Thermal Stability Characteristics of Some Resins from Chemically Modified PVC

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Synopsis

PVC has been modified by chlorine displacement reaction with *m*-aminophenol, bisphenol A, and phenophthalein. Sulfonation of these condensates yields bifunctional weak acid resins which do not exhibit $-SO_3H$ ionogenic group. Reaction of PVC with presulfonated bisphenol A, phenolphthalein, and phenol yields strong acid resins. Thermal stability characteristics of these various resins have been determined and the results indicate that such modifications improve the overall thermal stability of PVC.

INTRODUCTION

The inferior thermal stability of poly(vinyl chloride) (PVC) is one of the main factors limiting its applicability,[1] and many attempts have been made to improve this and related property of PVC by chemical modification.[1] The facile "Cl" displacement reaction involving PVC indicates the possibility of easy anchoring of desirable moieties on the PVC chain. Accordingly, we have been able to modify PVC by reaction with phenol (P), *m*-aminophenol (MAP), bisphenol A (BIS-A), and phenolphthalein (PHEN).[2,3] This research was actually initiated with a view to synthesizing strong acid resins[4] from PVC and eventually led us[5] to standardize the experimental conditions which would yield strong cation exchange resins from PVC.

The introduction of MAP, BIS-A, and PHEN in PVC chain leads to characteristic changes in the property of the base polymer.[2,3] Thus, all these PVC condensates, barring PVC–P, and the corresponding sulfonic acid resins, including that from PVC–P, are insoluble in all solvents for PVC. It may hence be expected that the modified PVC matrices are appreciably crosslinked (Fig. 1). This will imply an enhanced thermal stability since the applied thermal energy will have to rupture the various crosslinks introduced in the modified PVC network. To verify these ideas, we examined the thermal stability characteristics of these various PVC condensates. The salient features of the results are highlighted in this article.

EXPERIMENTAL

Materials

PVC (NOCIL, India, $\overline{M}_v = 8.6 \times 10^4$) was reprecipitated from alcohol–THF mixture several times. Ethylene diamine (EDA), used in some reactions as the base catalyst, was fractionally distilled before use. *m*-Aminophenol (BDH)
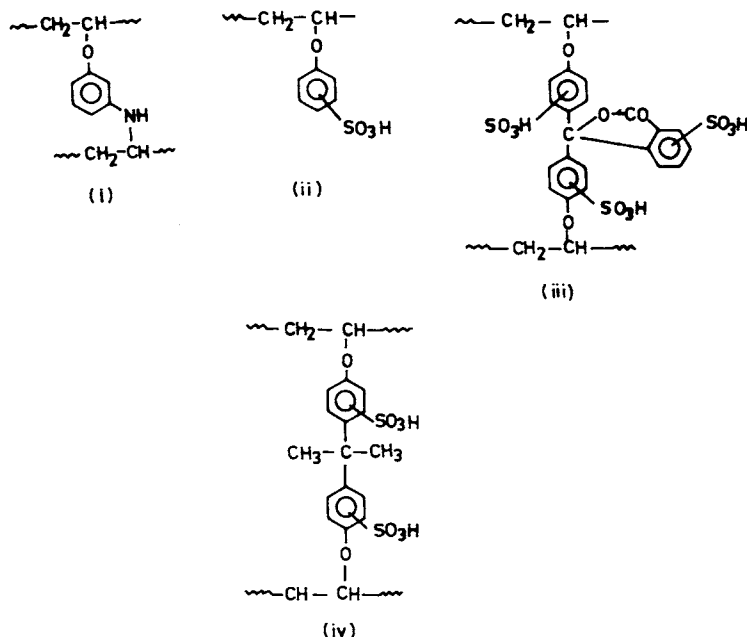
Fig. 1. Structures of PVC resins: (i) PVC–MAP; (ii) PVC–P–SO$_3$H; (iv); PVC–BIS–A–SO$_3$H; (iii) PVC–PHEN–SO$_3$H.

was recrystallized from alcohol before use. Bisphenol-A (BDH) and Phenol-phthalein (Merck) were used as supplied.

