

Comparative evaluation of thermal stabilities of novel sulphonic acid resins from anhydride modified polystyrene with commercial polystyrene based resins, Indion-225 and Zeo-carb 225

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Non-isothermal as well as isothermal stabilities of sulphonic acid resins from polystyrene, electrophilically substituted with phthalic anhydride, pyromellitic dianhydride, trimellitic anhydride and *cis*-1,2,3,6 tetrahydrophthalic anhydride have been studied and compared by d.t.a., t.g.a. and isothermal degradation of these resins at $250 \pm 10^\circ\text{C}$ for 72 h in air. The modified resins thus obtained exhibit better thermal stability relative to the unmodified sulphonated polystyrene. The d.t.a. and t.g.a. studies of the modified polystyrene based resins have revealed a better thermal stability compared to sulphonated polystyrene as well as commercial polystyrene divinyl benzene resins like Zeo-carb 225 and Indion 225 (available in India). Isothermal degradation of the commercial resins was studied at $250 \pm 10^\circ\text{C}$ for 72 h in air and the analysis of the degraded product has also been carried out. Finally, attempts have been made to rationalize these observations on the basis of the structural characteristics of all the resins.

(Keywords: non-isothermal stability; isothermal stability; anhydride-modified polystyrene resins; Indion 225; Zeo-carb 225)

INTRODUCTION

Biswas and Chatterjee¹ have recently presented the results of a comprehensive thermogravimetric analysis and hydrolytic stability studies of the four cation exchange resins prepared by sulphonation^{2,3} of polystyrene (PS), electrophilically substituted with phthalic anhydride (PA)⁴, trimellitic anhydride (TMA)⁵, *cis*-1,2,3,6 tetrahydrophthalic anhydride (THPA)⁶ and pyromellitic dianhydride (PMDA)⁴. The thermal behaviour of the above resins was rationalized on the basis of their structural characteristics.

The present paper highlights the non-isothermal as well as the isothermal stabilities of two commercial sulphonic acid resins from polystyrene-divinyl benzene such as Indion 225 and Zeo-carb 225. Also, this work offers an opportunity to compare the thermal stabilities of com-

mercial resins in detail with each other and with other polystyrene based sulphonic acid resins under identical experimental conditions. Finally, the thermal stability behaviour of all the resins was correlated on the basis of structural characteristics.

EXPERIMENTAL

Materials

The detailed synthesis of modified polystyrene polymers by electrophilic substitution with phthalic anhydride⁴, pyromellitic dianhydride⁴, trimellitic anhydride⁵, *cis*-1,2,3,6 tetrahydrophthalic anhydride and the corresponding sulphonated resins^{3,2,6} therefrom have already been described in earlier publications and their physico-chemical characteristics are listed in Table 1. Sulphonated polystyrene (PSS) of total capacity = 4.8 meq g^{-1} has been synthesized using the procedure of

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Table 1 Pertinent physico-chemical characteristics of anhydride modified sulphonated polystyrene

Resin	Physico-chemical characteristics		
	Total capacity (meq/g (dry))	Salt-splitting capacity (meq/g (dry))	Sulphur content (%)
Polystyrene pyromellitic dianhydride sulphonated (PSPMDAS)	5.75	4.58	16.42
Polystyrene phthalic anhydride sulphonated (PSPAS)	5.79	5.42	23.35
Polystyrene trimellitic anhydride sulphonated (PSTMAS)	5.49	4.98	15.58
Polystyrene tetrahydrophthalic anhydride sulphonated (PSTHPAS)	5.74	5.22	20.60

