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THERMOGRAVIMETRIC ANALYSIS OF TERPOLYMER RESINS DERIVED FROM O-AMINOPHENOL, DITHIOOXAMIDE AND FORMALDEHYDE

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ABSTRACT:

Terpolymers were prepared by the condensation of o-Aminophenol (o-A)-,dithiooxamide(D) and formaldehyde (F) in the presence of of hydrochloric acid (2M) as catalyst with varying molar ratio of reacting monomers. Terpolymers were characterized by their electronic absorption spectra, NMR spectra, IR spectra, elemental analysis and TGA. Molecular weight of terpolymer were determined by non-aqueous conductometric titration. The kinetic and thermodynamics parameters such as order of reaction, energy of activation, frequency factor, entropy charge , free energy change and apparent entropy change have been determined . Freeman Carroll and Sharp Wentworth method have been applied for the calculation of kinetic parameters while the data from the Freeman-Carroll method have been used up to determine various thermodynamics parameters. The static (isothermal) TG data were analysed by use of Sharp-Wentworth method were calculated and it was observed that the o-APDF-IV was more stable than those of o-APDF-I, o-APDF-II and o-APDF-III . This prediction on the basis of static TG data is an agreement with the prediction based on the activation energies and initial decomposition temperatures calculated from the dynamic TG curves.

Keywords:- Terpolymers, Synthesis, Resin, Thermal degradation, Kinetic parameters.

INTRODUCTION :

Many research is being directed towards the preparation of polymeric chains which are propagated because of the formation of metallic chelates, so that also synthetic resins derived from hydroxyl and amino compounds have attracted the attention of many research workers because of their versatile use as ion exchangers, photographic binders, thermal stabilizers, etc.

As the term implies, macromolecular science deals with compounds whose characteristic properties depend mainly on the extraordinary large size of the molecules and synthetic polymeric or macromolecular compounds lies between 104 and 107 polymeric materials received attention and importance only in the recent years. Condensation of phenol or hydroxybenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydroxybenzoic acid and urea/thiourea with formaldehyde /trioxane in presence of acid yields a terpolymer. These terpolymers are reported to have better acid resistance, better thermal stability and electrical properties than those of phenol-formaldehyde type copolymers.

Terpolymer are macromolecular entities which form an integral part of the backbone. Terpolymers are found to be amorphous powder or crystalline resinous in nature and form special class of polymers which are widely known for their uses. Condensation of phenol or hydrobenzoic acid with formaldehyde in presence of acid afforded a polymer, while condensation of hydrobenzoic acid and biuret with formaldehyde or trioxane in presence of acid as catalyst yields a Terpolymer. These Terpolymer have better thermal stability and electrical properties than those of phenol -

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formaldehyde type copolymers. The terpolymers can be used as ion-exchangers, semi-conductors, antioxidants, hardening agents, molding materials, rectifiers, dyes, fungicides in plants and living tissues.

In this paper we describe the study of Freeman-Carroll (1) and Sharp-Wentworth (2) methods to evaluate activation energy and thermal stability of newly synthesized terpolymer resin. The o-APDF terpolymer resins have been synthesized by the condensation process and purified. These are yellow color and are soluble in DMF, DMSO, aqueous KOH, and NaOH and insoluble in almost all organic and inorganic solvents.

EXPERIMENTAL

Chemicals : All the chemicals used were of Analytical R. grade.

Instruments used:

The apparatus required for a thermogravimetric analysis consists of the components.

1) A sensitive analytical balance.
2) A furnace.
3) A furnace temperature controller program
4) A recorder which provide a plot of sample. The plot is known as thermogram.

This is the entire experimental set-up for the thermogravimetric analysis, known as thermobalance. A wide range of commercial instruments are available and all of these have many common features. The thermograms of the terpolymer resins under present investigation were carried out at Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Anand, Gujarat.

Synthesis of o-Aminophenol(o-A)-Dithiooxamide(D)-Formaldehyde (F) Terpolymer Resin.

The four different types of o-APDF terpolymer resins have been successfully synthesized and abbreviated as given in Table 1.

Synthesis of o-APDF-I terpolymer resin

A mixture of ortho amino phenol (1.09gm, 0.1 mol), and dithiooxamide (1.20 gm, 0.1 mol) and formaldehyde (7.50 ml, 0.2 mol) in molar ratio of 1:1:2 in the presence of 2M (200 ml) HCl as a catalyst has been prepared in round bottom flask. The resultant mixture was refluxed over an oil bath for heating at 122°C ± 2°C for 5 hrs with occasional shaking to ensure thorough mixing. The temperature of oil bath was controlled electrically with the help of dimmerstat. The resinous sticky brown solid mass obtained was immediately removed from the flash as soon as the reaction period was over and then its purified. Excellent yield of terpolymer resin can be obtained by this reaction. The reaction is shown as follows in Fig. 1.

Purification of Resins :

The solid product was repeatedly washed with cold distilled water, dried in air and powdered with the help of agate mortar and pestle. The powder was washed many times with hot water followed by methanol to remove the unreacted starting materials, if any. The properly washed powder was dried in vacuum desicator over unhydrous calcium chloride. The resin was further purified by reprecipitation technique. The terpolymer was dissolved in 8% NaOH, filtered and reprecipitated by dropwise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with rapid stirring to avoid the lump formation. The process of reprecipitation was repeated twice. The terpolymer resin o-APDF-I so obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum dessicator over anhydrous calcium chloride.

Similarly other terpolymer resins o-APDF-II, o-APDF -III and o-APDF -IV were synthesized by varying molar properties of starting materials such as (2:1:3), (3:1:4) and (4:1:5) respectively by varying little experimental condition during polycondensation reaction of reacting materials.

