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Development of banana/glass short hybrid fiber reinforced nanochitosan polymer composites

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ABSTRACT

Natural fiber reinforced composites have attracted the attention of research community mainly because they are turning out to be an alternative solution to the ever depleting petroleum sources. Various natural fibres such as jute, sisal, palm, coir and banana are used as reinforcements. In this paper, banana fibres and glass fibers have been used as reinforcement. The aim of this present study was to develop a polymer made up of banana/glass fiber reinforced nanochitosan composites. The nanochitosan was prepared using polyphosphoric acid and composites of nanochitosan were prepared with short fibers of banana and glass in the presence of crosslinking agent glutaraldehyde. The prepared glass and banana fiber reinforced nanocomposites were characterized using different analytical tools such as FT-IR, XRD, TGA and DSC. The FT-IR studies reveal the formation of nanocomposites. The observed results of TGA and DSC show that the addition of glutaraldehyde along with the nanosized chitosan has increased the thermal stability.The XRD results indicate the change in crystallinity of nanocomposites.

Keywords: Banana fiber, glass fiber, nanocomposites, characterisation.

INTRODUCTION

Lignocellulosic biomass is the most abundant material in the world. Much work is done in the application of natural fibre as reinforcement in polymer composites [1]. There is a growing interest in the use of natural fibers as reinforcing components for both thermoplastic and thermoset matrices, because of the ideal benefits offered by natural fibers such as convenient renewability, biodegradability, and environmentally friendliness [2]. A great interest towards the development of composite materials reinforced with natural fibers has emerged in the last decade [3-5]. According to the Food and Agricultural Organization (FAO), each year farmers harvest around 35 million tons of natural fibers from a wide range of plants and animals. The term natural fibers is used to designate numerous kinds of fibers that are naturally produced by plants, animals and minerals [6]. The natural fibers such as sisal, coir, jute, ramie, pineapple leaf, and kenaf have the potential to be used as reinforcement materials in composites.

The growing interest in lignocellulosic fibres is mainly due to their economical production with few requirements for equipment and low specific weight, which results in a higher specific strength and stiffness when compared to synthetic fibers. The inherent polar and hydrophilic nature of lignocellulosic fibres and the non-polar characteristics of most thermoplastics results in compounding difficulties leading to non-uniform dispersion of fibres within the matrix which impairs the efficiency of the composite. This is a major disadvantage of natural fibre reinforced composites.

Another problem is that the processing temperature of composites is restricted to 200˚C as vegetable fibres undergo degradation at higher temperatures; this restricts the choice of matrix material [7]. Another setback is the high moisture absorption of natural fibres leading to swelling and presence of voids at the interface, which results in poor mechanical properties and reduces dimensional stability of composites. It is quite clear that the advantages outweigh the disadvantages and most of the shortcomings have remedial measures in the form of chemical treatment [8].

In India, banana is abundantly cultivated. Banana fiber can be obtained easily from the plants which are rendered as waste after the fruits have ripened. So banana fiber can be explored as a potential reinforcement. Banana fiber, a ligno-cellulosic fiber, obtained from the pseudo-stem of banana plant (*Musa sepientum*), is a bast fiber with relatively good mechanical properties. Banana fiber possesses good specific strength properties comparable to those of conventional materials like glass fibers [9-11]. Furthermore, this materials has a lower density than glass fiber [12]. However banana fibers are associated with some challenges including high moisture uptake low thermal stability and low bonding with polymers.

The glass fiber is blended with a thermoplastic fiber as a route to a perform material that could be easily shaped and molded into its final form without the need for a resin. Such composites are desirable because of their high strength, low cost and good fatigue resistance. Additionally glass fibers have good impact strength, good chemical and corrosion resistance, good electrical resistance, low dielectric constant and good dimensional stability. In the present study banana and glass fiber reinforced nanochitosan polymer composites were prepared and its mechanical strength was tested.

