Polymers from Renewable Resources. V. Synthesis and Characterization of Thermosetting Resins Derived from Cashew Nut Shell Liquid (CNSL)-Furfural-Substituted Aromatic Compounds

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SYNOPSIS

A number of resins were synthesized by reacting cardanol, a byproduct of the cashew industry, with furfural and substituted aromatic compounds in the presence of acid and basic catalysts. The resins were characterized by IR and NMR spectra 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. A plausible degradation mechanism is suggested. © 1994 John Wiley & Sons, Inc.
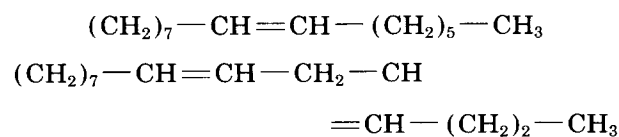
INTRODUCTION

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.[1-8] By renewable resource is meant agricultural products, i.e., materials that are synthesized by sunlight. One such agricultural product is cashew nut shell liquid[9-17] (CNSL), which is a byproduct 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 western and eastern coasts of India. The state of Orissa has a vast coastal area situated onside the Bay of Bengal and cashew trees are abundantly grown in this coastal region.
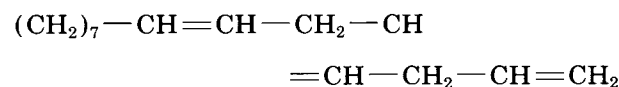
The major components of CNSL have been characterized by Tyman,[18] Murthy et al.[19] and Varma and co-workers[20] using ultraviolet, infrared, ^{1}H-NMR, and chromatography.[21,22] CNSL contains four major components, i.e., cardanol, cardol, anacardic acid, and 6-methyl cardol, whose structures are given below:

Anacardic Acid   Cardanol   Cardol   6 methyl Cardol
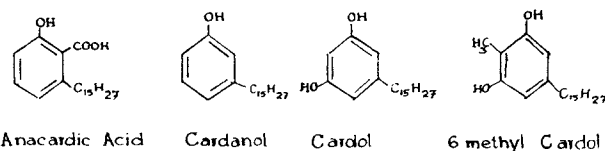
Of the above four components, anacardic acid is the most important component of CNSL. Anacardic acid decarboxylates on heating to give cardanol or 3-pentadecadienyl phenol. The side-chain C_{15} could be $(CH_2)_{14}-CH_3$:

$$(CH_2)_7-CH\!=\!CH-(CH_2)_5-CH_3$$
$$(CH_2)_7-CH\!=\!CH-CH_2-CH$$
$$=\!CH-(CH_2)_2-CH_3$$

or

$$(CH_2)_7-CH\!=\!CH-CH_2-CH$$
$$=\!CH-CH_2-CH\!=\!CH_2$$

Although a variety of R groups could be possible, all have *meta* substitution and a 15-carbon chain length. Tyman and Jacobs[21] showed that the relative proportion of unsaturated components of anacardic acid are mono-ene (38.7%), di-ene (16.3%), and tri-ene (45.1%). Hence, cardanol is a potential re-

newable monomeric source for the synthesis of a variety of speciality polymers. Many patents and reviews have been published on cardanol-based polymers.[23-26]

CNSL and its polymeric products find a wide variety of applications in industry. Polymeric products include friction-lining materials, surface coatings, paints and primers, varnishes, lacquer specialty coatings, adhesives, and binders. CNSL also has been used as a basic raw material for a vast number of industrially important chemical and chemical intermediates. A few of these includes fungicides, bacteriocides, and insecticides.

