

Synthesis and Characterization of Resin Copolymer Derived From Cardanol-Furfural –Urea/Thiourea

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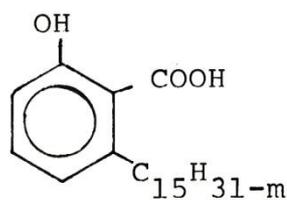
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Abstract: A number of resins were synthesized by reacting cardanol, (a byproduct of the cashew industry) with furfural and urea / thiourea in the presence of acid and base catalyst. The resins were characterized by FTIR spectrum and shown to be selective ion exchangers for certain metal ions. A batch equilibrium method was used for studying the selectivity of the metal ions. The thermal behavior of the resins was also studied with plausible degradation mechanism is suggested. The degree of crystallinity of resin copolymers have been studied by X-ray diffraction. The SEM of the resins have been studied.

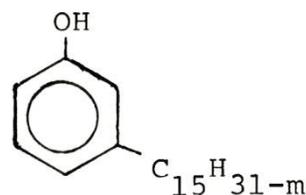
I. Introduction

In recent years, the synthesis of polymers from renewable resources has attracted the attention of many research workers because of the escalating price of petrochemicals (1-17) . By renewable resource is meant agricultural products, i.e., materials that are synthesized by sunlight. One such agricultural product is cashew nut shell liquid (CNSL), which is a by product of the cashew industry and contained in the soft honeycomb structure between the outer shell and the kernel of the cashew nut. The cashew nut tree (*Anacardium occidentale* linn) grows at altitudes below 1000 feet along with the by Eastern and western coasts of India .The state of Odisha has vast costal area situated outside the Bay of Bengal and cashew trees are abundantly grown in this costal region.

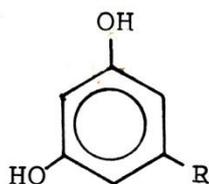
The major components of CNSL have been characterized by Tyman(18),Murthy et al(19). and Verma and co-workers(20) using ultraviolet ,infrared, H-NMR ,and chromatography(20-22) ,CNSL contains four major components, i.e. anacardic acid cardanol, cardol and 6-metyl cardol, whose at structures are given below:



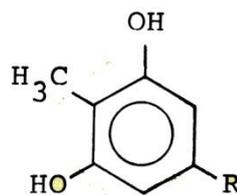
Anacardic acid



Cardanol



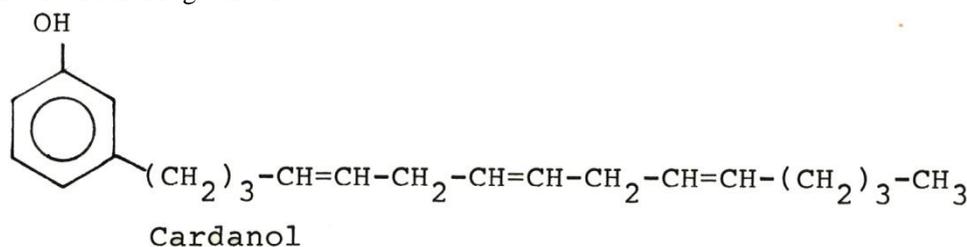
Cardol



6-methyl cardol

Of the above four components, anacardic acid is the most important component of CNSL .Nayak and Lenka (23-34) have reported the synthesis and characterization of a large number of resin using a multitude of hydroxyl aromatic compounds, furfural /formaldehyde in the presence of acid and base as the catalysts. They have reported, thermal ion-exchange properties bactericidal and fungicidal properties of the resins.

The structure of cardanol is given below:



II. Extraction Of Cardanol

Cashew nut shell liquid (CNSL) was obtained from M/S Dheer Gramodyog Ltd., Kanpur, India, Cardanol was obtained by double vacuum distillation of CNSL at 3-4 mm Hg and the fraction distilled at 230-240⁰ C was collected .The saponification value, viscosity ,specific gravity ,and moisture content were determined by the standard procedure (ISI –standard 840-1964) and reported in Table I .

Table-I : Properties of CNSL and cardanol

Sl. No.	Properties	CNSL	Cardanol
01	Colour	Dark brown	Dark brown
02	Specific gravity	0.965	0.870
03	Viscosity	226	39
04	Saponification value	122	23
05	Iodine value	276	275
06	Moisture content	2.2	2.4

Synthesis of Resin Copolymers

A mixture of cardanol (4 m. mole), furfural (40m.mole) and urea (4 m. mole) was refluxed at 120⁰ C for 5-7 hrs. in the presence of 4N NaOH (2mL) with periodic shaking .After completion of the reaction, the contents were extracted with ice-cold water, filtered and washed repeatedly with hot water to remove the unreacted materials .The product was dried in vacuum .Some of the resins were also prepared using HCl,H₂SO₄ and H₃PO₄ as the catalyst .The physicochemical properties of the resins are shown in Table II.