MATERIALS AND METHODS

Materials

Chitosan was kind gift from Indian Sea Foods, Cochin, Kerala. Banana Fibers was purchased from Vibrant Nature, Chennai, India and Glass Fibers was obtained from Placon Agencies, Chennai. All the chemicals used in the present work were of analytical grade.

Preparation of nanochitosan

Nanochitosan was prepared by sol-gel method using polyphosphoric acid. About 15g of chitosan was dissolved in 3 litres of conductivity water containing 60 ml of 2% v/v acetic acid .The above solution was stirred well for 45 minutes. Then to the above prepared chitosan solution, 12 gms of sodium hexametaphosphate dissolved in 1600 ml of conductivity water was added dropwise. A milky coloured emulsion like appearance was obtained. This solution was then allowed to settle as suspension by adding conductivity water in excess for 24 hours. After this process is over, the supersaturated solution was then decanted.

Preparation of fiber composites

The banana and glass fibers were cut into very small pieces of approximately 0.25 cm length to be used as dust fibers and three cm length for using as short fibers. The nanochitosan was dispersed in minimum amount of water. The above dispersed nanochitosan solution and the fibers was then mixed and blended in different proportions. The binary composites of nanochitosan were prepared with banana and glass fiber in the two different forms using short and dust fiber of glass and banana in the ratio 30:1 and 30:2 in the presence of crosslinking agent glutaraldehyde. This mixture was then stirred for 30 minutes using the high speed mixer Remi motor (200 rpm, 30 min) which was then stored overnight. It was then poured into the petridishes and allowed to dry.

Glass fiber nanochitosan composites:

a. Short fiber:	b. Dust fiber:
NC+GF(30:1)	NC+GF(30:1)
NC+GF(30:2)	NC+GF(30:2)

Banana fiber nanochitosan composites:

a. Short fiber:	b. Dust fiber:
NC+BF(30:1)	NC+BF(30:1)
NC+BF(30:2)	NC+BF(30:2)

FTIR Studies of blends.

FT-IR Measurements were performed with the fiber composites using Thermo Nicolet AVATAR 330 spectrophotometer in 4000 – 400cm^{-1} wavenumber range using KBr pellet method.

TGA

Thermogravimetric analysis of the nanocomposite fibers (cut into small flakes) was conducted on a SDT Q600 V8.0 Build 95 instrument in the temperature range of 50^{o} to 800^{o}C at the heating rate of 20˚K/min.

X – Ray Diffraction Studies

X–ray diffraction (XRD) studies of fiber nanocomposites was performed with the X-ray powder diffractometer (XRD – SHIMADZU XD – D1) using a Ni – filtered Cu Kα X–ray radiation source. Banana fiber in the form of short non woven fibers (3mm) was used in this work.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

Figure-1 shows the FT-IR spectra of pure nanochitosan. The IR spectra of nanochitosan (Figure 1) shows prominent peak at 3385.92 cm^{-1} corresponding to –OH stretching of axial OH group, -NH stretching. Peak obtained at 2908.57cm^{-1} corresponds to the aliphatic –CH asymmetric stretching. Certain peaks observed at 1635.20cm^{-1}, 897 cm^{-1} corresponds to –NH bending and C-C stretching. The FT IR spectra of NC+GF (30:1) (figure 2) shows prominent peak at 3436.08 cm^{-1} corresponding to –OH stretching of axial OH group, -NH stretching. Peak at 2926.20cm^{-1} corresponds to the aliphatic –CH stretching. The peak at 1632.98cm^{-1} corresponds to –NH bending and the peaks at 614cm^{-1} corresponds to out of plane bending. A similar type of results was observed in the case of NC+GF (30:2) nanocomposite (Figure-3). The FT-IR spectral details of NC+GF (30:1) (dust fiber) and NC+GF (30:2)(dust fiber) was represented in the figure-(4)-(5).The FT-IR spectra of NC+GF (dust fiber) (30:1) shows prominent peak at various wave number values such as 3454.10 cm^{-1} , 2925.03cm^{-1}, 776.59cm^{-1},476.82 and 416.70 cm^{-1}.These observed peaks indicate the presence of intermolecular hydrogen bonded OH stretching, aliphatic –CH asymmetric stretching, NH bending and C-C bending.