Recently, Varma and co-workers,[20] on the basis of the fragmentation pattern of mass spectra and NMR spectra, predicted the structure of cardanol to be
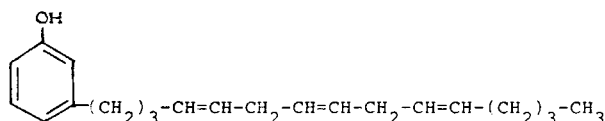
This is a phenolic compound having free *ortho* and *para* positions that could be used for the manufacture of a large number of phenolic resins for many uses. O'Connor and Blum[25] reported on the thermal stability of some resins by condensing cardanol with formaldehyde. Pillai and co-workers[24] reported on GPC studies on the cationic polymerization of cardanol initiated by borontrifluoride diethyl etherate. Pillai and co-workers[23] also reported on the synthesis and characterization of flame-retardant polymers from cardanol. Misra and Pandey[27] reported on the kinetics of the formaldehyde condensation of cardanol. Manjula[17] studied the oligomerization of cardanol using an acidic catalyst such as sulfuric and phosphoric acid and reported that BF_3OEt_2 is a good cationic initiator for the polymerization of cardanol. Recently, Sathiyalekshmi[26] reported on the structure and properties of CNSL–novalac resins prepared using succinic acid as the catalyst. Nayak and co-workers[28-40] reported on the synthesis and characterization of a large number of resins using a multitude of hydroxy aromatic compounds, formaldehyde/furfural, and substituted aromatic compounds in the presence of acids and bases as catalysts. They also reported on the thermal, ion-exchange properties, and microbiological properties of the resins.

This laboratory has taken up a project for the preparation of a large number of phenolic resins from renewable resources using cardanol as the base material to study their thermal, ion-exchange, and antimicrobial properties. It has also been planned

to use furfural for the synthesis of resins. Furfural, a renewable resource, is produced from vegetable waste like cane sugar, bagasse, rice hulls, maize cobs, and other such cellulosic waste materials. This communication presents the results of the resins synthesized by condensing cardanol, furfural, and hydroxy aromatic compounds as the comonomer in the presence of hydrochloric acid or certain bases as the catalyst. The IR and NMR spectra of the resins have been studied in order to ascertain the structure of the resin copolymers. The ion-exchange and the thermal properties of the resins are reported on herein.

EXPERIMENTAL

Cashew nut shell liquid (CNSL) was obtained from Kerala Cashew Development Corp. Quinol, India. Cardanol was obtained by double vacuum distillation of CNSL at 3–4 mm Hg and the fraction distilled at 230–240°C was collected. The saponification value, iodine value, viscosity, specific gravity, and moisture content were determined by the standard procedure (ISI-standard 840-1964) and are reported in Table I.

Synthesis of Resins

A mixture of cardanol (4 mmol), substituted aromatic compound (4 mmol), and furfural (40 mmol) was refluxed at 120°C for 5–7 h in the presence of 4N NaOH (2 mL) 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 as the catalyst. The physicochemical properties of the resins are shown in Table II.

Characterization of Resins

The hydroxy group content was estimated by acetylation with acetic anhydride/pyridine. The iodine

Table I   Properties of Cardanol and CNSL

Properties	CNSL	Cardanol
Color	Dark brown	Dark brown
Specific gravity	0.965	0.870
Viscosity	226	39
Saponification value	122	23
Iodine value	276	275
Moisture content	2.2	2.4

Table II Physicochemical Properties of Resins Prepared from Cardanol–Furfural–substituted Aromatic Compounds

Sample No.	Name of Comonomer	Catalyst Used	Yield (%)	Decomposition Temp (°C)
SCF 1	p-Hydroxyacetophenone	HCl	80	> 360
SCF 2	o-hydroxybenzoic acid	NaOH	70	> 360
SCF 3	p-methylbenzoic acid	HCl	75	> 360
SCF 4	Acetylsalicylic acid	HCl	75	> 360
SCF 5	p-Aminobenzoic acid	NaOH	60	310
SCF 6	o-chlorobenzoic acid	HCl	75	> 360
SCF 7	o-Aminobenzoic acid	HCl	75	> 360
SCF 8	Phenolphthaline	HCl	70	> 360
SCF 9	p-Chlorobenzoic acid	HCl	70	> 360
SCF 10	2-4-Dihydroxyacetophenone	HCl	75	> 360
SCF 11	p-Hydroxybenzoic acid	HCl	70	> 360
SCF 12	o-Hydroxyacetophenone	HCl	75	> 360
SCF 13	p-Hydroxybenzoic acid	NaOH	60	280
SCF 14	o-Hydroxybenzoic acid	HCl	65	> 360
SCF 15	α-Naphthol	HCl	70	> 360
SCF 16	Resorcinol	HCl	70	> 360
SCF 17	Bisphenol-A	HCl	80	> 360
SCF 18	Bisphenol-A	NaOH	60	310
SCF 19	β-Naphthol	HCl	65	> 360
SCF 20	p-Aminobenzoic acid	HCl	70	> 360

value was determined using Wiji's method. The IR spectrum was taken using a Nicolet DX-FTIR spectrophotometer. The thermal behavior was assessed on a DuPont 951 thermal analyzer at a heating rate of 10°C/min in air.

