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Thermal Studies Of Different Agrowaste Reinforced Novolac Composites Prepared Under Isothermal Conditions.

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ABSTRACT

The objective of this study is to evaluate the thermal properties of agro waste reinforced novolac composites derived from bagasse or cane chaff (CC), aloe vera (AV) and rice husk (RH) for potential applications as heat resistant and flame retardant materials. In this investigation the three bio polymeric composites were prepared by condensation method with weight ratio 1:1 (resin: biomass). Various spectral techniques like FTIR and SEM are employed for structural confirmation of composites. The thermal stability, flame retardancy and thermal degradation mechanism of the composites with different biomass have been evaluated by thermo gravimetric analysis (TGA). It is observed that bio composite of novolac prepared with rice husk has remarkably higher thermal stability and improved flame retardancy in comparison with the other two eco composites.

Keywords: Agro waste; Thermal stability; Flame retardancy; Thermo gravimetric analysis; Eco composites;

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INTRODUCTION

Agro waste refers to waste generated from plants such as plant fibers, leaves, hulls etc. Although not classified as hazardous waste, wastes produced from cereal crops make up a great volume of waste materials. Approximately 880 million tons [1] of cereals are produced world wide of which 18-22 million tons [2] of rice husk is produced in India alone. Traditionally, agro waste materials are used as bedding for animals and live stock feeding, burned in fields or added into soil as green fertilizer. Recent studies have documented other uses of these agro wastes such as soil conditioners or fertilizers, bio fuels, thermo plastics, activated charcoal and components of other composite materials [3]. The demand for natural/wood fiber composites in various applications such as automotive components, building materials and the aerospace industry is increasing due to ecological and environmental advantages of these over conventional composites. However, the advantages of composites are overshadowed by their easy combustibility and low stability in high temperatures as compared to metals. More recently attention has been directed towards preparing heat resistant and flame retardant advanced composites. The crushed remnants of sugarcane stacks left after the extraction of juice are called bagasse or cane chaff (CC or B₁). It is usually burnt in sugarcane industry to produce sugar. Its composite with phenolic resin prepolymer results in stable biomass composite having broader applications in industrial and home appliances [4].

Aloe Vera (aloe barbadensis miller) which is grown as medicinal plant is a member of family 'liliaceae'. A thick epidermis that surrounds the mesophyl constitutes the leaves of aloe. The presence of polysaccharides account for most of the dry matter of parenchymal tissue of aloe vera with two main types of polymers, acemannan found inside cell protoplasts and wide variety of polysaccharides that form the net of cell wall consisting cellulose and hemi cellulose [5,6]. Being a lingo cellulose material (long fiber) aloe vera (AV or B₂) is a potential resource for forming composite with phenolic resin [7].

Rice husk (RH or B₃) is a lingo cellulose containing natural composite that exhibits many potential advantages eg renewable source, low price, bio degradability etc [8]. One of the current applications of RH is its incorporation into polymer matrices for the fabrication of RH – filled eco composites [9, 10, 11]. In this investigation the poly condensation between three different biomass like cane chaff (B₁), aloe vera (B₂) and rice husk (B₃) with substituted phenolic resin (resorcinol) prepolymer has been reported. Their structural confirmations have been obtained from FTIR & SEM studies. An extensive study of their thermal stability and flame retardancy has been reported from their thermo gravimetric studies. The different kinetic parameter has been evaluated and thermal degradation mechanism of biomass – composites has been proposed by using eighteen various kinetic models.

EXPERIMENTAL

Material

The three biomass resources chosen Cane chaff (B₁), aloe vera (B₂) and rice husk (B₃) were collected in dry condition, washed repeatedly in demineralized water, filtered and dried in sun light for seven days. Then the samples were powdered and purified with absolute

alcohol, then again dried in micro wave oven at 80 °C for 24 hrs. The chemicals used were resorcinol, formaldehyde, oxalic acid, sulfuric acid and different solvents used for testing solubility of samples. All the chemicals used were of analytical grade supplied by E. Merck.

Preparation of resins matrix

For synthesis of novolac resins the method adopted by Nayak & Co-workers [12] was followed. Solid novolac resins were prepared by addition of formaldehyde to a mixture of resorcinol and 2 N oxalic acid slowly with ratio (F: P<1) 1:1.22 and subsequent heating at 90 °C for 6 hrs using air condenser. During the reflux process, the mixture was shaken periodically. The resulting mixture was poured into ice cold water. The crystalline solid formed was washed with de ionized water repeatedly and finally dried in vacuum oven.

