

Thermal stability of *p*-xylene-formaldehyde resin and its derivatives

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Abstract. Nitrated and chlorinated derivatives of *p*-xylene-formaldehyde resin were prepared and the resin samples were characterised by IR and NMR spectra. The average molecular weight of the resin samples was determined by vapour pressure osmometry. Kinetic parameters were determined from differential thermal analysis and thermogravimetry using Chatterjee, Anderson-Freeman, Broido, Flynn and Wall, Reich and Kissinger methods.

Keywords. *p*-Xylene-formaldehyde resin ; average molecular weight ; thermogravimetry ; differential thermal analysis.

1. Introduction

Anderson (1962) compared the thermal stability of chlorinated phenol-silane co-polymers with that of unmodified chlorinated phenolic resins, and reported that the chlorinated phenol-silane co-polymers had better thermal stability. The thermal properties of a number of nitrosubstituted and analogous non-nitrosubstituted epoxide polymers have been investigated by Fleming (1969). There was a dramatic increase in char yield and a decrease in maximum rate of weight loss for nitrosubstituted systems compared to their non-nitrated analogs. It was therefore believed that the substitution on a polymer backbone played an important role in the thermal stability. In the present work, the derivatives of *p*-xylene-formaldehyde resins were prepared and their thermal behaviour studied.

2. Experimental

The chemicals used were of analytical grade. *p*-Xylene-formaldehyde (*p*-XF) resin was prepared using *p*-xylene, paraformaldehyde and *p*-toluenesulphonic acid as catalyst (Patel *et al* 1979). The soluble fraction of *p*-XF resin was used for the nitration and the chlorination.

2.1. Nitration reaction

A soluble fraction of *p*-XF resin (1 g) was taken in a 100 ml round bottom flask. To this 10 g of nitrating mixture (5 g H₂SO₄ and 5 g HNO₃) were added dropwise with vigorous stirring for 1 hr. The temperature was maintained between 0–5° C by external cooling. The contents of the flask were then heated at 85° C for 2 hr, during which period the reaction was complete. Thereafter, the contents of the flask were poured in crushed ice. The precipitates so obtained were washed several times with 10% sodium bicarbonate solution and then with hot distilled water to remove unreacted acids.

2.2. Chlorination reaction

p-XF resin (2.5 g) and phosphorus pentachloride (9 g) were taken in 50 ml round bottomed flask. The contents of the flask were heated to 195° C for 2 hr (Colson). It was then poured into ice cold distilled water. The precipitates obtained were washed with hot distilled water. Both the nitrated and the chlorinated resin samples were dried in vacuum oven at room temperature.

2.3. Characterisation

The IR absorption spectra of resins were scanned on a Carl Zeiss model UR-10. The NMR data were obtained using Varian A-60D spectrophotometer operating at an applied radio-frequency of 60 MHz. The average molecular weights (\bar{M}_n) of the resin samples were determined using a Hewlett-Packard model-302B vapour pressure osmometer. The Linseis thermobalance was used for thermogravimetry (TG) experiment and a micro DTA cell was used for differential thermal analysis (DTA) (Desai *et al* 1972).

3. Results and discussion

The results are given in tables 1 to 4. The yield of nitrated *p*-XF resin was 1.6 g, was insoluble and yellow amorphous in nature and melted at 183° C. Parent *p*-XF resin had a melting point of 105° C and an \bar{M}_n of 850. The yield of chlorinated *p*-XF resin was 3.5 g and it was soluble in toluene, benzene and chlorobenzene. It was yellow amorphous in nature having a melting point of 128° C and an \bar{M}_n of 1061.

The IR spectra of nitrated *p*-XF resin showed a strong absorption peak at 1542 cm⁻¹ due to the asymmetric stretching of –NO₂ group and the peak at 1350 cm⁻¹ was due to symmetric stretching of –NO₂ group. This clearly indicated the presence of nitro groups on aromatic nuclei.

Chlorinated *p*-XF resin showed a strong absorption band around 725 cm⁻¹, suggesting the presence of –CH₂Cl groups.

The NMR spectra of chlorinated *p*-XF resin showed a chemical shift at 4.8 ppm for methylene group attached to chlorine and aromatic ring. It confirmed the chlorination of methyl groups.

The above results showed that the number of repeat units in a chain of chlorinated *p*-XF resin was about 8 and the number of chlorine atom per molecule of

this resin was about 6. Nitrogen from the elemental analysis data of the nitrated *p*-XF resin was 3.5%.

