Full Length Review Article

A COMPARATIVE STUDY OF SPANI COMPOSITES AND SPANI NANOCOMPOSITES PREPARED FROM MUSA SAPIENTUM

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ABSTRACT

Our country India is the largest producer of banana (Musa sapientum) contributing to 27 % of total world production and so annually large amount of banana pseudo stem containing nearly 62 % cellulose fibers are left unused on the plantation floor to serve merely as organic manure. Thus it is relevant, important and also economically profitable for our country to make it an industrially acceptable reinforcing material. This paper dealt with the synthesis and comparative study of composite and nanocomposite of Musa sapientum with a thermoset of SPANI (substituted polyaniline) prepared from resorcinol-paranitroaniline -urea- formaldehyde (R-PNA-U-F). The presence of various active sites and percentage of carbon, nitrogen and oxygen were provided by FTIR and elemental analysis respectively. In order to explore the use of composites and nanocomposites for different household and industrial applications, their XRD and TGA were done to know their crystallinity and thermal behavior respectively. The kinetic studies were done using Friedman Technique. Nanocomposites was found to be more crystalline and thermally stable than the than composite itself. The reorientation and molecular rearrangement after being associated with the solvent molecules was responsible for the improved crystallinity and thermal stability of the SPANI nanocomposite over the SPANI composite.

INTRODUCTION

Currently research on nanocomposite materials is being oriented towards the use of lignocellulosic fibers in preference to synthetic fibers as reinforcements due to their low density, good mechanical performance, biodegradability and ultimate availability. The use of natural fibers derived from annually renewable resources as reinforcing fibers in matrix provides positive environmental benefits with respect to ultimate disposability and utilization of raw materials. Cellulose based natural fibers can be used successfully as reinforcements for different thermosets and thermoplastics (Vijay Kumar Thakur, 2010). Banana plant (Musa sapientum) fiber is a popular fiber in natural fiber field and polymer composites. It consists of α−cellulose (43.5-71.9%), hemicelluloses (24.1-32.4), lignin (16.0-32.8%) and other materials like ash, wax and moisture (Waleed k.El-zawawy, 2003). Since the availability of banana plant waste if profound in our country, one of the objectives of our investigation is to make this waste natural fiber as an

industrially acceptable reinforcing material which is also economically profitable for our country. Since nanocomposites have drawn attention of many researchers owing to their improved and superior properties never found in traditional bulk materials, in this study we aimed at comparing the crystallographic properties and thermal behavior and nano composites derived from lignocellulosic fibers of banana plant stem.

MATERIALS AND METHODS

Chemicals and materials required

The chemicals such as paranitroaniline (PNA), urea (NH_2CONH_2), formaldehyde (HCHO) and concentrated hydrochloric acid (HCl) were procured from Merck and used without purification. The fibers 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.

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Preparation of SPANI composite and SPANI nanocomposite

First SPANI composites (1B) was prepared using fibers of Musa sapientum (MS), with thermoset of SPANI (resorcinol-urea-paranitroaniline –formaldehyde), (presented in our earlier communication) by taking resin to biomass 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 90^0C for heating 8 hours (Swain *et al*., 2013). 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. Then dried sample was grounded to small pieces by using mortar and pestle. About 2gm of dried sample was placed in 25ml of ethanol and was subjected to sonication for 15minutes using a sonicator. Then the sample was filtered and dried in vacuum oven overnight. In this way SPANI nanocomposite (BNC) was prepared.

Testing methods

Elemental analysis of the samples were done using CHCNO 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. atmosphere under non isothermal conditions on TGA Q50V20.13 Build39 TA instruments 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 nanocomposite were studied in nitrogen USA at a heating rate of 10^0c/min in the temperature range 30^0-800^0C. The X-ray diffraction of the samples were carried out in powder mode using copper target in WXRD/Schimadzu/Japan at temperature 30^0C 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.

RESULTS AND DISCUSSION

Elemental analysis: The elemental composition of the composite and the nanocomposite is given in the Table 1. It is clear from this table that carbon and nitrogen percentage are higher in the SPANI nanocomposite than in SPANI microcomposite.