Synthesis and Sulfonation of PVC Condensates

PVC was first condensed[2,3] with MAP, BIS-A, and PHEN. Sulfonation of the PVC condensates was done by two procedures.[2,3,5] The essential conditions and relevant details of the syntheses are summarized in Table I, while Figure 1 presents the tentative structures of the PVC resins.

Characterization

IR Spectra. The IR spectra were obtained on a Perkin-Elmer 237 B grating spectrophotometer.

Thermogravimetry. TGA were performed on a ULVAC SINKURIKO analyzer, Model TGD-5000 under the following conditions: heating rate = 15°C/min; temperature range 0–1500°C; aerial atmosphere.

RESULTS AND DISCUSSION

General Characteristics of the Reactions

The condensations of the various bifunctional moieties with PVC proceed to ca. 80% yield in general.[2,3] In all instances except in PVC–P the materials are insoluble in chlorinated hydrocarbons, tetrahydrofuran, aromatic hydrocarbons, dimethyl formamide, and dimethyl sulfoxide. IR absorptions at 1450–1465 cm^{-1} in I–IV are consistent with the presence of benzene ring in

TABLE I
Experimental Conditions Used for the Synthesis of PVC Resins

Number	Reactants	Solvent	Time (h)	Temp (°C)	Product
1	PVC : MAP	THF	10	60	PVC–MAP (i)
	1 : 1.5 (w/w)				
2	PVC : BIS-A	THF	10	60	PVC–BIS-A
	1 : 1.5 (w/w)				
3	PVC : PHEN	THF	10	60	PVC–PHEN
	1 : 1.5 (w/w)				
4	(i) PVC–MAP : H_2SO_4[a]	—	10	60	PVC–MAP–S[b]
	1 : 60 (w/w)				
	(ii) PVC–BIS–A : H_2SO_4[a]	—	10	60	PVC–BIS–A–S[b]
	1 : 60 (w/v)				
	(iii) PVC–PHEN : H_2SO_4[a]	—	10	60	PVC–PHEN–S[b]
	1 : 60 (w/v)				
5	(i) BIS-A : H_2SO_4[a]	—	0.5	100	BIS-A–SO_3H
	1 : 4 (w/w)				
	(ii) PHEN : H_2SO_4[a]	—	0.5	100	PHEN–SO_3H
	1 : 4 (w/w)				
	(iii) P : H_2SO_4[e]	—	0.5	100	P–SO_3H
	1 : 4 (w/w)				
6	(i) PVC : BIS-A–SO_3H	THF	20	60	PVC–BIS-A–SO_3H[c] (iv)
	1 : 3 (w/w)				
	(ii) PVC : PHEN–SO_3H	THF	20	60	PVC–PHEN–SO_3H[c] (iii)
	1 : 3 (w/w)				
	(iii) PVC : P–SO_3H	THF	20	60	PVC–P–SO_3H[c] (ii)
	1 : 3 (w/w)				

[a]Sulfonation reactions have been carried out using fuming H_2SO_4 (98%).
[b]Symbols denote sulfonated resins which do not exhibit —SO_3H functional group but only —COOH and phenolic —OH groups.[3]
[c]Symbols denote resins exhibiting "—SO_3H" and phenolic —OH [6(i) and (iii)] groups.[5]

the PVC network. Further, phenolic–OH is indicated by absorptions at 1350–1400 cm^{-1} in all three structures. This feature indicates that all the functional "OH" groups have not necessarily participated in the "Cl" displacement reaction simultaneously with two PVC chains, so that some free "OH" groups show up in the IR absorptions.[2,3]

Sulfonation of PVC–MAP, PVC–BIS-A, and PVC–PHEN has been found[3] to yield products (PVC–MAP–S, PVC–BIS-A–S, and PVC–PHEN–S, Table I), which do not contain any —SO_3H group, but, on the other hand have "—COOH" or "phenolic OH" in the skeleton. This is ascribed to oxidative degradation of the resin during sulfonation[2,3] in air.[6]

The alternative procedure,[5] in which PVC was condensed with presulfonated BIS-A or PHEN and P (Table I), however, affords PVC-based strong acid resins. The details of ion-exchange characteristics of these resins have already been reported.[5]

