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### Synthesis and characterization of agro based biocomposite with amino resin.

M Panda<sup>a</sup>, S Parida<sup>b</sup>, A Parija<sup>c</sup>, SC Das<sup>c\*</sup>

<sup>a</sup>Department of chemistry, L.N.Mahavidyalaya, Patkura, Kendrapara, Orissa, India.

<sup>b</sup>Department of Chemistry, S.M. College, Asureswar, Cuttack, Orissa, India.

<sup>c</sup>Department of Chemistry, Salipur College, Salipur, Cuttack, Orissa, India.

#### ABSTRACT

Rice husk (RH), a naturally occurring biomass consists mainly of lignocelluloses and silica. With different weight percentage of 10, 30 and 50, this was reinforced into thio urea – formaldehyde polymer matrix. The biopolymer composites were characterized by FTIR and <sup>13</sup>C NMR technique. FTIR and X-ray diffraction studies of these biopolymer composites showed the presence of silica. Due to high silica content in RH, their addition to synthetic polymer has a marked effect on the flammability of the resultant composites. In this investigation the thermal property has been evaluated by thermogravimetric analysis which shows that the biocomposites undergo three stages of decomposition and the composite with 50% biomass was found to be more thermally stable than other composites. The thermograms show a decomposition of 5 – 7% at 100°C, 30 – 40% at 250°C 55- 60% at 400°C and 60 – 70% at 650°C. The kinetics of non – isothermal degradation of composites were studied by using various kinetic models. The kinetic parameters such as n, slope, Ea values were evaluated. The activation energy first increased and then gradually decreased as the reaction proceeded.

**Keywords:** Thiourea – formaldehyde polymer matrix, biopolymer, thermal analysis, thermosetting resin , kinetic parameters.

*\*Corresponding author*

Email: ctkscd@gmail.com



## INTRODUCTION

Recent investigations of polymer based composite materials have developed many methods for polymer formulations and have allowed the manufacture of new products with optimal properties for special applications [1, 2]. These composites in most cases have improved the product design and reduce the material and energy consumption. A special interest has grown in composites based on polymeric matrix reinforced with raw lignocellulosic materials such as wood fillers [3], jute, sisal, pine apple, wheat straw, almond husk or rice husk [4,5]. These fillers introduce some advantages compared to traditional inorganic fillers including their renewable nature, low density, non – abrasive properties, stiffness, reasonable strength, biodegradability and low cost [6-9].

In addition, the processing of these composite materials is flexible, economical, ecological and it is possible to use the same machinery employed with other traditional fillers.

In certain countries like China, Malaysia, Srilanka and India, rice husk (RH) is one of the biomass materials which is a byproduct from the rice industry. It has been produced in huge quantities every year. The addition of RH can promote the biodegradation process of the polymer matrix and also make the final materials to be economically more competitive.

This lignocellulosic material due to higher percentage of raw fibre, nitrogen, cellulose and hemicellulose, has several active sites which shows the interaction with the polymer at the interfacial region through covalent and hydrogen bonding [7]. The hemicellulose present composed mainly of pentosans and hexosans, contain a large number of hydroxyl groups which could serve as reaction sites with various functional groups in the thermoset system. Lignin present in RH can be used as a coupling agent due to its low polarity [10].

Flammability is the important criteria for choosing a polymer for its application. The flame retardancy of the polymer can be increased by the incorporation of different types of flame retardant additives. Rice husk is proved to be effective than other chemical flame retardants because they have negative impact on environment and health [11].

## MATERIALS AND METHODS

### *Rice Husk (Biomass)*

Rice husk, an agricultural waste product of rice grain, obtained by dehusking of rice which was thoroughly washed with deionised water, filtered and dried in sunlight for seven days. It was ground to powder like form and was purified with absolute alcohol. Then it was kept in vacuum oven for 48 hours to keep it free from any organic and atmospheric impurities.

### **Chemicals**

Thiourea, formaldehyde, sulphuric acid and oxalic acid. All are of analytical grade obtained from E.Merck Chemicals.

### **Preparation of thiourea – formaldehyde resin.**

0.1 mol. of thiourea was taken in a clean and dry 100 ml flask with about 2 ml of formaldehyde and 2 ml of 2N H<sub>2</sub>SO<sub>4</sub>. The mixture was heated to 80°C for about 6 h by using air condenser. The polymer obtained was washed with deionised water and alcohol to remove unreacted monomer. The resulting polymer was dried and kept in vacuum oven.

### **Preparation of risk husk – resin composite**

The dried and powdered form of RH was mixed with the resin in different weight proportion like 10, 30 and 50 and was taken in a 200 ml flask with 2N H<sub>2</sub>SO<sub>4</sub> as catalyst. The mixture was heated to 80°C for 8 h by using the method reported by Das and coworkers [12]. Dark brown coloured composite was obtained which was filtered, washed repeatedly with deionised water and with absolute alcohol and then dried which was made available for further analytical tests.

### **Characterization**

#### *FTIR*

The FTIR spectra of RH and composites were recorded by using Bruker IFS – 66V infrared spectro meter in the scanning range from 4000 cm<sup>-1</sup> to 500cm<sup>-1</sup> where test pellets were prepared with analytical KBr crystals.

