12.1 conclusions

Bio-based materials have opened new corridors and technical applications in the vast area of polymer science. The scope of renewability and economic viability have feathered this branch of science further. Fibre composites offer unique applications in plastic and wood industries, automobiles, aircrafts, housing and many other ordinary pulses of human life. The surprising metamorphosis that the fibres can bring about in the ordinary routine of life deserves more and more elaborate studies. This enquiry has to be parallel with the studies on natural fibres which are now under utilised. Such studies are sure to shower surprising returns.

Cellulose micro and nano fibrils of banana fibres were isolated using high pressure hydrothermal process. Characterization of the synthesized micro and nanofibrils was done by different modern techniques. The chemical composition of macro, micro and nano fibres were determined using ASTM standards. From the chemical examination, major constituents of these fibres were found to be cellulose. The percentage of cellulose components were found to be increased during steam explosion and acid hydrolysis. The lignin and hemicellulose components were found to be decreased from macro to the nano fibres. The IR studies give evidence for the dissolution and chemical modification that occurred during steam explosion and further treatment of the fibres including both steam explosion and acid hydrolysis.
The morphological structures of the macro to nano fibres were compared. The observed fibre diameter of macro to nano fibres were 80 µm, 10 µm and 50 nm respectively. XRD studies were done to investigate the fibre size and percentage crystallinity of the modified fibres. The XRD studies also revealed that there is a reduction in the size of fibres during steam explosion in alkaline medium and reduction in size to the nanometer range during repeated steam explosion in acidic medium. The percentage crystallinity of the fibres was also found to be increased from steam exploded fibres to repeated steam explosion in acidic conditions. It was observed that the nano fibres show a highly crystalline structure. The crystallinity was found to be increased from micro to nano structure. This higher crystallinity was due to the more efficient removal of noncellulosic polysaccharides and dissolution of amorphous zones by acid hydrolysis combined with steam explosion. AFM analysis also showed that there was reduction in the size of banana fibres to the nanometer range (below 40 nm). TEM analysis also supported the evidence for the formation of nanofibrils of banana fibres by repeated steam explosion in acidic conditions. The average length and diameter of the developed nanofibrils were found to be between 200-250 nm and 4-5 nm, respectively. Overall polarity of the fibres was found to increase when the fibre diameter was decreased. The surface acidity was proved to be increasing from macro to nano scale as the IEP value decreased. Substantial increase in thermal stability was observed from macro to nano fibres which proved the high thermal stability of nanofibres to processing conditions of biocomposite preparation. The results of solvatochromism and zetapotential corroborate with FTIR results.
Several chemically modified banana fibres were characterized using solvatochromic, contact angle and electrokinetic measurements. Removal of the fatty substances and waxes from the fibres increases the relative amount of adsorbed water. Grafting with silane, acetic anhydride, and benzoyl chloride decreases the amount of adsorbed water. Empirical polarity parameters were calculated in terms of the Kamlet-Taft solvent polarity scale. The HBD ability was found lowest for benzyolated fibre. Electrokinetic measurements revealed that the chemical treatments given to banana fibre increased the IEP value. Alkali treated fibre showed a lower IEP value when compared to other chemically treated fibres. This implies that the acidity of alkali treated fibre is higher compared to other treatments. All the modified fibres show a peak in the measured acidic range. The results obtained were found to be consistent with the solvatochromic measurements. The AFM roughness analysis revealed that the fibre surface roughness is reduced by chemical treatment presumably due to the removal of cell wall and waxy topography. The different chemical nature of the surface structure was displayed by atomic force measurements and the hydrophilicity or hydrophobicity of the treated fibre was emphasised. The presence of Si-O-Si bonds, Si-O-cellulose and ester bonds confirmed that silane coupling agent and benzyolated group were effectively held on the fibre surface through condensation with cellulose hydroxyl groups. The changes in the surface properties was ascertained by contact angle measurements. Hydrophilic character of the cellulose fibres decreased after acetylation, benzoylation and silanation.

All these measurements are very efficient techniques to investigate the various changes effected by different chemical modifications which are
necessary to improve the compatibility of fibres and polymer matrices for making eco-friendly and low cost composite materials. The banana fibre surface modifications influence these measurements significantly.

