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HUMIC SUBSTANCES AS NEW STABILISERS FOR POLYVINYLCHLORIDE

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ABSTRACT

Three types of humic substances were extracted from an imperfectly drained marsh in Iraq as humic acid, fulvic acid and humin. These humic substances show great efficiency in increasing the thermal stability of polyvinylchloride, i.e., increasing the decomposition temperature, decreasing the rate of decomposition and reducing the rate and percentages of HCl loss.

INTRODUCTION

Chemical structure investigations of humic substances have shown that they contain about 32% phenolic acids, quinones and several structures capable of interacting with metal ions, metal oxides and metal hydroxides forming different metal organic complexes [1–4]. Interaction between humic substances and metal ions has been described by many authors as ion exchange, surface adsorption, chelating, coagulation and peptization [5–7].

It is well known that most PVC stabilisers contain one or more of these structures, i.e., metal chelates, quinones, substituted phenols, metal soaps, etc. [8,9]. Because of previous results, we have studied in the present work the efficiency of humic substances as stabilisers for PVC.

EXPERIMENTAL

Materials

Polyvinylchloride

Sicron type 548, *k*-value 70 was supplied by the Iraqi petrochemical complex. The polymer samples were reprecipitated from tetrahydrofuran by petroleum ether in order to remove any commercial additives.

Humic materials

The humic substance was extracted from the Al-Qurna Omm Al-shawage

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soil, an imperfectly drained marsh area at Basrah, Iraq. The extraction was carried out by dilute acid and alkaline solutions (10%) using usual extraction procedures generally accepted in soil science [1–7].

Three fractions were separated: (a) humic acid (HA), the soluble fraction from the humic substance in the dilute alkaline solution; (b) fulvic acid (FA), the soluble fraction from the humic substance in both diluted acid and base solution; (c) the unfractionated mixture which contains HA, FA and humin. The three fractions were purified, dried and analysed by atomic absorption, ESR and elemental analysis. The samples were then used as stabilisers for PVC.

The total organic content of the soil was ~ 28% (w/w) as determined thermogravimetrically.

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 the measurements were carried out in the presence of air against standard α-Al_2O_3.

The stabilised PVC samples were prepared by mixing the reprecipitated polymer powder with predetermined quantities of stabilisers.

RESULTS AND DISCUSSION

The thermogravimetric analysis results show that even low percentages of humic substances ($< 1\%$) have a remarkable effect on increasing the stability of PVC. Typical thermograms are shown in Figs. 1–3 for the mixed humic substance, humic acid and fulvic acid, respectively. Thus the decomposition temperature, as measured from DTG, increases by about 50°C, while the rate of decomposition at the decomposition temperature decreases from 1.63 to 0.73% min^{-1}. On the other hand, the thermogravimetric analysis results (TG) show that these stabilisers have a significant effect on reducing the rate and percentage of HCl loss as shown in Table 1.

The mixed humic substance shows greater efficiency as a stabiliser than both fulvic and humic acids.

The thermal stability of the humic substances was also studied, the results obtained are shown in Fig. 4 and Table 2. Fulvic acid shows greater stability than humic acid.

It is expected that the mechanism of stabilisation with these stabilisers could be a chain breaking mechanism due to the presence of quinonic and substituted phenolic groups. The stabilisers might have an effect on retarding

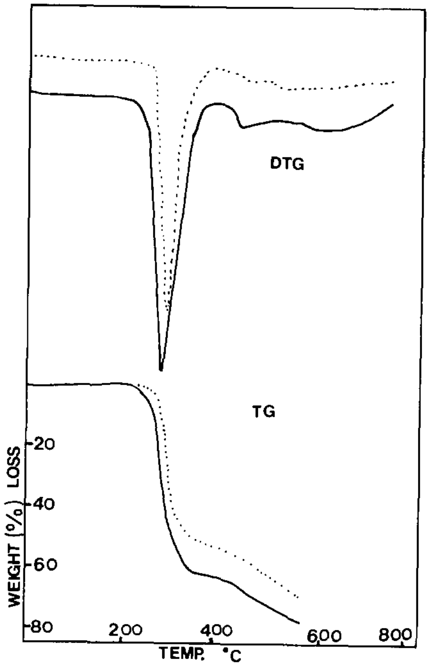

Fig. 1. Typical TG curves for (———) PVC and (· · · · · ·) PVC stabilised with 1% humic acid.