RESULTS AND DISCUSSION

Infrared Studies

The polycondensation reaction of cardanol with furfural and para-hydroxyacetophenone may be represented as follows:
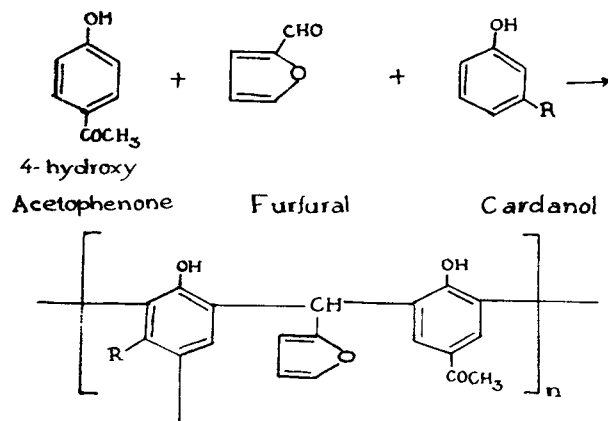

The IR spectrum of one of the resin copolymers prepared by condensing cardanol, furfural, and the

substituted hydroxy aromatic compound is shown in Figure 1. The structure of the repeat units as represented above were identified from the IR spectra of the copolymer. The bands in the region 3300–3421 cm^{-1} indicate the presence of the hydroxyl group. The peaks at 1605–1700 cm^{-1} are assigned to the

stretching of the
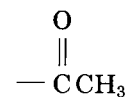
group. The strong intensity peak at 1580 cm^{-1} is due to the vibration of the aromatic —C=C— linkages. The peak in between 2925 and 3003 cm^{-1} is due to —CH— stretching of the furanyl ring. The presence of a medium-intensity band at 920 cm^{-1} is due to a trans double bond in aliphatic side chains of the cardanol moiety. The peak around 699–703 cm^{-1} is due to the —CH— out-of-plane bending in a monosubstituted furanyl ring.

¹H-NMR Study

The NMR spectrum of the copolymer prepared by condensing cardanol with substituted hydroxy aromatic compounds and furfural was determined in
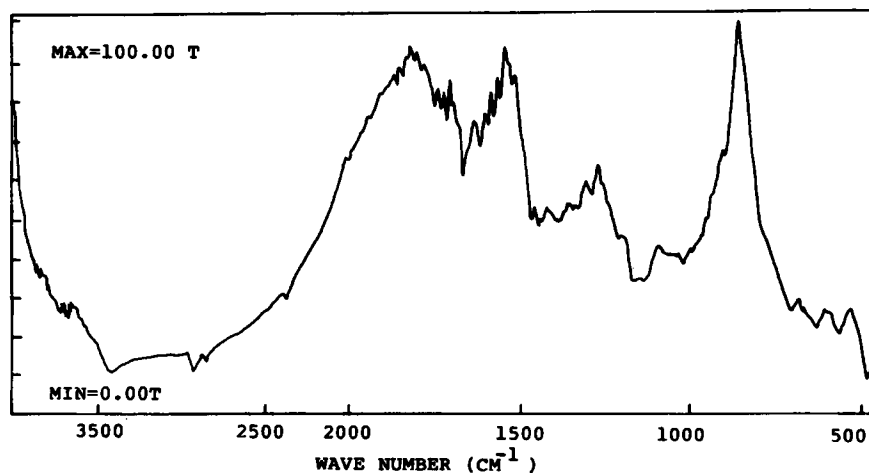
Figure 1   IR spectrum of SCF-1 copolymer (cardanol-furfural-p-hydroxyacetophenone).

CDCl$_3$. The NMR spectrum showed the presence of aromatic protons and methyl protons. Aromatic protons appeared as a multiplet in the range 6.65–7.72 ppm. Olefinic protons appeared in the range 4.93–5.45 ppm. Methylene protons appeared in the range 0.83–2.77 ppm. The peaks around the region 6.4 ppm are due to the phenolic hydroxyl group. The peak at 5.1 ppm is due to the methylene proton of long alkyl side chain. The peaks around 0.4–2.4 ppm are due to the aliphatic long chain of the cardanol moiety. The small peak at 0.8 ppm represents the terminal methyl group of the chain.