#### *<sup>13</sup>C NMR*

The <sup>13</sup>C NMR spectra were obtained with JEOL GSX – 400 spectrometer by using DMSO as solvent.

#### *TGA*

Thermogravimetric analysis of the biomass and composites were taken by using NETZSCHSTA 409 C/CD at a heating rate of 10K / min over a temperature range of 0-650°C in nitrogen atmosphere.

#### *XRD*

The XRD measurement was done in powder XRD mode in D8 ADVANCE, BRUKER using copper target.

## RESULT AND DISCUSSION

### Physico – chemical properties

Table (1) indicates the physico chemical properties of biomass and composites. The data reveals that all composites are crystalline in nature and insoluble in most of the organic solvents. However they are partially soluble in DMSO and DMF. The solubility parameter of the reported composites shows the non polar characteristics of the materials.

### Spectral analysis

The FTIR spectra of biomass (RH) and the three composites are shown in fig. 2(a), 2(b) and 2(c) and presented on table – 2. The spectrum of RH and the assignment of a peak at  $796\text{cm}^{-1}$  due to C – H bending vibration. A peak at  $1076\text{ cm}^{-1}$  shows C – O (str) vibration. A sharp peak at  $1646\text{ cm}^{-1}$  is due to N-H stretching vibration. A peak at  $1735\text{ cm}^{-1}$  is due to C = O (str) of carbonyl group. A peak due to C – H stretching vibration appears at  $2855\text{ cm}^{-1}$  and a broad peak at  $3430\text{cm}^{-1}$  shows O – H stretching due to alcoholic group. The spectrum of the composite shows the following peaks. A peak at  $1081\text{ cm}^{-1}$  is due to C – O stretching vibration. A sharp peak due to C = C ring stretching appears at  $1440\text{ cm}^{-1}$ . The peaks at  $1537\text{cm}^{-1}$  and  $1624\text{cm}^{-1}$  are due to N – H bending vibration coupled with C=C. The peak at  $2927\text{cm}^{-1}$  arises due to C – H stretching vibration. A sharp peak at  $3313\text{cm}^{-1}$  is due to N – H stretching (hydrogen bonded).

The FTIR study shows strong evidence of formation of biomass – resin matrix with different weight proportion because of active sites present in biomass. On comparison, the most obvious features in increased absorption in C = C region which shows more crosslinking with greater percentage of biomass. The peak at  $3430\text{ cm}^{-1}$  and at  $1735\text{ cm}^{-1}$  of biomass, missing in the spectra of composites is a clear indication of polymeric association of biomass with the polymer matrix through covalent and hydrogen bonding. Peaks of biomass at  $1076\text{ cm}^{-1}$ ,  $717\text{cm}^{-1}$  and  $488\text{ cm}^{-1}$  shows the presence of silica.

The successful formation of composites is also supported by  $^{13}\text{C}$  NMR analysis. Fig 3(a) and 3 (b) shows the various NMR peaks and the assignment of the peaks are given in Table – 3. In case of composite AR3 the peaks between 39.45ppm to 40.54ppm indicates the presence of tertiary carbons and the carbon atoms containing  $\text{NH}_2$  groups. A peak at 48.24 is due to  $\text{CH}_2 - \text{CH}_2$  linkage. The presence of C – O oxygen bearing  $\text{SP}^3$  hybridised carbon atom is shown in the peak at 52.75 ppm. The presence of N – C – O linkage is shown at 69.12 ppm. A peak at 184.15ppm is due to  $\text{SP}^2$  hybridized carbon in C = S group. In case of AR1 and AR2, similar peaks are observed with slight change in chemical shift.

X-ray diffraction analysis of composite with 50 weight percent biomass shows the presence of silica from typical silica characteristic at a peak between  $20\text{-}35^\circ$  shown in fig-4 [13].

### Thermal analysis

The thermal degradation of rice husk and rice husk – filled eco-composites were studied by using thermo gravimetric analysis in nitrogen atmosphere. The corresponding weight retention (TG) and derivative of weight retention (DTG) curves are shown in fig 5(a) and 5(b).

TG curves show the decomposition of biomass and also composites in three distinct stages. A minor weight loss up to 6% at a temperature 100°C is due to loss of moisture and volatile impurities. About 60 – 70% decomposition is marked at a temperature range of 600 – 650°C. Data shown in table – 4 indicates that the composites with a higher weight percentage of biomass show less percentage of decomposition. At temperature above 500°C, the residual weight of RH stabilized at about 16 wt % which agrees with the silica content in RH as reported in literature [14]. As the samples were heated close to 270°C, the RH component started to decompose and the decomposed byproducts including silica were formed. The silica ash gradually accumulated on the polymer matrix which delays the degradation process and makes the polymer more thermally stable.

