fibresremoves certain portion of hemicelluloses, lignin, adhesive pectin, waxy epidermal tissue and oil covering materials.It reducesfibre diameter and thereby increasesits aspect ratio. It also removes natural and artificial impurities and as a result, surface of the areca fibres became physically rough.This in-turn enhanced chemical interlocking between the alkali treated areca fibres and the thermoplastic polypropylene matrix [34, 40, 61, 92, 95, 102-107, 157-158]. Hence, alkali treated areca -polypropylene composites showed increased tensile strength, flexural strength and impact strength values when compared with that of untreated areca -polypropylene composites of corresponding fibre loadings.

3.3.4.3Permanganate Treated Areca–Polypropylene Composites

Based on hypothetical model given by various researchers [124, 156], a possible hypothetical model of interface of potassium permanganate treated areca fibres with PP matrix can be represented as follows.



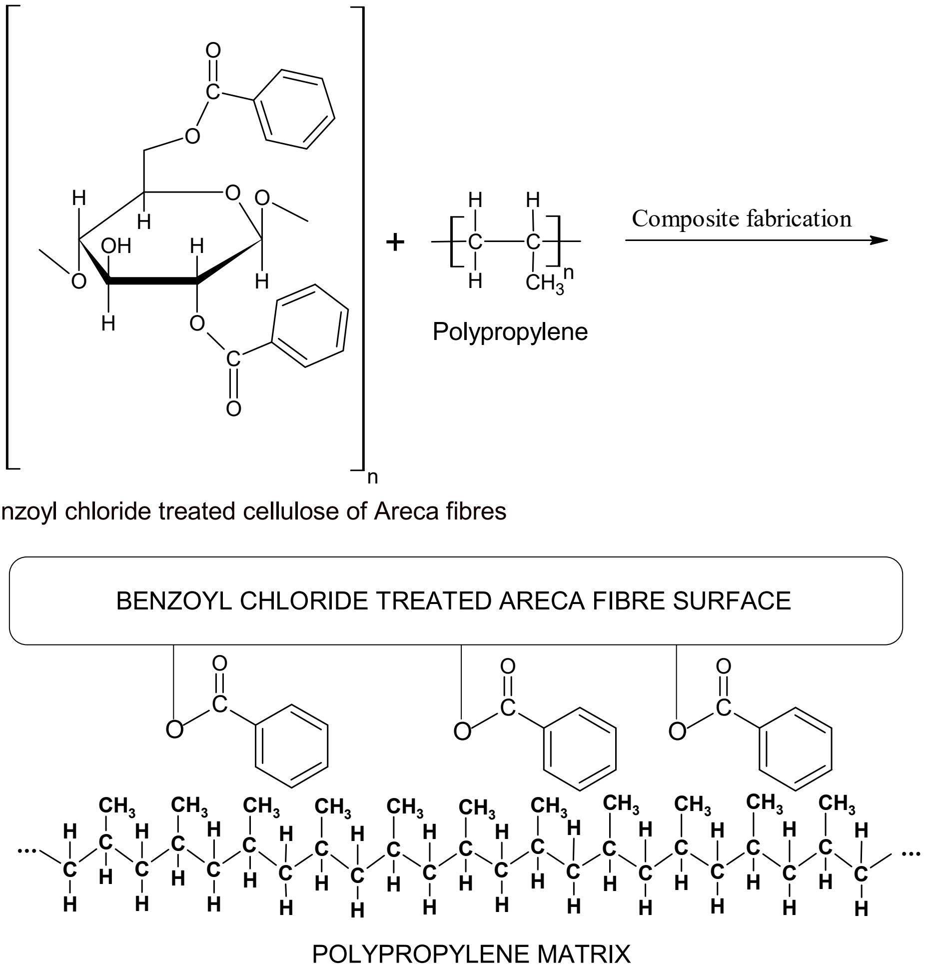
Scheme 3.3 Hypothetical model of interface of potassium permanganate treated Areca fibre - PP composites

Potassium permanganate treatment of areca fibresproduces highly reactive permanganate ions (Mn^{3+}) that reacts with cellulosehydroxyl groups of areca fibres and forms cellulose-manganate for initiating graft copolymerization. This treatment in-turn enhances chemical interlocking at the interface. Permanganate ions also react with the lignin constituents and carve the fibre surface and as a result, areca fibre surface became physically rough. This treatment reduces hydrophilic nature of areca fibres, improves interfacial interlocking at the interface and provides better adhesion with the thermoplastic polypropylene polymeric resin [34, 40, 67, 92, 95, 102-103, 108-110, 159].Because of this, potassium permanganate treated areca fibre reinforcedpolypropylene composites showed increased tensile strength, flexural strength and impact strength values when compared with that of untreated areca fibre reinforcedpolypropylene composites of respective fibre loadings.

3.3.4.4 Benzoylated Areca – Polypropylene Composites

Based on hypothetical model given by various researchers [124, 156], a possible hypothetical model of interface of benzoylated areca fibresurface having reactive C_6H_5COO- groups with the polypropylene polymer matrix can be schematically given as follows.

Extractable materials such as lignin, waxes and oil covering materials are removedby alkali pre-treatment of areca fibres. Then, benzoyl chloride reacts with this alkali pre-treated areca fibres and forms ester linkage and benzoyl groups are attached onto the cellulose backbone of areca fibres.

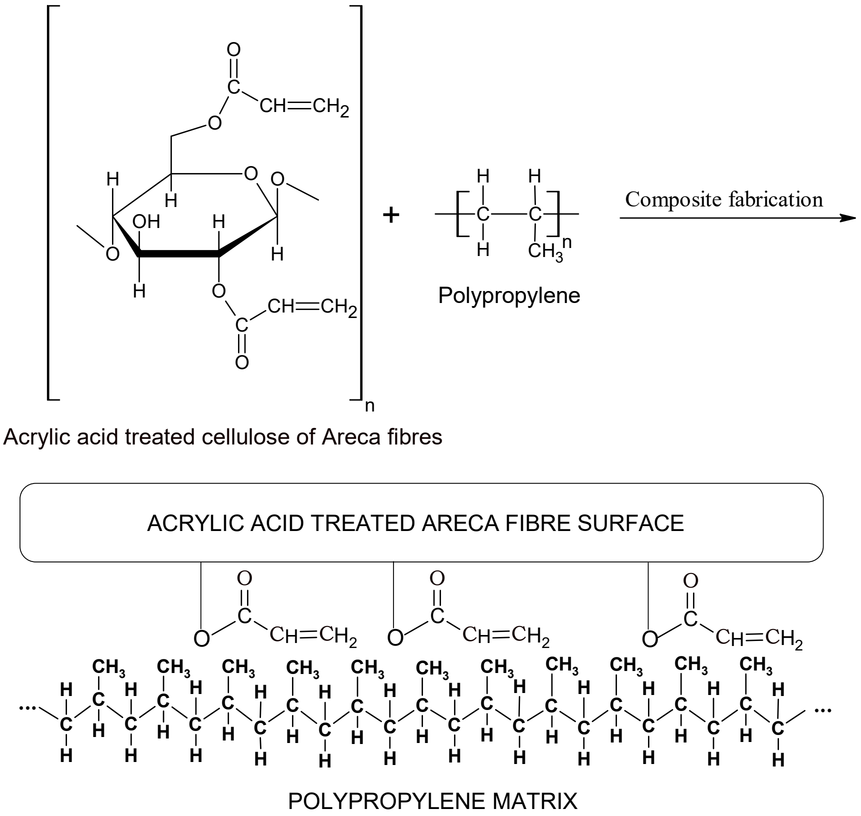


Scheme3.4 Hypothetical model of interface of benzoylated Areca fibre - PP composites

Due to the introduction of hydrophobic groups onto areca fibre surface, moisture resistance property of areca fibres is increased andcompatibilityof areca fibres with polypropylene polymer matrix is improved. The treated areca fibre surface became physically rough. Hence, benzoylation treatment improved chemical interlocking at the interface and provided effective fibre surface area for good adhesion with the matrix [34, 40, 57, 61, 95, 102-103, 105, 111, 159]. As a result, benzoylated areca fibre reinforced polypropylene composites showed increased tensile strength, flexural strength and impact strength values when compared with that of untreated areca fibre reinforced polypropylene composites of corresponding fibre loadings.

3.3.4.5 Acrylated Areca – Polypropylene Composites

Based on hypothetical model given by various researchers [124, 156], a possible hypothetical model of interface of acrylic acid treated areca fibre surface having reactive CH_2=CHCOO- groups with the polypropylene polymer matrix is shown in Scheme 3.5.



Scheme 3.5 Hypothetical model of interface of acrylated Areca fibre - PP composites

During acrylic acid treatment, there is replacement of hydrophilic hydroxyl groups by hydrophobic ester groups and most of the hemicelluloses and lignin are removed. Hence, effective fibre surface area for good adhesion with the thermoplastic polypropylene polymer matrix is increased and stress transfer capacity at the interface is enhanced[34, 40, 95, 102-103, 112-113]. As a result, for acrylic acid treated areca -polypropylene composites, higher tensile strength, flexural strength and impact strength values are observed when compared with that of untreated areca -polypropylene composites.

Amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced polypropylene composites with 60% fibre loading showed maximum tensile strength and flexural strength valuesfollowed by benzoyl chloride treatment, potassium permanganate treatment and alkali treatment.Similarly, amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced polypropylene composites with 50% fibre loading showed maximum impact strength valuesfollowed by benzoyl chloride treatment, permanganate treatment and alkali treatment.

This observed result is in good agreement with the experimentally determined tensile strength values and decomposition temperature values of the untreated and all chemically treated areca fibres which are shown in Table 3.5.

Table 3.5 Tensile strength values and decomposition temperature values of Areca fibres

Areca Fibre	Tensile strength (N/mm^2)	Decomposition temperature, (°C)
Untreated	116.93	322.2
6% Alkali treated	100.13	346.0
0.5% $KMnO_4$ treated	108.02	350.4
Benzoylated	110.34	350.7
5% Acrylated	112.42	351.1

Thedecreased tensile strength values observed after each chemical treatment of areca fibres is due to the removalof most of the fat, lignin, pectin and oil covering the external surface of the fibre cell wall. This in-turn improves the fibre adhesive quality in combination with the polymer matrix. Further, after chemical treatments, the thermal stability of all chemically treated areca fibres is improved which in-turn improves the properties of polymer composites.

Amongst all the chemical treatments carried out, higher tensile strength and decomposition temperature values were showed by areca fibres treated with acrylic acid followed by benzoyl chloride, potassium permanganate and sodium hydroxide treatments. Hence, acrylated areca fibre reinforced polypropylene composites showed higher tensile strength, flexural strength and impact strength values followed by benzoylated areca-polypropylene, permanganate treated areca-polypropylene and alkali treated areca-polypropylene composites.

The above said results clearly evidenced that chemical treatments are very effective in surface modification of areca fibres and in improving the polymer composite properties such as tensile strength, flexural strength and impact strength of areca fibre reinforced polypropylene composites.

3.3.5 Effect of Fibre Loadings on Areca Fibre Reinforced Polypropylene Composite Properties

With increase in fibre loading from 40% to 60%, the tensile strength and flexural strength values of untreated and all chemically treated areca fibre reinforced polypropylene composites increased and beyond 60% fibre loading, the tensile strength and flexural strength showed a decline. That is areca fibre reinforced polypropylene composites exhibited a maximum tensile strength and flexural strength values at 60% fibre loading. This is because of better areca fibre distribution in polypropylene matrix, less fibre fractures and effective transfer of load from polypropylene matrix to areca fibres at 60% fibre loading.

The observed increase in tensile strength and flexural strength values with chemical modifications and as well as with increase in fibre loadings up to 60% is in good agreement with the results reported in literature[30, 58-63, 67, 69, 73].

The decrease in tensile strength and flexural strength values for untreated and all chemically treated areca fibre reinforced polypropylene composites beyond 60% fibre loading is due to the fact that the melted polypropylene could not reach each of the areca fibre surface because of smaller amount of thermoplastic polypropylene matrix material and also, there is poor interfacial adhesion and inefficient stress transfer from matrix to fibres at 70% fibre loading[160].The factors contributing to the lower tensile strength and flexural strength values beyond 60% may be due to the random alignment of short areca fibres and the presence of voids in the areca fibre reinforced polypropylene composites[161].

With increase in fibre loading from 30% to 50%, the impact strength of all untreated and chemically treated areca fibre reinforced polypropylene composites increased but beyond 50% fibre loading, the impact strength values showed a decline. That is areca fibrereinforced polypropylene composites exhibited maximum impact strength values at 50% fibre loading. This is due to the fact that with increase in fibre loading, more force is required to pullout the fibres and hence increases the impact strength.

The observed increase in impact strength values with chemical modifications and as well as with increase in fibre loadings up to 50% is in good agreement with the results reported in literature [73, 75-77]. It has also been reported that high fibre content increases the probability of fibre agglomeration and further it results in regions of stress concentration and requires less energy for crack propagation [162].These results suggest that the areca fibre reinforced polypropylene composites are capable of showing high impact strength values because of strong interfacial bonding between the areca fibres and polypropylene matrix.

The decrease in impact strength beyond 50% may be due to the micro spaces between the areca fibres and the thermoplastic polypropylene matrix which initiates micro cracks on impact and results in crack propagation leading to failure [77].

Hence, these chemically treated areca fibre reinforced polypropylene composites with appropriate fibre loadings are best suitable for light weight materials industries.

3.4 CONCLUSION

Chemical modification of natural fibre would remove the impurities like pectin, fat and lignin present in the fibre. On the other hand, a rougher fibre surface may result after the chemical treatment due to the introduction of some reactive groups onto the fibre. From these studies, it is clearly concluded that chemical treatments of areca fibres are of greater importance in modifying the fibre surface, in reducing the hydrophilic nature of the fibre, in enhancing the fibre matrix adhesion and thereby increasing the properties of polymer composites. Tensile strength, flexural strength and impact strength values of areca fibre reinforced polypropylene composites are increased after chemical modification.Maximum value of tensile strength and flexural strength is observed at 60% fibre loading and maximum value of impact strengthis observed at 50% fibre loadingfor all untreated and chemically treated areca fibre reinforced polypropylene composites. Amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced polypropylene composites showed maximum tensile strength, flexural strength and impact strength values followed by benzoylated areca-polypropylene, potassium permanganate treated areca-polypropylene and alkali treated areca-polypropylene composites.Hence, areca fibre reinforced polypropylene composites can be effectively used in light weight materials industries.

CHAPTER 4

CHARACTERIZATION OF ARECA FIBRE REINFORCED THERMOPLASTIC ELASTOMERIC POLYMER COMPOSITES

4.1 INTRODUCTION

In this chapter fabricationprocess of untreated, alkali treated, potassium permanganate treated, benzoyl chloride treated and acrylic acid treatedareca fibre reinforced thermoplastic elastomeric natural rubber composites with 40%, 50%, 60% and 70% fibre loadings have been discussed. The determination of tensile strength, flexural strength and impact strength of untreated and allchemically treated areca fibre reinforced natural rubber composites aredone under 40%, 50%, 60% and 70% fibre loadingsby following ASTM standard procedures.The effect of chemical treatments and the effect of fibre loadings on the properties of untreated and all chemically treated areca fibre reinforced natural rubber composites are studied.

4.2MATERIALS AND METHODS

4.2.1Thermoplastic Elastomeric Polymer Matrix

Natural Rubber (NR) granules were obtained from Akolite Synthetic Resins, Mangalore. Natural Rubbergranules used for this study were ISNR 5(Indian Standard Natural Rubber-5) grade and light in colour.

4.2.2 Natural Rubber Matrix.

Thermoplastic elastomers like rubbers are materials thatunite the easyprocessing capability of thermoplastics and the elastic behaviour of rubbers.In this study, natural rubber is used as a thermoplastic elastomeric matrix material for the fabrication of areca fibre reinforced polymer composites. Natural Rubber is a linear polymer consisting of unsaturated hydrocarbon called isoprene (2-methyl-1,3-butadiene). There may be as many as 11,000 to 20,000 isoprene units in a polymer chain of natural rubber.The chemical structure of natural rubber is given in Fig: 4.1.

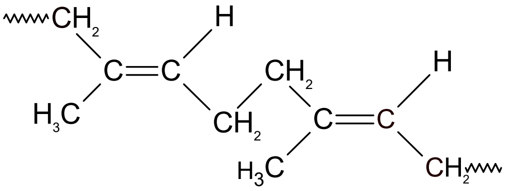


Fig: 4.1 Chemical structure of Natural Rubber

Natural Rubber isdefined as a material that is capable of recovering from largedeformations quickly and forcibly. It isobtained from a tropical rubber tree (Hevea brasiliensis) inthe form of milky white fluid known as field latex. Latex contains 30%-40% of rubber as a colloidal solution in water. Latex is obtained by making a cut in the rubber tree and is shown in Plate 4.1.

Plate 4.1 Natural Rubber in the form of latex from rubber tree

4.2.3 Properties of Natural Rubber

- Specific gravity of natural rubber is 0.915.
- Elasticity is the most significant property of natural rubber. When stretched it expands and attains its original state when released andthis property is due to its coil-like structure.

- Natural Rubberpossesses high tensile strength and modulus due to strain-induced crystallization and also it possesses good crack propagation resistance.
- Natural rubber shows enhanced building tack, which is necessary in many products like tyres,hoses, belts etc.
- The natural resilience of rubber is associated to molecular flexibility, amorphous structure and very low intermolecular force of attraction. Hence natural rubber exhibits quick and easy response to force and release of force [163].
- Natural Rubber is produced by plants and hence it is renewable, inexpensive and creates no health risk problems.

Clonally variation, period and use of yield stimulants, tapping system and means of preparation affects the molecular weight, distribution of molecular weight and non-rubber constituents of natural rubber [164]. Hence,natural rubber obtained from the same batch has been used in this study.

The specifications of natural rubber granules are given in the following Table 4.1.

Table 4.1Specifications of Natural Rubber

Parameters	**Value**
Dirt content, % by mass	0.03
Volatile matter, % by mass	0.50
Nitrogen, % by mass	0.30
Ash, % by mass	0.40
Initial plasticity number, P_0	38
Plasticity Retention Index	78

4.2.4 Fabrication of Areca Fibre Reinforced Natural Rubber Composites

The fabrication of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced natural rubber composite plates was carried out by compression molding technique. The areca fibrewas used as reinforcement material and the natural rubber granules were taken as matrix material. The weight fractions such as 40%, 50%, 60% and 70% of areca fibres were carefully controlled during the mixing of two ingredients. The resulting material was compression molded to the dimension of 300 x 300 x 5.0 mm^3. The composite preparation process was performed in the following order. First, the heat press was pre-heated to 60 °C. Then the pressure was set as 0 MPa and the temperature was raised to 100 °C. After that the pressure was raised to 5 MPa and the compounding temperature was raised to a certain degree such as 130°C, 140°C, 150°C or 160 °C respectively. Further, raised the pressure to 15 MPa, maintained the pressure andtemperature for 30 min. Finally, lowered the pressure to 0 MPa, lowered the temperature to 30 °C and composite plate was removed from the heat press. The composite specimens were post cured for 48 h before the test [103, 165-166].

4.2.5 Characterization of Areca FibreReinforced Natural Rubber Composites

Tensile strength, flexural strength (3-point stating bending test) and impact strength of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced natural rubber composites were measured by using ASTM standard procedures at a standard laboratory atmosphere of 30±2 °C and 65% relative humidity (RH 65%).At least five replicate composite specimens were tested and the results were given as an average of tested composite specimens.

4.2.5.1 Tensile Strength Testing

Untreated and all chemically treated areca fibre reinforced natural rubber composite specimens fabricated for the tensile strength test were cut and the measurement was carried out according to ASTM D3039 standard procedures. A rectangular shape specimen with the total length of 250 mm, gauge length of 150 mm, width of 50 mm and a uniform thickness of 5.0 mm was considered for the test. The composite specimen was loaded in the Universal Testing Machine until the failure of the specimen occurred.