Preparation of biomass composites

For the preparation of biomass composites the method adopted by Das & Co workers [4] was followed. The dried, powdered (0.01-0.5 mm diameter) form of B₁, B₂ & B₃ were separately mixed with solid resin pre polymers in weight ratio 1:1 in a covered Petri dish. The reflux process was started by using 1 M oxalic acid as the catalyst over a temperature of 120 °C for 6-8 hrs. The final products were purified, vacuum distilled and dried. The three composites prepared were RB₁, RB₂ and RB₃.

Spectral Studies

FTIR

FTIR spectra were obtained on resin, biomass and composites in potassium bromide pellets using Bruker IFS-66 V infra-red spectrometer.

SEM

Scanning electron micrographs of the resin and composites were obtained using a JOEL-JSM 35 CF scanning electron microscope at an acceleration of 10 KV.

Thermal studies

The TGA thermo grams of the three composites were obtained with PERKIN-ELMER, USA (Model: Pyris 1 TGA) at a heating rate of 10 °C / min over a temperature of 0 – 650 °C in nitrogen atmosphere.

RESULTS AND DISCUSSION

Spectral analysis

FTIR spectra of three biomass (B₁, B₂, B₃) and their composites (RB₁, RB₂, RB₃) are shown in fig 1 (a), (b), (c),(d), (e), (f) and data are represented in table-1 .FTIR spectrum of resin is shown in fig 1 (g) for comparison.

Table 1: FTIR data of biomass and composites

Name of the compound	Peak in cm ⁻¹	Assignments
B ₁ (Cane-Chaff)	608.2 (sh) 1053.2 (sh) 1113.2(sh) 1160.8 (sh) 1250.6 (sh) 1377.1 (sh) 1509.4 (sh) 1637.9 (sh) 1736.6 (sh) 2931.3 (sh) 3400.6 (sh)	May be C-X stretching C-O stretching vibration May be C=O stretching couple with adjacent C-C stretching Presence of sulphonamides which arises from asymmetric and symmetric SO ₂ stretching C-O stretching vibrations C-H bending vibrations NH ₂ or NH bending involves coupling between N-H bending and other fundamental vibrations C=O conjugation with phenyl or olefinic linkage C=O stretching C-H stretching May be O-H stretching absorption band
B ₂ (Aloe vera)	839 889 1077 1150 1317 1618	Aromatic nucleus containing C-H vibrations at 1,3-disubstitution May be due to aromatic C-H bending vibrations May be due to N-H bending vibrations for primary amine May be C-O stretching coupled with adjacent C-C stretching vibrations May be C-H bending vibrations May be due to conjugated C=C stretching found at lower frequency for amines.
	2922 3428 (w)	May be C-H stretching vibrations O-H stretching band in alcohols
B ₃ (Rice-Husk)	1076 (sh) 1646 (sh) 1735 (sh) 2123 (sh) 2333 (sh) 2855 (sh) & 2925 (sh) 3430 (w)	C-O stretching in acid anhydrides =C=C= stretching vibrations Due to carbonyl (=C=O) stretching vibrations -C≡ C- stretching vibrations Due to -C≡ N stretching vibrations Due to C-H stretching vibrations O-H stretching band in alcohols
RB ₁ (Composite of resin with cane-chaff)	890 (sh) 1028.7 (sh) 1072.2 (sh) 1372.1 (sh) 1441 (sh) 1609.6 (sh) 3345.9 (w)	May be aromatic C-H bending vibrations May be C-O stretching vibrations C-O stretching coupled with adjacent C-C stretching. C-H bending vibrations C-C stretching in 1,3 disubstituted benzene nucleus Conjugated C=O stretching O-H stretching band in alcohols (showing hydrogen bonding)
RB ₂ (Composite of resin with Aloe vera)	670 829 1127 1703 3108	May be C-H stretching vibrations Aromatic nucleus containing C-H bending vibrations at 1,3-disubstitution May be C-O stretching coupled with adjacent C-C stretching. Due to C=O stretching in esters May be due to C=C stretching
RB ₃ (Composite of resin with rice husk)	1069 1285 1618 1741 3420(w)	C-O stretching in acid anhydrides Aromatic C-O stretching vibrations Due to C=C ring stretching Due to C=O stretching band in esters O-H stretching band in alcohols showing hydrogen bonding.