Striking observation for the stability of eco-composites has been marked from DTG curves of Fig 5 (b). Peak (1) at about 330°C belongs to the decomposition of RH. Component peaks (2, 3, 4) for the composites have been shifted to higher temperature which reflects the improved thermal stability of polymer matrix due to incorporation of RH [15, 16]

### Study of Degradation Mechanism

The evaluation of Kinetic parameters and study of degradation mechanism of the biomass composites have been derived by using eighteen various kinetic models. For the characterization of rice husk composites thermal stability, two divergences among the studies are obvious, the first is the choice of kinetic models used to describe the pyrolysis kinetics and the second is the calculation of the kinetic parameters. All  $g(\alpha)$  functions as presented in Table-5 were plotted against  $1/T$  to calculate the correlation coefficient of linear regression  $R^2$ .  $\alpha$  is the degree of decomposition at a particular value of temperature. From the linear relationship between  $\log g(\alpha)$  and  $1/T$  at selected range of temperature we evaluate  $E_a$  from the slopes. The magnitude of the  $E_a$  values is expected to reflect the extent of cross linking of the resins which indicates that the extent of curing has a significant influence on the calculated  $E_a$  values. The kinetic parameters including activation energy ( $E_a$ ), temperature range of decomposition, methods chosen are presented in table-6

A perusal of the results indicated in table- 6 shows that in case of all the composites, the decomposition patterns for the temperature range 0 – 150°C shows the loss of moisture and associated volatile impurities which follows  $F_{3/2}$  mechanism. The decomposition pattern for the temperature range 150°C – 350°C follows  $F_2$  mechanism. Above 350°C again the composite follows  $F_{3/2}$  mechanism. The nucleation process between the resin and biomass molecule involves conversion of a small volume of reactant into a stable particle of product and continued reaction (growth) occurs preferentially at the interfacial zone of contact between these two phases. The most accepted model  $F_2/F_{3/2}$  indicates that the initiation of reaction occurs at a phase boundary and advances into the unreacted zone of the sample. The kinetic characteristics of the overall rate process are determined by the geometrical

mode of advance of the reaction interface from these boundaries towards the centre of unreacted zone and beyond the temperature range of 500°C, the polymer matrix undergoes fractionation resulting in the formation of monomer constituents vapors.

### **Flammability of the composites**

Flammability of the composites were studied by calculating oxygen index from the value of char residue as indicated in the respective thermo grams. It is found that rice husk filled composites are less prone to flame compared to polymer matrix without biomass. The composite with higher weight percentage of RH requires more oxygen and has higher flame retardancy. Van krevelen found a significant correlation between the char residue and the O.I. of polymers. [17] This linear relationship can be represented by the formula.

$OI = [17.5 + (0.4 \times CR)] / 100$  Where CR is the char residue as a percentage by weight. Table – 7 shows the value of oxygen index which proves the fire retardancy character of composites.

### **CONCLUSION**

In this investigation, the thermal degradation of rice husk – filled thiourea – formaldehyde resin was studied. It was observed that combustion behaviour of the composite is retarded with incorporation of RH, due to presence of silica in the biomass. The thermal properties TG and DTG show that the thermal decomposition process of polymer matrix had been delayed irrespective of RH Content in the eco-composites. Prominent flame retardant effect has been achieved by increasing the RH content. It can be concluded that the mechanism for the improved flame retardancy and thermal behaviour was due to the thermal shielding and diffusion barrier effect caused by silica layer during combustion. The evaluation of kinetic parameters by using eighteen kinetic models reveals that higher  $E_a$  values are observed in case of composites containing higher weight percent of biomass. This might be due to the presence of more reactive sites which increases the extent of crosslinking. The kinetics of thermal degradation found to be best described by kinetic equations of n-th order  $F_n$  mechanism.

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Fig-1: FTIR Spectrum of Biomass (Rice Husk)

