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Dehydrochlorination of Poly(viny1 Chloride) in Pyridine. III. Thermal and Mechanical Properties

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Dehydrochlorination of Poly(vinyl Chloride) in Pyridine. III. Thermal and Mechanical Properties

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ABSTRACT

The thermal properties of dehydrochlorinated PVC (DHPVC) were evaluated. From thermogravimetric analysis (TGA) and differential thermal analysis (DTA), a larger decrease in thermal stability of dehydrochlorinated PVC than of PVC was observed. Thermal stability of DHPVC increased continuously with an increase in dehydrochlorination temperature and dilution of the reaction solution during dehydrochlorination. However, with an increase in dehydrochlorination time, an increase in thermal stability after an initial drop was obtained. The highly cross-linked product separated from the reaction solution at higher dehydrochlorination temperatures showed a lower thermal stability than that of corresponding soluble DHPVC. The stress-strain behavior of dehydrochlorinated PVC samples was also studied.

INTRODUCTION

Dehydrochlorination of PVC results in the development of conjugated double bonds [1], chain scission, and cross-linking [2] in PVC chains. These structural changes, which take place during dehydrochlorination, are supposed to affect the physical properties of PVC. Shindo et al. [3] attempted to study the thermal and mechanical properties of DHPVC, but no detailed study has been done so far.

In our previous work [4, 5] PVC was dehydrochlorinated in pyridine, and the effect of dehydrochlorination conditions on the structural changes taking place during dehydrochlorination was evaluated. The present investigation was undertaken to study the changes in thermal and mechanical properties of PVC under dehydrochlorination conditions.

EXPERIMENTAL

Material

DHPVC was obtained by thermal dehydrochlorination of PVC in pyridine solution under a nitrogen atmosphere. Experimental details were given earlier [4].

Thermogravimetric Analysis

Thermogravimetric analysis was carried out on a Stanton Redcroft TG-750 thermobalance in a nitrogen atmosphere. The samples were heated at a uniform heating rate of 10°C/min from room temperature to 800°C. Primary thermograms were obtained by plotting the residual weight against temperature.

Differential Thermal Analysis

DTA analysis was carried out by using a Stanton Redcroft DTA 673-4 instrument with alumina as the reference in vacuum. Samples were heated from room temperature to 450°C at a heating rate of 10°C/min.

Color Development Studies

Color development studies were carried out using an electrothermal melting point apparatus at a heating rate of 5°C/min.

Mechanical Properties

Stress-strain behavior was determined using an Instron tester at 25°C/65% RH and microdumbbells die-cut from films cast from a 2% solution in THF. Load-elongation curves were obtained with the

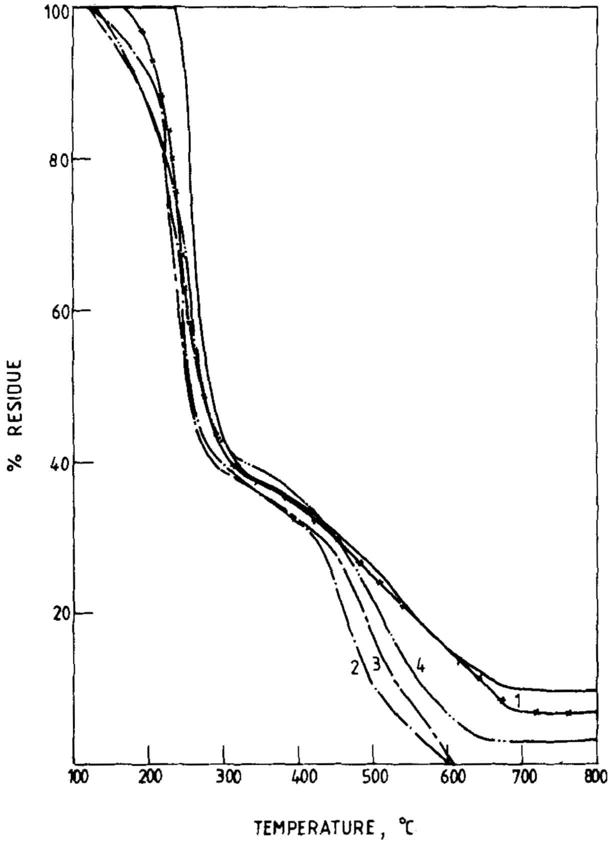

FIG. 1. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) at 120°C. Change in primary thermogram with dehydrochlorination time of (1) 45, (2) 90, (3) 135, (4) 180 min. (—) PVC.