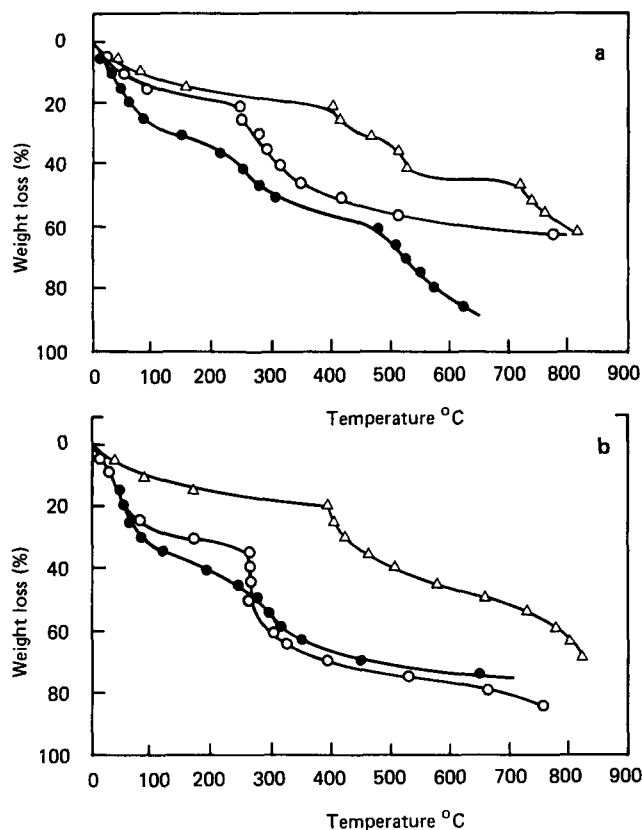


Figure 1 T.g.a. curves of (●): PSS; (○): Indion 225; and (△): Zeo-carb 225. (a) in air, (b) in nitrogen

Vasudevan *et al.*⁷. Sulphonated styrene-divinyl benzene copolymers of commercial importance, Indion 225 and Zeo-carb 225, were received from Ion-Exchange (India) Ltd. and Iono-Chem (India) Ltd. The resins were used after vacuum drying at 60°C.

I.R. spectra

I.R. Spectra were recorded on a Perkin-Elmer 237B Grating I.R. spectrophotometer with KBr pellets.

Thermal characteristics

The thermal studies of Indion 225, Zeo-carb 225 and PSS were carried out both in air and nitrogen with a Stanton Red Croft TG-750 (U.K.) model up to 1000°C. The d.t.a. studies were carried out with a Stanton Red Croft DTA (U.K.) model at temperatures up to 500°C in air.

The t.g.a. data of PSPAS, PSTMAS, PSPMDAS and PSTHPAS (using the present instrument) have been

Table 2 Comparative studies of d.t.a. peaks of the resins

Polymer	D.t.a. peak at temperature (°C)	
	Endotherm (°C)	Exotherm (°C)
PSPAS	70	530 (Sharp)
PSTMAS	70	490 (Sharp)
PSTHPAS	120	470 (Sharp)
PSPMDAS	140	240 (Broad)
Indion 225	{ 55 (small) 250 (sharp)	-
Zeo-carb 225	{ 132 (small) 393 (sharp)	-
PSS	175 (sharp)	-

reported elsewhere¹, which will be referred to for comparative evaluation.

In all the cases heating rate was 10°C min⁻¹.

Isothermal degradation studies

Known weights of Indion 225 were heated in air in a muffle furnace at 250°C ± 10°C. At time intervals of 12 h, 24 h, 32 h and 72 h the weight losses were determined.

The isothermal stability studies of PSPAS, PSTMAS, PSPMDAS, PSTHPAS under same experimental conditions have been reported earlier¹ which will be repeated for comparative evaluation.

The i.r. spectra of resin residues, left after 72 h of isothermal heating, were recorded and the pH metric titration of the same was also carried out following the common procedure^{8,9}.

RESULTS AND DISCUSSION

Thermogravimetric analyses

Figure 1 presents the thermograms of PSS, Indion 225 and Zeo-carb 225 in air and in nitrogen atmosphere. Table 2 compares the thermal stability of PSS, Indion 225 and Zeo-carb 225 with the corresponding data for PSPAS, PSTMAS, PSPMDAS and PSTHPAS both in air and in nitrogen, atmosphere. Table 2 summarizes the d.t.a. characteristics of PSS, Indion 225, Zeo-carb 225 and those of PSPAS, PSTMAS, PSPMDAS and PSTHPAS. However, it is clear from Figure 1 that the thermal stability of Zeo-carb 225 is much higher than that of Indion-225 from the very beginning. Again, the latter shows a better thermal stability compared to PSS throughout the curve. Also, it appears from Figure 1 that the thermal stability of Indion 225 is much higher in air than in nitrogen, after a weight loss of 20%. The maximum weight loss is 60.7 (771°C) in air compared to 85% (755°C) in nitrogen. Therefore, it appears from the t.g.a. curve of Indion 225 that in air some oxidative degradation takes place which restricts the normal trend of weight loss which is observed in nitrogen atmosphere.

The t.g.a. curves of PSS, both in air and nitrogen atmosphere show a 30% weight loss at 152°C and 87°C respectively. This weight loss may be due to the loss of inherent moisture. In air, the thermal stability of PSS is considerably high (up to 70% weight loss). But the maximum weight loss in nitrogen atmosphere is higher than that in air.

