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POLYMERS FROM RENEWABLE RESOURCES. XI. SYNTHESIS AND CHARACTERIZATION OF THERMOSETTING RESINS DERIVED FROM CARDANYL ACRYLATE-FORMALDEHYDE-SUBSTITUTED AROMATIC COMPOUNDS

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ABSTRACT

A large number of resins have been synthesised by condensing cardanyl acrylate, a derivative of cardanol (a constituent of Cashewnut Shell Liquid) with formaldehyde and substituted aromatic compounds in the presence of acids as catalyst. The resins have been characterized by IR spectra. The thermal behaviour of the resins have also been studied. The kinetic parameters for the degradation of the resins have also been evaluated by using computer analysis, the LOTUS package, method.

INTRODUCTION

In the recent years, the synthesis of polymers from renewable resources has attracted the attention of many research workers (1-4) because of its substitutes for the petrochemical derivatives. Renewable resources means agricultural products i.e. materials that are synthesised by sunlight. One such agricultural product is Cashewnut Shell Liquid (CNSL). The major components of CNSL have been charcterized by Tyman (5) and Verma and coworkers (6) using ultraviolet, infrared, H'-NMR and chromatography. The four major components are cardanol, cardol, anacardic acid and 6-methyl cardol. Mishra and Pandey (7) reported the kinetics of formaldehyde condensation of cardanol. Manjula (8-9) has studied the oligomerization of cardanol using acids as catalysts. The structure of cardanol was reported by Verma and co-workers (6). Sathyalekshmi (10) reported the structure and properties of CNSL-novalac resins prepared by using succinic acid as catalyst. John and Pillai (11) have reported the synthesis of a vinyl monomer, viz. cardanyl acrylate and its suspension polymerization to get crosslinked beads. Nayak and Lenka (12-15) have reported the synthesis and characterization of a large number of resins using multitude of hydroxy aromatic compounds, formaldehyde/furfural and substituted aromatic compounds. They have also reported the synthesis and characterization of resins reacting cardanol with formaldehyde and substituted aromatic compounds in the presence of acids and basesas catalysts. This communication reports the synthesis and characterization of resins obtained by condensation of cardanyl acrylate with substituted aromatic compouds and formaldehyde.

EXPERIMENTAL

Cardanyl acrylate was prepared and purified by the method reported by John and Pillai (11).

Synthesis of Resin : A mixture of cardanyl acrylate (4m mol) substituted aromatic compounds (4m mol) and formaldehyde (40m mol) with 1% hydroquinone was refluxed at 110°C for 4-6 hour in the presence of 2ml of HCl (6N) or H_2SO_4 (6N) with periodical shaking. The physico-chemical properties of the resins are furnished in Table-1. At the end of the reaction, the contents were extracted with ice-cold water, filtered and washed with hot water to remove the unreacted materials. The product was dried in vacuum.

Solvent Absorptivity Behaviour of Resin : Different amounts of resins were stored in 3 ml of different solvents overnight. Excess solvent present on the surface resins was removed with filter paper. Then, it was weighed and absorptivity of solvents (SA%) was calculated using the following equation.

$$SA\% = \frac{W_2-W_1}{W_1} \times 100$$

where W_1 is the weight of dry sample and W_2, the weight after the absorption of solvent. The data are furnished in Table-2.

IR spectra was taken on a Nicolet DX-IR spectrophotometer. Thermal analysis was carried out using a Dupoint 951 thermal analyser at a heating rate of 10°C/min in nitrogen.

RESULTS AND DISCUSSION

The resin copolymer (I) was synthesised by condensing cardanyl acrylate with p-aminobenzoic acid and formaldehyde in the presence of acids as catalyst. The schematic presentation of the preparation of resin copolymer is shown in Scheme-1.

TABLE-1

PHYSICOCHEMICAL PROPERTIES OF RESINS PREPARED FROM CA-FOR-SUBSTITUTED AROMATIC COMPOUNDS.