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RESULTS AND DISCUSSION :

Thermogravimetry Of o-APDF Terpolymer Resin

The thermogravimetric analysis of o-APDF terpolymer resins has been carried out in the temperature range of 40°C to 800°C. The thermograms of o-APDF terpolymer resins are shown in Fig. 2, 3, 4 and 5. The thermogram of o-APDF terpolymer shows three steps in the decomposition reaction after initial loss of water molecular.

Thermogravimetry of o-APDF-I terpolymer resin

Thermogram of o-APDF-I terpolymer resin is given in Fig. 2, depicts three steps in decomposition reaction, after loss of one crystalline water molecule entrapped in the polymer molecule (5.94% found and 6.64% calculated). The first step of decomposition starts from 110°C to 150°C, corresponding the gradual mass loss of 17.82% found and 18.18% calculated, which may be due to the gradual loss of one hydroxyl group and one Amino (-NH-) group attached to aromatic benzene ring. The second step of degradation starts from 150°C to 530°C corresponding the rapid mass loss of 89.10% found and 88.40% calculated which may be due to the degradation of one aromatic benzene ring. The third step of decomposition starts from 530°C to 800°C, corresponding to slow loss of 94.26% found and 100.00% calculated, due to the degradation of side chain and Dithiooxamide moiety consequently the residue is left behind. Which is of carbon moiety The thermal degradation by increasing temperature may be due to the increasing strain and unstability and cross linking of molecule by increasing thermal vibration. To decrease the strain and to maintain stability the resin undergoes degradation.

Thermogravimetry of o-APDF-II terpolymer resin

Thermogram of o-APDF-II is shown in Fig. 3, showing three stage decomposition, in the temperature range of 40°C-800°C after initial mass loss of crystalline water molecule (3.96% found and 4.59% calculated). The first step of decomposition starts from 140°C to 250°C corresponding the mass loss of 16.50% found and 16.84% calculated, which may be due to loss of the hydroxyl groups and two Amino (-NH-) groups attached to aromatic benzene ring, may be due to increasing strain by thermal vibrations. The second step starts from 250°C to 560°C, corresponding the mass loss of 92.40% found and 92.28% calculated which may be due to degradation of two aromatic benzene nuclei, may be due to unzipping strain and unstability in the molecule. The third step of degradation starts from 560°C to 800°C, corresponding to the mass loss equal to 95.73% found and 100.00% calculated, which may be due to the degradation of side chain and dithiooxamide moiety and consequently the residue left over is carbon moiety.

Thermogravimetry of o-APDF-III terpolymer resin

Thermogram of o-APDF-III terpolymer resin is shown in Fig. 4, in the temperature range of 40°C to 800°C, showing three stage decomposition reaction with initial loss of one water molecule corresponding the loss of 3.30% found and 3.50% calculated. The first step of decomposition starts from 145°C to 280°C, corresponding to the loss of mass equal to 16.50% found and 16.16% calculated, which may be due to the degradation of two hydroxyl and two Amino (-NH-) groups attached to two aromatic benzene rings, may be due to increasing cross linking, strain and unstability by thermal vibrations. The second step decomposition starts from 280°C to 590°C, when the molecule loss it's fine structures, cross linking, strain and unstability may increased, which result of showing the mass loss equal to

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94.38% found and 94.2147% calculated which may be due to the degradation of three aromatic benzene rings. The third step starts from 590°C to 800°C, when the strained molecule suffer unzipping of cross linking, leading to the mass loss of 97.50% found and 100.00% calculated, may be due to degradation of side chain and Dithiooxamide moiety consequently the residue left behind.

Thermogravimetry of o-APDF-IV terpolymer resin

Thermogram of o-APDF-IV terpolymer resin is shown in Fig. 5, in the temperature range of 40°C to 800°C, showing three stages in the decomposition reaction with initial loss of water molecule corresponding the mass loss of 2.64% found and 2.83% calculated. The first stage of decomposition starts from 150°C to 290°C, which is corresponding to the mass loss (15.84% found and 15.74% calculated) of four hydroxyl and four (-NH-) groups attached to four aromatic benzene nucleus, may be due to increasing cross linking, strain and unstability in the molecule by increasing thermal vibration due to increasing temperature in the molecule. The second step of decomposition starts from 290°C to 600°C, when strain increases high, leading to the mass loss equal to 95.70% found and 95.37% calculated, which may be due to the degradation of four aromatic benzene rings. The third and last step decomposition may be due to the loss of side chain and dithiooxamide moiety, when the strained molecule suffer unzipping of cross linking, leading to the mass loss equal to 98.62% found and 100.00% calculated and consequently the residue left behind is carbon moiety.

The results of thermogravimetric analysis of o-APDF terpolymer resins and species degraded with their corresponding percentage mass loss are given in Table 3.62. By using thermal decomposition data the graphs were plotted by applying Sharp-Wentworth method (Fig. 6) and activation energy was calculated, found to be in good agreement with the activation energy calculated by Freeman-Carroll method . The thermal activation energy plot and Freeman-Carroll plots for o-APDF terpolymer resin have depicted in Fig. 7 to 8 respectively. The thermogravimetric parameters have been calculated on the basis of thermal activation energy of using Freeman-Carroll method. The various kinetic parameters such as change in energy (ΔS) free energy change (ΔF) frequency factor (Z) and apparent entropy (S*) are given in Table 3.

DISCUSSION :

By using thermal decomposition data and then applying the Sharp-Wentworth method (a representative Sharp-Wentworth plot of o-APDF - (1) polymer is shown in Fig.6) activation energy is calculated which is in agreement with the activation energy calculated by Freeman-Carroll method (Table2). A representative thermal activation energy plot(Fig.7) and Freeman-Carroll plot(Fig.8) for the polymer has been shown. Thermodynamic parameters have been calculated on the basis of thermal activation energy. These values are given in Table2.

