Thermal Non-oxidative Degradation of PVC and Stabilizing Action of Various Surfactants Salts of Fatty Acids

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ABSTRACT

Surfactant salts of 3 different fatty acids (i.e., stearic, palmitic and lauric acids) with lead and metals of group IIB were prepared, and the effect of the size of cations and the nature of anions on dehydrochlorination process involved during degradation of polyvinyl chloride, using conductivity and thermogravimetric techniques, have been studied. The effectiveness of these salts depends upon the electronegativity of the metal ion and even more on the hard acid character. The size of the cation also plays an important part, and metal stearates are found to be more effective in blocking the zip elimination of hydrochloric acid as compared to the corresponding palmitates and laurates due to their relatively large sizes.

Key Words: thermal degradation, polyvinyl chloride, dehydrochlorination, stabilization action, fatty acids salts

INTRODUCTION

Polyvinyl chloride (PVC) is one of the most important commercial polymers used in the world. Outdoor exposure of PVC, however, causes both thermal and photooxidation. The stability, degradation and stabilization of PVC have attracted the interest of many polymer scientists and technologists since long and they are still the subject of research and development projects worldwide [1–4]. The elementary process involved in degradation of PVC has been investigated by various techniques, e.g., dehydrochlorination [5–9], TGA [10], IR [11], NMR [12], ESR [13] and mass spectroscopy [14].

Thermal non-oxidative degradation is generally believed to proceed by random unimolecular elimination of hydrochloric acid (HCl), because initiation occurs at the structural defects of polymer. The dehydrochlorination of chain may begin with an ionic molecular mechanism [15], when splitting out of hydrogen chloride molecule leads to lower energy state on account of formation of conjugated double bonds (Scheme I).

This process continues until polarization, as a result of electronegativity of chlorine atom, is compensated by the resonance energy produced by polyene linkages (Scheme II).

Such self-stabilization by polyene structure is possible only at low temperature. However, at normal temperature the HCl produced may interact with conjugated chains thus reducing the effective size of polyene linkages. This in turn causes further dehydrochlorination. Thermal stability of PVC can

Scheme I

Scheme II

be improved using various types of stabilizers which can quench the HCl produced.

In the present study surfactants such as the salts of three different fatty acids, for example, stearic acid, palmitic acid and lauric acid with Pb and metals of group IIB are prepared and the effect of size of cation on the dehydrochlorination process is studied. The value of 'n' in $(CH_3 (CH_2)_n COO)M$ is systematically reduced from 34 to 10.

The nature of anion on HCl elimination process involved during thermal non-oxidative degradation has also been studied. Conductometric and thermogravimetric techniques are used to study the degradation process in PVC.

EXPERIMENTAL

Materials
PVC white powder of analytical grade was obtained from BDH Chemicals Ltd, England. The number average molecular weight of PVC was $100,000 \pm 100$. The particle size data are given as follows:

100% passes B.S. 60 mesh ($\leq 250\mu$ of particle size)
74% passes B.S. 200 mesh ($\leq 75\mu$ of particle size)

Stearic, palmitic and lauric acids (AR-grade) obtained from BDH Ltd were used as such. The materials KOH, $CdCl_2$, $HgCl_2$, $ZnCl_2$ and $Pb(NO_3)_2$ used for the preparation of fatty acids' salts were of AR-grade. They were obtained from Merck and used as such. De-ionized water was used for the measurement of HCl.

Preparation and Purification of Stabilizers
Stearic, palmitic and lauric acids were dissolved separately in water containing 5% KOH. This gave the potassium salt of the respective acid. The salts $CdCl_2$, $HgCl_2$ and $ZnCl_2$ were dissolved separately in distilled water to prepare their solution. The solution of each potassium salt of acids was added to these chloride solutions separately. Since the stearate, palmitate and laurate salts of these metals are insoluble in water, the precipitation occurred in each case. $Pb(NO_3)_2$ was used to prepare Pb salts of fatty acids. The precipitates were then filtered and purified by washing repeatedly with distilled water to remove last traces of KCl and KNO_3. The precipitates were finally dried in a vacuum desiccator at 60 °C until a constant weight was obtained.

Degradation Measurements
The thermal non-oxidative degradation was performed in a glass reactor placed in an oven at 190 $\pm$ 2 °C. Pure PVC was mixed in molar ratio of 5 parts per hundred (pph) of metal salts of stearic, palmitic and lauric acids. One gram of the sample was subjected to heat and HCl produced was carried by preheated nitrogen gas to a conductivity cell. The gas was absorbed in de-ionized water at a constant temperature and conductivity was measured with the help of a sensitive AC Wheatstone Bridge Model RC-18A, using a cathode ray oscilloscope. From the conductance measurement, percentage dehydrochlorination of the sample versus time was obtained.

