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SYNTHESIS AND CHARACTERISATION OF BIOCOMPOSITES AND NANOBIOCOMPOSITES PREPARED FROM *MUSA SAPIENTUM*

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ABSTRACT

Banana, a tropical and subtropical plant of genus Musae consists of highly vascular system. The study of chemical composition on banana stem reveals the presence of nearly 62% of cellulosic fibres in it. For this reason it has been used as reinforcing fibres in the formation of composites. The present paper deals with the preparation of biocomposite and nanobiocomposite from banana plant fibre with thermoset prepared from Resorcinol-Paranitroaniline –Urea formaldehyle (R-PNA-U—F) and its nanoform. The presence of various active sites and percentage of carbon, nitrogen and oxygen were provided by FTIR and elemenal analysis respectively. In order to explore the use of biocomposites and nanobiocomposites for different household and industrial applications, their XRD and TGA were done to know their crystallinity and thermal behavior. The Kinetic Study were done using Friedman Technique. XRD Study reveals that the nanobiocomposites are more crystalline than composite itself .The increased adhesion between the nanoresin copolymer and the banana plant waste is responsible for the improved thermal stability of nanobiocomposite over the composite.

KEY WORDS

Crystallinity, Musa sapientum, nanobiocomposite, thermogravimetry and XRD

1. INTRODUCTION

The study and utilization of natural polymers such as in various fields go back to ancient times as man's early scientific activities [1-2] various examples can be found in domestic life all around the world regarding effective utilization of various natural fibres.[3-5] However the availability of a large number of synthetic materials and their biochemical properties has changed the market for natural polymers. It is only during last few years that the significance of ecofriendly materials has been realized all over the world to a greater extent [6-8] Natural fibres have greater advantages over synthetic fibres due to their affordability biodegradability , ease of processing and [9 - 11]mostly due to their eco friendliness as they can be derived from renewable resources [12-14]In recent years greater attention has been paid to their use in a number of applications including their use as reinforcing material for polymer matrices with thermosets and thermoplastic matrices[15].Plant waste fibres have the composition, properties and structure that make them suitable for uses such as composite, textile, pulp and paper manufacture. Natural fibres such as flax, hemp, straw, kenaf, jute and sisal are usually listed raw materials when used as reinforcing phase in composites[16] (Siqueira et al- 2010). Most important constituents of natural fibres are cellulose, hemi cellulose, lignin, wax etc. At the molecular scale, cellulose is a polysachharide composed of glucose molecules linked by glycoside bonds. It contains many hydroxyl groups which can provide active sites for hydrogen bonding with matrix [17] (nanoresin copolymer/resin copolymer).

To overcome the limitations of traditional micrometer-scale composites, there has been push for increasing interest in reinforcing composite materials with nano sized particles as nanocomposites can provide extraordinary properties never found in conventional composites. In view of this the authors have taken a novel attempt to synthesize and characterize biocomposites and nanobiocomposites using cellulose fibres of banana plant stem (containing about 62 % cellulose) [18] as reinforcing starting material. The reactivity/chemical composition and use of different sites of banana plant have been investigated by several workers [19- 21]. Our country India is the largest producer of banana contributing to 27% of total worlds production[21] and so large quantities of banana stem (9.8 lakh tones) are left unused on the plantation floor to serve merely as an organic manure. Thus since the availability of banana plant waste is profuse in our country, it is relevant, important and also economically profitable for our country to make it an industrially acceptable reinforcing material which is also one of the objective of present investigation.

2. MATERIALS AND METHODS

2.1 chemicals and materials required:

The chemicals such as paranitroaniline (PNA), urea (NH_2CONH_2), formaldehyde (HCHO), 2N hydrochloric acid (HCl) were procured from Merck and used without purification. The fibres of banana plant waste collected from Musae sapientum (MS), the most common species in India were chopped into small pieces (2-3 inch) and then were washed with deionised water, filtered with ordinary filter paper and then sun dried for seven days. They were grounded to powder form and purified with absolute ethanol.