Thermal Stability Characteristics

Figures 2–4 represent the thermograms of the various PVC-based condensates prepared as above, along with the same for unmodified PVC. Clearly, the
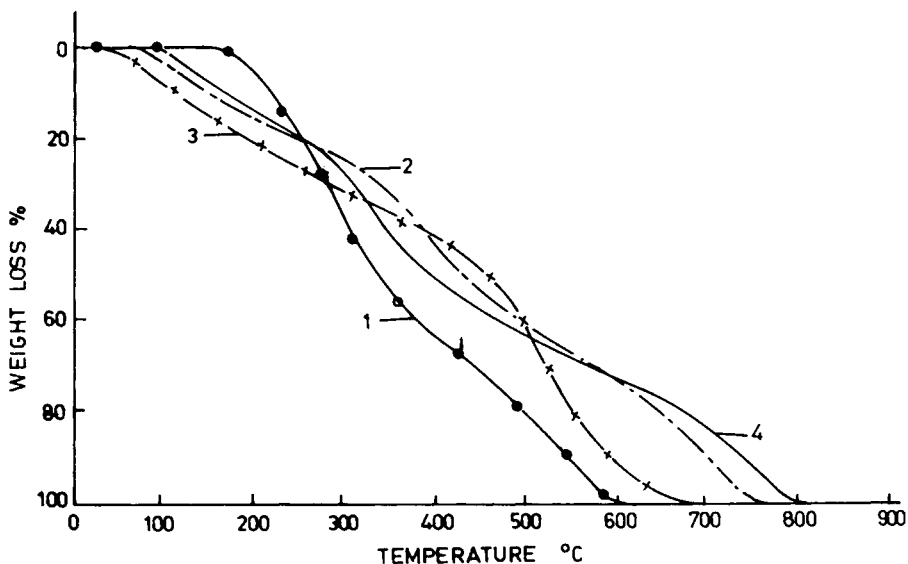
Fig. 2. Percent weight loss vs. temperature curves for (1) PVC; (2) PVC–MAP; (3) PVC–MAP–S; (4) PVC–P–SO$_3$H.

chemical modification considerably improves the overall thermal stability of the base polymer. The thermal stability characteristics are now compared system wise.

PVC. The PVC thermogram obtained in the present study agrees essentially with the literature.[7] PVC undergoes endothermic dehydrochlorination[8,9] in the range 200–320°C and depolymerization reaction reportedly starts at
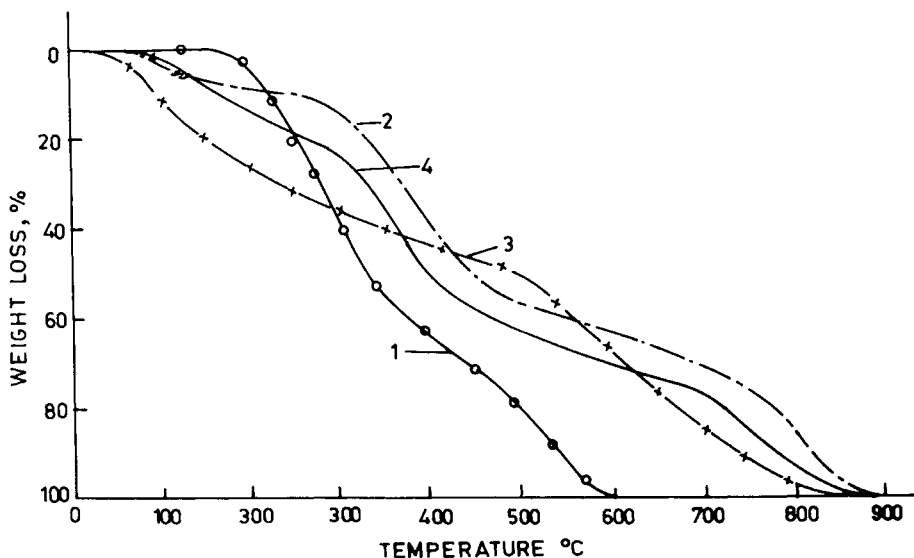