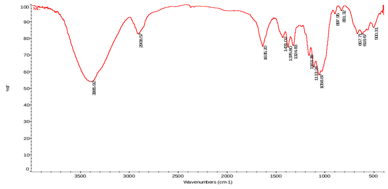
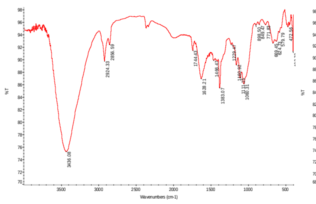
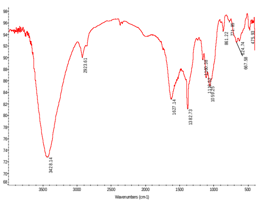
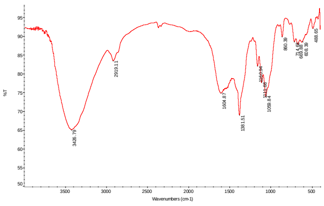


Figure-1







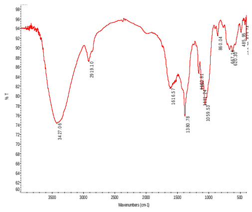


Figure-2 Figure-3 Figure-4 Figure-5

Figure-6-9 shows the FT-IR spectra of NC+BF (30:1), NC+BF (30:2), NC+BF (30:1) (dust fiber) and NC+BF (30:2) (dust fiber) respectively. The FT-IR spectra of nanochitosan banana fiber composites prepared in different ratios shows prominent peak at 3446.01 cm^{-1} corresponding to –OH stretching of axial OH group. The peak obtained at 2925.31cm^{-1} was attributed to the aliphatic –CH stretching. Certain peaks observed at 1089.81 cm^{-1} corresponds to C–O stretching and the peak obtained at 780.01 cm^{-1} corresponds to N-H bending. On comparing the FT-IR spectral results of the nanochitosan glass fiber composites and nanochitosan banana fiber composites prepared in different ratios with pure nanochitosan it was observed that some more additional peaks were observed in the case of fiber nanocomposites corresponding to the groups present in the glass fiber and banana fiber. In addition to this, the intensity of the OH bands has also increased when compared to the pure nanochitosan .These FT-IR spectral results indicate that there are no significant conformational differences between nanochitosan and the composites

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formed. There are no significant differences in the major bands, however there are shift differences in the peak intensities which indicate changes in the amount or concentration.

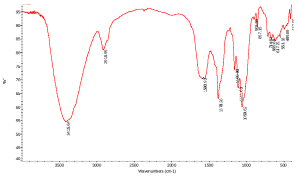


Figure-6

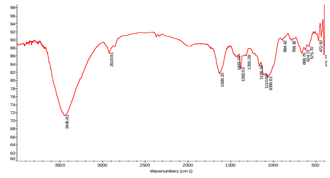


Figure-7

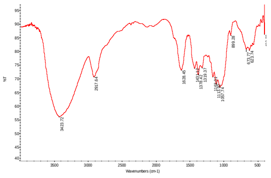


Figure-8

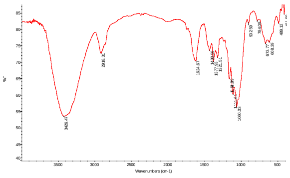


Figure-9

TGA

The TGA thermogram details of NC+GF (short fiber) (30:1), NC+GF (30:2) (short fiber), NC+GF (30:1)(dust fiber), NC+GF (30:2) (dust fiber) and NC+BF (short fiber) (30:1), NC+BF (30:2) (short fiber), NC+BF (30:1)(dust fiber) and NC+BF (30:2) (dust fiber) was represented in the Table-1-2 ,Figures-10(a-h).