2.2 preparation of composite:

Two types of biocomposites (A and B**)** were prepared using fibres of Musae sapientum(MS), one(sampleA) with thermoset copolymer resin T(resorcinol-urea-paranitroaniline – formaldehyde) and another (sampleB) with nano resin copolymer (N1), the nano form of the thermoset T [22], (presented in our earlier communication) by taking resin to biomas ratio 1:1 proportion by weight in presence of 2N HCl using the linkage of formaldehyde by usual reflux condensation polymerization method at a temperature of 90^{0}C for heating 8 hours[22]. The samples prepared were washed several times with deionised water and ethanol to remove the impurities (if any) and then dried in vacuum oven at room temperature overnight.

2.3 Testing methods:

Elemental analysis of the samples were done using CHNSO elemental analyser, Thermo Finnigan. The FTIR study of the samples were done using Perkin Elmer model no. RX-1 in the scan range 4000 cm^{-1} to 500 cm^{-1} to ascertain the presence of various active sites. About 0.1-0.5 mg of samples were pressed to discs by mixing with potassium bromide under pressure in vacuum to form transparent discs. The thermal stability of the composite and nano composite were studied in nitrogen atmosphere under non isothermal conditions on TGA Q50V20.13 Build39 TA instruments USA at a heating rate of 10^{0}C/min in the temperature range 30^0-800^{0}C. The X-ray diffraction of the samples were carried out in powder mode using copper target in WXRD/Schimadzu/Japan at temperature 30^{0}C for structural identification and degree of crystallinity . The voltage setting was at 40 KV and current setting was at 30mA. The XRD patterns were obtained in the scan range 2^0 to 80^0.

3. RESULTS AND DISCUSSION

3.1 elemental analyses: The elemental composition of the Biocomposite and nanobiocomposite are given in the **Table-1**. It is clear from this table that carbon and nitrogen percentage are higher in the nanobiocomposite than in microbiocomposite.

3.2 **FTIR study** : FTIR spectrum of sample A(composite) and sample B (nano composite), represented in **Fig-1 (A), Fig-1(B)** respectively are clear indicative of presence of various active sites like ⁻phenolic -OH , aromatic nucleus**,** aromatic nitro group and many more (**Table-2**).The absence of absorption band due to N-H stretching as expected spectrum for $-NH_2$ group, confirms the linkage of - NH_2 group of paranitoaniline with other monomers.

