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Degradation of Barium-Cadimium Stabilized PVC in Solution

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Summary

The degradation kinetics of PVC stabilized with barium and cadmium stearate has been studied in solution in inert atmosphere. Formation of HCl and metal chloride was followed along with the changes of UV and visible spectra. It has been shown that reaction between the stabilizer and labile chlorines originally present is insufficient to explain stabilization.

Introduction

Despite of the waste number of papers and patents about barium and cadmium containing PVC stabilizers their stabilization mechanism and kinetics are not completely understood. Based on infrared and radioactivity measurements exchange of labile chlorines for ester groups by the stabilizer was proposed about twenty years ago (FRYE and HORST 1959, 1960). Exchange reaction was also demonstrated (TRAN VAN HOANG et al. 1976) with 4-chloro-2-hexene, a model compound of allylic chlorine in PVC. At present, this mechanism is widely accepted (NASS 1976) though there are authors who bafflingly neglect this possibility (PROHASKA and WYPYCH 1979). Another recent paper (CZAKÓ et al. 1979) concluded that exchange cannot be the predominant mechanism of stabilization.

On "solid" PVC samples (i.e., powder, milled sheet etc.) HCl formation kinetics, together with the measurement of stabilizer consumption and metal chloride formation was thoroughly studied (NAGATOMI and SAEKI 1962, OCSKAY et al. 1971, CZAKÓ et al. 1977). Only few measurements were carried out in solution (BRAUN and HEPP 1973, 1978), despite of the fact that problems arising from inhomogeneity and sample morphology are absent in solution.

In this study the formation of HCl and metal chloride as well as of polyenes was followed during the

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degradation of 1,2,4-trichlorobenzene solution of PVC stabilized by barium and cadmium stearate.

Experimental

The PVC sample Ongrovil S 470 was an industrial suspension polymerisate (kindly supplied by Borsod Chemical Works). Degradation was carried out in carefully purified 1,2,4-trichlorobenzene (TCB). Barium and cadmium stearate were laboratory products. Two master batches were prepared with the Ba and Cd soap, respectively, by dry blending. 1 g of the master batch contained 0.05 mmole stabilizer. Weighed amounts of the master batches were placed in the reaction vessel and unstabilized PVC was added to round up the total weight of PVC to 625 mg (10 mmole VC units). Then 30 cm^3 TCB was poured on the powder, the vessel deoxygenated by a stream of Ar or N_2 and placed in the 200°C thermostated oil bath. In case of higher stabilizator concentrations the stabilizers were weighed directly into the reaction vessel.

HCl evolution was followed conductometrically. In separate experiments the UV and visible spectra of samples from the solution (diluted in 1:1 ratio with tetrahydrofuran) were recorded from time to time. The concentration of polyenes was calculated from the UV spectra as described earlier (TÜDŐS et al. 1974).

The amount of metal chlorides formed were determined in separate experiments. After a predetermined time the heat treatment was stopped, 10 cm^3 distilled cyclohexanone was added, the chlorides were extracted by water and titrated with 0.01 n $AgNO_3$ using a RADELKIS OP-930 automatic burette and conductometric end point detection.

Results and Discussion

The HCl formation kinetics from unstabilised and Ba-Cd stabilised PVC are shown on Fig.1, together with the amount of chloride formed. The limiting value of the chloride formed, measured subsequent to the induction period was about 85% of the theoretical. Four stages can be distinguished on the chloride curve. The first 0.05 mole % chloride is formed relatively fast, within about 30 min. In the second period the chloride formation rate is considerably slower and nearly constant, the second 0.05 mole % is formed in about 60 min. The degradation rate is $8.3 \cdot 10^{-6}$ min^{-1}, about 6 times lower than in case of unstabilized PVC; a similar value was obtained by TROITSKII et al. 1977, in case of tin stabilizers. Then, the stabilizer becoming exhausted,

