International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 382-393, 2017

Thermal and Kinetics studies of diazotised resins from renewable resource

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Abstract : As an alternate to the use of conventional reinforcing synthetic resins, biobased resins were synthesized from renewable resources such as cardanol and furfural. Cardanol is the meta- substituted phenolic compound isolatedfrom cashew nut shell liquid (CNSL), a byproduct of cashew industry. P-chloroaniline has been diazotised and coupled with cardanol to prepare diazotised p-chloroanilinecardanol dye (bio monomer). The obtained dye has been condensed with furfural inpresence of 3N.H_2SO_4 to give diazotized p-chloroanilinecardanol furfural (homo polymer) resin.The condensedresin has been allowed to react with urea, ethylene glycol, resorcinol and o-hydroxy benzoic acid to form various copolymer resins. These resins have been characterized by Fourier Transform-Infrared spectroscopy (FT-IR),^{1}H-Nuclear Magnetic Resonance spectroscopy (^{1}H-NMR),X-ray diffraction (XRD), Thermogravimetric Analysis (TGA) and Differential thermal analysis (DTA)studies.XRD techniques are used to distinguish the state of polymer, i.e. crystalline or amorphous etc., to calculate percentage crystallinity. The energy of activation for different stages of polyurethane degradation is determined by Coats-Redfern integration method which involves different kinetic models.

Keywords : cardanol, crystallinity, X-Ray diffraction, energy of activation.

Introduction

Newer moleculesincluding small molecules and polymers, identified from renewable resources have attracted muchattention recently because oftheir ease, yearly renewability, high similarity and potential biodegradability[1].Among different renewable resources, cashew nut shell liquid (CNSL), a naturally occurring phenols and furthermore highabundantand agricultural by-product in tropical countries including India.CNSL can be regarded as a multipurpose and vital raw material for wide applications in the form of brake linings, surface coatings, paints, and varnishesas well as in polymer production [2].Variousresearchers have starting at now analysed its extraction [3], chemistry and composition [4]. As per literature, CNSL is already in use in the manufacture of peculiar phenolic resins for lamination and as friction materials [5].CNSL can conceivablysupplant phenol in numerous applications with equivalent or better outcomes. CNSL contains four major components namely, 3-pentadecenyl phenol (cardanol), 5-pentadecenyl resorcinol (cardol), 6-pentadecenyl salicylic acid (anacardic acid) and 2-methyl-5-pentadecenyl resorcinol (2-methyl cardol).

Cardanol is a byproduct from the cashew processing industry and is the principle constituent of CNSL [6]. With its reactive functional benzene ring, phenolic hydroxyl and unsaturated alkyl chain group, cardanol serves as a natural and renewable chemical feedstock to fine chemical products, such as solvents, paints, varnishes, surfactants, plasticizers [7],friction materials [8], andflame retardants [9].Manjula et al.[10] studied the kinetics and mechanism of oligomerization of cardanol over acid catalysts. Nayak and co-workers [11] have reported the synthesis and characterization of a large number of resins using a multitude of hydroxy aromatic compounds, formaldehyde/furfural, and substituted aromatic compounds. Mohapatra et al. [12] have studied the thermal properties of resins derived from 4-hydroxy acetophenone-furfural-substituted benzoic acids. Swain et al. [13] have also reported the synthesis and characterization of cardanol based resins in the presence of acids and bases as catalyst. Resins derived from CNSL/cardanol are widely employed in the field of surface coatings, adhesives, and laminates, and have various miscellaneous applications [14]. The synthesis of cardanol–formaldehyde resins have been reported earlier[15].However, these have some limitations, like weak chemical stability, low flexibility, and weak impact resistance [16].Therefore, the cardanol–formaldehyde resins may be further modified by replacing formaldehyde with furfural in the presence of a relevant catalyst to improve the chemical and mechanical stability of such cardanol based resins.Furfural, the heteroaryl aldehyde, is obtained as an agricultural waste product which has anconsiderable application in the formation of resins [17]. Moreover, furfural, being aproduct of vegetable origin and availablein virtually unlimited quantities, is a much more cost-effective aldehyde than formaldehyde.Numerous resins have been prepared by using cardanyl acrylate and furfural in the presence of an acid catalyst and a selective organic compound, and their thermal propertieshave been studied [18].The mechanical and thermal properties of cardanol–furfural resins were found to be superior when compared with the literature[19,20]on phenol–formaldehyde resins.However, reports regarding the diazotized cardanol furfural resins are verydefined. In the present study, diazotized p-chloroanilinecardanol furfural resin has been synthesized and characterized. Further thermal and kinetic studies on the synthesized resins also evaluated

Materials and methods

Cardanol was obtained from M/s Satya Cashew Chemicals Ltd, Chennai, Furfural (A.R. grade, 99 %) was obtained from M/s Qualikems Fine Chemicals Pvt. Ltd., New Delhi, India was used for formulation. Sodium nitrite, potassium hydroxide and methanol were received from M/s BDH Ltd (India). O-hydroxy benzoic acid, resorcinol, urea & ethylene glycol were received from E.Merck, (Germany).The chemicals were used as received. Infrared spectra were taken in a Shimadzu-FT-IR spectrophotometer by KBr pellet method. ^{1}H-NMR spectra were recorded using Bruker300 MHz ^{1}H-NMR spectrometer. XRD patterns of the resins were collected using a PANalytical X'Pert Pro MPD θ/θ goniometer with Cu-Kα radiation, and fixed slit incidence (0.5 deg. divergence, 1.0 deg, anti-scatter, specimen length 10 mm) and diffracted (0.5 deg anti-scatter, 0.02 mm nickel filter) optics. Percentage of crystallinity[21] and crystalline index [22] were calculated using the following equation:

