

Degradation of Poly(vinyl chloride) in the Presence of 9-(2,3-Epoxypropane)carbazole Studied by Means of TGA/FTIR

KRZYSZTOF PIELICHOWSKI,^{1*} JAN PIELICHOWSKI,¹ and IAN HAMERTON²

¹Department of Chemistry, Technical University, 31-155 Kraków, Poland; and ²Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, United Kingdom

SYNOPSIS

Blends containing poly(vinyl chloride) and 9-(2,3-epoxypropane)carbazole in different weight ratios were subjected to investigations using thermogravimetric analysis coupled with Fourier transform infrared spectroscopy. The effect of additive on the polymer degradation process was studied. It was found that 9-(2,3-epoxypropane)carbazole causes an increase in the onset temperature of hydrogen chloride emission by about 20–25°C. Finally, the mechanisms of stabilization were proposed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Many workers have investigated the mechanisms of degradation and all aspects of the stabilization of poly(vinyl chloride) (PVC), resulting in numerous publications.^{1–6} The main reason for this research is the drive to improve the relatively low thermal stability of this bulk polymer. The general features of the degradation mechanism have been explained in the literature. It has already been found and confirmed that the evolution of hydrogen chloride (dehydrochlorination) plays a key role, followed by the formation of double bond sequences, which are responsible for discoloration and decrease in the polymer's mechanical properties. A knowledge of this phenomena does not, however, explain the general trends. The majority of PVC-stabilizer systems were developed empirically. For the most part, these are metal carboxylate stabilizers whose synergistic effect could only be explained after it became clear that esterification of the polymer to form PVC-carboxylate esters had occurred.⁷ The most important problem associated with the prediction of the thermal behavior of a stabilized polymeric material is

caused by multicomponent formulation of the stabilizer. Different mechanisms, from various components of such a stabilizer, running separately or affecting each other, are responsible for the global effect. It requires much effort to distinguish and identify the individual reactions. From a different perspective, it seems logical to investigate separately the substances which, taking into account mechanisms (or the most probable mechanisms), are able to react with HCl and, thus, facilitate its removal from the system.

Continuing our previous work,⁸ in which it has been proven that carbazole can act as a secondary stabilizer, we present in this article the influence of 9-(2,3-epoxypropane)carbazole on PVC during the process of thermal degradation. Considering the structure of this multifunctional compound, it can be expected that 9-(2,3-epoxypropane)carbazole reacts with HCl and polymer chain even more readily and efficiently than its precursor—carbazole.

EXPERIMENTAL

Materials

The samples were prepared by dilution of PVC-E (from Zakłady Chemiczne Tarnów S.A., Fikentscher number = 70) with 9-(2,3-epoxypropane)carbazole in dimethylsulphoxide (DMSO). The solvent was

* To whom correspondence should be addressed at the Institute of Organic Chemistry & Technology, Technical University, Ul. Warszawska 24, 31-155 Krakow, Poland.

Table I Characteristics of the Samples

Sample No.	Weight Content of 9-(2,3-Epoxypropane)carbazole [%]
1	poly(vinyl chloride)
2	9-(2,3-epoxypropane)carbazole
3	1.0
4	2.0
5	3.0
6	4.0

then removed under vacuum. A description of the samples is given in Table I.

9-(2,3-Epoxypropane)carbazole was prepared using the modification of the method of Pielichowski and Chrzaszcz:⁹ in a round-bottomed flask equipped with an efficient stirrer and an upright condenser 30 mL of 45% solution of NaOH, 5 g (0.03 mol) of carbazole, and 10 mL of DMSO were added. The mixture was vigorously stirred for 30 min. Then, at room temperature, a mixture of 3 mL (0.038 mol) of epichlorhydrin and 3 mL of DMSO was added within 30 min. The content of the flask was poured into water, then the crude solid product was filtered, washed until neutral pH was obtained, and dried. Crude product (6.9 g, yield 89.5%) was obtained, which was then recrystallized from methanol—mp 105–107°C.

