ISSN (e): 2250 – 3005 || Volume, 05 || Issue, 06 || June – 2015 ||
International Journal of Computational Engineering Research (IJCER)

Synthesis and characterization of resin copolymer derived from cardanol-furfural/ formaldehyde –p-hydroxy benzoic acid.

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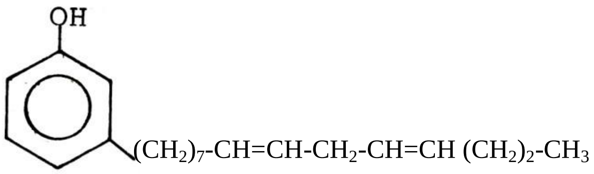
***ABSTRACT*:**
Some of resin copolymers have been synthesized by refluxing cardanol, which is a major constituent of Cashew nut Shell Liquid (CNSL), with furfural/formaldehyde and p-hydroxy benzoic acid in presence of different acid and base catalysts. The resins have been characterized by FTIR spectra. The thermal behaviors of the resins have been studied and the kinetic parameters as well as plausible degradation mechanism have been suggested. In addition to this XRD and SEM of the copolymers have been studied.

I. INTRODUCTION

Cashew nut shell liquid (1-5) (CNSL) and its polymeric product find a wide variety of applications in industries (8-10). The main constituents of CNSL are anacardic acid, cardol, cardanol and 6-methyl cardol. On heating, anacardic acid is decarboxylated to cardanol which is a n-penta decadienyl phenol. Its aliphatic side chain usually consists of mixture of one, two and three double bonds in a linear chain. These components of CNSL have been characterized by a number of techniques including proton NMR, ultraviolet (UV), infrared (IR) and chromatography.



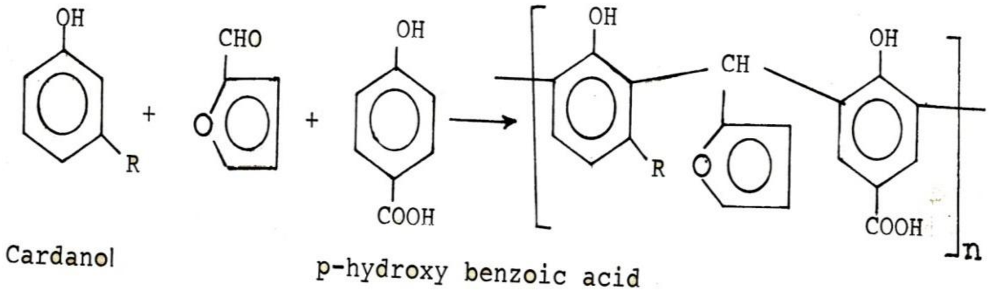
Although a tot of work has been carried out on phenol-formaldehyde polymers which have great deal of importance as materials, the area of synthetic resins derived from renewable resources like CNSL has not been widely exploited. Recently Misra and Pandey (11) reported the kinetics of formaldehyde condensation of cardanol. Manjula has studied the oliqomerization of cardanol using acid catalyst.(12,13) Recently Varma and coworkers(14), on the basis of the fragmentation pattern of mass spectra and NMR spectra proposed the structure of cardanol. O' Connor and Blum (15) have reported the thermal stability of some resins by condensing cardanol formaldehyde. Pillai et al (16, 17) have reported the GPC studies on the cationic polymerization of cardanol initiated by Boron trifluoride diethyl etharate. Sathiyalekshmi (18) reported the, structure and properties of CNSL-novalac resins prepared using succinic acid as the catalyst. Nayak and Lenka (19-30) have reported the synthesis and characterization of a large number of resins using a multitude of hydroxy aromatic compounds, formaldehyde/furfural in the presence of acid and base as the catalysts. They have reported, thermal, ion-exchange properties, bactereocidal and fungicidal properties of the resins. This communication presents the synthesis and characterization of resins obtained by condensation of cardanol-formaldehyde-p-hydroxy benzoic acid.

