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THERMOGRAVIMETRIC ANALYSIS OF $ZnCl_2$ CATALYZED DEGRADATION OF PVC

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The kinetic parameters of dehydrochlorination (DHCL) process of PVC and PVC mixed with different amount of $ZnCl_2$ have been determined by using thermogravimetric analysis. These values have been compared with those obtained by using UV-visible spectroscopic analysis of PVC film containing $ZnCl_2$ degraded at different temperatures. The values of apparent activation energy (E_a) decreases with the increase of the amount of $ZnCl_2$ and the values obtained in the present work are in reasonable comparison with previous works. The catalytic effect of $ZnCl_2$ on PVC DHCL process is explained here.

Keywords: dehydrochlorination process, kinetics, PVC, $ZnCl_2$ catalyzed degradation

Introduction

PVC is one of the most widely used industrially important polymer. It stands second in the world considering the use and consumption of synthetic material. Although it has numerous excellent properties degradation takes place at a considerable rate at the usual temperature of processing which can reduce the useful life of the material. During its thermal degradation elimination of HCl occurs and subsequent formation of conjugated double bond takes place [1–4]. The evolved HCl further catalyzes the degradation reaction. The catalytic effect of HCl is due to the secondary bond association of polar HCl molecule [5–8] with the double bond. This sort of association reduces the effective size of conjugation in the polyene linkage thus reducing the self-stabilization of the partly degraded PVC chain and making the allylic chlorine more labile. In order to reduce the autocatalytic effect of HCl and to terminate the upzipping of the chain stabilizers are used. There is an important class of these metal carboxylates [9–11] extensively used not only as stabilizers but also as lubricants for PVC. The stabilization action of the metal carboxylates is generally explained on the basis of

i) Frye and Horst Mechanism
ii) Reaction of metal carboxylates with HCl

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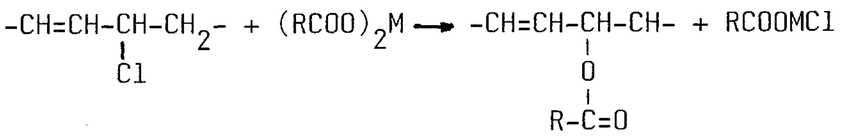
Frye and Horst Mechanism

Frye and Horst [12] suggested that the replacement of the labile chlorine atoms of the polymer with more stable group e.g. carboxylates prevent the initiation of zip-elimination of HCl.



$$-CH{=}CH-\underset{\substack{|\\ Cl}}{CH}-CH_2- + (RCOO)_2M \longrightarrow -CH{=}CH-\underset{\substack{|\\ O\\ |\\ R-C=O}}{CH}-CH- + RCOOMCl \qquad (I)$$

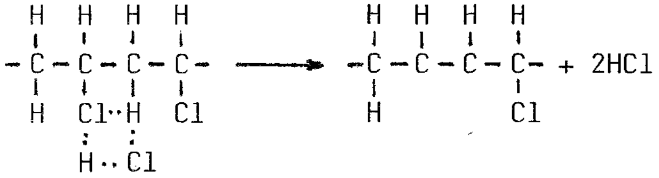
The presence of such groups also acts as a 'catch or block' for zipping i.e., they terminate sites in the polymer backbone.

Reaction of metal carboxylates with HCl

The metal carboxylates may react with HCl

$$(RCOO)_2M + 2HCl \rightarrow 2RCOOH + MCl_2 \qquad (II)$$

and the absorption of HCl from the polymer matrix reduces the probability of the reaction



$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ -C- & C- & C- & C- \\ | & | & | & | \\ H & Cl\cdot\cdot & H & Cl \\ & \vdots & \vdots & \\ & H\cdot\cdot & Cl & \end{array} \longrightarrow \begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ -C- & C- & C- & C- \\ | & & & | \\ H & & & Cl \end{array} + 2HCl \qquad (III)$$

thereby reducing its catalytic activity [13, 14].