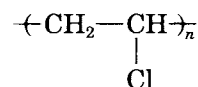
Analytical Techniques

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer 7 thermogravimetric analyzer. The conditions were: heating rate 50 K/min, sample weight ca. 5 mg, nitrogen flow 40 cm³/min. Al₂O₃ was used as a reference material. Infrared spectra were recorded using a Perkin-Elmer 1725X FTIR spectrometer interfaced with an IBM PS-2 computer. The thermogravimetric analyzer 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.

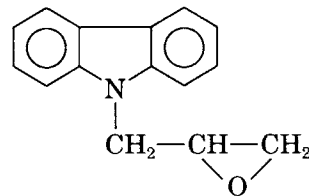
RESULTS AND DISCUSSION

The substances under investigation were of the general formula:

(i) PVC



(ii) 9-(2,3-epoxypropane)carbazole (EPC)



Considering the chemical structure of 9-(2,3-epoxypropane)carbazole, it was expected that reactions with HCl could take place. It would lead to differences in the thermal degradation process in comparison to the pure PVC sample, observed using TGA and FTIR.

Initially, sample 1 (PVC) was investigated. The TGA results reveal that it was stable up to 290°C. Above this temperature, a rapid mass loss was observed that reached about 64% of initial mass up to 400°C. From the FTIR data can be found that the first peaks corresponding to HCl in the vapor were found at 320°C, with a maximum at 360°C.

The next step was the investigation of thermal behavior of 9-(2,3-epoxypropane)carbazole. It underwent a practically one-step degradation, starting at 220°C (Fig. 1). Up to a temperature of 345°C, the mass loss of 87% was observed. The char residue at 400°C was found to be 6% of the initial sample mass. Analysis of the FTIR results leads to the conclusion that at 255°C the evolution of 1-chloro-2-propanol begins, which was identified according to ref. 10. FTIR spectra are displayed in the form of a stacked plot on Figure 2.

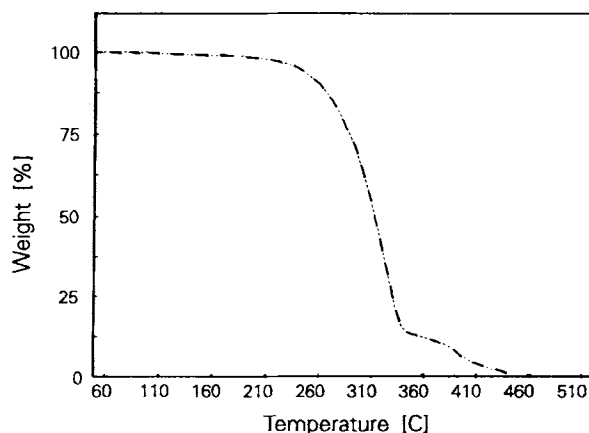


Figure 1 Thermogravimetric curve of sample 2.