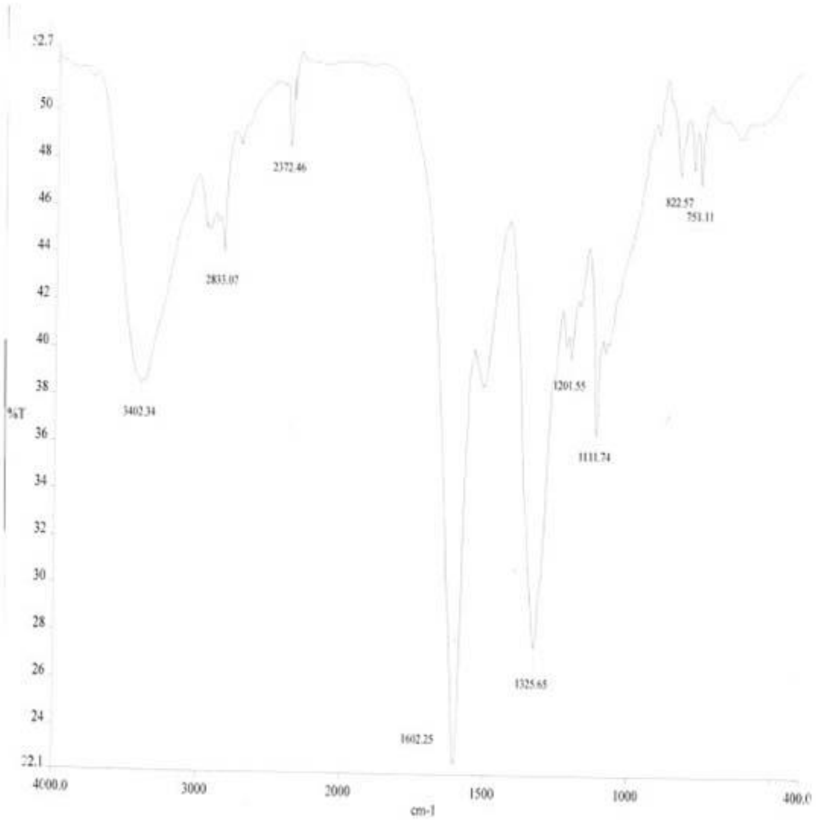

Fig.1(a) FTIR spectrum of biocomposite(A)

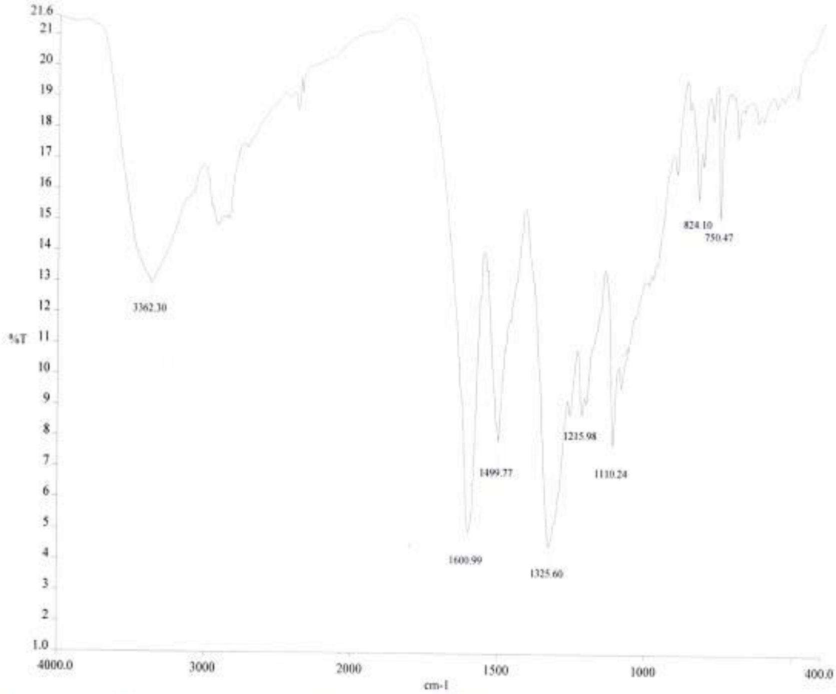

Fig.1(b). FTIR spectrum of nanobiocomposite(B)

3.3 TGA study: **Fig (2)** represents the thermogravimetric curves of composites in micro scale and nano scale. The percentage of weight loss at different temperature values is represented in **Table-3**. The initial mass loss up to 5-6% is due to loss of moisture entrapped or water of crystallization associated with the composites or other volatile impurities present in them. The onset of initial loss is quicker in microcomposite (A) than nanocomposite (B). The second step decomposition involving breaking or cleavage between the MC fibre and the thermoset is comparatively slower in nanocomposite(B) than composite(A) The higher decomposition temperature of the nanocomposite confirms its more compactness than the microcomposite. This may be due to strong bonding between hydroxyl group of cellulose and that of the nanoresin coplolymer. For both these samples the degradation of polymeric chain commences after 350^{0}C and is slow. There is marked difference in percentage of weight loss over the entire temperature range for these samples. The nanocomposite is found to be comparatively thermally more stable and compact than the microcomposite.