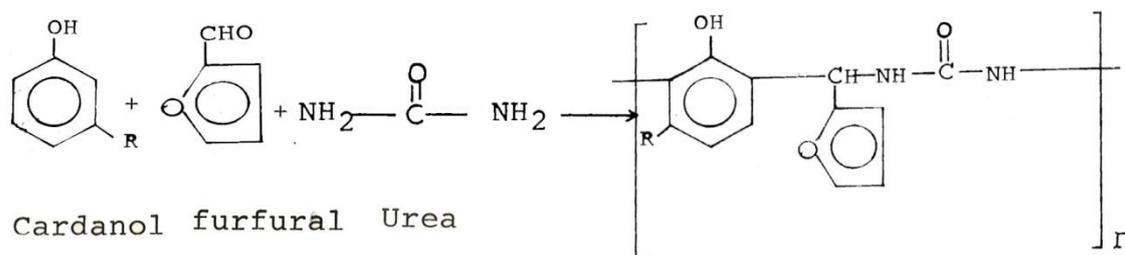


Table II: Physico –chemical properties of resins prepared from cardanol – furfural – urea

Sl. No.	Sample Composition	Name of comonomer	Catalyst used	Yield (%)	Decomposition temp. (°C)
01	Cardanol+furfural	Urea	HCl	80	>360
02	Cardanol+furfural	Urea	KOH	80	>360
03	Cardanol+furfural	Thiourea	H ₂ SO ₄	80	>360
04	Cardanol+furfural	Thiourea	NaOH	70	>360
05	Cardanol+furfural	Urea	H ₃ PO ₄	85	>360
06	Cardanol+furfural	Urea	CH ₃ COOH	75	>360
07	Cardanol+furfural	Thiourea	H ₃ PO ₄	85	>360
08	Cardanol+furfural	Thiourea	CH ₃ COOH	75	>360

FTIR studies

The high intense peak (Fig.1) at 2921.9 Cm⁻¹ is due to C-H stretching in aromatic ring. The band 2852 Cm⁻¹ shows the presence of methylene bridge .The peak in the region at 1587.6 Cm⁻¹ assigned to the vibration of the aromatic –C=C- linkages as well as N-H bending .The peak at 1455.1 Cm⁻¹ is due to C-O stretching of ester or alcohol. The and at 965.9 Cm⁻¹ is due to trans double bond in the side chain of cardanol moiety .The peak at 748.6 Cm⁻¹ due to C-H out of plane bending in medium intense band at 693 Cm⁻¹ is due to C-H out of

plane bending vibration in monosubstituted furanyl ring .The peak at 478.7 Cm⁻¹ is due to out of plane bending.

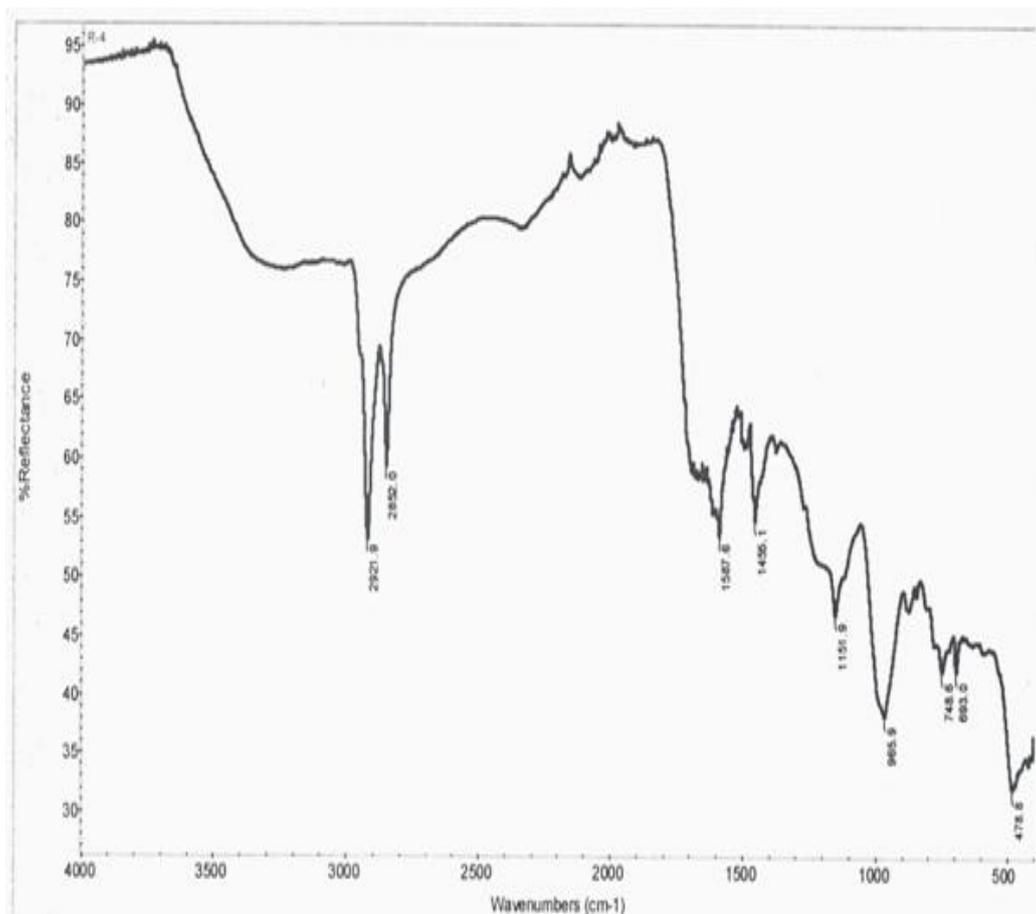


Fig-1 FTIR spectra of the resin prepared from cardanol- furfural –urea

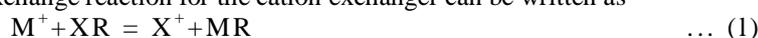
Table-III

Sl. No.	Wave No. (Cm ⁻¹)	Functional group
01	2921.9	C-H stretching
02	2852.0	C-H stretching(SP ³ carbon)
03	1587.6	C=C stretching
04	1455.1	C-H asymmetric stretching
05	1151.9	C-O stretching of ester or alcohol
06	965.9	Out of plane /CH=CH trans unsaturation
07	748.6	Monosubstituted aromatic ring typically have out – of – plane bending
08	693.0	Monosubstituted aromatic ring typically have out – of – plane bending
09	478.7	Out of plane bending

Ion-exchange Properties of the Resins .