By using the data of the Freeman-Carroll method various thermodynamic parameters have been calculated (Table 2). The values of these thermodynamic parameters for all the tercopolymers are about the same. The similarity of the values indicates a common reaction mode. From the abnormally low values of frequency factor, it may be concluded that the decomposition reaction of o-APDF polymers can be classed as a 'slow' reaction. There is no other obvious reason.

The activation energy calculated by Sharp-Wentworth method and Freeman-Carroll method are in good agreement. The sequence of thermal stability is found to the o-APDF-I < o-APDF-II < o-APDF-III < o-APDF-IV. The sequence of thermal stability is predicted on the basis of

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increasing initial and half decomposition temperature as well as on the increasing melting points. The removal of water molecule is the initial slow mass loss, which may due to the water entrapped in terpolymer resin, hence the water is probably considered as a crystal water. Finally residue remained ascribed as dithiooxamide moiety. The various kinetic parameters calculated by Freeman-Carroll method are about same, indicating common mode of decomposition reaction. Abnormally the low values of frequency factor may be indicated that the decomposition reaction can be classed as slow reaction. The slow reaction is also predicted by negative values of entropy change. The negative values means the disorder is less and the reaction in carried by more order manner, making it slower. The graphs obtained by Sharp-Wentworth and Freeman-Carroll methods are fairly good straight liners or linear by ignoring some abnormal points, indicating that the decomposition does not obey first order kinetics perfectly [3,4,5,6,7,8,9,10,11,12,13,14,15,16]. However no unique conclusion can be drawn from the TGA study as the decomposition reaction perhaps is very complicated.

On the basis of all the physico-chemical and spectral evidences and foregoing results and discussion the most probable structures have been proposed for o-APDF terpolymer resins under investigations as shown in Fig. 9.

REFERENCES:

E. S. Freeman and B. Carroll, J. Phys.Chem. 62, 394 (1958).

J. B. Sharp and S. A. Wentworth, Anal.Chem. 41 2060 (1969).

Kirsten Skogerson, Mark Downey, Marica Mazz, “Rapid determination of phenolic component in red wine from UV-visible spectra,” American J. Ecology and Viticulture, 58, 318-325 (2007).

Bhave N. S., Iyar V. N., J. Thermal Analysis, 32, 1367-1377 (1987).

Chatterjee S.K.; Gupta N.D.; J. Polym. Sci. Part A -I (11) 1216 (1973).

Gurnule W. B., Ph.D. Thesis, RTM Nagpur University, Nagpur (1999).

Gurnule W. B. Juneja H. D., Paliwal L. J., Oriented J. Chem., 15(2), 283-288 (1999).

Jadhao M. M., Ph.D. Thesis, RTM Nagpur University, Nagpur (2005).

Lingala P.S., Juneja H. D., Paliwal L. J., Proc. Nat. Acad. Sci. Ind., 71(A), III, 205-212 (2001).

Lingala P. S., Ph.D. Thesis, RTM Nagpur University, Nagpur (2003).

Michael P.E.P., Barbe J.M., Juneja H.D., Paliwal L.J., Europ. Polym. J., 43, 4995-5000 (2007).

Pal T. K., Kharat R. B., J. Ind. Chem. Soc., 27A, 85 (1988).

Pal T. K., Ph.D. Thesis, RTM Nagpur University, Nagpur, (1988).

Rusli Daik, Maniam S., Malaysian J. of Chem., 9(1), 016-021 (2007).

Pancholi H. B., Patel M. M., Thermochemica Acta, 191, 227-233 (1991).

Patel K. D., Patel M. M., Synth. React. Inorg. Mat. Org. Chem., 23(2), 299-325 (1993).

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Table 1
Synthesis and Physical Data of o-APDF Terpolymer Resins

Terpolymer Resin Abbreviation	Reactants			Molar ratio	Catalyst 2M/HCl (ml)	Reflux Temp. (K)	Time (hr)	Yield (%)	Melting point (K)
	Ortho amino phenol o-AP (mol)	Dithiooxamide D (mol)	Formal dehyde F (mol)						
o-APDF-I	0.1	0.1	0.2	1:1:2	200	393	5	80	386
o-APDF-II	0.2	0.1	0.3	2:1:3	200	393	5	82	393
o-APDF-III	0.3	0.1	0.4	3:1:4	200	393	5	84	390
o-APDF-IV	0.4	0.1	0.5	4:1:5	200	393	5	85	389

Table 2
Thermogravimetric Data and Decomposition Temperature Range of o-APDF Terpolymer Resins

Terpolymer Resins	Loss of crystalline water molecule		Decomposition step, temperature range (°C), mass loss (%) and species degraded						Mass of residue leftover (%)
			First Step (loss of methyl & hydroxyl group)		Second Step (loss of aromatic phenyl nucleus)		Third Step (loss of side chain of oxamide)		
	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	
o-APDF-I	40-110	5.94(F) 6.64C)	110-150	17.82(F) 18.18(C)	150-530	89.10(F) 88.40(C)	530-800	94.26(F) 100.00(C)	5.74(F) 0.0(C)
o-APDF-II	40-140	3.96(F) 4.59(C)	110-250	16.50(F) 16.84(C)	250-560	92.40(F) 92.28(C)	560-800	95.73(F) 100.00 (C)	4.27F) 0.0(C)
o-APDF-III	40-145	3.30(F) 3.50(C)	145-280	16.50(F) 16.16(C)	280-590	94.38(F) 94.21(C)	590-800	97.30F) 100.00 (C)	2.70(F) 0.0(C)
o-APDF-IV	40-150	2.64 (F) 2.83(C)	150-290	15.84(F) 15.74(C)	290-600	95.70(F) 95.37(C)	600-800	98.62F) 100.00 (C)	1.38(F) 0.0(C)