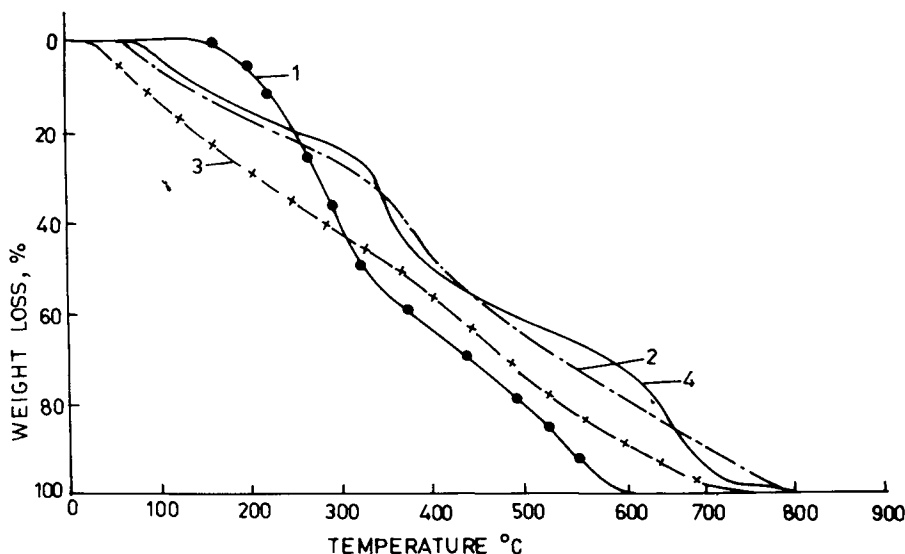Fig. 3. Percent weight loss vs. temperature curves for: (1) PVC; (2) PVC–BIS-A; (3) PVC–BIS-A–S; (4) PVC–BIS-A–SO$_3$H.

Fig. 4. Percent weight loss vs. temperature curves for (1) PVC; (2) PVC–PHEN; (3) PVC–PHEN–S; (4) PVC–PHEN–SO$_3$H.

around 350°C. In the presence of oxygen[6,9] oxygenated structures, such as peroxide, hydroxyl, or carbonyl functionalities are introduced in the PVC chain and all these groups interact with neighboring "Cl" atoms and accelerate loss of HCl. Also, mixture of unsaturated carbon—carbon backbone[10] and any unconverted PVC partly chars and undergoes oxidative degradation[10] to small fragments. The broad endotherm at 260°C and the sharp exotherm at 495°C appear to correspond to these reactions.[10]

PVC–MAP and PVC–MAP–S. Figure 2 reveals that the initial decomposition temperature follows the trend:

$$\text{PVC } (200°C) > \text{PVC–MAP } (100°C) > \text{PVC–MAP–S } (55°C)$$
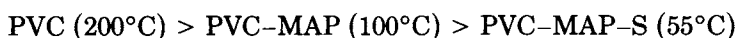
PVC undergoes 50% weight loss in the temperature range 200–300°C, while PVC–MAP or PVC–MAP–S do so gradually over a much wider temperature, 50–450°C. This indicates a lower rate of endothermic dehydrochlorination corresponding to peaks at 300 and 340°C, respectively (Table II), which is obviously due to a much decreased amount of available

$$-\text{CH}_2-\overset{\displaystyle |}{\underset{\displaystyle \text{Cl}}{\text{CH}}}-$$
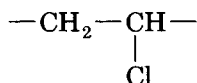
moieties in the modified network.

The second inflection in the TG curve (300–800°C range) is accompanied by a strong exothermic peak at 640°C (PVC–MAP) and at 525°C (PVC–MAP–S), which is due to oxidative degradation of the PVC–MAP condensates. Relevantly, the occurrence of the exothermic peak at a lower temperature in PVC–MAP–S compared to PVC–MAP is significant. During treatment with fuming H$_2$SO$_4$ during sulfonation, PVC–MAP undergoes some oxidative