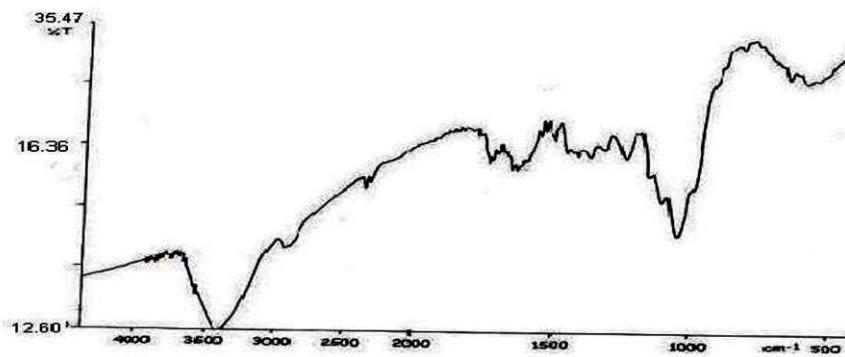


Fig: 1 (a) FTIR Spectrum of Biomass B1 (Cane-chaff)

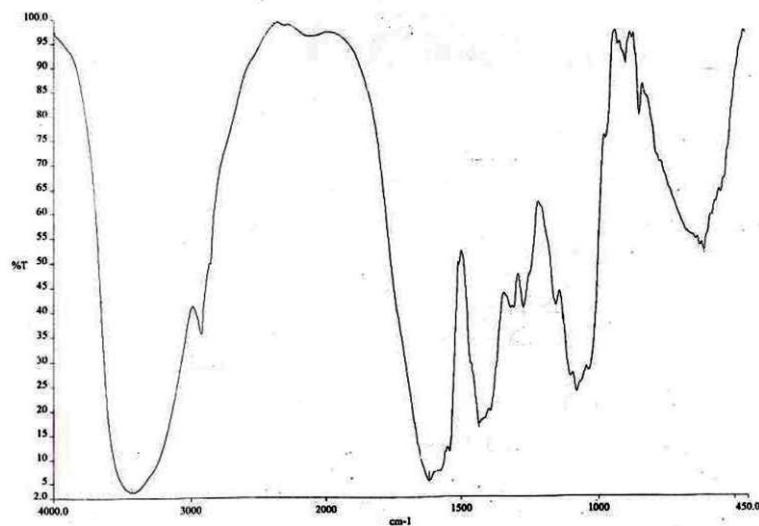


Fig: 1 (b) FTIR Spectrum of biomass B2 (Aloe vera)

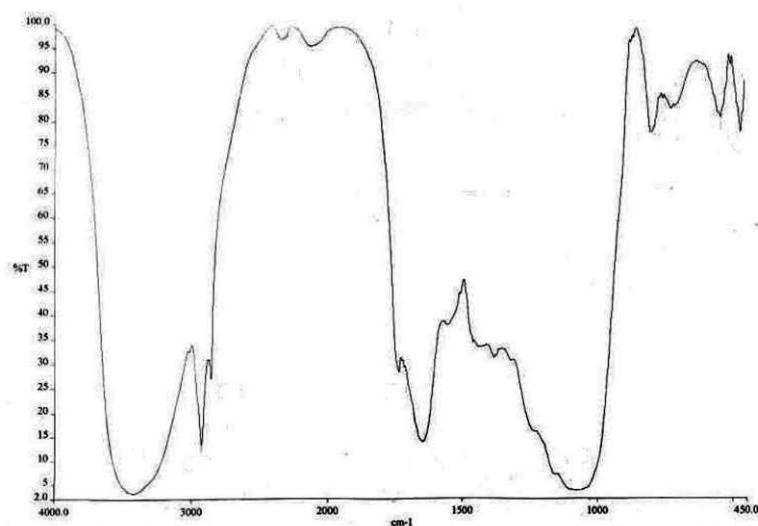


Fig: 1 (c) FTIR Spectrum of Biomass B3 (Rice husk)

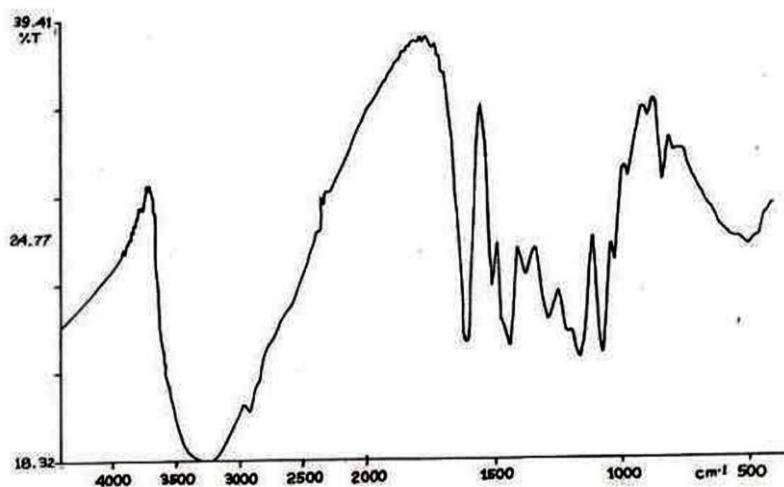


Fig:1(d) FTIR Spectrum of composite RB1 (Resin + Cane chaff)