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

Sample	Nitrogen	Carbon	Hydrogen
Microcomposite (1B)	5.89	43.94	4.666
Nanocomposite (BNC)	2.216	75.65	10.907

FTIR study: FTIR spectrum of sample 1B(SPANI composite) and sample BNC (SPANI nanocomposite), represented in fig-1(a), fig-1(b)respectively are clear indicative of presence of various active sites like, aromatic nucleus, aromatic nitro group and many more (Table 2). The absence of absorption band due to N-H stretching as expected doublet for -NH$_2$

group, confirms the linkage of - NH$_2$ group of paranitoaniline with other monomers. Similarly the appearance of peak due to C=C stretching vibration of phenyl nucleus at 1602.25cm^{-1} in sample 1B and at1589cm^{-1} in sample BNC confirms the incorporation of phenyl nucleus in the polymeric backbone through condensation of raw materials(MS) with thermoset of paranitroaniline (PNA)- urea (NH$_2$CONH$_2$)- formaldehyde (HCHO)-resorcinol.

Table 2(a). FTIR data of composite (1B) showing presence of various active groups

Frequency value(cm^{-1})	Probable assignment
3402.34(m)	N-H$_{st}$ secondary amines
2833.04	-CH$_2$ symmertric stretching
1602.25	-C-Hstr .aromatic ring
1325.25	-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 composite (BNC) showing presence of various active groups

Frequency value(cm^{-1})	Probable assignment
3340.0	N-H stretching 2^0 amines/intramolecular H-bond in cellulose
2915.8	C-H stretching vibration of cellulose/hemicelluloses
1655	C=O of aromatic ring
1589	C-C stretching(in ring) aromatic
1392.5	-N-O asymmetric stretching due to nitro compounds
1496.6	Lignin components
1289.1	-C-N stretching
1256.4	C-H bending -
1081.4	C-C/C-O stretching
1199.4	C-O-C etheral linkage
896.3	β- glucosidic linkage
822.2	paradisubstituted benzene
425.749	disubstituted benzene

Usually a weak band appears at 2350-2360cm^{-1}for parent cellulose of banana pulp due to O-H stretching vibration of intermolecular and intramolecular hydrogen bonded OH group in cellulose (Ibrahim, 2002). The absence of these bands in both these samples indicates the participation of OH group in the bond formation process.

XRD analysis: A comparative XRD graph of sample 1B (SPANI composite) and sample BNC (SPANI nanocomposite) is 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 1B (SPANI composite) and sample BNC (SPANI nanocomposite) are calculated using Debye-scherrer equation(1) (Suresh Kumar, 2010).

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

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 (Cukα₁=1.54056 A°)

Crystallinity

The percentage of each of these samples that is crystalline can be calculated from equation (2) (Suresh Kumar, 2010).

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

Where Xc 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 BNC(SPANI nanocomposite) than sample1B (SPANI composite). The crystallite size ranges from 4.52nm to37.21 nm in case microcomposite and from 6.7nm to 199nm in case of nanocomposite.

The degree of crystallinity ranges from 4.527 to 22.36 to in SPANI composite (1B) and from 0.023 to 216 in SPANI nanocomposite (BNC). There is both increase in degree of crystallinity and crystallite size for each of the respective peaks in nanocomposite. The SPANI nanocomposite (BNC) tends to be more crystalline in nature than the SPANI composite (1B) which may be due to more orderly arrangement of the constituent particles within the crystal after being associated with the solvent molecules to form macro crystalline structure.

TGA study: Fig (4) represents the comparative thermogravimetric curves of composites and nanocomposite. The percentage of weight loss at different temperature values is represented in Table 4. The onset of initial loss is quicker in SPANI composite (1B) than in SPANI nanocomposite (BNC).The initial mass loss up to 5-6% is due to loss of moisture entrapped or water of crystallization associated with the samples or other volatile impurities present in them. It normally occurs at room temperature and 150^{0}C. The second step decomposition involving breaking or cleavage between the MC fibre and the thermoset T is comparatively slower in

Table 3. XRD peak fit parameters for composite (1B) and nanocomposite (BNC) showing improved crystallinity and crystallite size of nanocomposite than composite

