



J. Chem. Pharm. Res., 2010, 2(3):193-205

ISSN No: 0975-7384
CODEN(USA): JCPRC5

Synthesis and thermal properties of polyurethanes from Cardanol-furfural resin

S. Gopalakrishnan^{a,*} and R. Sujatha^a

^a*Department of Pharmaceutical Chemistry, Manonmaniam Sundaranar University, Tirunelveli, Tamilnadu, India*

ABSTRACT

Cardanol, a meta substituted phenol is a renewable organic resource obtained as a byproduct of the cashew industry. It is used for the production of polyurethanes. The cardanol-furfural resin has been synthesized by the condensation of cardanol with furfural in the presence of adipic acid catalyst and using varied molar proportion of the reacting monomers. The synthesized cardanol-furfural resin has been characterized by different physico-chemical techniques. The characterized furfuralated cardanol novolac resin has been condensed with toluene diisocyanate to produce hard segment polyurethanes. Soft segment polyurethanes are prepared by condensing the commercial polyol, polypropylene glycol-1200 (PPG-1200) with toluene diisocyanate and cardanol-furfural resin. Thermal stabilities of the polyurethanes were determined by Differential thermal analysis (DTA) and Thermo gravimetric analysis (TGA). Thermal decomposition curves were studied carefully with minute details. The Horowitz - Metzger and Broido methods have been used in the present investigation to calculate thermal activation energy. Thermal activation energy (E_a) calculated with above two mentioned methods are in close agreement.

Key words: Cardanol, polyurethane, polypropylene glycol – 1200, thermo gravimetric analysis, activation energy.

INTRODUCTION

In recent years, the utilization of bioresources to obtain polyurethanes has attracted much attention. There has been a large number of works based on polymers from Cashew Nut Shell Liquid derivatives appeared in the literature. Cardanol, a natural meta substituted alkyl phenol from Cashew Nut Shell Liquid (CNSL), an agricultural byproduct abundantly available in India

and can be regarded as a versatile and valuable raw material for polymer production [1-4]. The unique structural feature that makes cardanol an interesting monomer is the presence of a long alkyl group in the meta position. Alkyl groups are known to improve the solubility alignment properties, dielectric properties and gas permeability properties of polymers. Numerous studies have been carried out using the reactivity of the hydroxyl group in cardanol [5-11]. The synthesis, mechanical and thermal properties of polyurethanes based on cardanol formaldehyde resin have been reported earlier [12-15]. Hydroxyalkylated cardanol-formaldehyde resins have been used for the synthesis of polyurethanes with good thermal and mechanical properties. Other than formaldehyde, aldehydes like acetaldehyde, propionaldehyde and benzaldehyde are also used for resin formation [16-18]. But they are not widely used. Furfural, the heteroaryl aldehyde is obtained as an agricultural waste product which has an extensive application in the formation of resins [19]. Several 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 properties were studied [20]. A number of semi-interpenetrating polymer networks (semi-IPNs) have been synthesized using polyurethane and cardanol derivatives like acetylated cardanol and phosphorylated cardanol and also by condensing cardanol-formaldehyde-p-hydroxyacetophenone or furfural novolac resins with polyurethanes prepared from castor oil and diisocyanates [21]. Thermal properties of the semi- interpenetrating networks composed of castor oil polyurethanes and cardanol- furfural resin have been studied [22].

In the present study, cardanol-furfural resins have been synthesized using adipic acid catalyst and used for the production of polyurethanes. The physico-chemical characteristics of the resins and also the thermal properties of the polyurethanes have been evaluated.

EXPERIMENTAL SECTION

Cardanol was obtained from M/s Sathya Cashew Pvt.Ltd., Chennai, India. Furfural (A.R.grade) was received from M/s S.D.Fine Chemicals. Adipic acid and toluene diisocyanate were received from E.Merck(Germany), Methanol(BDH) was used to dissolve the catalyst.PPG-1200 was received from Aldrich Chemicals(USA) and dibutyltin dilaurate was received from Fluka Chemie (Germany).The chemicals were used as received.

Infrared spectra were taken in a Shimadzu 8400 S FT IR Spectrophotometer ($4500-350\text{cm}^{-1}$) by Neat/KBr methods. $^1\text{H-NMR}$ spectra were recorded using a Bruker Avance III 400MHz FT NMR spectrometer. Thin layer chromatographic separation was carried out in three different solvent systems. Specific gravity, iodine value, hydroxyl value and intrinsic viscosity of the resin were determined according to the IS Standard 840-1964.Molecular weight of the resin was determined by gel permeation chromatography using μ -styragel columns, 100A^0 and 500A^0 UV detector and 280nm filter. The polyurethanes were subjected to differential thermal analysis (DTA)/ thermo gravimetric analysis (TGA) studies at a rate of $20^\circ\text{C}/\text{min}$ in air using Universal V4.3A TA instruments.

Synthesis of cardanol-furfural resin

Novolac resins (AR1, AR2 and AR3) with mole ratios, 1:0.9, 1:0.8 and 1:0.7 of cardanol to furfural were prepared using adipic acid as catalyst. The catalyst (1% based on cardanol) was dissolved in 3 ml methanol under warm conditions. Cardanol was taken in a three- necked round bottom flask equipped with a Liebig condenser, mechanical stirrer and thermometer. Furfural was added to the cardanol through a dropping funnel along with the catalyst. The reaction was carried out at temperature 120°C for 4 h and then at 140°C for 2 h. The reaction resulted in the formation of multinuclear cardanol- furfural resins. The initial P_H of the reaction mixture was 4

which lowered to 2 on the completion of the reaction. The resins were purified by dissolving in toluene and by precipitating it with distilled water. Then the resins were collected and dried using a rotary evaporator under vacuum and analysed.