Ion-exchange Properties of the Resins

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 used in the present investigation for this study.

Effect of Electrolyte on the Metal Uptake

The effect of different electrolytes, such as chloride, sulfate, and nitrate ions at various concentrations, on uptake of several metal ions by the resin copolymer is furnished in Table III. Perusal of the results (Fig. 2) indicates 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 sulfate ion. These trends may be explained in the light of the stability constants of these complexes. The sulfate ion might form rather strong chelates with the above metal

ions, whereas the other ions under investigation form weak chelates and, therefore, might not be expected to influence the position of metal chelate equilibrium to the extent to be expected by the sulfate ion.

Rate of Metal Uptake

The dependence of the rate of the metal-ion uptake on the nature of the metal ion is represented in Table IV. The rates of metal adsorption of the resins were determined to find the shortest time period for which equilibrium could be established. The results indi-
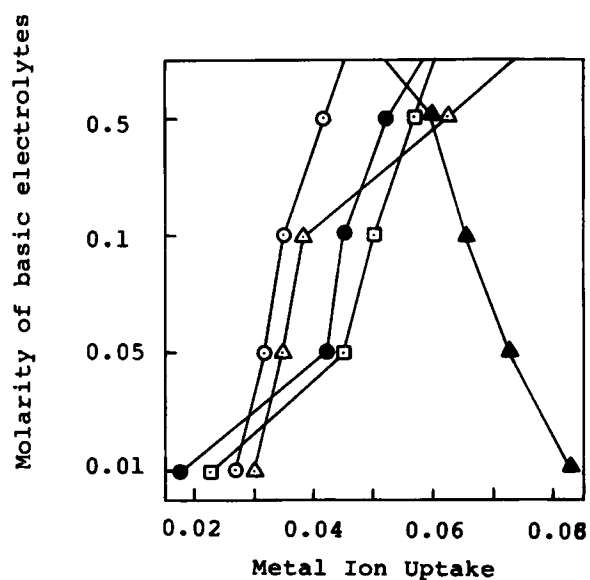

Figure 2   Millimoles of Cu^{2+} per 25 mg of SCF-2 resin. Adsorption of Cu^{2+} by cardanol-furfural-o-hydroxybenzoic acid resin.

Table III   Evaluation of the Effect of Different Electrolytes on Uptake of Several Metal Ions[a]

Sample No.	Metal Ion	Electrolytes (mol/L)	pH	Weight (mmol) of Metal Ion Uptake in Presence of				
				$NaNO_3$	NaCl	KNO_3	KCl	Na_2SO_4
SCF 2	Cu^{2+}	0.01	10	0.0277	0.0302	0.0176	0.023	0.0831
		0.05		0.0327	0.0327	0.0428	0.0453	0.0730
		0.1		0.0352	0.0378	0.0452	0.0504	0.0655
		0.5		0.0428	0.063	0.0529	0.0579	0.0604
SCF 2	Zn^{2+}	0.01	6	0.0182	0.0182	0.0156	0.0156	0.0520
		0.05		0.0234	0.0208	0.0338	0.0208	0.0416
		0.1			0.0312	0.0442	0.0260	0.0390
				0.0312				
		0.5		0.0364	0.039	0.0494	0.0312	0.0280
SCF 2	Co^{2+}	0.01	6	0.0273	0.0182	0.0139	0.0205	0.0364
		0.05		0.041	0.0228	0.0208	0.025	0.025
		0.1		0.0433	0.0342	0.0232	0.0319	0.0228
		0.5		0.0592	0.0387	0.0278	0.0387	0.0159
SCF 2	Mg^{2+}	0.01	10	0.0105	0.0105	0.008	0.0134	0.0182
		0.05		0.0124	0.0124	0.0105	0.0153	0.0144
		0.1		0.0144	0.0134	0.0124	0.0158	0.0134
		0.5		0.0153	0.0144	0.0134	0.0211	0.0105
SCF 2	Mn^{2+}	0.01	10	0.121	0.1342	0.1276	0.1474	0.1408
		0.05		0.1342	0.1386	0.1364	0.143	0.1342
		0.1		0.1386	0.1464	0.1386	0.1408	0.1272
		0.5		0.1408	0.1474	0.1452	0.154	0.1232

[a] Volume of electrolyte solution = 25 mL; time = 24 h; volume of metal ion solution = 1 mL; room temperature $[M(NO_3)_2]$ = 0.1 mol/L.

cate that different ions require different time periods for the establishment of equilibrium. The rates of metal uptake follow the order $Cu^{2+} > Mn^{2+} > Co^{2+} > Mg^{2+} > Zn^{2+}$ and are shown in Figure 3.