Sample name	Nature	2θ in degrees	β(FWHM) in degrees	Degree of crystallinity (X$_C$)	Average degree of crystallinity	Crystallite size in nm	Average crystallite size in nm
1B	Composite	7.2859	0.28	0.629	0.22486	28.569	13.596
		15.537	0.36	0.296		22.361	
		16.46	0.95	0.016		8.4793	
		18.115	0.40	0.216		20.203	
		21.033	0.72	0.037		11.258	
		21.812	0.84	0.023		9.8716	
		22.41	1.8	0.0023		4.527	
		24.05	0.68	0.0439		11.894	
		25.31	0.55	0.083		14.886	
		26.38	0.22	1.298		37.216	
		44.22	0.51	0.104		16.874	
		64.57	0.53	0.092		17.792	
		77.68	0.55	0.083		18.607	
BNC	Nanocomposite	9.891	0.04	216	29.22	199.2	66.40
		11.53	0.06	64		133.0	
		12.97	0.07	40.303		114.1	
		13.77	0.14	5.03		57.1	
		15.32	0.3	0.512		26.7	
		16.34	0.42	0.186		19.1	
		18.22	0.22	1.298		36.5	
		21.36	0.38	0.2519		21.2	
		22.03	0.84	0.0233		9.6	
		22.59	1.2	0.008		6.7	
		23.69	0.14	5.0379		57.9	
		24.47	0.28	0.629		29.0	
		25.70	0.07	40.303		116.3	
		26.78	0.260	0.7865		31.3	
		34.13	0.06	64		138.4	

Table 4. Weight loss (%) pattern (concise data) at different temperature ranges showing higher thermal stability of nanocomposite than composite

Sample	Nature	100^{0}C	200^{0}C	300^{0}C	400^{0}C	500^{0}C	600^{0}C	700^{0}C	790^{0}C
1B	composite	3.02	11.27	36.96	54.2	59.09	63.58	67.13	72.64
BNC	nanocomposite	2.76	6.31	29.75	49.144	54.09	58.95	63.13	66.36

Table 5. Order of reaction determined from the rmogravimetry analysis

Sample	Nature	Temperature range	Order of reaction
1B	composite	0^0—600^{0}C	1.092
BNC	nanocomposite	0^0—600^{0}C	0.942
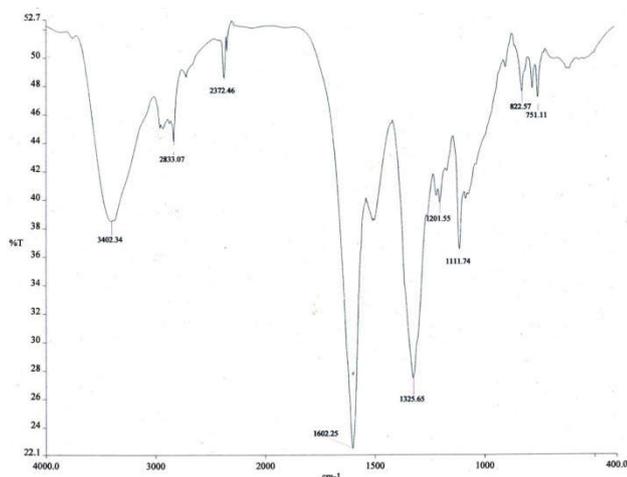
Figure 1(a). FTIR spectrum of sample 1B
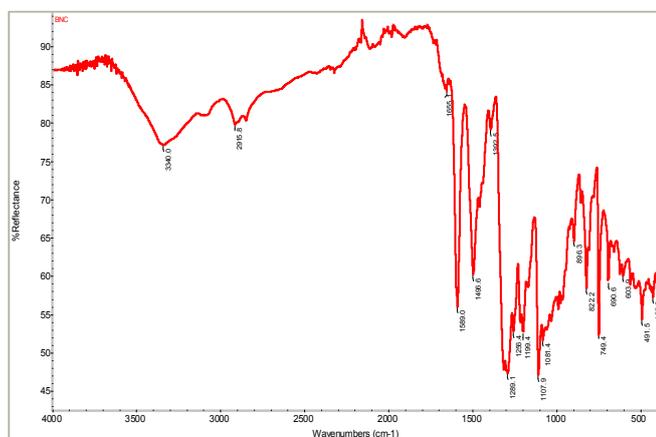
Figure 1(b). FTIR spectrum sample BNC
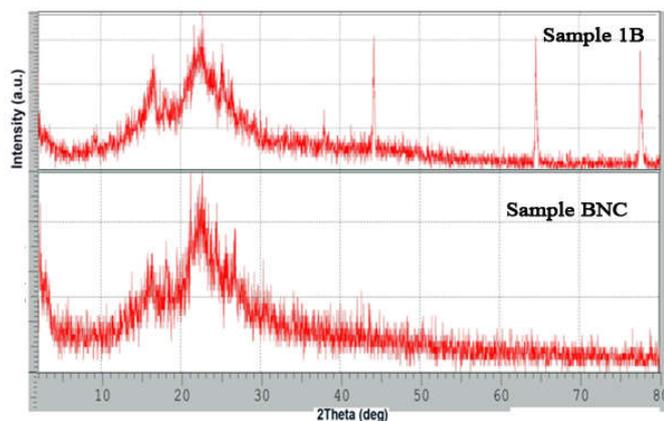
Figure 2. A copmpararive XRD graph showing higher crystallinity of sample BNC over sample 1B