Synthesis of resins:

Method-1

A mixture of cardanol (4 m. mole), furfural (40 m. mole) , and p-hydroxy benzoic acid (4 m. mole) was refluxed at 110°C for about 6-8 hours in presence of 2 ml of NaOH (4N) with periodical shaking. At the end 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. The physico-chemical properties of the resins are furnished in Table-2. The dried resin was weighed and mixed with different percentage of hexarnethylenetetramine (HMTA) which acts as curing agent and powdered and kept in the ovan for first one hr. at 100^0 C and post cured further 1 hr. at 120^0 C.

The poly condensation reaction of cardanol with furfural (40 m. mole), and p-hydroxy benzoic acid may be represented as follows.



Method-2

Reagents taken

i) Cardanol - 1.192 gm

ii) Formaldehyde - 3.84 gm

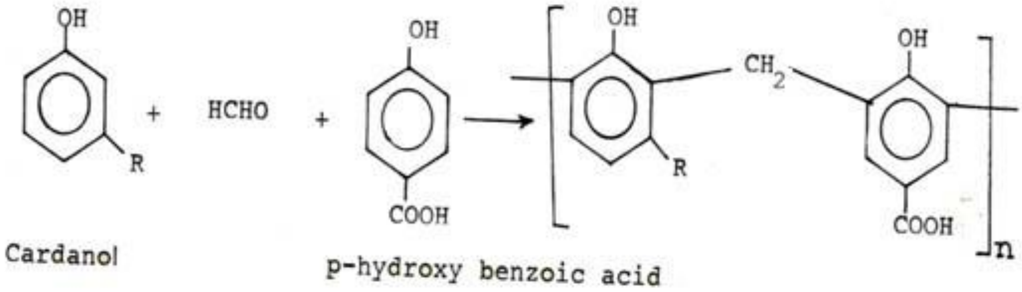
iii) p-hydroxy benzoic acid - 0.552 gm.

Catalyst used: - HCl (4N) 2 ml

Condensation of cardanol- formaldehyde and p-hydroxy benzoic acid in presence of acid catalyst.

Procedure : A mixture of 1.192 gm (4 m. mole) of cardanol, 3.84 gm (40 m. mole) of formaldehyde and 0.552 gm (4 m. mole) of p-hydroxy benzoic acid were refluxed for 2-3 hrs at 80-100°C in presence of 2 ml of (4N) HCl catalyst with periodical shaking. After completion of reaction, the product was washed with 10% NaOH then hot water in order to remove the basic and unreacted impurities, filtered and the residue was dried in vacuum at 60°C, and then collected.

Polycondensation reaction for above method may be represented as follows:



PHYSICO- CHEMICAL PROPERTIES OF CARDANOL-FURFURAL-P-HYDROXY BENZOIC ACID.

Table-1

Sl. No.	Name of comonomer	Catalyst	Duration of heating	Colour	Structure	Solubility	Yield (%)	Decomposition of temp. (^{0}c)
01	Cardanol+formaldehyde+ p-hydroxy benzoic acid	HCl	3	Brown	Crystalline	DMF*	70	>360
02	Cardanol+formaldehyde+ p-hydroxy benzoic acid	H_2SO_4	3	Reddish	Crystalline	DMF*	60	>360
03	Cardanol+formaldehyde+ p-hydroxy benzoic acid	NaOH	6	Brown	Crystalline	DMSO*	65	>360
04	Cardanol+formaldehyde+ p-hydroxy benzoic acid	KOH	6	Brown	Crystalline	DMSO*	60	>360
05	Cardanol+formaldehyde+ p-hydroxy benzoic acid	H_3PO_4	2	Brown	Crystalline	DMSO*	70	>360
06	Cardanol-furfural- p-hydroxy benzoic acid	HCl	2	Brown	Crystalline	DMSO*	65	>360
07	Cardanol-furfural- p-hydroxy benzoic acid	$H_2\,SO_4$	2	Reddish	Crystalline	DMSO*	60	>360
08	Cardanol-furfural- p-hydroxy benzoic acid	KOH	6	Brown	Crystalline	DMSO*	70	>360

* - represents partially solvents.