Synthesis of Hard segment and Soft segment polyurethanes

Hard segment polyurethanes (AR1T, AR2T and AR3T) were synthesized by treating the vacuum dried cardanol-furfural resin (0.1 mole) with toluene diisocyanate, keeping the isocyanate index (NCO/OH mole ratio) constant at 1.4. The reaction was carried out at room temperature in the presence of dibutyl tin dilaurate as catalyst. The number of hydroxyl groups (N) can be derived from the equation

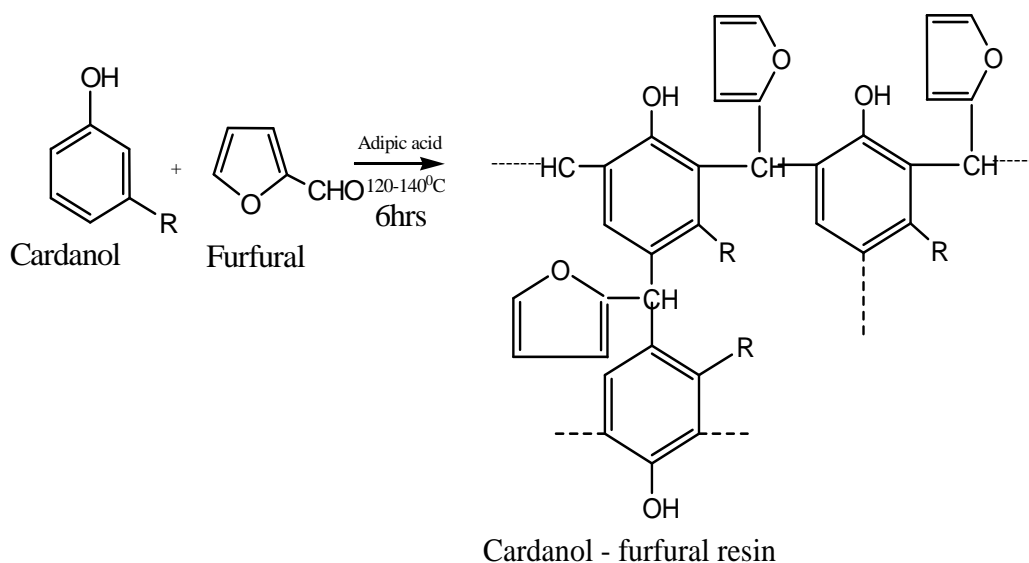
$$N = \frac{w (M + 42N)}{56 W}$$

where N is the number of hydroxyl groups, w the amount of KOH required for the hydrolysis of acetyl derivative of the resin and W the weight of acetyl derivative of the resin and M is the molecular weight of the resin.

Similarly 0.1 mole of commercially available polyol, polypropylene glycol-1200 (PPG-1200) was also condensed with the diisocyanate along with 0.1 mole of the synthesized cardanol-furfural resin in the presence of dibutyl tin dilaurate, keeping the isocyanate index 1.4 to get the soft segment polyurethanes. These are designated as AR1TP1, AR2TP1 and AR3TP1. The polyurethanes formed were then allowed to cure for 48 hours in a flat surface without any disturbance. The polyurethanes were again cured in a vacuum oven at 80°C for 48 h and used to evaluate its thermal properties.

RESULTS AND DISCUSSION

The synthesis of cardanol-furfural resins under various mole ratios of cardanol:furfural leads to ortho-para substituted products. Though adipic acid has ortho orientation effect, all the mole ratios of cardanol:furfural enables ortho-para substitution during the initial furfurylation as well as subsequent condensation of furfurylated cardanol. The synthesis of cardanol-furfural resin is presented in Scheme 1.



Scheme 1. Formation of cardanol-furfural resin

Physico-chemical characteristics of cardanol-furfural resin

All the synthesized resins are reddish brown in colour. The specific gravity and intrinsic viscosity of the cardanol-furfural resin are greater than that of the cardanol-formaldehyde resin and cardanol. The decrease in the iodine value is observed which may be due to the steric effect in the cardanol-furfural resin during the addition of iodine monochloride. The number of hydroxyl groups present in the resin is only the –OH groups in the benzene rings.

Thin layer chromatographic study of the resin in three different solvent systems (100% Benzene, 1:1 Benzene: Chloroform and 8:2 Petroleum ether (40-60°C): Diethyl ether) showed a distinct single spot, and the R_f value for cardanol -furfural resin is different from that of cardanol indicating the formation of the product. The results are presented in Table-1.

Table-1 Physico-chemical characteristics of cardanol-furfural resin

Properties	Cardanol	Cardanol-furfural resin		
		AR1 1:0.9	AR2 1:0.8	AR3 1:0.7
Colour	Dark brown	Reddishbrown	Reddishbrown	Reddishbrown
Odour	Phenolic	Phenolic	Phenolic	Phenolic
Specific gravity(g/cc at 30°C)	0.9230	0.9651	0.9601	0.9548
Viscosity(intrinsic)	0.0309	0.048	0.046	0.0415
Iodine value	221.5	212.3	219	203.5
Hydroxyl value	181.7	130.5	149	137
Molecular weight	302	2105	1814	1403
Number of hydroxyl groups	1	5	5	4
Thin layer chromatography: R_f values				
(i)100% Benzene	0.71	0.67	0.68	0.65
(ii)Benzene:chloroform(1:1)	0.58	0.53	0.55	0.54
(iii)Pet.ether:Diethylether(8:2)	0.74	0.65	0.69	0.67

FT IR and $^1\text{H-NMR}$ spectroscopy of cardanol-furfural resin

The FT IR spectra of all the cardanol-furfural resin samples are almost identical in all respects. The phenolic hydroxyl band is observed at 3396 cm^{-1} . The peaks at 3006.8 cm^{-1} and 2852 cm^{-1} are the aromatic CH stretching and aliphatic CH stretching respectively. The CH_2 peaks are found at 2925 cm^{-1} while the CH_3 peaks are seen at 2854 cm^{-1} and are confirmed by the presence of their deformative peaks at 1424 cm^{-1} and 1460 cm^{-1} respectively. The sharp peak at 729 cm^{-1} indicates the ortho substitution at benzene nuclei and the sharp peak at 869 cm^{-1} indicating the para substitution at benzene nuclei. The FT IR spectrum of cardanol- furfural resin is presented in Fig.1.