Table-1

SAMPLE	%Weight Loss	Decomposition Temperature(˚C)
NC+GF(short fiber) (30:1)	10	180
	20	225
	30	278
NC+GF(short fiber) (30:2)	10	270
	20	319
	30	344
NC+GF (dust fiber) (30:1)	10	218
	20	262
	30	300
NC+GF (dust fiber) (30:2)	10	190
	20	248
	30	292

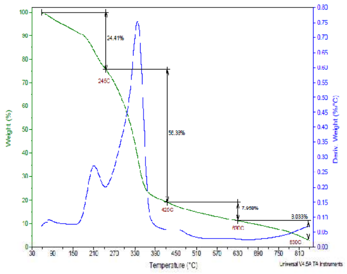


Figure-10 (a)

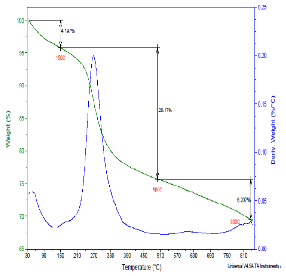


Figure-10(b)

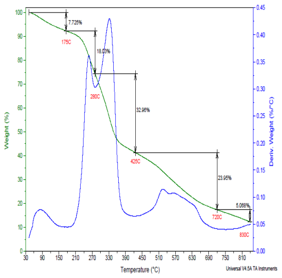


Figure-10(c)

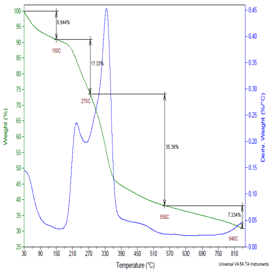


Figure-10(d)

Table-2

SAMPLE	%Weight Loss	Decomposition Temperature(˚C)
NC+BF(short fiber) (30:1)	10	205
	20	258
	30	355
NC+BF(short fiber) (30:2)	10	260
	20	400
	30	470
NC+BF (dust fiber) (30:1)	10	284
	20	682
	30	700
NC+BF (dust fiber) (30:2)	10	105
	20	260
	30	370

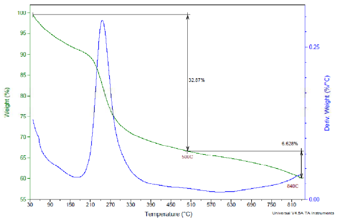


Figure-10(e)

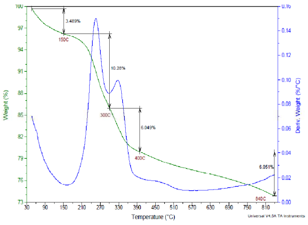


Figure-10(f)

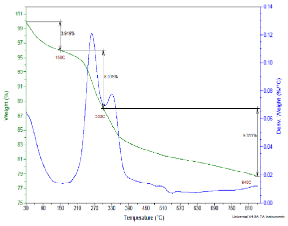


Figure-10(g)

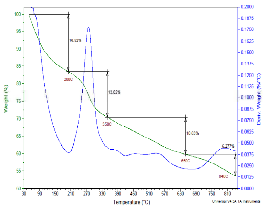


Figure-10(h)

The initial weight loss obtained in the region of 50–100˚C was mainly due to moisture evaporation and water adsorbed to the fiber. The degradation of fiber reinforced nanocomposite in the temperature region ranging from 220–300 ˚C was mainly attributed to thermal depolymerization of hemicellulose and the cleavage of glycosidic linkages of cellulose. The broad peak obtained in the region from 200 to 500˚C was contributed by lignin components and the degradation of cellulose take place between the temperature ranges from 275˚C and 400˚C.

From the results of TGA it was observed that in the case of composites of nanochitosan with glass fibre an increase in the amount of glass fibre (ratio) increases the thermal degradation, where as in the dust forms it decreases. In case of the composites of nanochitosan with banana fibre an increase in the amount of banana fibre in short form as well as dust form increases the degradation temperature. On comparing the results of TGA of glass fiber composites with banana fiber, it was concluded that the nanochitosan with banana fibre composites have higher thermal stability in terms of higher degradation temperature than the nanochitosan with glass fibre composites. This was confirmed from the amount of residue remained at the end of the experiment and the various decomposition temperatures.