$$\text{Percentage of crystallinity } (X_c) = \frac{I_c}{I_c + I_a} X\ 100$$

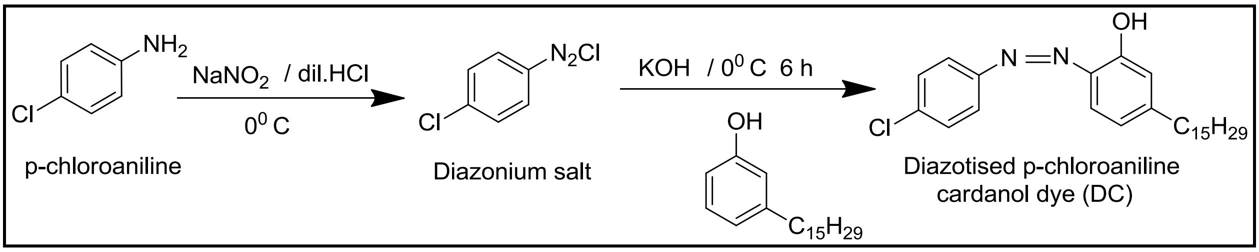
$$\text{Crystallinity Index (CI) } = \frac{I_c - I_a}{I_c}$$

where$I_c$and I_a are the intensity of crystalline and amorphous peaks.

TGA and DTA of all resins have been performed at a rate of 20 °C/min in nitrogen using a Universal V4-3A TA instrument (model SDTQ 600). Thermograms were interpreted and analyzed to obtain information about thepercentage weight loss at varioustemperatures. The kinetic parameters and the activation energy (Ea) have beencomputedfrom the data obtained from the thermograms. It helps us to determine the thermal stability of resins.

Synthesis of diazotised p- chloroanilinecardanol dye (DC)

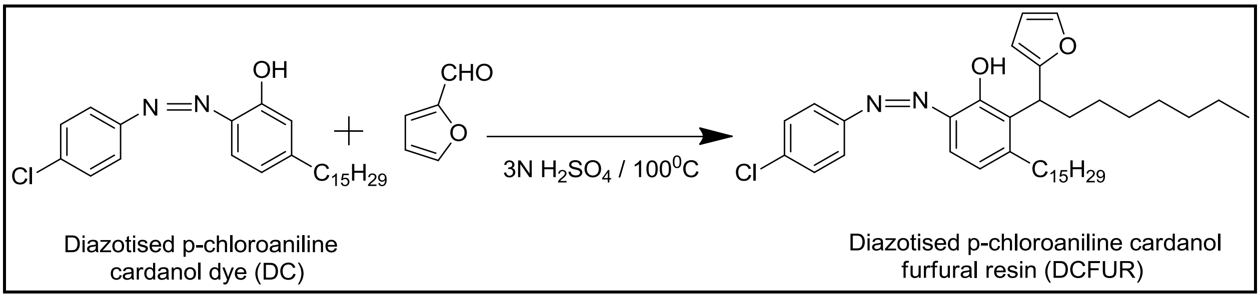
2.2 g of p-chloroanilinein 10ml con.HCl and 10ml hot distilled water was added with 1.2 g of sodium nitrite solution in water at 0 °Cand stirred for 5 mins at that temperature. To the above, 5 g of cardanol, dissolved in an ice cold solution of alcoholic potassium hydroxide, was added in drops. Then thereaction mixturewas stirred for 6 hours at room temperature which yielded a red colored diazotised p-chloroanilinecardanol dye (biomonomer). Then the red dyewas washed thoroughly with water and dil.HCl and then dried at room temperature. The resulting red colored dye (DC) was recrystallized using methanol-water mixture.



Synthesis of biomonomer DC

Synthesis of diazotised p- chloroaniline cardanol furfural resin (DCFUR)

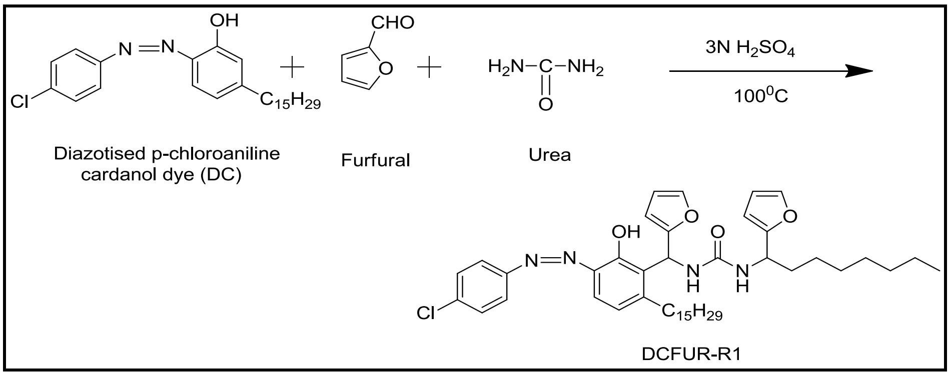
2.15 g of DC was treated with 3 ml of furfural in presence of 2 ml of 3N H_2SO_4at 100 °C for 6 hours. A dark reddish black colored resin, (diazotised p-chloroaniline cardanol furfural resin-DCFUR) obtained was dried in air after thoroughly washed with dil NaOH.