4.2.5.2 Flexural Strength Testing

Three – point static flexural tests of untreated and all chemically treated areca fibre reinforced natural rubber composites were taken according to ASTM D790-10 standard procedure using a Universal Testing Machine at a crosshead speed of 10 mm/min.The specimens fabricated for the flexural test were cut with help of zig saw and the composite specimen dimensions used were 80mm x 10 mm x 5 mm.

4.2.5.3 Impact Strength Testing

Dynamic Charpy Impact tests of untreated and all chemically treated areca fibre reinforced natural rubber composite specimens were conducted on a notched composite specimen according to ASTM D6110-10 using a Universal Impact Testing Machine. The width and depth of each specimen was measured with a micrometer screw gauge to the nearest of 0.01 mm and the length was measured to the nearest of 0.1 mm with digital caliper. The dimensions of the specimens used were 130 mm x 12.5 mm x 5 mm.

4.3 RESULTS AND DISCUSSION

4.3.1 Tensile Strength of Areca – Natural Rubber Composites

The force per unit area (N/mm^2 or MPa) required for breaking the composite material is known as tensile strength. The aim of tensile test is to evaluate the strength ofbonding between the untreated, alkali treated, permanganate treated, benzoylated and acrylated areca fibres and the thermoplastic elastomeric natural rubber matrix.

It has been reported that the modulus of natural rubber decreases with increasing temperature in the range of 130-210 °C [167]. The higher compounding temperatures induce higher rubber fluidity and lead to enhanced dispersion of the liquid rubber among the areca fibres, resulting in improved integration between the areca fibres and NR matrix. To study the effect of compounding temperature on tensile strength of untreated areca fibre reinforced natural rubber composites, the composites reinforced with 60% fibre loading at different temperatures such as 130 °C, 140 °C, 150 °C and 160 °C were prepared for the measurements. Each piece of the fabricated areca – NR composite plate was cut into five specimens. Each result is an average of five measurements and is shown in Table 4.2.

Table 4.2Effect of molding temperature on tensile strength

Molding Temperature (°C)	**Tensile Strength (N/mm^2)**	**Elongation at Break (%)**
130	126.02	15.48
140	130.25	17.42
150	125.24	18.48
160	127.68	16.94

The tensile strength results showed that there was no considerable difference among the four composite samples. The reason may be contributed to the limited temperature differences among the four groups. Hence, compounding temperature, 130 °C will be recommended for cost-effective consideration. Hence, untreated and all chemically treated areca fibre reinforced natural rubber compositeswith 40%, 50%, 60% and 70% fibre loadings were fabricated at a compounding temperature of 130 °C [165]. From the fabricated composites, test specimens were cut to size according to the

ASTM standard procedures and were evaluated for tensile, flexural and impact properties.

The tensile strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced natural rubber composites under 40%, 50%, 60% and 70% fibre loadings are given in Table 4.3. An immense influence on tensile strength of areca fibre reinforced natural rubber composites was observed with respect to fibre content and chemical modifications of areca fibres.

Table 4.3 Tensilestrength values of Areca - NR composites

Areca fibre	**Tensile strength values in N/mm^2 at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	87.24	112.28	126.48	108.32
6% Alkali treated	92.26	116.82	130.82	109.26
0.5% Potassium permanganate treated	94.28	118.28	134.56	110.52
Benzoyl chloride treated	94.86	118.98	138.52	112.26
5% Acrylic acid treated	96.86	122.84	140.82	113.56

The effect of chemical treatments on tensile strength of untreated,6% sodium hydroxide treated, 0.5% permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca -NR composites with 40%, 50%, 60% and 70%fibre loadings are shown in Fig: 4.2.

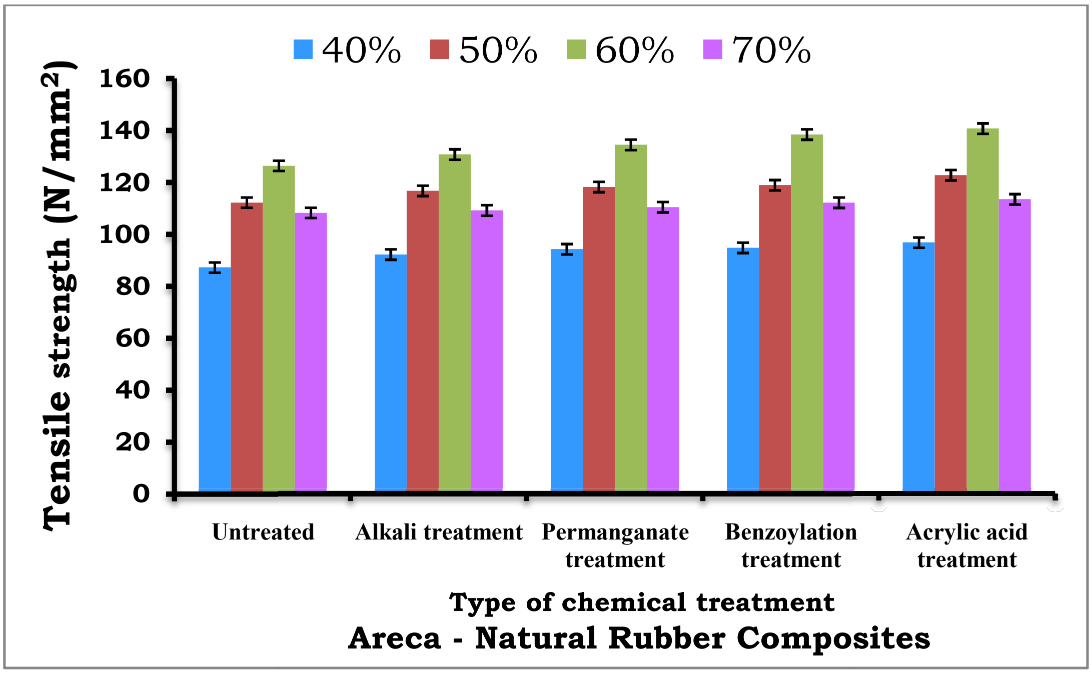


Fig: 4.2 Tensile strength of Areca – Natural Rubbercomposites with different fibre loadings

The tensile strength of untreated areca fibre reinforcednatural rubber composites with 60% fibre loading increased by 44.97% compared to 40% fibre loading, 12.65% compared to 50% fibre loading and for 70% fibre loading, tensile strength decreased by 14.35% when compared to 60% fibre loading.

The tensile strength of 6% sodium hydroxide treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 41.79% compared to 40% fibre loading, 11.98% compared to 50% fibre loading and for 70% fibre loading, tensile strength decreased by 16.48% when compared to 60% fibre loading.

The tensile strength of 0.5% potassium permanganate treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 42.72% compared to 40% fibre loading, 13.76% compared to 50% fibre loading and for 70% fibre loading, tensile strength decreased by 17.87% when compared to 60% fibre loading.

The tensile strength of benzoyl chloride treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 46.03% compared to 40% fibre loading, 16.42% compared to 50%

fibre loading and for 70% fibre loading, tensile strength decreased by 18.96% when compared to 60% fibre loading.

The tensile strength of 5% acrylic acid treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 45.39% compared to 40% fibre loading, 14.64% compared to 50% fibre loading and for 70% fibre loading, tensile strength decreased by 19.36% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced natural rubber composites with 60% fibre loading showed 3.43%, 6.39%, 9.52% and 11.34% increase in tensile strength values respectively when compared to untreated areca fibre reinforced natural rubber composites with same 60% fibre loading [103].

4.3.2 Flexural Strength of Areca – Natural Rubber Composites

Flexural strength is the capacity of the material to resist deformation under load. It is highly important to know the weight bearing capacity of many materials.The flexural strength values of untreated, 6% sodium hydroxide treated, 0.5% permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca - NR composites under 40%, 50%, 60% and 70% fibre loadings are given in Table 4.4.

Table 4.4 Flexural strength values of Areca -NR composites

Areca fibre	**Flexural strength values in N/mm^2 at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	86.02	110.24	118.26	84.02
6% Alkali treated	86.28	110.86	120.52	84.28
0.5% Potassium permanganate treated	88.02	112.26	122.68	86.02
Benzoyl chloride treated	90.24	112.86	122.98	86.52
5% Acrylic acid treated	92.54	114.86	128.52	86.68

The effect of chemical treatments on flexural strength of untreated,6%

sodium hydroxide treated, 0.5% permanganate treated, benzoyl chloride treated and 5% acrylic acid treatedareca -natural rubber composites with different fibre loadings are depicted in Fig: 4.3.

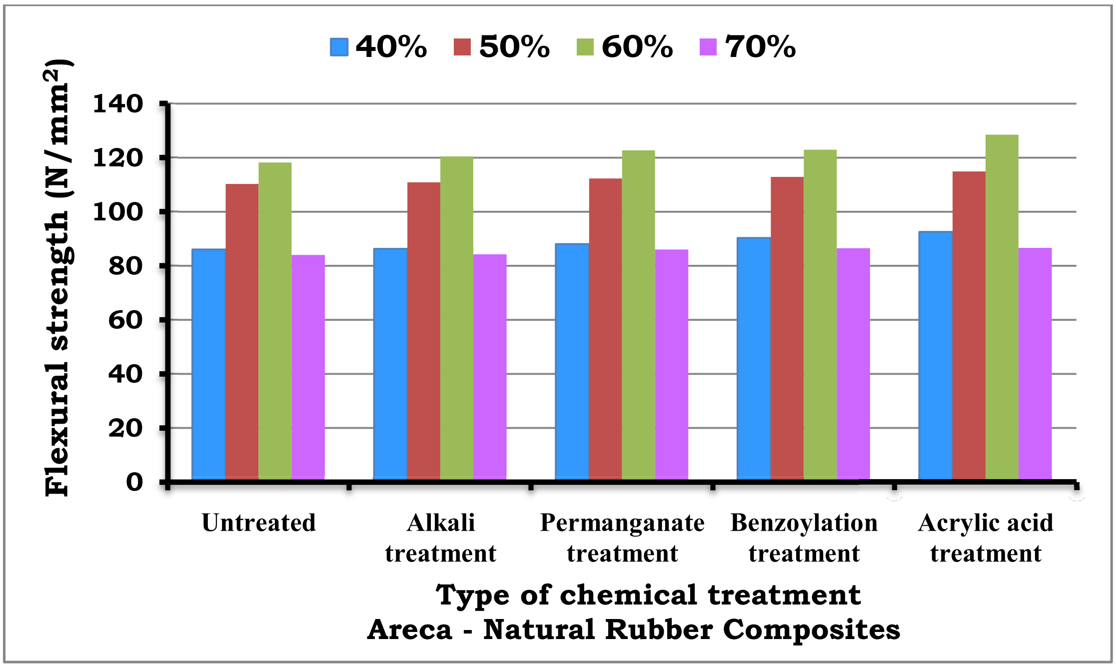


Fig: 4.3 Flexural strength of Areca – Natural Rubber composites with different fibre loadings

It wasobserved that the fibre content and chemical modifications of areca fibregreatly influenced the flexural strength of areca - natural rubber composites.The flexural strength of untreated areca fibre reinforcednatural rubber composites with 60% fibre loading increased by 37.48% compared to 40% fibre loading, 7.28% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 28.95% when compared to 60% fibre loading.

The flexural strength of 6% sodium hydroxide treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 39.68% compared to 40% fibre loading, 8.71% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 30.07% when compared to 60% fibre loading.

The flexural strength of 0.5% potassium permanganate treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 39.38% compared to 40% fibre loading, 9.28% compared to 50% fibre loading and for 70% fibre loading,flexural strength decreased by 29.88% when compared to 60% fibre loading.

The flexural strength of benzoyl chloride treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 36.28% compared to 40% fibre loading, 8.97% compared to 50% fibre loading and for 70% fibre loading,flexural strength decreased by 29.65% when compared to 60% fibre loading.

The flexural strength of 5% acrylic acid treated areca fibre reinforced natural rubber composites with 60% fibre loading increased by 38.88% compared to 40% fibre loading, 11.89% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 32.56% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced natural rubber composites with 60% fibre loading showed 1.91%, 3.74%, 3.99% and 8.68% increase in flexural strength values respectively when compared to untreated areca - NR composites with same 60% fibre loading [164].

4.3.3Impact strength of Areca – Natural Rubber composites

Impact strength is the capacity of the material to withstand a suddenly applied load and is expressed in terms of energy.Impact strength is determined by Charpy Impact test. The impact strength is calculated as the ratio of impact absorption to test specimen cross-section(J/mm^2). It is very vital to know the optimum fibre loading to get superior impact properties [155].

Impact strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treatedareca fibre reinforced natural rubber composites with fibre loadings of 40%, 50%, 60% and 70% are given in Table 4.5.

It was observed that areca - NR composites with 60% fibre loadings showed maximum impact strength valueswhen compared to areca fibre reinforced natural rubber composites with other fibre loadings.Irrespective of chemical treatment, all chemically treated arecafibre reinforced NR composites showed higher impact strength values than the untreated arecafibre reinforced natural rubber composites.

Table 4.5 Impact strength values of Areca - NR composites

Areca fibre	**Impact strength values in J/mm^{2}at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	10.26	12.24	14.56	10.22
6% Alkali treated	10.85	12.84	15.02	10.42
0.5% Potassium permanganate treated	12.04	13.52	16.24	10.86
Benzoyl chloride treated	12.86	13.96	17.86	11.02
5% Acrylic acid treated	13.26	14.82	20.22	12.24

The impact strength of untreated and all chemically treated areca fibre reinforced natural rubber composites with 40%, 50%, 60% and 70% fibre loadings areshown in Fig: 4.4.

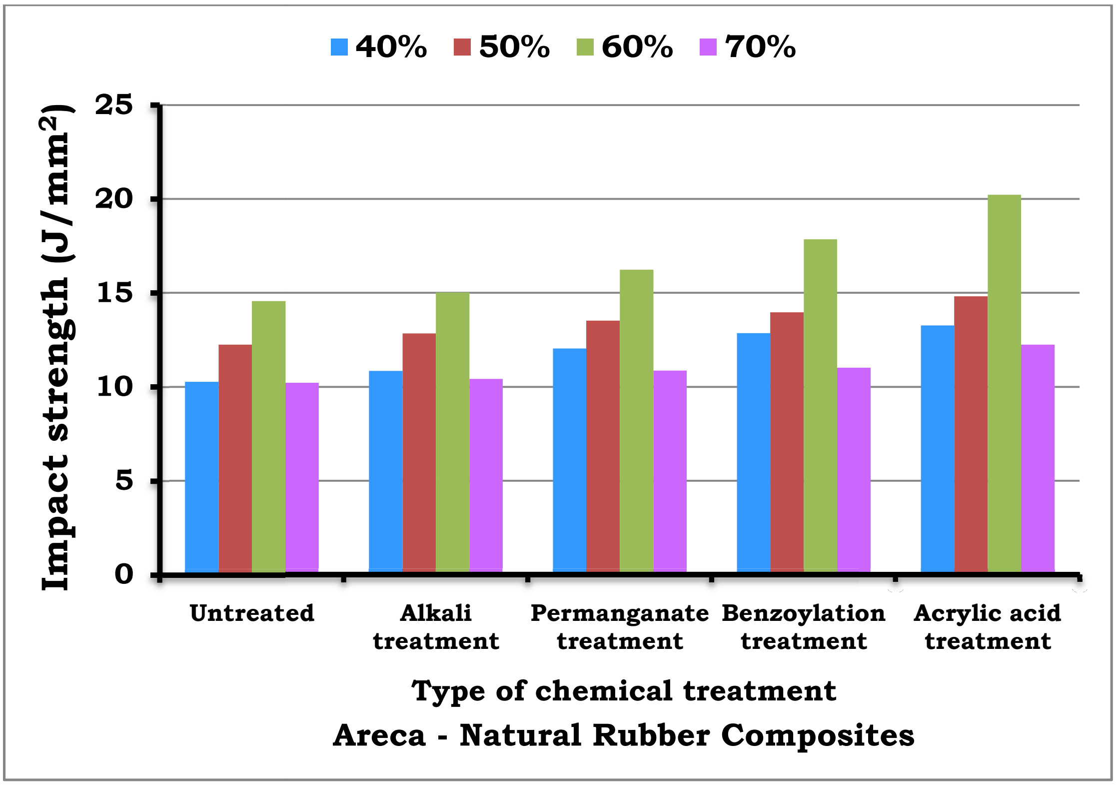


Fig: 4.4 Impact strength of Areca –Natural Rubbercomposites with different loadings

In case of untreated areca fibre reinforced natural rubbercomposites, the impact strength of 60% fibre loading increased by 41.91% compared to 40% fibre loading, 18.95% compared to 50% fibre loading and for 70% fibre loading, it decreased by 29.81% when compared to 60% fibre loading.

In case of 6% sodium hydroxide treated areca fibre reinforced natural rubbercomposites, the impact strength of 60% fibre loading increased by 38.43% compared to 40% fibre loading, 16.98% compared to 50% fibre loading and for 70% fibre loading, it decreased by 30.63% when compared to 60% fibre loading.

For 0.5% potassium permanganate treated areca fibre reinforced natural rubber composites, the impact strength of 60% fibre loading increased by 34.88% compared to 40% fibre loading, 20.12% compared to 50% fibre loading and for 70% fibre loading, it decreased by 33.13% when compared to 60% fibre loading.

In case of benzoyl chloride treated areca fibre reinforced natural rubber composites, the impact strength of 60% fibre loading increased by 38.88% compared to 40% fibre loading, 27.94% compared to 50% fibre loading and for 70% fibre loading, it decreased by 38.30% when compared to 60% fibre loading.

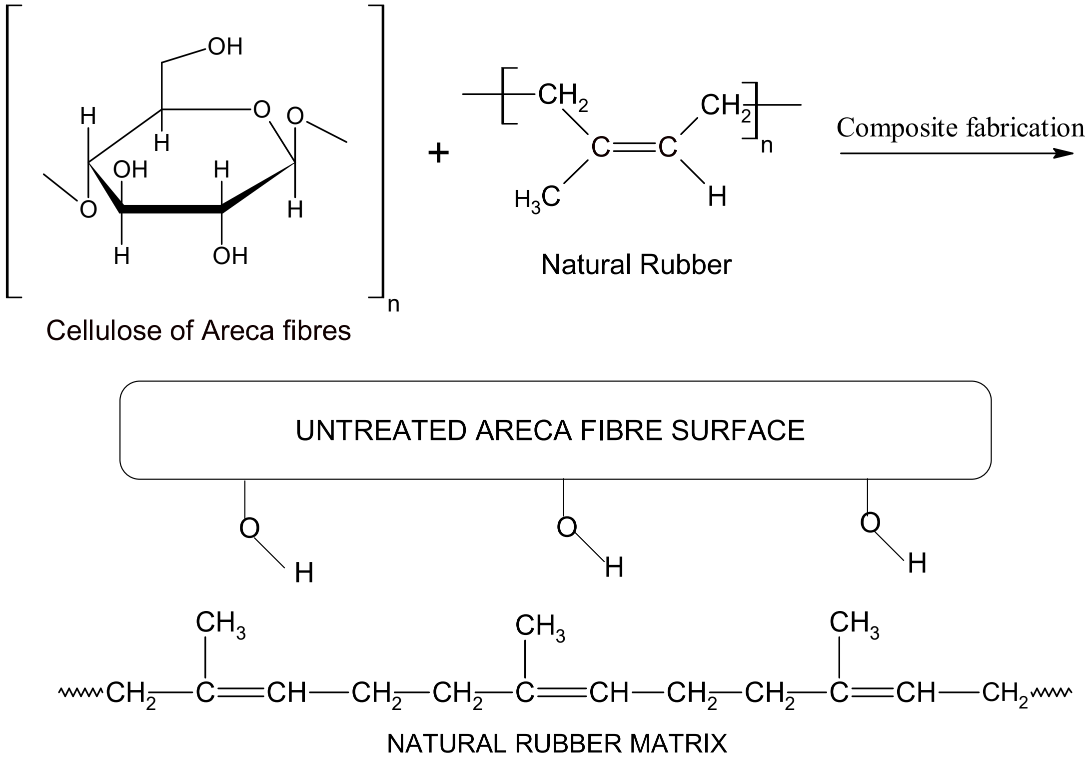
For5% acrylic acid treated areca fibre reinforced natural rubbercomposites, the impact strengthof 60% fibre loading increased by 52.49% compared to 40% fibre loading, 36.44% compared to 50% fibre loading and for 70% fibre loading, it decreased by 39.47% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca -NR composites with 60% fibre loading showed 3.16%, 11.54%, 22.66% and 38.87% increase in impact strength values respectively when compared to untreated areca fibre reinforced NR composites with same 60% fibre loading [166].