II. FTIR ANALYSIS

The structure of the cardanol-furfural-p-hydroxy benzoic acid was identified from the spectral data from the fig.1. The band near 3369.9 cm^{-1} is due to O-H stretching in phenolic OH group. The strong peak at 2833.6 cm^{-1} indicates the C-H stretching of methylene linkages. A medium absorption band at 1667.1 cm^{-1} is due to C-O stretching in –COOH. The peak at 1585.2 cm-^{1} is due to carboxylate anionic stretching vibration. The alkene disubstitution is identified by the peak at 1514.9 cm^{-1}. The peak at 1414.2 is due to C-H asymmetric stretching. The band at 1158.9 cm^{-1} is due to C-O stretching of ester or alcohol. The peak at 1098 cm^{-1} is due to C-O stretching. The intense peak at 842.7 cm^{-1} is due to CH=CH trans un saturation. The peak 760.7 cm^{-1} is due to monosubstituted aromatic ring typically have out of plane bending.

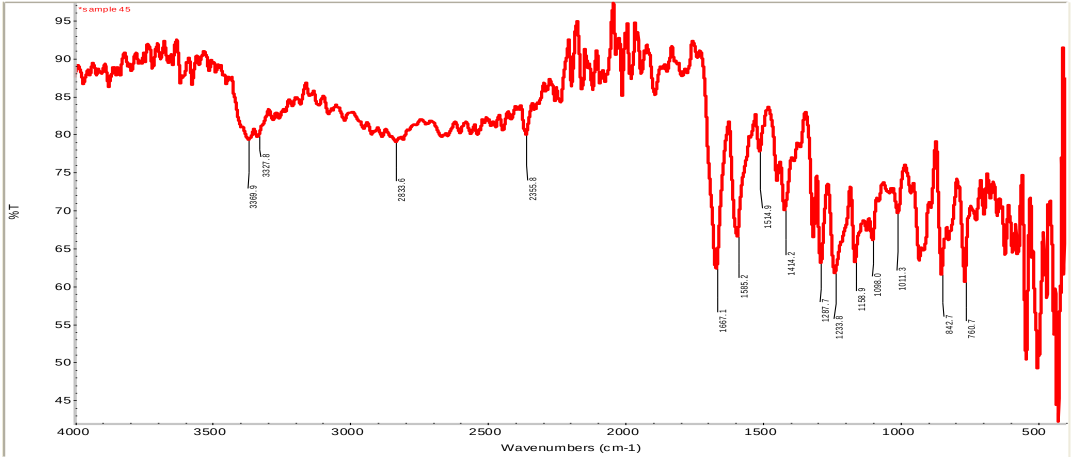


Fig-1. IR Spectra of the resin prepared from cardanol-furfural-p-hydroxy benzoic acid.

Table 2

Sl. No.	Wave No. (Cm^{-1})	Functional group
01	3369.9	O-H stretching in cardanol part
02	2833.6	C-H stretching(SP^3 carbon)
03	1667.1	-C-O stretching in –COOH group
04	1585.2	C=C stretching in aromatic ring and N-H bending
05	1514.9	C=C ring stretching
06	1414.2	C-H asymmetric stretching
07	1158.9	C-O stretching of ester or alcohol
08	1098.0	C-O stretching
09	842.7	Out of plane /CH=CH trans unsaturation
10	760.7	Monosubstituted aromatic ring typically have out – of – plane bending

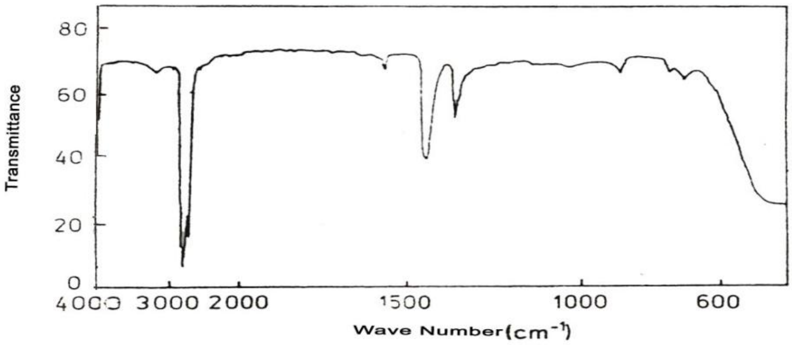


Fig-2 IR spectra of the resin prepared from cardanol- formaldehyde –p-hydroxy benzoic acid.