F = found, C = calculated

Table 3
Results of Thermogravimetric Analysis of o-APDF Terpolymer Reins

Terpolymer resins	Half decomposition Temp. (K)	Activation energy Ea (KJ)/mol		Entropy change □S (J)	Free energy □F (KJ)	Frequency factor (Z) (Sec.$^{-1}$)	Apparent entropy (S*) (KJ)	Order reaction (n)
		FC	SW					
o-APDF-I	633	23.41	23.74	-163.956	97.314	659	-19.149	0.98
o-APDF-II	673	25.64	24.41	-164.521	100.375	705	-19.11	0.97
o-APDF-III	683	26.72	26.61	-165.092	102.548	785	-19.03	0.95
o-APDF-IV	688	27.25	27.51	-165.662	104.721	812	-19.02	0.94

SW – Sharp-Wentworth Method FC – Freeman–Carroll Method

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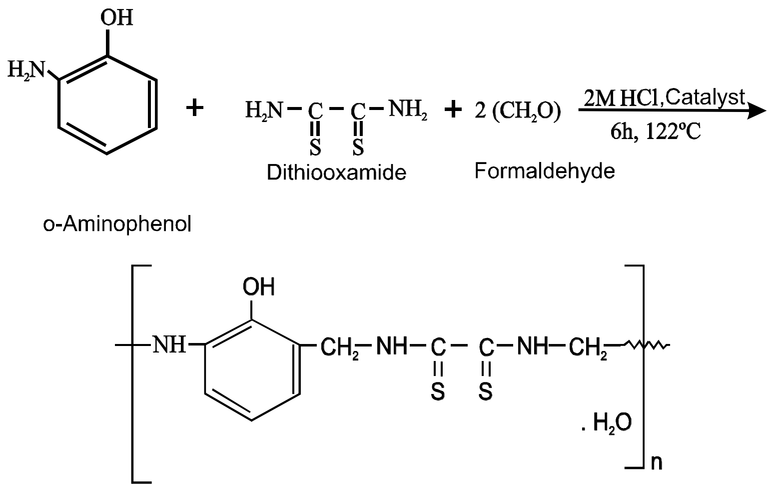

o-APDF Terpolymer

Fig. 1. Reaction and Suggested Structure of Representative o-APDF-I Terpolymer Resin

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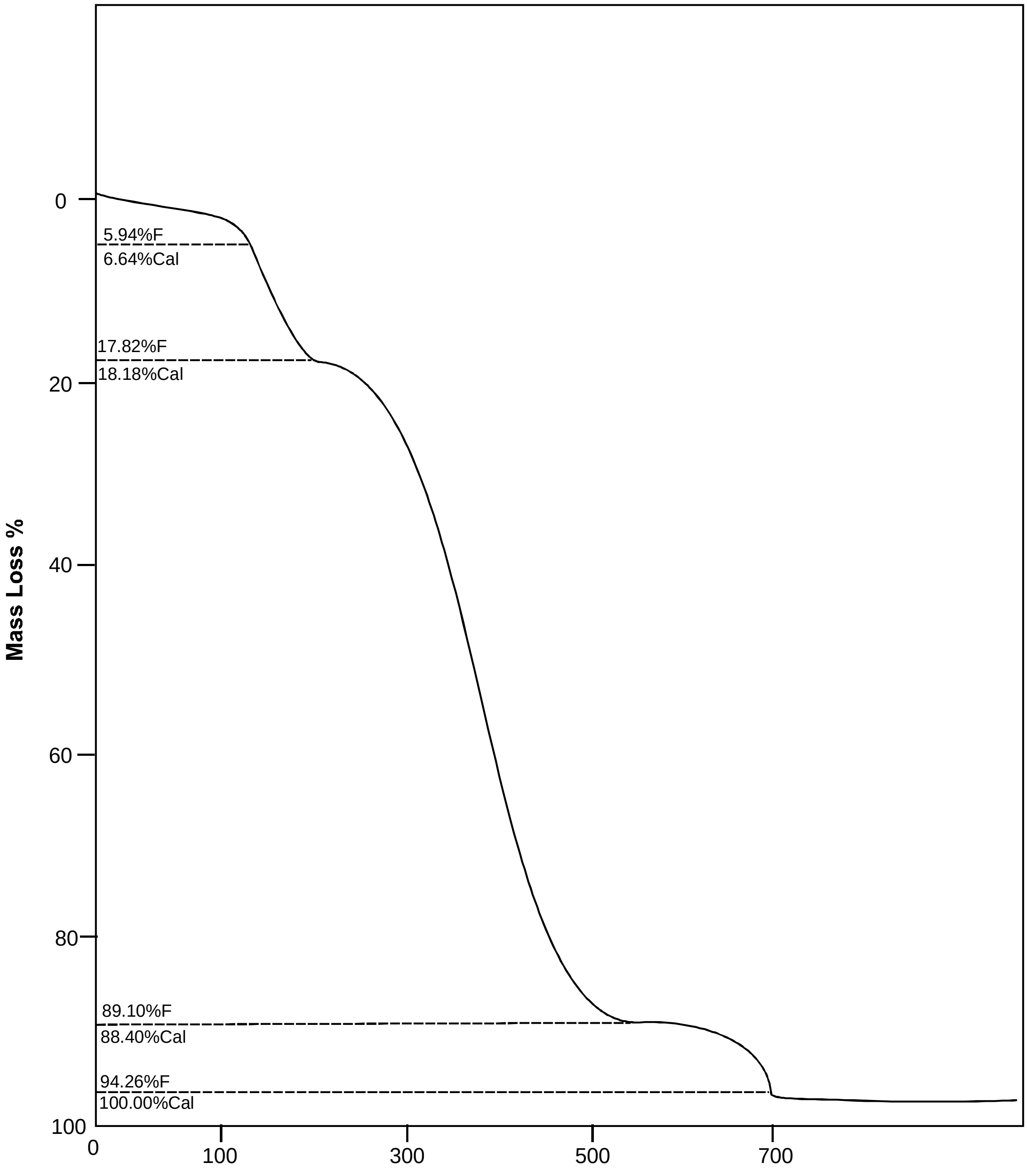