4.3.4 Effect of Chemical Treatments on Areca Fibre Reinforced Natural Rubber Composite Properties

4.3.4.1 Untreated Areca – Natural Rubber Composites

In the composites, polymeric matrix molecules may be anchored to the fibre surface by chemical reaction or by adsorption and this determines the extent of interfacial adhesion.Based on hypothetical model given by various researchers [103, 124, 156], the possible hypothetical model of interface of untreated areca fibre – natural rubber matrix can be written as follows.



Scheme 4.1 Hypothetical model of interface between cellulose-OH of untreated Areca fibres with Natural Rubber matrix

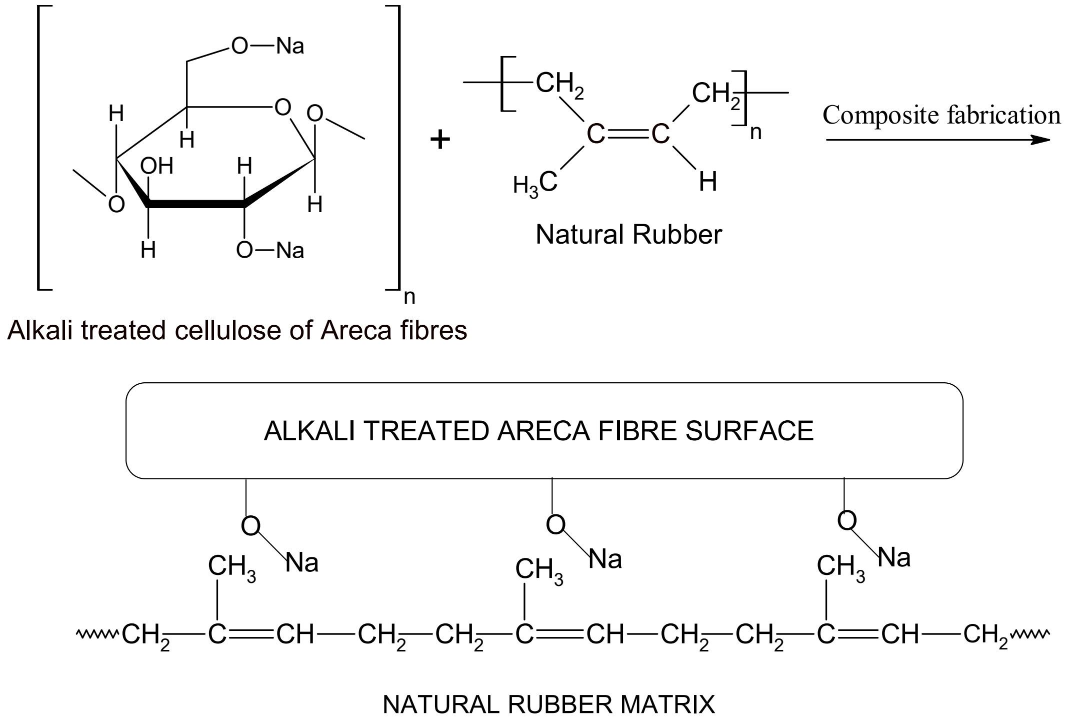
The main problem in natural fibre filled rubber is its incompatibility between the hydrophilic nature of areca fibres and the hydrophobic nature of rubber, and as a result, it merely possesses adhesion, leading to poor properties such as tensile strength, flexural strength and impact strength to the composites.

4.3.4.2Alkali Treated Areca – Natural RubberComposites

The properties of short areca fibre reinforced natural rubber composites depend on various factors such as the aspect ratio of fibre, length of fibre, content of fibre, fibre orientation and dispersion and fibre-rubber adhesion [168]. Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of alkali treated areca fibre surface having reactive -ONa groups with thermoplastic elastomeric natural rubber polymeric matrix can be schematically represented as follows.

The alkali treatment of areca fibres changed the orientation of highly packed crystalline cellulose and forms an amorphous region. This provides more access for the penetration of chemicals and there is a formation of Fibre-cell-O-Na groups between the cellulose molecular chains of areca fibres. The alkali treatment takes out certain portion of hemicelluloses, lignin, adhesive pectin, waxy and oil covering materials.Due to this, hydrophilic hydroxyl groups are reduced and areca fibres moisture resistance property is increased. It also reduced arecafibre diameter and thereby increased its aspect ratio (length/diameter ratio).

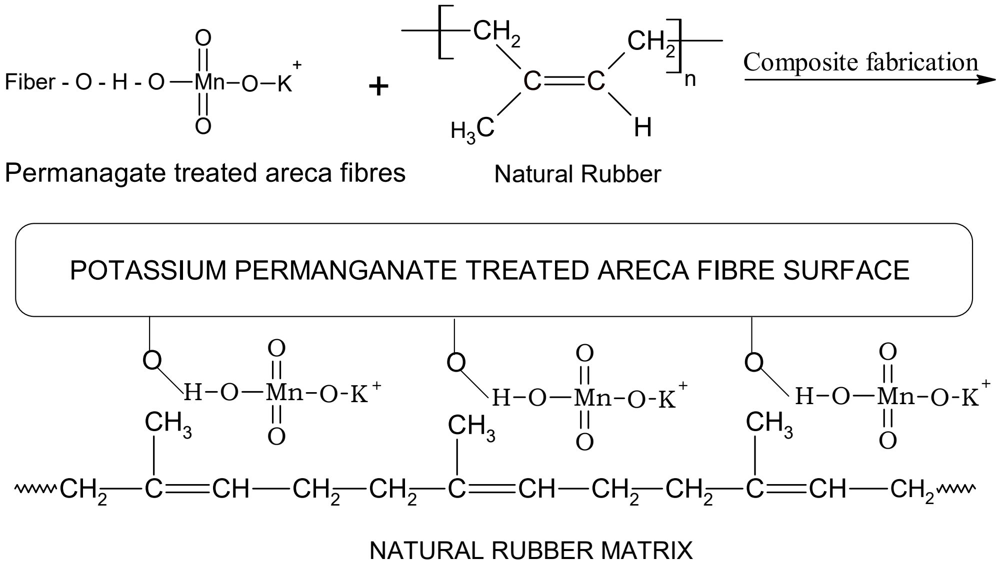
As a result, reactive areca fibre surface area for good adhesion with the natural rubber matrix is increased and chemical interlocking at the interface is improved [34, 40, 61, 92, 95, 102-107, 157-158, 166]. Hence, sodium hydroxide treated areca fibre reinforced natural rubber composites resulted in increased tensile strength, flexural strength and impact strength values when compared with that of untreated areca fibre reinforced natural rubber composites of corresponding fibre loadings.



Scheme 4.2 Hypothetical model of interface of alkali treated Areca fibre – NR composites

4.3.4.3 Potassium Permanganate Treated Areca – Natural RubberComposites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of potassium permanganate treated areca fibres with thermoplasticelastomeric natural rubber polymer matrix can be schematically represented as follows.



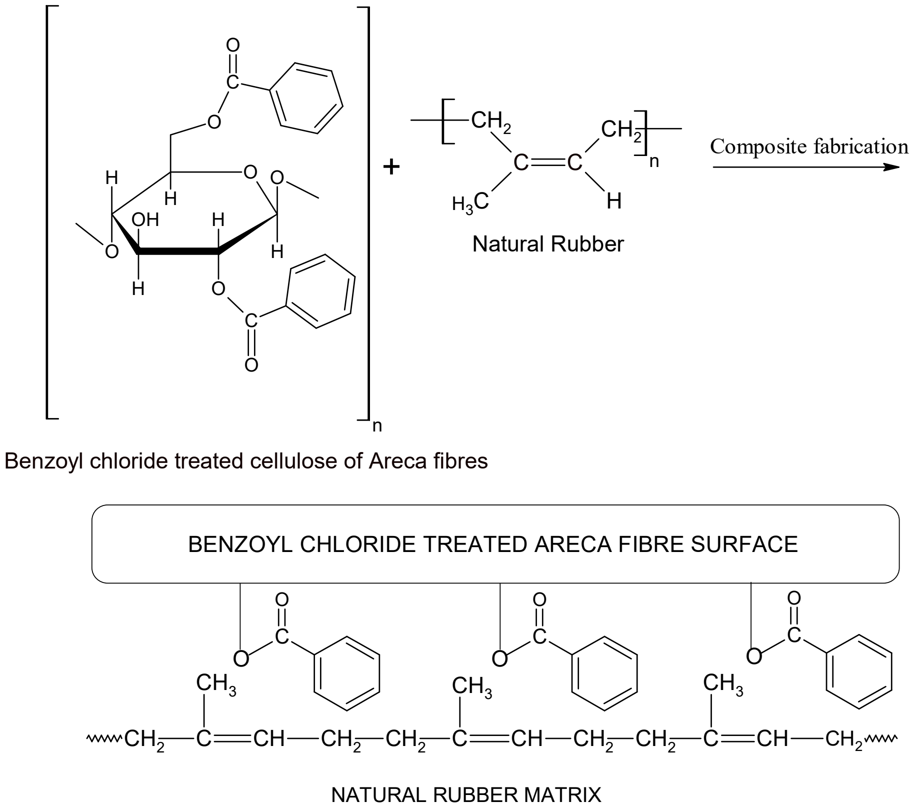
Scheme 4.3 Hypothetical model of interface of potassium permanganate treated Areca fibre – NR composites

Potassium permanganate treatment produces highly reactive permanganate ions and cellulose manganate is formed as a result of reaction of this highly reactive permanganate ion (Mn^{3+}) with cellulose of areca fibres. Permanganate ions also react with lignin constituents and carve the areca fibre surface. As a result, areca fibre surface became physically rough, its moisture resistance property is improved and thus improved chemical interlocking at the interface and provided better adhesion with the polymeric resin natural rubber[34, 40, 67, 92, 95, 102-103, 108-110, 159, 166].

Because of this, potassium permanganate treated areca fibre reinforcednatural rubber compositesshowed increased tensile strength, flexural strength and impact strength values when compared with that of untreated areca fibre reinforcednatural rubbercomposites of respective fibre loadings.

4.3.4.4 Benzoylated Areca – Natural RubberComposites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of benzoyl chloride treated areca fibresurface having reactive C_6H_5COO- groups with the thermoplastic elastomeric natural rubberpolymeric matrix can be schematically given as follows.



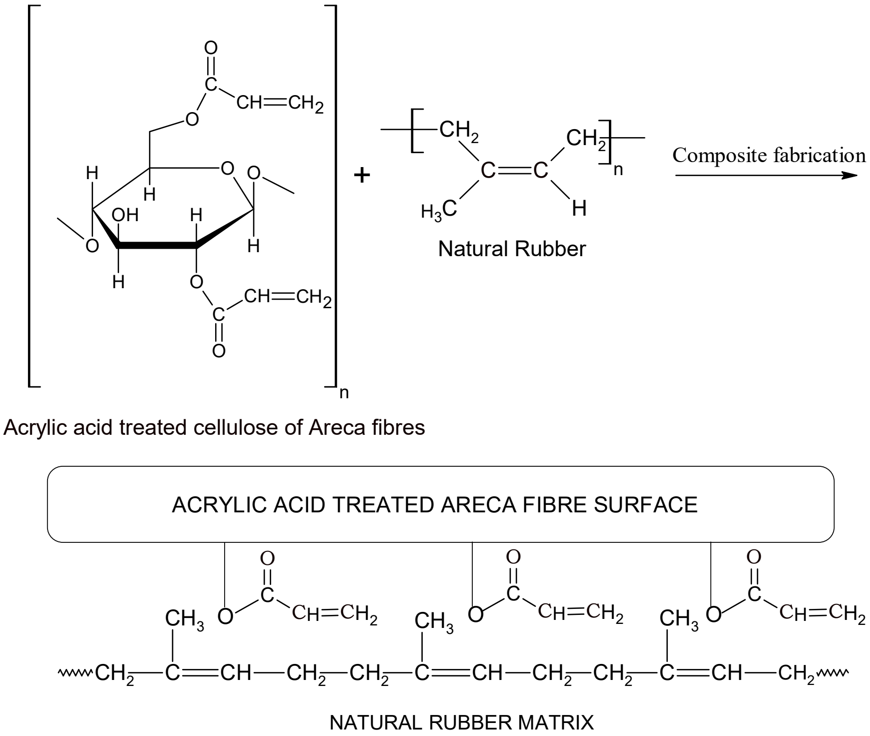
Scheme4.4 Hypothetical model of interface of benzoylated Areca fibre – NR composites

There is a formation of ester linkage with areca fibres due tobenzoylation treatmentand benzoyl groups are attached on to the cellulose backbone of areca fibres. Extractable materials such as lignin, waxes and oil covering materials areisolated. Hence, the benzoylated areca fibre surface became physically rough and hence moisture absorption of benzoylated areca fibres is decreased.

Further, it enhancedchemical interlocking at the interface and provided effective fibre surface area for good adhesion with the natural rubber polymeric matrix[34, 40, 57, 61, 95, 102-103, 105, 111, 159, 166].As a result, benzoylated areca fibre reinforced natural rubber composites showed augmented tensile strength, flexural strength and impact strength values when compared with that of untreated areca fibre reinforced natural rubbercomposites of respective fibre loadings.

4.3.4.5 Acrylated Areca – Natural RubberComposites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of acrylic acid treated areca fibre surface having reactive CH_2=CHCOO- groups with thermoplastic elastomericnatural rubber polymer matrix is shown in Scheme 4.5.



Scheme 4.5 Hypothetical model of interface of acrylated Areca fibre - NR composites

During acrylic acid treatment, there is replacement of hydrophilic hydroxyl groups by hydrophobic ester groups and most of the hemicelluloses and lignin are removed. Acrylated areca fibre surface became physically rough. Hence, effective fibre surface area for good adhesion with the polymeric matrix is increased, chemical interlocking at the interfaceis improved and stress transfer capacity at the interface is enhanced[34, 40, 95, 102-103, 112-113, 166]. As a result, for acrylic acid treated areca fibre reinforced natural rubber composites, higher tensile strength, flexural strength and impact strength values are observed when compared with that of untreated areca fibre reinforced natural rubber composites of corresponding fibre loadings.

Amongst all the chemical treatments carried out, higher tensile strength and decomposition temperature values were showed by areca fibres treated with acrylic acid followed by benzoyl chloride, potassium permanganate and sodium hydroxide treatments as indicated in Table 3.5. Hence, amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced natural rubber composites showed maximum tensile strength, flexural strength and impact strength values followed by benzoylated areca-NR, potassium permanganate treated areca-NR and alkali treated areca-NR composites.

These results clearly evidenced that chemical treatments are very effective in surface modification of areca fibres and in improving the tensile strength, flexural strength and impact strength of chemically treated areca fibre reinforced natural rubber composites.

4.3.5 Effect of Fibre Loadings on Areca Fibre Reinforced Natural Rubber Composite Properties

With increase in fibre loading from 40% to 60%, the tensile strength, flexural strength and impact strength values of all untreated as well as chemically treated areca fibre reinforced natural rubber composites are increased and beyond 60% fibre loading, the tensile strength, flexural strength and impact strength showed a decline. That is areca fibre reinforced natural rubber composites exhibited maximum tensile strength, flexural strength and impact strength values at 60% fibre loading. This is because of better fibre distribution in matrix, less fibre fractures and effective transfer of load from matrix to fibres at 60% fibre loading. It has also been reported that high fibre content increases the probability of fibre agglomeration and further it results in regions of stress concentration and requires less energy for crack propagation [162].As fibre loading increases, more force is required to pullout the fibres and thereby increases the tensile strength, flexural strength and impact strength.

The observed increase in tensile strength, flexural strength and impact strength values with chemical modifications and as well as with increase in fibre loadings up to 60% is in good agreement with the results reported in literature[30, 58-63, 67, 69, 73, 75-77].These results suggest that the areca fibre reinforced natural rubber composites are capable of showing higher values because of strong interfacial bonding between the chemically treated areca fibres and thermoplastic elastomeric natural rubber matrix.

Further, in the case of composites with 40% and 50% fibre loadings, lesser areca fibre fraction is used and these areca fibres are serving as the crucial reinforcement in the natural rubber composites and hence, the reduced fibre amount resulted in a significant decrease in tensile strength, flexural strength and impact strength values compared to areca fibre reinforced natural rubber composites with 60% fibre loading [165].

The decrease in tensile strength,flexural strength and impact strength values for all untreated as well as chemically treated areca fibre reinforced natural rubber composites beyond 60% fibre loading is due to fact that the melted rubber could not reach each of the areca fibre surface because of smaller amount of matrix material and also, there is poor interfacial adhesion and inefficient stress transfer from matrix to fibres at 70% fibre loading [160]. The factors contributing to the lower tensile strength,flexural strength and impact strength values at 70% fibre loading may also be due to the random alignment of short areca fibres and the presence of voids in the areca fibre reinforced natural rubber composites [161]. The decrease in impact strength may be due to the micro spaces between the fibre and the matrix which initiates micro cracks on impact and results in crack propagation leading to failure [77].

So, these chemically treated areca fibre reinforced natural rubber composites with 60% fibre loadings are best suitable for applications where high tensile strength, flexural strength and impact strength values are required.

4.4 CONCLUSION

Due to chemical treatments, there is introduction of some reactive groups onto the areca fibre surface. And also, the impurities like pectin, fat and lignin present in the areca fibresare removed by chemical treatments. Further, a rougher fibre surface is formed after all the chemical treatments. From these studies, it is clearly concluded that chemical treatments of areca fibresare of greater importance in modifying the areca fibre surface, in reducing the hydrophilic nature of arecafibres, in enhancing the areca fibre–polymer matrix adhesion and thereby increasing the properties of areca fibre reinforced natural rubber composites. Maximum values of tensile strength, flexural strength and impact strengthare observed at 60% fibre loading for all untreated as well as chemically treated areca fibre reinforced natural rubber composites. Amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced natural rubber composites of 60% fibre loading showed maximum tensile strength, flexural strength and impact strength values followed by benzoyl chloride treated areca – natural rubber,potassium permanganate treated areca – natural rubber and alkali treated areca – natural rubber composites at the same 60% fibre loading. Hence, areca fibre reinforced natural rubber composites can be considered as a very promising material for the fabrication of light weight materials and can be effectively used in vibration dampers, tyres, hoses and belts.

CHAPTER 5

CHARACTERIZATION OF ARECA FIBRE REINFORCED THERMOSET POLYMER COMPOSITES

5.1 INTRODUCTION

In this chapter, fabricationprocess of untreated,alkali treated, potassium permanganate treated, benzoyl chloride treated and acrylic acid treated areca fibre reinforced thermoset polymer composites such as areca – epoxy and areca – urea formaldehyde composites with different fibre loadings have been discussed.Curing reactions of epoxy resin and urea formaldehyde resin in presence of hardener are studied. The investigation of polymer composite properties such as tensile strength, flexural strength and impact strength of untreated and above said chemically treated areca fibre reinforced epoxy and areca fibre reinforced urea formaldehyde polymer composites are done under 40%, 50%, 60% and 70% fibre loadings. The tensile strength of untreated areca fibre reinforced epoxy composites under 10%, 20%, 30%, 40%, 50%, 60% and 70% have also been determined. The effect of chemical treatments and the effect of fibre loadings on the properties of all fabricated areca - epoxy and areca - urea formaldehyde polymer composites are studied.

5.2MATERIALS AND METHODS

5.2.1Thermoset Polymer Matrix

Epoxy resin and Urea Formaldehyde (UF) resin were obtained from Akolite Synthetic Resins, Mangalore.