Table 3

Sl. No.	Wave No. (Cm^{-1})	Functional group
01	3400	O-H stretching in phenolic OH group
02	3040-3010	-C=C- stretching in alkene
03	2920-2860	C-H stretching in methylene linkage
04	1598	Carboxylate anionic stretching vibration
05	1460-1440	C-H bending in side chain alkane
06	1385-1380	The phenolic O-H bending and C-O stretching
07	780-680	Bending vibration of C-H group

Thermogravimatric (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-p-hydroxy benzoic acid 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 .

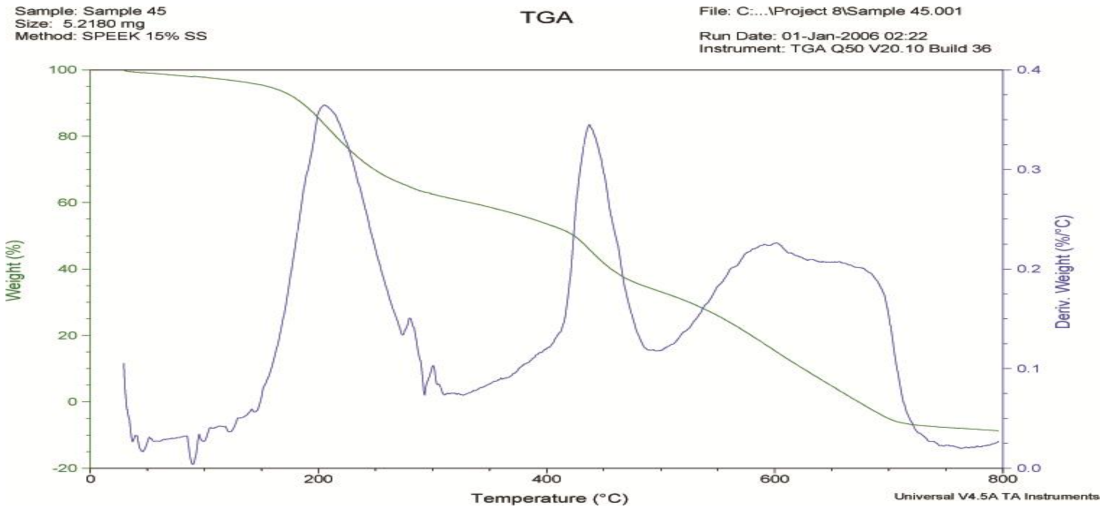


Fig-3 Thermogram of copolymer (cardanol-furfural-p-hydroxy benzoic acid).

Percentage of weight loss of resin for every 50 degree interval

Table-4

Sl. No.	Temperature Celsius in degree	% of weight loss
01	50	1
02	100	3
03	150	5
04	200	15
05	250	30
06	300	38
07	350	41
08	400	45
09	450	55
10	500	65
11	550	71
12	600	82

III. Result & Discussion:

From the TG curve of resin copolymer prepared from cardanol-furfural and p-hydroxy benzoic acid in presence of NaOH catalyst, it was observed that about 50-55% of weight loss occurs up to 400^{0}C. 70-75% 0f weight loss occurs up to 600^{0}C. Copolymer prepared in presence of acid catalyst like H_2SO_4 or H_3PO_4 is more thermally stable than Copolymer prepared in presence of base catalyst like NaOH or KOH it may be due to greater degree of crosslinking and greater dehydration reaction.

IV. X-RAY DIFRACTION:

There are three major aspects of investigating the crystal structure of resin copolymers prepared from cardanol-formaldehyde/furfural- substituted aromatic acids/alcohols. These are (i) degree of crystallinity, (ii) lattice size, (iii) ctystallite orientation. Hermans (20) and Karst and Flaschner (21) developed quantitative methods for determination of the degree of crystallinity(Xcr) 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 (22) developed a better method for the determination of Xcr by introducing crystal defect concept which was subsequently simplified and computed by Vonk(234) Hindlesh(24)developed a peak resolution technique to find out Xcr values . Crystalline size can be determined by Scherrers' Formula (25).