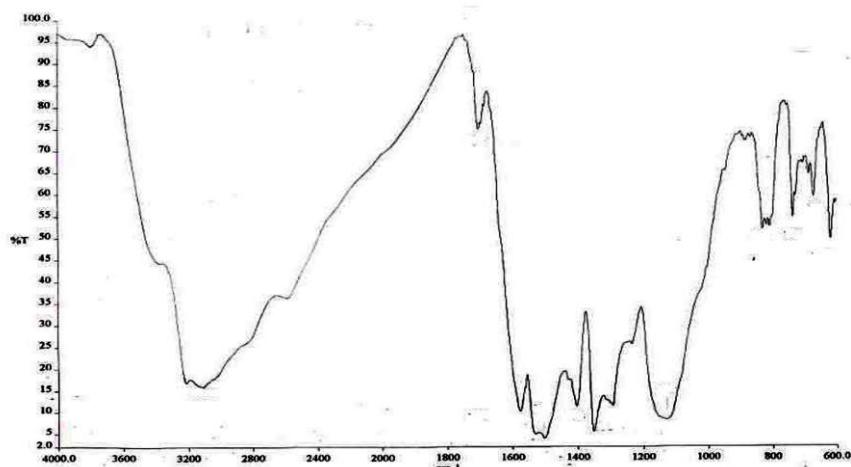


Fig 1(e) FTIR Spectrum of composite RB2 (Resin + Aloe vera)

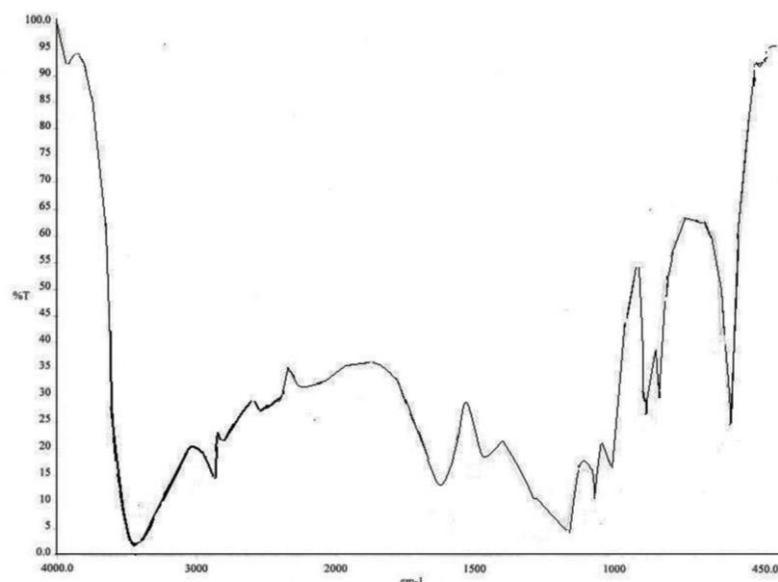


Fig: 1(f) FTIR Spectrum of composite RB3 (Resin + Rice husk)

In FTIR spectrum of B₁ [fig 1(a)] the presence of active sites like carboxylic acid (-COOH) and carbonyl (C=O) group are indicated by the peaks at 3400.6 cm⁻¹ and 1736.6 cm⁻¹ respectively. In fig 1 (b), FTIR spectrum of B₂, the peaks at 3428 cm⁻¹ and 1618 cm⁻¹ indicate the functional sites like -COOH and -CO-NH are present in it. A broad peak at 3430 cm⁻¹ in FTIR spectrum of B₃ [fig 1(c)], indicates the presence of alcoholic -OH, an active site for reaction. Two peaks at 2855 cm⁻¹ and 2925 cm⁻¹ indicate alkyl C-H group. The most informative peak is seen at 1735 cm⁻¹ which is due to C=O (carbonyl) stretching frequencies. The other peaks at 1070 cm⁻¹ and 1646 cm⁻¹ are indicative of the presence of active sites like NH₂ and C=C.

