EFFECTS OF ALKALINE EARTH METAL STEARATES ON THE DEHYDROCHLORINATION OF POLY(VINYL CHLORIDE)

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Abstract

The thermo non-oxidative degradation of PVC and the effects of alkaline earth metal (Be, Mg, Ca, Ba) stearates were studied by thermogravimetry in the temperature range 150 to 500°C. The alkaline earth metal stearates were observed effectively reduce the dehydrochlorination of PVC. The synergistic effects of combinations of these salts with lead stearate were also studied and are discussed. Kinetic parameters such as the activation energy, order of reaction and Arrhenius factor were calculated by the Coats and Horowitz methods. The results showed that these metal stearates increase the activation energy required for the dehydrochlorination of PVC.

Keywords: PVC, kinetics

Introduction

Poly(vinyl chloride) (PVC) is one of the most frequently used plastics, with many applications in various industrial branches. The wide applicability of PVC is due to its mode of modification by various additives, its chemical resistance and its low production costs. PVC and its various formations do not burn readily, but decompose to give toxic and corrosive products, which constitute a crucial problem as concerns their use. At temperatures above 150°C, the elimination of HCl occurs and, as a result of this, the formation of polyene sequences take place. Colour formation may lead to drastic changes in the physical and chemical properties of PVC, these being unacceptable for the appearance of the material in many applications. The process of degradation has been studied by various workers, and three different mechanisms, based on different active cen-

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tres, mainly radical, ionic and molecular, have been suggested [1–4]. Stabilizers are used to terminate the unzipping of the chain and also to reduce the autocatalytic effect of HCl produced as a result of degradation. Metal carboxylates are extensively used not only as stabilizers, but also as lubricants [5–7]. Metal carboxylates inhibit the evolution of HCl and colour formation during the processing of PVC. The aim of this paper is to study the stabilization effects of various alkaline earth metal stearates on the dehydrochlorination of PVC in an inert atmosphere.

Experimental

Chemicals and reagents

Chemicals and reagents used: stearic acid (Sigma, Item No. 1259); potassium hydroxide (Merck, Item No. 5021); calcium chloride dihydrate (Sigma, Item No. C3881); barium chloride dihydrate (Sigma, B0750), magnesium chloride hexahydrate (Merck, 5831); beryllium chloride (Fluka, Item No. 14220) and poly(vinyl chloride) (BDH, molecular weight 100 000±200, viscosity No. 150/R to 1961(E);87, particle size: 100% passes through B.S. 60 mesh, while 74% passes through 200 mesh.

Preparation of metal stearates

Potassium stearate was obtained by dissolving 5.689 g of stearic acid in 200 ml of alkaline water containing 1.122 g of potassium hydroxide. 200 ml of the metal chloride solution (0.1 M) prepared in distilled water was added to a solution of the potassium salt and precipitation occurred. The precipitates of metal stearates were filtered off, washed with water, and dried under vacuum until constant mass was obtained.

Preparation of samples

0.001 moles of metal stearate was mixed with 10 g of PVC by grinding the required amounts in an agate mortar for 10–15 min. In order to study the synergistic effects of the alkaline earth metal stearates with lead stearate, 0.0005 moles each of alkaline earth metal stearate and lead stearate were mixed with 10 g of PVC.

The TG curves were recorded on the Shimadzu TG-31 system with a R-122T recorder. A heating rate of 2 deg·min^{-1} was employed and 15 mg samples were used in order to obtain high resolution. All experiments were performed in nitrogen at a flow rate of 40 ml·min^{-1}.

Results and discussion

TG curves for PVC and PVC mixed with different metal stearates are shown in Figs 1–2. It is evident from the TG curves that the degradation of PVC occurs in two distinct steps. The first loss in mass, in the temperature region 180 to 300°C, is due to the dehydrochlorination of PVC. The second loss in mass, above 300°C, is due to the evolution of volatile products formed by the cyclization of short polyene linkages [8–11]. Comparison of the TG curves for pure PVC and for PVC samples containing different metal stearates shows that all these metal stearates act as excellent stabilizers and effectively reduce the dehydrochlorination of PVC in the temperature range 180 to 270°C. It is also observed that the temperature at which dehydrochlorination starts is increased. This means that alkaline earth metal stearates reduce the catalytic effect of HCl on PVC degradation, which is due to the interaction of HCl with the double bond of the dehydrochlorinated chain [12–16].
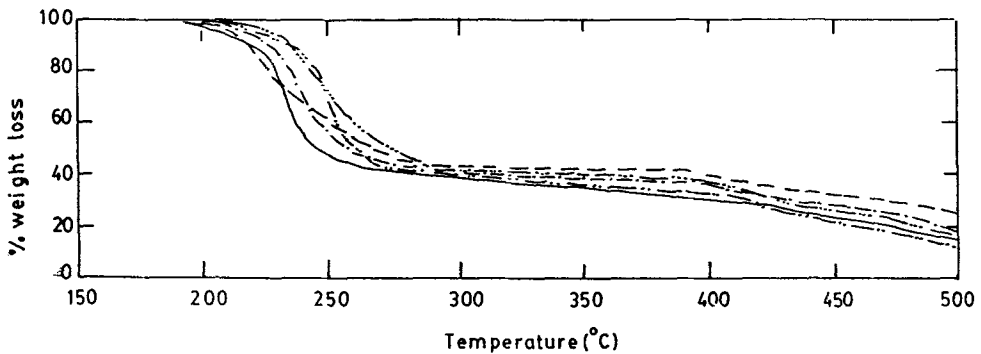