Sample Resin	% yield	Decomposition Temp.(°C)	Colour	Structure	Solubility
CA-FOR-PHBA^a	75	>250	Black	Crystalline	DMF*, Toluene*
CA-FOR^a	60	>250	Black	Crystalline	DMF*
CA-FOR-PABA^a	72	>250	Black	Crystalline	DMF*
CA-FOR-OCBA^a	61	>250	Black	Crystalline	Toluene*
CA-FOR-$_b$-Naphthol^b	60	>250	Brown	Crystalline	DMF*

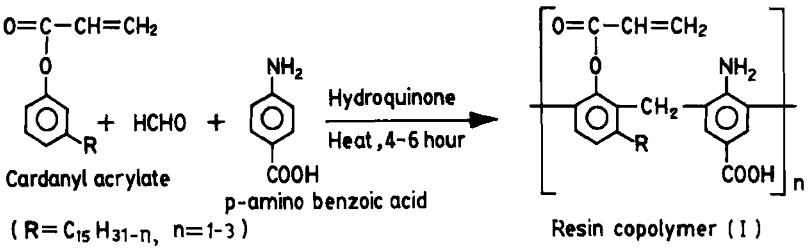
CA - Cardanylacrylate, FOR - Formaldehyde, PHBA - Parahydroxy benzoic acid, PABA - Para amino benzoic acid, OCBA - Orthochloro benzoic acid, a - HCl medium, b - H_2SO_4 medium.
* - Partially soluble.

TABLE-2

SOLVENT ABSORPTIVITY OF RESINS

Name of resin	Name of Solvent					
	DMF			Toluene		
	W_1(mg)	(W_2)mg	SA%	W_1(mg)	W_2(mg)	SA%
CA-OHBA-FOR	400	600	50	600	900	50
CA-FOR	600	800	33.3	400	550	37.5
CA-FOR-PABA	400	550	37.5	300	420	40
CA-FOR-OCBA	450	700	55.5	350	520	50

[CA - Cardanylacrylate, FOR - Formaldehyde, OCBA - Orthochloro benzoic acid, PABA - Para amino benzoic acid, OHBA-Orthohydroxy benzoic acid.]



Scheme I

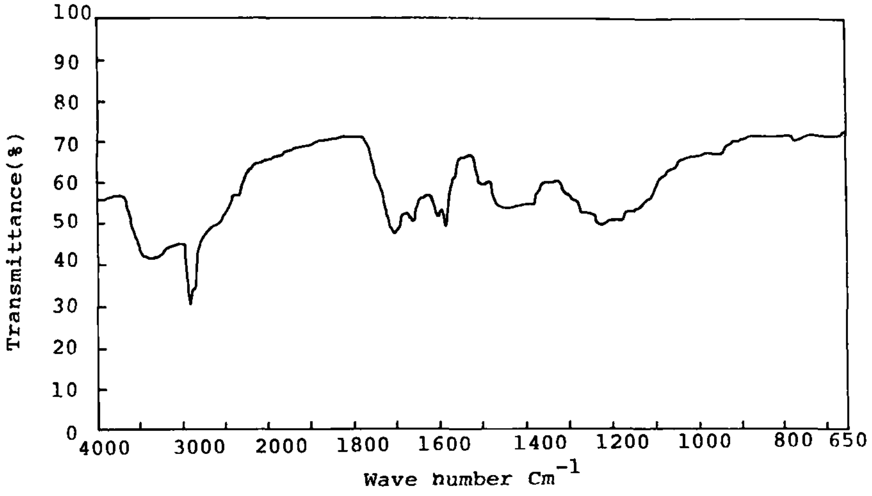


Fig.1 : IR-Spectra of CA-FOR-PABA

IR Study : The IR spectra (fig.1) of the resin copolymer (I) shows a strong peak at 2920 cm^{-1} , which indicates that the -CH- stretching from $-CH_2-$ linkage. A medium band at 3040-3010 cm^{-1} is due to alkene disubstitution. A peak at 3400 cm^{-1} indictes the N-H stretching of the amino ($-NH_2$) group. A band at 1605 cm^{-1} is due to the carboxylate anionic $(-C\overset{O}{\underset{O}{<}}-)$ stretching vibration.

A peak at 1720 cm^{-1} is due to C=O stretching, which is a lower one due to conjugation of the unsaturation with the carbonyl group. A peak at 1660 cm^{-1} is the indication of the double bond of acrylic moiety.