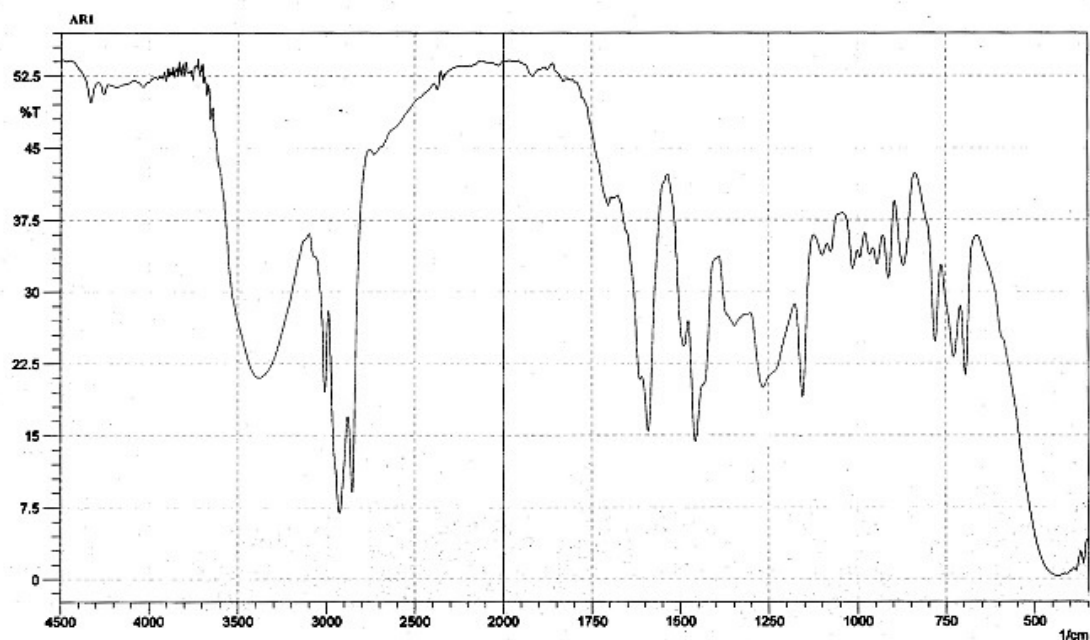


Fig.1 FT IR spectrum of cardanol-furfural resin

In the $^1\text{H-NMR}$ spectra of cardanol-furfural resin samples, the peak at 6.60-7.40 δ is due to aromatic protons of benzene and furan ring, the peak around the region 6.50 δ is due to phenolic hydroxyl, the peak at 4.90-5.30 δ is due to methylene ($\text{C}=\text{CH}_2$) proton of long alkyl side chain originally present in cardanol and the peak at 0.80-2.83 δ is due to the long aliphatic side chain. The peak at 0.80 δ is due to terminal methyl group of the chain. The strong peak at 1.30 δ is attributed to the long chain (more than five methylene groups) of the side chain. The peak at 2.82 δ also indicates the methine proton of $(\text{C}_6\text{H}_5)_2\text{-CH-C}_4\text{H}_3\text{O}$ for the bridge between two phenyl rings and one furan ring. The $^1\text{H-NMR}$ spectrum of cardanol-furfural resin is presented in Fig. 2.

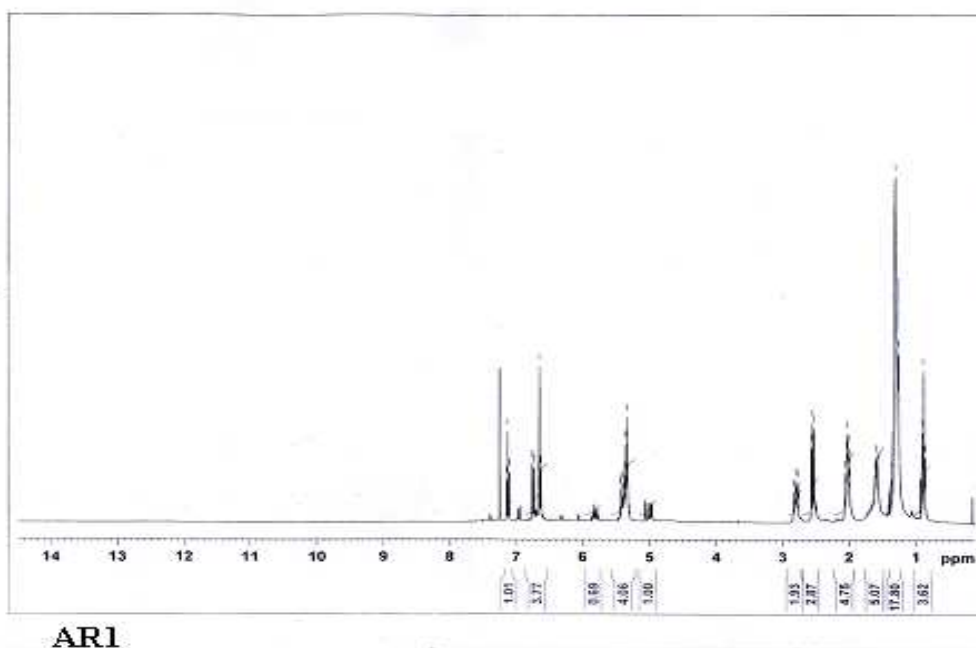


Fig. 2 $^1\text{H-NMR}$ spectrum of cardanol- furfural resin

Synthesis of polyurethanes

One of the most widely used techniques to obtain polyurethanes is the one-shot technique, which consists of the very efficient mixing, in one step only, in a short time, of all of the raw materials involved in polyurethane preparation: polyol, chain extender and the diisocyanate [23]. The condensation reaction between cardanol-furfural resin and diisocyanate can lead to the formation of stable urethane linkages. The condensation reaction was found to be exothermic. Dibutyl tin dilaurate catalyst was used and the reaction completed within 10 min. The ratio of concentrations of diisocyanate to hydroxyl groups (1:1.4) was chosen so that the excess of diisocyanate present leads to the formation of terminal isocyanate groups. The final curing of the reaction product leads to the formation of allophanate linkages with the reaction involving terminal isocyanate groups with active hydrogen present in urethane groups of the polymer.