Shimadzu TGA-31 thermogravimetric system was also used to follow thermal degradation of PVC. Changes in mass of the system versus

temperature were plotted. The weight of 45 mg sample was used in each experiment and the nitrogen gas flow rate was maintained at 40 mL per min.

RESULTS AND DISCUSSION

The results obtained during the thermal non-oxidative degradation have been given in Figure 1 where percentage dehydrochlorination is plotted against time. Degradation of pure PVC shows a sigmoidal curve which means that HCl produced during the degradation process autocatalyzes the reaction. The HCl elimination from the polymer causes conjugation of the polyene linkages which grow until the chain is stabilized by the resonance

energy. However, HCl once produced, can interact with the double bond of polyene linkage, and thus reduces the effective size of polyene linkage. When the size of polyene linkage is reduced the allylic chlorine becomes destabilized and HCl is further eliminated. This catalytic effect of HCl has been confirmed by various workers [1−4, 8].

Zinc, cadmium, mercury and lead salts of higher fatty acids were used and their effect on reducing the catalytic effect of HCl produced was examined in the present study. The size of anion was also changed by increasing the number of CH_2 units, and for this purpose metal salts of stearic, palmitic and lauric acids were used.

Figure 1 also shows the degradation of PVC mixed with 5 pph of three salts of fatty acids, for example, Pb-stearate, Pb-palmitate and Pb-laurate. It is clear from the figure that the rate of dehydro-chlorination decreases and the induction period increases (Table 1) with each salt. This is attribut-ed to the fact that HCl, which acts as catalyst

Figure 1. Degradation of PVC at 190 °C; PVC pure •, PVC+Pb-stearate (5pph) ▲, PVC+Pb-laurate (5pph) ■, PVC+Pb-palmitate (5pph) ○.
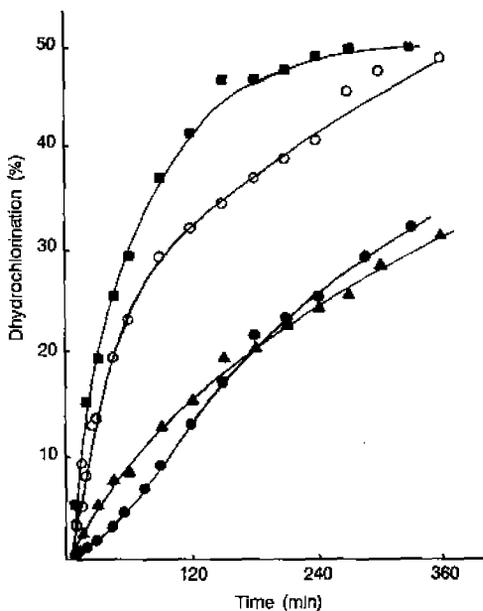
Figure 2. Degradation of PVC at 190 °C; PVC pure •, PVC+Zn-stearate (5pph) ▲, PVC+Zn-laurate (5pph) ■, PVC+Zn-palmitate (5pph) ○.

Table 1. Induction period for various salts of fatty acids, in thermal non-oxidative degradation of PVC.

Metal	Electronegativity	Electronic structure	Induction period (at 190 $^\circ$C) min.		
			stearate	palmitate	laurate
Zn	1.6	2,8,18,2	4	4	4
Cd	1.7	2,8,18,18,2	33	–	–
Hg	1.9	2,8,18,32,18,2	12	10	7
Pb	1.8	2,8,18,32,18,4	35	25	22
PVC (pure)	–	(Induction period, 5 min.)	–	–	–

during the degradation of PVC, reacts with Pb-salts of fatty acid producing lead chloride, the mobility of which is much less than HCl and thus catalytic effect on degradation due to HCl is reduced. The replacement of labile chlorine in the chain with the bulky ester group of the salt also blocks the initiation of the zip elimination of HCl.

This reversible blocking mechanism [17, 18] in the present work was found to be more efficient with the bulkier ester group as the effective stabilizing action of the Pb salts was found in the order: stearate>palmitate>laurate.

Figure 2 shows the degradation of PVC mixed with 5 pph of Zn-salts of fatty acids. It is evident that Zn-palmitate and Zn-laurate increase the dehydrochlorination process. Zn-stearate was also found to increase the dehyrochlorination in the initial period of degradation. Zn-salts are supposed to react with HCl produced, to give their respective salts. However, $ZnCl_2$ formed during the reaction acts as a catalyst for substitution reaction in the absence of a nucleophilic reagent and helps towards further dehydrochlorination. Zinc salts, therefore, were not found as effective stabilizers in PVC at this particular stabilizer concentration used.