The mechanical properties of banana fibre/PF resin composites fabricated by RTM and CM techniques were analysed as a function of fibre length and fibre loading. The tensile, flexural and impact behaviour of the composites were characterized. Tensile and flexural properties were found to be higher in RTM composites than CM composites at all fibre loading. At higher fibre length the stress value was lowered due the entanglements and fibre curling. The optimised fibre length was 30 mm. It was found that increasing the fibre content had a positive effect on tensile and flexural strength. The tensile and flexural properties increased with fibre loading upto 40 wt% for both RTM and CM techniques and then decreased with an increase in fibre loading. At low fibre loading the fibre may act as a flaw in the matrix, reducing the tensile strength of the composite. The matrix is not restrained by enough fibres and highly localised strain occurs in the matrix at low stresses, causing the bond between matrix and fibre to break, leaving the matrix diluted by non reinforcing debonded fibres at low fibre content. As the fibre concentration increases, the stress is more evenly distributed and the strength of the composite increases. At higher fibre loading there is a strong tendency for fibre-fibre interaction. This leads to poor wetting of fibres and fibre dispersion. Even if fibre / matrix bonding is present poorly dispersed fibres give rise to fibre-fibre interactions and reduce the load bearing capabilities of the fibres and there by reduce the available stress transfer area. The impact strength of RTM composites are slightly lower than that of CM composites. SEM indicated that the extent of fibre pull out was lower for RTM
Conclusions and future scope of the work

Composites than CM composites. The void content is comparatively less in the composites prepared by RTM. Thus fibre/matrix interaction is substantially improved in RTM composites. It can be concluded that the mechanical properties of the composites are intimately dependent on the fabrication techniques. The tensile strength and Young’s modulus value of the composites are compared with the theoretical predictions. Experimental values were seen to agree with the theoretical predictions at lower fibre loading but deviate slightly from ROM, series and Hirsch’s model at higher fibre loading. The parallel model show large positive deviation from the experimental value. The presence of voids, fibre/fibre interaction, critical fibre length, non-uniformity of the fibre and the surface irregularities of the fibre greatly influence the tensile properties of the composites. These reasons can be accounted for the deviation from theoretical predictions.

Banana fibres have been subjected to chemical modifications like alkali treatment, benzoylation, acetylation, formic acid, KMnO₄ and silane treatments. The surface morphology is studied using FTIR and SEM. The chemical structure of treated fibres was remarkably changed as indicated by IR spectra. Of the various chemical treatments, the fibre/matrix adhesion is higher in the case of NaOH treated fibre composite. The SEM micrograph indicates a reduction in the thickness of the fibre upon alkali treatment. This may be due the leach out of alkali soluble fractions like waxy layer, lignin and hemicellulose. More-over the treatment produces a number of small voids on the surface of the fibre that promote mechanical interlocking between the fibre and the matrix. Tensile strength, flexural strength, Young’s modulus and flexural modulus are found to be maximum in the case of NaOH treated fibre composites. The reduction in the hydrophilicity during
benzoylation, acetylation and silane treatment made the fibre less compatible with hydrophilic PF. This can be attributed to the decreased mechanical properties of the above treated composites. When the composites were fabricated by RTM, a marked improvement in the tensile and flexural properties was observed and these composites had lower impact strength than CM composites. The low impact strength is due to the high bonding of the fibre with phenolic resin which resulted in a fracture of fibre at the crack plane without any fibre pull out. A significant part of the energy absorption during impact takes place through the fibre pull out process. Less fibre pull out occurred in RTM composites due to high interfacial bonding. The fracture of the fibres occurred at the crack plane.

Dynamic mechanical analysis of neat PF and randomly oriented short banana fibre/PF composites were investigated with reference to varying fibre content and different chemical modification. The viscoelastic properties had been evaluated as a function of temperature and frequency. DMA results revealed that the incorporation of fibre into the PF matrix gives rise to an increase of the storage modulus and the maximum value was for composite having a fibre content 40 wt% irrespective of the fabrication method. With an increase of temperature, the storage moduli of both treated and untreated composites decreased due to the deterioration of the fibre/matrix adhesion at higher temperatures. The loss modulus curves broadened compared to neat PF matrix. The tan δ value was lowered as the fibre content increased and is attributed to better fibre/matrix interaction. The SEM micrographs supported the above observations. Chemical modifications like alkali, KMnO₄ and formic acid treatments of the fibre were found to improve the interfacial bonding of the fibre with the resin. The Tₐ obtained from loss modulus and
tan δ curves indicated a shift towards higher temperature. Storage moduli of these treated composites were increased. Among the chemically treated composites highest storage modulus and glass transition temperature were obtained for alkali treated composites. The high values of the composite were supported by the fact that the load transfer between the fibre and the matrix occurred through the strong fibre-matrix interface. Cole-cole plot of the composites showed the heterogeneous nature of the system. The experimental storage modulus and tan δ values of the composites were compared with the theoretical models and it was found that the experimental values deviate from theoretical models indicating the heterogeneous nature of the composites. RTM fabricated composites showed better performance compared to CM composites.