Spectral characteristics of Polyurethanes

Almost all of the Infrared research on polyurethanes has focused on two principal vibrational regions: the N-H stretching vibration (3200-3500 cm^{-1}) and the carbonyl C=O stretching vibration (1700-1730 cm^{-1}) [24,25]. Polyurethanes are capable of forming several kinds of hydrogen bonds due to the presence of a donor N-H group and a C=O acceptor group in the urethane linkage. It is well known that in hydrogen bonded urethane N-H and C=O bands appear at lower wave numbers than those in free ones [26].

The FT IR spectra of the synthesized hard and soft polyurethanes are shown in Fig. 3a and Fig. 3b respectively. The characteristic absorption at 3301 cm^{-1} corresponding to urethane linkage (-NH stretching, bonded), which is broadened due to the formation of hydrogen bond with a carbonyl group. There is a band at 1720 cm^{-1} , which is attributable to free C=O urethane groups and the band at 1645 cm^{-1} corresponding to C=O stretching (bonded) in urethane and 1537 cm^{-1} corresponding to N-H bending in urethane.

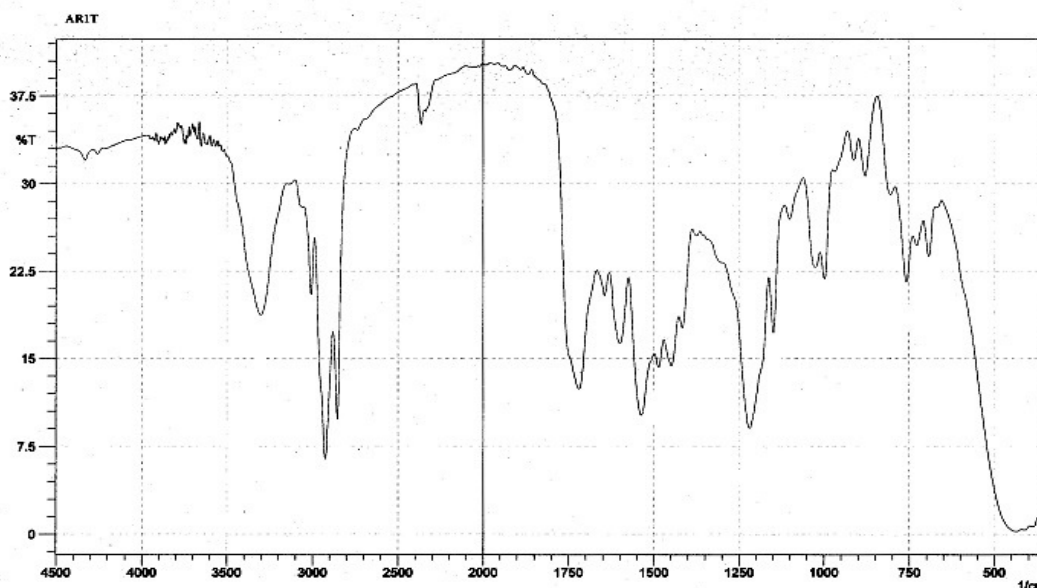


Fig. 3a FTIR spectrum of hard segment polyurethane

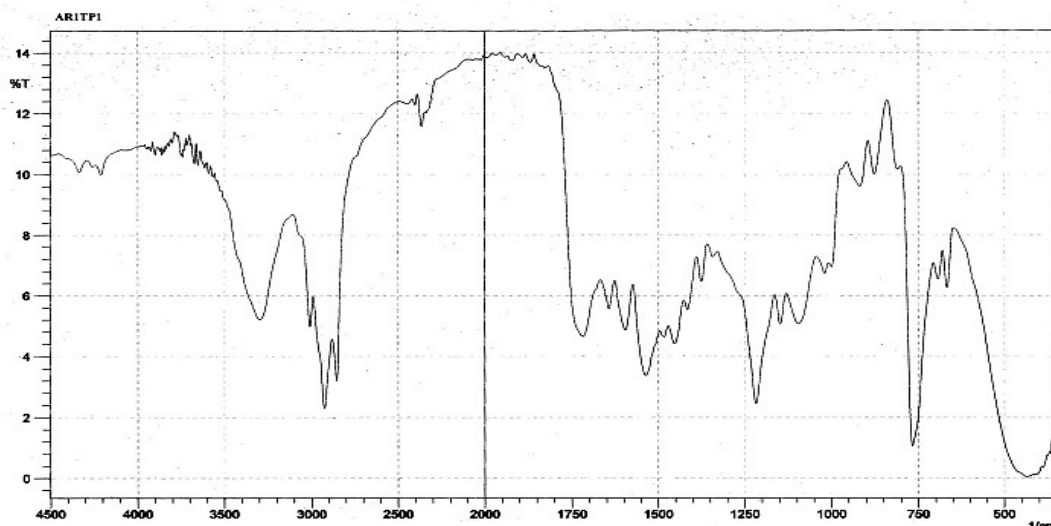


Fig. 3b FTIR spectrum of soft segment polyurethane

Thermal properties of polyurethanes

DTA/TGA thermograms of cured hard and soft polyurethanes are presented in Fig. 4a, 4b, 4c and Fig.5a, 5b, 5c respectively. The hard segment polyurethanes show three exotherms, a very weak one around 325 °C and two strong exotherms around 468 °C and 553 °C. The weak exotherm is due to the cleavage of meta substituted alkyl side chain of the phenyl ring. The soft segment polyurethanes show three or four weak exotherms between 300 °C and 465 °C and a strong one around 560 °C. The soft segment polyurethanes thermally degraded successively after the cleavage of meta-substituted alkyl side chain due to the presence of the commercial polyol, polypropylene glycol-1200 in the temperature range 300 °C -465 °C. The hard segment polyurethanes show lesser number of exotherms in comparison with that of the soft segment polyurethanes, due to higher crosslink density.

