Studies on Thermo-Oxidative Degradation of Poly Vinyl Chloride

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Introduction

This susceptibility of PVC to degradation is attributed to the defective chemical structure of the polymer. These defects include allylic chlorine in the chain [1], end groups [2], copolymerization of oxygen during polymerization [3,4], and probably head to head structure and chloromethyl side chain branching [5,6,7]. In thermal non-oxidative degradation dehydrochlorination from the main chain takes place either by ionic or radical mechanism resulting in doubly bonded conjugated polyenes [8].

$$-CH_2-CH(Cl)-CH_2-CH(Cl)-CH_2-CHCl \longrightarrow -\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}- + HCl$$

The presence of oxygen further accelerates dehydrochlorination resulting the chain session. The mechanism of thermo-oxidative degradation is not certain, however Gupta and Pierre [9] have proposed a mechanism in which oxygen has been found to react with the radicals generated in PVC to form unstable peroxy linkages. Stabilizers are

$$-CH_2-CH-CH_2-CH(Cl)- \xrightarrow{O_2}$$

$$CH_2-CH-CH_2-CH(Cl)-$$

$$\xrightarrow{RH} CH_2-CH(OOH)-CH_2-CH(Cl)- + R^{\cdot}$$

added to PVC to perform preventive and curative functions like binding or neutralization of HCl [10] exchange of labile chlorine atoms [11,12,13] and addition at the damage sites like double bonds [14,15].

Though extensive studies have been made on the mechanism of degradation and stabilization of PVC, however these involve relatively sophisticated chemical, spectroscopic and other methods. Oxygen flask technique has already been used successfully in the determination of chlorine in PVC [16], it was also employed in this study. It was hoped that it will be a simple and convenient method for the rapid assessment of PVC degradation during processing and for the evaluation of effectiveness of stabilizers

Experimental

PVC

Powdered PVC sample obtained from "Pakistan PVC Limited" was purified by making a solution in pure tetrahydrofuran and reprecipitating it using methanol. Polymer sample was dried under vacuum at 90°C. The molecular weight of the polymer using viscometery technique was found to be 35600.

Stabilizers

Lead, iron and zinc stearates were prepared by the precipitation method [16]. Stearic acid was added to KOH solution (concentration not exceeding 5%). Once the potassium stearate was formed, about 10-15% solution of metal salt was added to precipitate out metal stearate. The slurry containing about 10% metal stearate was filtered and washed with excess of water to remove any soluble salts. It was dried and then used in PVC.

Degradation and Stabilization Studies

Degradation of virgin PVC and PVC compositions with 3 phr (part per hundred) of various stabilizers was carried out at 100°, 150°, 170° and 200°C. Temperature of 100°C and 150°C was obtained in a thermostated oven (±1°C) whereas a heating mantle with an insulation arrangement was used to maintain the temperature at 170°C and 200°C (± 2°C). About 30 mg. of the sample was taken at various time intervals, burnt in an oxygen flask and the solution was analysed for chlorine content by potentiometric titrations. The virgin and degraded samples were also analysed spectroscopically using Beckman IR-20A spectrophotometer.

Results and Discussion

Results obtained in degradation experiments are reported in Table 1. Percent loss of chlorine for virign PVC at various temperatures is plotted as function of time in Fig.1. The amount of HCl evolved increased with increasing temperature. PVC was kept at 100°C for a week, but no HCl was detected, though the sample turned yellowish after this long exposure which seems to be due to the

Table 1: Themo-oxidative degradation of PVC compositions at 150°C

Time hour	PVC + Zinc stearate	PVC + Lead stearate
1.	0	0.0
2.	0	0.0
3.	0.4	0.0
4.	0.7	0.0
5.	2.2	0.0
7.	2.6	0.0
9.	2.8	0.0
11.	3.0	0.0
15	3.0	0.0
18.	2.93	0.0
31.	2.0	0.2
37.	3.2	0.4
53.	10.6	1.1
62.	12.1	1.2
69.	17.4	1.6
91.	20.8	3.2
115.	23.5	4.0
145.	26.2	5.8

formation of peroxy linkages. A comparison I.R. spectra of polymer with that of unexposed polymer shows an additional carbonyl peak at 1730 cm^{-1} while there was no change in the C-Cl absorption peak, meaning this bond is still intact. Induction period for the evolution of HCl is reduced as the temperature is raised. This induction period is followed by a rapid loss of HCl, which further accelerates the dehydrochlorination process. Induction period for various PVC compositions is given in Table 2.