The water absorption kinetics of banana fibre reinforced PF composites were analyzed at different temperatures 25, 50 and 90°C. The effects of fibre loading, and chemical modification of fibres on the water absorption of the composites were evaluated. Neat PF resin shows minimum water absorption and as the amount of hydrophilic cellulose fibre increased the water uptake also increased. The investigation revealed that as the fibre content increased, the water uptake also increased and leveled off at longer times irrespective of the fabrication method. The fibre reinforced composites were found to absorb water very rapidly at the initial stage and later a saturation level was attained without any further increase in water sorption. Water sorption of RTM composites were comparatively less than that of CM composites due to the lower void content and high fibre/matrix interaction compared to CM composites. The values of diffusion coefficient, sorption coefficient, permeability coefficient and mole percent uptake at equilibrium of alkali
treated fibre reinforced composite were found to be lower than that of untreated and other treated composites irrespective of the fabrication techniques. This is explained by enhanced bonding between fibre and matrix through chemical treatment. As a result of chemical treatment the hydroxyl groups of cellulose binds with the matrix by hydrogen bonding and good fibre/matrix adhesion is established. Therefore, the chances of hydroxyl groups coming in contact with water molecules are reduced considerably. The analysis also proved that water absorption was increased in the case of benzoylated, acetylated and silanised fibre composites. After these chemical treatments the fibre surface becomes hydrophobic, which decreases the fibre/matrix interaction, thus facilitating void formation and enhances watersorption. The sorption coefficient and permeation coefficient increased with increase in fibre loading. Diffusion studies revealed that the interfacial adhesion plays a vital role in the water transport process. Fickian model was used to study the diffusion process in banana fibre reinforced PF composites and revealed deviation between experimental values and theoretical predictions. This may be due to the deviation of diffusion from Fickian behaviour. Scanning electron micrographs of fracture surfaces of RTM and CM composites indicated that fibre splitting and more fibre pull out occurred for CM composites. Thus fibre/matrix interaction substantially improved in RTM composites. Finally, it is highly relevant to add that water transport studies could be used as a probe to evaluate the strength of the interfacial adhesion in cellulose fibre reinforced polymer composites.

Cellulose nano particles are inherently a low cost material which is available from a variety of natural sources and in a wide variety of aspect ratios ~200nm long and 5nm in diameter. They are an attractive nano material for
multitude of potential applications in a diverse range of fields. Mechanical properties of micro and nano composites are improved with the incorporation of fibres and the nanocomposites exhibit mechanical properties greater than micro and macro composites and may lead to improved light weight PF composites for application in automobile parts. Mechanical properties of the nanocomposites showed significant increase in tensile and modulus values when only small quantities (10wt%) of nanofibres were added. This is due to good interfacial adhesion between the fibres and matrix. The stress increases linearly with strain at low elongation and more strength is shown for nano composites. More than 10 fold increase in strength and modulus is realised by the addition of only 10wt % of the nanofibres. When the fibre content of the nanofibre is 12wt% of the PF composite, the impact strength of the system is 123% higher than that of the pure matrix system. However the tensile strength, Young’s modulus and elongation at break of the nanocomposite exhibit a maximum when the nanofibre is 10 wt% of the composite. Micro and nanofibres were separated from banana fibre by steam explosion method. Macro, micro and nano fibre reinforced PF resin composites were prepared using these fibres. The effects of filler loading were investigated. The nanofibres improve their compatibility with PF resin matrix. The dispersability of micro and nano fibrils decreases at higher wt% due to agglomeration. The stiffness and ductility of the micro and nano composites also were found to increase. The reinforcement effect depends largely on matrix ductility. i.e, the resistance to crack the propagation. Above 40 wt% for macro, 20 wt% for micro and 10wt% for nano, the mechanical properties decrease due to fibre to fibre contact that occurs when the fibre mat impregnated with resin is pressed in the mould to prepare composite laminates. The crystallinity and elongation at break were lower for
microcomposites than nanocomposites due to entanglements of the microfibrils which are more pronounced at higher fibre content. The thermal stability of the composites has been investigated by TGA. The thermal stability is more pronounced for nano composites.

