Thermochimica Acta, 80 (1984) 317–321
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS AND CHARACTERISATION OF SOME NEW STABILISERS FOR POLYVINYLCHLORIDE

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(Received 11 May 1984)

ABSTRACT

Some new stabilisers having a chelating polymeric structure were synthesised and characterised, i.e., 8-hydroxyquinoline-formaldehyde chelating resins of Cd, Zn, and Pb. The efficiency of these new stabilisers was studied with respect to PVC. The stabilised PVC samples showed outstanding thermal stability as studied by thermogravimetric techniques, i.e., the percentage of HCl evolved reduced remarkably with increasing polymer decomposition temperature.

INTRODUCTION

During an earlier research programme it was shown that polymeric stabilisers are very efficient at increasing the stability of bisphenol-A polycarbonates [1] and polyethylene [2].

In this paper the thermal stability of PVC stabilised with some new stabilisers having a chelating polymeric structure is illustrated.

This research is in line with the mechanism of PVC degradation due to the autocatalytic effect of HCl [3]. Therefore, most of the PVC stabilisers are HCl acceptors [4].

EXPERIMENTAL

Materials

PVC. Sicron type 548 FM *K* value = 70, was supplied by the Iraqi Petrochemical Complex. The polymer was reprecipitated from tetrahydrofuran by petroleum ether in order to remove any commercial additives.
8-Hydroxyquinoline. Supplied by BDH.

0040-6031/84/$03.00

The other chemicals and solvents were used as supplied by Fluka.

Synthesis and characterisation of 8-hydroxyquinoline–formaldehyde (I)

The five-necked reaction vessel was charged with 0.05 mol of 8-hydroxyquinoline, 0.013 mol of NaOH, and 0.22 mol of formaldehyde as formalin solution (37–40% w/v).

The reaction mixture was refluxed, the viscosity of the mixture increased progressively until a very viscous solution was formed, then the polymerisation was stopped.

The product was neutralised, purified, then dried under vacuum for 24 h. The polymer was characterised by elemental analysis and spectroscopy. Calc.: C, 77.12; H, 5.26; N, 8.18; Found: C, 78.22; H, 4.95; N, 7.97%.

Synthesis of the chelating polymers

The quinoline–formaldehyde resin (I) was transferred to the chelating polymer for Zn, Cd, and Pb by shaking the polymer powder (I) with the metal nitrate solutions at pH 10–11 for 48 h. The product was washed with distilled water to remove the unchelated metal ions. The chelating polymeric products were analysed by atomic absorption, elemental analysis, thermogravimetry (TG) and IR spectroscopy.

The percentages of the metals found by elemental analysis were: Pb, 25.8; Cd, 30.85; Zn, 17.27%. From the elemental analysis results the percentage of chelated metal was determined for each metal; i.e., 47, 78, and 62% for Pb, Cd and Zn, respectively. Comparative results were obtained from the atomic absorption analysis.

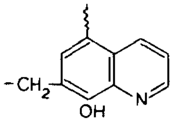
Thermogravimetric analysis

The thermal analysis tests were carried out on a MOM derivatograph thermoanalyser, which measures TG, DTG, DTA and temperature simultaneously.

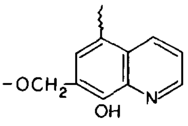
The measurements were carried out by increasing the temperature of the sample at a steady rate (10 °C min^{-1}) until the sample was substantially decomposed. All measurements were carried out against standard α-Al_2O_3 in air.

RESULTS AND DISCUSSION

The mechanism of formation of 8-hydroxyquinoline–formaldehyde resin is expected to be similar to that of phenol–formaldehyde in the presence of base catalysts, which has previously been well established [5]. Two types of interlinkage groups are expected to be present in this polymer, structures (**a**) and (**b**). The type of interlinkage group will not affect the chelating characteristics of the polymer (structure **c**).