Different peaks found in FTIR spectra of composites (RB₁, RB₂, RB₃) shown in fig-1 (d),(e), (f) indicate the successful incorporation of biomass into the resin matrix. Decrease in the height of broad peaks at 3345.6 cm⁻¹ [fig 1(d)] and 3430 cm⁻¹ [fig 1(f)] in composites RB₁ & RB₃ indicates decrease in number of free -OH groups due to formation of linkage of biomass with the polymer matrix by covalent and hydrogen bonding. The peaks at 1736.6 cm⁻¹ of B₁ and 1735 cm⁻¹ of B₃ are absent in their composites (RB₁ and RB₃) indicating the loss of carbonyl functionality due to formation of composites.

A stretching frequency at 1703 cm⁻¹ in FTIR spectrum of composite RB₂ shows the presence of ester group. This group is formed due to condensation of phenolic -OH of resin pre polymer and -COOH group of biomass B₂. The formations of composites in all the cases are supported by the fact that the shape of peaks near 1600 cm⁻¹ and in the range 1300-1100cm⁻¹ change because of the increase of connection between the aromatic rings as the cure rate increases.

In order to evaluate changes in the surface morphology of polymer composites, resorcinol-formaldehyde resin and composites with different biomass were analyzed by scanning electron microscopy. The SEM image of pure resin and its composites (RB₃, RB₂ & RB₁) are shown in fig 2(a), 2(b), 2(c) & 2(d).SEM images of resin and composites also confirm the incorporation of biomass in the resin matrix. These results evidently demonstrate the difference between surface morphology of resin and composites depending upon the nature of interfacial interaction between resin and biomass.

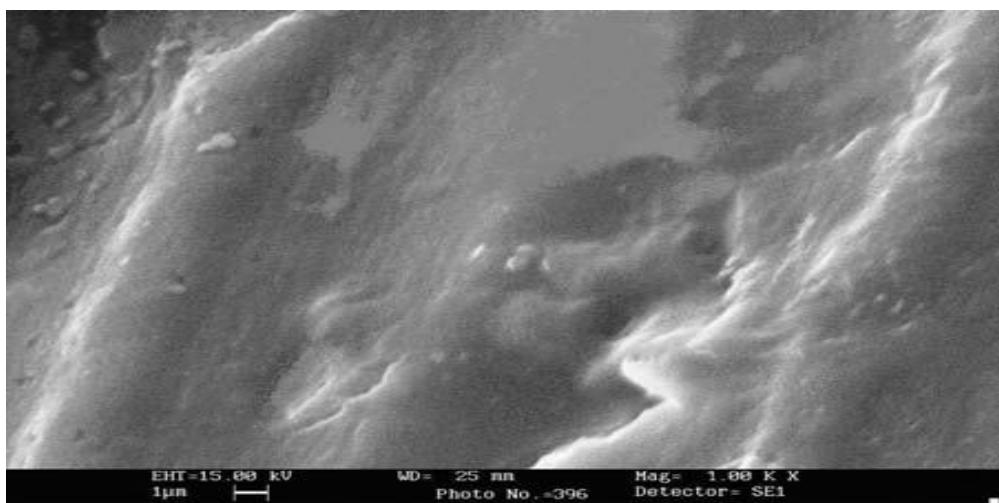


Fig 2(a): SEM image of Pure Resin

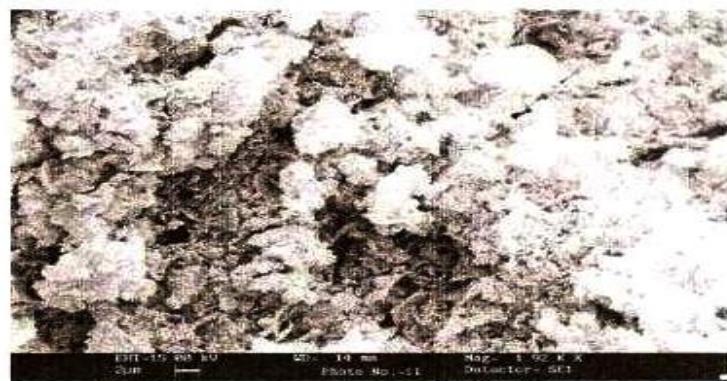


Fig: 2(b) Scanning electron micrograph of composite RB3
(Resin+Rice husk)