All properties like mechanical, thermal, dynamic mechanical fracture properties etc are affected by the reinforcing particles. It can be concluded that properties of composites made by nano particle reinforcement are better than the composites made by micro and macro particles. Phenolic resin matrix has higher bond strength with fibre due to the possible reaction between the methylol group of the resin with the hydroxyl group of cellulose. These properties together with the inexpensive nature of the indigenous fibre make the composite attractive for industrial application. The surface topology of banana fibre/PF composite has a smooth surface finish and wood-like appearance. The results suggest that banana fibre reinforced PF composites have an edge over the conventional materials used in building industry.

Untreated macro fibre/PF sample subjected to cold water ageing has shown a 30% decrease in tensile strength where as nanofibre/PF sample has shown 10% decrease. The water molecules act as a plasticizer by influencing the fibres, matrix and interface simultaneously and disturbing the mechanical integrity of the composite system. Fibre/ PF debonding may be initiated by the development of osmotic pressure pockets at the surface of fibres due to the leaching of water soluble substances from the fibre surface.

The nano fibrils provide stable and substantial reinforcement which is more resistant to all ageing process when compared with macrofibres and microfibrils. Nanofibril composites are stronger also. On examination the PF
matrix of the composite will not degrade much due to long term ageing because it showed no significant water uptake or strength loss. Macrifibril/PF composites suffered maximum strength loss followed by microfibril/PF composites in all the ageing process. The extent of mechanical properties decrease with increasing ageing time were relatively small for nanofibril composites over microfibril and macrofibril composites. Mercerisation indicates good fibre/matrix bonding. Fibre modification using silane coupling agent decreases the fibre/matrix adhesion due to its hydrophobic nature which leads to poor interaction with the hydrophilic matrix. In all the specimens the same PF resin is used as the matrix. But the composites showed significant variation in strength. Therefore, the studies on ageing show that the strength loss in all the composites appeared to be due to weakening and degradation of the fibre and not due to the matrix. This is consistent with the fibre pulled out SEM of the fracture surface. In soil aged composites and outdoor weathered composites, the cellulose fibrils protrude from the surface giving the surface a rough nature. The reinforcement by fibre makes the PF composites biodegradable. Alkali treated samples show minimum degradation in comparison with all other ageing processes. This study indicates that mercerised nano banana fibre reinforced PF composite can withstand normal exposure to environment without much appreciable change in tensile strength.

Thermal stability of untreated and treated banana fibres and their composites has been investigated by TGA. As the fibre loading increases, the weight loss at a particular temperature is simultaneously geared up. This happens at all temperatures due to the low thermal stability of banana fibre compared to PF resin. A gradual weight loss is observed starting at around 300°C for all the
composites. This initial weight loss is possibly due to the degradation of the lignin, hemicellulose etc present in the fibres, which continues for some period at a very slow rate. Because the actual decomposition of the cured composites begins at elevated temperatures, the weight loss occurs at a faster rate. The intersection point between the initial slope and the slope followed after the fast decomposition basically provides primary onset of the decomposition temperature. The thermal stability of the fibres was increased by chemical treatment. This may be attributed to the reaction between cellulosic hydroxyl group of the fibre and the coupling agents. These bulkier groups restrict the segmental mobility, thereby increasing the stiffness of the cellulose backbone. It is also partially due to the fact that some of the components of the fibre, such as lignocellulose, that degrade at a lower temperature may be extracted during alkali pre treatment. The composite samples reinforced with alkali, KMnO₄ and formic acid treated fibre provide a higher degradation temperature in comparison with the untreated composites. The removal of hemicellulose, pectin, waxes etc which increase the crystallinity as a result of alkali treatment of the banana fibre improves the interfacial bonding in the composite as understood from the weight loss and peak temperatures. At higher temperature region the thermal degradation increases compared to untreated one due to the removal of lignin and cuticle layer of fibres during each treatment. Upon these treatments, the percentage weight loss and percentage residue are decreased and the thermal stability of the composites were increased. During benzylation, acetylation and silane treatment the hydrophilicity of the fibre surface is decreased and the void content and moisture content increased. This leads to weak chemical boning at the fibre/matrix interface. Hence the degradation takes place at an earlier temperature compared to untreated composite. In the DTG curves the initial
depression is due to water evaporation. The two main degradation peaks are due to fibre degradation and the resin disintegration. The first peak of all composites varies slightly which depends on the fibre treatment. Second peak which is due to PF resin is not affected considerably by the fibre reinforcement.