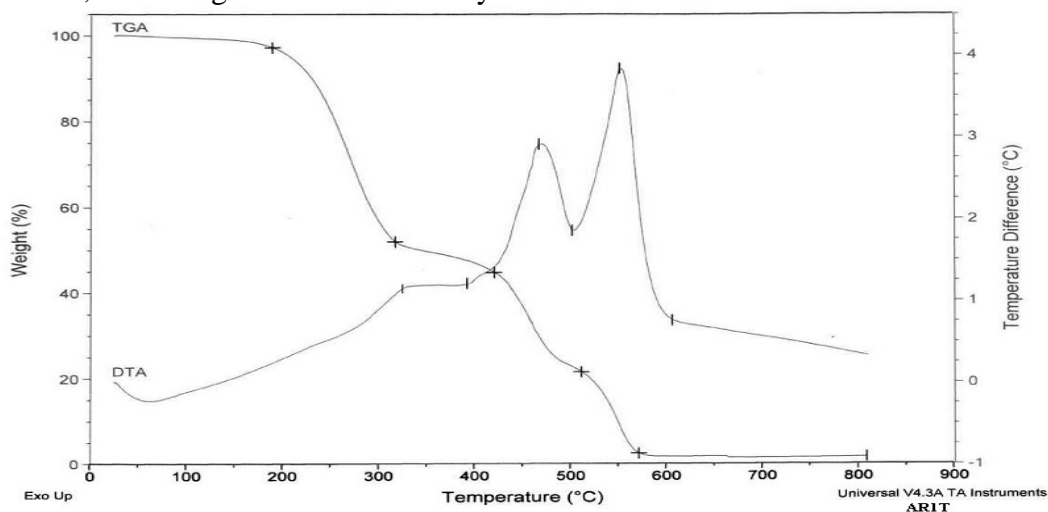
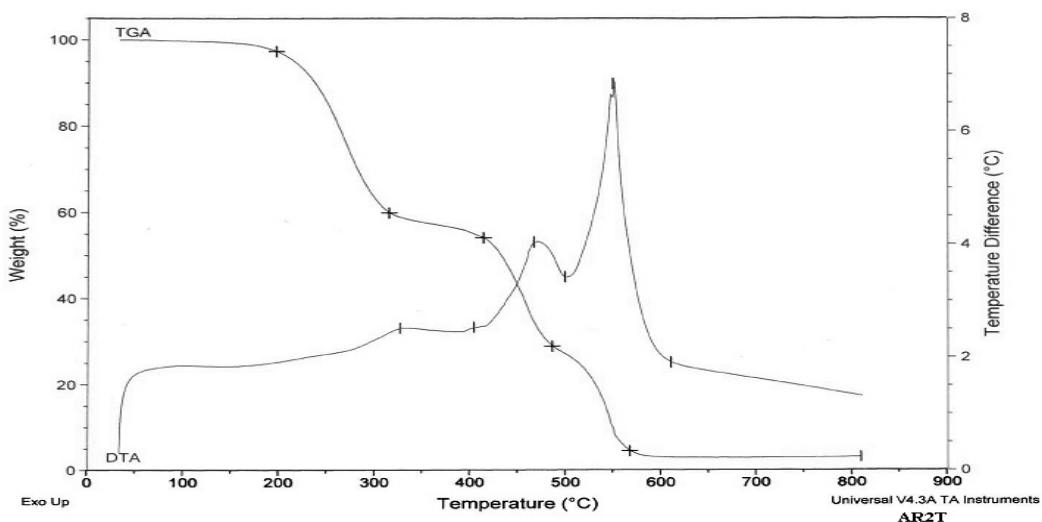
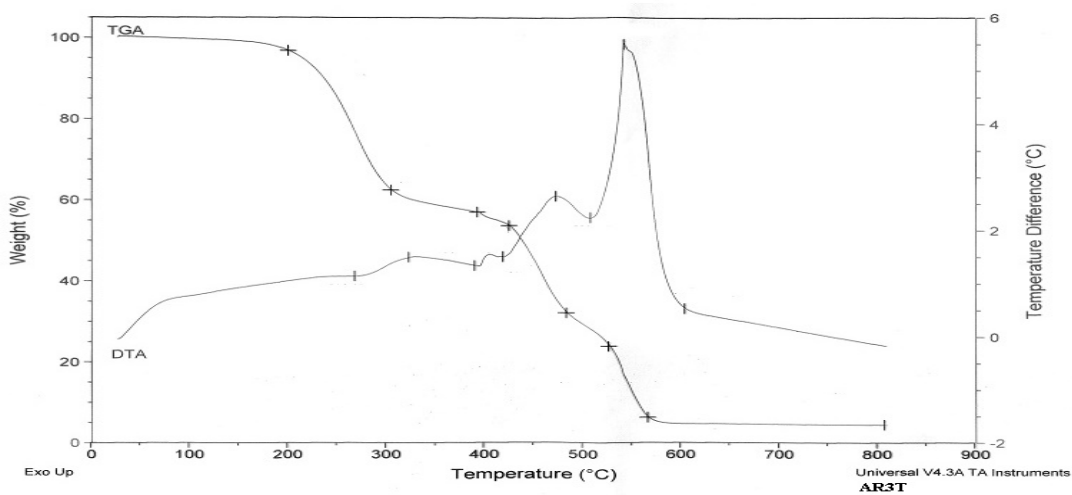
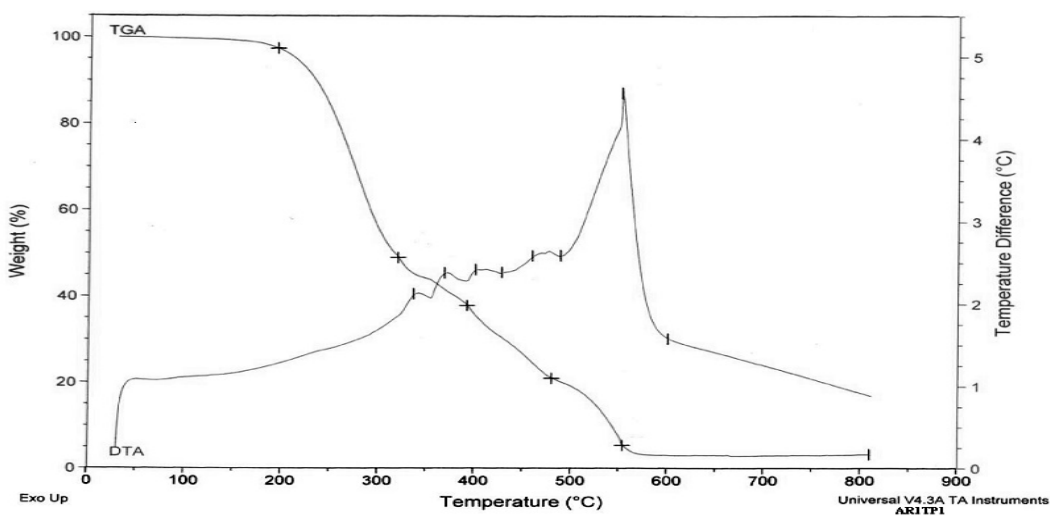
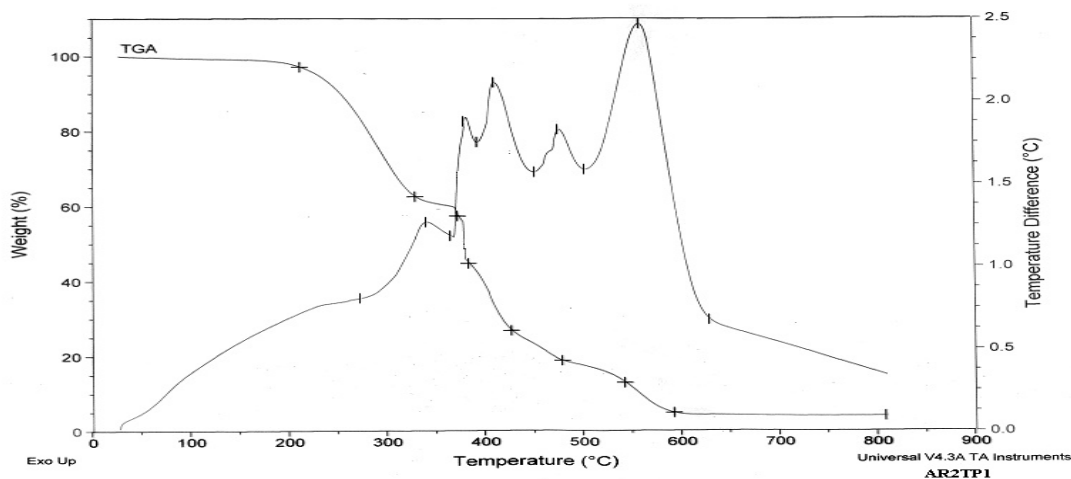
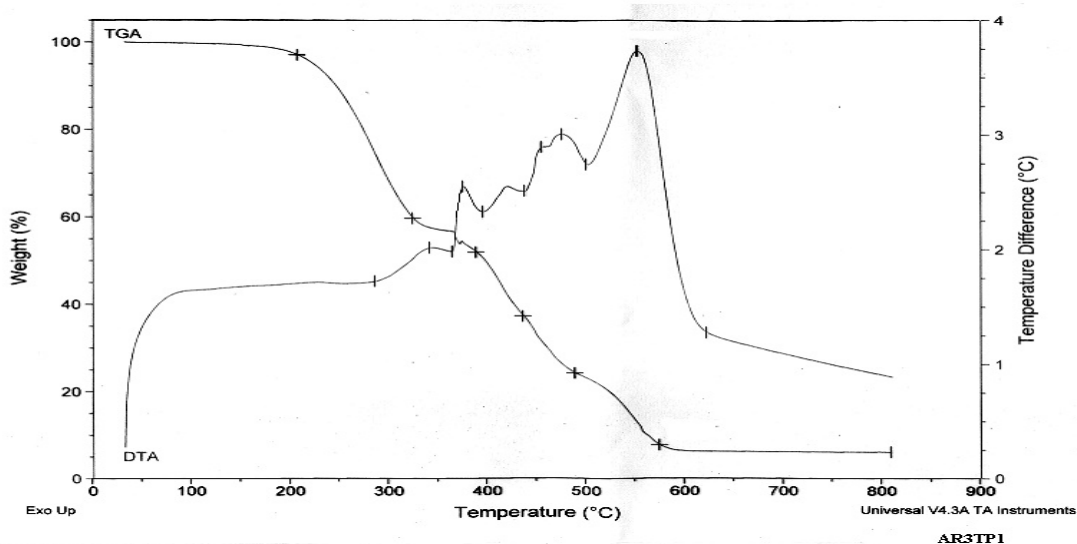