Thermogravimetric Analysis of the Resins : Thermogravimetry is a technique in which the mass of the material under investigation is continuously followed as a function of temperature and time as it is heated or cooled at the predetermined rate. Thermogravimetric analysis of polymers were followed using a computer analysis method, the LOTUS package for assigning the kinetic mechanism. A novel computerised LOTUS method has been applied for the evaluation of the various kinetic parameters. Sbirrazzuole et al (16) have discussed the validity and application of various methods. Nair and Madhu Sundrar (17) have shown a linear relationship between log g(α) and the reciprocal temperature. This procedure has led to a simple application of regression analysis between log g(α) and reciprocal

TABLE-3

KINETIC FUNCTIONS (INTEGRAL DIFFERENTIAL FORMS) USED FOR THE DATA ANALYSIS

Function	Name of the function	g (α)	f (α)	Rate controlling process
MPL^1	Mampel Power Law, n=1	$-\ln(1-\alpha)$	$(1-\alpha)$	Chemical reaction
MPL^0	Mampel Power Law, n=0	α	1	Chemical reaction
$MPL^{1/3}$	Mampel Power Law, n=1/3	$3[1-(1-\alpha)^{1/3}]$	$(1-\alpha)^{1/3}$	Chemical reaction
$MPL^{1/2}$	Mampel Power Law, n=1/2	$2[1-(1-\alpha)^{1/2}]$	$(1-\alpha)^{1/2}$	Chemical reaction
$MPL^{2/3}$	Mampel Power Law, n=2/3	$3/2[1-(1-\alpha)^{2/3}]$	$(1-\alpha)^{2/3}$	Chemical reaction
MPL^2	Mampel Power Law, n=2	$(1-\alpha)^{-1} - 1$	$(1-\alpha)^2$	Chemical reaction
R_2	Contracting Cylinder	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Phase-boundary reaction, symmetry
R_3	Contracting sphere	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Phase-boundary reaction, spherical symmetry.
A_2	Avrami-Erofeev equation(n=2)	$[-\ln(1-\alpha)^{1/2}]$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	Assumes random nucleation and its subsequent growth, n=2.
A_3	Avrami-Erofeev equation(n=3)	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	Assumes random nucleation and its subsequent growth, n=3.
A_4	Avrami-Erofeev equation(n=4)	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	
D_2	Valensi (Barrer) Equation	$\alpha+(1-\alpha)\ln(1-\alpha)$	$[1-\ln(1-\alpha)]^{-1}$	Two dimensional difusion, Cylindrical Symmetry.
D_3	Jander Equation.	$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}$	Three-dimensional diffusion.
D_4	Ginstling-Boknshtein equation	$1-2\alpha/3-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	Three-dimensional diffusion, Spherical Symmetry.

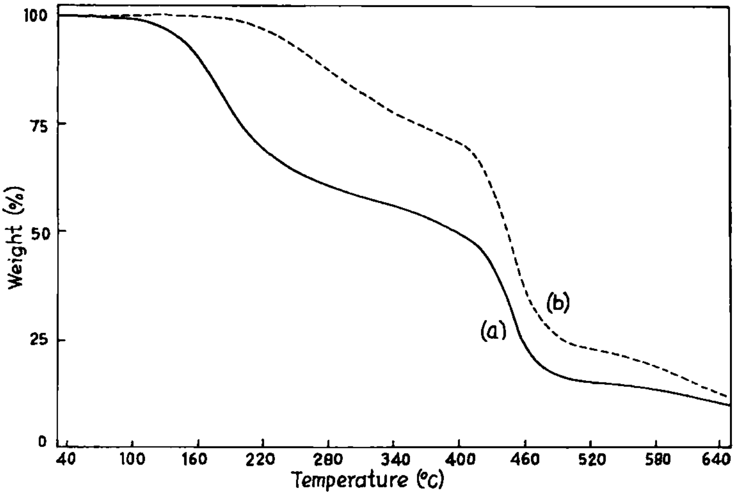


Fig. 2 (a) Thermogram of CA-FOR-OCBA.
(b) Thermogram of CA-FOR.

temperature and assigns the kinetic mechanism to the model with a regression value R close to unity. The program is written using LOTUS-MACROS for analysis of T.G. by fourteen kinetic models given in Table-3. Based on spread sheet analysis, a package for fixing kinetic mechanism for non-isothermal process has been developed. Necessary cell relationships have been used to evaluate different log g(α) for different temperatures.