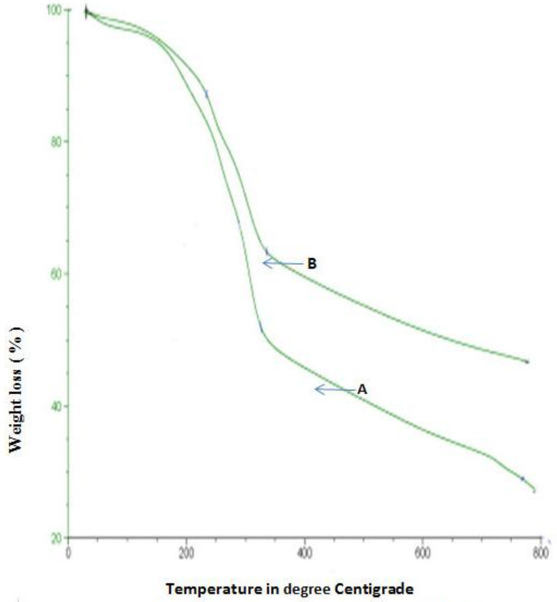

Fig :2. TGA Curve of Biocomposite (A) & Nanobiocomposite (B) showing greater thermal stability of Nanobiocomposite (B)

Kinetic study of thermal degradation reaction : The order of reaction and activation energy of thermal degradation reaction for the composite and Nanocomposites were calculated from thermochemical data using Friedman technique[23] and is represented in **Table(4).** The order of reaction is as expected, since it is a well known fact that the decomposition of copolymers do not obey first order kinetic perfectly.[24]

3.4 XRD analysis: The XRD graph of sample A (composite) and sample B (nanocomposite) are given in **Fig-3**. As is observed from the XRD graph that both these samples are not perfectly crystalline as superposition of both sharp and diffused scattering occurs.There exists some non crystalline region in even the mostly highly crystalline structure. The crytstallite dimension of sample A(microcomposite) and sample B (nanocomposite) are calculated using Debye-scherrer equation(1) [22]

$$Dhkl=\frac{k\lambda}{\beta'\cos\theta} \qquad \text{-------------}\ (1)$$

Where $\beta^{|}$=B-b, $\beta^{|}$=FWHM (full width at half maximum) for each peak

B= Line width
b= instrumental broadening
K= Shape factor = 0.9
θ= Bragg's angle (degree)

λ=wave length of X-ray radiation
($Cuk\alpha_1$=1.54056 A°)

Crystallinity

The percentage of each of these samples that is crystalline can be calculated from equation (2) [22]

$$x_c = \left(\frac{0.24}{\beta'}\right)^3 \qquad \text{------------- (2)}$$

Where X_c is degree of crystallinity From the calculated data (table-3) it is concluded that the degree of crystallinity as well as crystallite size is comparatively higher in case of sample B (nanobiocomposite) than sample A (microbiocomposite). The crystallite size ranges from 4-37 nm in case microbiocomposite and from 22-54 nm in case of nanobiocomposite. As there is both increase in degree of crystallinity and crystallite size for the respective peaks in nanobiocomposite , the cellulosic fibres of Musae sapientum are expected to be better incorporated into matrices of nanoresin copolymer (thermoset N1) as compared to the copolymer resin (thermoset T)[25] . The high degree of crystallinity of nanobiocomposite (sample B) explores the solid Behaviour for synthesizing some novel materials. The microcomposite (sample A) tends to be more amorphous in nature. This may be due to poor adhesion between fibres of MS and the thermoset T. The degree of crystallinity and crystallite size are enhanced in case of nanobiocomposite as compared to micro biocomposite.