DSC

DSC is an analytical tool which helps to understand the thermal behavior of polymers and composites. It helps in finding glass transition temperature and polymer composites. The glass transition temperature (Tg) is the temperature at which the material undergoes a structural transition from an amorphous solid state (glassy state) to a more viscous (rubbery) state. Below Tg, films are rigid and brittle, whereas above it films become flexible and pliable. Figures:11(a-h) represents the DSC curve of NC+GF (short fiber) (30:1), NC+GF (30:2) (short fiber), NC+GF (30:1)(dust fiber), NC+GF (30:2) (dust fiber) and NC+BF (short fiber) (30:1), NC+BF (30:2) (short fiber), NC+BF (30:1)(dust fiber) and NC+BF (30:2) (dust fiber) respectively.

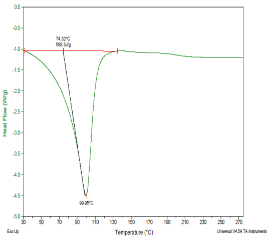
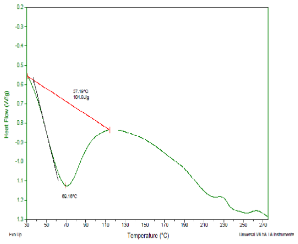


Figure-11(a)



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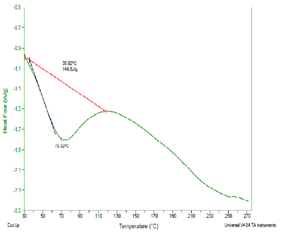

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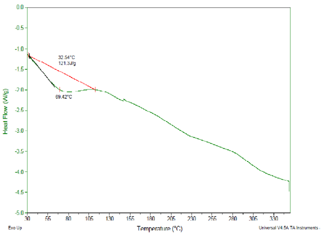
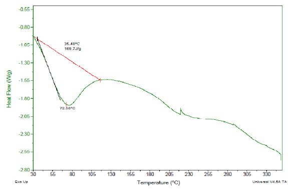


Figure-11(d)



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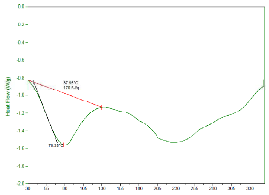

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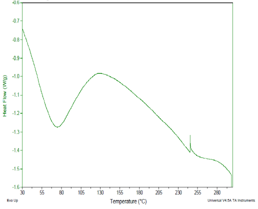

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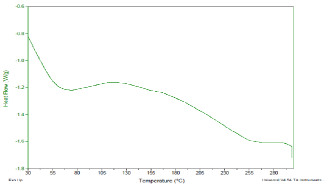


Figure-11(h)

The DSC curve of NC/GF short and the dust forms prepared in the ratio of (30:1, 30:2) shows an endothermic peak at various temperatures such as 99.9˚C, 69.1˚C, 70.3˚C, and 69.4˚C respectively, where as for NC/BF the endothermic peaks are observed at 72.5˚C, 78.3˚C, 75.2˚C and 73.2˚C respectively. The glass transistion temperature of the glass fiber reinforced composites was found to be around 130˚C in case of both short fiber and dust fiber whereas in the case of banana fiber reinforced composites the glass transistion temperature was found to be around 135˚C. On comparing the glass transistion temperature of glass fiber reinforced composites with the banana fiber reinforced composites it was concluded that the bananafiber reinforced composites was found to be highly thermally stable than the glass fiber reinforced composites.

XRD

XRD has been one of the most widely used methods for materials, especially metal and inorganic materials. The crystalline phases and their relative contents in materials can be quantitatively obtained by the diffraction peak location, diffraction peak number and relative intensity of XRD pattern. The XRD spectral details of NC+GF (short fiber) (30:1), NC+GF (30:2) (short fiber), NC+GF (30:1)(dust fiber), NC+GF (30:2) (dust fiber) and NC+BF (short fiber) (30:1), NC+BF (30:2) (short fiber), NC+BF (30:1)(dust fiber) and NC+BF (30:2) (dust fiber) was represented in the Table-3,Figures-12(a-h).