Previous studies [15] using DHCL technique show that when Zinc carboxylate was used as stabilizer, after a certain period of time when the rate of thermal DHCL was very small, an abrupt increase in HCl, production and degradation of the material took place and PVC was found to turn black immediately after this period. This may be due to the reaction in which $ZnCl_2$ reacts with HCl producing a stable $H^+ZnCl_3^-$ complex thus catalyzing the DHCL process.

In this present work the kinetic parameters of the DHCL process of PVC and PVC mixed with different amounts of $ZnCl_2$ (1, 2 and 3 mole%) were determined by using thermogravimetric analysis in a temperature range of 150° to 350°C. Values of E_a obtained so are compared to those obtained recently [16] by using UV-visible spectroscopic technique where E_a was determined from the temperature dependence of the rate of the colour development of PVC films containing various amounts of $ZnCl_2$. The values obtained in both studies are in good agreement with each other.

Experimental

Thermogravimetric analysis of pure PVC and PVC mixed with different amounts of $ZnCl_2$ was carried out.

Chemicals used

Poly Vinyl Chloride (PVC)

Analytical grade PVC supplied by BDH Ltd. with the following specifications was used:

Molecular weight	100,000 ± 20
Viscosity number	[ISO/R 174 to 1961 (E)]
Particle size	100% passes B. S 60 mesh 74% passes B. S 200 mesh.

Zinc Chloride ($ZnCl_2$)

Zinc chloride (anhydrous) of analytical grade obtained from E. Merck was used.

Samples for TG were prepared by mixing $ZnCl_2$ homogeneously in various proportions (1, 2 and 3 mole%) under dry and inert atmosphere. Thermal analysis of these samples was carried out using Netzsch simultaneous thermal analyzer STA 429, in static air. Approximately 32 mg of the sample was placed in the crucible and heated in the temperature range 150° to 350°C with a heating rate of 2 deg/min.

Results and discussion

The percent weight loss against temperature for pure PVC and PVC mixed with different proportions of $ZnCl_2$ from 150° to 350°C are shown in Fig. 1. The weight of the sample decreases slowly as the degradation starts and then sharply over a temperature range of 230° to 270°C. Finally it levels off. This is the first stage of the degradation where the decrease in weight is primarily due to the DHCL process. The %loss for different samples are given in Table 1. As the amount of $ZnCl_2$ in PVC decreases the loss in weight occurs earlier. In order to calculate the kinetic parameters of the DHCL process the following methods were used:

i) H. H. Horwitz *et al.* [17]
ii) A. W. Coats *et al.* [18].

The values of the kinetic parameters are given in Table 2. It is evident from the stable that E_a of the DHCL process decreases with the increase of the amount of $ZnCl_2$. The values obtained by these two methods differ only ±2.5%.

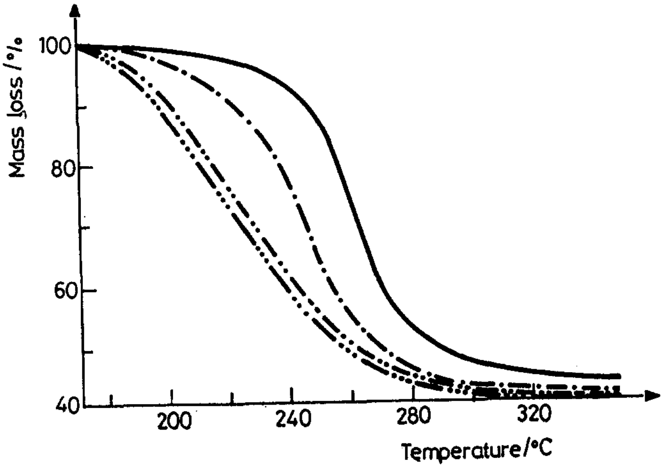


Fig. 1 TG curve for PVC (——) and PVC mixed $ZnCl_2$: 1 mole% (– · – · –); 2 mole % (– · · – · · –); 3 mole% (– · · · – · · · –)