Cd-stearate was found to be a good stabilizer for PVC as it is shown in Figure 3. The induction period of dehydrochlorination here increased from 5 to 33 min as compared to pure PVC. Cadmium, being more electronegative as compared to Zn, forms a stable $CdCl_2$ and it is more effective in quenching the HCl produced during the reaction and thus reducing the catalytic effect of HCl on

dehydrochlorination process.

Figure 4 shows the effect of Hg-salts of fatty acid on dehydrochlorination of PVC. Hg-stearate was more effective than Hg-palmitate and Hg-laurate. The same trend was observed in Zn-salts of fatty acid. Comparing the stabilization effect of Zn-, Cd- and Hg-stearates, it is found that Cd-stearate is a more effective stabilizer in these series (Figure 5). The metals Zn, Cd and Hg lie in the 2nd group and electronegativity of these metals is
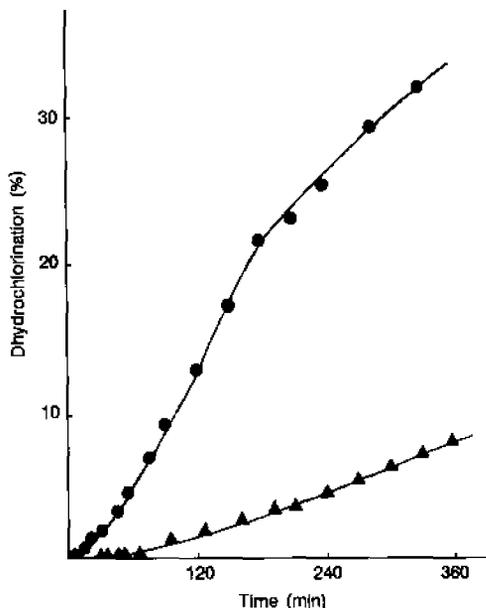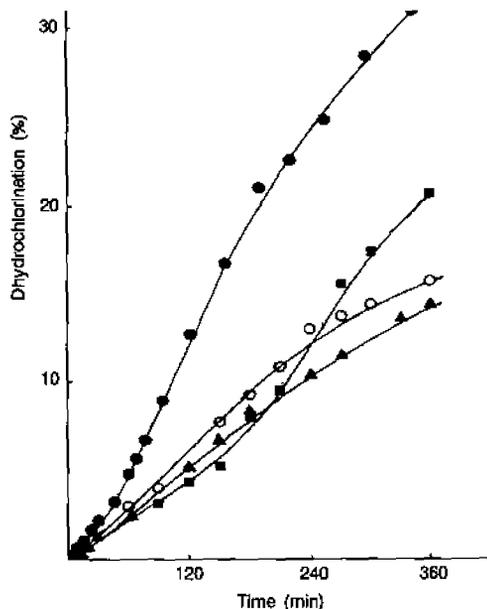

Figure 3. Degradation of PVC at 190 $^\circ$C; PVC pure •, PVC+Cd-stearate (5pph) ▲.

in the order of Hg>Cd>Zn. The ease with which a stable metal chloride is formed is also in the same order and it is expected that Hg-stearate should act as a better stabilizer than Cd-stearate. However, because Hg exists in two oxidation states, so at high temperature there may exist an equilibrium between these two states:

$$2HgCl_2 \rightleftharpoons HgCl + HgCl_3$$

Ionic species thus produced can decrease stabilization effect on PVC and can cause further dehydrochlorination by ionic mechanism.

Thermogravimetric analysis was also carried out for pure PVC and PVC mixed with metal stearates under inert atmosphere. Figure 6 shows TGA curves where the weight loss of the sample versus temperature has been plotted. It is clear from the Figure 6 that the degradation of PVC starts around 180 °C. As the temperature is increased from 180 °C, PVC loses its weight due to

elimination of HCl and the process continues until the temperature of nearly 320 °C is achieved. The weight loss in this region i.e., 180−320 °C is mainly due to the dehydrochlorination process already studied by conductometric technique. The results obtained in this region show that the PVC mixed with Zn-stearate begins to lose its weight at a lower temperature than that of pure PVC. However, with Cd-stearate the weight loss was observed at a higher temperature as compared to that in pure PVC. The stabilizing effect of Hg-stearate was less than that of Cd-stearate. TGA curves also confirm the results obtained by the dehydrochlorination studies.