Numerous theories has developed in order to explain the relative affinity of various cations. Out of all, one is commonly accepted model, the ion-exchanger is considered as Donnan equilibrium, the reaction between dissolved compound and the compound comprised of resins exchanger and the ion which it contains. The resin thus is effectively an insoluble ion of the opposite polarity from that which it exchanges.

The ion exchange reactions with few exceptions are reversible. The exchange of ions is stoichiometric and the stoichiometric exchange reaction for the cation exchanger can be written as



The influence of various electrolytes in the selectivity of ions , rate of metal uptake, and distribution (D) between the copolymer and solution containing the metal ions was investigated. A number of metal ions were in the present investigation for this study.

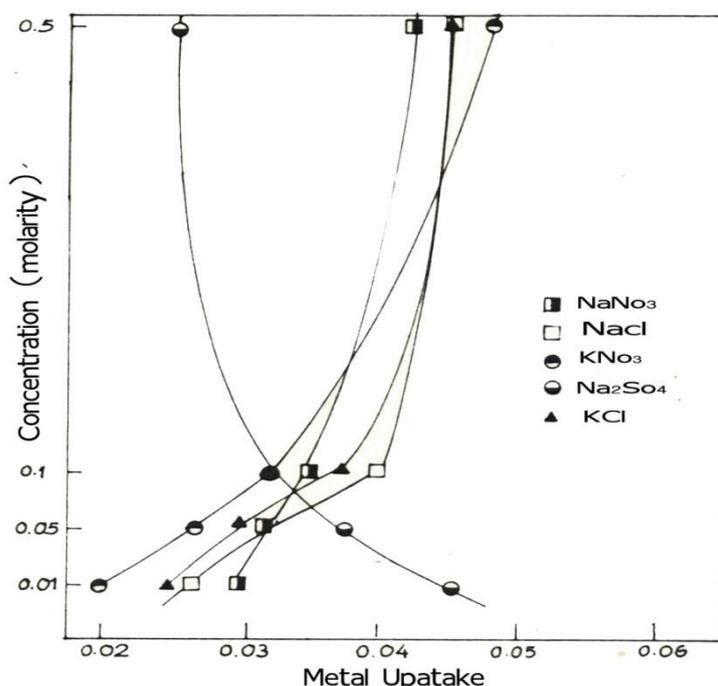


Fig 2: Adsorption of metal ion (Cu^{2+}) by the copolymer [Cardanol – furfural –urea] at various strength of different electrolytes .

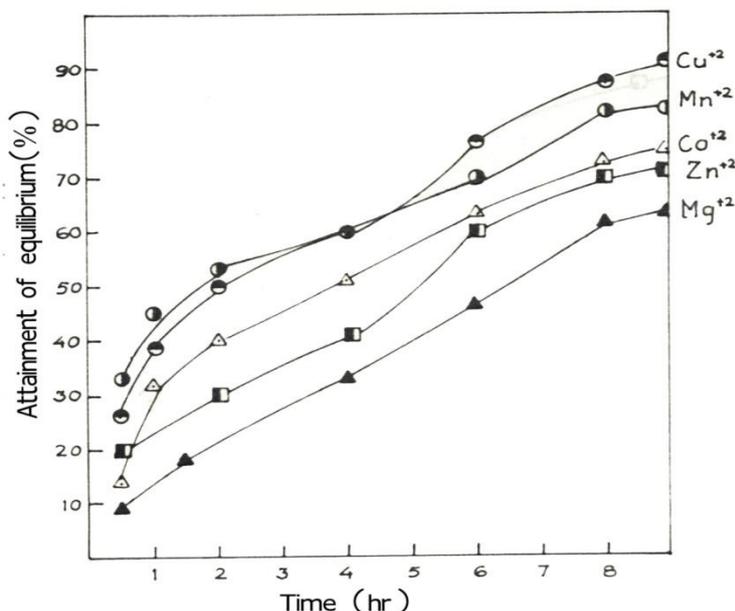


Fig 3 : Rate of different metal uptake by the copolymer (Cardanol –furfural-urea)

Table-iv comparison of rates of metal ion uptake in different times*

Sl. No.	Name of resin	Metal ion	% of metal ion uptake at different time(h)						
			0.5	1	2	4	6	8	10
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
01	Cardanol – furfural- Urea	Cu^{2+}	27.6	38.9	50.1	60.2	76.4	87.6	92.1
		Co^{2+}	13.2	33.3	40.1	53.4	63.4	73.4	75.1
		Zn^{2+}	20.1	30.1	30.1	40.1	60.1	70.1	72.2
		Mn^{2+}	32.1	45.2	51.7	58.1	70.8	82.2	85.3
		Mg^{2+}	12.3	28.3	35.7	42.9	57.2	64.2	70.5