5.2.2 Hardener

In this study, araldite hardener HY951 (N,N'-bis(2-aminoethyl)ethane-1,2-diamine, $C_6H_{18}N_4$) and hardener ammonium chloride (NH_4Cl) were used as curing agents for the preparation of Areca – Epoxy and Areca – Urea Formaldehyde polymer composites respectively and they were obtained from Akolite Synthetic Resins, Mangalore.In the curing process of epoxy resin and urea formaldehyde resin,curing agents (hardeners) play a significant role because these curing agents relate to the curing kinetics, reaction rate, gel time, degree of cure, viscosity, curing cycle and the final properties of the cured products.The chemical structure of araldite hardener HY951 is given in Fig: 5.1.

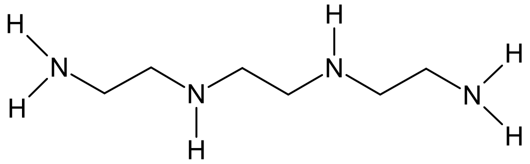


Fig: 5.1 Chemical structure of araldite hardener HY951

(N, N'-bis (2-aminoethyl) ethane-1, 2-diamine)

5.2.3 Epoxy Resin.

Epoxy resin is the most commonly used thermoset resin in composite fabrication technology. Epoxy resin possesses tailored elasticityand excellent finishing due to the presence of stable ether linkages. The chemical structure of epoxy resin is given in Fig: 5.2.

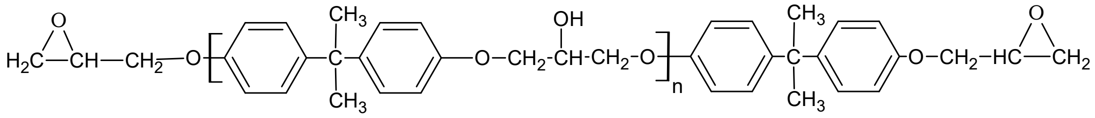


Fig: 5.2 Chemical structure of Epoxy resin

The polar nature (-O and –OH groups) of the molecule produces excellent adhesionquality.The raw uncured resin molecules present in a thermoset epoxy resin are cross linked through a catalytic exothermic chemical reaction and creates extremely strong bonds to one another and the resin changes from a liquid state to a solidstate. Moulds made from epoxy resins are employed for the production of components for air-crafts and automobiles.

5.2.3.1 Properties of Epoxy Resin

Epoxy resin possesses the properties such as good chemical, environmental and moisture resistance, good resistance to solvents and corrosives, good thermal stability,good electrical insulating properties, long shelf life, low shrinkage during cure and good mechanical and fatigue strength properties.The properties of epoxy resin are given in Table 5.1.

Table 5.1Properties of Epoxy resin

Properties	Epoxy resin
Density (g/cm^3)	1.15-1.20
Water absorption (%)	0.15-0.52
Tensile strength (N/mm^2)	45-60
Young's modulus (N/mm^2)	1371
Elongation at break (%)	4

5.2.4 Urea – Formaldehyde Resin

Urea formaldehyde (UF)resins accounts for over 80% of amino resins. The synthesis of UF resin involves the formation of monomethylol urea and other intermediates such are dimethylol urea, trimethylol urea and tetramethylol urea based on reaction conditions such as pH, temperature and the ratio of formaldehyde to urea [169-172]. The chemical structure of monomethylol urea is given in Fig: 5.3.

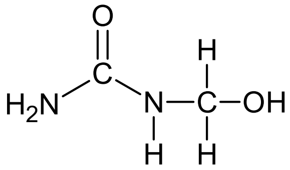


Fig: 5.3 Chemical structure of Monomethylol Urea

5.2.4.1 Properties of Urea Formaldehyde Resin

Low price, absence of colors in cured polymer, low cure temperature, resistance to micro organisms and abrasion, hardness and good thermal properties are the superior qualities of ureaformaldehyde resin.The properties of urea formaldehyde resin are given in Table 5.2.

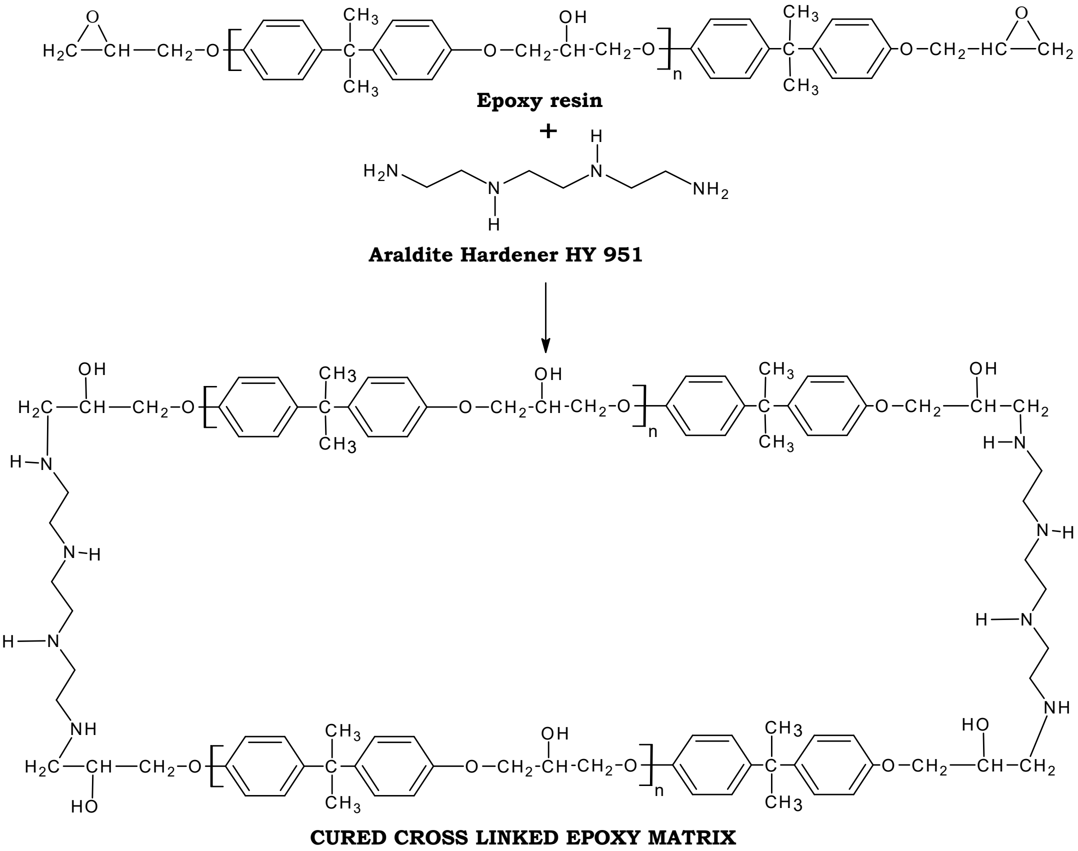
Table 5.2 Properties of Urea Formaldehyde resin

Properties	Urea Formaldehyde resin
Density (g/cm^3)	1.260 - 1.262
pH	7.5 - 8.0
Tensile strength (N/mm^2)	20-25
Tensile modulus (N/mm^2)	75 - 90
Elongation at break (%)	5.5
Viscosity (cps)	200 - 300
Pot life (days)	60

5.2.5 Curing Reaction of Epoxy Resin

The curing reaction of epoxy resin is the process by which an epoxide group present in the epoxy resin and the curing agents with or without the catalysts are transformed from low-molecular-weight to a highly cross linked structure. Epoxy resin can react with both nucleophilic curing reagents and electrophilic curing agents due to the presence of 1, 2-epoxide groups in the epoxy resin. Because of high electro negativity of an oxygen atom, the chemical bonds between oxygen and carbon atoms in the 1, 2-epoxide groups are polar bonds and hence the oxygen atom becomes partially negative and the carbon atoms become partially positive. And also, the strained (unstable) nature of the epoxide ring favors the easy attack of polar groups (nucleophiles) on it and facilitates the ring opening reaction of epoxy group. The chemical structures of the epoxides also have significantconsequences on the curing reactions. More details about the relative reactivity of various epoxides with different curing agents and the orientation of ring opening of epoxides are given by Tanaka and Bauer [173]. It is concluded from their studies that the electronwithdrawing groups present in the epoxides would increase the rate of reaction when cured with nucleophilic reagentsand would decrease the rate of reaction of epoxides when cured with electrophilic curing agents.

Many poly-functional curing agents with active hydrogen atoms such as polyamines, polyamides and polyphenols perform nucleophilic addition reaction with epoxides.Based on the mechanism of curing reaction ofdifferent epoxy resin/amine systems proposed by various researchers [173-176], the possible curing reaction of epoxy resin in presence of araldite hardener HY951 (N,N'-bis(2-aminoethyl)ethane-1,2-diamine)may be written as follows.



Scheme 5.1 Curing reaction of Epoxy resin

5.2.6 Curing Reaction of Urea Formaldehyde Resin

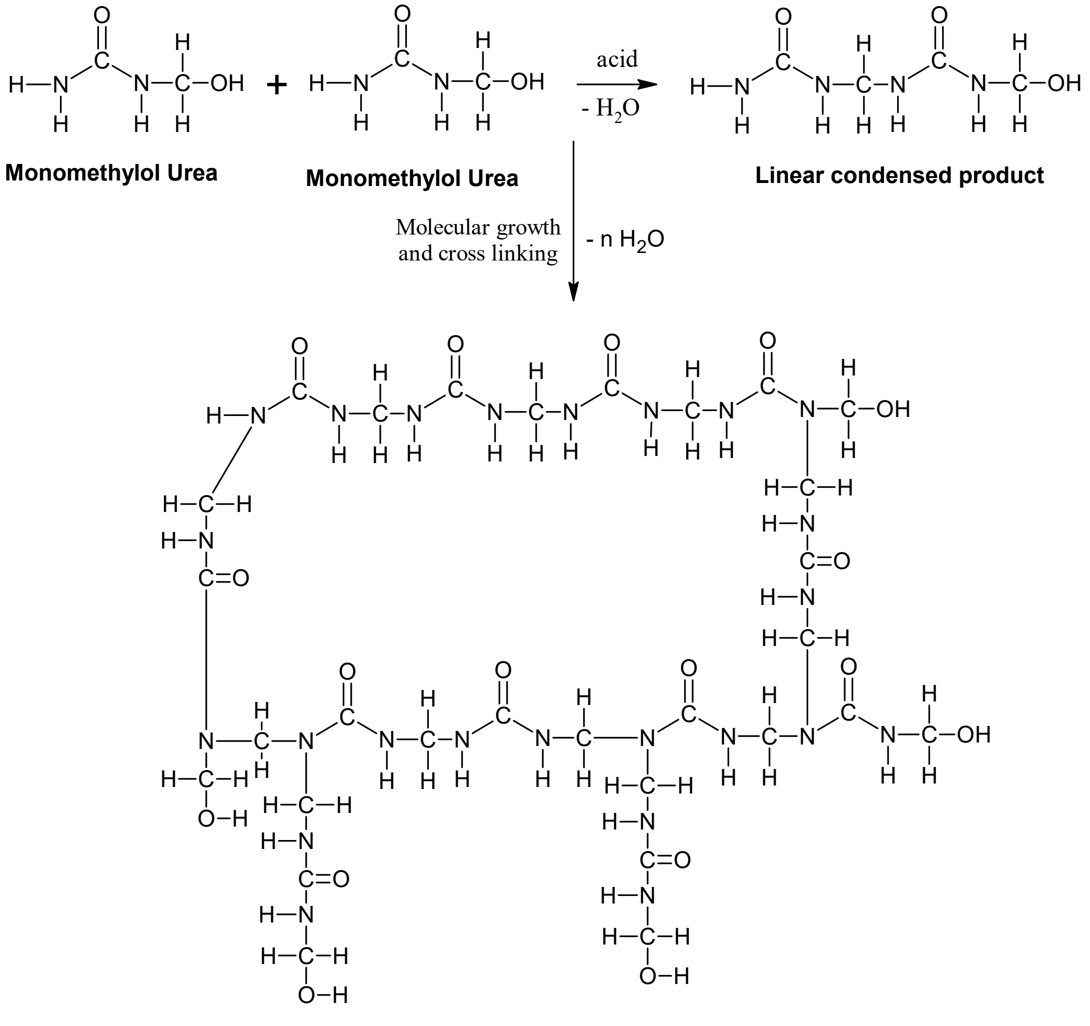
The curing reaction of Urea Formaldehyde resin is the process by which the low molecular weight methylol derivatives of urea are transformed to a highly cross linked network structure in presence of curing agents like NH_4Cl. NH_4Cl has a strong catalyzing effect on reactants in urea formaldehyde resin systems.

$$4\ NH_4Cl + 6\ HCHO \longrightarrow 4\ HCl + (CH_2)_6N_4 + 6\ H_2O$$

Scheme 5.2 Reaction of hardener - NH_4Cl with formaldehyde

The effect of hardener, ammonium chloride on urea formaldehyde resin curing is to release hydrochloric acid by reacting with free formaldehyde present in the urea formaldehyde resin, so that the released H^+ ions from HCl favors the condensation polymerization reaction of monomethylol urea. And also, by the addition of NH_4Cl hardener, pot life and rate of curing of urea formaldehyde resin can be regulated [177].

Condensation polymerization reaction of urea formaldehyde resin involves condensation reaction between the nucleophilic nitrogen of monomethylol urea and the electrophilic carbonyl carbon of the formaldehyde in presence of hydrochloric acid released by hardener NH_4Cl to form polymer molecules either in linear or cured network (cross linked) molecular structure [169-172].



Scheme 5.3 Curing reaction of Urea - Formaldehyde resin

5.2.7 Fabrication of Areca Fibre ReinforcedEpoxy and Areca Fibre ReinforcedUrea Formaldehyde Composites

The fabrication of untreated,6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforcedepoxy and areca fibre reinforcedurea formaldehyde composite process was performed by compression molding technique. First, resin and its corresponding hardener were mixed in 10:1 ratio. One half of the resin was placed inside the mixing chamber for about 1 min at 20 RPM; then areca fibres were added over a period of 2 min. Then, the other half of the resin was placed inside the mixing chamber and the mixing speed was increased to 30 RPM for 5 min. The resulting material was compression molded at a pressure of 0.5 MPa using a Santec compression molding press. Finally, the composites were post-cured at room temperature for 15 days. The weight fractions 40%, 50%, 60% and 70% of areca fibre was carefully controlled during the mixing of two ingredients. The moulds have been prepared with dimensions of 300 × 300 × 10 mm^3 [92, 95, 102].

And also, untreated areca fibre reinforced epoxy composites with 10%, 20%, 30%, 40%, 50%, 60% and 70%fibre loadings which were post-cured at a room temperature for 15 days were fabricated to test tensile strength only. Similarly, another set of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced epoxy composites with 40%, 50%, 60% and 70%fibre loadings which were post-cured at a room temperature for 18 days werealso fabricated to test tensile strength only.

5.2.8 Characterization of Areca Fibre ReinforcedEpoxy and Areca Fibre Reinforced Urea Formaldehyde Composites

Mechanical properties such as tensile strength, flexural strength (3-point stating bending test) and impact strength of untreated, 6% alkali treated, 0.5% permanganate treated, benzoyl chloride treated and 5%

acrylic acid treated areca fibre reinforced epoxy andareca fibre reinforced UF composites were measured by following ASTM standard procedures at a standard laboratory atmosphere of 30±2 °C and 65% relative humidity (RH 65%).At least 5 replicate specimens were tested and the results were presented as an average of tested specimens.

5.2.8.1 Tensile Strength Testing

Untreated and all chemically treated areca - epoxy and areca – UF polymer composite specimens prepared for the tensile strength test were cut and the measurement was carried out according to ASTM D638 [Type III] standards. A dumbbell shape specimen with the total length of 250 mm, a gauge length of 100 mm, width of 22 mm at gauge length section and 35 mm width at gripping section and a uniform thickness of 10 mm was considered for the test. The composite specimen was loaded in the Universal Testing Machine until failure of the specimen occurred.

5.2.8.2 Flexural Strength Testing

Flexural test of untreated and all chemically treated areca - epoxy and areca – UF polymer composites was performed by using 3-point bending method on a Universal Testing Machine (Instron 5566) according to ASTM D790-03 procedure. Specimens prepared for the flexural test were cut with help of zig saw and the dimensions of the specimen used were 160 mm length, 50 mm width and 10 mm thickness. The specimens were tested at a crosshead speed of 2 mm/min.

5.2.8.3 Impact Strength Testing

Impact energy absorbed by untreated and all chemically treated areca - epoxy and areca – UF polymer composite specimens was determined by performing Charpy method of impact testing methods as per ASTM-D256-90 standard procedures with notched specimens using Instron Pendulum Tester (9050 Manual Model). The width and depth of each specimen was measured with a micrometer screw gauge to the nearest of 0.01mm and the length was measured to the nearest of 0.1 mm with digital caliper. The mean specimen dimensions were used to calculate impact strength. Specimen of length of 55 mm with square cross section of 10 mm side and U notch made at the center of the specimen for a depth of 5 mm was considered for the impact test.

5.3 RESULTS AND DISCUSSION

5.3.1 Tensile Strength Values

5.3.1.1 Tensile strength of Areca – Epoxy Composites

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of composite materials used instructural applications. The force per unit area (N/mm^2 or MPa) required to breakcomposite material is the ultimate tensile strength or tensile strength at break.

The effect of areca fibre loadings on tensile strength of untreated areca fibre reinforced epoxy composites which were post cured for 15 days is given in the following Fig: 5.4.

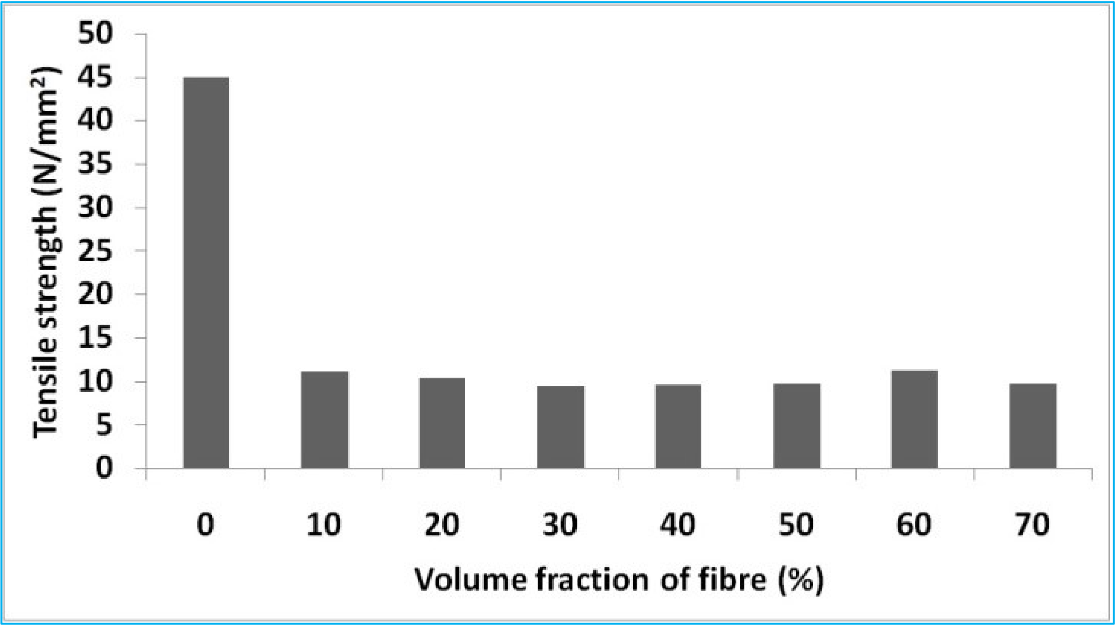


Fig: 5.4 Tensile strength of untreated Areca – Epoxy composites

It was clearly understood that the tensile strength of areca fibre reinforced epoxy composites was less than that of epoxy matrix. There was no significant difference in tensile strength of composites madeby reinforcing untreated areca fibres with different fibre loadings. The highesttensile strength, 11.37 N/mm^{2}was obtained for 60% fibre loading with anextension of 9 mm. The factorscontributing to the lower tensile strength values may be due to the random alignment ofshort areca fibres and the presence of voids in the composites [161]. The untreated, 2%, 4%, 6%, 8% and 10% NaOH treated and 0.5% $KMnO_4$ treated areca fibre reinforced epoxy composites which were post-cured at a room temperature for 15 dayswith 60% fibre loadings were prepared for the tensile strength measurement test [92].The resultsobtained for the above said areca-epoxy composites are shown in Table 5.3.