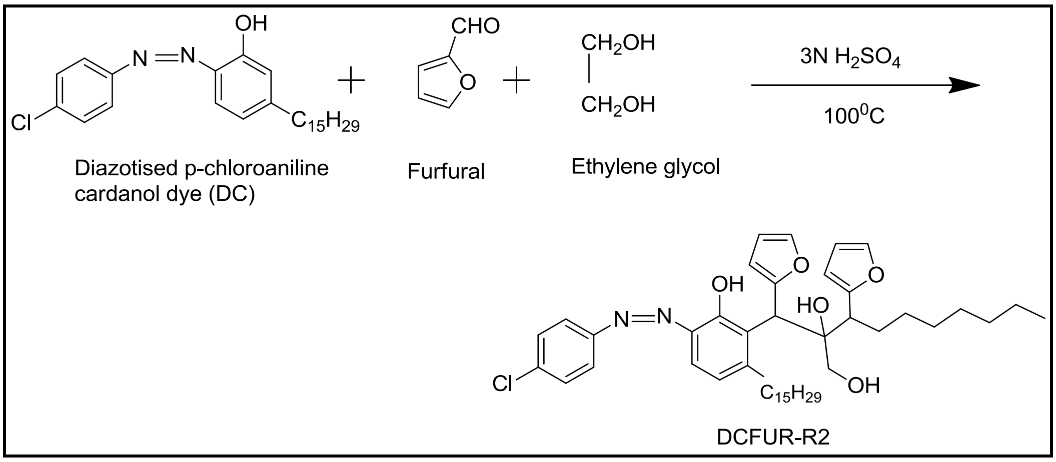
Synthesis of homopolymer resin DCFUR

Synthesis of diazotised p- chloroaniline cardanol - furfural organic compound resins

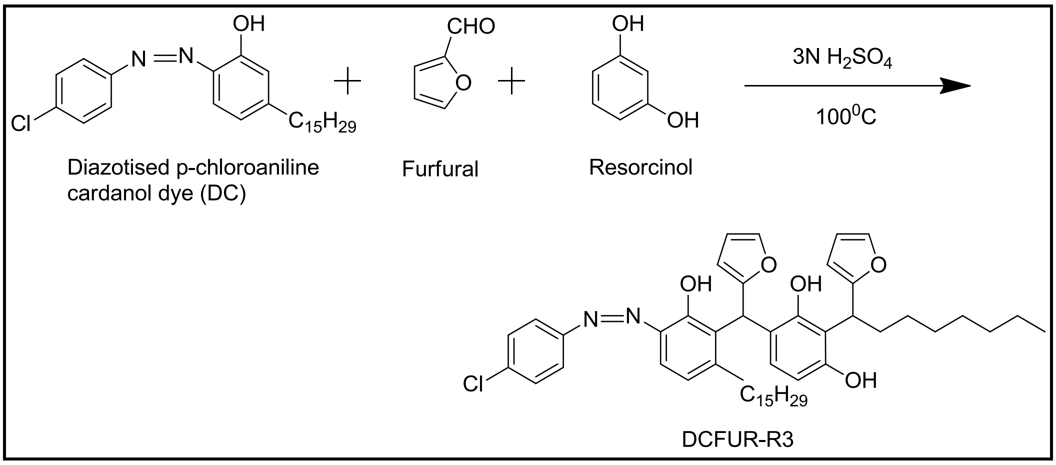
2.15 g of DC was stirred with3 ml furfural and 0.54 g ureain presence of 2 ml 3N H_2SO_4 at 100 °C using mechanical stirrer for about 6 hours. The resulted copolymer resin (DCFUR-R1) was dried in vacuum at room temperature after washed well with dil.NaOH and then with hot distilled water. Three more resins wereprepared using of 0.75 g of ethylene glycol (DCFUR-R2), 0.52 g of resorcinol (DCFUR-R3) and 0.76 g o-hydroxy benzoic acid (DCFUR-R4) instead of urea by adopting the same experimental procedure.