Effect of Electrolyte on the metal uptake

The effect of different electrolytes, such as chloride, sulphate, and nitrate ions at various concentrations, on uptake of several metal ions by the resin copolymer is furnished in Table IV .Perusal of the

results (Fig.2) indicated that the amount of Cu^{2+} , Zn^{2+} , Mg^{2+} , Co^{2+} and Mn^{2+} adsorbed by the resin copolymer as noted in Table III increases with increase in concentration of electrolyte, but a decreasing trend is noticed in the case of the sulphate ion. These trend may be explained in the light of stability constants of these complexes. Rate of metal uptake

The dependence of the rate of the metal ion uptake on the nature of the metal ion is represented in Fig.3. The rate of metal adsorption of the resins were determined to find the shortest time period for which equilibrium could be established. The results indicates that different metal ions require different time period for the establishment of equilibrium. The rate of metal uptake at definite period follow the order $\text{Cu}^{2+} > \text{Mn}^{2+} > \text{CO}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+}$. And are shown in Figure .3

The rmogravimetric (TG) Analysis Of The Resins.

On the basis of the above observed trend in weight loss with temperature. A plausible degradation mechanism of the resin copolymers prepared by condensing cardanol-furfural-urea-substituted aromatic compounds may be due to

- (1) Chain fragmentation and post curing controlled by the unreacted methylol groups;
- (2) Thermal reforming, controlled by the free radicals formed, and
- (3) Ring stripping, depending upon the elemental composition .

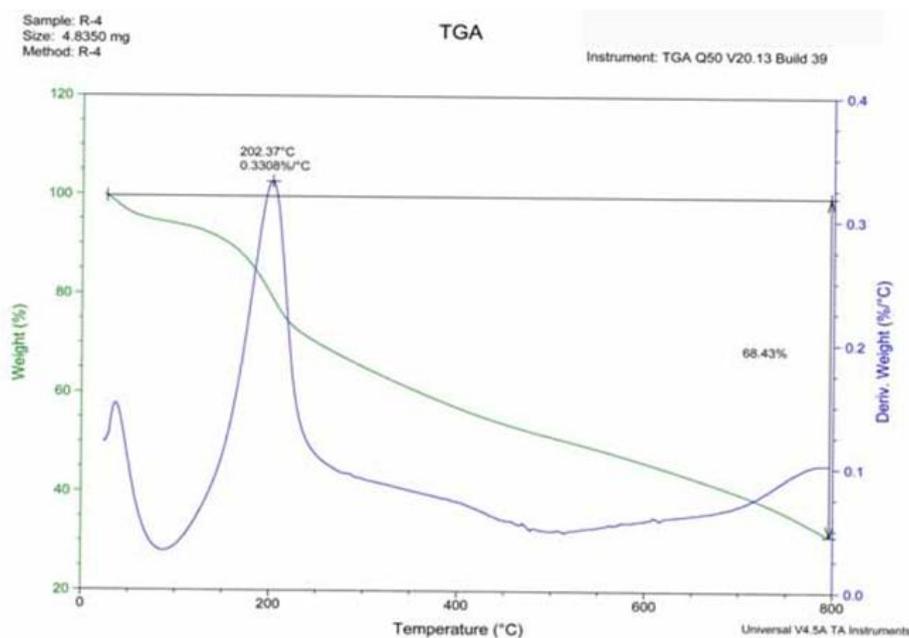


fig-4: Cardanol - furfural - urea

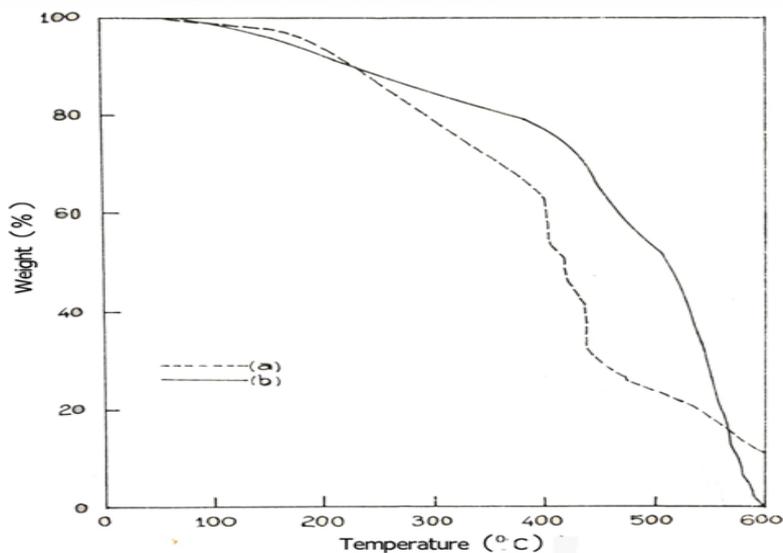


Fig. 5: Thermogram of copolymers

- a) Cardanol – furfural –o-hydroxy benzoic acid
- b) Cardanol – furfural – p-hydroxy acetophenone