Fig. 2. Decomposition Pattern of o-APDF-I Terpolymer Resin

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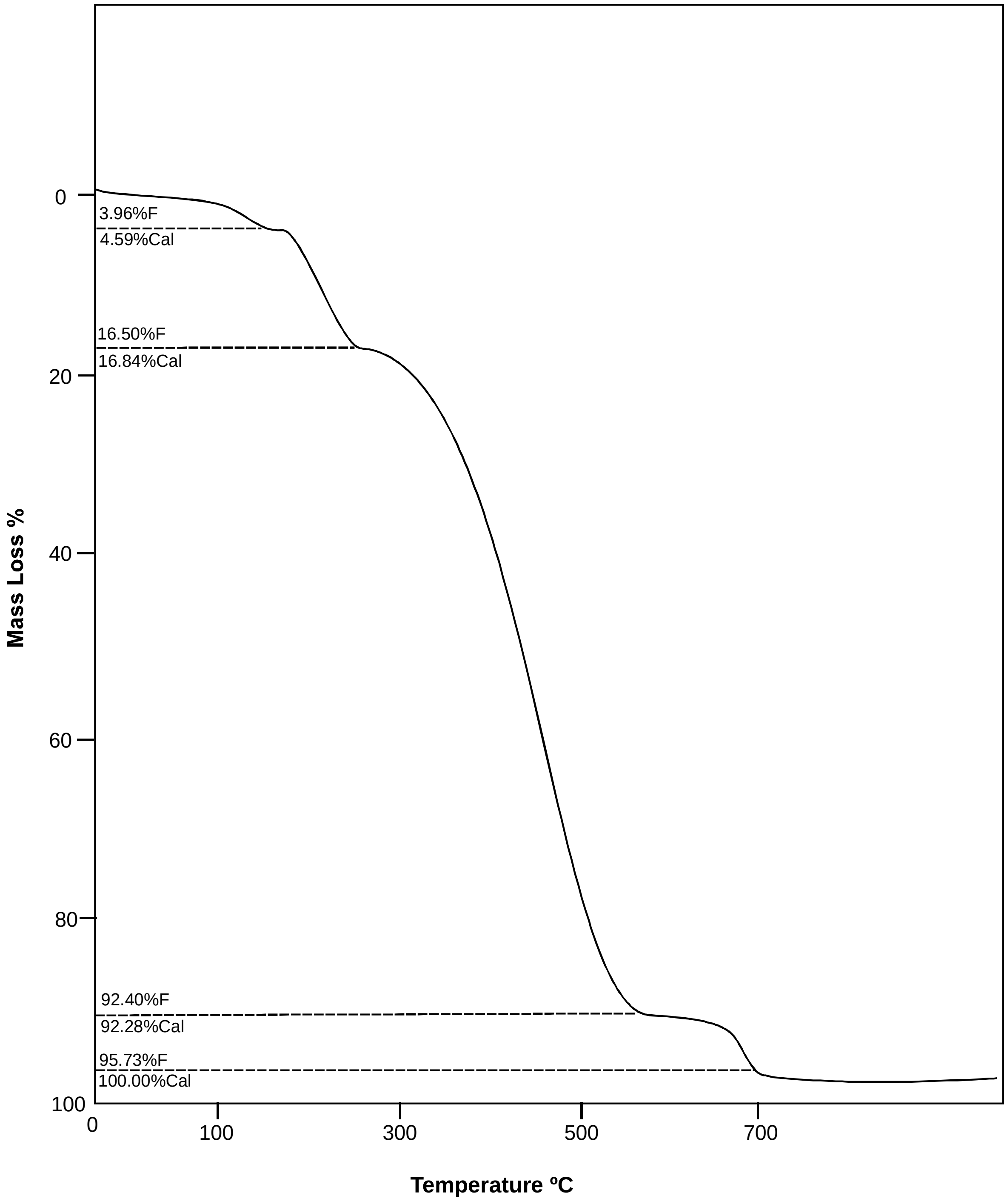