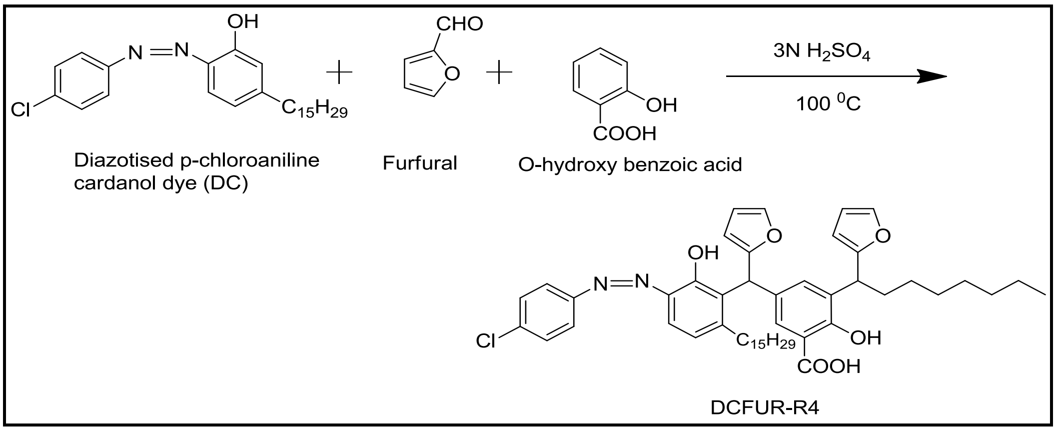
Synthesis of copolymer resin DCFUR-R1



Synthesis of copolymer resin DCFUR-R2



Synthesis of copolymer resin DCFUR-R3



Synthesis of copolymer resin DCFUR-R4

Characterization

FT-IR spectra of resins

FT-IR spectra of the five resins are displayed in Fig.1. A broad absorption band at 3488cm^{-1}is alloted to the stretching vibrations of hydrogen bonded phenolic hydroxyl group. A strong peak at 2932 cm^{-1}corresponds the symmetrical CH_2 stretching of the side chain of cardanol and the peak at 2834cm^{-1} corresponds the presence of methylene bridge. The peak at 1459cm^{-1} confirmsazo group. The peak at 1679cm^{-1}is due to the C=O stretching frequency of acyclic urea group and the peak at 1181cm^{-1} is dueto the C-N stretching present in urea.The peak at 1087 &1203cm^{-1} attributed to the C-O stretching frequency of aliphatic alcohol. The peak at 1248cm^{-1} is aroused due to the free O-H inplane bending of resorcinol.The peak at 1118cm^{-1}corresponds to the C-O stretching frequency ofcarboxylic acid.

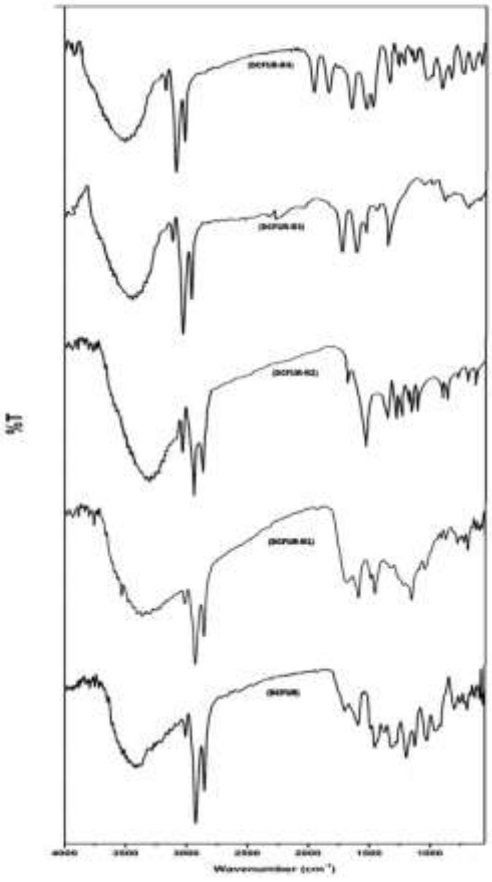


Fig. 1 FT-IR spectrum of resins.

^{1}H-NMR spectra of resins

^{1}H-NMR spectra of the five resins are presented in Fig.2. The peak at 1.2-2.5 ppm shows the methylene group of the side chain of cardanol.The peak at 2.1 ppm shows the OH group of the aliphatic alcohol.The multipletsat 2.8 ppm are owing to the presence of methylene protons and the peak at 1.8 ppm corresponds to the presence ofmethyl protons.The singlet at 5.0 ppm corresponds the phenolic OH group. The peaks between 7.1-7.6 and 6.6-6.7 ppm correspondsto the presence of aromatic protons. The peak at 10.9 ppm shows the OH group of the carboxylicacid.