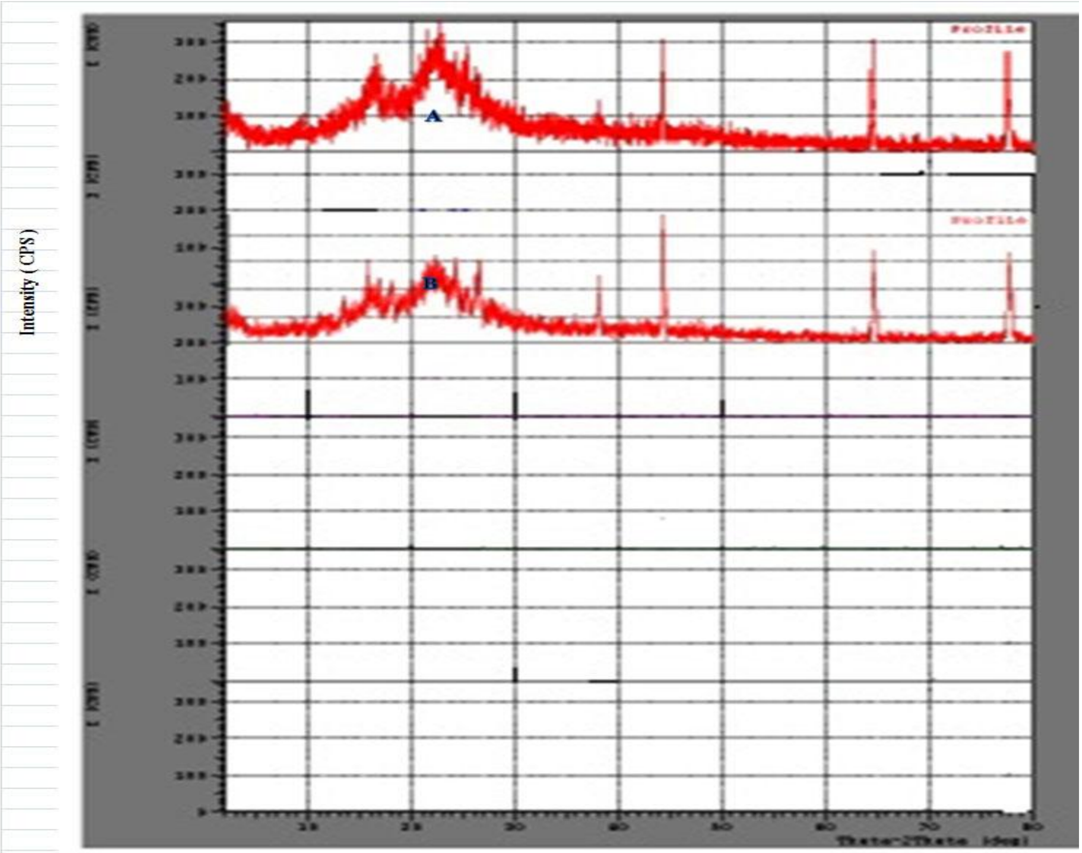

Fig.3. XRD graph showing higher crystallinity of Nanobiocomposite (B) than Biocomposite (A).

Table -1 Elemental composition (% of carbon, nitrogen & hydrogen)

sample	nitrogen	carbon	hydrogen
Microcomposite(A)	**5.89**	**43.94**	**4.666**
Nanocomposite(B)	11.453	57.94	5.844

Table2(a): FTIR data of microcomposite (A)

Peaks(cm^{-1})	Probable assignments
3402.34	(m)N-H $_{str}$ secondary amines
2833.04	-CH_2- symmetric stretching
1602.25	-C-Hstr. Aromatic ring
1325.65	-N-O, Aromatic nitro compound
1201.55	C-N- stretching / C-H- bending
1111.74	C-O bending
822.57	-C-H /monosubstituted C=C
751.11	Monosubstituted aromatic ring out of plane

Table 2(b): FTIR data of nano composite (B)