The kinetic parameters of *p*-XF resin and its derivatives obtained from TG thermograms at different heating rates (RH) and using the Chatterjee (1965) method are given in tables 1 a to 1 c. In *p*-XF resin the decomposition temperature ranges were different for different heating rates (*cf* table 1a). A two-step degradation was observed at all the four heating rates. The decomposition of *p*-XF resin started from $\sim 145^\circ$ and ended at $\sim 630^\circ$ C. The weight loss involved in the first step decomposition ranged from ~ 30 to $\sim 45\%$ and the corresponding energy of activation E_A , ranged from ~ 18 to ~ 20 kcal mol⁻¹ for the RH of 6.5° to 1.0° C min⁻¹ respectively. The major decomposition was noted in the second step and the E_A values ranged from ~ 23 to ~ 30 kcal mol⁻¹. The reaction approached nearly first order kinetics for both the steps. The Arrhenius frequency factors, A_0 min⁻¹, varied to a considerable extent for all the RH.

Nitrated *p*-XF resin sample decomposed in the range of $\sim 195^\circ$ to $\sim 670^\circ$ C. The ΔT varied from $\sim 335^\circ$ to $\sim 475^\circ$ at various RH. The decomposition occurred in a single step corresponding to 100% weight loss for all the RH. E_A varied from ~ 18 to ~ 21 kcal mol⁻¹ in the case of different RH. The order of reaction, n , and the A_0 varied significantly.

Table 1a. Kinetic parameters (TG).

R.H. (°C min ⁻¹)	Amount (mg)	Decompo- sition temperature range (°C)	ΔT (°C)	Weight loss (%)	E_A (kcal mol ⁻¹)	Order of reaction n	Frequency factor A_0 min ⁻¹
6.5	50	165-395	455	45	18.4	1.14	6.58×10^6
		395-620		55	24.3	1.14	7.54×10^6
	25	160-395	470	45	18.0	1.14	4.93×10^6
		400-630		55	23.2	1.14	7.27×10^6
4.0	50	145-310	405	36	19.0	1.19	4.98×10^6
		315-550		64	26.3	1.19	2.31×10^{10}
	25	145-310	415	36	18.8	1.19	0.08×10^6
		320-560		64	27.0	1.19	8.2×10^{10}
2.5	50	155-315	410	30	19.5	1.01	5.17×10^{10}
		320-565		70	28.0	1.14	2.68×10^{14}
	25	150-315	415	30	20.0	1.01	1.18×10^{10}
		320-565		70	28.5	1.14	6.15×10^{14}
1.0	50	185-365	405	30	20.5	1.06	6.32×10^2
		365-590		70	30.1	1.18	4.49×10^8
	25	180-355	410	30	20.6	1.06	6.97×10^8
		365-590		70	30.3	1.18	8.69×10^7

Method : Chatterjee (1965).

System : *p*-xylene formaldehyde resin.

Table 1b. Kinetic parameters (TG).

R.H. (°C min ⁻¹)	Amount (mg)	Decompo- sition temperature range (°C)	ΔT (°C)	Weight loss (%)	E_A (kcal. mol ⁻¹)	n	A_0 (min ⁻¹)
6.5	50	195-665	470	100	19.9	1.17	3.43×10^4
	25	195-670	475	100	18.4	1.17	2.04×10^4
4.0	50	195-585	400	100	20.6	1.34	3.00×10^7
	25	195-585	390	100	20.4	1.34	2.05×10^7
2.5	50	225-560	335	100	18.4	1.09	1.98×10^6
	25	225-560	335	100	18.5	1.09	9.08×10^6
1.0	50	225-575	350	100	19.8	1.30	7.6×10^8
	25	225-575	350	100	20.6	1.30	7.34×10^8

Method : Chatterjee (1965).

System : Nitrated *p*-XF resin.

Table 1c. Kinetic parameters (TG).