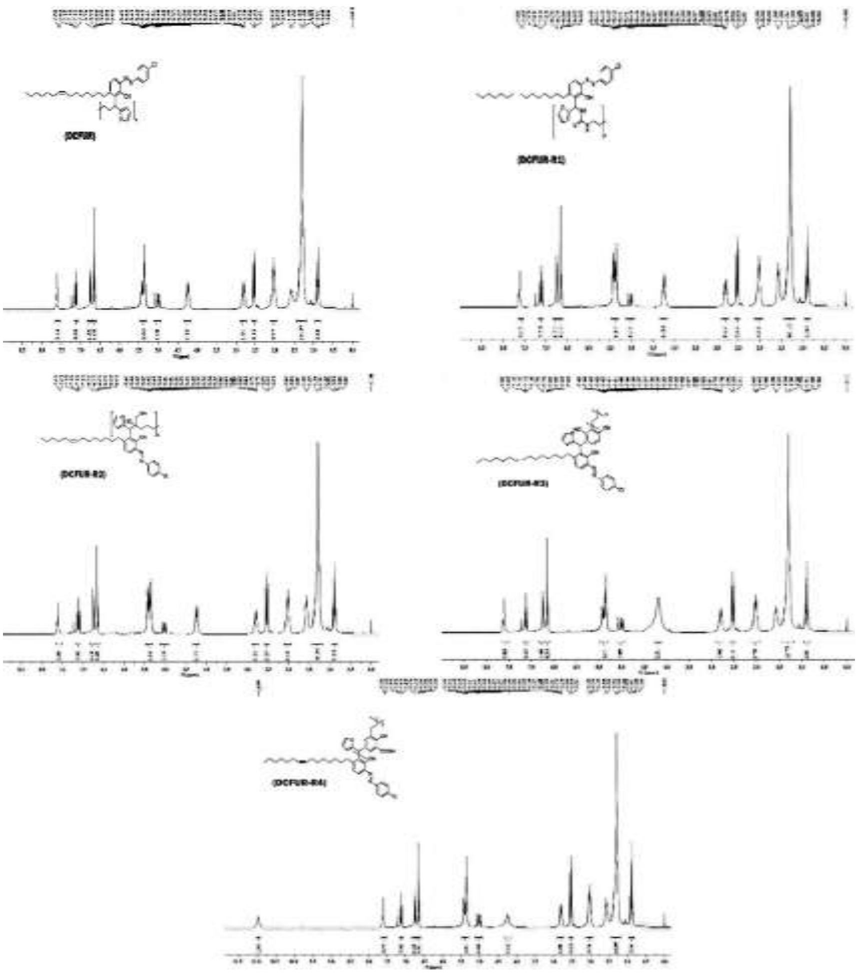


Fig.2. ^{1}H-NMR spectrum of resins

X-ray Diffraction studies

X-ray diffraction results of the five synthesized resins are presentedin Table 1.The majority of the polymershave both crystalline and amorphous regions. The occurrence of both types of features in the polymer indicates that ordered and disordered regions coexistin crystalline polymers.Cardanol-furfural resins are generally crystalline in nature. The assimilation of additionalmonomers to phenol furfural back bone disturbeditscrystallinity [23].It is evident from the Table.1 that the five resins DCFUR, DCFUR-R1, DCFUR-R2, DCFUR-R3 and DCFUR-R4 show 80.58%crystallinity,72.31% crystallinity, 76.78% crystallinity, 81.25%crystallinity and 82.21% crystallinity repectively. The crystallinity index of the resins DCFUR, DCFUR-R1, DCFUR-R2, DCFUR-R3 and DCFUR-R4 are found to be 0.759, 0.617, 0.698, 0.769 and 0.784 respectively. The XRD patterns of the five resins are presented in Fig. 3.Thepercentage of crystallinity of the resins decreases oncopolymerization. In case of DCFUR-R1 and DCFUR-R2, the percentage of crystallinity was decreased by adding urea and ethylene glycol as co-monomers. The decrease in crystallinity could be attributed to the presence of aliphatic compounds that are added as co-monomers in the sample. In case of DCFUR-R3 and DCFUR-R4, the percentage of crystallinity was found to increase on adding resorcinol and o-hydroxy benzoic acid as co-monomers and this could be due to the presence of aromatic compound as co-monomers in the copolymer resins.

Table1. Percentage of crystallinity and crystalline index of the resins

Resin	**Intensity of peak**		**Percentage of crystallinity (X_c)**	**Crystallinity index (CI)**
	Crystalline (I_c)	**Amorphous(I_a)**		
DCFUR	1245	300	80.58	0.759
DCFUR-R1	1251	479	72.31	0.617