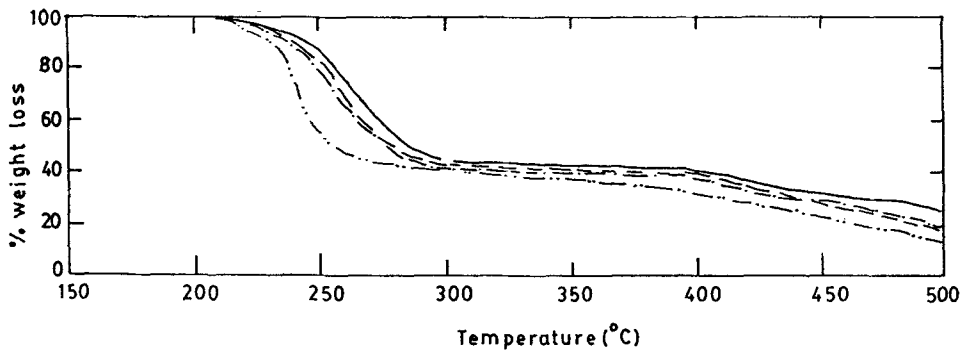Fig. 1 TG curves for PVC (————), and for PVC mixed with Ba-stearate (– – – –), Ca-stearate (– · – · – ·) or Mg-stearate (– ·· – ·· –)

Fig. 2 TG curves for PVC mixed with (Ba + Pb)-stearates (– · – · – ·), (Ca + Pb)-stearates (– – – –) or (Mg + Pb)-stearates (– ·· – ·· –)

These metals stearates effectively quench HCl and so less HCl is available in the polymer matrix to interact with the double bond of the dehydrochlorinated polymer chain. For this reason, the long polyene linkages become stabilized and the dehydrochlorination which occurs due to the reduced destabilized polyene linkages is also reduced. Analysis of the TG traces shows that the stability sequence of the alkaline earth metal stearates is not the same, although the concentrations of these metals in the PVC lattice are nearly the same. The stability of the alkaline metal stearates decreases in the sequence Be > Mg > Ca > Ba. This reveals that metals with a high electronegativity or charge density (see in Table 1) act as good HCl quenchers and effectively reduce the catalytic effect of HCl on the thermal degradation of PVC. Therefore, beryllium and magnesium, which have high charge densities, act as good HCl acceptors and reduce the elimination of HCl which occurs due to the interaction of HCl with the double bond of the dehydrochlorinated polymer chain, and make the PVC chain thermally stable.

Table 1 Values of electronegativity and charge density of alkaline earth metals

Metal	Charge density	Electronegativity
Be^{2+}	6.45	1.5
Mg^{2+}	3.08	1.2
Ca^{2+}	2.02	1.0
Ba^{2+}	1.48	0.9

The synergic effects of the alkaline earth metal stearates with lead stearate in a molar ratio of 1:1 were also studied. These combinations of metal stearates stabilize PVC more than do the alkaline earth metal stearates alone. The synergism may be due to complex formation in which chloride-stearate interchange leads to regulation of the stabilizer [17–19]. The alkaline earth metal exchanges its stearate moiety for labile chlorine or for the chloride of lead chloride, and the lead stearate reacts with the HCl evolved during degradation and reduces its catalytic activity.

The kinetic parameters for the dehydrochlorination process were also calculated by using the Horowitz [20] and Coats methods [21]. The values obtained for the order of reaction, Arrhenius factor and energy of activation are given in Table 2. For pure PVC, the order of reaction for dehydrochlorination was found to be one and the activation energy observed was quite close to the values obtained by many others [22, 23]. The small difference in the energy of activation may be due to various factors, including mainly differences in particle size and experimental environment. This is confirmed by Danforth [24], who studied

Table 2 Values of kinetic parameters for the dehydrochlorination of PVC and PVC mixed with different alkaline earth metal stearates