Finally, the t.g.a. curves of Zeo-carb 225 show a weight loss of ca. 10% at 80°C in air and at 87°C in nitrogen atmosphere. A trend of enhanced thermal stability in air is observed in Zeo-carb 225 after 26% weight loss. Therefore, it may be concluded that enhanced thermal stability in air is characteristic of PS-DVB sulphonic acid resins. Bothe *et al.*¹⁰ have noticed that the unsulphonated polymer changes colour on heating and becomes liquid, while the sulphonated cation exchanger retains its spherical form. According to them the complex degradation behaviour of the polystyrene-divinyl benzene sulphonic acid resins is due to the formation of sulphones. A review of the above t.g.a. analysis data together with the above information leads to the probability of -COOH acid group formation by splitting one side of the ladder junction of divinyl benzene which is a double chain polymer. Simultaneous formation of the sulphone linkage

allows the resin to retain its pearl nature.

In the next stage of our present work, the comparative evaluation of thermograms of PSS, Indion-225 and Zeo-carb 225 with that of PSPAS, PSTMAS, PSPMDAS and PSTHPAS have been shown in Tables 3 and 4.

It is also important to note that T_0 (the temperature up to which the basic structure of a polymer is retained) of PSPAS, PSPMDAS, PSTMAS and PSTHPAS are (~300°C) observed to be greater than that of Indion 225 (~250°C) but less than that of Zeo-carb 225 (~400°C). In N_2 the gross weight loss of PSPMDAS is 58% (895°C) whereas for Zeo-carb 225 and Indion 225 the weight losses are 70% (820°C) and 88% (812°C) respectively. Therefore, the thermal stabilities of PSPMDAS, Zeo-carb 225 and Indion 225 lie in the order:

$$\text{PSPMDAS} > \text{Zeo-carb 225} > \text{Indion 225}$$

The maximum thermal stability of PSPAS is quite low (100%, 629°C). The same for PSTMAS and PSTHPAS are 75% (734°C) and 75% (896°C) respectively. Therefore, the thermal stabilities of PSTHPAS and Zeo-carb 225 are more or less the same. Also, it appears in PSPMDAS that, interchain crosslinking through pyromellitic dianhydride has better effect in thermal stability than that observed through divinyl benzene in Zeo-carb 225.

It is interesting to note that the maximum thermal stability of PSPMDAS in air is deteriorated to a value of 78% weight loss at 923°C, which is due to the effect of aerial oxygen on $C=O$ of quinonic structure and may cause major degradation, whereas in Zeo-carb 225 the presence of air has increased the thermal stability. Ultimately in air, a more or less similar thermal stability is

Table 3 Thermal stability* of polystyrene based sulphonic acid resins

Resin	Temperature (°C) for weight loss (%)										Maximum weight loss
	10	20	30	40	50	60	70	80	90	100	
PSS	35	58	87	193	275	311	448	-	-	-	836 (78%)
PSPAS	51	75	280	326	366	457	536	362	389	629	629 (100%)
PSTMAS	51	94	306	341	511	594	676	-	-	-	734 (75%)
PSTHPAS	80	107	232	391	430	504	739	-	-	-	896 (75%)
PSPMDAS	92	237	280	361	637	-	-	-	-	-	895 (58%)
ZC 225	87	391	420	504	653	780	820	-	-	-	820 (70%)
IN 225	35	58	170	264	264	303	391	663	-	-	812 (88%)

* Thermal stability in nitrogen atmosphere

Table 4 Thermal stability* of polystyrene based sulphonic acid resins

Resin	Temperature (°C) for weight loss (%)										Maximum weight loss
	10	20	30	40	50	60	70	80	90	100	
PSS	35	59	152	254	301	476	522	567	-	-	655 (86%)
PSPAS	51	94	341	376	425	522	545	562	571	-	580 (98%)
PSTMAS	51	94	326	361	400	494	549	576	596	639	629 (100%)
PSTHPAS	69	101	237	356	420	532	567	611	672	-	730 (95%)
PSPMDAS	103	254	291	381	549	804	-	-	-	-	923 (78%)
ZC 225	80	400	462	518	732	812	-	-	-	-	812 (60%)
IN 225	51	248	380	311	415	771	-	-	-	-	820 (61%)

* Thermal stability in air

Table 5 Effect of temperature on the weight loss of resins

Resin	% Weight loss at different time interval			
	14 (h)	24 (h)	36 (h)	72 (h)
PSPAS	64.8	64.8	77.8	89.4
PSTMAS	72.2	73.0	74.9	89.1
PSTHPAS	62.8	63.2	73.8	85.8
PSPMDAS	70.9	71.3	71.9	73.9
Indion 225	70.66	70.66	70.4	70.138

Table 6 Characteristic i.r. absorptions (cm^{-1})

	Bands	Assignments
Indion 225	{ 1035 1600	Sharp and broad for $-SO_3H$ $C=C$ aromatic stretching
Indion 225 after heating	{ 1035 1700 1600	Very small for $-SO_3H$ Small but sharp for $-COOH$ $C=C$ aromatic stretching