Fig. 3. Decomposition Pattern of o-APDF-II Terpolymer Resin

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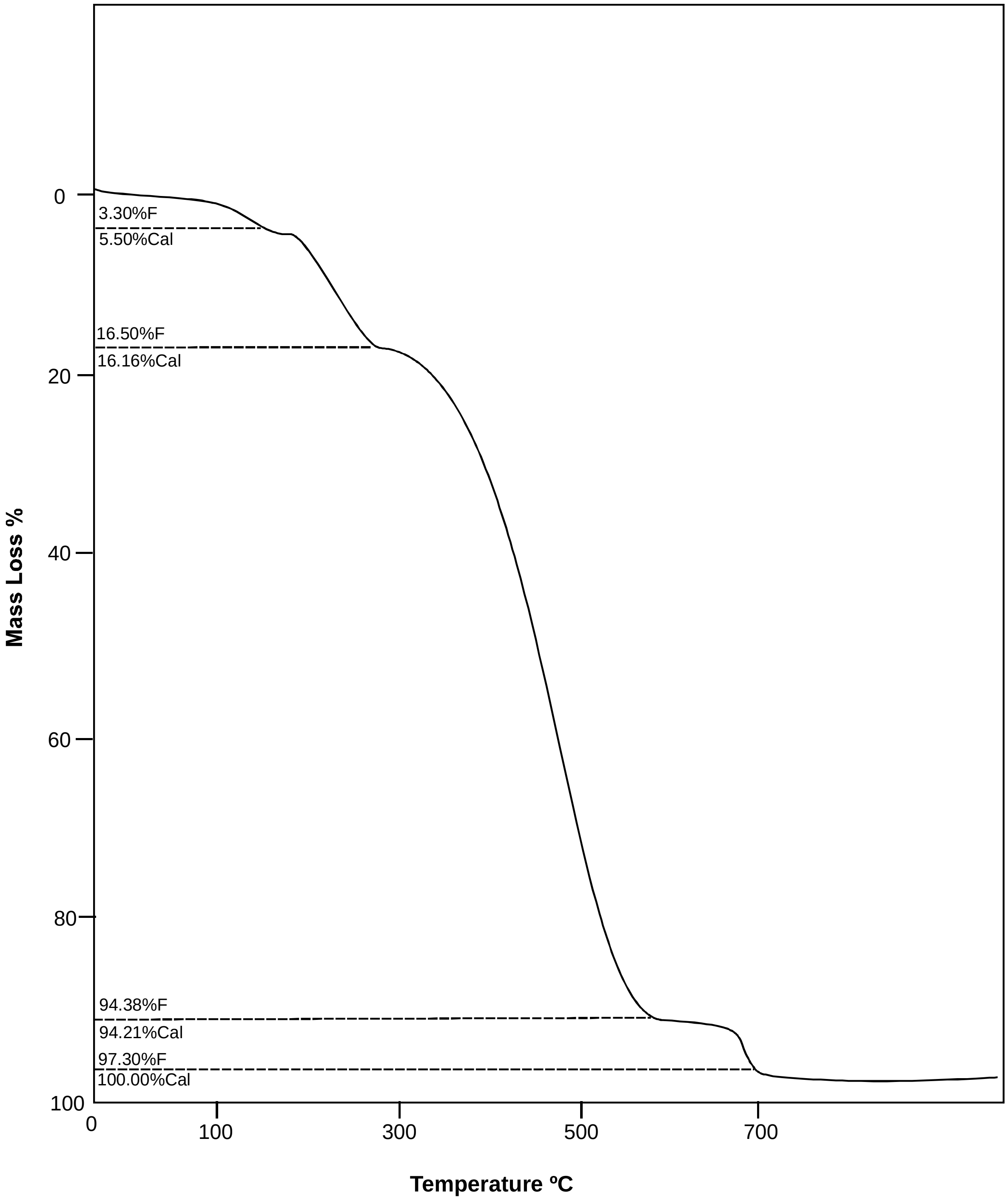

Fig. 4. Decomposition Pattern of o-APDF-III Terpolymer Resin

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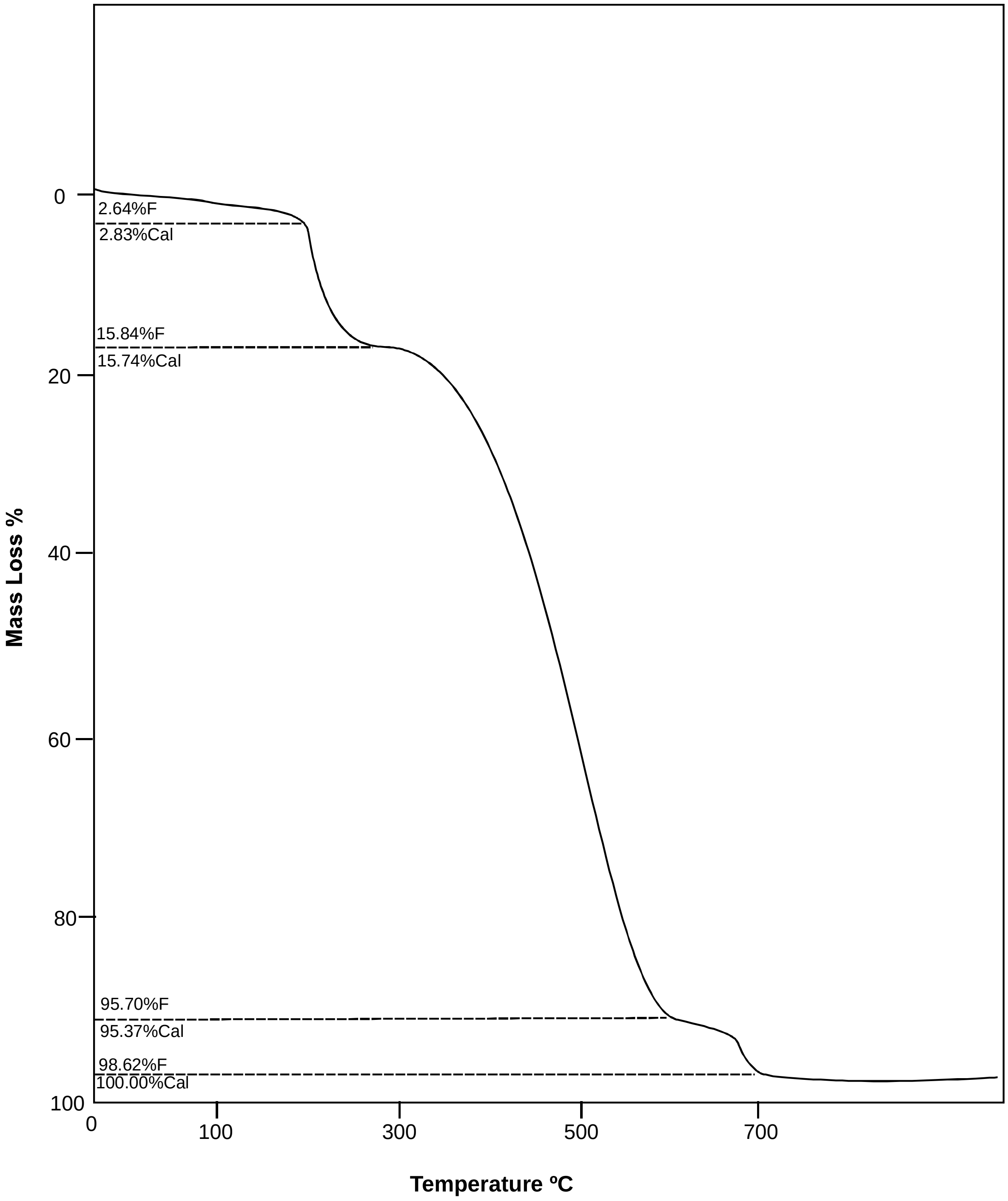