Table 1 Percent change in mass: PVC and PVC containing $ZnCl_2$ during heating

Temp. / °C	% Weight retained			
	PVC	$ZnCl_2$ (mole %)		
		1	2	3
180	99.9	99.7	99.5	98.5
190	99.6	98.6	95.8	95.07
200	99.3	97.5	91.5	89.5
210	99.0	96.3	85.7	83.7
220	97.7	91.5	77.5	73.5
230	96.7	87.8	68.5	66.1
240	94.4	77.5	61.5	58.6
250	88.5	65.6	55.6	53.5
260	73.1	54.0	49.5	48.0
270	56.7	48.2	47.0	46.0
280	51.8	45.1	44.5	43.5
290	48.2	43.7	43.0	42.0
300	46.2	42.6	42.5	41.5

Table 2 The kinetic parameters of the dehydrochlorination process

Methods	Kinetic parameters	PVC	$ZnCl_2$ (mole %)		
			1	2	3
Coats	E_a / kJ mol^{-1}	160.53	120.08	104.64	76.20
et al. [18]	n	1	1	1	1
Horwitz	E_a / kJ mol^{-1}	164.82	123.95	108.00	79.83
et al.[17]	Z / s^{-1}	$2.941 \cdot 10^{15}$	$5.035 \cdot 10^{11}$	$2.639 \cdot 10^{10}$	$1.513 \cdot 10^{10}$

Table 3 Variation of E_a with different proportion of $ZnCl_2$ in PVC [16]

$ZnCl_2$ wt%	Activation energy (E_a) / kJ·mol^{-1}
10.3	57.20
6.5	74.00
3.2	84.2
1.6	99.70

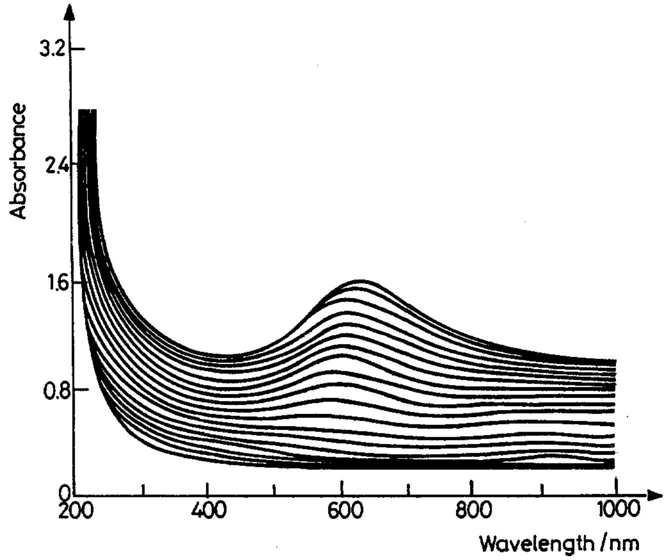


Fig. 2 UV-visible spectra of PVC film containing $ZnCl_2$ (10.3 wt%) degraded at 70°C. Increasing absorbances correspond to successive scans at 10 min intervals [16]

Recently E. D. Owen [16] has reported the E_a values by using $ZnCl_2$ in PVC. UV-visible spectroscopy of PVC films containing various amounts of $ZnCl_2$ were

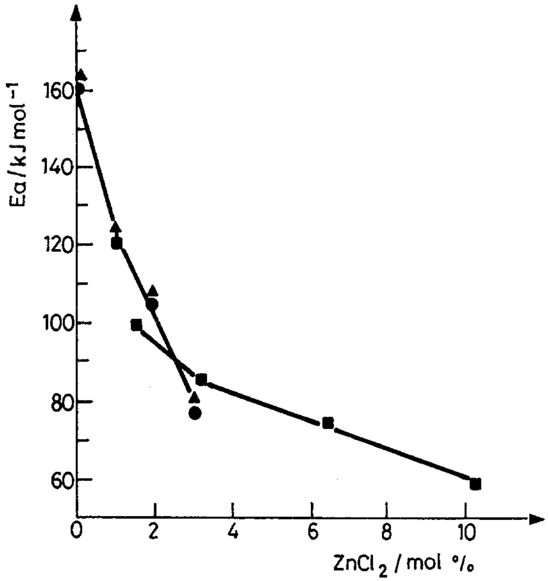


Fig. 3 Plot of E_a *vs*. $ZnCl_2$ (mole %) in PVC for values of E_a in the present work obtained by the methods due to H. H. Horwitz *et al.*; A. W. Coats *et al.* E_a values as reported by E. Owen [16]