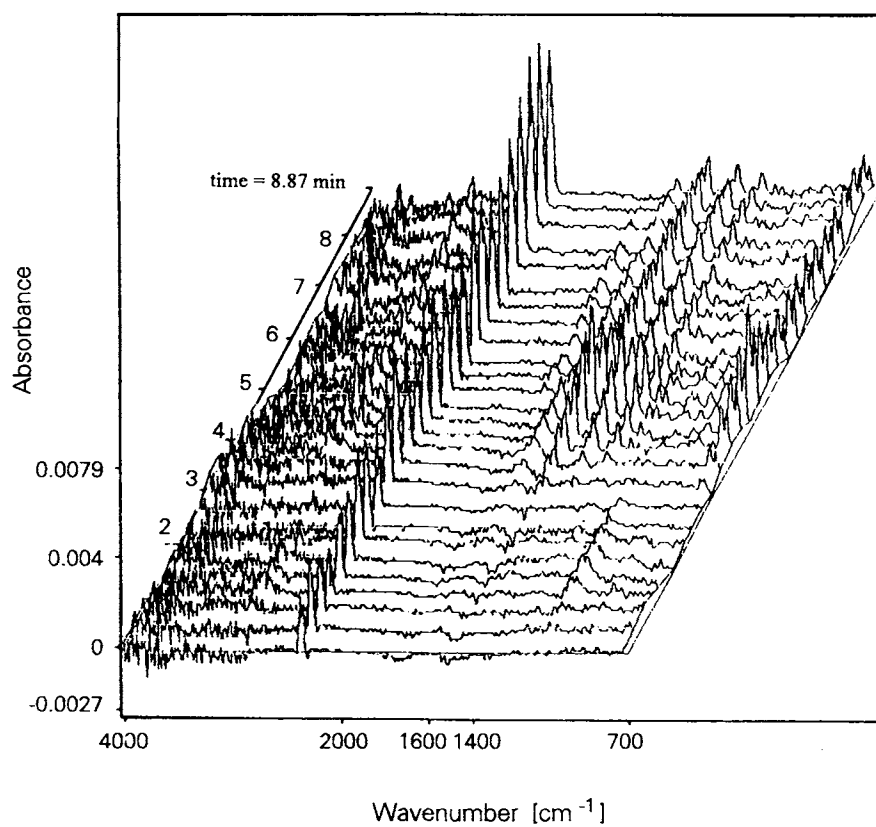


Figure 2 Stacked plots of FTIR spectra of sample 2 from 0 to 8.87 min.

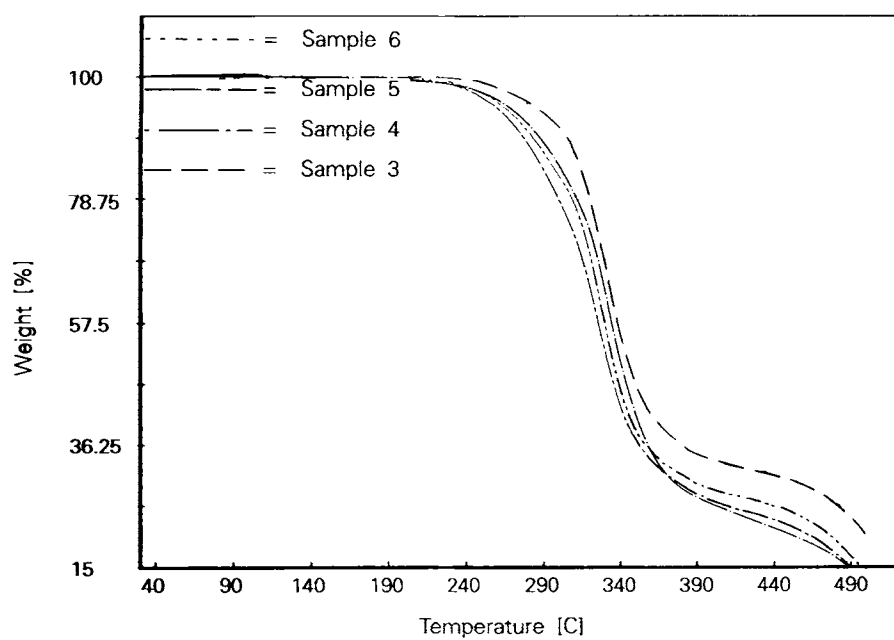


Figure 3 Thermogravimetric curves of samples 3, 4, 5, and 6.

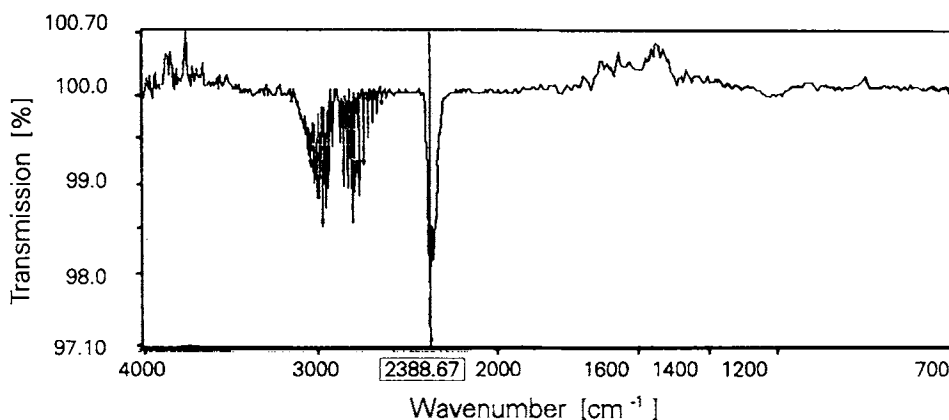


Figure 4 FTIR spectrum of sample 6 at 375°C.