R.H. (°C min ⁻¹)	Amount (mg)	Decompo- sition temperature range (°C)	ΔT (°C)	Weight loss (%)	E_A (kcal. mol ⁻¹)	n	A_0 (min ⁻¹)
6.5	50	150-250	485	14	15.6	1.59	2.46×10^8
		265-635		86	20.3	0.77	1.44×10^9
	25	150-255	485	17	15.3	1.59	2.49×10^8
		270-635		83	20.6	0.77	1.64×10^9
4.0	50	130-320	495	30	16.0	1.13	3.87×10^4
		325-625		70	21.8	1.13	3.67×10^4
	25	130-325	490	30	16.2	1.13	1.80×10^4
		325-620		70	22.0	1.13	3.76×10^4
2.5	50	170-395	415	30	17.5	1.38	2.10×10^8
		395-585		70	23.6	1.22	1.19×10^7
	25	170-410	415	30	17.9	1.38	2.10×10^9
		410-585		70	23.9	1.22	2.19×10^7
1.0	50	150-310	410	30	20.0	1.69	2.92×10^7
		320-560		70	26.0	1.22	3.46×10^{10}
	25	150-325	410	30	20.2	1.69	1.28×10^8
		330-560		70	26.3	1.22	3.05×10^9

Method : Chatterjee (1965).

System : Chlorinated *p*-XF resin.

Chlorinated *p*-XF resin decomposed in two steps. The decomposition of the resin started at $\sim 150^\circ\text{C}$ and ended at $\sim 560^\circ\text{C}$. Nearly 30% weight loss was noted in the first step degradation. The E_A values for two steps ranged from ~ 15 to ~ 26 kcal mol $^{-1}$. The major decomposition was observed in the second step, and the E_A values ranged from ~ 20 to ~ 26 kcal mol $^{-1}$ at various RH used for the study. In chlorinated *p*-XF resin the values of n and A_0 showed great variation. From the thermal study of these three resin samples, it was noted that chlorination of *p*-XF resin decreased its thermal stability as noted from the values of the starting decomposition temperature, whereas nitration of the *p*-XF resin resulted in increase of its thermal stability. The stability as revealed from the TG has the following order :

Nitrated *p*-XF > *p*-XF > chlorinated *p*-XF.

In the absence of the data on the volatile product of the decomposition, it is premature to offer explanation on the thermal stability of these resins.

Table 2 shows the kinetic parameters obtained from TG thermogram obtained at various RH for *p*-XF resin and its nitrated and chlorinated derivatives and

Table 2. Energies of activation (TG).

Name of the resin	R.H. ($^\circ\text{C min}^{-1}$)	Amount of resin (mg)	Energy of activation E_A (kcal mol $^{-1}$)			n	
			Broido method	Flynn-Wall method	Anderson-Freeman method		
<i>p</i> -XF resin	6.5	25	14.6	36.1	22.2	1.00	
		50	14.5	36.1	23.5	1.15	
	4.0	25	14.9		23.4	1.76	
		50	14.7		23.9	1.36	
	2.5	25	16.5		24.3	1.36	
		50	16.3		25.8	1.35	
	1.0	25	19.3		26.2	1.15	
		50	19.2		26.3	1.73	
	Nitrated <i>p</i> -XF resin	6.5	25	18.3	37.8	24.2	1.53
			50	19.0	38.0	24.2	1.19
4.0		25	20.0		26.1	1.6	
		50	20.9		26.7	1.5	
2.5		25	18.4		23.3	0.93	
		50	20.7		23.9	0.83	
1.0		25	18.6		25.3	0.75	
		50	20.1		26.7	0.84	
Chlorinated <i>p</i> -XF resin	6.5	25	13.9	21.5	19.3	0.91	
		50	14.9	22.8	18.9	0.81	
	4.0	25	17.4		20.2	1.11	
		50	17.5		20.8	1.36	
	2.5	25	18.7		22.3	1.27	
		50	18.4		20.7	0.99	
	1.0	25	19.7		23.0	1.11	
		50	19.1		24.5	1.33	

System : *p*-XF resin and its derivatives.

using the methods of Broido (1969), Flynn and Wall (1966) and Anderson and Freeman (1961). For *p*-XF the E_A values obtained by the Broido method varied from ~ 15 to ~ 19 kcal mol⁻¹ as the RH decreased from 6.5° to 1.0° C min⁻¹ respectively. The E_A from Flynn-Wall method was 36 kcal mol⁻¹, whereas from the Freeman-Anderson method it was fairly constant viz., 24 kcal mol⁻¹.

Similarly E_A for nitrated *p*-XF resin obtained using Flynn-Wall method was higher (~ 38 kcal mol⁻¹) than that obtained using Freeman-Anderson method which in turn, was higher than that using Broido method.