Table 5.3 Tensile strength values of 15 days post-cured Areca – Epoxy composites

Areca Fibre	Tensile strength (N/mm^2) of areca –epoxy composites (60% fibre loading)
Untreated	11.37
2% NaOH treated	13.75
4% NaOH treated	13.64
6% NaOH treated	14.54
8% NaOH treated	13.87
10% NaOH treated	12.73
0.5% $KMnO_4$ treated	10.90

The significant increase in tensile strength was noticed for alkali treatedareca fibre reinforced epoxy composites. It has been understood that the areca-epoxy composites prepared byreinforcing areca fibres treated with 6% NaOH bear the maximum load of 3.2 KNwith an extension of 5 mm. The tensile strength of alkali treated areca fibre reinforced epoxy compositeswas found to be increased with increasing concentration of NaOH up to 10%. That is, thetensile strength increased by 21%, 20%, 28%, 22%and 12% for compositesprepared by reinforcing areca fibres treated with 2%, 4%, 6%, 8% and 10% NaOHrespectively when compared to untreated areca – epoxy composites. This implied that the alkali treatment removed most of the fat, lignin, pectin and oil covering the external surface of the fibre cell wall and thus improved the fibre adhesive quality in combination with the epoxy matrix. The improved interlockingcaused by the denser NaOH between the areca fibres and the epoxy matrix may be favourableto the tensile strength of the areca fibre reinforced epoxy composites [92].

The tensile strength, however, drops by 5% and 14% respectively for epoxy composites prepared with 8% and 10%NaOH treated areca fibres when compared with epoxy composites prepared with 6% NaOH treated areca fibres. The smaller tensile strength denotes the degradation of areca fibres ontreatment with denser alkali. Severe alkali treatment induces larger fibrillation and hence, reduces the fibre efficiency in the composite strengthening [114]. The tensile strength of 0.5% permanganate treated areca-epoxy composites with60% fibreloading was found tobe 10.90 N/mm^2 with a displacement of 6 mm and the tensile strength valuewasmarginallylower than that ofuntreated areca–epoxy composites [92].

The tensile strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced epoxy composites which were post-cured at a room temperature for 18 daysunder 40%, 50%, 60% and 70% fibre loadings are given in Table 5.4.

It was observed that the areca fibre content and the chemical modifications of areca fibres greatly influenced the tensile strength of 18 days post cured areca fibre reinforced epoxy composites.

Table 5.4Tensilestrength values of 18 days post-cured Areca - Epoxy composites

Areca fibre	Tensile strength values in N/mm² at given fibre loadings (wt %)			
	40%	50%	60%	70%
Untreated	20.18	21.48	22.37	19.86
6% Alkali treated	20.68	25.18	29.09	19.64
0.5% Potassium permanganate treated	21.28	26.56	32.04	20.52
Benzoyl chloride treated	22.06	28.58	34.06	20.84
5% Acrylic acid treated	24.84	30.26	36.58	22.52

The effect of chemical treatments on tensile strength of untreated,6% alkali treated, 0.5% permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca - epoxy composites with 40%, 50%, 60% and 70%fibre loadings are depicted in Fig: 5.5.

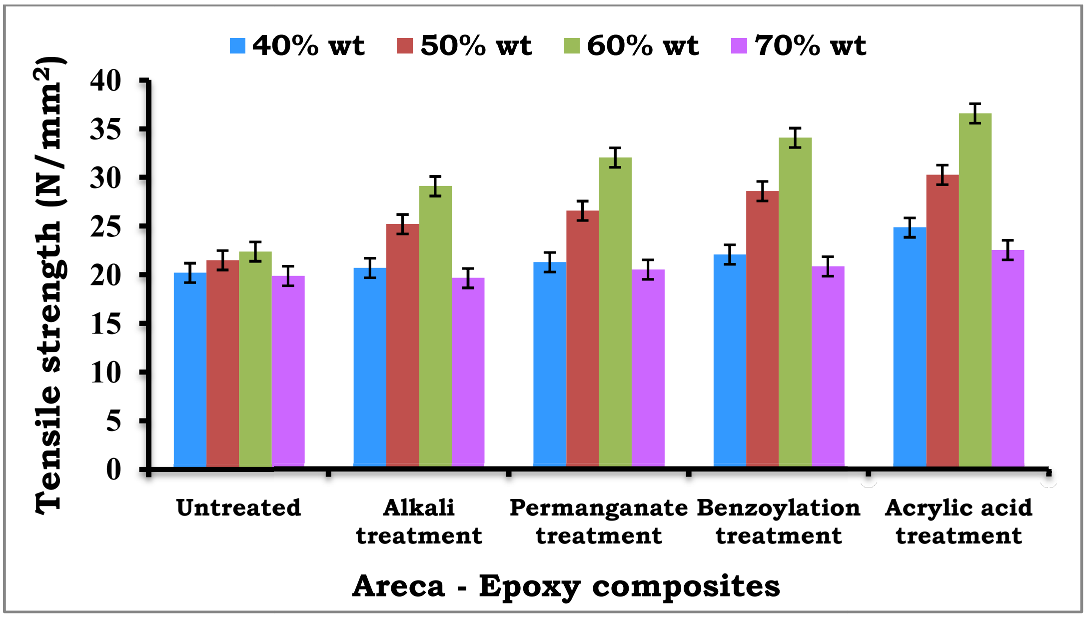


Fig:5.5Tensile strength of Areca - Epoxy composites with different fibre loadings

The tensile strength of untreated areca fibre reinforced epoxy composites with 60% fibre loading increased by 10.85% compared to 40% fibre loading, 4.14% compared to 50% fibre loading and for 70%

fibre loading,tensile strength decreased by 11.22% when compared to 60% fibre loading.

The tensile strength of 6% sodium hydroxide treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 40.67% compared to 40% fibre loading, 15.53% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 32.49% when compared to 60% fibre loading.

The tensile strength of 0.5% potassium permanganate treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 50.56% compared to 40% fibre loading, 20.63% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 35.96% when compared to 60% fibre loading.

The tensile strength of benzoyl chloride treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 54.40% compared to 40% fibre loading, 19.17% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 38.81% when compared to 60% fibre loading.

The tensile strength of 5% acrylic acid treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 47.26% compared to 40% fibre loading, 20.89% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 38.44% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced epoxy composites with 60% fibre loading showed 30.04%, 43.23%, 52.26% and 63.52% increase in tensile strength values respectively when compared to untreated areca fibre reinforced epoxy composites with same 60% fibre loading.

5.3.1.2 Tensile strength of Areca – UF Composites

The tensile strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced urea formaldehyde composites which were post cured at a room temperature for 15 days under 40%, 50%, 60% and 70% fibre loadings are given in Table 5.5.

Table 5.5Tensilestrength values of Areca - UF composites

Areca fibre	Tensile strength values in N/mm² at given fibre loadings (wt %)			
	40%	**50%**	**60%**	**70%**
Untreated	15.24	16.86	24.56	16.24
6% Alkali treated	15.98	17.52	26.52	16.86
0.5% Potassium permanganate treated	16.56	18.98	28.32	17.02
Benzoyl chloride treated	16.96	20.56	30.86	18.2
5% Acrylic acid treated	18.28	22.56	32.52	18.96

The effect of chemical treatments on tensile strength of untreated and all chemically treated areca fibre reinforced UF composites with 40%, 50%, 60% and 70%fibre loadings are depicted in Fig: 5.6.

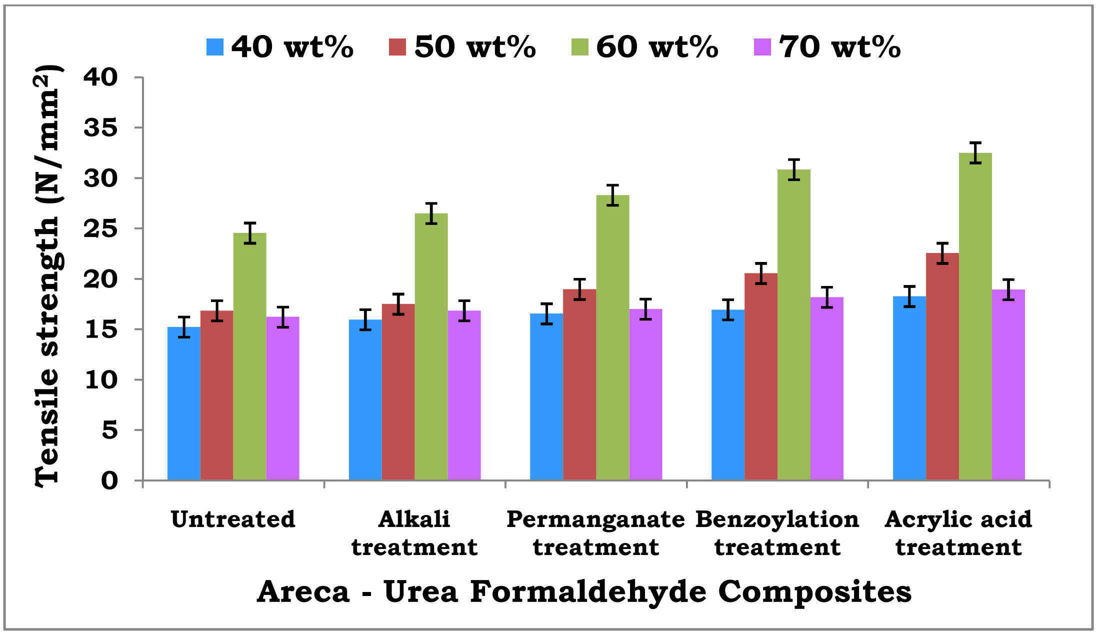


Fig:5.6 Tensile strength of Areca –UF composites with different fibre loadings

It wasseen that the areca fibre content and the chemical modifications of areca fibres greatly influenced the tensile strength of areca fibre reinforced UF composites. The tensile strength of untreated areca fibre reinforced UF composites with 60% fibre loading increased by 61.15% compared to 40% fibre loading, 45.67% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 33.87% when compared to 60% fibre loading.

The tensile strength of 6% alkali treated areca fibre reinforced UF composites with 60% fibre loading increased by 65.96% compared to 40% fibre loading, 51.37% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 36.43% when compared to 60% fibre loading.

The tensile strength of 0.5% potassium permanganate treated areca fibre reinforced UF composites with 60% fibre loading increased by 71.01% compared to 40% fibre loading, 49.21% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 39.90% when compared to 60% fibre loading.

The tensile strength of benzoyl chloride treated areca fibre reinforced UF composites with 60% fibre loading increased by 81.96% compared to 40% fibre loading, 50.10% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 41.02% when compared to 60% fibre loading.

The tensile strength of 5% acrylic acid treated areca fibre reinforced UF composites with 60% fibre loading increased by 77.90% compared to 40% fibre loading, 44.15% compared to 50% fibre loading and for 70% fibre loading,tensile strength decreased by 41.70% when compared to 60% fibre loading.

NaOH, $KMnO_4$, C_6H_5COCl and $CH_2{=}CHCOOH$ treated areca fibre reinforced UF composites with 60% fibre loading showed 7.98%, 15.31%, 25.65% and 32.41% increase in tensile strength values respectively when compared to untreated areca fibre reinforced urea formaldehyde composites with same 60% fibre loading.

5.3.2Flexural Strength Values

5.3.2.1 Flexural Strength of Areca - Epoxy Composites

Flexural strength is the material's ability to bend without undergoing major deformities. It is the maximum stress experienced by the material at the point of rupture. The flexural strength values of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca - epoxy composites which were post cured at a room temperature for 15 days under 40%, 50%, 60% and 70% fibre loadings are given in Table 5.6.

The effect of chemical treatments on flexural strength of untreated and all chemically treated areca fibre reinforced epoxy composites with different fibre loadings are depicted in Fig: 5.7.

Table 5.6 Flexural strength values of Areca-Epoxy composites

Areca fibre	**Flexural strength values in N/mm^2 at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	30.24	38.48	42.68	24.28
6% Alkali treated	52.54	61.28	84.86	26.84
0.5% Potassium permanganate treated	54.38	64.96	88.98	27.26
Benzoyl chloride treated	56.02	66.58	94.28	28.46
5% Acrylic acid treated	57.54	68.52	96.84	28.98

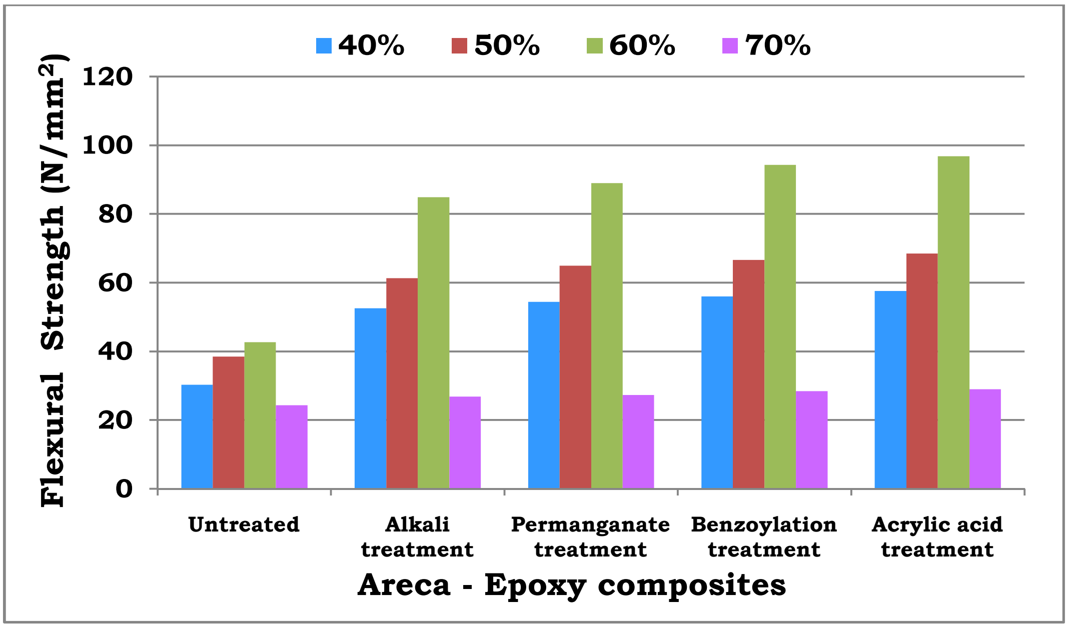


Fig:5.7 Flexural strength of Areca -Epoxy composites with different fibre loadings

It wasnoticed that the areca fibre content and the chemical modifications of areca fibres greatly influenced the flexural strength of areca fibre reinforced epoxy composites.The flexural strength of untreated areca fibre reinforced epoxy composites with 60% fibre loading increased by 41.13% compared to 40% fibre loading, 10.91% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 43.11% when compared to 60% fibre loading.

The flexural strength of 6% alkali treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 61.52% compared to 40% fibre loading, 38.48% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 68.37% when compared to 60% fibre loading.

The flexural strength of 0.5% potassium permanganate treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 63.63% compared to 40% fibre loading, 36.98% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 69.36% when compared to 60% fibre loading.

The flexural strength of benzoyl chloride treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 68.30%

compared to 40% fibre loading, 41.60% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 69.81% when compared to 60% fibre loading.

The flexural strength of 5% acrylic acid treated areca fibre reinforced epoxy composites with 60% fibre loading increased by 68.30% compared to 40% fibre loading, 41.33% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 70.07% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced epoxy composites with 60% fibre loading showed 98.83%, 108.48%, 120.90% and 126.90% increase in flexural strength values respectively when compared to untreated areca fibre reinforced epoxy composites with same 60% fibre loading [95].

5.3.2.2 Flexural Strength of Areca - UF Composites

The flexural strength values of untreated, 6% sodium hydroxide treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced UF composites which were post cured at a room temperature for 15 days under 40%, 50%, 60% and 70% fibre loadings are given in Table 5.7.

Table 5.7 Flexural strength values of Areca-UF composites

Areca fibre	Flexural strength values in N/mm^2 at given fibre loadings (wt %)			
	40%	**50%**	**60%**	**70%**
Untreated	28.56	30.58	32.52	24.56
6% Alkali treated	28.96	32.58	34.86	26.28
0.5% Potassium permanganate treated	30.26	34.56	36.82	28.82
Benzoyl chloride treated	32.56	35.02	42.52	29.02
5% Acrylic acid treated	34.96	36.28	46.84	30.24

It wasunderstood that the arecafibre content and the chemical modifications of areca fibres greatly influenced the flexural strength of areca - UF composites.The effect of chemical treatments on flexural strength of untreated and all chemically treated areca -UF composites with 40%, 50%, 60% and 70% fibre loadingsare depicted in Fig: 5.8.

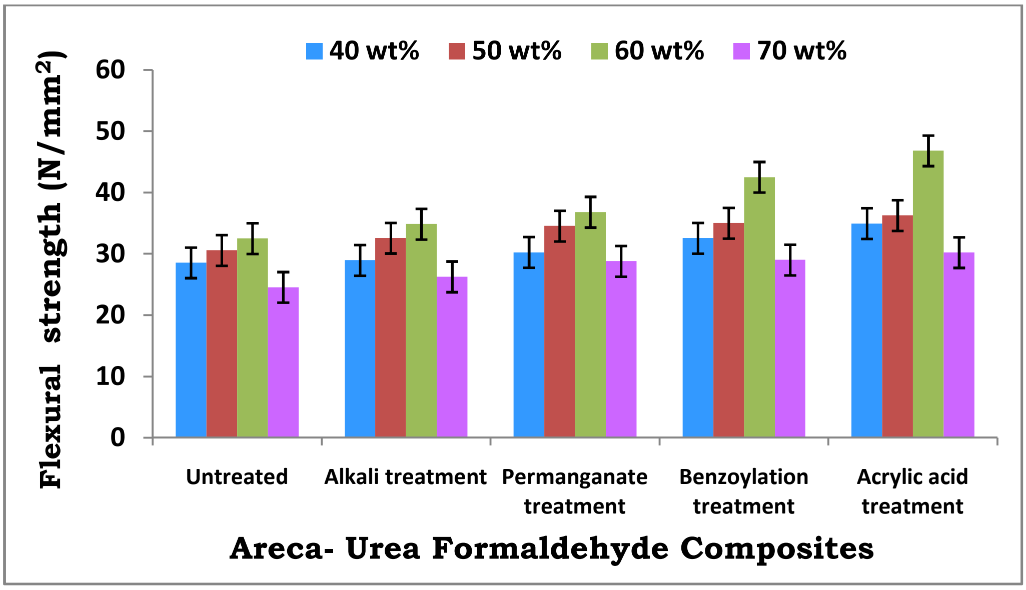


Fig: 5.8Flexural strength of Areca - UF composites with different fibre loadings

The flexural strength of untreated areca fibre reinforcedurea formaldehyde composites with 60% fibre loading increased by 13.87% compared to 40% fibre loading, 6.34% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 24.48% when compared to 60% fibre loading.

The flexural strength of 6% alkali treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading increased by 20.37% compared to 40% fibre loading, 6.99% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 24.61% when compared to 60% fibre loading.

The flexural strength of 0.5% potassium permanganate treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading increased by 21.68% compared to 40% fibre loading, 6.54% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 21.72% when compared to 60% fibre loading.

The flexural strength of benzoyl chloride treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading increased by

30.59% compared to 40% fibre loading, 21.42% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 31.75% when compared to 60% fibre loading.

The flexural strength of 5% acrylic acid treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading increased by 33.98% compared to 40% fibre loading, 29.10% compared to 50% fibre loading and for 70% fibre loading, flexural strength decreased by 35.44% when compared to 60% fibre loading.

NaOH, $KMnO_4$, C_6H_5COCl and CH_2=CHCOOH treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading showed 7.20%, 13.22%, 30.75% and 44.03% increase in flexural strength values respectively when compared to untreated areca fibre reinforced UF composites with same 60% fibre loading.