(a)



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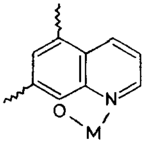

(c)

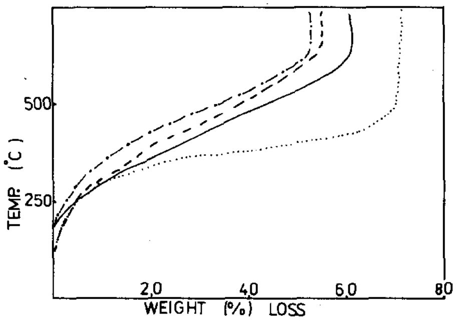

Fig. 1. Typical thermogravimetric curves for the stabilisers: (· · · · · ·) commercial stabiliser (neutral lead stearate); (———) Pb-chelated polymer; (— — —) Zn-chelated polymer; (· — · — ·) Cd-chelated polymer.

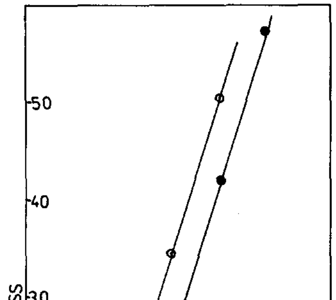

Fig. 2. The effect of chelating stabiliser on the (%) HCl evolved as measured thermogravimetrically: (○) PVC; (●) PVC+0.83% Cd-chelating stabiliser.

TABLE 1

Some thermal stability characteristics of PVC stabilised with different stabilisers

Thermal characteristics	PVC	PVC + Zn-chelated polymer (wt.%)			PVC + Pb-chelated polymer (wt.%)			PVC + Cd-chelated polymer (wt.%)			PVC + comm. stab. [a] (wt.%)		
		0.83	1.67	3.33	0.83	1.67	3.33	0.83	1.67	3.33	0.83	1.67	3.33
Decomposition temp. (°C) from:													
DTG	270	275	275	285	275	275	280	275	280	285	285	285	290
TG	250	250	250	255	250	250	255	250	250	255	250	250	255
Total HCl loss (%)	63.33	61	60.25	58	60	62	61.4	61.67	61.33	60.33	62	62	61
HCl loss (%) at (°C):													
260	18.5	17.5	14	12.5	14	12.5	11.5	9.5	9	5.8	15	13	12
270	26.3	25.5	24.3	24	24	23.5	22.5	17	16	15.3	24.67	22	21.67
280	34.8	34	33.3	32.5	34	33	32.5	25.5	25	21.3	31.67	30	29.67

[a] Neutral lead stearate stabiliser.

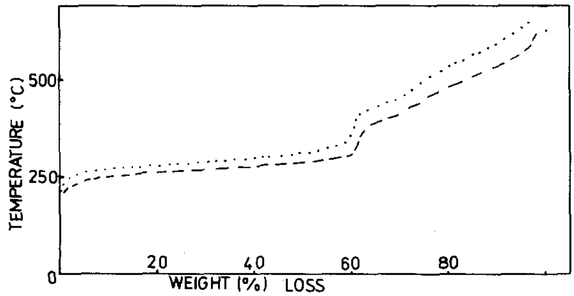

Fig. 3. Typical thermogravimetric curves for PVC (— — —) and PVC stabilised with 0.83% Cd-chelating stabiliser (· · · · · ·).

Concerning the percentage of the chelated metals on the polymer chains, it was found to be strongly dependent on the pH of the solution.

The chelated polymeric stabilisers were thermally more stable than the metal soaps now used commercially as stabilisers [6] for PVC; typical thermograms are shown in Fig. 1.

The TG results show that these stabilisers have a significant effect on reducing the percentage HCl loss, it decreases to about one third of its original value in the case of the Cd-chelating stabiliser; typical results are shown in Table 1 and Fig. 2.

On the other hand, these stabilisers increase the decomposition temperature of PVC as measured from TG and DTG; typical thermograms are shown in Fig. 3.

We think that the stabilisation efficiency of these stabilisers is due to the neutralisation of the HCl produced from the dehydrochlorination reactions of the polymer chains; either by their reaction via chelated metal ions and/or by reaction with the basic part of the quinoline structure, forming quinoline hydrochloride. The phenolic groups could also take part in the stabilisation process of the polymer as chain-terminating stabilisers, the behaviour of which is well-known with the substituted phenols now used commercially as stabilisers [7].

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