Distribution of the Metal Ion at Different pH Levels

Table V represents the effect of pH on the distribution ratios of the metal ions between an aqueous solution and the CNSL resin. The data indicate that the relative amount of the metal ion taken up by the copolymer increases with increase in pH of the medium (Fig. 4). The investigation was carried out up to a definite pH value for a particular metal ion to prevent the hydrolysis of metal ions at higher pH. All the ions have low distribution ratios at pH 4. This may be attributed due to a low stability constant.

The results of this study are helpful in selecting

Table IV   Comparison of Rates of Metal-ion Uptake in Different Time[a]

Sample No.	Metal Ion	% of Metal-ion Uptake at Different Times (h)					
		0.5	1	2	4	6	8
SCF 2	Cu^{2+}	55.84	61.79	67.64	82.35	91.12	94.15
	Co^{2+}	31.31	37.36	56.31	68.69	75	87.63
	Zn^{2+}	7.14	21.42	28.85	35.71	50	63.31
	Mn^{2+}	7.54	9.43	16.98	81.11	84.90	90.56
	Mg^{2+}	12.41	24.83	37.25	56.20	68.62	81.04

[a] (mmol metal ion adsorbed ×100)/(mmol metal ion adsorbed at equilibrium); $[M(NO_3)_2]$ = 0.1 mol/L; volume = 1 mL; $NaNO_3$ = 1 mol/L; volume = 25 mL room temperature.
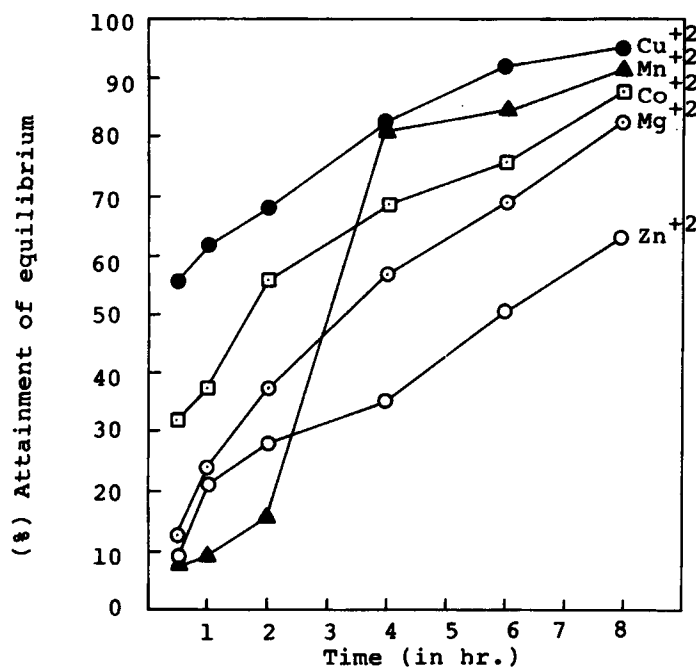
Figure 3   Rates of metal uptake of cardanol–furfural–o-hydroxybenzoic acid resin for 0.1M solution of Mn^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, and Zn^{2+} nitrate.

the optimum pH for selective uptake of a specific metal ion from mixtures of different ions.

Thermogravimetric (TG) Analysis of the Resins

The TG thermogram of eight resin copolymers are represented in Figures 5 and 6 to give a comparative picture regarding the thermal stability of the resin copolymers. The characteristic thermal data are represented in Table VI with the weight loss at different temperatures and decomposition ranges.

A cursory glance at Table VI indicates that all the resins under investigation decompose in three distinct stages. About a 10% weight loss occurs for all the resins up to 200°C. This may be attributed to the moisture retained in the sample. Except for the resin prepared by condensing cardanol–furfural–*para*-methylbenzoic acid, all the seven resins reported in Table VI decompose by about 20% at 300°C. The resin prepared by condensing cardanol–furfural–*ortho*-hydroxybenzoic acid decomposes very rapidly thereafter: 60% at 400°C and 75% at 500°C. All other resins decompose about 40–60% at about 500°C. All the resins degrade very quickly after 500°C, and 100% decomposition occurs around 600°C.