Regression analysis is carried out for 1/T and log g (α), the regression value is given by;

$$R^2 = \frac{XY-n\bar{X}\bar{Y}}{(X^2-n\bar{X}^2)(Y^2-n\bar{Y}^2)} \qquad (8)$$

Slope is given by $a = \bar{y}-b\bar{x}$ whose $x = 1/T$, $y = \log g(\alpha)$ where n is the number of observations. The mechanism having R^2 close to unity is chosen. The program mainly takes into account the data entry, the temperature range in °C, the rate of heating q and the values. It evaluates the values of log g (α) and 1/T and carries out regression analysis for 1/T vs log g(α). The program gives the results of slopes, constants and R^2 values corresponding to each of the mechanism and also plots graphs for each of the mechanism and prints out the results. We have to use two important methods i.e. Coats and Redfern and L.Riech to calculate the

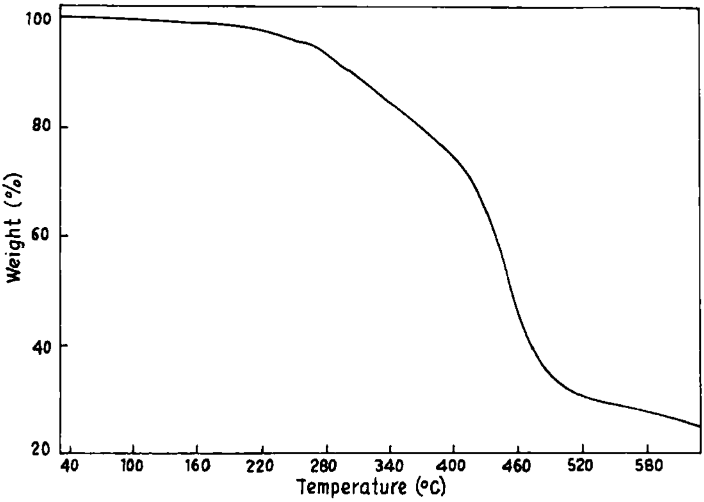


Fig.3 Thermogram of CA-FOR-PHBA.

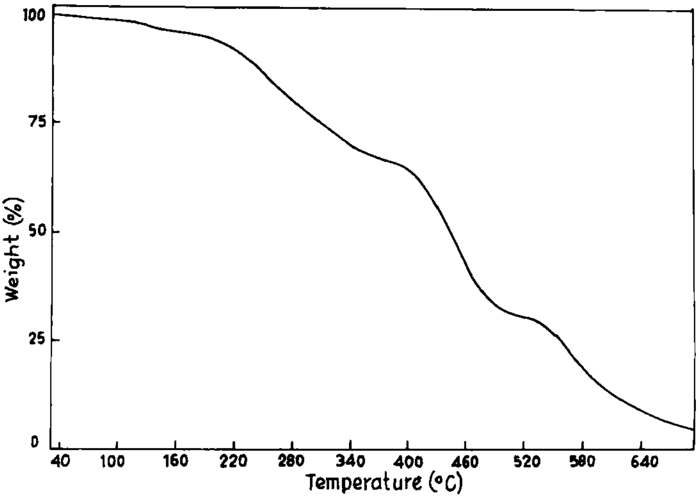


Fig.4 Thermogram of CA-FOR-PABA.