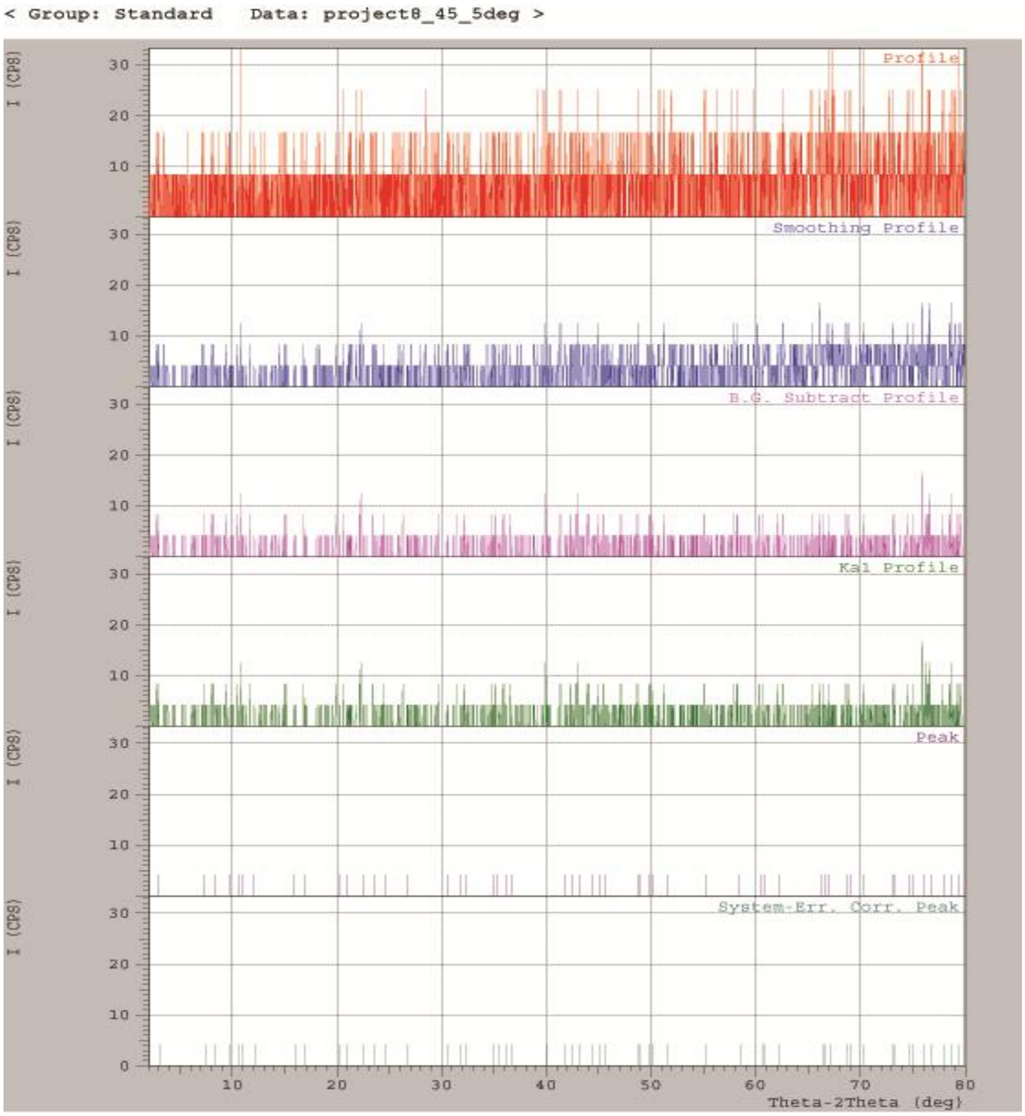
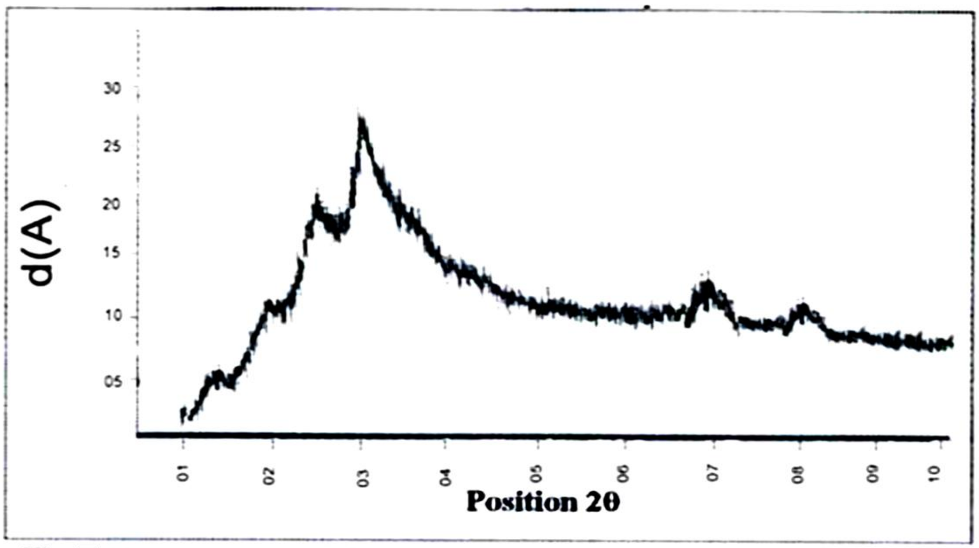