5.3.3Impact Strength Values

5.3.3.1 Impact Strength of Areca - Epoxy Composites

Impact strength is the capability of a material to absorb shock and impact energy without breaking. The impact value of a material changes with changes in temperature. Generally, at lower temperatures, the impact energy of a material is decreased.Charpy Impact test determines the amount of energy absorbed in Joules by a material during fracture and it is a measure of materials toughness. A material's toughness is its ability to absorb energy during plastic deformation. It acts as a tool to study brittle - ductile transition. Brittle materials have low toughness and they can endure a small amount of plastic deformation. On impact, the energy of the pendulum is transferred to the test specimen and a part of the energy is consumed during fracture of the specimen. The impact strength of natural fibre reinforced polymer composites depends upon fibre aspect ratio and fibre rigidity. The impact strength is calculated as the ratio of impact absorption to test specimen cross-section(J/mm^2).

Impact strength of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced epoxy composites with 40%, 50%, 60% and 70% fibre loadings which were post cured at a room temperature for 15 days are given in Table 5.8.

It was observed that areca fibre reinforced epoxy composites with 60% fibre loading showed maximum impact strength valueswhen compared to areca fibre reinforced epoxy composites with other fibre loadings. Irrespective of the chemical treatment, all chemically treated areca- epoxy composites showed higher impact strength values than the untreated areca- epoxy composites of respective fibre loadings.

Table 5.8 Impact strength of Areca - Epoxy composites

Areca fibre	**Impact strength values in J/mm^{2}at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	08.64	09.68	10.24	07.64
6% Alkali treated	90.62	10.28	21.22	09.54
0.5% Potassium permanganate treated	10.42	12.68	22.64	10.24
Benzoyl chloride treated	11.56	14.58	24.56	10.86
5% Acrylic acid treated	12.54	16.24	28.28	11.56

The impact strengthof untreated and all chemically treated areca fibre reinforced epoxy composites with 40%, 50%, 60% and 70% fibre loadings are illustrated in Fig: 5.9.

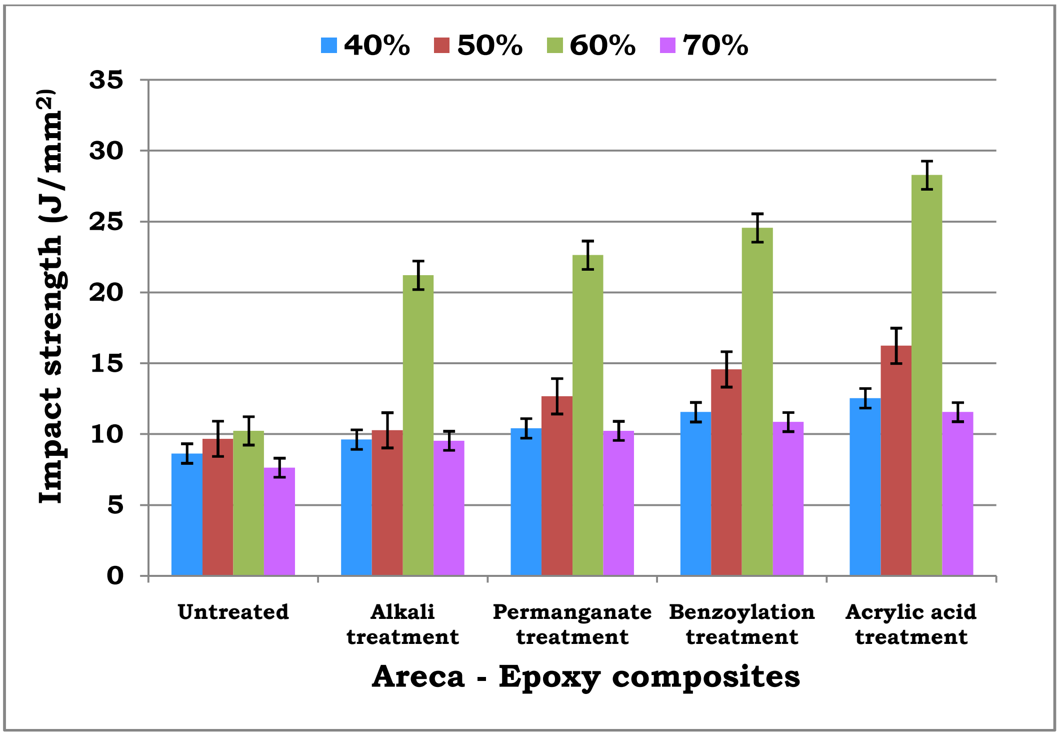


Fig:5.9 Impact strength ofAreca -Epoxy composites with different loadings

In case of untreated areca fibre reinforced epoxy composites, the impact strength of 60% fibre loading increased by 18.52% compared to 40% fibre loading, 5.79% compared to 50% fibre loading and for 70% fibre loading, it decreased by 25.39% when compared to 60% fibre loading.

In case of 6% alkali treated areca fibre reinforced epoxy composites, the impact strength of 60% fibre loading increased by 120.58% compared to 40% fibre loading, 106.42% compared to 50% fibre loading and for 70% fibre loading, it decreased by 55.04% when compared to 60% fibre loading.

For 0.5% potassium permanganate treated areca fibre reinforced epoxy composites, the impact strength of 60% fibre loading increased by 117.27% compared to 40% fibre loading, 78.55% compared to 50% fibre loading and for 70% fibre loading, it decreased by 54.77% when compared to 60% fibre loading.

In case of benzoyl chloride treated areca fibre reinforced epoxy composites, the impact strength of 60% fibre loading increased by

112.46% compared to 40% fibre loading, 68.45% compared to 50% fibre loading and for 70% fibre loading, it decreased by 55.78% when compared to 60% fibre loading.

In 5% acrylic acid treated areca fibre reinforced epoxy composites, the impact strengthof 60% fibre loading increased by 125.52% compared to 40% fibre loading, 74.14% compared to 50% fibre loading and for 70% fibre loading, it decreased by 59.12% when compared to 60% fibre loading.

Sodium hydroxide, potassium permanganate, benzoyl chloride and acrylic acid treated areca fibre reinforced epoxy composites with 60% fibre loading showed 107.23%, 121.09%, 139.84% and 176.17% increase in impact strength values respectively when compared to untreated areca fibre reinforced epoxy composites with same 60% fibre loading [102].

5.3.3.2 Impact Strength of Areca-Urea Formaldehyde Composites

Impact strength of untreated, 6% alkali treated, 0.5% potassium permanganate treated, benzoyl chloride treated and 5% acrylic acid treated areca fibre reinforced urea formaldehyde composites which were post cured at a room temperature for 15 days with 40%, 50%, 60% and 70% fibre loadings are given in Table 5.9.

Table 5.9 Impact strength of Areca - UF composites

Areca fibre	**Impact strength values in J/mm^{2}at given fibre loadings (wt %)**			
	40%	**50%**	**60%**	**70%**
Untreated	07.86	08.78	09.82	07.64
6% Alkali treated	08.26	09.28	10.24	08.02
0.5% Potassium permanganate treated	10.02	10.26	12.08	09.28
Benzoyl chloride treated	10.86	12.46	14.28	10.24
5% Acrylic acid treated	12.28	14.86	18.96	10.98

It was observed that areca fibre reinforced urea formaldehyde composites with 60% fibre loading showed maximum impact strength valueswhen compared to areca fibre reinforced Urea Formaldehyde composites of other fibre loadings. Irrespective of the chemical treatment, all chemically treated arecafibre reinforced urea formaldehyde composites showed higher impact strength values than the untreated arecafibre reinforced urea formaldehyde composites of respective fibre loadings.

The impact strengthof untreated and all chemically treated areca fibre reinforced Urea Formaldehyde composites with 40%, 50%, 60% and 70% fibre loadings are illustrated in Fig: 5.10.

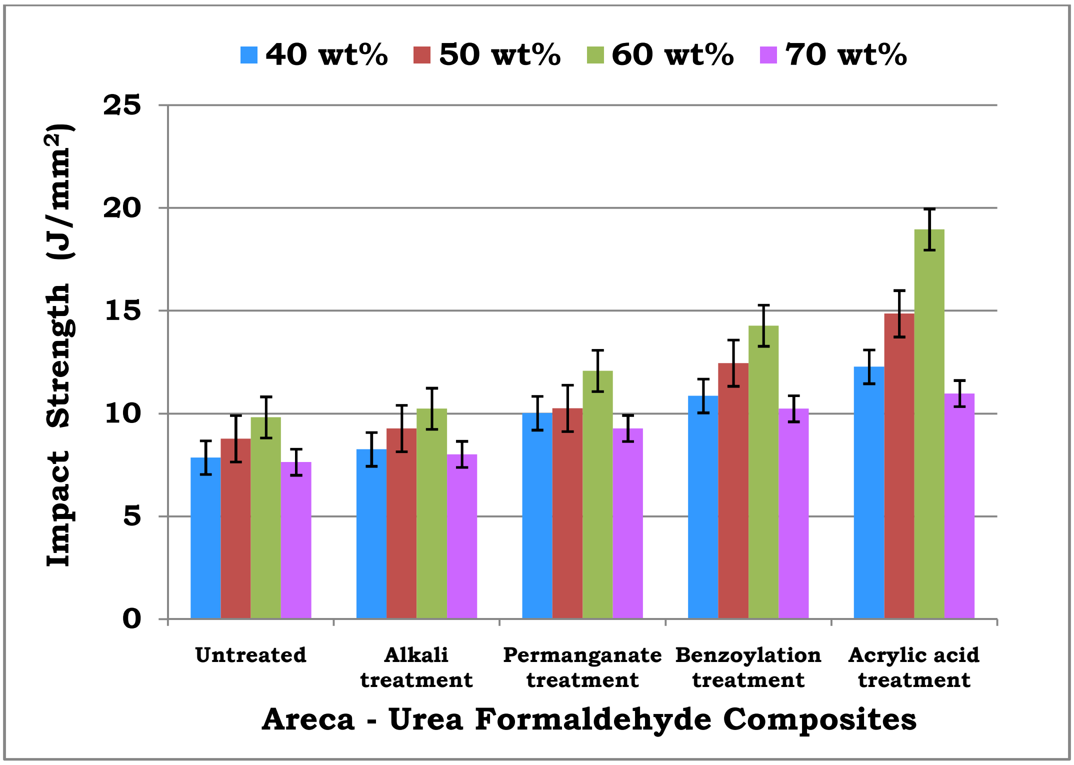


Fig:5.10 Impact strength ofAreca - UF composites with different loadings

In case of untreated areca - UF composites, the impact strength of 60% fibre loading increased by 24.94% compared to 40% fibre loading, 11.85% compared to 50% fibre loading and for 70% fibre loading, it decreased by 22.20% when compared to 60% fibre loading.

In case of 6% alkali treated areca fibre reinforced urea formaldehyde composites, the impact strength of 60% fibre loading increased by 23.97% compared to 40% fibre loading, 10.34% compared to 50% fibre loading and for 70% fibre loading, it decreased by 21.68% when compared to 60% fibre loading.

For 0.5% potassium permanganate treated areca fibre reinforced urea formaldehyde composites, the impact strength of 60% fibre loading increased by 20.56% compared to 40% fibre loading, 17.74% compared to 50% fibre loading and for 70% fibre loading, it decreased by 23.18% when compared to 60% fibre loading.

In case of benzoyl chloride treated areca fibre reinforced urea formaldehyde composites, the impact strength of 60% fibre loading increased by 31.49% compared to 40% fibre loading, 14.61% compared to 50% fibre loading and for 70% fibre loading, it decreased by 28.29% when compared to 60% fibre loading.

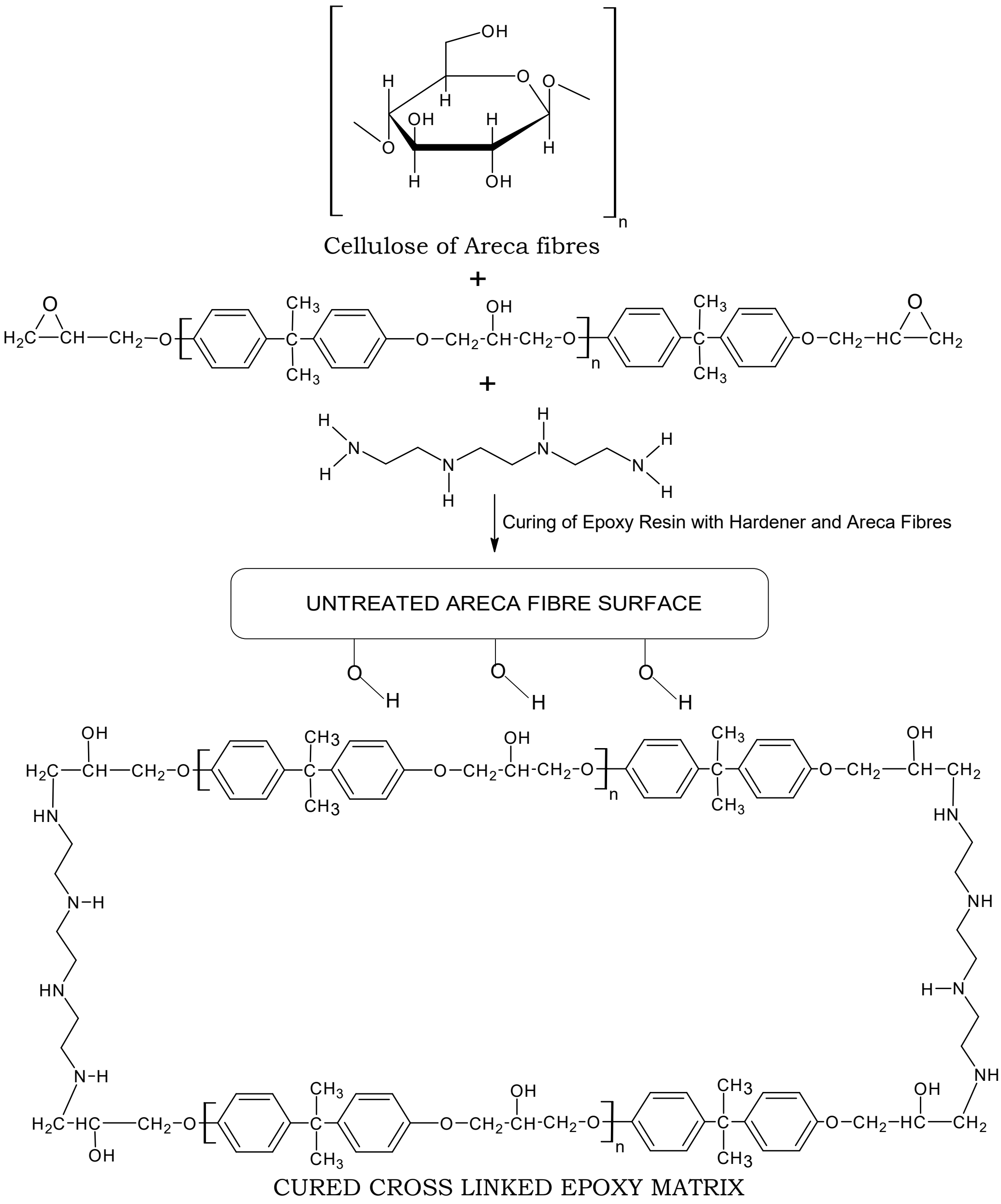
In case of 5% acrylic acid treated areca fibre reinforced urea formaldehyde composites, the impact strengthof 60% fibre loading increased by 54.40% compared to 40% fibre loading, 27.59% compared to 50% fibre loading and for 70% fibre loading, it decreased by 42.09% when compared to 60% fibre loading.

NaOH, $KMnO_4$, C_6H_5COCl and CH_2=CHCOOH treated areca fibre reinforced urea formaldehyde composites with 60% fibre loading showed 4.28%, 23.01%, 45.42% and 93.08% increase in impact strength values respectively when compared to untreated areca -urea formaldehyde composites with same 60% fibre loading.

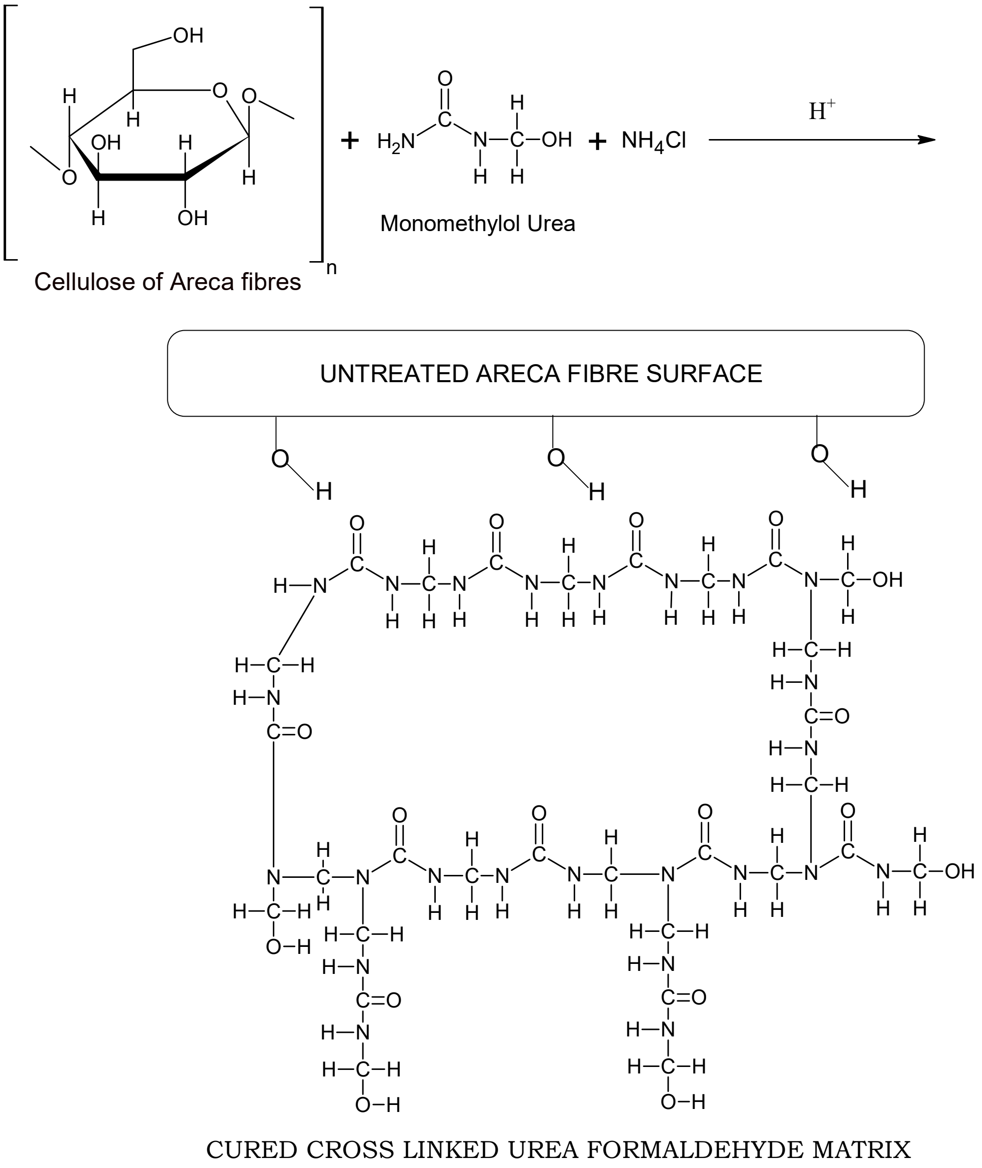
5.3.4 Effect of Chemical Treatments on Areca - Epoxy and Areca – Urea Formaldehyde Composite Properties

5.3.4.1 Untreated Areca – Epoxyand Areca – UF composites

In the composites, polymer matrix molecules may be anchored to the fibre surface by chemical reaction or adsorption and this determines theextent of interfacial adhesion. Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of untreated areca fibre – epoxy and untreated areca fibre – urea formaldehyde composites can be given as follows.



