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TG/FT-IR STUDIES OF POLY(VINYL CHLORIDE) BLENDS

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Abstract

Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG/FT-IR) was used to investigate the stabilizing action of 3-(2,4-dibromophenylazo)-9-(2,3-epoxypropane)carbazole on the degradation of poly(vinyl chloride) (PVC). It was found that this secondary stabilizer increases the initial temperature of hydrogen chloride evolution (the main process responsible for PVC decomposition), thereby allowing its application for novel PVC systems with enhanced thermal stability. The application of TG/FT-IR technique for study of the thermal properties of polymeric materials offers additional characterization options in comparison with thermogravimetry, if used alone.

Keywords: blends, PVC, stabilization, TG/FT-IR

Introduction

For the characterization of polymeric materials, thermogravimetry (TG) has proved to be a useful technique for probing the compositions and degradation routes of these highly-organized structures [1, 2]. Even more information can be gained if TG is coupled with Fourier transform infrared spectroscopy (FT-IR). TG/FT-IR is a combined technique for determining sample mass change with respect to temperature and for identifying the volatile decomposition products. Since it is possible to operate at modest, controlled temperatures and heating rates, the thermal behaviour of polymers can be investigated before they undergo complete thermal degradation at high temperature. Another advantage stems from the on-line coupling: the emission of volatiles can be directly assigned to the respective temperatures and TG steps.

TG/FT-IR has been used for the thermal analysis of numerous polymers [3], such processes as curing reactions of epoxy resins [4] and the industrially-oriented recycling of synthetic undercoatings [5]. We have recently reported [6–9] investigations of poly(vinyl chloride) (PVC), one of the most important commercial polymers, blended with novel thermal stabilizers based on 9-(2,3-epoxypropanecarbazole). It has ben found that some derivatives of this com-

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pound exhibit properties of a secondary stabilizer, which allows their utilization to improve the inferior thermal properties of PVC. In the present investigation, the thermal behaviour of blends of PVC with 3-(2,4-dibromophenylazo)-9-(2,3-epoxypropane)carbazole have been studied by TG/FT-IR. Special attention was paid to the analysis of hydrogen chloride evolution since this process is believed to be the predominant one during the thermal decomposition of PVC.

Experimental

Materials

The samples were prepared by dilution of PVC-S (Zakłady Chemiczne w Tarnowie-Mościcach SA, of molecular mass $(\overline{M}n)$=46 000) with 3-(2,4-dibromophenylazo)-9-(2,3-epoxypropane)carbazole in dimethylsulfoxide. Casting films were then conditioned in vacuum for 2 weeks.

3-(2,4-Dibromophenylazo)-9-(2,3-epoxypropane)carbazole was obtained according to the procedure given in Refs [8, 9]. A description of the samples is given in Table 1.

Table 1 Characteristics of the samples used in this work

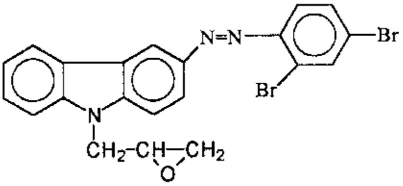
Sample No.	Concentration/wt % of additive in PVC	Additive
1	0 (pure PVC)	–
2	1	3-(2,4-dibromophenylazo)-9-(2,3-epoxypropane)carbazole
3	5	
4	10	

Techniques

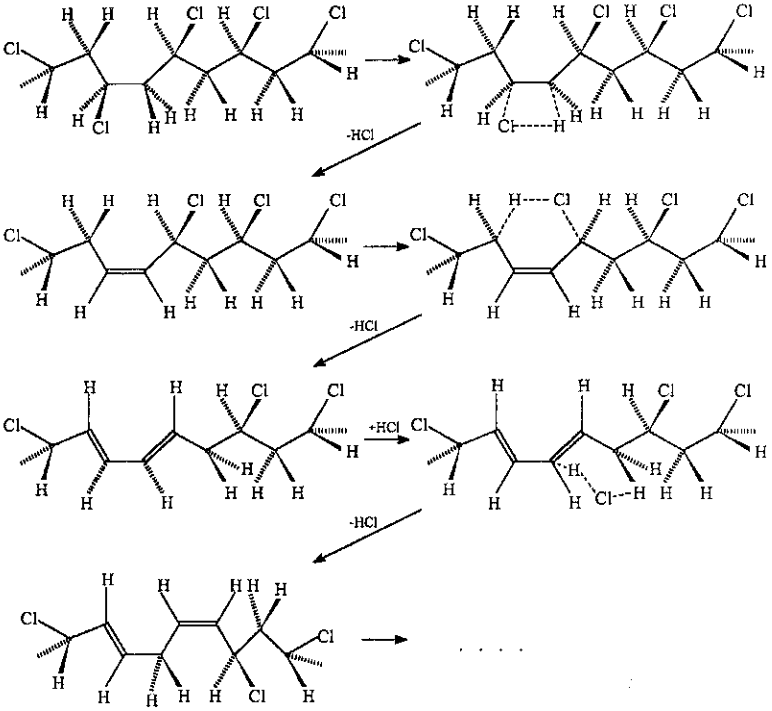
TG analysis was carried out with a Perkin-Elmer TG analyser. The conditions were: heating rate=10 or 50 K min^{-1}, sample mass ~5 mg, and nitrogen flow= 50 cm^3 min^{-1}. FT-IR spectra were recorded with a Perkin-Elmer 1725X FT-IR spectrometer. The TG analyser (P-E 7) and spectrometer were suitably coupled (connecting heated gas line temperature=220°C) to enable the passage of evolved products from the furnace to the gas cell over a short path, in order to minimize secondary reactions or condensation on the cell walls.