following settings on the Instron tester: gauge length = 2 cm, crosshead speed = 0.5 cm/min, and chart speed = 20 cm/min on a full-scale load of 2 kg.

RESULTS AND DISCUSSION

Thermal Stability

The thermal characteristics of PVC and DHPVC were evaluated by studying their TGA thermograms.

TABLE 1. Variation in Thermal Properties with Dehydrochlorination Time. Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) at 120°C

Dehydrochlorination time (min)	Degree of dehydrochlorination (x, %)	$\overline{M}_w$	Percentage of double bonds (P_n, %)[a]	IDT (°C)	T_{50} (°C)	IPDT (°C)
PVC	-	96,500	0.23	235	290	346
45	2.13	85,900	0.40	170	275	332
90	3.42	66,800	0.45	120	259	318
135	3.62	109,300	1.20	120	259	315
180	4.53	192,100	2.28	127	270	326

[a] Number of double bonds per 100 monomer units of a polymer chain of PVC.

Effect of Dehydrochlorination Time on Thermal Stability

The effect of dehydrochlorination time on the thermal stability of PVC has been investigated. Primary thermograms of PVC and DHPVC samples are presented in Fig. 1.

A two-step decomposition was observed in PVC. The major decomposition started at 245°C and the polymer attained some stability at around 345°C when about 60% of the decomposition was over. Dehydrochlorination of PVC occurred with a major weight loss during this period. Further, slow decomposition started at around 450°C and an almost negligible residue was left at 690°C. The decrease in the rate of HCl evolution was the result of intermolecular interaction of the double bonds formed in the first step of degradation. The two-step decomposition of PVC was retained in the dehydrochlorinated products, except there was a decrease in degradation temperatures with an increase in dehydrochlorination time (Fig. 1). The initial decomposition temperature (IDT), the temperature corresponding to 50% decomposition (T_{50}), and the integral procedural decomposition temperature (IPDT) decreased continuously with an increase in dehydrochlorination time (Table 1). However, the DHPVC prepared at 180 min showed an increase in IDT, T_{50}, and IPDT.

The decrease in thermal stability of DHPVC may be attributed to (1) the additional labile sites (allylic chlorines) formed in PVC chains due to partial dehydrochlorination, and (2) to chain scission during dehydrochlorination. The improvement in thermal stability