On the basis of the above observed trend in weight loss with temperature, a plausible degradation mechanism of the resins prepared by condensing cardanol–furfural-substituted aromatic compounds

may be represented as consisting of three steps, viz.: (a) chain fragmentation and postcuring controlled by the unreacted methylol groups; (b) thermal reforming, controlled by the free radicals formed; and
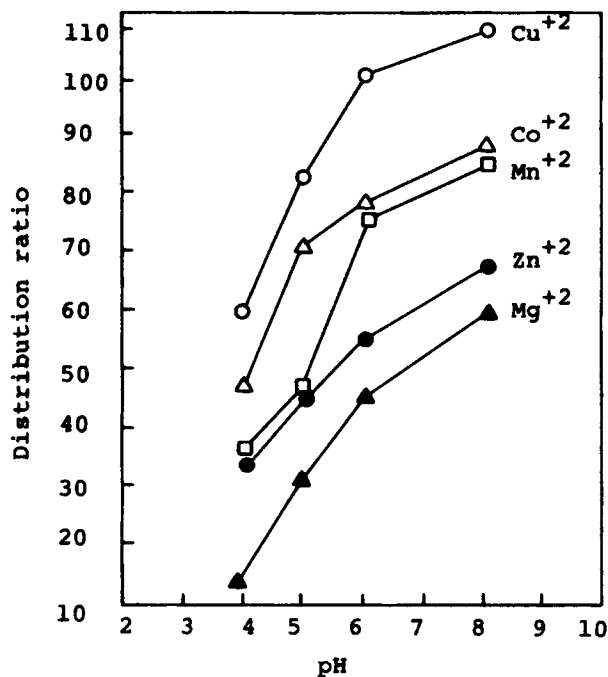

Figure 4   Distribution ratio of Co^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, and Mg^{2+} nitrates at different pH.
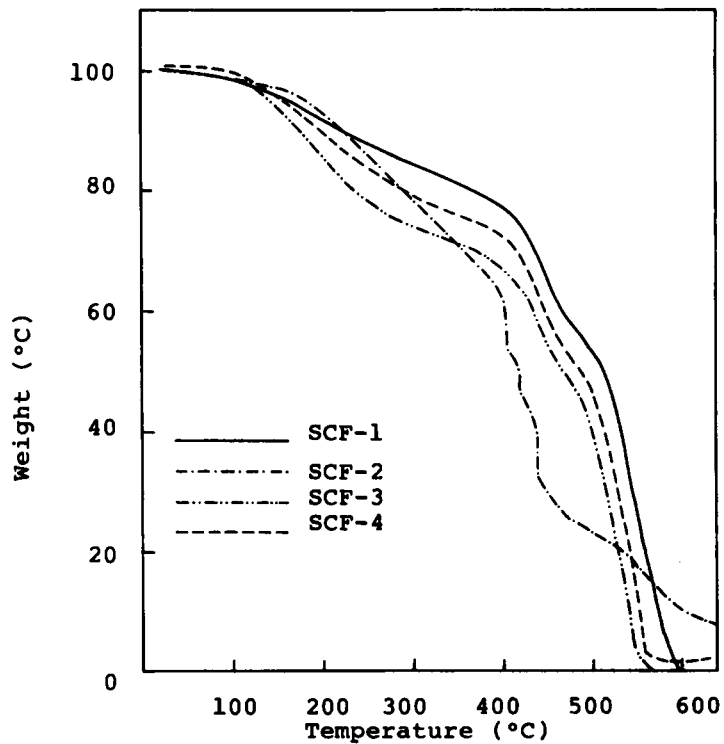
Figure 5   TG thermogram of copolymers.

(c) ring stripping, depending upon the elemental composition.