casted from THF and were degraded at various temperatures. The successive scans of the UV-visible spectra with an interval of 10 minutes (Fig. 2) were taken thus measuring the rate constant of the reaction at one temperature, from the temperature dependence of the rate constant E_a of the process was calculated. These values are given in Table 3. The values obtained in the present work are given in comparison to these values in Fig. 3. It is clear from Fig. 3 that the values of E_a are reduced with the increase in the proportion of $ZnCl_2$ in PVC. However, the relative decrease in E_a becomes less with the increased amount of $ZnCl_2$.The DHCL process occurring in PVC is influenced by various factors i.e.,

i) DHCL occurs in the structural defects in PVC and in structures containing oxygen

ii) Random DHCL of the PVC chain

iii) The catalytic effect of HCl

iv) The catalytic effect of $ZnCl_2$.

The dynamic changes in the morphology of the polymer with the degradation time and its dependence on the initial composition of the polymer sample also play an important role in relative contribution of the above mentioned reactions. These effects are considered important particularly when the degradation is done in the powder or the film forms. Increase in the degradation time decreases the cohesive energy density (C.E.D.) of the material whereby the HCl may not be retained in the polymer matrix to the same extent as at the beginning of the DHCL process. $ZnCl_2$ and PVC mixtures are not considered to be thermodynamically compatible either and the increased proportion of $ZnCl_2$ helps HCl release from the film or from the solid mixture. It seems that different processes (i) and (iv) take place simultaneously but in different proportions and with the increase of $ZnCl_2$ content, the process (iv) occurs faster. However, the HCl release from the polymer matrix with the increased proportion of $ZnCl_2$ may reduce the reaction III in a later stage of the degradation.

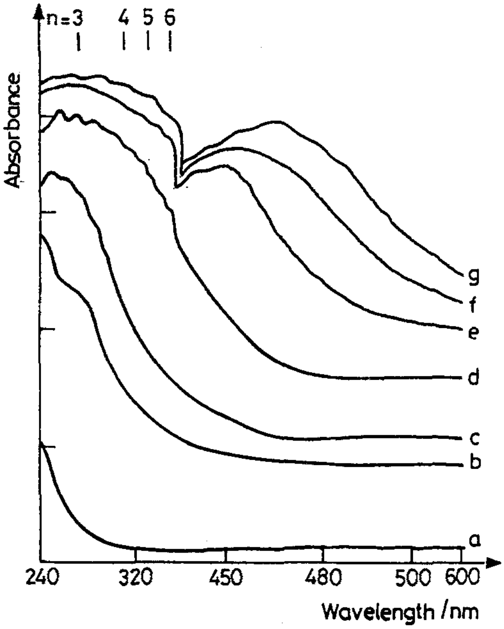
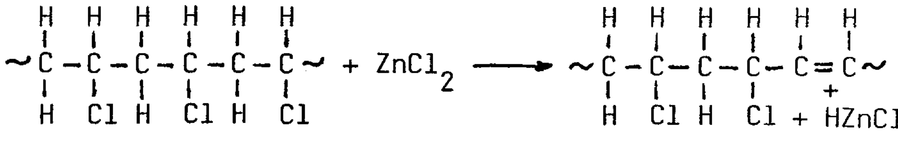


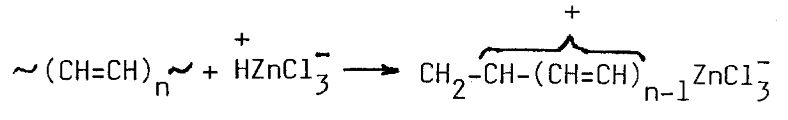
Fig. 4 UV-visible spectra of PVC film containing $ZnCl_2$ (1 mole %) degraded at 180°C for (a) 0 min; (b) 1 min; (c) 5 min; (d) 30 min; (e) 60 min; (f) 90 min; (g) 120 min