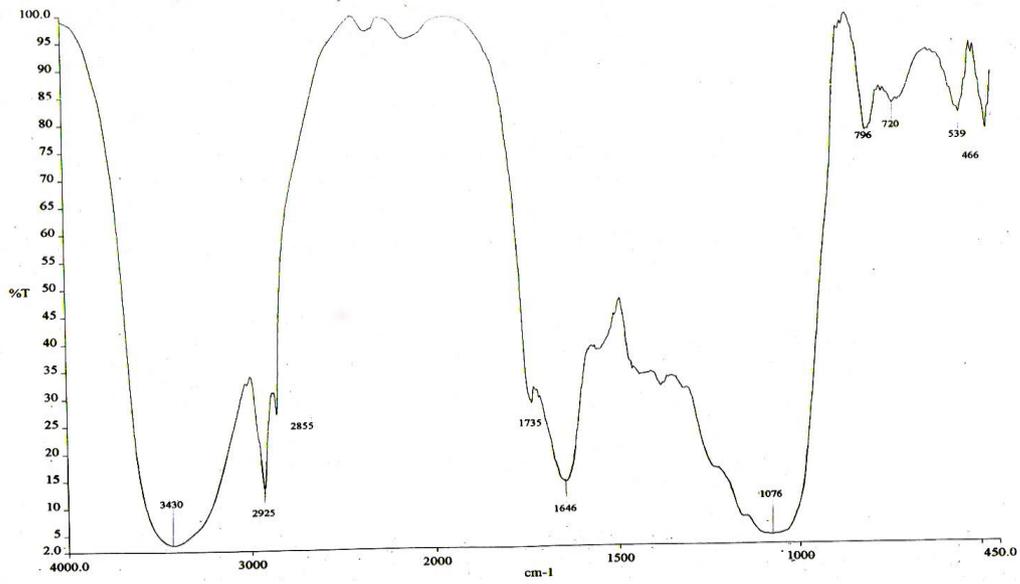


Fig-2 (a) : FTIR Spectrum of AR<sub>1</sub>

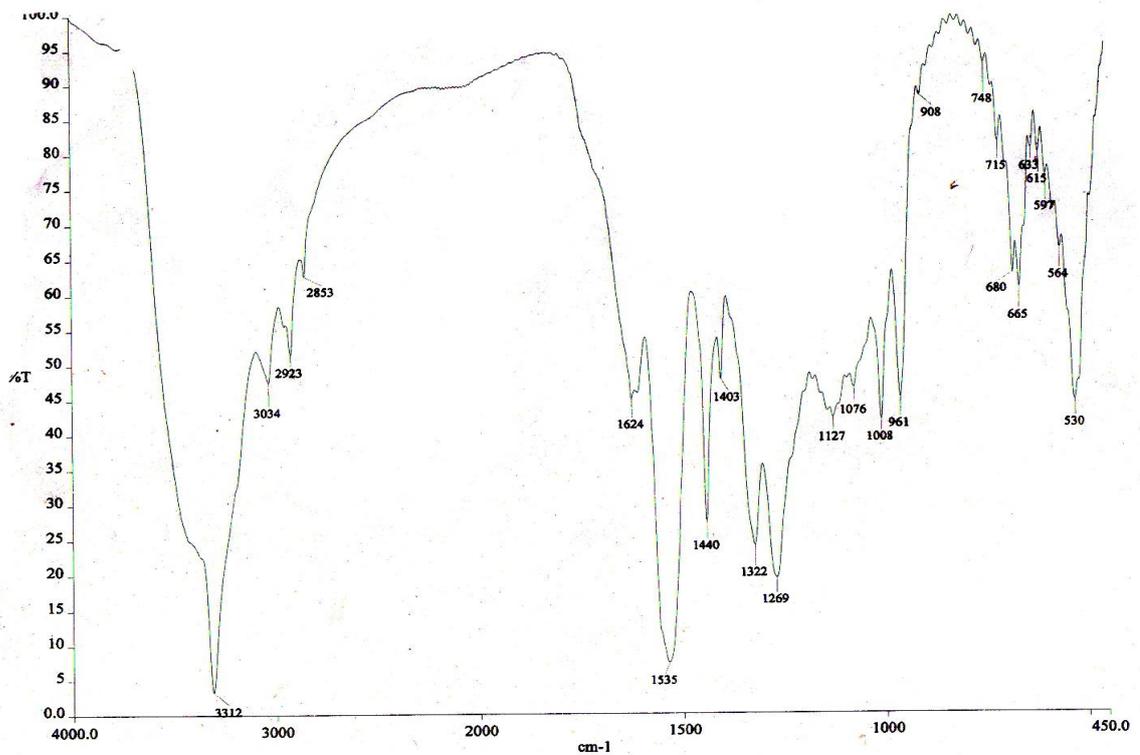