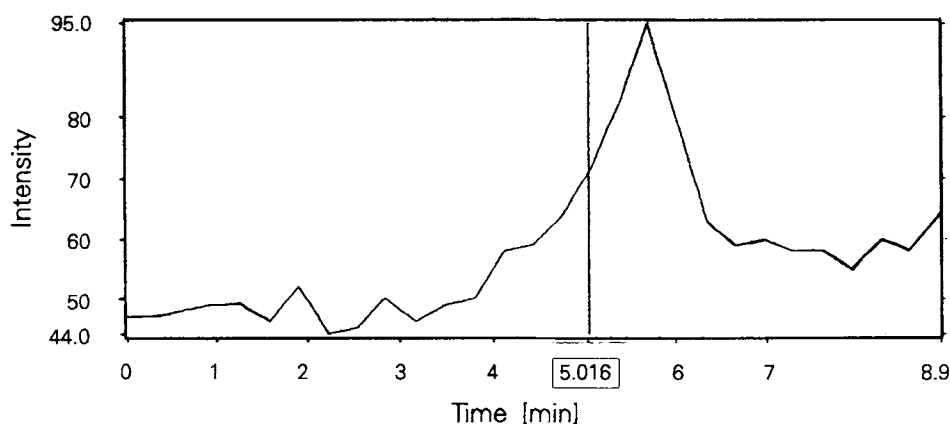


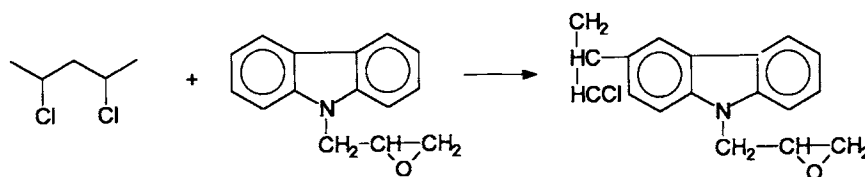
Figure 5 A Gram-Schmidt chromatogram of sample 5.

Among the samples of PVC-EPC blends (sample 3, 4, 5, and 6), sample 3 turned out to be the most stable one. The TGA profiles of all the samples investigated are very similar in the shape, with differences in initial degradation temperature (IDT) values laying in the range of 3–15°C (Fig. 3). The main degradation process occurred in the range of 250–380°C, reaching its maximum rate at about 330°C that was found from the first derivatives of the weight loss curves.

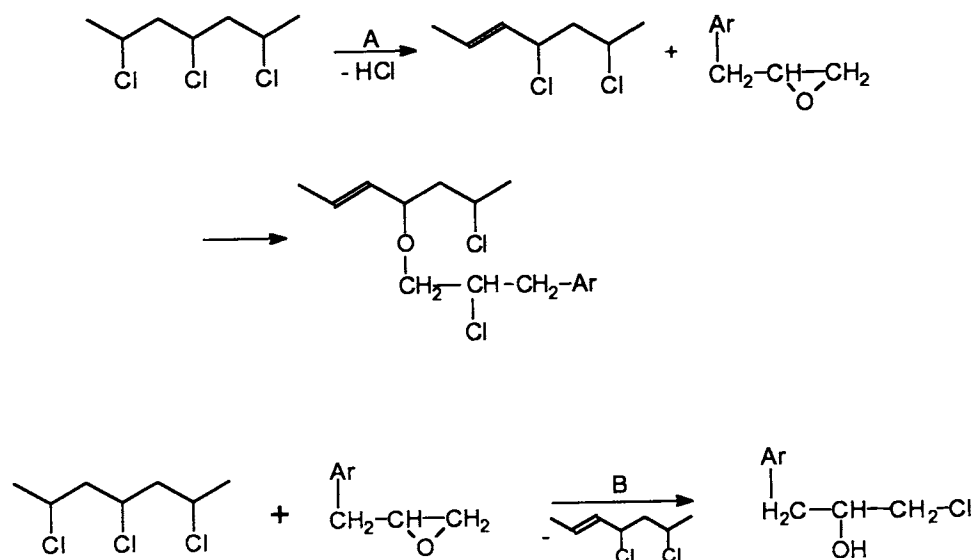
Analysis of the FTIR data allowed us to obtain information about HCl emission. For samples 5 and 6, first HCl peaks were detected at 340–345°C, having their maxima at 375°C (Fig. 4). Additionally,