DCFUR-R2	1290	390	76.78	0.698
DCFUR-R3	910	210	81.25	0.769
DCFUR-R4	1410	305	82.21	0.784

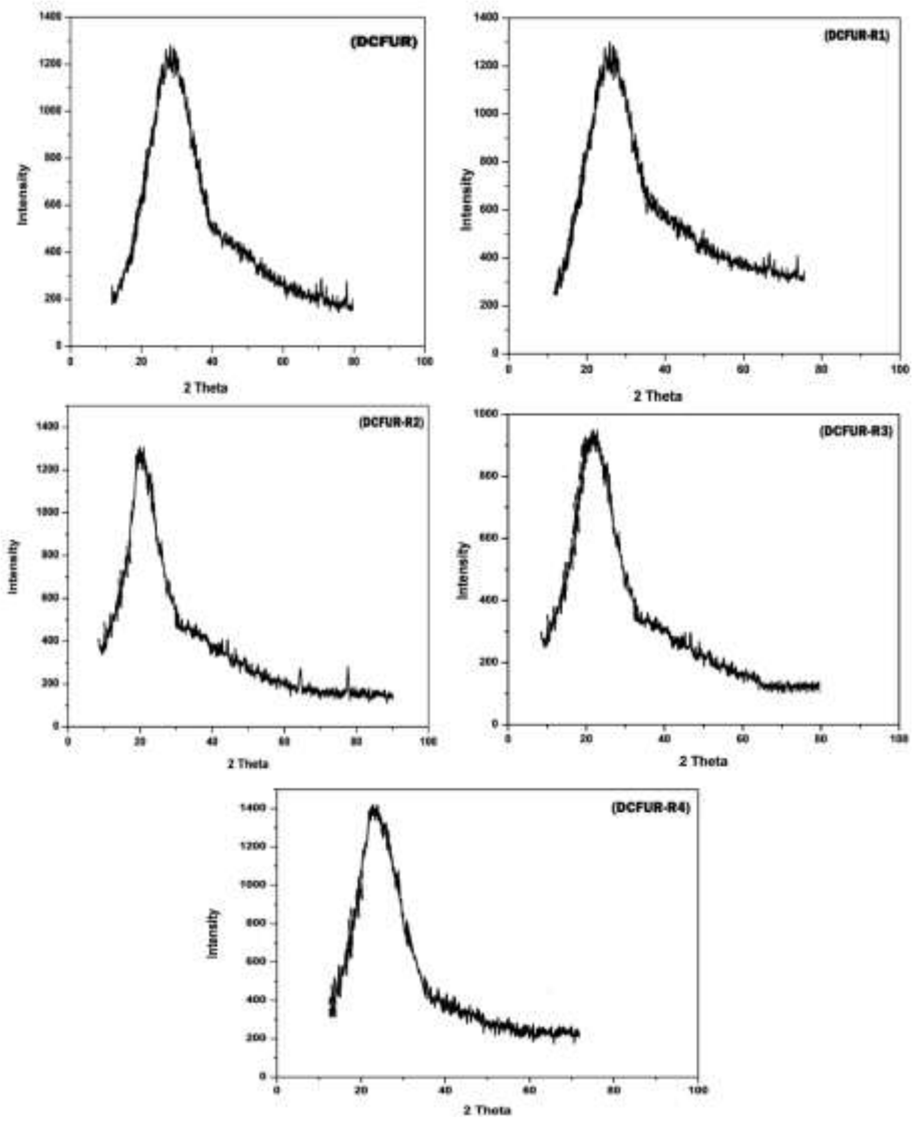


Fig. 3XRD pattern of resins

Thermogravimetric analysis

Thermograms of the resins arepresented in Fig. 4. The thermogravimetric analysis (Table2)revealsthat the resins were decomposed in two different steps. In the first step of thermal degradation, 100-200°C, weight loss upto 8% is observed in allthe resins.The initial weight loss upto 8% around 100-200 °C is observed in all our samples, which may be due to the presence of moisture in the sample. The gradual weight loss in the temperature range200-400 °C could be due to the thermal degrdation caused in the sample. The gradual weight loss in the temperature range200-400 °C could be due to the thermal degrdation caused in the sample, which might have occured in different modes such as dehydration, demethylation, decarboxylation, decrosslinking and chain scissions. The degradation occurred in different forms as dehydration, demethylation, decarboxylation, decrosslinking and chain scissions. The resins DCFUR, DCFUR-R1, DCFUR-R2, DCFUR-R3 and DCFUR-R4 are thermally more stable up to 400 °C.Finally, a rapid weight loss to 90% of the original sample weight was observed around 400 - 500 °C, which could be accounted for the depolymerisation and the cleavage segmentation of the aromatic ring in an oxydegradative approach.

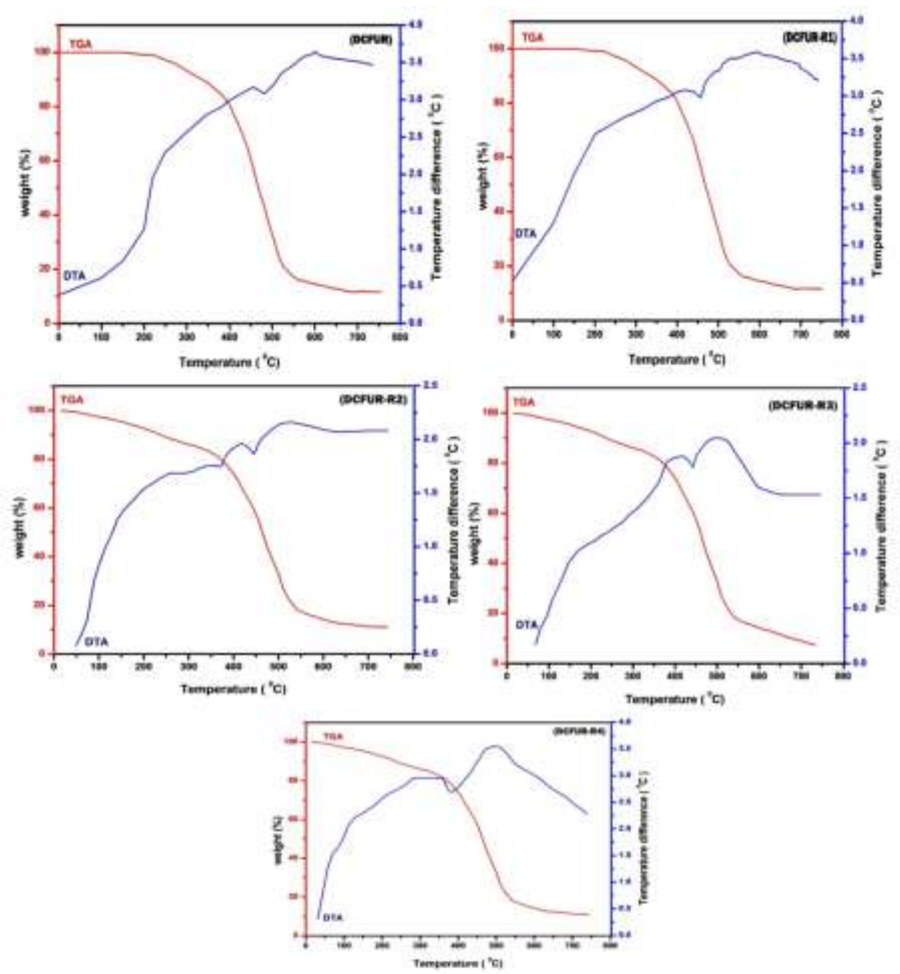


Fig.4TGA & DTA curves of resins

Table2.Thermogravimetric analysis of the resins

Resin	% of weight loss at different temperature (°C)						
	100	200	300	400	500	600	700
DCFUR	1	4	8	17	79	86	89
DCFUR-R1	3	5	11	24	83	91	94
DCFUR-R2	3	5	15	22	82	90	94
DCFUR-R3	0	2	10	21	76	83	84
DCFUR-R4	2	8	14	20	72	80	88

Differential thermal analysis

TGA studies have been supported by the DTA evaluation arrangement (Table 3). DTA curves are documentedconcurrently with TGA curves. In the DTA, the base line remains constant as long as there is no thermal transition in the sample. The first two peaks in the thermogram could be associated due to the first order phase transitions such as crystallization of different polymeric units and melting of the sample respectively. Followed by melting, the sample endure decomposition which is obvious from the broad peaks in the differential thermogram. The DTA curve of DCFUR shows two exotherms at 374 °C and 459 °C. The weak exotherm observed at 374 °C is due to the cleavage of meta-substituted alkyl side chain of the phenyl ring. Similarly, the resins DCFUR-R1, DCFUR-R2, DCFUR-R3 and DCFUR-R4 exhibited two exothermic peaks and the final degradation/decomposition of the resins have beennoticed at a higher temperature than that of the DCFUR.