Sample	Range of α studied	Redfern's method			Horowitz's method
		Order of reaction	A factor	Activation energy / kcal·mol⁻¹	Activation energy / kcal·mol⁻¹
PVC	0.50–1.20	1.00	$7.69 \cdot 10^7$	84.58±4.32	78.02±3.24
PVC + Be-stearate	0.60–1.40	1.00	$8.96 \cdot 10^{10}$	118.26±6.15	128.80±4.67
PVC + Mg-stearate	0.50–1.50	1.00	$2.31 \cdot 10^{10}$	108.22±5.41	118.41±3.98
PVC + Ca-stearate	0.75–1.10	1.00	$7.27 \cdot 10^9$	97.55±4.65	101.62±5.12
PVC + Ba-stearate	0.60–1.80	0.90	$2.15 \cdot 10^9$	92.63±5.34	84.80±5.09
PVC + Pb-stearate	0.80–1.20	0.95	$8.89 \cdot 10^9$	101.57±5.43	110.62±4.19

Table 3 Values of kinetic parameters for the dehydrochlorination of PVC mixed lead and alkaline earth metal stearates

Sample	Range of α studied	Redfern's method			Horowitz's method
		Order of reaction	A factor	Activation energy / kcal·mol⁻¹	Activation energy / kcal·mol⁻¹
(Be+Pb)-stearates	0.85–1.75	1.00	$3.91 \cdot 10^{10}$	137.26±11.78	149.16±14.54
(Mg+Pb)-stearates	0.80–1.70	0.95	$9.76 \cdot 10^{10}$	81.70±6.29	75.84±5.08
(Ca+Pb)-stearates	0.70–1.50	0.90	$3.19 \cdot 10^{11}$	113.65±9.17	126.51±7.67
(Ba+Pb)-stearates	0.60–1.40	1.00	$5.46 \cdot 10^9$	103.73±8.90	115.20±11.01

various PVC samples with different masses and found that the activation energy changes with the size of the sample.

The order of reaction for PVC samples containing different stabilizers was also found to be in the range of one (Table 2). This means that the mechanism of dehydrochlorination is not greatly affected by the addition of these metal stearates. It may be that these metal stearates merely quench HCl and stop further dehydrochlorination which occurs due to the process of autoacceleration.

The activation energies for PVC samples containing different stabilizers are found to be higher than that for pure PVC. The high activation energies indicate that the presence of metal stearates in the PVC matrix hinders its degradation. It is evident from the Table that the activation energies decrease in the sequence $Be > Mg > Ca > Ba$.
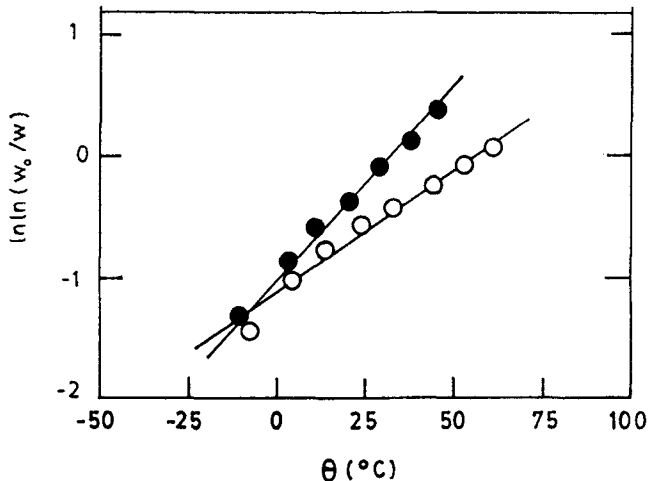

Fig. 3 Plots of ln (w_o/w) vs. θ for PVC (o) and for PVC + Be-stearate (•)

The high activation energies for beryllium and magnesium indicate that these metals act as good stabilizers and increase the activation energy required for the elimination of HCl, as discussed earlier.

The energies of activation for the mixed stearate samples are relatively high as compared with the PVC samples containing the alkaline metal stearates alone, except for magnesium. The high activation energies indicate that these mixed stearates effectively reduce the thermal degradation of PVC. The synergism may be due to complex formation in which chlorine–stearate interchange leads to regulation of the stabilizer, as discussed earlier. The order of reaction for PVC samples containing lead and alkaline metal stearate is also nearly one, as observed for all other samples.

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Zusammenfassung — Mittels TG wurde im Temperaturbereich 150 bis 500°C die thermische nichtoxidative Zersetzung von PVC und der Einfluß der Stearate von basischen Erdmetallen (Be, Mg, Ca, Ba) untersucht. Es wurde beobachtet, daß die Stearate von basischen Erdmetallen die Dehydrochlorierung von PVC effektiv herabsetzen. Auch der synergistische Effekt aus der Kombination dieser Salze mit Bleistearat wurde untersucht und diskutiert. Mittels der Methoden von Coats und Horowitz wurden außerdem kinetische Parameter, wie zum Beispiel Aktivierungsenergie, Reaktionsordnung und Arrhenius'scher Faktor berechnet. Die Ergebnisse zeigen, daß die Metallstearate die für die Dehydrochlorierung von PVC erforderliche Aktivierungsenergie anheben.