A study of the thermal degradation of poly(vinyl chloride) in the presence of carbazole and potassium carbazole using t.g.a./*FT*i.r.

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Thermal properties of blends containing poly(vinyl chloride) and carbazole or potassium carbazole in different molar ratios were investigated using thermogravimetric analysis coupled with Fourier transform infra-red spectroscopy. The effect of additives on the polymer degradation process, and especially on the evolution of hydrogen chloride, was studied. Finally, mechanisms of stabilization were proposed.

(Keywords: poly(vinyl chloride); thermal degradation; stabilization)

INTRODUCTION

The thermal degradation of poly(vinyl chloride) (PVC) has been the subject of numerous papers, which have been discussed in several excellent review articles[1-4]. It is well known that PVC undergoes dehydrochlorination followed by the formation of double bond sequences, which are responsible for subsequent discoloration and a decrease in its mechanical properties. The mechanism of this process is still the subject of debate: it may occur via a radical, ionic or a molecular route. The low thermal stability of PVC is thought to be caused by the whole range of irregular structures in the polymer, e.g. initiator residues and internal unsaturation. This hypothesis was confirmed by the comparison of thermal stability of PVC with some low molecular weight compounds taken as models for the 'ideal' PVC structure, e.g. 1,4,7-trichloropentane[2]. The main role of the stabilizer is to react with the liberated HCl and thus facilitate its removal from the system, since it has been shown to have a catalytic effect on the rate of the degradation reaction. Any substance (or group of substances) that is able to decrease the rate of dehydrochlorination could thus be considered as a potentially effective stabilizer. The use of thermal analysis coupled with spectroscopic techniques turned out to be particularly effective in the examination of such substances and the processes of stabilization.

The present work attempts to evaluate the influence of carbazole and potassium carbazole on PVC during the process of thermal degradation.

EXPERIMENTAL

Materials

The samples analysed in this work were prepared by dilution of PVC-E (from Hoechst, Fikentscher number = 65) with carbazole (from Merck) or potassium carbazole (from IChP) in dimethylsulfoxide. The solvent was then removed under vacuum. A description of the samples is given in *Table 1*.

Analytical techniques

Thermogravimetric analysis (t.g.a.) was carried out using a Perkin–Elmer 7 thermogravimetric analyser. The conditions were: heating rate, 10 and 50 K min^{-1}; sample weight, ~5 mg; nitrogen flow, 40 cm^3 min^{-1}. Al_2O_3 was used as a reference material. Fourier transform infra-red (*FT*i.r.) spectra were recorded using a Perkin–Elmer 1725X *FT*i.r. spectrometer interfaced with an IBM 55SX computer. The thermogravimetric analyser and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reaction or condensation on cell walls.

RESULTS AND DISCUSSION

The evolution of volatile products at a heating rate of 10 K min^{-1} was insufficient for the recording of *FT*i.r. spectra. An increase in the heating rate to 50 K min^{-1} allowed us to obtain a whole set of corresponding *FT*i.r. spectra and thermograms; the curves on the latter were respectively shifted towards the higher temperatures.

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Table 1 Characteristics of the samples used in this work

Sample no.	Mole ratio of PVC:additive	Additive
1	1:1	Carbazole
2	1:0.5	Carbazole
3	1:0.1	Carbazole
4	1:1	Potassium carbazole
5	1:0.5	Potassium carbazole
6	1:0.1	Potassium carbazole
7	PVC-E	–
8	Carbazole	–
9	Potassium carbazole	–

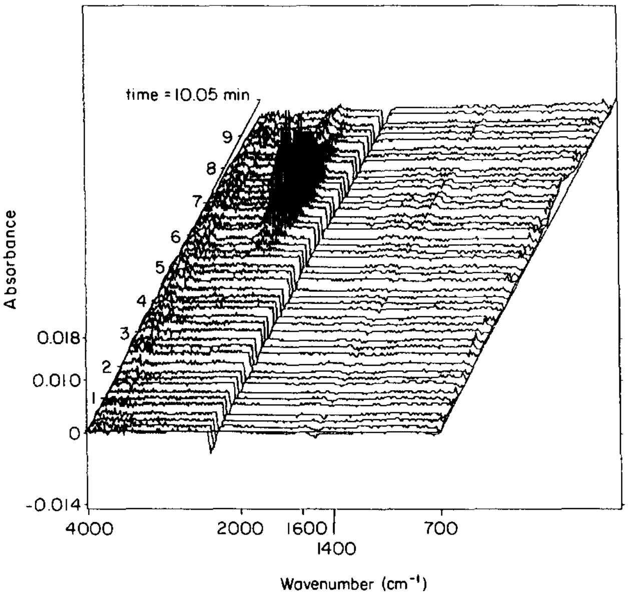


Figure 1 Stacked plots of *FT*i.r. spectra of PVC-E from 0 to 10.05 min

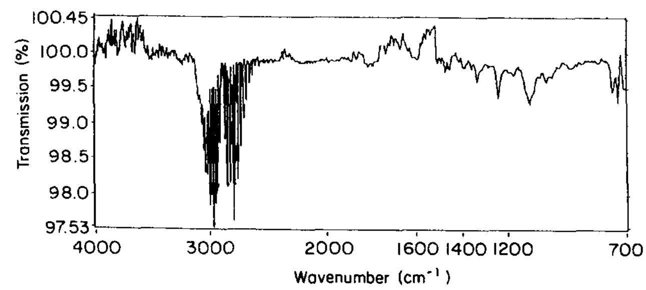


Figure 2 *FT*i.r. spectrum of sample 3 at 375°C after 6.755 min

Initially, the sample of PVC-E (sample 7) was analysed. Peaks corresponding to HCl in the vapour were found at 325°C, reaching a maximum at the height of gas emission at 380°C. A stacked plot of *FT*i.r. spectra is shown in *Figure 1*.