Scheme 5.4 Hypothetical model of interface between cellulose-OH of untreated Areca fibres with Epoxy matrix

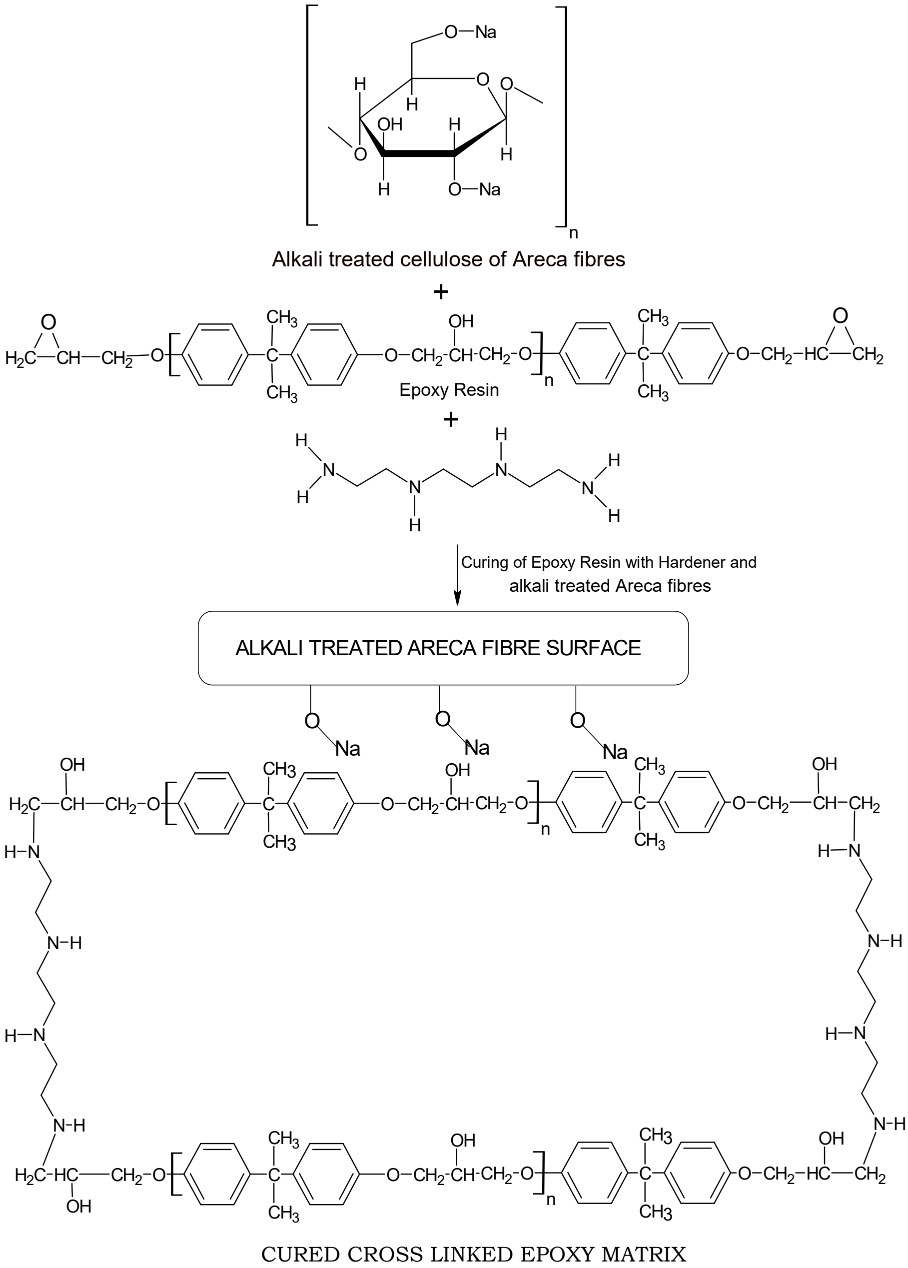


Scheme 5.5 Hypothetical model of interface between cellulose-OH of untreated Areca fibres with UF matrix

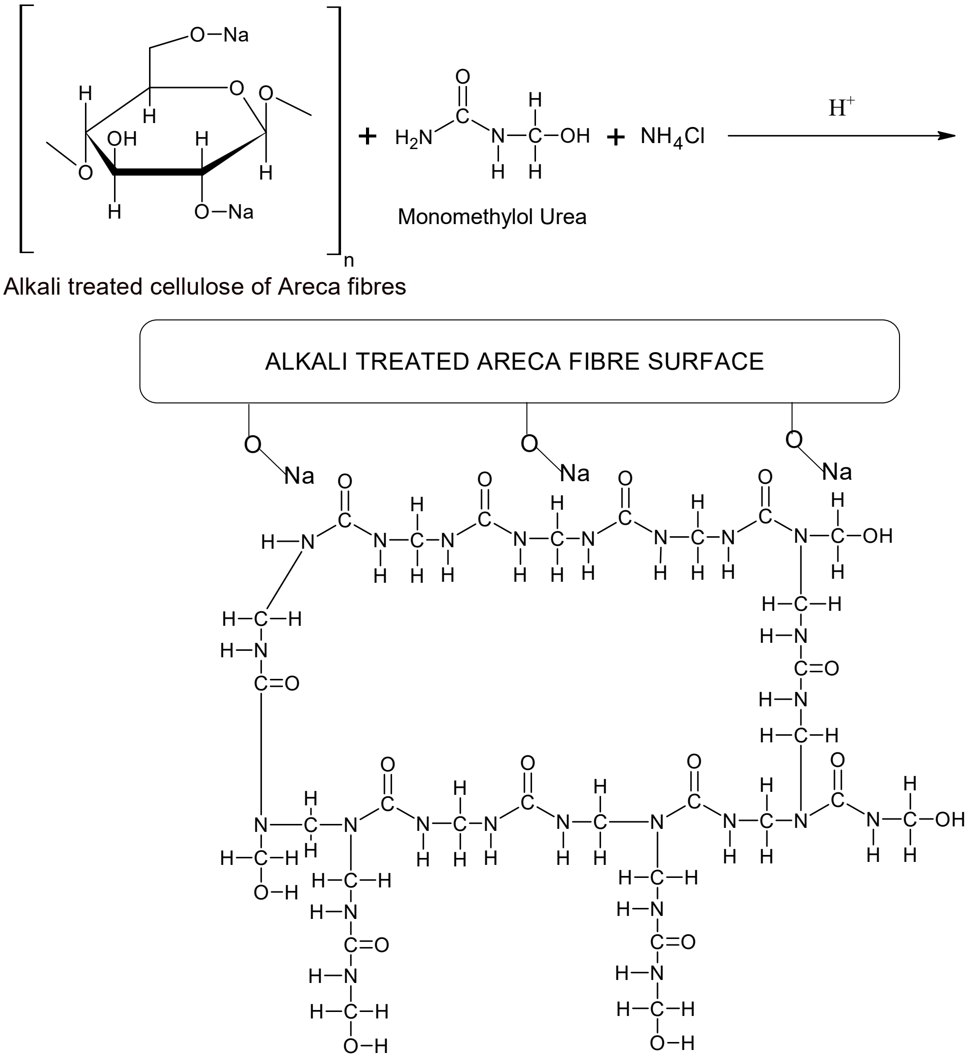
The interfacial strength of composites depends upon the surface topology of fibre and it is a very important factor.Untreated areca fibres are hydrophilic whereas the epoxy resin and UF resinare hydrophobic. This resulted in incompatibility between the areca fibre and epoxy resin and between the areca fibre and UF resin. Hence, the untreated areca fibre reinforced epoxy composites and untreated areca fibre reinforced urea formaldehyde composites indicated low tensile strength, flexural strength and impact strength values when compared with that of corresponding chemically treated areca - epoxy composites and chemically treated areca - UF composites respectively.

5.3.4.2Alkali Treated Areca – Epoxyand Areca – UF Composites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of alkali treated areca fibre – epoxy and alkali treated areca fibre – Urea Formaldehyde composites can be given as follows.



Scheme 5.6 Hypothetical model of interface of alkali treated Areca fibre - Epoxy composites



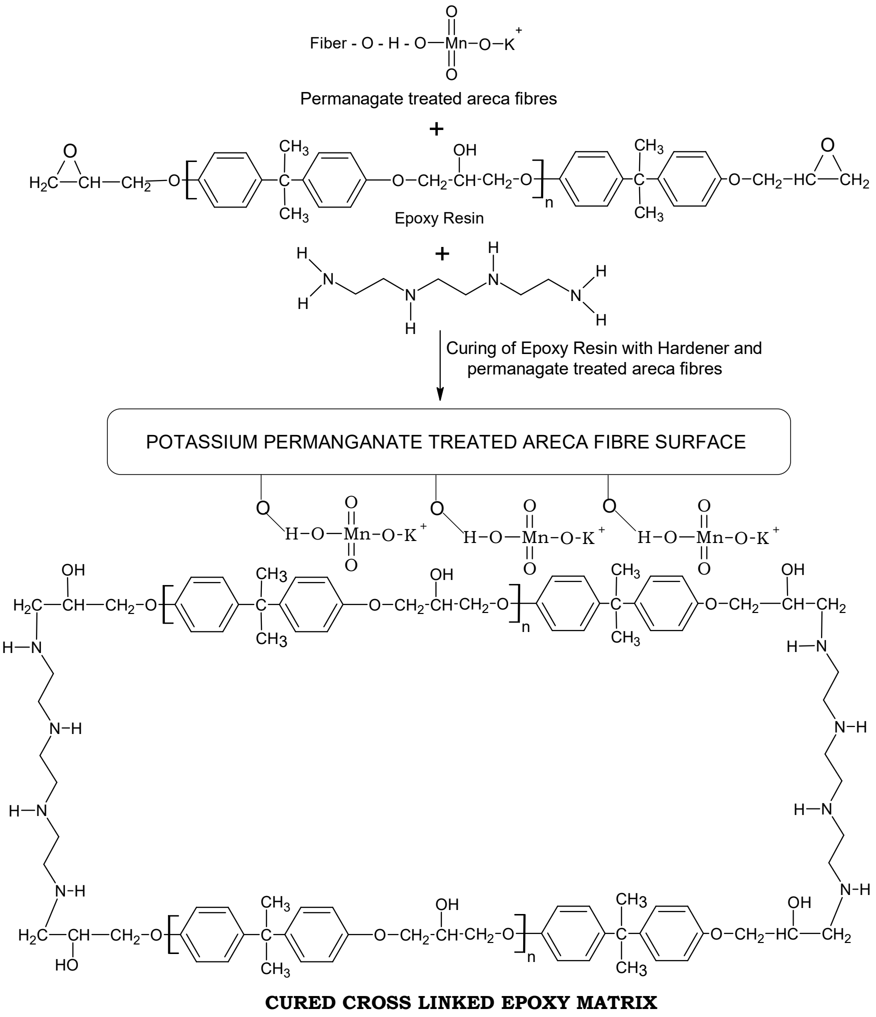
CURED CROSS LINKED UREA FORMALDEHYDE MATRIX

Scheme 5.7 Hypothetical model of interface of alkali treated Areca fibre - UF composites

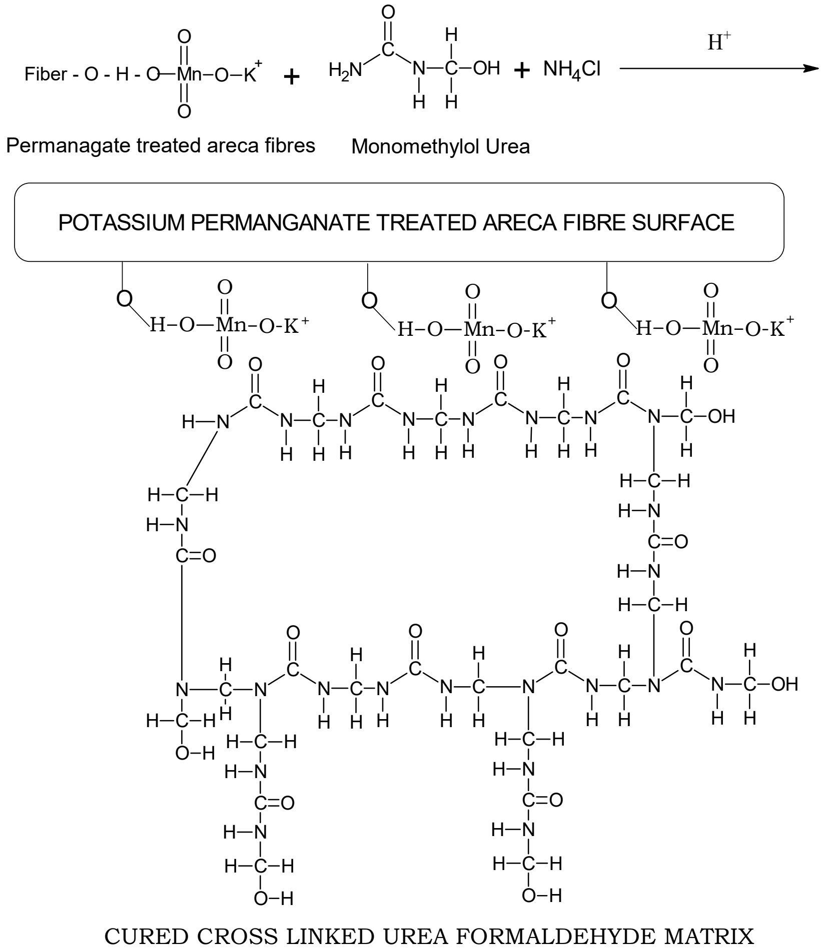
Alkali treatment of areca fibres takes out certain portion of hemicelluloses, lignin, adhesive pectin and waxy epidermal tissue, oil covering materials and impurities from the natural areca fibres and resulted in increment of cellulose exposed on the fibre surface and thereby increased the number of possible reaction sites. Also, mercerization improved the fibre wetting by fibrillation which in-turn increased effective surface area available for contact with wet polymer matrix.It also reduced fibre diameter and thereby increased its aspect ratio[34, 40, 61, 92, 95, 102-107, 157-158]. Hence, alkali treated areca fibre reinforced epoxy composites and alkali treated areca fibre reinforced urea formaldehyde composites showed increased tensile strength, flexural strength and impact strength values.

5.3.4.3Potassium Permanganate Treated Areca – Epoxyand Areca – UF Composites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of permanganate treated areca fibre – epoxy and permanganate treated areca fibre – urea formaldehyde composites can be given as follows.



Scheme 5.8 Hypothetical model of interface of permanganate treated Areca fibre - Epoxy composites

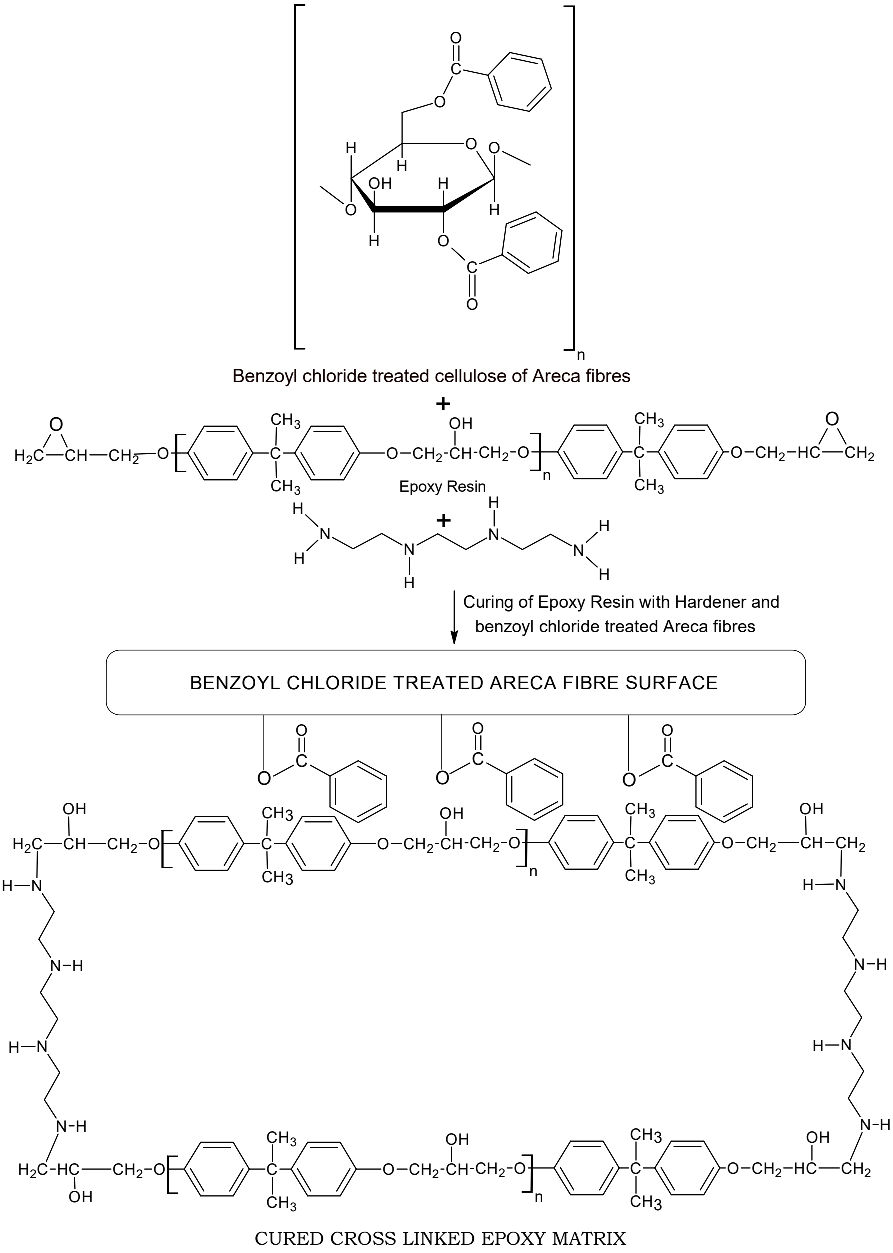


Scheme 5.9 Hypothetical model of interface of permanganate treated Areca fibre - UF composites

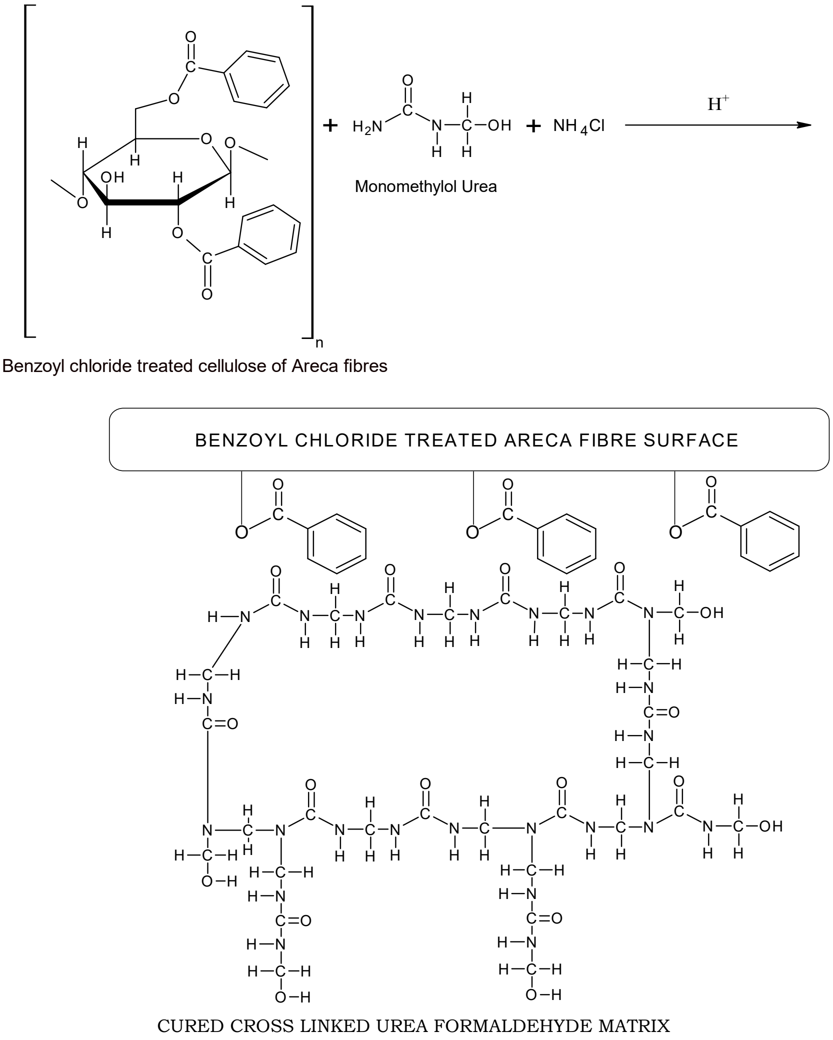
Cellulose-manganate is produced as a result of reaction of highly reactive permanganate ions (Mn^{3+}) with cellulose of areca fibres. Permanganate ions also react with lignin constituents and carve the areca fibre surface. As a result, areca fibre surface became physically rough. This improved interfacialchemicalinterlocking at the interface and provided better adhesion with the polymeric resin[34, 40, 67, 92, 95, 102-103, 108-110, 159].Because of this, permanganate treated areca fibre reinforced epoxy composites and permanganate treated areca fibre reinforced urea formaldehyde composites showed increased tensile strength, flexural strength and impact strength values.