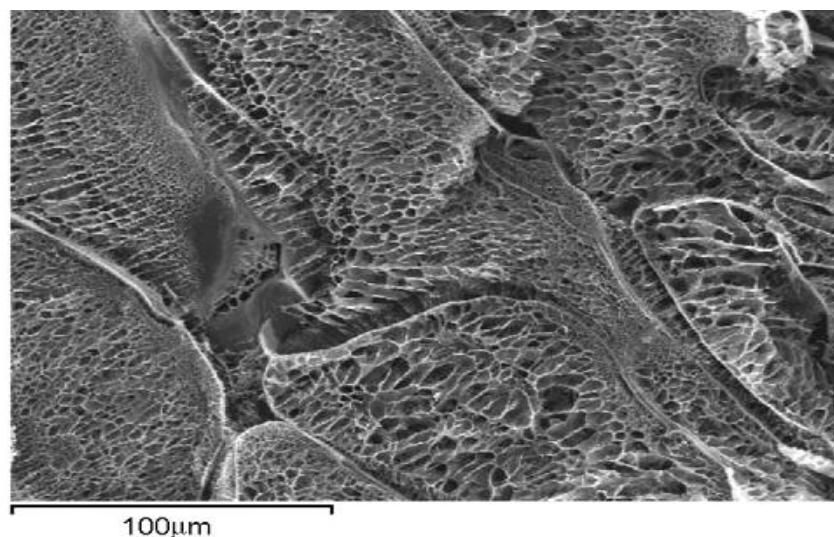


Fig 2(c): SEM image of RB2 (Resin + Aloe vera)

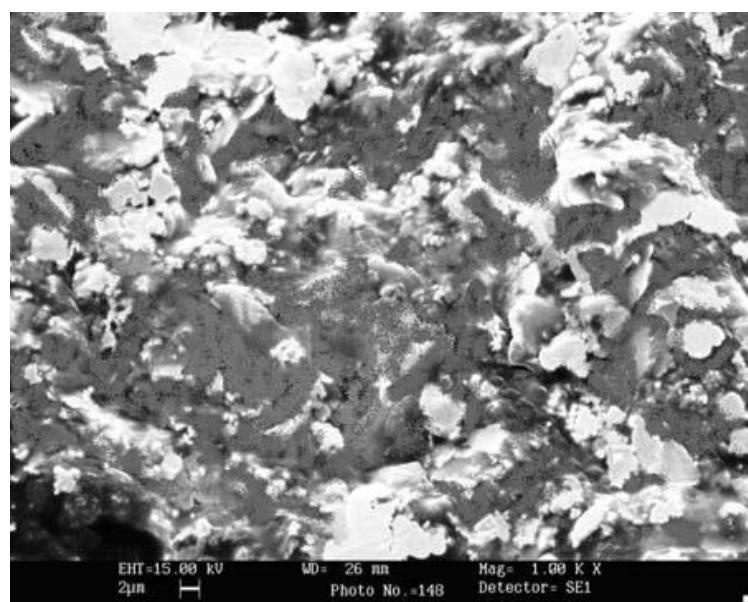


Fig 2 (d): SEM image of RB1 (Resin + Cane Chaff)

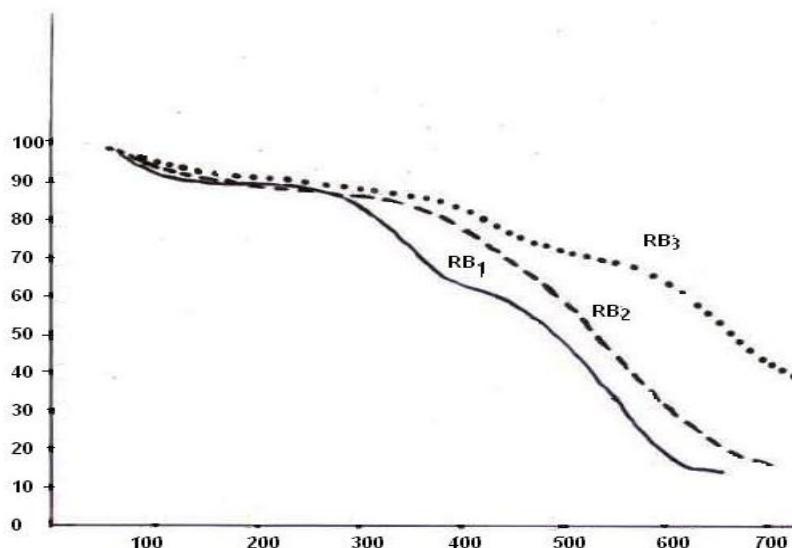


Fig 3 :- Thermograms of composites RB₁ ,RB₂ & RB₃

Thermal analysis

Thermal stability and flame retardancy

The thermal studies of three composites RB₁, RB₂ & RB₃ were investigated by means of thermo gravimetric analysis (TGA) in nitrogen atmosphere at a heating rate of 10 °C / min. The corresponding thermo grams are shown in fig-3.