Table3. Differential thermal analysis of the resins

Resin	1st exotherm (°C)	2nd exotherm (°C)
DCFUR	374	459
DCFUR-R1	419	493
DCFUR-R2	410	491
DCFUR-R3	421	490
DCFUR-R4	413	489

Kinetics studies

TGA data can be used for obtaining kinetic parameters of the thermal degradation of the polymer sample[24]. Experiments are of ten carried out under non-isothermal conditions[25]. In this method, the solid samples are subjected to a gradual temperature increase, usually as a linear function of time. By employing this technique, it is possible to determine the associated kinetic parameters (activation energy and pre exponential constant of the Arrehenius law as well as the kinetic function) related to the process mechanism.[26]. CNSL-furfural-substituted aromatic compound and the thermal stability of the seresins have been reported by Sahooetal[27].

Coats - Redfern method

Coats and Redfern expression, is the most used among the available methods[28]to evaluate the Arrhenius parameters as well as the kinetic models and also the mechanism of the degradation process. The parameters E_a and A can be calculated by testing different kinetic models g(α) [29]. For a first-order reaction process, Coats and Redfern provided an integral form of rate equation and it is represented as,

$$Log\ \frac{g(\alpha)}{T^2} = Log\frac{AR\ (1-\frac{2RT}{Ea})}{\Phi Ea} - \frac{Ea}{2.303RT}$$

Where,
T = Temperature
A = Pre-exponential term
R = Gas constant
Ea = Energy of activation
ϕ = Heating rate
and αis given by,

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f}$$

Where,
W0 = Initial weight of the sample
Wt = Residual weight of the sample at the temperature
Wf = Final weight of the sample.

The graphical representation of Logg (α)Vs1/T gives a straight line for the correct chosenform of g(α). According to the square dcorrelation coefficient values R^2, which is calculated for various possible kinetic function reveals that the decomposition processis followed first order kinetics[30]. Kinetics of thermal degradation of thesynthesized homopolymerand copolymerresins was followed undernon-isothermal condition and Coats-Redfern method was employed to determine the activation energy of there sin. Activation energy has been calculated and also the possible function of the kinetic modelis presented. Various kinetic functions used for the analysis are presented in Table 4. Regression analysis has been carried out for the five resins synthesized.