Results and discussion

The additive has the following structure:



As concerns the stabilizing action of this compound on the degradation of PVC, a possible reaction with evolved hydrogen chloride should be analysed as a prevailing process, since HCl emission is generally accepted as being responsible for subsequent polyene formation and the resulting rapid discolouration [10] (Scheme 1).



Hence, the primary action of an efficient PVC thermal stabilizer is to react with evolved HCl, thereby preventing delocalization and propagation of polyene structures.

Thermogravimetric analysis at a heating rate of 10 K min^{-1} reveals no substantial difference in the degradation routes up to 200°C (Table 2). The dehydrochlorination process can easily be followed by FT-IR analysis, as shown in Fig. 1.

On the basis of the summarized FT-IR spectra (stacked plot), it is possible to find the difference between the initial temperatures of HCl evolution from pure

Table 2 Results of the TG analysis of samples 1–4

Sample No.	$T_{5\%}$	$T_{10\%}$	$T_{20\%}$	$T_{30\%}$	$T_{40\%}$	Char residue/ % at 400°C
			°C			
1	162	293	309	318	343	37
2	251	280	298	307	331	36
3	212	252	270	277	284	37
4	213	259	263	285	306	35

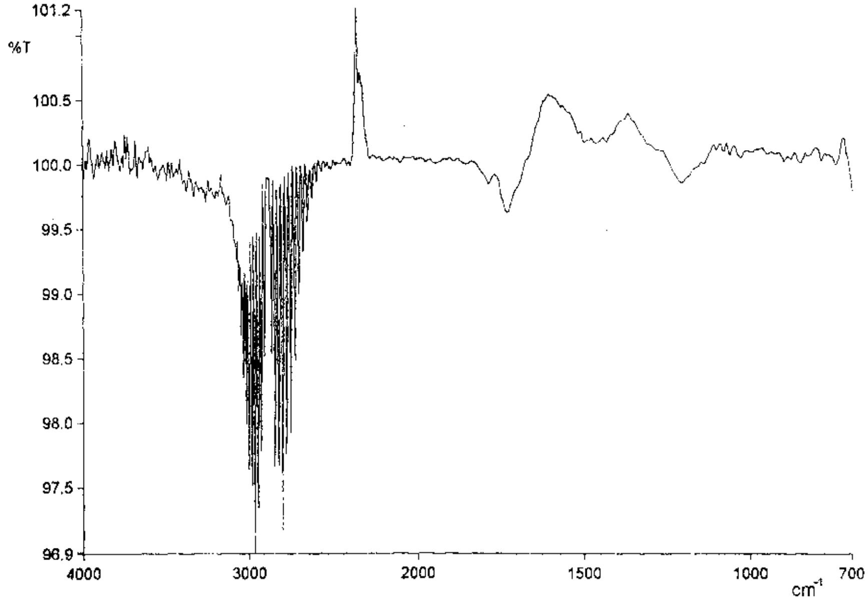


Fig. 1 FT-IR spectrum of sample 3 at 310°C

PVC and its blends; this was found in the case of 3-(2,4-dibromophenylazo)-9-(2,3-epoxypropane)carbazole blends to be in the temperature difference range of 10–15°C.

Conclusions

The coupling of a thermobalance with an FT-IR spectrometer offers additional characterization possibilities in comparison with the traditional TG technique, if used alone. This is particularly true for the evolution of strong IR absorbers, such as carbon dioxide, carbon monoxide and hydrogen chloride, provided that the experimental conditions are adequately maintained. By computeraided special procedures, such as spectral substraction and stripping, even complex degradation routes may be readily identified.

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