O'Connor and Blum[25] reported on the thermal analysis of some phenol–formaldehyde resins along with the cardanol–formaldehyde resins. Phenolic resins decompose at higher temperatures than do
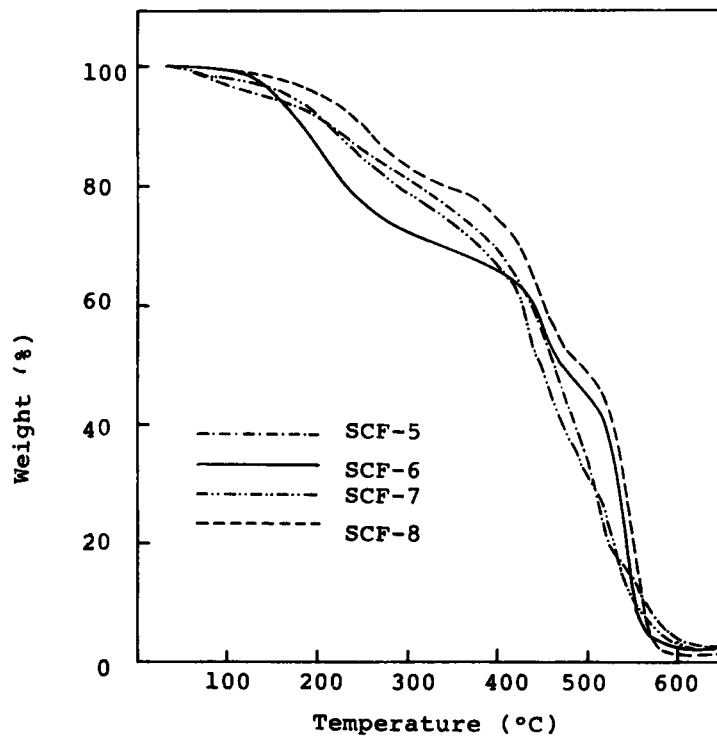

Figure 6   TG thermogram of copolymers.

Table V Distribution Ratio "D^*" of Different Metal Ions as Function of pH

| Sample No. | Metal Ion | Distribution Ratio of the Metal Ions at Different pH | | | |
		pH 4	pH 5	pH 6	pH 8
SCF 2	Cu^{2+}	60	82.21	100	108
	Co^{2+}	47.3	71.9	78.9	87.7
	Mn^{2+}	36	47.2	76.0	87.2
	Zn^{2+}	35.3	47.6	55.3	67.6
	Mg^{2+}	12	31.6	47.9	60.0

$$D^* = \frac{\text{mmol metal ion on the copolymer}}{\text{mmol metal ion in solution}} \times \frac{\text{volume of solution}}{\text{weight of copolymer}} ;$$

$[M(NO_3)] = 0.1$ mol/L; volume = 1 mL; $NaNO_3 = 1$ mol/L; volume = 25 mL; time = 24 h; room temperature.

Table VI Characteristic Thermal Data of the Resin Copolymers

| Sample No. | Decomposition Range (°C) | | | % of Weight Loss (±2%) up to Various Temperatures (°C) | | | | | |
	First	Second	Third	100	200	300	400	500	600
SCF 1	0–200	200–400	400–600	0	8	16	20	40	100
SCF 2	0–200	200–400	400–700	0	5	8	60	75	90
SCF 3	0–200	200–400	400–600	0	10	30	40	60	100
SCF 4	0–200	200–400	400–560	0	8	20	22	44	100
SCF 5	0–200	200–400	400–600	0	8	15	25	60	100
SCF 6	0–200	200–400	400–600	0	8	22	32	45	98
SCF 7	0–200	200–400	400–600	0	2	12	22	58	97
SCF 8	0–200	200–400	400–600	0	2	10	22	40	99

the cardanol-based resins. The thermal degradation pattern of phenol–formaldehyde resins has been thoroughly studied. The degradation takes place in two stages: The reaction is reported to take place through a thermooxidation process. Manjula et al.[41] reported that the decomposition temperature for 10 and 50% cardanol–formaldehyde and phenol–formaldehyde resins are 340 and 480°C and 485 and 830°C, respectively. This indicates that cardanol-formaldehyde has very poor thermal stability, poorer than that of phenol–formaldehyde resins. The difference in thermal stability is due to the structural difference of these two types of compounds. In the case of cardanol, there is a long hydrocarbon chain with a double bond (mono-ene) at the meta position. The degradation of this long hydrocarbon chain occurs at a very low temperature. By comparing the cardanol–formaldehyde thermogram with the cardanol-furfural thermogram, it is seen that the resin containing the furfural moiety decomposes at a relatively higher temperature than does the cardanol–

formaldehyde resin. This is because the furfural moiety in the resin backbone is more stable than is the methylene bridge present in the case of the formaldehyde resin.

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