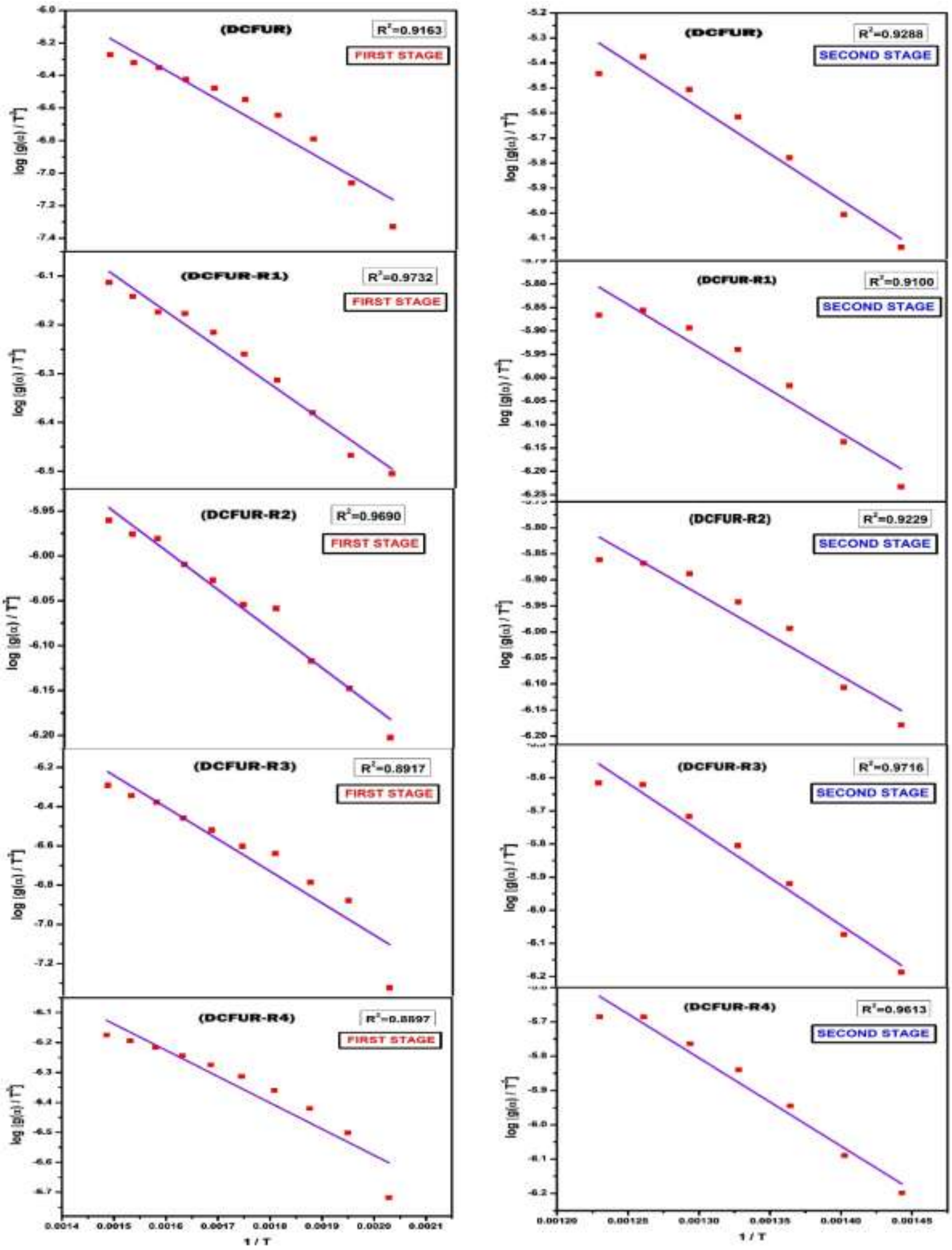


Fig. 5Coats-Redfern plot for resins (First Stage and Second Stage)

Table 4. Energy of activation for thermal degradation of resinswith maximum R^2 values by Coats - Redfern method

Resin	**First stage (220 – 400°C)**			**Second stage (420 – 540°C)**		
	R^2	**Ea (Kcal/mol)**	**Function**	**R^2**	**Ea (Kcal/mol)**	**Function**
DCFUR	0.9163	15.1730	D_2	0.9288	30.5705	$MPL^{2/3}$
DCFUR-R1	0.9732	6.2022	D_4	0.9100	15.1397	MPL^1
DCFUR-R2	0.9690	3.6082	D_2	0.9229	12.9947	MPL^0
DCFUR-R3	0.8917	13.5019	D_2	0.9716	23.7863	$MPL^{1/2}$
DCFUR-R4	0.8897	7.2830	D_3	0.9613	21.3337	$MPL^{2/3}$

Energy of activation for the first and second stage thermal degradation of resins has been calculated. The computerized plots based on Coats-Redfern equation is presented in Fig.5. Coats-Red fern plots are drawn for both homopolymer and co-polymer resins, and good fits are obtained for there action parametern = 1. Two distinct stages of decompositions are indicated in both cases and activation energies are deduced from the slope of the plots. A linear correlation is obtained by plotting the logarithm of heating rate against the reciprocal of the absolute temperature.

Evaluationofenergyofactivation

The energy of activation for the thermal degradation of hompolymer and copolymer resins is presented in Table4. The energy of activation Ea is lower for the first stage of degradation than the second stagein all the homopolymer and copolymer resins which showed that the first step is the fastest step.

Homopolymer resins show higher activation energy than copolymer resins. This may be due to the crystallinity of homopolymer resins. Greater the crystalline nature greater will be its activation energy [31]. The activation energy can be calculated from the slope of the best fitting linear regression according to the Coats-Redfern equation.

The energy of activation for the thermal degradation of resins with maximum R^2 values was given in Table 4. In the first stage, the activation energy of copolymer resins ranges between 3.6082 to 15.1730 Kcal/mol. A tendency of the activation energy to increase with the degree of degradation has been observed both in homopolymer and copolymer resins. In the second stage the activation energy of copolymer resins ranges between 12.9947 Kcal/mol to 23.7863 Kcal/mol. In general, copolymer resins containing aromatic compounds as co-monomers have higher activation energy than copolymer resins containing aliphatic compounds as co-monomer.In almost all the cases (Table. 4) the first stage of degradation follows complex diffusion mechanism, which is in accordance with investigation by Jabal et al [32]. As predicted by Nair et al [33], it is evident that the Mampel equation gives reasonable energy of activation and maximum R^2 values in the second stage of degradation for both homopolymer and copolymer resins. According to the squared correlation coefficient values R^2 which is calculated for various possible kinetic functions, it reveals that the decomposition process is most likely a first order kinetics.

Conclusion

Cardanol-furfural based resins were synthesized with good yield and well characterized.This proposed research may lead to a new platform in the field of resins based on renewable resources. The synthesized cardanol–furfural based resins have the potential to minimize the use of phenol resin based on petrochemical derivatives like phenol–formaldehyde resins.The higher R^2 value and energy of activation Ea values are calculated in the second stage of degradation. Among the synthesized resins, the derivatives havingaromatic compounds as co-monomers possesses higher activation energy when compared withresins having aliphatic compounds as co-monomer. Further, it hasbeen clearly understood from the Coats-Redfern method, the homopolymer and copolymer resins followed complex diffusion mechanism (D) in the first stage of degradation and Mample mechanism (MPL) in the second stage of degradation.X-ray diffraction patternshowed that the percentage of crystallinity was decreased by contributing aliphatic co-monomer such as urea and ethylene glycol, and the percentage of crystallinity was increased by contributing aromatic co-monomer such as resorcinol and o-hydroxybenzoic acid. The resins obtained urea and ethylene glycol has higher thermal stability than the resins from resorcinol and o-hydroxy benzoic acid and reason might be behind the absence of aromatic ring in urea and ethylene glycol.

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