Van Krevelen found a significant correlation between the char residue and O.I. of polymers [13]. The linear relationship can be represented by the formula.

$$OI = \frac{(17.5 + 0.4CR)}{100}$$

Where CR is the char residue as a percentage by weight.

In order to give a comparative picture of flame retardancy of the resin(R) and composites, characteristic thermal data including the oxygen index values (OI) are furnished in table-2. The oxygen index values have been calculated based on the carbonaceous char (residual weight at 650 °C indicated in thermo grams).

Table 2: Char yields and Oxygen index analysis of composites.

Name of the composites	Char yields at 650 °C (%)	Oxygen Index in %
RB ₁	14.7	23
RB ₂	20.3	25
RB ₃	53.2	38

RB₁: Composite of resin and cane chaff.

RB₂: Composite of resin and aloe Vera.

RB₃: Composite of resin and rice husk.

Table 3: Algebraic expressions of function $g(\alpha)$ and its corresponding mechanism

Sl No	Mechanism	Name of the function	$g(\alpha)$	Rate-determining mechanism
1. Chemical process or mechanism non-invoking equations.				
1	F3/2	One and a half order	$(1-\alpha)^{-1/2} - 1$	Chemical reaction
2	F2	Second Order	$(1-\alpha)^{-1} - 1$	Chemical reaction
2. Acceleratory rate equations.				
3	P1/2	Mampel Power Law	$\alpha^{1/2}$	Nucleation
4	P1/3	Mampel Power Law	$\alpha^{1/3}$	Nucleation
5	P1/4	Mampel Power Law	$\alpha^{1/4}$	Nucleation
3. Sigmoidal rate equations or random nucleation and subsequent growth.				
6	A1(F1)	Avrami-Erofeev equation($n=1$)	$-\ln(1-\alpha)$	Assumed random nucleation & subsequent growth.
7	A2	Avrami-Erofeev equation($n=2$)	$[-\ln(1-\alpha)]^{1/2}$	Assumed random nucleation & subsequent growth.
8	A3	Avrami-Erofeev equation($n=3$)	$[-\ln(1-\alpha)]^{1/3}$	Assumed random nucleation & subsequent growth.
9	A3/2	Avrami-Erofeev equation($n=1.5$)	$[-\ln(1-\alpha)]^{1/1.5}$	Assumed random nucleation & subsequent growth.
10	A4	Avrami-Erofeev equation($n=4$)	$[-\ln(1-\alpha)]^{1/4}$	Assumed random nucleation & subsequent growth.
4. Deceleratory rate equations.				
4.1. Phase boundary reactions.				
11	R2	Power law	$1-(1-\alpha)^{1/2}$	Contracting cylinder.
12	R3	Power law	$1-(1-\alpha)^{1/3}$	Contracting sphere.
4.2. Based on the diffusion mechanism.				
13	D1	Parabolic law	α^2	One-dimensional diffusion.
14	D2	Valensi (Barrer) equation	$\alpha + (1-\alpha)\ln(1-\alpha)$	Two-dimensional diffusion.
15	D3	Jander equation	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry
16	D4	Ginstling Brounstein equation	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion, cylindrical symmetry
17	D5	Zhuralev, Lesokin and Tempelman equation	$[(1/(1-\alpha))^{1/3}-1]^2$	Three-dimensional diffusion.
18	D6	Anti-Jander equation	$[(1+\alpha)^{1/3}-1]^2$	Three-dimensional diffusion.

It is evident from thermo grams that these composites exhibited good resistance to thermal decomposition up to 300-400 °C in nitrogen atmosphere and began to decompose gradually above that temperature. The residual weight (char residue) at 650 °C ranged from 14.7 % to 53.2 % in nitrogen atmosphere.

The exceptional high char yield of composite RB₃ at high temperature region is important showing the good thermal stability of this composite is attributed due to the following reasons.