Fig-2 (b) : FTIR Spectrum of AR<sub>2</sub>

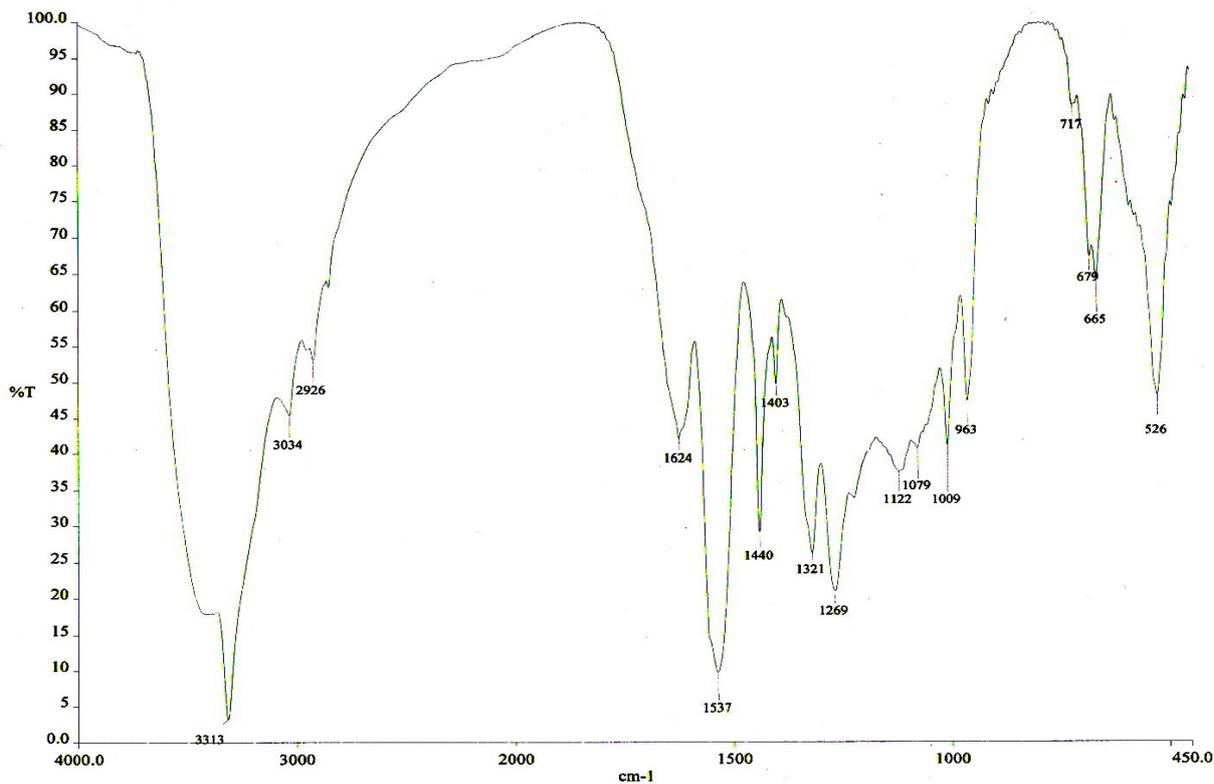
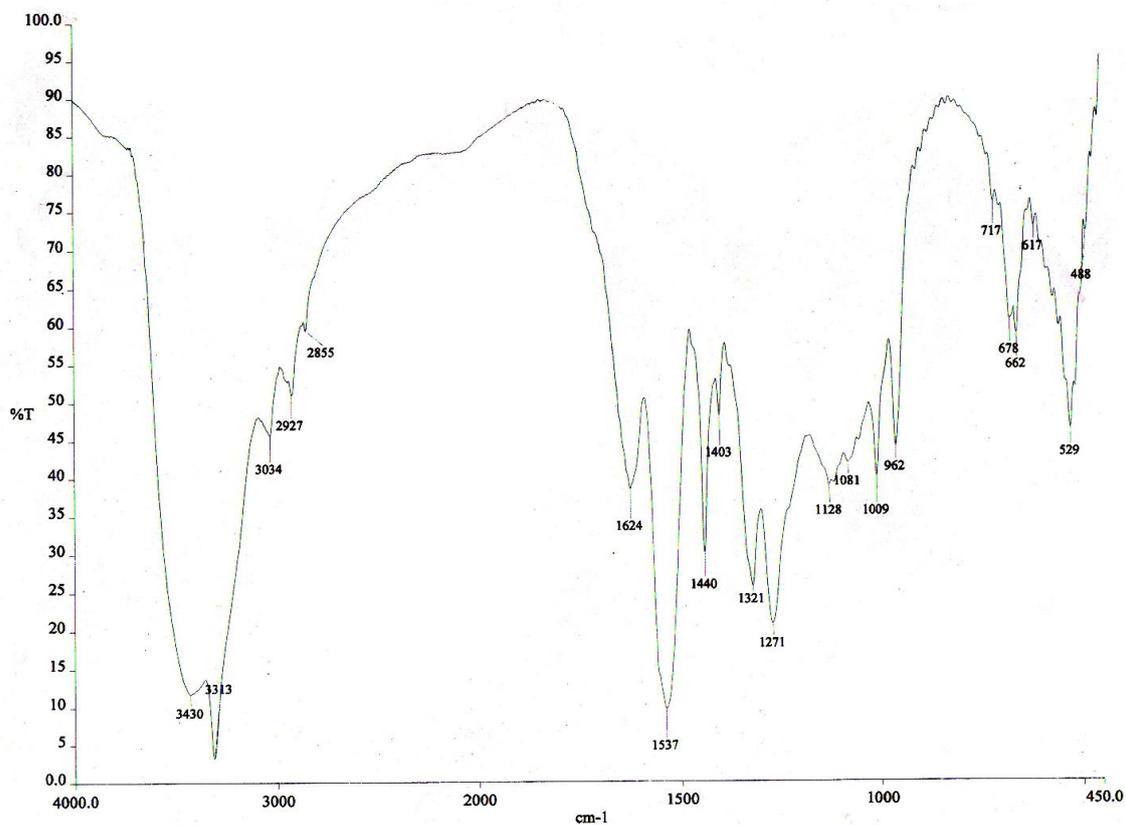
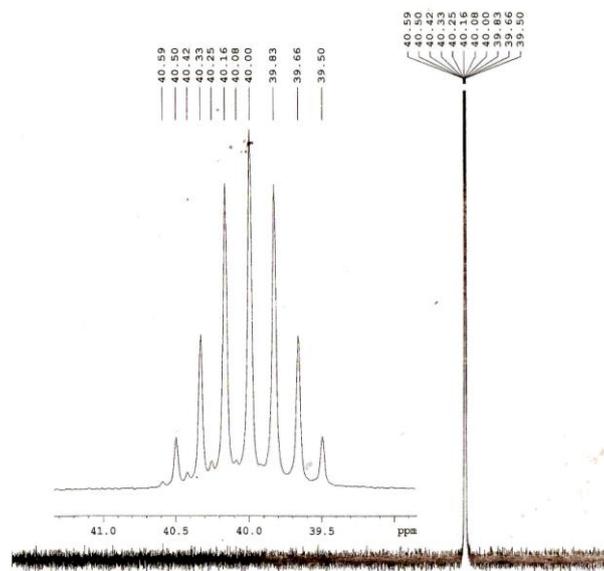