$ZnCl_2$ catalyzes the degradation reaction [19] by forming a stable complex of type $H^+ZnCl_3^-$ and creates a labile allylic chlorine in the PVC chain.



$$\sim\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}\sim+ZnCl_2\longrightarrow\sim\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-\underset{+}{\overset{H}{C}}=\overset{H}{C}\sim+HZnCl_3^-\qquad(IV)$$

$H^+ZnCl_3^-$ can interact with polyene linkages giving



$$\sim(CH{=}CH)_n\sim + \overset{+}{H}ZnCl_3^- \longrightarrow CH_2\text{-}\overset{+}{\overbrace{CH\text{-}(CH{=}CH)}}_{n-1}ZnCl_3^- \qquad (V)$$

where *n* is the average number of conjugated double bond. UV-visible absorbance spectrum (Fig. 2) in the range 610 nm has been reported [14] due to this complex formed during the degradation of PVC films containing $ZnCl_2$ at 70°C. In the present study [17], the effect of $ZnCl_2$ on PVC degradation was also studied under isothermal conditions by maintaining temperature at 180±2°C. Successive scans of the UV-visible spectra of the degraded film monitored the appearance of a broad absorption maxima at 440 nm (Fig. 4) in contrast to the previous studies where it was obtained at 610 nm. No such absorption spectra was observed when the pure PVC film was degraded (Fig. 5). As the degradation temperature is high i.e., 180°C in the present studies, the increased degradation rate resulted in high concentration of polyene linkages (with small polyene linkages in abundance as compared to the larger one). A shift in absorption is therefore observed from 610 nm to 440 nm, when the temperature of degradation was changed from 70° to 180°C because of the decrease in the value of $\bar{n}$ in the present work.

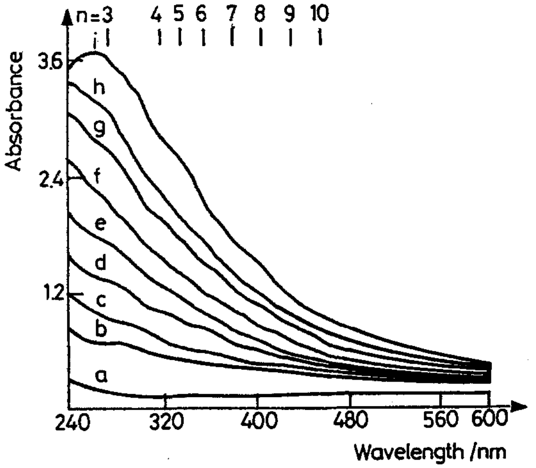


Fig. 5 UV-visible spectra of PVC film degraded at 180°C for
a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min; (f) 150 min; (g) 180 min; (h) 210 min; (i) 240 min

$ZnCl_2$ is an effective degrading catalyst. The catalytic activity is due to the formation of a stable complex(v), the formation of which is confirmed by UV-visible spectroscopy. A sharp decrease in the activation energy of the DHCL process is observed when it is mixed with PVC and these values are in reasonable comparison with that obtained by using an isothermal spectroscopic method.

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Zusammenfassung — Mittels TG wurden die kinetischen Parameter des Dehydrochlorierungsprozesses (DHCL) von PVC und von mit verschiedenen Mengen von $ZnCl_2$ versetztem PVC bestimmt. Diese Werte wurden mit denjenigen verglichen, die man bei der spektroskopischen Analyse der Zersetzung von $ZnCl_2$-haltigen PVC-Filmen bei verschiedenen Temperaturen im sichtbaren UV-Bereich erhalten hatte. Die Werte der scheinbaren Aktivierungsenergie (E_a) sinken mit zunehmendem $ZnCl_2$-Gehalt und die hier erhaltenen Werte sind vergleichbar gut mit denen der vorangehenden Arbeit. Der katalytische Effekt von $ZnCl_2$ auf PVC DHCL-Vorgänge wurde erklärt.