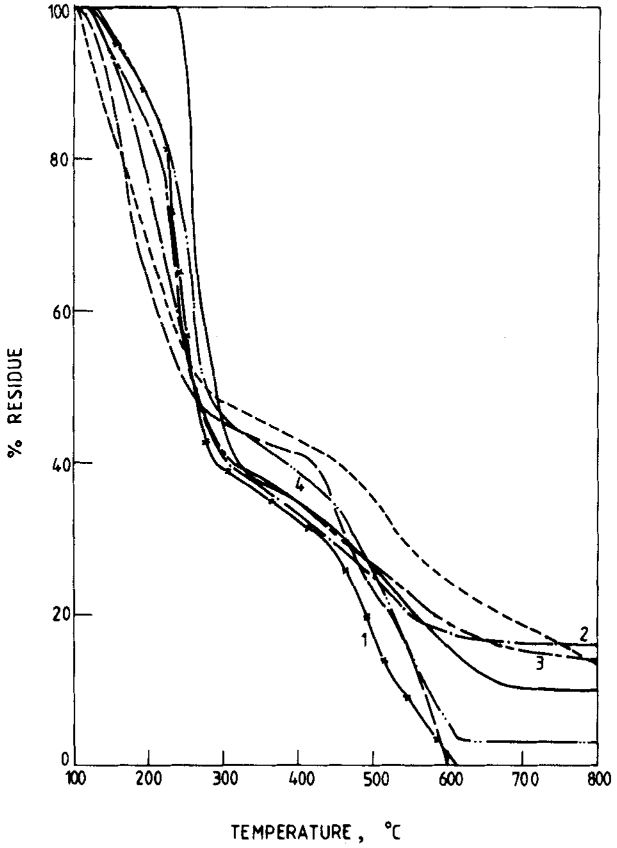

FIG. 2. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) for 135 min. Change in primary thermogram with dehydrochlorination temperature of: (1) 120, (2) 125, (3) 135, (4) 150°C. (– –) Separated highly cross-linked product at 135°C. (– – –) separated highly cross-linked product at 150°C. (—) PVC.

of DHPVC prepared at 180 min is perhaps due to cross-linking in the polymeric chains at long dehydrochlorination times.

Effect of Dehydrochlorination Temperature on Thermal Stability

The influence of the dehydrochlorination temperature on the thermal stability of PVC has been evaluated. Primary thermograms (Fig. 2)

TABLE 2. Variation in Thermal Properties with Dehydrochlorination Temperature. Thermal Dehydrochlorination of PVC in Pyridine (41.7 g/L) for 135 min

Sample	Dehydrochlorination temperature (°C)	Degree of dehydrochlorination (x, %)	$\overline{M}_w$	Percentage of double bonds (P_n, %)	IDT (°C)	T_{50} (°C)	IPDT (°C)
PVC	-	-	96,500	0.23	235	290	346
DHPVC	120	3.62	109,300	1.20	120	259	315
DHPVC	125	3.82	117,500	1.52	120	259	314
DHPVC	135	4.14	130,900	1.73	120	259	319
Separated highly cross-linked product	135	-	-	-	107	248	312
DHPVC	150	5.63	80,300	1.08	127	275	336
Separated highly cross-linked product	150	-	-	-	101	275	325

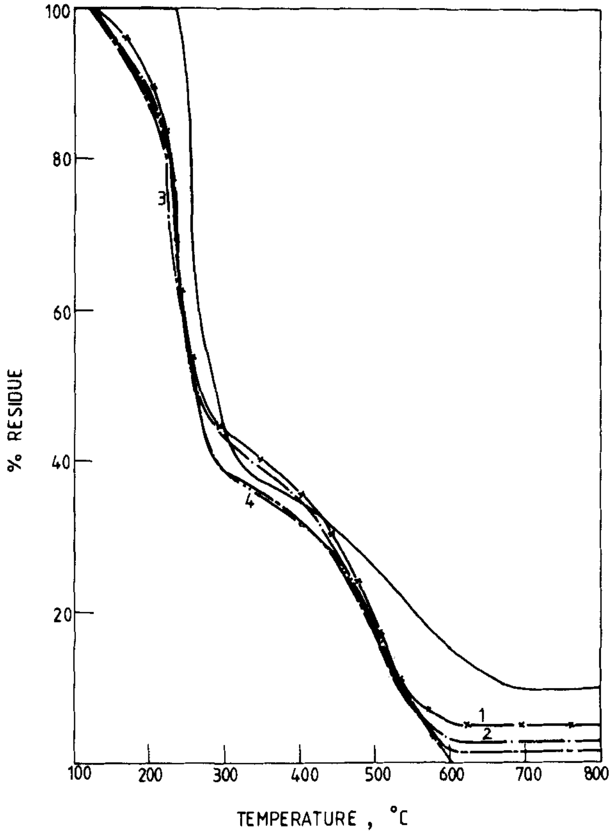

FIG. 3. Thermal dehydrochlorination of PVC in pyridine at 120°C for 135 min. Change in primary thermogram with PVC concentration of: (1) 25.0, (2) 28.0, (3) 31.3, (4) 41.7 g/L. (—) PVC.

and Table 2 show an increase in decomposition temperatures, IDT, and IPDT (i.e., an increase in thermal stability) of DHPVC with an increase in dehydrochlorination temperature.