The results obtained for various stabilizers at 150°C and 200°C are shown in Figs. 2 and 3 respectively. Effectiveness of lead stearate as a stabilizer is already known. This study also confirms that this stabilizer increases the induction period for the degradation of the polymer to about 50 minutes at 200°C. It shows the significance of this stabi-

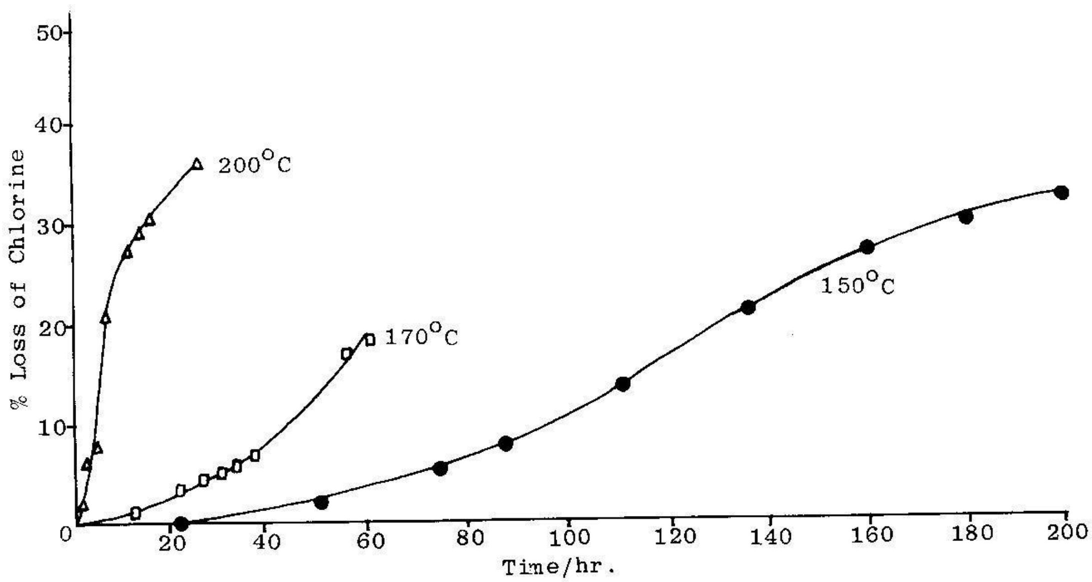

Fig. 1: Degradation of PVC at various temperatures.

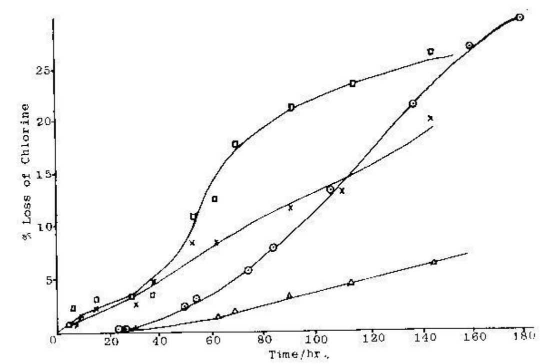

Fig.2 Degradation of various PVC composition at 150°C; PVC alone Θ, PVC with Zinc stearate □, Lead stearate Δ, Zinc and Lead stearates X.

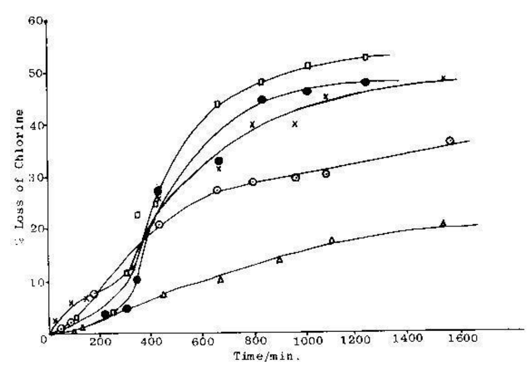

Fig.3: Degradation of various PVC compositions at 200°C; PVC alone Θ PVC with Zinc strearate □, Iron strerate O, Lead Stearate Δ, Zinc & Lead sterate X.

Table 2: Induction Period For Various PVC Samples

S.No.	Sample	Temperature/°C	Induction Period
1.	PVC	150	23 Hr.
2.	PVC	170	11 Hr.
3.	PVC.	200	15 Min.
4.	PVC + Zinc stearate.	150	3 Min.
5.	PVC + Zinc stearate,	200	10 Min.
6.	PVC + Zinc iron stearate	150	3 Min.
7.	PVC + iron stearate	200	3 Min.
8.	PVC + lead stearate	150	31 Hr.
9.	PVC + lead stearate	200	50 Min.
10.	PVC + zinc & lead stearate	150	3 Min.
11.	PVC + zinc & lead stearate	200	3 Min.

lizer in processing. Zinc stearate was found (Fig. 2 and 3), to accelerates the evolution of HCl. The induction period is reduced from 26 hrs. to 3 hrs. at 150°C and from 3 hrs. to 3 minutes at 200°C. This catalytic or destabilization effect of zinc stearate is attributed to the formation of zinc chloride which is a strong Lewis acid and in the absence of a nucleophilic reagent it is a powerful dehydrochlorination catalyst. Its accumulation in the Polymers mixture has deletrious effect on the thermal stability of the PVC resulting its blackening and crosslinking [13]. Almost similar results are obtained with iron stearate, through the extent of destabilization is less compared to zinc stearate. It is expected because zinc being more electro-negative than iron will be more effective in dehydrochlorination of PVC. When zinc and lead stearates were used together no synergistic effect was observed and the induction period was less compared to the lead stearate itself. This again is attributed to the destabilization effect of zinc chloride. For effective synergicism none of the stabilizer has to act as destablizer.

Our results indicate that oxygen flask technique is a useful method for assessing thermal stability of PVC and the effectiveness of stabilizers.

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