Thus banana fibre is a potential reinforcement in phenol formaldehyde resin and one of the fastest growing types of polymer additive.

**12.2 Future Scope**

The present work offers the scope for extensive studies in the macro, micro and nano fields.

1. The performance of composite system is highly influenced by the fibre/matrix interface. Hence a more detailed characterization of the interface between banana fibre and PF resin would be worth attempting. The interface can be further characterized by techniques such as electron spectroscopy for chemical analysis (ESCA), microbond test, and single fibre pull out test.

2. Recycling and burning characteristics of banana fibre reinforced PF composites can be examined.

3. Hybrid fibre composites with synthetic fibres can be developed and their performance can be evaluated.

4. Product Development-partition bands can be developed using these composites. Other useful products also can be manufactured using banana/sisal hybrid fibre reinforced polyester composites.
5. Processing techniques for banana fibre used currently are not economical and are time consuming. Better processing methods have to be found out and techniques developed for getting high quality fibres at a cheaper rate. In addition, economic processing methods for the composites have also to be developed.

6. Cellulose biopack for cosmetic applications

7. Development of dental bridges made out of nanofibres
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3. Contact angle measurements of untreated and chemically treated banana fiber, in the International Conference on National Polymers, Biopolymers, Biomaterials, their composites, Blends IPNs and Gels: Macro to Nano scale held at Kottayam during 19-21 November 2007

4. Electrokinetic studies of chemically modified banana fiber at the seminar on Nano technology for biomedical applications held at S N College, Chengannur on 17 & 18 March 2009
Curriculum Vitae

5. Polarity parameters of banana nano fiber at the 1st International conference on recycling and reuse of materials held at Kottayam from 17-19 July 2009

6. Contact measurements of banana fiber at the National Seminar sponsored by CSIR and STEC on ‘Major Trends in General and Applied Chemistry’ from March 25–27, 2008 at St. Thomas College, Kozhencherry, Kerala

7. Comparison of micro and nano fibrils of banana phenol formalehyde composites for hierarchial applications at the National seminar on “Recent trends in Organic Chemistry”, held at Christian College, Chengannur from 16-18 January 2009

8. Electrokinetic studies of chemically modified banana fiber at the seminar on Nano technology for biomedical applications held at S N College, Chengannur on 17 & 18 March 2009

9. Polarity parameters of banana nano fiber at the 1st International conference on recycling and reuse of materials held at Kottayam from 17-19 July 2009

10. National seminar “Wonders in nano science” held on 17-19th November 2009 at N.S.S.College, Pandalam

Posters presented in national/international conferences


2. Presented a poster on contact angle measurements of untreated and chemically treated banana fiber in the ICNP 2007, international Conference on National Polymers, Biopolymers, Biomaterials, their composites, Blends IPNs and Gels: Macro to Nano scale held in Kottayam during 19-21 November 2007

3. “Electrokinetic measurements” of banana nano fiber at the 1st International conference on recycling and reuse of materials held at Kottayam from 17-19 July 2009

4. “Mechanical properties and failure topography of banana fibre composites” at the Second International Conference on Polymer Processing and Characterisation (ICPPC-2009) held at Kottayam, from 15-17th January 2010

Workshop attended


Book Chapter

**Curriculum Vitae**

publications, Cincinnati Chapter 10 “coir and Hemp Fiber Reinforced polymer composites”


**Publications**


3. KN Indira, Kuruvilla Joseph, Laly A Pothen, Sabu Thomas, Influence of processing conditions in the physico-mechanical properties of banana-pf composites, Composites Part A (communicated)


6. K N Indira, Bibin Mathew Cherian, Laly A Pothan, Sabu Thomas, K. Joseph, Surface characteristics, spectroscopic investigations and thermal behaviour of banana fibres- macro to nano scale, Colloid and Interface Science (communicated)

7. K. N. Indira, Bibin Mathew Cherian, Laly A Pothan, Sabu Thomas, K. Joseph, Thermal stability and degradation of banana fibre/PF composites fabricated by RTM, Composite Science and Technology (communicated)


10. K. N. Indira, Bibin Mathew Cherian, Laly A Pothan, Sabu Thomas, K. Joseph, A comparative study of banana fibre/pf composites on the mechanical, thermal and viscoelastic properties-from macro to nano scales, Polymer Composites, (Communicated)