Fig. 4a DTA/TGA curves of AR1T

**Fig.4b DTA/TGA curves of AR2T****Fig. 4c DTA/TGA curves of AR3T****Fig.5a DTA/TGA curves of AR1TP1**

**Fig. 5b DTA/TGA curves of AR2TP1****Fig. 5c DTA/TGA curves of AR3TP1**

The TGA curves of polyurethanes showed that the hard and soft segment polyurethanes decompose in three or four distinct stages. The initial weight loss (about 3%) up to 200°C is attributed to the moisture retained in the sample. The hard segment polyurethanes decomposed around 40-50% at 400°C, but the soft segment polyurethanes decomposed around 50-60% at 400°C. Both the polyurethanes decomposed around 70-90% in the temperature range of 500-550°C. This is due to the strong network formed between polyurethane prepared from toluene diisocyanate and cardanol- furfural novolac resin. The first break of the TG curves around 200°C is due to the presence of moisture in the compound. The second break around 325°C is due to the decrosslinking or post curing process where about 35% weight loss occurs. The third break around 400°C indicates the decomposition of polyurethane moiety of the compound. And the last break around 550°C is due to disintegration of the resin moiety into simpler molecules.

It is observed from Table-2 that the hard segment polyurethanes are more stable than the soft segment polyurethanes due to higher cross link density of the former ones. Also the percentage of weight loss in the case of lower mole ratio of cardanol: furfural (1:0.7) derived polyurethanes

are comparatively lower than that of higher mole ratio of cardanol: furfural (1:0.9 and 1:0.8) derived polyurethanes indicating the higher stability of these polyurethanes.