Peaks(cm^{-1})	Probable assignments
3362.30	O-H-peak (Free)
1600.99	C-Hstr. Aromatic ring
1499.77	N-H in plane deformation(secondary amine)
1325.60	N-O, Aromatic nitro compound
1215.98	C-N- stretching / C-H- bending
1110.24	C-O bending
824.10	C-H /monosubstituted C=C
750.47	Monosubstituted aromatic ring / metadisubstituted benzene

Table 3: Weight loss (%) pattern (concise data) of the microcomposite and nanocomposite at different temperature range

Sample	Nature	100°C	200°C	300°C	400°C	500°C	600°C
A	Microcomposite	3.02	11.271	36.96	54.2	59.09	63.58
B	nanocomposite	1.76	8.36	29.75	49.23	54.81	59.64

Table-4: Kinetic parameters determined from thermogravimetry analysis

Sample	Nature	Temperature range	Order of reaction	Activation energy(KJ/mole)
A	Microcomposite	0^0—600^0C	1.092	0.283
B	nanocomposite	0^0—600^0C	0.942	0.111

Table-5 XRD peak fit parameters of the microcomposite and nanocomposite

Sample	Nature	2θ in degree	B (FWHM) in degree	Degree of crystallinity (X_C)	Crystallite size (D) in nm
A	Microcomposite (resin copolymer T + fibres of MS)	15.157	0.36	0.296	22.361
		16.46	0.95	0.016	8.479
		24.05	0.369	0.0439	11.89
		25.31	0.95	0.083	14.886
		26.31	0.40	1.298	37.216
		44.22	0.72	0.104	16.874
		64.57	0.84	0.092	17.792
		77.68	1.8	0.083	18.607
B	Nanoocomposite (nanoresincopolymer N1+fibres of MS)	15.86	0.173	2.669	46.508
		17.99	0.36	0.296	22.412
		24.09	0.22	1.129	37.04
		26.511	0.15	4.096	54.58
		38.00	0.188	2.080	44.44
		44.25	0.17	2.813	50.60
		64.58	0.183	2.255	51.51
		77.68	0.205	1.604	49.924

4. CONCLUSION

1. The present investigation is an extensive study between micro and nanocomposite prepared from banana plant fibres, copolymer resin and nano resin copolymer. The XRD and TG investigation concludes the more applicability of crystallinity and solid behavior of nanocomposites in comparison to microcomposites. The nanobiocomposite due to its high percentage of crystallinity can be modified to some novel biomaterials which will have wide household and industrial applications.
2. Regarding thermal behaviour, nano biocomposites are more resistible to thermal degradation than micro biocomposites so that nano biocomposites may be used as heat resisting materials.
3. It is an attempt to explore the possibilities of reusing waste banana fibres to useful household and industrial materials.
4. Phenolic resin polymers are replaced partially by a bio renewable molecules (Musa Sapientum) thereby getting a cost effective resin.

5. ACKNOWLEDGEMENTS

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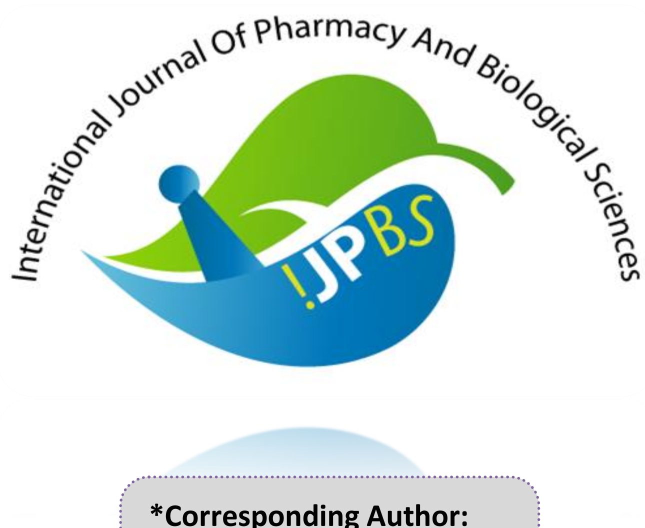

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