In the first group of samples (1, 2 and 3), sample 2 was the most stable, with an initial decomposition temperature (*IDT*) of 210°C. By considering the *FT*i.r. spectrum of sample 3, it was noticed that in this case dehydrochlorination occurred after 6.2 min, corresponding to a temperature of 340°C, having a maximum at 375°C (*Figure 2*). This corresponds to a mass loss of 15.5% from the t.g.a. curve, displayed in *Figure 3*. The rate of this process reaches a maximum at 375°C. Both values may be compared with the last stage of degradation from the t.g.a. curve.

Sample 6, from the second group of samples (4, 5 and 6), was found to be the most stable (*IDT*=210°C). The t.g.a. profiles of degradation samples 4 and 5 were very similar, displaying an initial 20% mass loss up to a temperature of 150°C. The maximum decomposition rates for both samples occurred in the temperature range 275–280°C. From i.r. results of sample 4, it was found that the first HCl peaks were detected at 340°C, reaching their maxima at 370°C. For sample 5, these values were 350 and 380°C, respectively. Analysis of the gas evolution chromatogram of sample 6 revealed that up to a temperature of 285°C, emission of volatile products remained practically nil (*Figure 4*).

It is important to point out that the initial temperatures of HCl emission are dependent on the sensitivity of the analytical equipment. Using another procedure, or a special technique, it is possible to detect HCl at lower temperatures, as described in the literature[4]. Our results, obtained under the same experimental conditions, enable us to estimate the relative influence of the chosen additives on the process of HCl evolution. Hence, on the basis of t.g.a. curves, essentially no decrease in mass loss was observed. Taking all the results into consideration leads to the conclusion that carbazole and potassium carbazole can act as secondary stabilizers. However, carbazole differs considerably from other secondary stabilizers that have a similar chemical structure, e.g. secondary amines. This is because of its acidic hydrogen atom ($pK_a = 7$).

The experimental results show that the use of carbazole and potassium carbazole as additives causes an increase

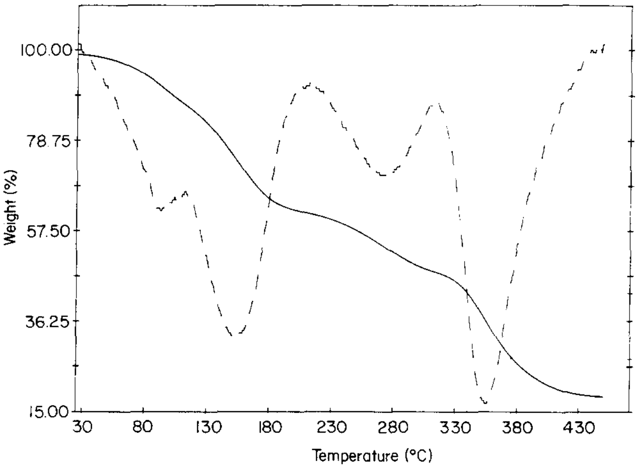


Figure 3 Thermogravimetric curve of sample 3: ——, weight loss curve; – –, first derivative of weight loss curve

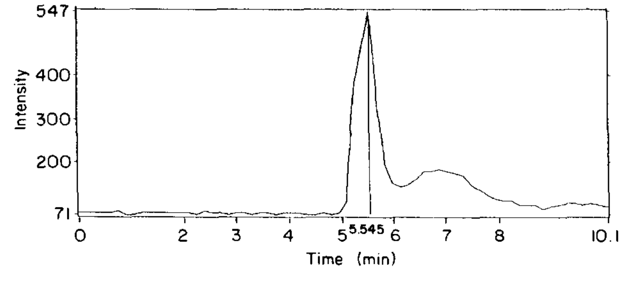
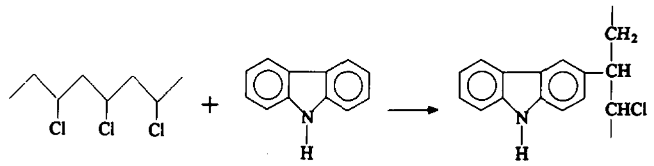
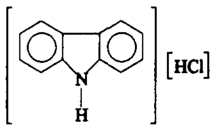


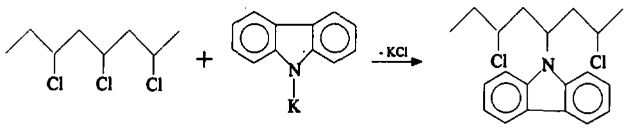
Figure 4 A Gram–Schmidt chromatogram of sample 6



Scheme 1



Scheme 2



Scheme 3

in the initial temperature of HCl emission. This is confirmed especially in the case of samples 3 and 5. A possible explanation for this phenomenon can be found by examination of the chemical structure and reactivity of the investigated compounds. Carbazole, as an aromatic compound, is able to react with double bonds of polyene sequences, i.e. an aromatic alkylation reaction (*Scheme 1*). Coordination of HCl in the form of a complex can be suggested as well, since carbazole is a Lewis acid, leading to the structure in *Scheme 2*. Taking into account potassium carbazole, a similar mechanism seems possible by its connection to the polymer chain in the reaction shown in *Scheme 3*. The steric hindrance afforded by the aromatic molecule blocks access to the adjacent chlorine atoms and also influences the polymer chain through electron interactions.

CONCLUSIONS

The reaction of carbazole and potassium carbazole with PVC causes the onset temperatures of HCl evolution to increase by about 15–20°C. The suggested mechanisms of stabilization should be confirmed in the presence of other substances (e.g. epoxy resins) and such studies are now in progress.

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