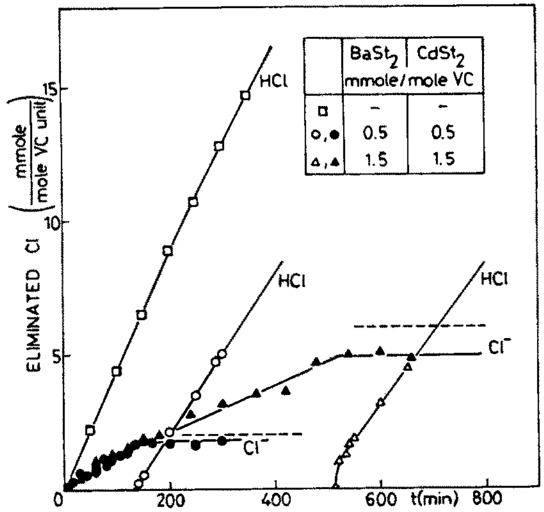

Figure 1. Metal chlorides and HCl formed from PVC stabilized with (0.5 mmole $BaSt_2$ + 0.5 mmole $CdSt_2$)/mole VC monomer unit (o and ●) and with (1,5 mmole Ba St_2 + 1.5 mmole $CdSt_2$)/ mole VC monomer unit (Δ and ▲). The HCl evolution curve of unstabilized PVC is included for comparison (+). Degradation at 200°C in TCB solution in inert atmosphere.

the chloride formation is accelerated again and gaseous HCl evolution starts. In the last stage, after the end of the induction period, the rate of HCl evolution is slightly lower than that of the unstabilized PVC at the same degradation time.

Similar results were obtained with higher stabilizer concentrations: the first part of the chloride formation curve did not change noticeably (Table 1), but the linear part became longer.

The reaction of the stabilizer with the labile chlorines originally present is not sufficient to explain this findings. It seems that the first step of dehydrochlorination, i.e. HCl elimination at defect sites or randomly, takes place also in presence of stabilizers. An effective stabilizer reacts, however, with that species which initiates the zip reaction (activated chain elimination) in the absence of the stabilizer, or it stops the zip after the formation of one or very few double bonds. With higher stabilizer concentrations the HCl evolution rate at the end of the induction period was much higher (Fig.1), but after a few minutes, i.e. at most after a few tenths of a percent conversion, it reached about the same steady state value for all stabilizer concentrations. At present we do not have a firm explanation of this finding. Similar behaviour was observed with higher Cd/Ba ratio at low stabilizer concentrations too. As an explanation the catalytic effect of $CdCl_2$ could be considered. It is difficult, however, to understand, that this does not last longer. We have to mention, that the solutions remained clear even after the exhaustion of the stabilizer, at least when their chloride binding capacity was not more than 6 mmole Cl/mole VC units. (Higher concentrations were not investigated up to exhaustion as their induction periodes were longer than 500 min.) This means that the metal chlorides remained dissolved in the solvent.

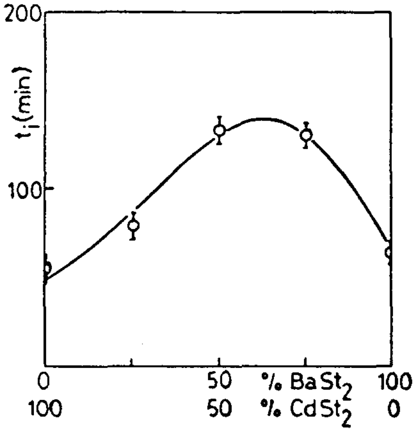

Figure 2. Dependence of the length of induction period on stabilizer composition. The total stabilizer concentration was 1 mmole/ mole VC monomer units.

The well known strong synergistic effect of barium and cadmium soaps is observed also in solution (Fig.2). Although the induction periodes of the samples stabilized with the same molar amount of Cd resp. Ba stearate do not differ much, the investigation of the UV and visible spectra shows marked difference in their way of action. Spectra are compared on Fig.3, indicating that cadmium containing stabilizers effectively inhibit polyene formation, while barium stearate, if used alone, only retards polyene formation to some extent and a considerable amount of polyenes is formed.