Fig-2 (c) : FTIR Spectrum of AR<sub>3</sub>



**Fig-3(a) : NMR spectrum of Rice Husk**



**Fig-3(b) : NMR Spectrum of (AR<sub>3</sub>)**

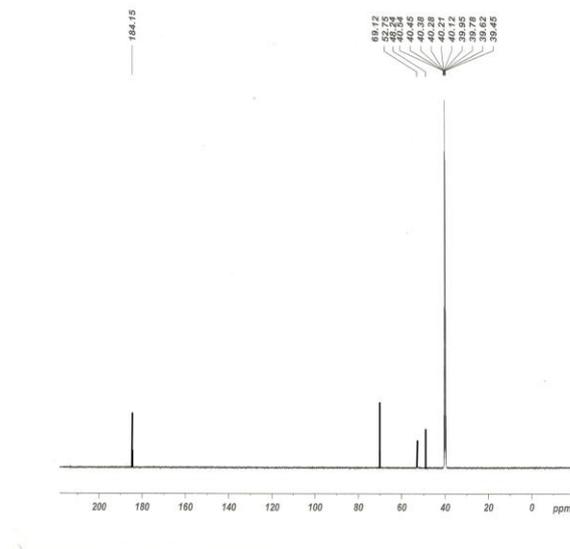


Fig – 4 : XRD Pattern of AR<sub>3</sub>

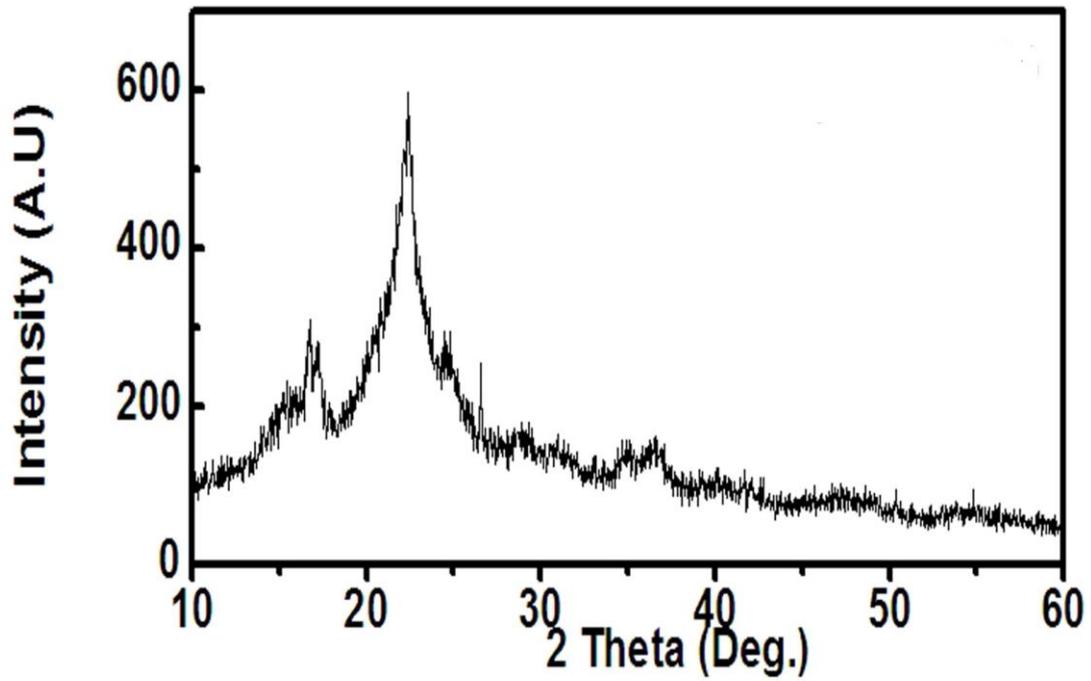


Fig –5 (a) : The thermogravimetric analysis curves of biomass and composites

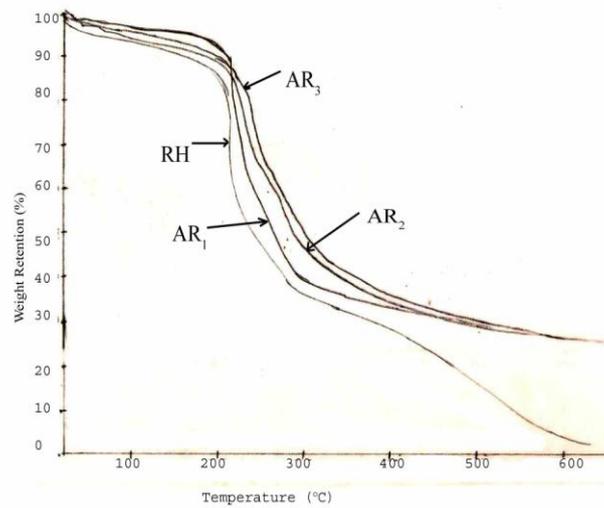
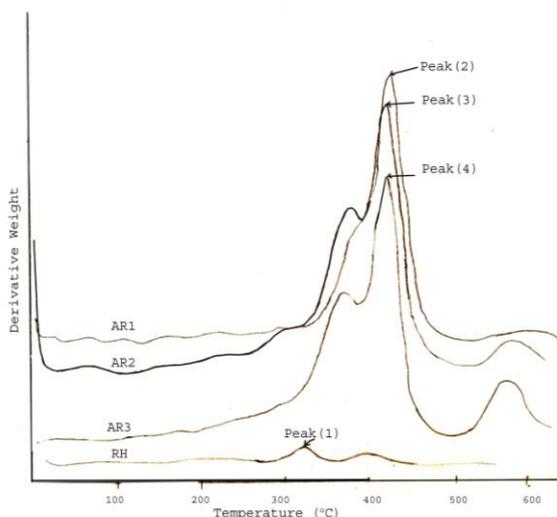