Fig. 5. Decomposition Pattern of o-APDF-IV Terpolymer Resin

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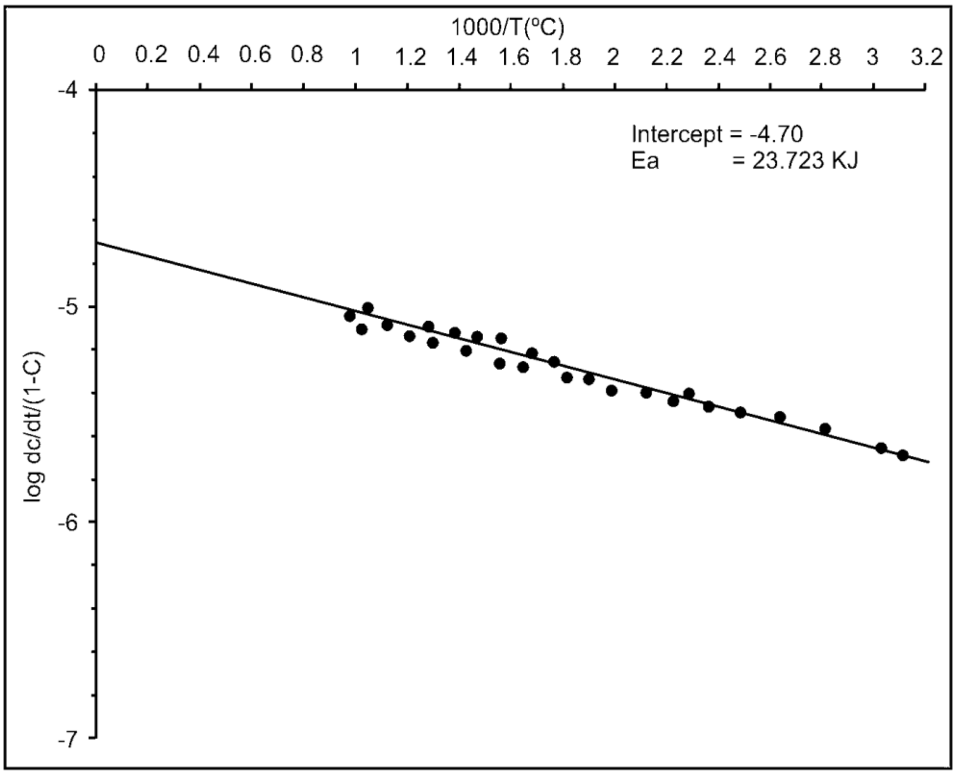

Fig.6. Sharp-Wentworth Plot of o-APDF-I Terpolymer Resin

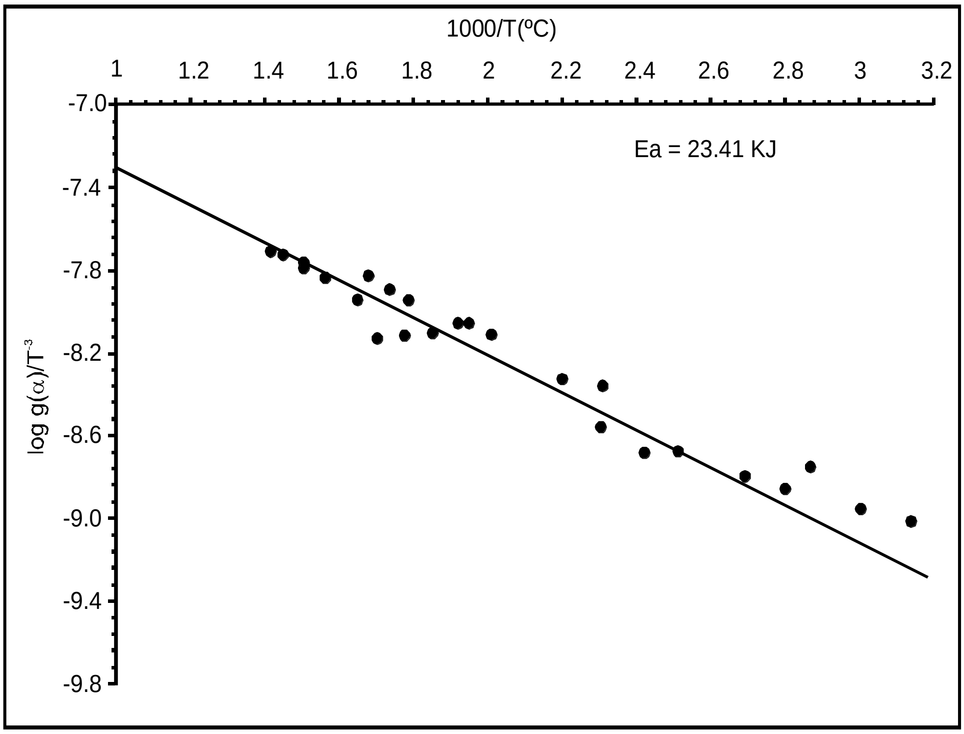

Fig.7. Thermal activation energy plot (Freeman-Carroll plot) of o-APDF-I terpolymer resin