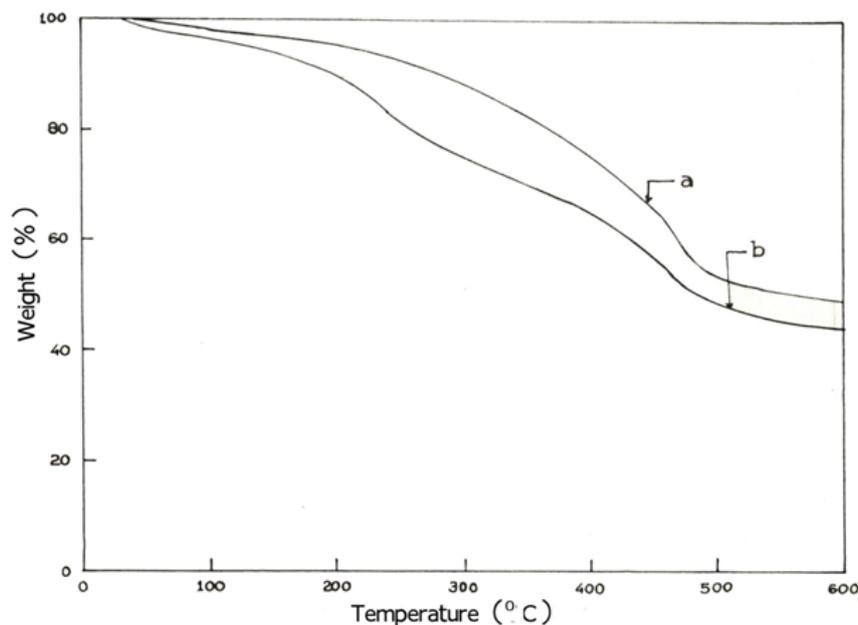


Fig. 6: Thermogram of the homopolymer

- a) Cardanol – furfural
- b) Cardanol – furfural – thiourea

III. Result And Discussion

On Comparison Of Thermal Stability Between The Resin Copolymers Prepared From Cardanol - Furfural - Substituted Aromatic Compounds And The Copolymers From Cardanol - Furfural - Urea / Thiourea, It Was Observed That Copolymers From Substituted Aromatic Compounds Are Less Thermal Stable Than The Copolymers From Urea / Thiourea, This May Be Due To The Greater Crosslinking In Case Of Urea / Thiourea Copolymers. From The Fig (4) Representing The TG Curve Of Cardanol - Furfural - Urea Copolymers Was Observed That Only 50-55% Of Weight Loss Occurs Up To 600°C But 95-100% Weight Loss Occurs Around 600°C For Cardanol - Furfural - Substituted Aromatic Compound, Copolymers From Fig.(5)

The Thermo Gravimetry (TG) Curve For The Homopolymer Prepared From Cardanol - Furfural (After Curing With HMTA) Was Shown In Fig.(6) And It Was Found That Homopolymers Are More Thermal Stable Than Corresponding Copolymers Because Only 48% Of Weight Occurs Around 600°C For Homopolymers.

From The Above Discussion It Was Found That, The Copolymers Prepared From Cardanol - Furfural - Urea / Thiourea Are More Thermally Stable Than Homopolymer, Homopolymers Are More Stable Than Cardanol - Furfural - Substituted Aromatic Compound Copolymers. In Addition With It Was Found That The Cured Copolymers Are More Thermally Stable Than The Non-Cured Copolymers. (Curing Of Copolymers Were Carried Out By Using HMTA).

Lastly, On Comparison With The Thermal Stability Between The Copolymer - Cardanol - Furfural – Urea In Presence Of H₃PO₄ And H₂SO₄ Than The Resin Prepared In Presence Of NaOH And KOH. This May Be Attributed That Greater Degree Of Crosslinking. We Conclude That The Copolymer Prepared From Cardanol-Furfural-Urea/Thiourea Are More Thermal Stable.

IV. X-Ray Diffraction Studies

Introduction

There are three major aspects of investigating the crystal structure of resin copolymers, These are (i) degree of crystallinity, (ii) lattice size, (iii) crystallite orientation. Hermans (1) and Karst and Flaschner developed quantitative methods for determination of the degree of crystallinity (X_{cr}) i.e. Relative proportion of crystalline domains in the crystalline - amorphous composite structure. These two methods define crystalline domains as those which contribute maxima in its X-ray diffraction curve and arrived at a crystalline proportion by comparison of the intensity of maxima considered to be contributed by the crystalline part of the substance and the intensity of the background scattering supposed to be due to amorphous regions. Ruland developed a

better method for the determination of Xcr by introducing crystal defect concept which was subsequently simplified and computed by Vonk Hindle developed a peak resolution technique to find out Xcr values .
 $N\lambda=2dsine$

Table-V The basic data of cardanol-furfural-thiourea is given in table-V

Sl. no.	Strongest peak no.	2 theta(deg)	d(A)	1/11	FWHM (deg)	Intensity (Counts)	Integrated Intensity(Counts)
1	1	2.4218	36.45076	100	0.00000	1	0
2	2	5.0723	17.40802	100	0.00000	1	0
3	3	6.3348	13.94122	100	0.00000	1	0