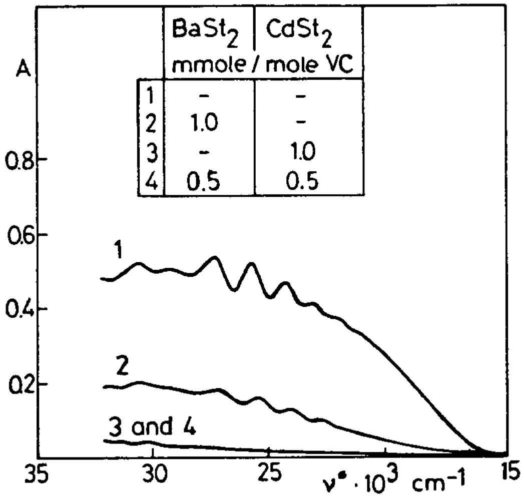

Figure 3. The UV and visible spectra of PVC degraded in TCB solution at 200°C for 45 min. The total stabilizer concentration was 1 mmole/mole VC monomer units. Spectra were taken in 1:1 mixture of TCB and THF, PVC concentration 10,4 g/dm^3.

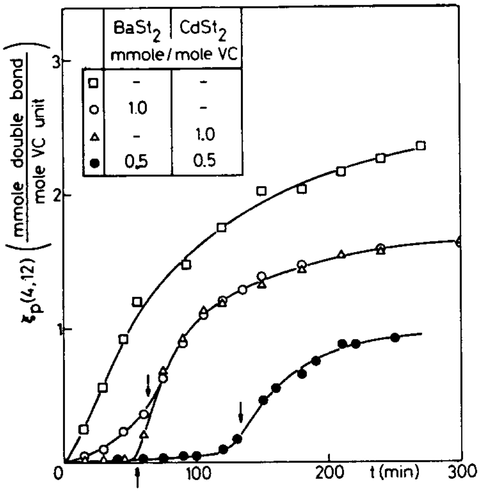

Figure 4. The amount of double bonds summarized for polyenes n = 4-12. The experimental conditions see at Fig.3. Arrows indicate the beginning of HCl evolution.

The sum of double bonds $\xi_p(4,12)$ found in polyenes n = 4-12 are plotted on Fig.4. In the case of unstabilized PVC, at early stages this sum represents about 50% of the total amount of double bonds, at later stages this ratio falls rapidly due to polyene consuming secondary reactions, e.g. cyclization (TÜDŐS et. al 1974). Fig.4 shows that with cadmium containing stabilizers polyene formation starts only when the stabilizer becomes exhausted, while with barium stearate the rate of polyene formation increases continuously with the consumption of the stabilizer. On the other hand, since cadmium stearate, when used alone, is consumed much faster than the mixed Ba-Cd stabilizer, and somewhat faster even than barium stearate alone, we have to conclude that in cadmium stabilized PVC the initiation of dehydrochlorination is faster than in the absence of cadmium. Similar findings were published in the case of "solid" PVC samples degraded in air VYMAZAL et al. 1980). This might be the effect of $CdCl_2$, but also the cadmium stearate or its hypotetical mixed chloride CdCl-stearate might catalyse initiation. At present the data do not allow to distinguish between these two possibilities. In the explanation of synergism also the possibility of complex formation between barium and cadmium salts can be taken into account, as similar complex formation was found in the case of Ca-Zn stabilizers (ONOZUKA and ASAHINA, 1969).

TABLE I

The amount of metal chlorides formed in 60 min at 200°C in the presence of Ba + Cd stearate (molar ratio 1:1)
PVC concentration: 0.33 mole VC units/l

Stabilizer concentration	Weight ratio of stabilizer to PVC	Theoretical chloride binding capacity	Found chloride
$\frac{\text{mmole}}{l}$	phr	$\frac{\text{mmole}}{\text{mole VC units}}$	$\frac{\text{mmole}}{\text{mole VC units}}$
0,33	1,1	2	0,76
0,67	2,2	4	0,85
1,00	3,3	6	0,95
1,67	5,5	10	0,82
3,33	11,1	20	0,93
5,00	16,6	30	0,84

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