TABLE-4

THERMAL DATA OF RESINS PREPARED FROM CARDANYL ACRYLATE - FORMALDEHYDE - SUBSTITUTED AROMATIC COMPOUNDS

Sl. No.	Name of Resin	Decomposition % at various Temperature Range (°C)					
		100	200	300	400	500	600
1.	CA-FOR-PHBA	3	5	15	33	80	92
2.	CA-FOR	0	3	17	31	76	84
3.	CA-FOR-PABA	3	10	25	35	68	87
4.	CA-FOR-OCBA	3	22	32	51	85	89

TABLE - 5

COATS AND REDFERN TREATMENT OF KINETIC PARAMETERS FOR THE DEGRADATION OF RESINS PREPARED FROM CA-FOR-PHBA

Function	Degradation Temperature Range in °C					
	100-300		310-410		410-600	
	R^2	E	R^2	E	R^2	E
MPL_0	.9646	8.9	.9355	11.9	.9423	7.63
$MPL_{1/3}$	.9844	5.1	.9779	6.1	.6770	1.01
$MPL_{1/2}$	.9852	6.2	.9653	7.7	.6247	1.0
$MPL_{2/3}$	.9827	6.8	.9582	8.6	.6417	2.2
MPL_1	.9782	7.4	.9508	9.6	.8128	3.7
MPL_2	.9072	14.4	.8932	20.5	.9864	2.7
R_2	.9827	6.8	.9582	8.6	.6417	2.2
R_3	.9782	7.4	.9508	9.6	.8128	3.7
A_2	.9447	3.3	.9008	4.6	.8475	2.2
A_3	.8967	1.5	.8283	2.2	.6733	0.5
A_4	.7321	0.62	.6481	1.0	.6605	1.0
D_2	.9889	14.4	.9752	17.8	.6969	4.6
D_3	.9823	17.1	.9607	21.9	.8996	10.4
D_4	.9874	15.34	.9703	19.1	.7966	6.3

E - activation energy (KCal/mole)

TABLE-6

L.RIECH TREATMENT OF KINETIC PARAMETERS FOR THE DEGRADATION OF RESINS PREPARED FROM CA-FOR-SUBSTITUTED BENZOIC ACID.

Sample Resin	Temp. range	Function	R^2	E(Kcal/mole)
CA-FOR-PHBA	100-310	MPL^0	.9920	7.3
	310-410	MPL^0	.9882	8.6
	410-600	MPL^2	.9889	30.3
CA-FOR	170-400	MPL^1	.9846	11.1
	400-470	MPL^0	.9868	13.1
	470-640	$MPL^{2/3}$	.9401	46.3
CA-FOR-PABA	100-220	MPL^0	.9627	4.24
	220-410	D_3	.9860	15.08
	410-570	MPL^0	.9561	5.9
	570-680	MPL^0	.9519	3.09
CA-FOR-OCBA	100-170	MPL^0	.9627	7.66
	170-210	MPL^1	.9776	4.27
	240-450	MPL^0	.9460	5.73
	450-640	$MPL^{2/3}$	.9426	3.52

energy of activation. The equations of the above two methods are represented as :

Coats and Redfern method -

$$\ln[G(\alpha)/T^2] = \ln \frac{A.R}{\beta E} \left(1- \frac{2RT}{E}\right) - E/2.3\ R \times 1/T$$

where = Rate of heating, R = Gas constant, A = Z = Collision frequency factor, E = Activation energy, 'E' is calculated from the straight line obtained by plotting ln (α/T^2) vs 1/T and ln A can be obtained from the intercept.

L-Reich Equation

$$\ln[G(\alpha)] = -E/R \times \frac{1}{T} + \ln \left[R/E \times \frac{A}{\beta} \times T_n^2\right]$$

where n' is the number of observations. The thermograms of four typical resins are presented in (fig. 2-4). The data showing the percentage of decomposition at various temperature ranges are furnished in Table-4.

The Table-5 gives the Coats and Redfern treatment of kinetic parameter for the degration of the resin prepared from cardanylacrylate - formaldehyde - parahydroxy benzoic acid.

A perusal of the results in Table-6 (L-Riech treatment of the kinetic parameters for the degration of resins) indicates that the resins decompose in three distinct stages. Taking the example of cardanyl acrylate - formaldehyde, it is seen that the first step is very fast and the last step is the slowest one. This is obvious considering the mechanism of the degradation of resins. The first step is the removal of water molecule absorbed in the resin.

In the last step, the degradation of resins takes place, which is very complicated and likely to be slow.

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