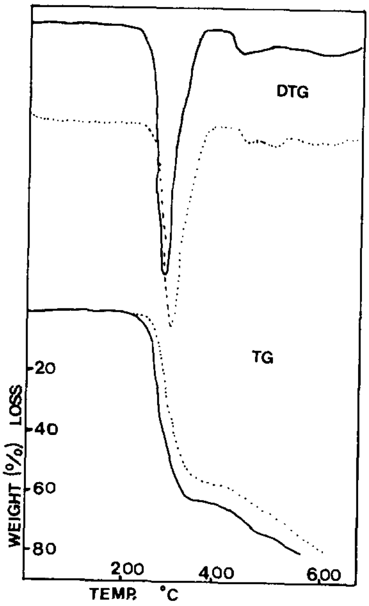

Fig. 2. Typical TG curves for (———) PVC and (· · · · · ·) PVC stabilised with 1% fulvic acid.

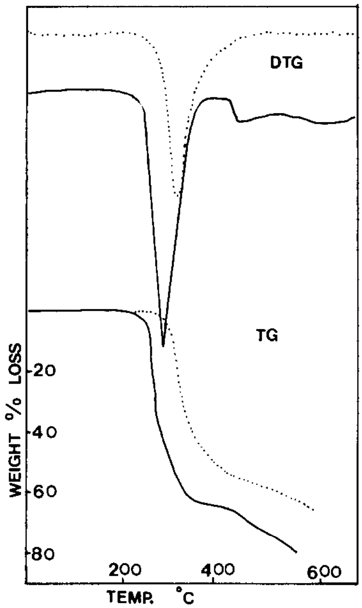

Fig. 3. Typical TG curves for (———) PVC and (······) PVC stabilised with 1% humic substance (mixture).

the autocatalytic effect of HCl evolved from the decomposition of PVC, since chelated metal structures already present in the humic substances are capable of reacting with the evolved HCl. This effect has been proved since we found that the stability of PVC increases with increasing concentration of

TABLE 1

The effect of stabilisers on the thermal stability characteristics of PVC

Temp. (°C)	HCl loss (%)			
	PVC	PVC + 1% stabiliser		
		HA	FA	Mixture
250	3	1	1	0
260	5	2	2	0
270	10	2	3	0.5
280	33	5	5	1.0
290	39	13	14	1.0
300	47	35	33	5.0
Total HCl loss	63	57	57	53
Decomp. temp. from DTG (°C)	265	280	300	310
Rate of decomposition at decomp. temp. (% min^{-1})	1.63	1.09	0.73	0.73

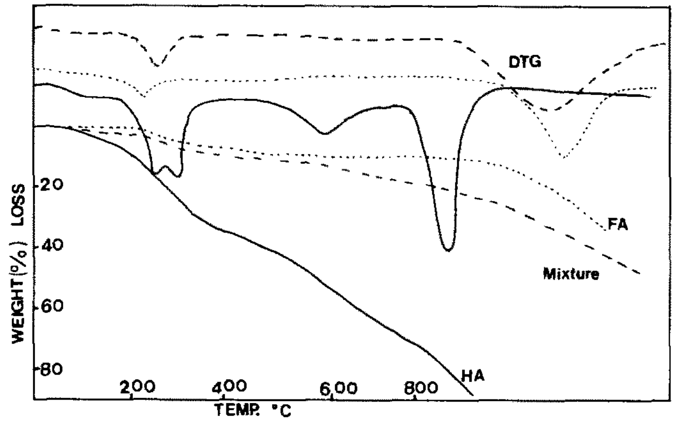

Fig. 4. Typical thermogravimetric curves for the humic substances. (———) Humic acid, (— — —) humic substance (mixture) and (······) fulvic acid.

TABLE 2

Some thermal stability characteristics of the humic substances

	Humic acid	Fulvic acid	Mixture
Decomp. temp. from DTG (°C)	230	220	270
Rate of decomposition at decomp. temp. (% min^{-1})	0.108	0.018	0.018

metal chelated structures in the humic substance. The effect and mechanism of metal complexes on the stability of polymers has been studied by many investigators [10,11].

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