Table 4: Thermo gravimetric Analysis Data

Name of the Compound	Temp in °C	Function/ Mechanism	Activation energy(kJ.mol ⁻¹)	Correlation coefficient (R ²)
RB ₁ (Composite of resin and Cane-Chaff)	0-150	F3/2	0.2438	0.9475
	150-360	D6	5.0087	0.6864
	360-510	D6	19.1821	0.9960
	510-600	F1	51.0237	0.9844
RB ₂ (Composite of resin and aloe vera)	0-150	F3/2	0.1439	0.9723
	150-300	D6	4.0579	0.9950
	300-450	D2	5.2488	0.9393
	450-600	D3	14.0921	0.9978
RB ₃ (Composite of resin and rice husk)	0-150	F3/2	0.2612	0.9381
	150-350	D6	3.9740	0.9289
	350-500	D6	21.9127	0.9961
	500-600	D3	50.3995	0.9956

Rice husk has been reported to contain metallic constituents such as Si, K, Ca, Na, Fe, Mg, Mn, Al, Zn, Co, Cu and Ni.[14]. Additionally, silicon is made up of amorphous silica in rice husk as is evident from XRD analysis. [15] During thermal degradation at about 250 °C the RH (rice husk) component started to decompose and decomposed byproducts (including silica residues) were formed, before the on-set of resin degradation. The silica ash accumulated forms a protective network which can stabilize against or delay the thermo oxidation process. [16] The inertness and rigidity of the silica skeleton after thermal degradation was also reported by Kaupp [17] which was further confirmed by SEM observations made by Anshu Bharadwaj and his co-workers [18]. It appears that the role of silica is more than just a geometric shield to the combustible material in the sample. It appears that silica forms molecular bond with carbon which is not easily broken. As organic materials, the polymers and the wood fibers are very sensitive to flame. Improvement of flame retardancy of composite materials have become more and more important in order to comply with the safety requirements of the wood fiber composite products. The burning process is comprised of five fundamental steps which are heating, decomposition, ignition, combustion and propagation. Flame retardancy can be achieved by the disruption of burning process at any of these stages that can lead to the termination of the process before actual ignition occurs. The flame retardant property of three composites RB₁, RB₂ & RB₃ were evaluated by measuring their oxygen index values(%) which were between 23 and 38. Generally materials exhibiting OI values above 26 should demonstrate self-extinguishing behavior [19]. So the composites of aloe vera and rice husk have good flame retardant properties.

Thermo gravimetric analysis and kinetic studies

The evaluation of kinetic parameters and study of degradation mechanism of the biomass composites have been derived by using eighteen various kinetic models which are shown in table-3. In all cases a computerized developed lotus package method by Mohanty and Rao [20] has been used for the evaluation of kinetic parameters.

The values of energy activation(E) corresponding to a co-relation co-efficient (R^2) close to unity were chosen with respect to the said kinetic model as represented in table-4 to explain the kinetics of the degradation mechanism. The details of the literature of the mechanism have been given in our earlier publication [21].

A perusal of the results indicated in table-4 shows that in case three composites, $F_{3/2}$ model is applicable in the decomposition patterns for the temperature range up to 150°C . $F_{3/2}$ model has been used to determine activation energy values with respect to highest co-relation co-efficient up to the temperature range of 150°C . This model proves that the initiation of the reaction occurs at a phase boundary and advances into the unreacted zone of the sample.

The decomposition pattern in case of all the composites with the temperature ranges from 150°C to 350°C follow D_6 model. The nucleation process between the resin copolymer and biomass molecule involves conversion of a small volume of reactant into a stable particle of the product and continued reaction (growth) occurs preferentially at the interfacial zone of contact between these two phases.

The decomposition pattern of the composites follow $F_1\&D_3$ models above 500°C indicating the formation of monomer constituent vapors leaving behind char residue.

Initial nucleation, growth expression and final termination of the composite matrix have been concluded from the kinetic studies of the biomass composites.

CONCLUSION

The work reported here focused on the preparation of resin composites with three different biopolymers (cane chaff, aloe vera & rice husk) and extensive study of their thermal stability, flame retardancy and thermal degradation mechanism.

The following conclusions are made from the investigation.

- Different natural fibers can be successfully incorporated into thermosetting resin matrix like phenolics and substituted phenolics by condensation method using acid catalyst as is evident from spectral studies.
- Bio polymeric composites with phenolics are having higher thermal stability than the biopolymers themselves.
- It opens a new opportunity for production of cost effective (as it uses wastes) heat resistant advanced polymeric composites having manifold applications such as automotive components, building materials and aerospace industry.
- From the study of thermo grams it is concluded that an agro waste like rice husk can be used as an additive in polymer matrix producing a better flame retardant and heat resistant polymeric composite.
- Further investigations are in progress by changing the nature of biomass to other agricultural and industrial waste products locally available.

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