An increase in the number of double bonds with an increase in dehydrochlorination temperature [5] was supposed to decrease the thermal stability of DHPVC. On the contrary, an increase in thermal stability was observed, perhaps due to an increase in cross-linking reactions with an increase in dehydrochlorination temperature.

An interesting phenomenon was observed by studying the thermal stability of a highly cross-linked product separated from the reaction solution at higher reaction temperatures during dehydrochlorination.

TABLE 3. Variation in Thermal Properties with Concentration. Thermal Dehydrochlorination of PVC in Pyridine at 120°C for 135 min

PVC concentration (g/L)	Degree of dehydrochlorination (x, %)	$\overline{M}_w$	Percentage of double bonds (P_n, %)	IDT (°C)	T_{50} (°C)	IPDT (°C)
PVC	-	96,500	0.23	235	290	346
25.0	5.10	70,100	0.87	127	264	329
28.0	4.34	83,700	0.89	127	264	322
31.3	3.82	100,600	0.98	120	264	315
41.7	3.62	109,300	1.20	120	259	315

A larger decrease in the IDT, T_{50}, and IPDT of a cross-linked product separated at 135 and 150°C was observed than of the corresponding soluble DHPVC. The separated highly cross-linked material may contain shorter chains instead of long molecular chains, which decrease the thermal stability to a great extent.

Effect of Concentration on Thermal Stability

Variation in the thermal stability of PVC with dilution of the reaction solution during dehydrochlorination has also been studied. From the thermograms in Fig. 3 and from Table 3, an increase in the thermal stability of DHPVC with dilution of the reaction solution was observed.

The decrease in the number of double bonds with dilution [5] may be responsible for the increased thermal stability.

In general, PVC on dehydrochlorination becomes less stable thermally than the original PVC.

DTA was also used to evaluate the thermal stability of DHPVC. In DTA thermograms of PVC and DHPVC (Fig. 4) no clear T_g but only a broad shift in base line, indicative of T_g, was obtained in the range 70-80°C. The thermograms also showed that the onset of decomposition of PVC occurs at 243°C and the peak decomposition at 270°C; the onset of decomposition of DHPVC is at 120°C and the peak decomposition at 157°C. Again, a decrease in thermal stability of DHPVC is apparent.

Color development studies were carried out to observe the difference in the thermal stability of PVC and DHPVC at a low extent of heat degradation. The discoloration of PVC and DHPVC [prepared in pyridine solution (41.7 g/L) at 135°C and 135 min] with temperature is

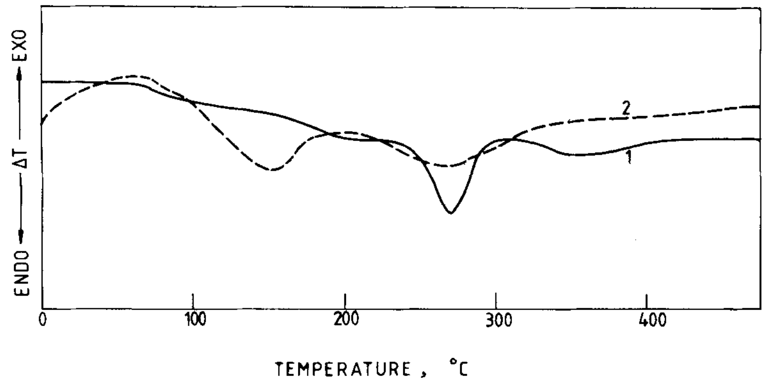

FIG. 4. DTA thermograms of (1) PVC, (2) DHPVC [prepared in pyridine solution (41.7 g/L) at 120°C and 180 min].

TABLE 4. Temperature (°C) at Color Changes

	Pink	Orange	Red	Brown	Black
PVC (colorless)	180	220	250	280	300
DHPVC (pink)	-	-	140	170	270

given in Table 4. These results indicate the poor thermal stability of DHPVC compared to PVC in the early stages of heat degradation. Color development studies have also been carried out by Thame et al. [6] on PVC and grafted PVC.