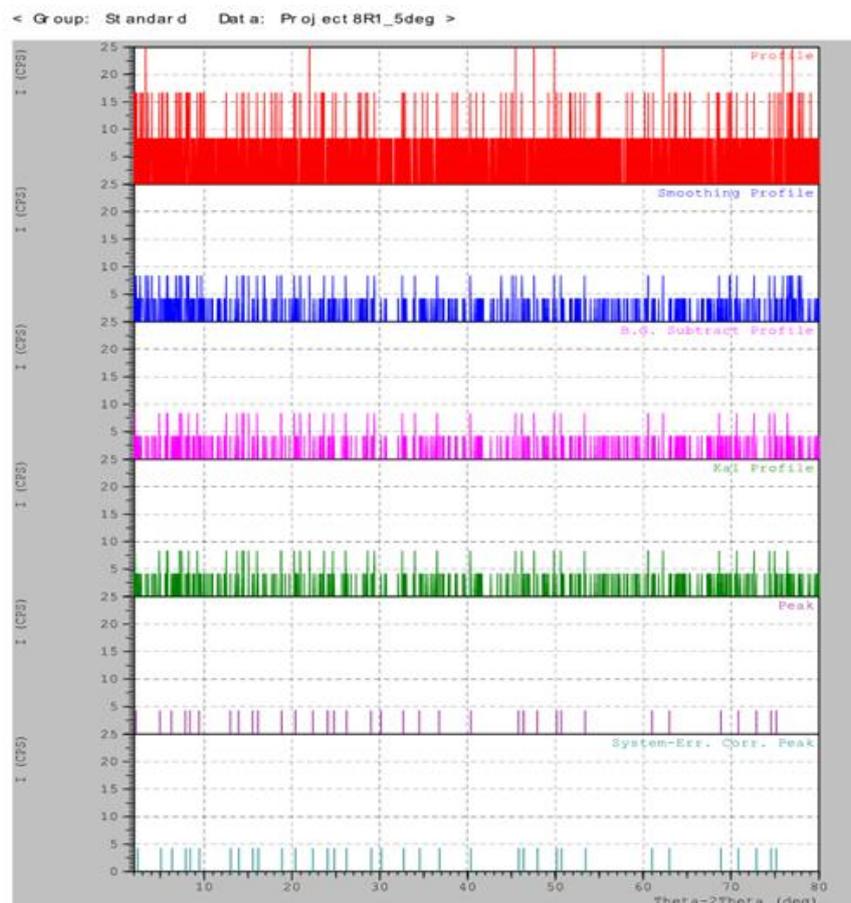


Fig-7

4.3. Result And Discussion:

In the present investigation, Ruland and Vonk method has been employed for calculating the degree of Crystallinity (Xcr) values but Bragg’s equation indicated the presence of two sets of reflection planes corresponding to the 2θ values of 20 and 80. This is more clearly observed from above data and in fig-7.

Scanning electron microscope (sem)

Introduction

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm).