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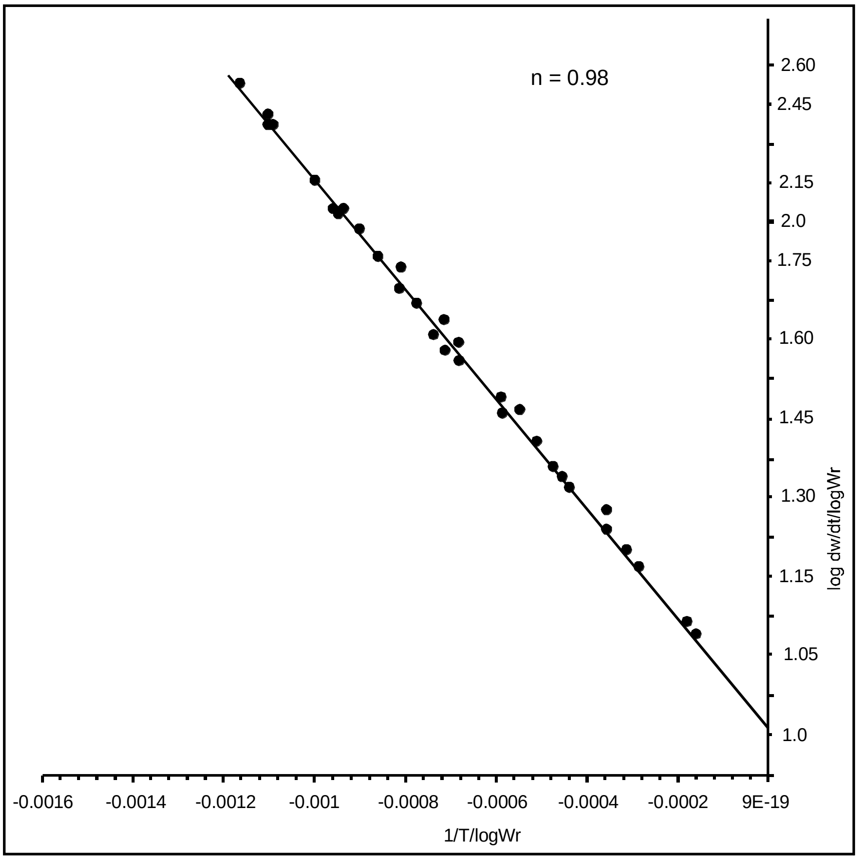

Fig.8. Freeman-Carroll Plots of o-APDF-I Terpolymer Resin

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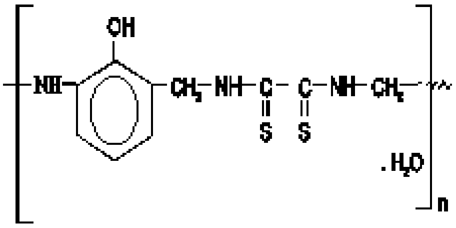
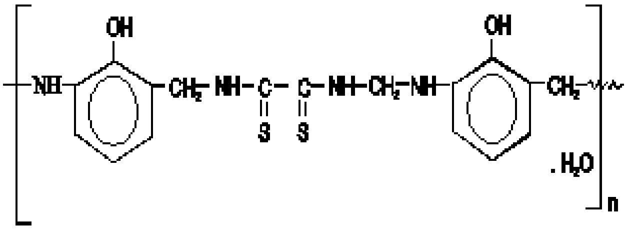


o-APDF-1 (1:1:2)



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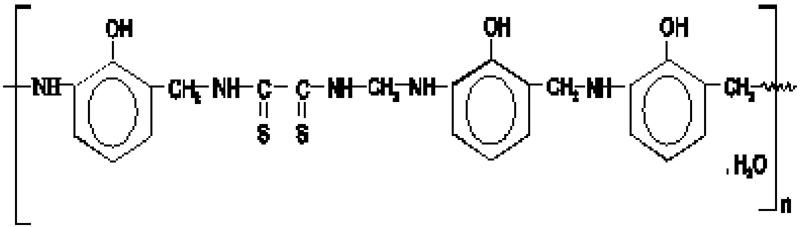
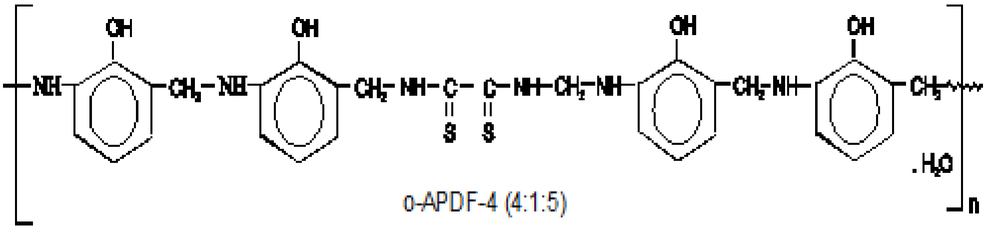


o-APDF-3 (3:1:4)



o-APDF-4 (4:1:5)

Fig. 9. Structures of o-APDF Terpolymer Resins

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