Stress-Strain Behavior

The stress-strain response of PVC and DHPVC samples has been investigated.

Figure 5 summarizes the effect of dehydrochlorination time on the stress-strain behavior of PVC. Decreases in breaking stress, yield stress, and elongation were observed with an increase in dehydrochlorination times. However, the DHPVC prepared at long dehydrochlorination times showed some improvement in mechanical properties.

With an increase in dehydrochlorination temperature, increases in breaking stress and yield stress of DHPVC were observed along with a decrease in elongation (Fig. 6).

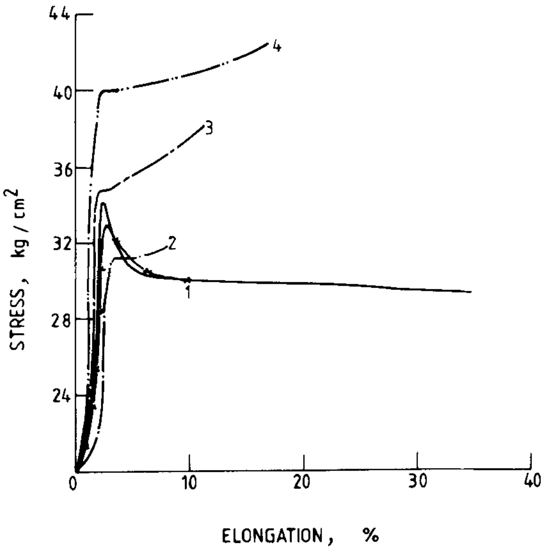

FIG. 5. Variation in stress-strain behavior with dehydrochlorination time of: (1) 45, (2) 90, (3) 135, (4) 180 min. (—) PVC. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) at 120°C.

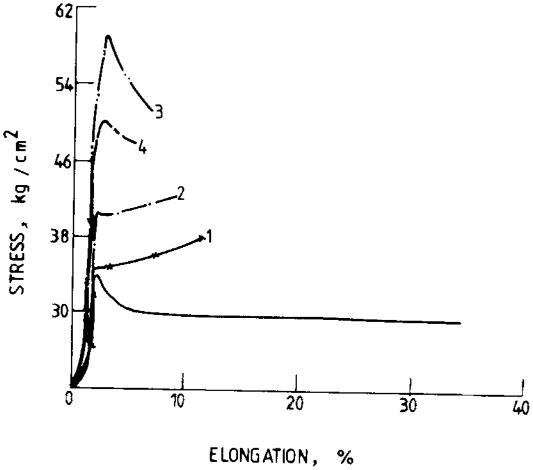

FIG. 6. Variation in stress-strain behavior with dehydrochlorination temperature of: (1) 120, (2) 125, (3) 135, (4) 150°C. (—) PVC. Thermal dehydrochlorination of PVC in pyridine (41.7 g/L) for 135 min.

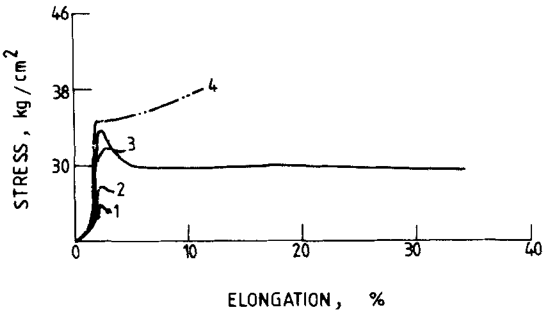

FIG. 7. Variation in stress-strain behavior with PVC concentration of: (1) 25.0, (2) 28.0, (3) 31.3, (4) 41.7 g/L. (—) PVC. Thermal dehydrochlorination of PVC in pyridine at 120°C for 135 min.

Dilution of the reaction solution during dehydrochlorination decreased breaking stress, yield stress, and elongation continuously (Fig. 7).

The loss in the mechanical properties of PVC during dehydrochlorination may be attributed to chain scission reactions. The increase in breaking stress and yield stress along with the decreased elongation of DHPVC are explained by the cross-linking reactions occurring during dehydrochlorination.

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