Fig.4



Fig·5 :XRD Pattern of Cardanol- Furfural-P-hydroxybenzoic acid

The basic data of cardanol-furfural-p-hydroxy benzoic acid I

Table-5

Sl. no.	Strong-est peak no.	2 theta(deg)	d(A)	I/II	FWHM (deg)	Intensity (Counts)	Integrat-ed Intensity(Counts)
1	1	3.1121	28.36693	100	0.00000	1	0
2	2	7.3851	11.96071	100	0.00000	1	0
3	3	8.3187	10.62034	100	0.00000	1	0

V. Result and discussion.

In the present investigation, Rulandand Vonk method has been employed for calculating the degree of Crystallinity (Xcr) values but Bragg's equation and Debye Scherer equation indicated the presence of two sets of reflection planes corresponding to the 2Θ values of 2^0 and 80^0.This is more clearly observed from the data given in table-5and also in fig.4&5.

A polymer can be considered partly crystalline and partly amorphous too much crystallinity of substance causes brittleness. The crystallinity part gives sharp narrow diffraction peak and the amorphous part gives very board peak. The relation between the intensities can be used to calculate the degree of crystallinity.

VI. SCANNING ELECTRON MICROSCOPE (SEM) :

A Scanning Electron Microscope (SEM) is type of a electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample surface topography and composition. The electron beam is generally scanned in a raster scan patteren, and the beams position is combined with the detected signal to produce an image. SEM can achive resolution better than nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions and at a wide range of elevated temperature. 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).