gas evolution chromatogram of sample 5 showed that the maximum of emission of all volatile products occurs at ca. 350°C, above the temperature of maximum degradation rate and well below the maximum of HCl emission (Fig. 5). For samples 3 and 4, HCl evolution begins at 330°C.

It should be pointed out that the initial temperatures of the hydrogen chloride emission depend on degradation conditions (heating rate, sample mass, sample geometry, etc.) and on the sensitivity and speed of analysis by the analytical equipment. It can be assumed in our investigation that the heating rate played the dominant role. It can be clearly seen that the TGA curves are shifted towards higher



Scheme 1



Scheme 2

temperatures in comparison to any other obtained at the lower heating rate: the detection of the volatile species was also supposedly delayed. If another procedure or degradation technique is used, the first traces of HCl can be found in lower temperatures.² Our results, obtained under the same experimental conditions, enable us to estimate the relative influence of the additive on the process of PVC degradation.

Summarizing the results, it can be seen that the addition of EPC does not improve the global thermal parameters (e.g., IDT) of the degradation process. It could, however, be predicted knowing its thermal behavior alone. On the other hand, EPC significantly influences the evolution of hydrogen chloride. It should be pointed out that its impact on HCl emission makes it a good prospect for its applications in conjunction with any other stabilizer. One can also not exclude the possible synergistic effects, because many stabilizer systems act not only through HCl removal, as, for example, organotin compounds.^{11,12}

A possible explanation of the influence of EPC on the emission of HCl can be drawn from the chemical structure and reactivity of this compound. There are three places in the structure of EPC molecule that can be assumed to react with evolved HCl

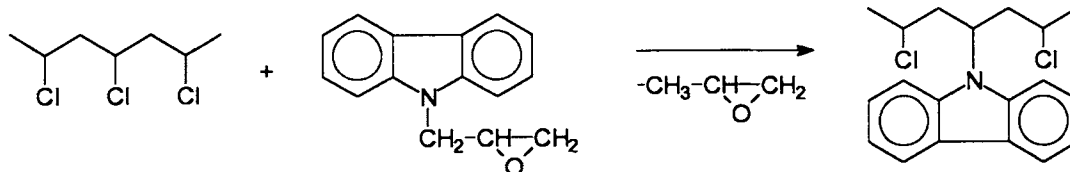
or with "defects" in the PVC structures, thus, indirectly facilitating HCl removal.

The first one (displayed in Scheme 1) concerns the aromatic ring and its reaction with the double bond of polyene sequences of partially degraded PVC. The second is connected with the epoxy group, leading either to the formation of allylic chloro ethers (path A on the Scheme 2), as found in model studies of epoxy compounds,² or to 1-chloro-2-propanol derivatives (Path B on the Scheme 2).

Scheme 3 presents connection of the molecule, which is formed after breaking of C—N bond in EPC, to the polymer chain. This is accompanied by emission of propylene oxide, which was identified according to ref. 10.

CONCLUSIONS

The reaction of EPC with PVC causes an increase in the onset temperature of HCl emission by about 20–25°C. It is a promising result and, therefore, our current research is focussed on new stabilizing systems, in which EPC can act as a secondary stabilizer.



Scheme 3

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