Table 1 shows the induction period (observed at 190 °C), electronic structure and electronegativity for various metal salts. As it is clear from the table that the induction period in general is decreased when we reduce the number of CH_2 groups in the cation attached with particular metal i.e., going from stearate to laurate. In case of Hg

Figure 4. Degradation of PVC at 190 °C; PVC pure ●, PVC+Hg-stearate (5pph) ▲, PVC+Hg-laurate (5pph) ■, PVC+Hg-palmitate (5pph) ○.
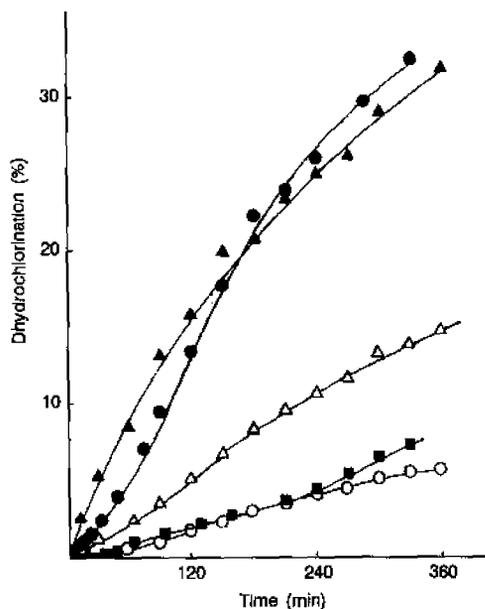

Figure 5. Degradation of PVC at 190 °C; PVC pure ●, PVC+Zn-stearate (5pph) ▲, PVC+Hg-stearate (5pph) △, PVC+Cd-stearate (5pph) ■ PVC+Hg-stearate (5pph) ○.
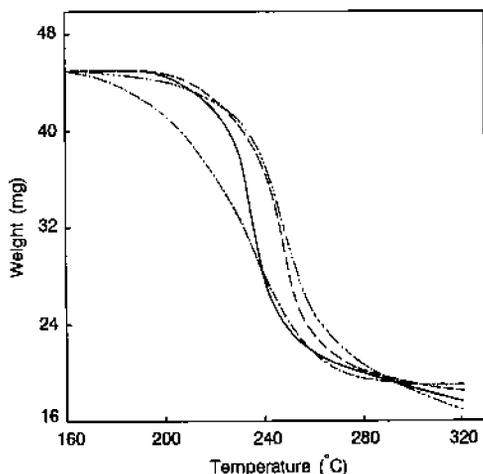
Figure 6. Thermogravimetric analysis; PVC pure ——, PVC+Cd-stearate (5pph) — — —, PVC+Zn-stearate (5pph) —·—·—·, PVC+Hg-stearate (5pph) —···—···.

the induction period reduces from 12 to 7 min when the size of the ethylene linkage was reduced from 17 to 11. Similar trend was obtained with Pb-salts. However, with Zn the induction periods recorded for metal stearate, palmitate and laurate were the same. It may be due to small experimental error involved during the degradation study. The most probable reason for the decrease in the induction period is the thermal instability of metal laurates and palmitates as compared to stearates. The small size of $(CH_2)_n$ chain makes them relatively less effective to block the HCl zipping elimination. Also the smaller chains make these salts more volatile at high temperature. These types of salts, therefore, can be used as stabilizers during the processing where polymer is subjected to heat only for a short period. The nature of anion plays an important part in stabilizing PVC. Hard acid metals form stable chlorides and thus by combining with HCl reduce its mobility and thus its catalytic effect on PVC degradation. Transition metals which have the capability of forming complexes with chlorine also have the ability to quench the effect of HCl. The amount of stabilizer added also plays an important role. Small amount

of Zn-stearate has previously been found to stabilize PVC [20–22]. As the amount of Zn-stearate used was higher in the present study, so $ZnCl_2$, once formed in excess, destabilized PVC by interacting with double bond of polyene linkage. In our recent studies on the effect of $ZnCl_2$ on degradation of PVC using UV-visible spectrophotometry we have shown the interaction of the polyene linkage with $ZnCl_2$ [25, 26]. Formation of a stable complex has been reported which creates a labile chlorine in the PVC chains. The labile chlorine once produced initiates zip opening in chains thus increasing the degradation rate of PVC [22–24]. The catalyzing effect of $ZnCl_2$ was found to be much more than of $CdCl_2$ [27, 28].

CONCLUSION

In stabilizing PVC the nature of anion plays an important role in these salts of fatty acids. The HCl produced which has a catalytic effect on degradation is absorbed more effectively by the metals with hard acid character, and such anions are therefore more effective in reducing the thermal degradation. The bulkier ester groups in the salt, that is, stearates, due to their size, were more effective in blocking the zip elimination of HCl as compared to the palmitates or laurates.

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