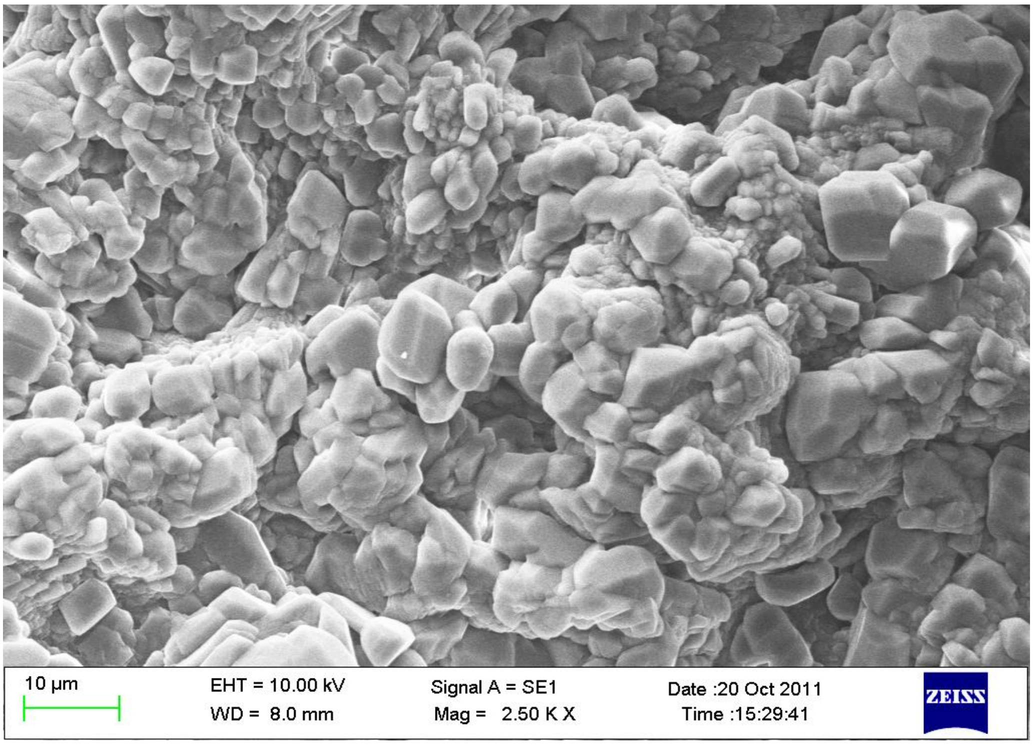


Fig. 6 Cardanol-furfural-p-hydroxy benzoic acid

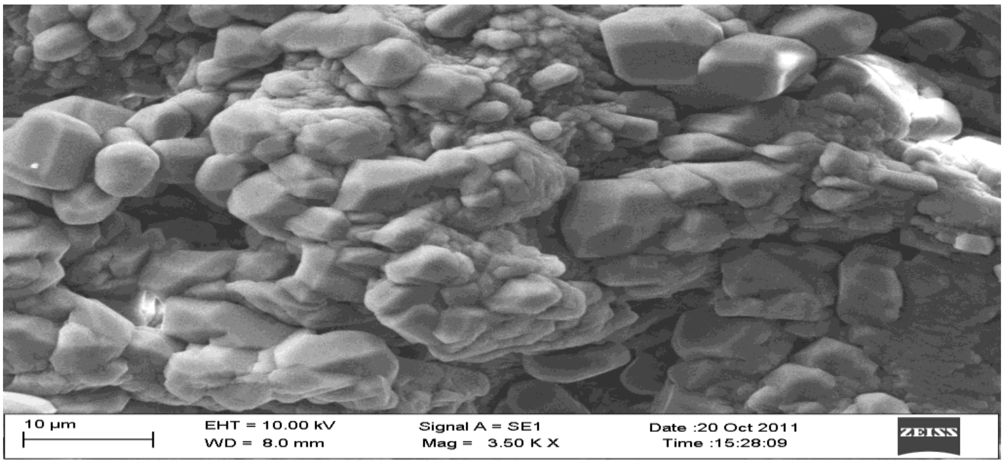


Fig.7 Cardanol-furfural-p-hydroxy benzoic acid.

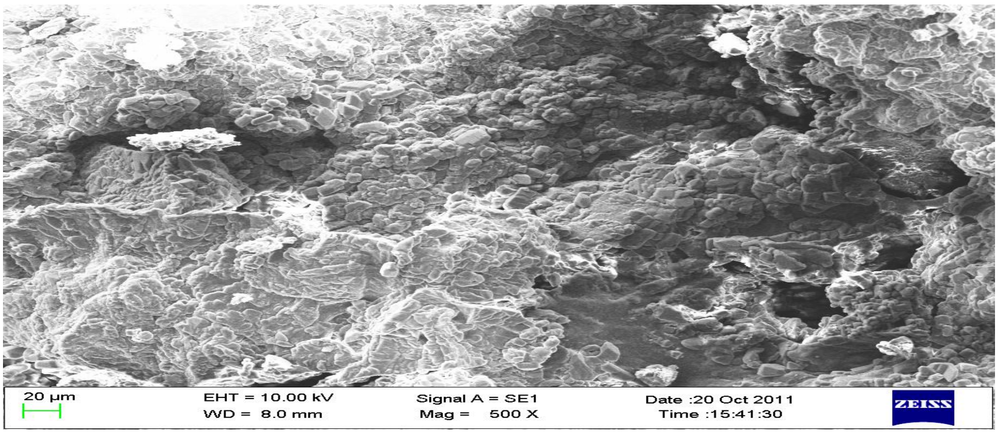


Fig.8 Cardanol-furfural-p-hydroxy benzoic acid.

VII. 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 caradnol – furfural–p-hydroxy benzoic acid. It has been studied from ZEISS instrument from CIPET (LARPM) in fig. (6-8).

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