No such regularity was observed in the E_A values for the chlorinated *p*-XF resin sample when heated at different RH. From the thermal decomposition of these resin samples, it is noted in general that the E_A values obtained using any one method, for a particular resin sample, is found to decrease with the increasing heating rates. This trend is predominant in *p*-XF and chlorinated *p*-XF resin samples as compared to the nitrated *p*-XF resin. It should be mentioned that *p*-XF and chlorinated *p*-XF resin samples were soluble in some solvents, whereas the nitrated *p*-XF resin sample was not. The thermal behaviour of the former resin samples carried out at different RH could be interpreted as follows :

When the rate of heating is slow, the heat absorbed by the resin sample might be utilised in regrouping the molecules. If the relaxation time, τ is smaller than the time during which heat is delivered to the sample, the molecules will have time to regroup and the heat capacity will change gradually. At a high heating rate, the time for regrouping will be less and the heat is directly imparted to break the bonds in the molecules.

In the present study, the *p*-XF and the chlorinated *p*-XF resin, samples being soluble, might be more flexible in nature than the nitrated *p*-XF resin sample. Hence the decreasing trend of E_A with the increasing RH might be ascribed to the molecular rearrangement of flexible ones.

The kinetic parameters obtained from DTA curves using Reich (1969) methods are given in table 3. The DTA thermograms of all the three resin samples obtained at RH (a) 1°, (b) 2°, (c) 4° and (d) 6.5° C min⁻¹ were exothermic in nature and all peaks were associated with humps (*h*). For *p*-XF resin, the temperature for the hump and the maxima at different RH was (a) 350°, 460°, (b) 365°, 480°, (c) 350°, 490° and (d) 400°, 510° C respectively.

The E_A values for *p*-XF resin obtained using the Reich method ranged from ~ 64 to ~ 57 kcal mol⁻¹ and the decomposition reaction followed nearly first order kinetics. The range of E_A for the nitrated *p*-XF sample was from ~ 36 to ~ 41 kcal mol⁻¹, and the decomposition also followed nearly first order kinetics; while the E_A values for the chlorinated *p*-XF samples ranged from ~ 58 to ~ 39 kcal mol⁻¹ and had similar value of n .

The E_A values for all the three resin samples obtained using the Kissinger (1956) method had the following trend and followed nearly first order kinetics in general.

Nitrated *p*-XF (~ 19.0 kcal) > *p*-XF (~ 18.0 kcal)

> chlorinated *p*-XF (~ 17.5 kcal).

Summarising the kinetic parameters obtained from DTA curves using Reich and Kissinger methods, the Reich method deals with the energy of activation

Table 3. Kinetic parameters (DTA).

Name of the resin	Rate of heating (°C min ⁻¹)	Peak temp. (°C)	E_A (kcal mol ⁻¹)		n	
			Reich	Kissinger	Reich	Kissinger
<i>p</i> -XF resin	6.5	400 (<i>h</i>) 510	56.9	18.0	1.24	0.81
	4.0	350 (<i>h</i>) 490	58.3		1.27	0.81
	2.5	365 (<i>h</i>) 480	60.3		1.26	0.86
	1.0	350 (<i>h</i>) 460	64.4		1.01	0.99
Nitrated <i>p</i> -XF resin	6.5	385 (<i>h</i>) 525	40.9	19.1	1.14	0.90
	4.0	380 (<i>h</i>) 515	35.8		1.05	1.15
	2.5	375 (<i>h</i>) 460	40.2		1.18	1.07
	1.0	370 (<i>h</i>) 450	36.4		1.05	1.24
Chlorinated <i>p</i> -XF resin	6.5	385 (<i>h</i>) 500	39.1	17.5	1.24	1.04
	4.0	325 (<i>h</i>) 485	40.9		0.97	1.43
	2.5	325 (<i>h</i>) 475	46.0		0.93	1.26
	1.0	310 (<i>h</i>) 450	58.4		1.30	1.23

System : *p*-XF resin and its derivatives.

for a single thermogram obtained at a single heating rate, whereas the Kissinger method involves many thermograms at different heating rates keeping other experimental conditions constant. This method assumes that the activation energy is the same for the decomposition of the sample at different heating rates.

The trend observed in the E_A using the Reich method from DTA study carried out at different RH show that *p*-XF and chlorinated resins are more flexible than the nitrated *p*-XF resin sample.

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