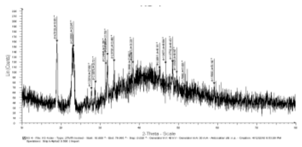
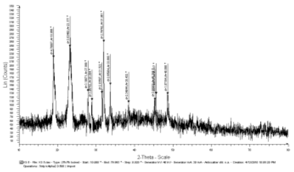


Figure-12(a)



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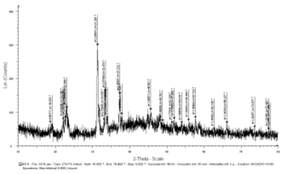

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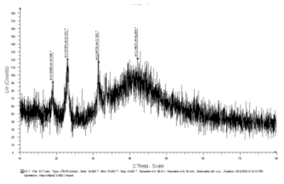

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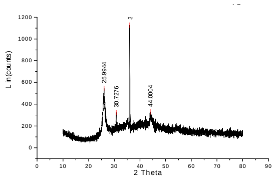

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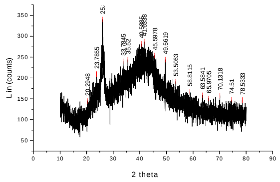

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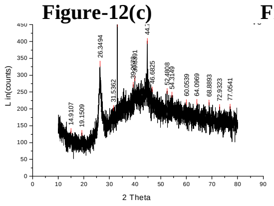

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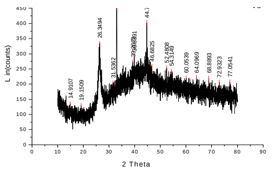

Figure-12(h)

TABLE:3

BINARY COMPOSITES	COMPOSITION	% OF CRYSTALLINITY	
		SHORT FIBER	DUST FIBER
NC+GF	30:1	25.2	18.3
NC+GF	30:2	24.6	23.3
NC+BF	30:1	10.9	11.1
NC+BF	30:2	19.9	15.5

X-ray diffraction pattern of polymer contain both sharp as well as diffused bands. Sharp bands correspond to crystalline orderly regions and diffused bands correspond to amorphous regions [13]. The crystallinity is calculated by separating intensities due to amorphous and crystalline phase on diffraction phase. Computer aided curve resolving technique is used to separate crystalline and amorphous phases of diffracted graph. After separation, Percentage of crystallinity X_c % is measured as ratio of crystalline area to Total area.

$X_c\% = Ac/Ac+Aa \times 100.$
where
A_c= Area of crystalline phase
A_a= Area of amorphous phase
X_c= Percentage of crystallinity

Small Angle X-ray Scattering (SAXS), Infrared Spectroscopy, can also be used to measure crystallinity [14]. From the XRD results of table 3 and figures-12(a-h), it was observed that the % degree of crystallinity was found to be higher in case of short fiber when compared to dust fiber. Moreover the composites made up of glass fiber reinforced with nanochitosan has more crystallinity in terms of better strength compared to banana composites reinforced nanochitosan [15, 16]. From the results the dust fiber fiber composite is having more amorphous region which can be useful for the wastewater remediation. The banana fiber is a low cost, good biosorbent [17], it efficiency was further improved during the composite formation.

CONCLUSION

The prepared nanocomposites have been expected to have improved mechanical properties. The FT-IR results of fiber reinforced nanocomposites show that there were no significant differences in the molecules and the bondings in the composites when compared to the novel materials such as banana fiber, glass fiber and nanochitosan. From the XRD results it was concluded that the glass fibre reinforced composites has more crystallinity, showing better strength and higher dispersion than banana fiber composites. The results of TGA and DSC indicate that the nanochitosan with banana fibre composites have higher thermal stability in terms of higher degradation temperature than the nanochitosan with glass fibre composites.

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