5.3.4.4Benzoyl Chloride Treated Areca – Epoxyand Areca – UF Composites

Based on hypothetical model given by various researchers [103, 124, 156], a possible hypothetical model of interface of benzoyl chloride treated areca fibre – epoxy and benzoyl chloride treated areca fibre – urea formaldehyde composites can be given as follows.



Scheme 5.10 Hypothetical model of interface of benzoyl chloride treated Areca fibre - Epoxy composites

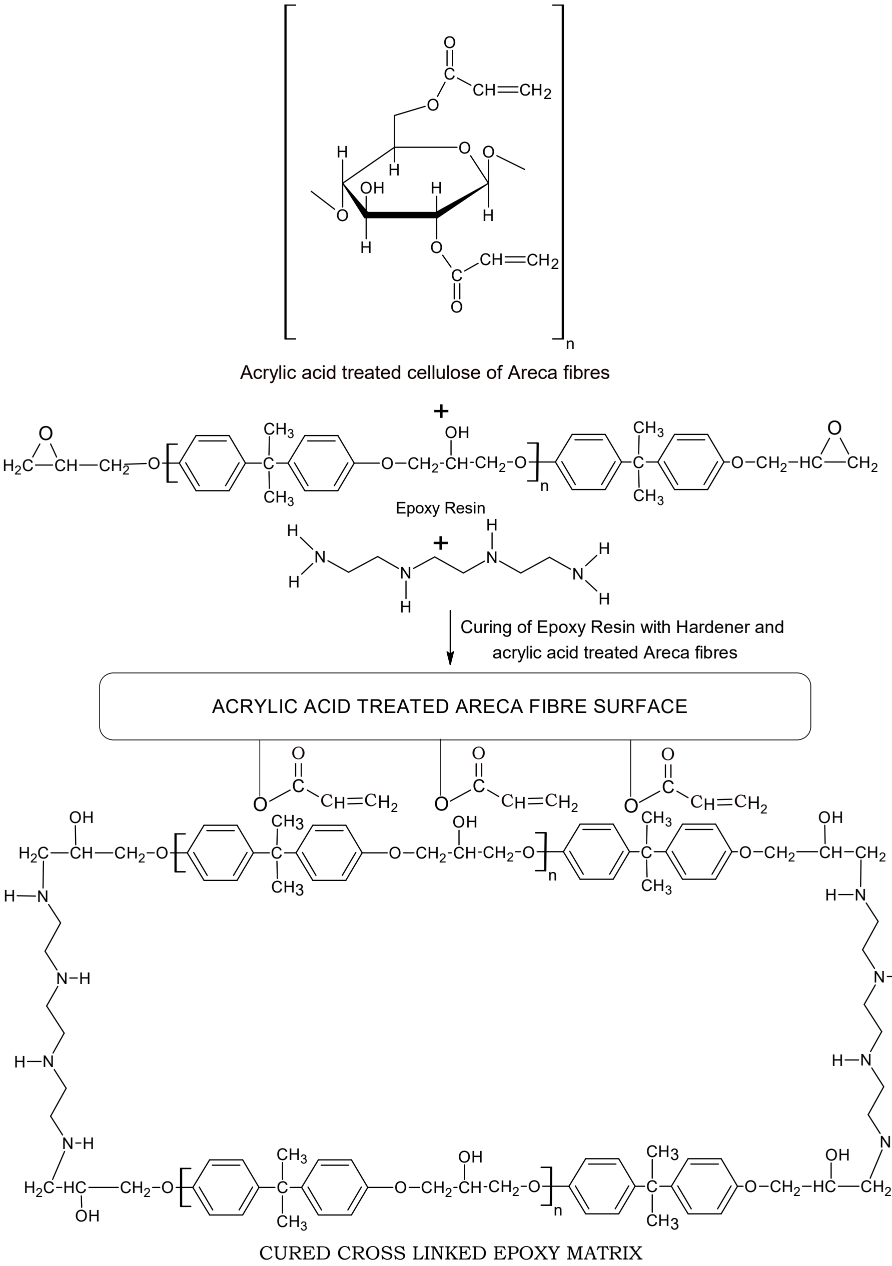


Scheme 5.11 Hypothetical model of interface of benzoyl chloride treated Areca fibre - UF composites

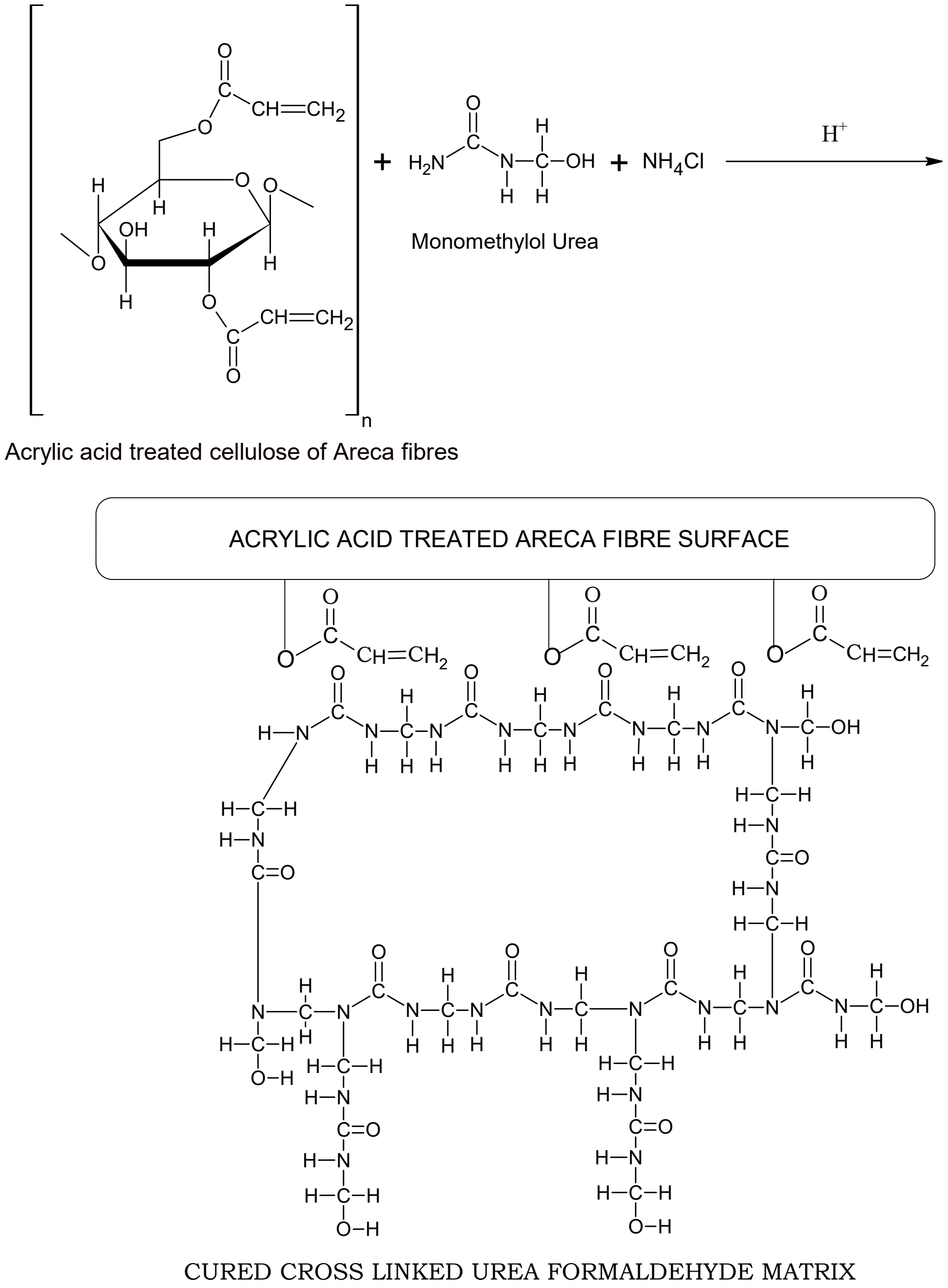
Benzoyl chloride treatment resulted in an introduction of benzoyl groups attached on to the cellulose backbone of areca fibres. Extractable materials areisolatedand hence benzoylated areca fibre surface became physically rough. Soit improved chemical interlocking at the interface and provided effective fibre surface area for good adhesion with the polymer matrix[34, 40, 57, 61, 95, 102-103, 105, 111, 159]. As a result, benzoylated areca - epoxy composites and benzoylated areca -UF composites showed increased tensile strength, flexural strength andimpact strength values.

5.3.4.5 Acrylic Acid Treated Areca – Epoxyand Areca – UF Composites

Based on hypothetical model given by various researchers [103, 124, 156], the possible hypothetical model of interface of acrylic acid treated areca fibre – epoxy and acrylic acid treated areca fibre – urea formaldehyde composites can be given as follows.



Scheme 5.12 Hypothetical model of interface of acrylic acid treated Areca fibre - Epoxy composites



Scheme 5.13 Hypothetical model of interface of acrylic acid treated Areca fibre - UF composites

A region where the reinforcing natural lignocellulosic fibres and the polymeric matrix phase are chemically and/or mechanically combined or otherwise indistinct is referred to as interface. During acrylic acid treatment, most of the hemicelluloses and lignin are removed and there is replacement of hydrophilic hydroxyl groups by hydrophobic ester groups in the areca fibres. As a result, effective areca fibre surface area available for good adhesion with the polymer matrix is increased and stress transfer capacity at the interface is enhanced[34, 40, 95, 102-103, 112-113]. Hence, for acrylic acid treated areca fibre reinforced epoxy composites and acrylic acid treated areca fibre reinforced urea formaldehyde composites, higher tensile strength, flexural strength and impact strength values are observed.

Amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced epoxyand acrylic acid treated areca fibre reinforced urea formaldehyde composites of 60% fibre loadings showed maximum tensile strength, flexural strength and impact strength valuesfollowed by benzoyl chloride treatment, potassium permanganate treatment and alkali treatment.

This may be due to the fact that amongst all the chemical treatments carried out, higher tensile strength and decomposition temperature values were showed by areca fibres treated with acrylic acid followed by benzoyl chloride, potassium permanganate and sodium hydroxide as indicated in Table 3.5. Hence, acrylated areca - epoxy and acrylated areca - urea formaldehyde composites showed higher tensile strength, flexural strength and impact strength values compared to any other chemical treatment.

These results clearly indicated that chemical treatments are very efficient in surface modification of areca fibres and in enhancing the tensile strength, flexural strength and impact strength values of areca fibre reinforced epoxy and areca fibre reinforced UF composites.

5.3.5 Effect of Fibre Loadings on Areca - Epoxy and Areca – Urea Formaldehyde Composite Properties

With increase in fibre loading from 40% to 60%, the tensile strength, flexural strength and impact strength values of untreated as well as all chemically treated areca - epoxy and areca – urea formaldehyde composites were increased and beyond 60% fibre loading, the tensile strength, flexural strength and impact strength showed a decline. That is areca fibre reinforced epoxy and areca fibre reinforced urea formaldehyde composites exhibited maximum tensile strength, flexural strength and impact strength values at 60% fibre loading. This is because of better fibre distribution in matrix, less fibre fractures and effective transfer of load from matrix to fibres at 60% fibre loading. As fibre loading increases, more force is required to pullout the fibres and thereby increases the tensile strength, flexural strength and impact strength values.

The observed increase in tensile strength, flexural strength and impact strength values with chemical modifications and as well as with increase in fibre loadings up to 60% is in good agreement with the results reported in literature[30, 58-63, 67, 69, 73, 75-77].

The decrease in tensile strength, flexural strength and impact strength values for untreated as well as chemically treated areca - epoxy and areca -urea formaldehyde composites beyond 60% fibre loading is due to poor interfacial adhesion and inefficient stress transfer from matrix to fibres at 70% fibre loading[160].The factors contributing to the lower tensile strength and flexural strength values may be due to the random alignment of short areca fibres and the presence of voids in the areca-epoxy and areca-UF composites[161]. The decrease in impact strength values may be due to the micro spaces between the fibre and the matrix which initiates micro cracks on impact and results in crack propagation leading to failure [77].

Hence, chemically treated areca-epoxy and areca-UF composites with 60% fibre loadings are best suitable for industrial applications.

5.4 CONCLUSION

From these studies, it is clearly concluded that chemical treatments of areca fibres are of greater importance in changing the fibre surface, in reducing the hydrophilic nature of areca fibres, in enhancing the fibre - matrix adhesion and thereby increasing the properties of areca - epoxy and areca – urea formaldehyde composites. Maximum values of tensile strength, flexural strength and impact strength were observed at 60% fibre loadings for all untreated and chemically treated areca - epoxy and areca - urea formaldehyde composites.

Amongst all the chemical treatments carried out, acrylic acid treated areca - epoxy and acrylic acid treated areca -UF composites of 60% fibre loading showed maximum tensile strength, flexural strength and impact strength values followed by benzoyl chloride treatment, permanganate treatment and alkali treatment at the same 60% fibre loading. Hence, based on the availability, low cost and good strength characteristics, areca – epoxy and areca – urea formaldehyde composites can be considered as a very promising material and can be effectively used in light weight materials industries.

SUMMARY, CONCLUSION AND RECOMMENDATIONS

- The studies on size distribution of areca fibres indicated that areca fibres can be approximated as cylindrical shape with an average length of 39 mm and with an average diameter of 0.347 mm and giving aspect ratio, L/D of 112.39.
- The chemical composition of areca fibres has been determined experimentally and the areca fibres composed of 55.82% cellulose, 34.28% hemicelluloses, 6.82% lignin, 1.80% moisture content and 1.28% ash content.
- Tensile strength values of all chemically treated areca fibres are found to be marginally lower than that of untreated areca fibres and this may be due to the removal of most of the fat, lignin and pectin covering the external surface of the fibre cell wall, which would in turn, improves areca fibres adhesive quality in combination with the polymer matrix.
- The surface modification of areca fibres is carried out by chemical treatments such as 6% alkali treatment, 0.5% potassium permanganate treatment, benzoyl chloride treatment, 5% acrylic acid treatment and acetic anhydride treatment.
- The chemical reactions of areca fibres with $NaOH$, $KMnO_4$, C_6H_5COCl, $CH_2=CHCOOH$ and $CH_3COOCOCH_3$ have been explained.
- After all the chemical treatments, areca fibre surface became physically rough and clean. That is areca fibre surface became more uniform due to the elimination of micro voids and stress transfer capacity between the ultimate cells improved.
- Further, chemical treatments of areca fibres resulted in exposure of more reactive groups on the fibre surface and hence there is increase in effective fibre surface area for good adhesion with the polymer matrix.
- FTIR studies confirmed the chemical modifications of areca fibres. And also, the FTIR spectra of untreated and all chemically treated

areca fibres showed absorption bands characteristic of chemical groups of lignocellulosic fibre components such as cellulose, hemicelluloses, lignin and pectin.

- TGA-DTG studies revealed the improved thermal stability for all chemically treated areca fibres andthis may be due to the introduction of new reactive chemical moieties into the areca fibres.
- XRD studies showed marginal decrease in the crystallinity for all chemically treated areca fibres. This may due to the swelling of fibres, partial removal of cementing materials and introduction of bulky groups into the cellulose molecular chains in a micro fibril which would destroy the orderly packing of cellulose chains.
- SEM image analysis indicated the changes in surface topography for all chemically treated areca fibres and this in-turn confirmed the chemical modifications of areca fibres.
- Water absorption studies indicated the decrease in moisture absorption values for all chemically treated areca fibres and this may be due to the replacement of hydrophilic hydroxyl groups by hydrophobic chemical groups by respective chemical treatments. Further, chemical treatments destroyed the cellular structure of areca fibres and reduced the void content and this in turn reduced the moisture uptake of chemically treated areca fibres.
- Chemical treatments of areca fibres are of greater importance in modifying the fibre surface, in reducing the hydrophilic nature of the fibre, in enhancing the fibre-matrix adhesion and thereby increasing the properties of areca fibre reinforced thermoplastic, thermoplastic elastomeric and thermoset polymer composites.
- With respect to chemical modifications of areca fibres and areca fibre content, a significant influence on tensile strength, flexural strength and impact strength values of areca–polypropylene, areca–natural rubber, areca-epoxy and areca–urea formaldehyde composites were observed.
- Irrespective of chemical treatment, all chemically treated areca–

polypropylene, areca–natural rubber, areca-epoxy and areca–urea formaldehyde composites showed improved tensile strength, flexural strength and impact strength values.

- With increase in fibre loading from 40% to 60%, the tensile strength and flexural strength values of untreated and all chemically treated areca–polypropylene composites have been increased and beyond 60% they showed a decline.
- With increase in fibre loading from 30% to 50%, the impact strength of untreated and all chemically treated areca – PP composites have been increased and beyond 50% they showed a decline.
- Amongst all the chemical treatments carried out, acrylated areca-polypropylene composites of 60% fibre loading showed maximum tensile strength and flexural strength values followed by benzoyl chloride treatment, permanganate treatment and alkali treatment.
- Amongst all the chemical treatments carried out, acrylic acid treated areca-polypropylene composites of 50% fibre loading showed maximum impact strength values followed by benzoyl chloride treatment, permanganate treatment and alkali treatment.
- With increase in fibre loading from 40% to 60%, the tensile strength, flexural strength and impact strength values of untreated and all chemically treated areca -natural rubber composites have been increased and beyond 60% they showed a decline.
- Amongst all the chemical treatments carried out, acrylic acid treated areca fibre reinforced natural rubber composites of 60% fibre loading showed maximum tensile strength, flexural strength and impact strength values followed by benzoyl chloride treatment, permanganate treatment and alkali treatment.
- Curing reaction of epoxy resin in presence of araldite hardener HY951 and curing reaction of urea formaldehyde resin in presence of ammonium chloride hardener have been explained.
- With increase in fibre loading from 40% to 60%, the tensile strength, flexural strength and impact strength values of untreated

and all chemically treated areca–epoxy and areca–urea formaldehyde composites have been increased and beyond 60% they showed a decline.

- Amongst all the chemical treatments carried out, acrylic acid treated areca-epoxy composites and acrylic acid treated areca–urea formaldehyde composites of 60% fibre loading showed maximum tensile strength, flexural strength and impact strength values followed by benzoyl chloride treatment, potassium permanganate treatment and alkali treatment.
- Thus, the successful fabrications of new class of thermoplastic, thermoplastic elastomeric and thermoset resin based polymer composites reinforced with areca fibres have been done.
- Based on studies, it is very clear that areca fibres can be effectively used as a potential reinforcement for Polypropylene matrix, Natural Rubber matrix, Epoxy resin and Urea Formaldehyde resin.
- Hence, areca fibre reinforced polymer composites can be considered as a very promising material for the fabrication of light weight materials and can be effectively used in industrial sectors like automobile body building, packaging, office furniture, partition panels andfor making value added items like thick boards, fluffy cushions,non-woven fabrics and thermal insulators.
- The present work can be continued by blending areca fibres with other natural fibres.
- The present wok can also be continued by using high quality polymer resin systems to fabricate areca composites of superior properties.
- New products based on these areca fibre reinforced polymer composites have to be developed.

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