TABLE II
DTA Characteristics of PVC Resins

| Resin	DTA Peak Temperature (°C)	
	Endothermic	Exothermic
PVC	260	495
PVC–MAP	300	640
PVC–MAP–S	340	525
PVC–BIS-A	290	780
PVC–BIS-A–S	300	738
PVC–BIS-A–SO$_3$H	190	740
PVC–PHEN	280	615
PVC–PHEN–S	305	545
PVC–PHEN–SO$_3$H	180	690
PVC–P–SO$_3$H	200	700

cleavage as evident from the appearance of "—COOH" or "phenolic OH" functional groups in PVC–MAP–S.[2,3,5]

PVC–BIS-A, PVC–BIS-A–S and PVC–BIS-A–SO$_3$H. Figure 3 reveals the following trend in the initial decomposition temperature

PVC (200°C) > PVC–BIS-A–SO$_3$H (115°C) > PVC–BIS-A (100°C)

> PVC–BIS-A–S (60°C)
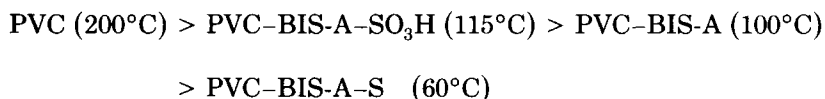
The first inflections in the TG curves in all three systems clearly indicate a much flatter rate of weight loss accompanying dehydrochlorination (ca., endothermic peaks at 290, 300, and 200°C, respectively, Table II). The second inflections (ca., 300–800°C) are accompanied by the appearance of very strong exothermic peaks (740–780°C, Table II) signifying complete oxidative degradation. As with PVC–MAP–S, the exotherm for PVC–BIS-A–S occurs at a lower' temperature than PVC–BIS-A, indicating oxidative cleavage during sulfonation which forms —COOH or phenolic OH groups in PVC–BIS-A–S.

PVC–PHEN, PVC–PHEN–S, and PVC–PHEN–SO$_3$H. Figure 4 indicates that the initial decomposition temperatures follow the trend:

PVC (200°C) > PVC–PHEN–SO$_3$H (115°C) > PVC–PHEN (100°C)

> PVC–PHEN–S (60°C)
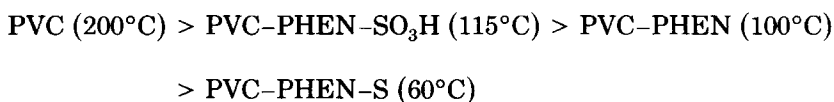
As with the other systems, the first inflection in the TG curve is accompanied by the appearance of endothermic peaks (Table II), while the second inflection (300–800°C) corresponds to complete oxidative rupture (Table II). Also, as expected, PVC–PHEN–S exotherm peaks at a lower temperature (545°C) than PVC–PHEN (615°C).

PVC–BIS-A–SO$_3$H, PVC–PHEN–SO$_3$H, and PVC–P–SO$_3$H. The aforementioned results indicate that the sulfonic acid resins from modified PVC have improved thermal stability more or less comparable to the same for modified unsulfonated product. This is reasonable since PVC has been con-

densed with the presulfonated BIS-A or PHEN, thereby eliminating the possibility of oxidative degradation during sulfonation.

The case of PVC–P–SO₃H resin (Fig. 2) is interesting. The condensation of PVC with monofunctional phenol yields soluble PVC–P. Apparently, PVC is unlikely to get crosslinked with the phenol, which perhaps explains the easy solubility of PVC–P. PVC–P–SO₃H, on the other hand, is insoluble in common solvents for PVC, due possibly to the incorporation of additional —SO₃H moieties in the polymer. The overall thermal stability of PVC–P–SO₃H is also characteristically high as compared to PVC (Fig. 2). The thermogram exhibits two inflections, with the endothermic peak at 200°C between 100 and 300°C, and the strong exothermic 700°C peak in the range 300–800°C.

CONCLUSIONS

Strong acid resins prepared by the reaction between PVC and presulfonated phenol, bisphenol A, and phenolphthalein exhibit improved overall thermal stability compared to PVC. A variety of desirable groups can thus be introduced into PVC by a rather simple procedure developed in this research. While the overall thermal stability is improved, the degradation in the modified resin, nevertheless, continues. Unfortunately, this will limit the possible high temperature application of these materials inasmuch as the accompanying weight losses would affect the use properties of these resins.

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