Fig – 5(b) : DTG curves of biomass and composites



RH : Rice Husk  
 AR<sub>1</sub> : Composite with 10% RH  
 AR<sub>2</sub> : Composite with 30% RH  
 AR<sub>3</sub> : Composite with 50% RH

Table – 1: PHYSICO – CHEMICAL PROPERTIES

Name of the compound	Colour	Structure	Solubility				Percentage yield
			CCl <sub>4</sub>	DMSO	DMF	Ethyl Alcohol	
RH	Dark Brown	Crystalline	—	±	—	—	—
AR <sub>1</sub>	Brownish white	Crystalline	—	±	±	—	72.2
AR <sub>2</sub>	Dark Brown	Crystalline	—	±	±	—	74.5
AR <sub>3</sub>	Dark Brown	Crystalline	—	±	±	—	79.6

RH : Rice Husk (biomass)  
 AR<sub>1</sub> : Composite with 10% biomass.  
 AR<sub>2</sub> : Composite with 30% biomass.  
 AR<sub>3</sub> : Composite with 50% biomass.  
 DMSO : Dimethyl Sulphoxide.  
 DMF : Dimethyl formamide.  
 + : Soluble  
 ± : Partially Soluble  
 — : Insoluble

Table – 2: FTIR data of biomass and composites

Name of the compound	Peaks (cm <sup>-1</sup> )	Probable assignments
RH	720 – 796	C – H bending vibration due to aromatic nucleus
	1076	C – O (Str) Vibration
	1646	C = C (Str) Conjugated
	1735	C = O (Str) of Carbonyl group
	2855	C – H (Str) Vibration
	3430 (w)	O – H (Str) of alcoholic group
AR <sub>1</sub>	1076	C – O (str) Vibration
	1440	C = C ring Stretching
	1535	N – H bending vibration
	1624	N-H bending vibration coupled with olefinic linkage
	2923	C – H (Str) Vibration
	3312(s)	N – H (Str) hydrogen bonded
AR <sub>2</sub>	1079	C – O (str) Vibration
	1440	C = C ring Stretching
	1537	N – H bending vibration
	1624	N-H bending vibration coupled with olefinic linkage
	2926	C – H (Str) Vibration
	3313(s)	N – H (Str) hydrogen bonded
AR <sub>3</sub>	1081	C – O (str) vibration
	1440	C = C ring Stretching
	1537	N – H bending vibration
	1624	N-H bending vibration coupled with olefinic linkage
	2927	C – H (Str) Vibration
	3313(S)	N – H (Str) hydrogen bonded

RH :Rice Husk (biomass), AR<sub>1</sub> : Composite with 10% biomass, AR<sub>2</sub> : Composite with 30% biomass, AR<sub>3</sub> :Composite with 50% biomass.

 Table – 3: <sup>13</sup>C NMR data of biomass and composites

Name of the compound	Peaks in ppm	Conclusion
RH	39.50 – 40.16	May be tertiary carbon, no oxygen attached
	40.25 – 40.59	- NH <sub>2</sub> group
AR <sub>1</sub>	39.45 – 40.12	May be tertiary carbon ,no oxygen attached
	40.21 – 40.54	carbon attached to NH <sub>2</sub> group
	48.04	CH <sub>2</sub> linkage
	52.72 – 53.02	C – O oxygen bearing carbon ,SP <sup>3</sup> hybridised
	69.07	Due to N – C – O Linkage
AR <sub>2</sub>	184.15	SP <sup>2</sup> hybridised carbon in thiocarbonyl (C=S) group
	39.43 – 40.10	May be tertiary carbon, no oxygen attached
	4.27 – 40.44	carbon attached to NH <sub>2</sub> group
	49.04	CH <sub>2</sub> linkage
	52.84	C – O oxygen bearing carbon SP <sup>3</sup> hybridised
	69.12	Due to N – C – O Linkage
AR <sub>3</sub>	184.15	SP <sup>2</sup> hybridised carbon in thiocarbonyl (C=S) group
	39.45 – 40.12	May be tertiary carbon, no oxygen attached
	40.21 – 40.54	carbon attached to NH <sub>2</sub> group
	48.24	CH <sub>2</sub> linkage
	52.75	C – O oxygen bearing carbon ,SP <sup>3</sup> hybridised
	69.12	Due to N – C – O Linkage
	184.15	SP <sup>2</sup> hybridised carbon in thiocarbonyl (C=S) group

RH: Rice Husk (biomass), AR<sub>1</sub> :Composite with 10% biomass.  
AR<sub>2</sub> : Composite with 30% biomass, AR<sub>3</sub> :Composite with 50% biomass.