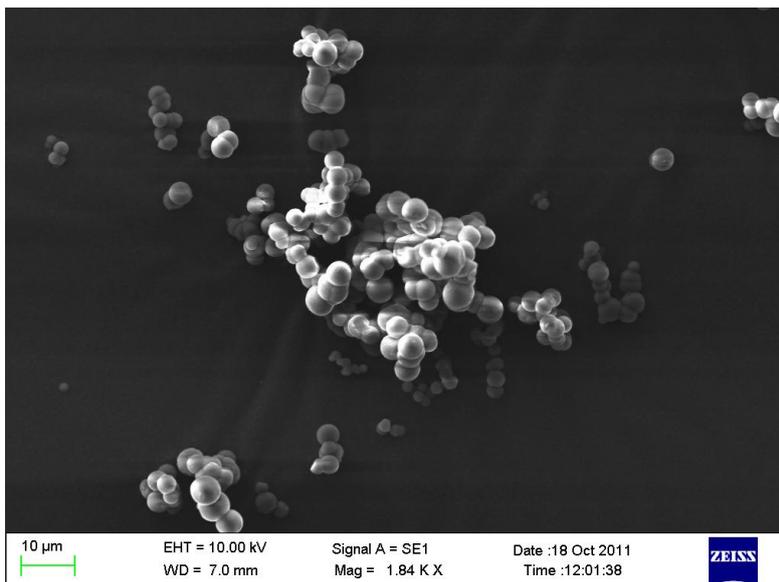


Fig-8, Cardanol-furfural-Urea

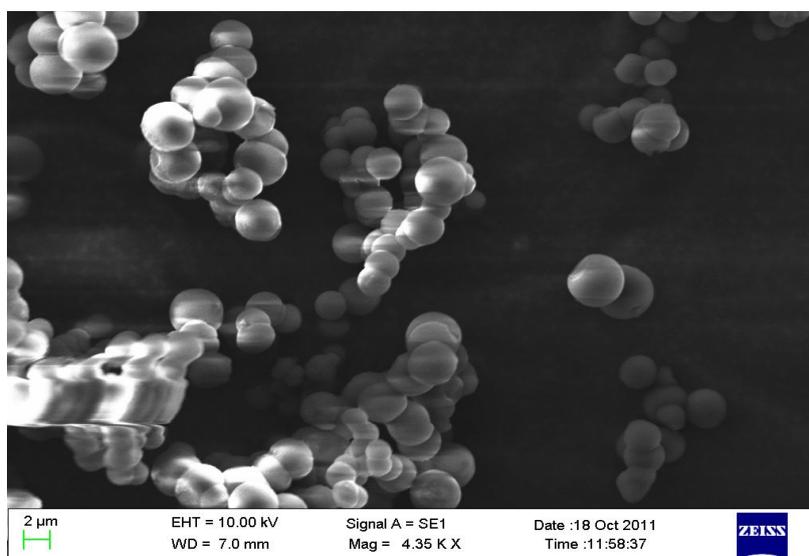


Fig-9, Cardanol-furfural-Urea

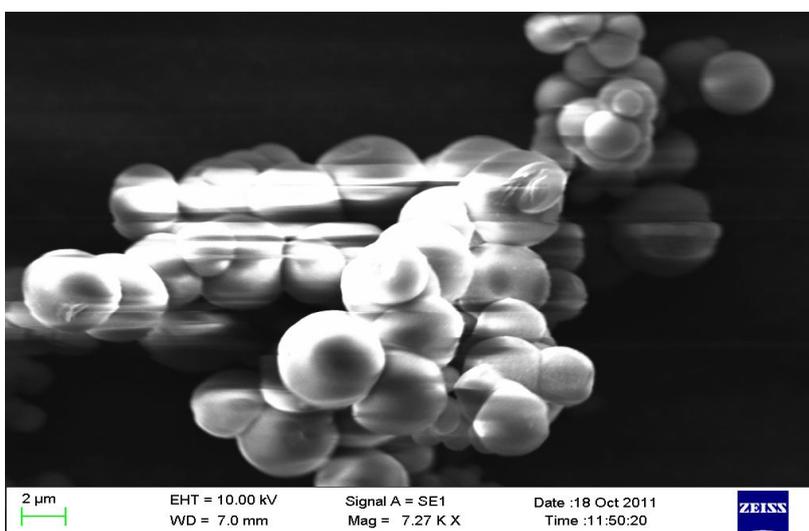


Fig-10, Cardanol-furfural-Urea

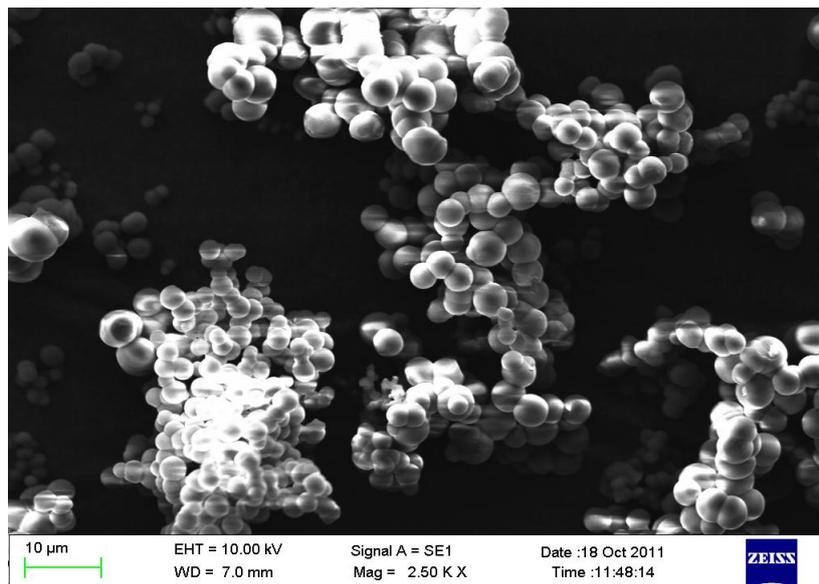


Fig-11, Cardanol-furfural-Urea

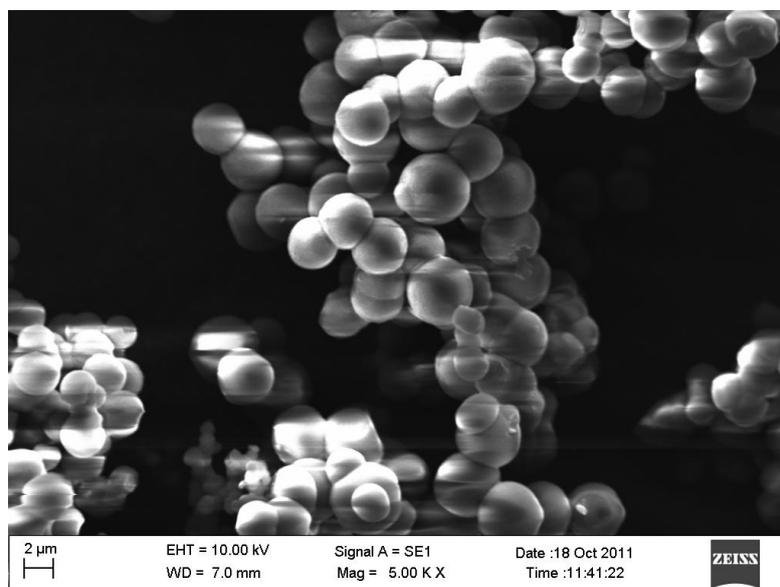


Fig-12, Cardanol-furfural-Urea

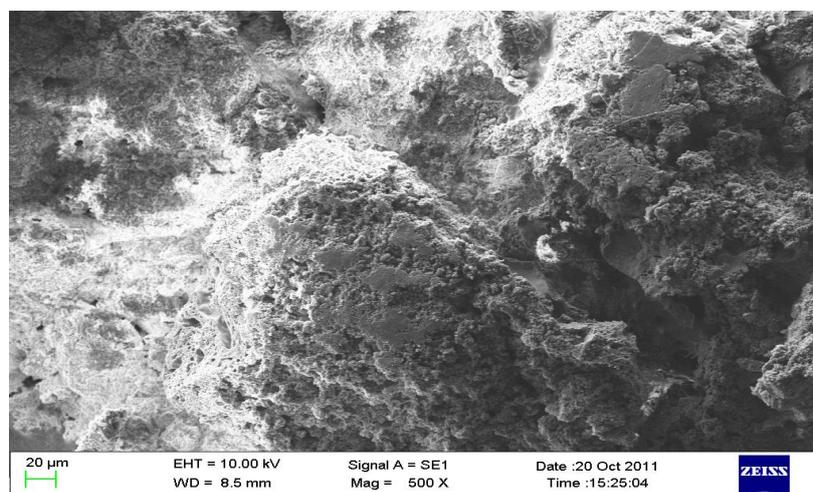


Fig-13, Cardanol-furfural-Urea

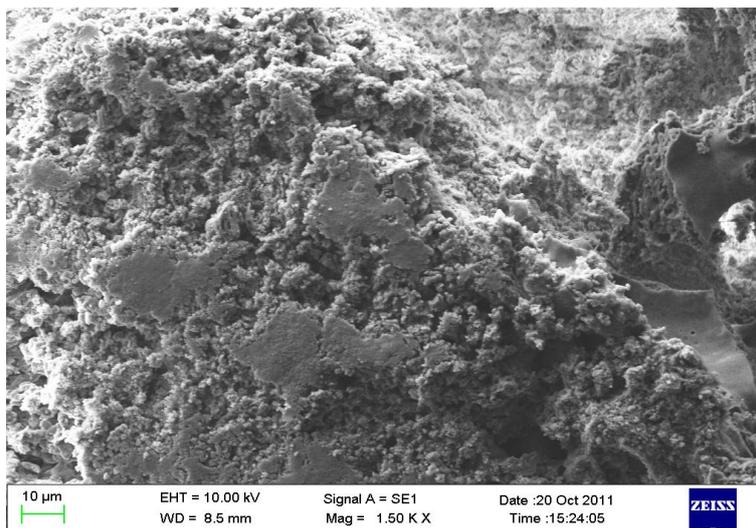


Fig-14, Cardanol-furfural-Urea

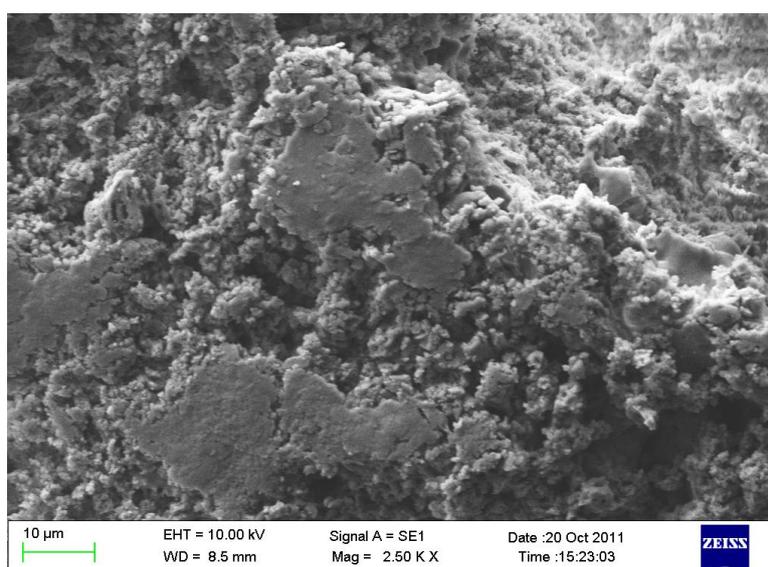


Fig-15, Cardanol-furfural-Urea

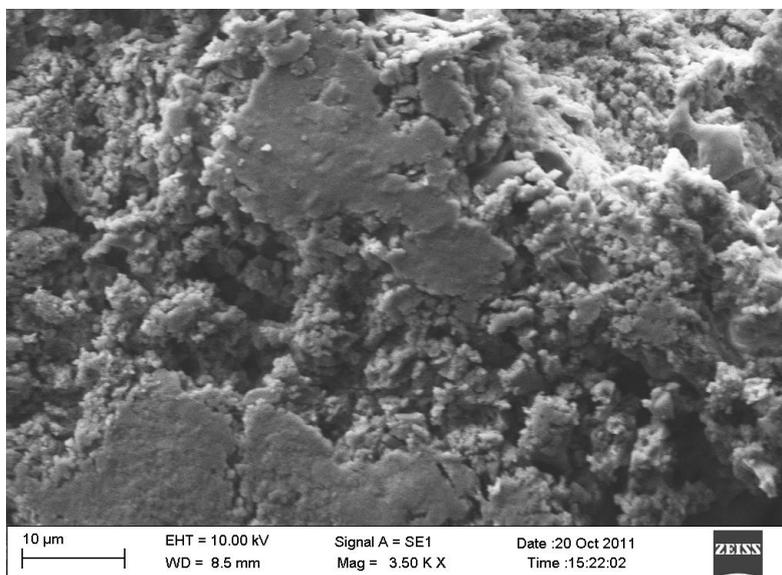


Fig-16, Cardanol-furfural-Urea

V. Result And Discussion

The SEM is routinely used to generate high-resolution images of shapes of resin copolymer and to show spatial variations in chemical compositions: 1) acquiring elemental maps or spot chemical analysis using EDS, 2) discrimination of phases based on mean atomic number (commonly related to relative density) using BSE and 3) compositional maps based on differences in trace element “activators” (typically transition metal and Rare Earth elements) using CL. The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure of resin copolymer cardanol – furfural – thiourea and cardanol-furfural-urea. It has been studied from ZEISS instrument from CIPET (LARPM) in fig.(8-16)

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