Table-2 TGA characteristics of polyurethanes

Polyurethanes	Percentage of weight loss at different temperatures									
	100°C	150°C	200°C	250°C	300°C	350°C	400°C	450°C	500°C	550°C
AR1T	-	-	2	15.8	39	49	52	62.3	75.8	87.5
AR2T	-	-	2.5	13	35.7	42	44	57.5	71.8	88
AR3T	-	-	3	13.2	34.8	40	42.5	53.5	70	84.5
AR1TP1	-	-	3	14	44.5	56	64	72.9	79	93
AR2TP1	-	-	1	7.5	26	38	58	75	81	89.5
AR3TP1	-	-	2	10	29.5	42	49.4	64.2	76	86

A mathematical interpretation of thermo gravimetric curves is used to determine kinetic parameters of thermal decomposition reactions. Horowitz and Metzger [27] have demonstrated the method of calculation of energy of activation of polymeric substances. The equation used for the calculation of energy of activation (E_a) was,

$$\ln \ln \left(\frac{W_0}{W_t} \right) = \frac{E_a \theta}{RT_s^2}$$

where $\theta = T - T_s$; W_0 is the initial weight; W_t is the weight at any time t ; T_s is the peak temperature; and T is the temperature at particular weight loss. A plot of $\ln \ln (W_0)/(W_t)$ vs. θ gives an excellent approximation to a straight line. From the slope, the activation energy is calculated. Representative plot is shown in Fig.6. The calculated values for the activation energy of decomposition by Horowitz-Metzer method are presented in Table-3.

The activation energy associated with each stage of decomposition was also evaluated by the well-known Broido method [28]. The equation used for the calculation of activation energy (E) was,

$$\ln \ln \left(\frac{1}{Y} \right) = \left(\frac{-E_a}{R} \right) \frac{1}{T} + \text{Constant}$$

where

$$Y = \frac{W_t - W_\infty}{W_0 - W_\infty}$$

where, $W_0 - W_\infty$ is the fraction of the number of initial molecules not yet decomposed; W_t the weight at anytime t ; W_∞ the weight at infinite time (= zero) and W_0 the initial weight. A plot of $\ln \ln (1/Y)$ vs. $1/T$ gives an excellent approximation to a straight line. The slope is related to the activation energy. Representative plot is shown in Fig.7. The calculated values for the activation energy of decomposition by Broido method are presented in Table-3.

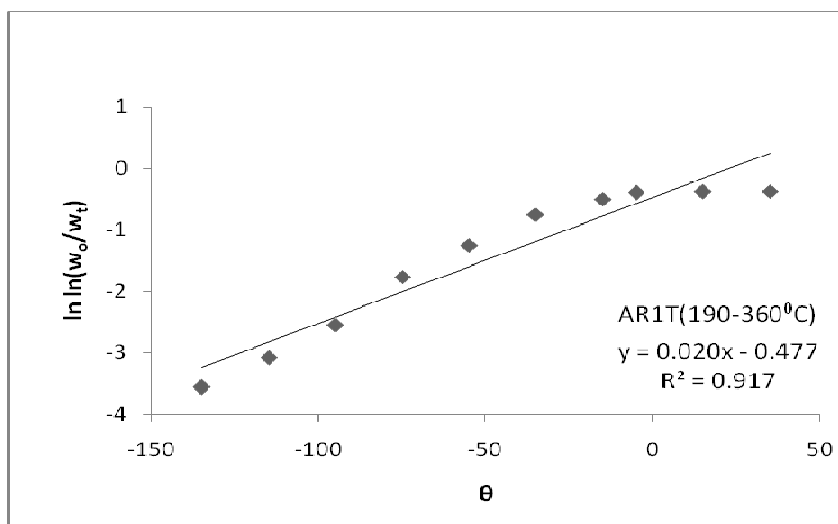


Fig. 6 Representative Horowitz-Metzer plot.

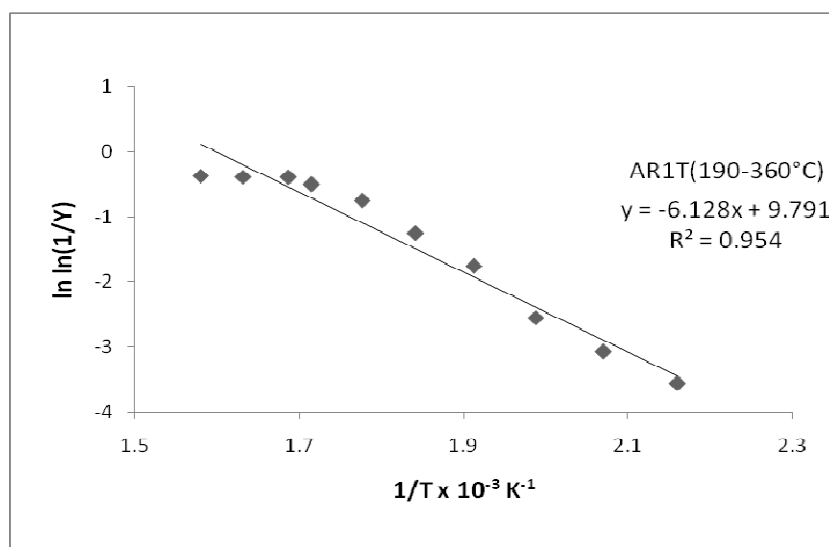


Fig.7 Representative Broido plot

The results indicate that in the case of hard polyurethanes, the activation energy is lowest in the temperature range of 380-470°C indicating that this is the fastest step. This is bound to happen since in the first stage the decrosslinking of the long alkyl side chain occurs and in the last stage the decomposition of polyurethane moiety occurs. By judging the activation energy in the three temperature ranges, it could be predicted that the first and last steps are slow compared to the second step where the breaking up of urethane linkages take place. In the case of soft polyurethanes, the second and third steps are considered to be fast processes since their activation energies are less compared to the first step.