SPANI nanocomposite (BNC) than SPANI composite (1B). For both these samples the degradation of polymeric chain commences after 350^0C and is slow. There is a remarkable difference in percentage of weight loss over the gamut of temperature for these samples. The higher decomposition temperature of the nanocomposite confirms its more compactness than the composite. The enhanced thermal stability of SPANI nanocomposite (BNC) may be due to the fact that after being associated with the solvent molecules reorientation and structural rearrangement takes place at the

molecular scale which increases the compactness as well as the particle size of the sample (BNC).
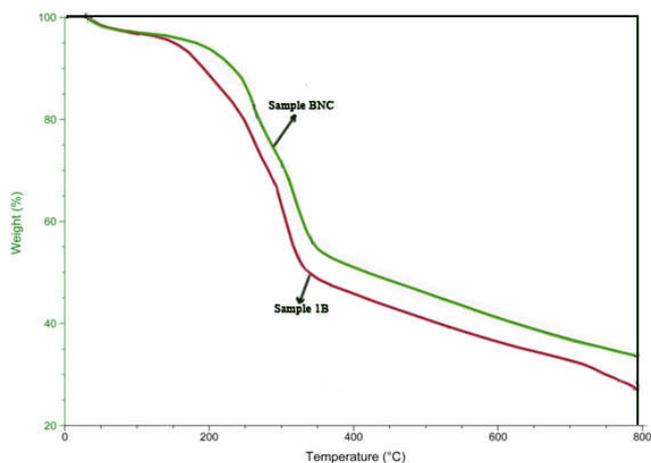
Figure 3. A compararive TGA graph showing higher thermal stability of sample BNC over sample 1B

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 thermo chemical data using Friedman technique (Pawan P. Kalbende, 2013), and is represented in Table 5, (Ibrahim *et al*., 2002). 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 (Sanjiokumar *et al*., 2011).

Conclusion

- The present investigation is an extensive study between micro and nanocomposite prepared from banana plant fibres and copolymer resin. The effect of sonication on crystallographic properties and thermal degradation behavior of the composite of Musae sapientum were analysed. The sonication improved crystallite size as well as crystallinity of the sample. The thermal stability also improved remarkably. The nanocomposite due to its high degree of crystallinity can be modified to some novel biomaterials which will have wide array of household and industrial applications.
- Since nanocomposite are more resistible to thermal degradation than the composite, they may be used as heat resisting materials.
- It is an attempt to explore the possibility of reusing agricultural waste of Musa sapientum to useful household and industrial materials.
- Phenolic resin polymers are replaced partially by a biorenewable molecules (Musa sapientum) thereby getting a cost effective resin.

Acknowledgements

REFERENCES

Ibrahim, M. 2002. *Preparation of cellulose and cellulose derivative azocompounds,*Cellulose, 9, 337.

Pawan, P. Kalbende, Mangesh, V. Tarase, and Anil. B. 2013. Zade, preparation, *Characterization and thermal studies of p-nitrophenol- based copolymer, Journal of Chemistry, volume 2013.* article ID 846327 9

Sanjiokumar, S. Rahangdale, and Wasudeo, B. Gurnule, 2011. Antimicrobial activity and thermal properties of copolymer resin derived from 2, 2'- dihydroxybiphenayl, dithaiooxamide and formaldehyde, Scholars Research Library, Der Pharma Chemical, 3 (4) : 314-322.

Suresh Kumar G, E KGirija and A Thami Zhavel, 2010. Synthesis *and characterization of bioactive hydroxyapatite-calcite nanocomposite for biomedical applications, Journal of colloid and interface science*, 349, 56-62.

Swain, P.P., Das, S.C. 2013. *Synthesis and characterization of nanoresin copolymer prepared from paranitro aniline, resorcinol and urea,* International journal of research in pharmaceutical and biological sciences, *Vol. 4(2),* Apr-Jun.

Vijay Kumar Thakur and Amar Singh Singha, 2010. *Physico-chemical and Mechanical Characterization of Natural Fibre Reinforced Polymer Composites,* Iran Polym j,*19,*(1), 3-16.

Waleed, k. El-zawawy and Maha M. Ibrahim, 2003. *Synthesis and characterization of cellulose resins,* polymers for advanced technologies,14, 623-631.

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