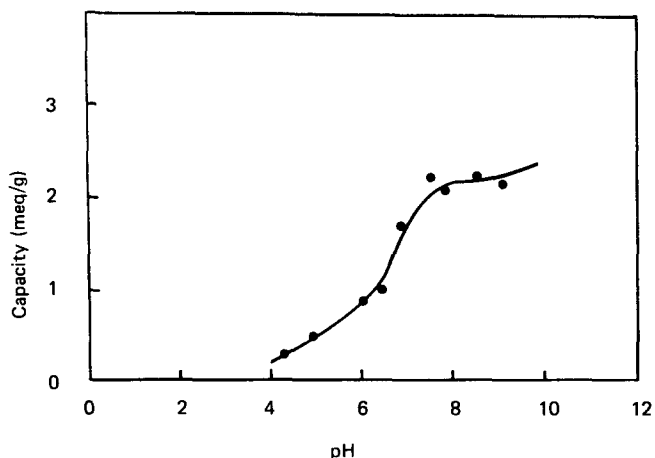


Figure 2 Capacity vs. equilibrium pH curve of Indion 225 (after 72 h heating at $250^\circ C \pm 10^\circ C$ in air)

observed in the case of PSPMDAS and Zeo-carb 225. In Indion 225 the maximum weight loss is 61% (820°C). The trend in thermal stability in air is:



In air the maximum weight losses of PSPAS, PSTMAS, PSTHPAS are comparatively high compared to Indion 225.

Isothermal decomposition of the resin

For practical applications of the resins and to get additional support for the decomposition process suggested as above, isothermal measurement of Indion 225 was carried out for a sustained period in atmosphere. Table 5 compares the effect of heating on weight loss of Indion 225 in air at $250^\circ \pm 10^\circ\text{C}$ with that of PSPAS, PSTMAS, PSTHPAS and PSPMDAS at different time intervals viz. 14 h, 24 h, 32 h and 72 h. These data reveal that in general 60–70% degradation occurs for all the cases in 14 h, about 25% PSPMDAS is retained even after 72 h as against 10% of the other three anhydride modified sulphonic acid resins. A very small increase in weight is observed in the case of Indion 225 from 32 h of heating.

The i.r. spectra of Indion 225 left after 72 h of heat treatment were also recorded and compared with the i.r. spectra of the original resin (Table 6) which suggests the appearance of a small but prominent peak at 1700cm^{-1} corresponding to the $-\text{COOH}$ group. The broad stretching band due to $-\text{SO}_3\text{H}$ group at 1040cm^{-1} and 1200cm^{-1} practically disappear.

To identify the nature of the resin left after isothermal degradation studies, pH-metric titration was performed (Figure 2). The weak acid nature of the material is apparent from the titration curve which reveals a single

inflection, $\text{p}K = 6.33$, as calculated by the procedure of Helfferich⁹. The literature data⁹ for $\text{p}K$ of $-\text{COOH}$ acid are in the range 4–6.

Hence, all the factors justify the partial formation of $-\text{COOH}$ group during heat treatment on Indion 225.

CONCLUSION

Anhydride modified sulphonic acid resins from PS, especially PSPMDAS exhibit better thermal stability than the unmodified styrene based resins.

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REFERENCES

- 1 Biswas, M. and Chatterjee, S. *J. Macromol. Sci. Chem.* 1984, **A21**, 1501
- 2 Biswas, M. and Chatterjee, S. *J. Appl. Polym. Sci.* 1982, **27**, 4645
- 3 Biswas, M. and Chatterjee, S. *J. Appl. Polym. Sci.* 1984, **29**, 829
- 4 Biswas, M. and Chatterjee, S. *J. Appl. Polym. Sci.* 1982, **27**, 3851
- 5 Biswas, M. and Chatterjee, S. *Angew. Makromol. Chem.* 1983, **113**, 11
- 6 Biswas, M. and Chatterjee, S. *Eur. Polym. J.* 1983, **19**(4), 317
- 7 Vasudevan, P. and Sujakumar, S. *Angew. Makromol. Chem.* 1979, **75**, 195
- 8 Biswas, M. and John, K. J. *Angew. Makromol. Chem.* 1978, **72**, 52
- 9 Helfferich, F. 'Ion Exchange', McGraw-Hill, New York (1962)
- 10 Bothe, N., Döscher, F., Klein, J. and Widdecke, H. *Polymer* 1979, **20**, 850
- 11 Ghatge, N. D. and Khune, G. D. *Angew. Makromol. Chem.* 1979, **79**, 93