**Table – 4: Concise TG data of biomass and composites**

Temperature °C	Percentage decomposition			
	RH	AR <sub>1</sub>	AR <sub>2</sub>	AR <sub>3</sub>
100	5.2	6.0	5.6	6.7
250	20.0	45.0	30.0	28.0
400	70.0	63.0	55.0	54.0
650	95.5	76.0	63.0	60.0

RH : Rice Husk (biomass), AR<sub>1</sub>: Composite with 10% biomass.

AR<sub>2</sub> : Composite with 30% biomass, AR<sub>3</sub> : Composite with 50% biomass.

**Table-6: Degradation Kinetics data**

Name of the compound	Temperature (°C)	Function	Activation energy (KJ/Mole)	Correlation coefficient (R <sup>2</sup> )
AR <sub>1</sub>	0-150	F <sub>3/2</sub>	0.1917	0.994
	150-350	F <sub>3/2</sub>	7.1312	0.953
	350-500	F <sub>3/2</sub>	2.894	0.982
	500-650	F <sub>3/2</sub>	5.542	0.6083
AR <sub>2</sub>	0-150	F <sub>3/2</sub>	0.3009	0.9332
	150-350	F <sub>2</sub>	36.012	0.9674
	350-500	F <sub>3/2</sub>	2.198	0.9721
	500-650	F <sub>3/2</sub>	2.137	0.979
AR <sub>3</sub>	0-150	F <sub>3/2</sub>	0.437	0.9682
	150-350	F <sub>2</sub>	38.548	0.9516
	350-500	F <sub>3/2</sub>	2.532	0.9862
	500-650	F <sub>3/2</sub>	2.398	0.9867

AR<sub>1</sub>: Composite with 10% biomass, AR<sub>2</sub> : Composite with 30% biomass.

AR<sub>3</sub> : Composite with 50% biomass.

Table – 5: Algebraic expression of function &  $g(\alpha)$  and its corresponding mechanism [18-21]

Sl. No	Mechanism	Name of the Function	$g(\alpha)$	Rate determining Mechanism
<b>A (Based on the diffusion mechanism)</b>				
1	$D_1$	Parabola Law	$\alpha^2$	One – dimensional diffusion
2	$D_2$	Valensi (Barrer) equation	$\alpha + (1 - \alpha)\ln(1 - \alpha)$	Two dimensional diffusion
3	$D_3$	Jander Equation	$[1 - (1 - \alpha)^{1/3}]^2$	Three dimensional diffusion spherical symmetry
4	$D_4$	Ginstling – Brounstein equation	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$	Three dimensional diffusion cylindrical symmetry
5	$D_5$	Zhuravlev, Lesokin, Tempelman equation	$[(1 - \alpha)^{-1/3} - 1]^2$	Three dimensional diffusion
6	$D_6$	Anti – Jander equation	$[(1 + \alpha)^{1/3} - 1]^2$	Three dimensional diffusion
<b>B (Random nucleation and subsequent growth)</b>				
7	$A_1$	Avrami – Erofeev equation	$-\ln(1 - \alpha)$	Assumed random nucleation and its subsequent growth (n=1)
8	$A_{3/2}$	Avrami – Erofeev equation	$[-\ln(1 - \alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth (n=1.5)
9.	$A_2$	Avrami – Erofeev equation	$[-\ln(1 - \alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth (n=2)
10	$A_3$	Avrami – Erofeev equation	$[-\ln(1 - \alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth (n=3)
11	$A_4$	Avrami – Erofeev equation	$[-\ln(1 - \alpha)]^{1/4}$	Assumed random nucleation and its subsequent growth (n=4)
<b>C (Phase boundary equation) :</b>				
12	$R_2$	Power law	$[1 - (1 - \alpha)]^{1/2}$	Contracting cylinder (Cylindrical symmetry)
13	$R_3$	Power law	$[1 - (1 - \alpha)]^{1/3}$	Contracting cylinder (Spherical symmetry)
<b>D (Acceleratory rate equation) :</b>				
14	$P_{1/2}$	Mampel Power Law	$\alpha^{1/2}$	Nucleation
15	$P_{1/3}$	Mampel Power Law	$\alpha^{1/3}$	Nucleation
16	$P_{1/4}$	Mampel Power Law	$\alpha^{1/4}$	Nucleation
<b>E (Chemical process or Mechanism (non – invoking equation))</b>				
17	$F_2$	Second Order	$(1 - \alpha)^{-1} - 1$	Chemical reaction
18	$F_{3/2}$	One and a half order	$(1 - \alpha)^{-1/2} - 1$	Chemical reaction

Table – 7: Data of Oxygen Index (OI)

Name of the compound	Temperature	Char residue as %	Oxygen index (decimal value)
AR <sub>1</sub>	650°C	24	.271
AR <sub>2</sub>	650°C	37	.323
AR <sub>3</sub>	650°C	40	.335

AR<sub>1</sub>: Composite with 10% biomass,

AR<sub>2</sub>: Composite with 30% biomass.

AR<sub>3</sub>: Composite with 50% biomass.

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