Table-3 Activation energy of decomposition for hard and soft segment polyurethanes

Polyurethanes	Decomposition Temperature range (°C)	Peak temperature Ts °C	Method	Activation energy in Kcal/mol	% residue left
AR1T	190-360	325	B	12.1763	
			HM	14.5665	
	421-511	468	B	8.668	

	511-571	553	HM B HM	8.728 18.148 18.821	1.629
AR2T	200-360	327	B HM	12.369 14.3779	3.064
	410-490	467	B HM	9.688 9.792	
	500-570	551	B HM	18.086 18.888	
AR3T	200-360	324	B HM	11.5107 13.3049	4.495
	410-480	473	B HM	9.692 9.974	
	500-570	542	B HM	14.241 14.532	
AR1TP1	195-355	337	B HM	13.096 16.192	3.261
	390-480	460	B HM	5.153 4.694	
	480-560	553	B HM	6.622 7.312	
AR2TP1	210-360	341	B HM	13.981 17.966	3.969
	380-480	412	B HM	8.6162 8.101	
	490-590	560	B HM	8.284 8.273	
AR3TP1	200-360	342	B HM	13.287 16.458	6.108
	390-480	477	B HM	8.049 8.9319	
	490-580	552	B HM	8.423 8.126	

*B-Broido**HM- Horowitz & Metzger*

CONCLUSION

The development of novel polyurethanes from cardanol- furfural resin is reported. The thermal activation energy (E_a) calculated with Horowitz – Metzger and Broido methods are in close agreement. The energy of activation (E_a) is higher for the first stage than the second stage of degradation in all the polyurethanes. The energy of activation (E_a) for the first stage of decomposition of both hard and soft segment polyurethanes is almost the same. But the energy of activation (E_a) for the second and third stages of decomposition of hard segment polyurethanes is higher than that of the soft segment polyurethanes. The hard segment polyurethanes are having higher crosslink density. So energy needed to break the core structure is high when compared to that of soft segment polyurethanes. It is concluded that the hard segment polyurethanes are thermally more stable than the soft segment polyurethanes and also the lower mole ratio of cardanol: furfural (1:0.7) derived polyurethanes are comparatively more stable than that of the higher mole ratio of cardanol: furfural (1:0.9 and 1:0.8) derived polyurethanes.

Acknowledgements

One of the authors(RS) wish to thank the University Grant Commission, New Delhi, the director of Collegiate Education, Chennai and the Principal, Sarah Tucker College, Tirunelveli for selecting under FDP Programme.

REFERENCES

- [1] MS Patel; VS Patel and RG Patel. *J. Therm. Anal.*, **1989**, 35, 47.
- [2] JP Pillot; MDM Vanthanh; J Gerval and J Dunogues. *Euro. Poly. J.*, **1989**, 25, 285.
- [3] S Manjula; C Pavithran; CKS Pillai and VG Kumar. *J. Mater. Sci.*, **1991**, 26, 4001.
- [4] S Manjula; VG Kumar and CKS Pillai. *J. Appl. Polym. Sci.*, **1992**, 45, 309.
- [5] ND Ghatge and BM Shinde. *J. Elastomers*. **1979**, 111, 48.
- [6] ND Ghatge and SV Vailva. *Die Aggewandte Macromoleculare chemie.*, **1975**, 43, 1.
- [7] S Manjula; CKS Pillai and VG Kumar. *Thermochim. Acta.*, **1990**, 159, 255.
- [8] G John and CKS Pillai. *Makromol. Chem. Rapid. Commun.*, **1992**, 13, 255.
- [9] V Madhusudhan and BGK Murthy. *Prog. Org. Coat.*, **1992**, 20, 63.
- [10] RS Balakrishna; MN Satyanarayana; BB Vishwanath and MM Shrisalkar, *J. Appl. Polym. Sci.*, **1990**, 41, 1365.
- [11] R Antony. *J. Polym. Sci.*, **1993**, 31, 3187.
- [12] K Sathyalekshmi and S Gopalakrishnan. *Plast Rubber Compos.*, **2000**, 29(2), 63.
- [13] CV Mythili; A Malar Retna and S Gopalakrishnan. *Bull. Mater. Sci.*, **2004**, 27(3), 235-241.
- [14] CV Mythili; A Malar Retna, and S Gopalakrishnan. *J. Appl. Polym. Sci.*, **2005**, 98, 284-288.
- [15] Kattimuttathu I Suresh and Vadi S Kishanprasad. *Ind. Eng. Chem. Res.*, **2005**, 44, 4504-4512.
- [16] A Gardziella; L Pilato and A Knop, Phenolics Resins, Springer, Berlin, **1999**.
- [17] SP Potnis and BV Sharma. *Pop. Plast.*, **1969**, 13, 8.
- [18] N Tripathy and PK Choudhary. *Ind. J. Appl. Chem.*, **1961**, 24, 9.
- [19] LH Brown. *Ind. Eng. Chem.* **1952**, 44, 2672.
- [20] TK Das; D Das; BN Guru, KN Das and S Lenka. *Polym.-Plast. Technol. Eng.*, **1998**, 37, 427.
- [21] DK Mohapatra; D Das; PL Nayak and S Lenka. *J. Appl. Polym. Sci.*, **1998**, 70, 837.
- [22] DK Mishra; BK Mishra; S Lenka and PL Nayak. *Polymer Engineering and Science.*, **1996**, 36, 8.
- [23] Z Wirpsza, Polyurethanes: Chemistry, Technology, and applications, Kemp, T.J., Ed, Ellis Horwood, Newyork, **1993**.
- [24] DJ Skrovanek; SE Howe; PC Painter and MM Coleman. *Macromolecules.*, **1985**, 18, 1676.
- [25] F Papadimtrakopoulos; E Sawa and W J MacKnight, *Macromolecules.*, **1992**, 25, 4682.
- [26] RW Seymour; G M Estes and SL Cooper. *Macromolecules.*, **1970**, 3, 579.
- [27] HH Horowitz and Metzger. G. Esso Res Engg Co., Linden, NJ, *J Anal Chem.*, **1963**, 35, 1464.
- [28] A Broido. *J polym Sci.*, **1969**, 7, 1761.