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Thermal behaviour of fulvic and humic acids in comparison with a maleic anhydride oligomer

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Abstract

The thermal behaviour of samples of maleic anhydride oligomer (MAO), fulvic acid (FA) and humic acid (HA) of well-known origins has been studied. FA crystallizes very easily: m.p. = 441 K, melting $\Delta H = 230.5$ J g^{-1}. The thermogravimetric analysis revealed similar behaviour for FA and MAO, which decompose with comparable rates. In contrast, the decomposition of HA proceeds more slowly and with formation of a 10–20% residue.

INTRODUCTION

In a previous work, analogies between fulvic and poly(maleic) acids have been demonstrated. In particular, some similarities in the IR spectra and gas chromatograms of maleic anhydride oligomer (MAO) and fulvic acid (FA) have been emphasized [1]. FA and MAO show similar activities in metal binding. In particular, MAO grafted onto polystyrene provides a very effective binding agent for lead and other heavy metals [2–4].

The analogies found have not been related to the true structure of FA. To date the structure of FA has not been completely clarified. Most of the evidence indicates that FA is a polymeric material of low molecular weight

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ranging from a few hundred to several thousand. The carbon skeleton of FA consists of a broken network of poorly condensed aromatic rings with an appreciable number of disordered aliphatic chains and alicyclic structures. FA contains several oxygen-containing functional groups such as carboxyl, carbonyl, phenolic and methoxy groups [5].

In a previous work [6] the structure of an oligomer of maleic anhydride was studied, mainly by means of mass spectroscopy and ^{13}C NMR. On the basis of the quoted works and because olefinic carboxylic sequences have been suggested as one of the building blocks of humic materials [1,7], the oligomer of well-known structure can be used as a model to investigate the chemical and physical properties of FA.

The aim of this work is to compare the thermal behaviour of MAO with those of FA and humic acid (HA) of well-known origins.

EXPERIMENTAL

Materials

The FA and HA were extracted from a soil from Tradate (VA), Italy. MAO was obtained by polymerizing maleic anhydride in acetone solution at 25 °C in the presence of pyridine [8]. The molecular mass of FA was 500–1000 and that of MAO was 574 (mass spectroscopy). Table 1 lists the elemental analyses of these substances.

Procedure

DSC curves were obtained on a Perkin–Elmer DSC-2 instrument equipped with a Perkin–Elmer Thermal Analysis Data Station 3600. Samples of 0.3–3.5 mg were weighed in aluminium pans. The instrument was preset at 323 K and the sample was heated at 20 K min^{-1} (dynamic test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output. Thermogravimetric curves were obtained on a Perkin–Elmer TGS-2 instrument under air or nitrogen at 20 K min^{-1}.

TABLE 1

Elemental analysis of FA, HA and MAO

Sample	C (%)	H (%)	N (%)	S (%)
FA	42.82	4.46	4.20	0.55
HA	42.53	5.11	4.68	0.50
MAO	53.02	3.61	2.60	–

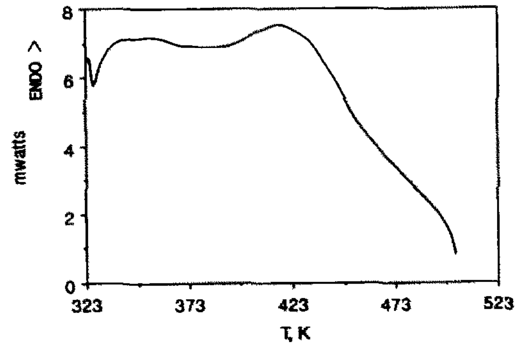

Fig. 1. Dynamic DSC curve of MAO; scanning rate, 20 K min^{-1}.

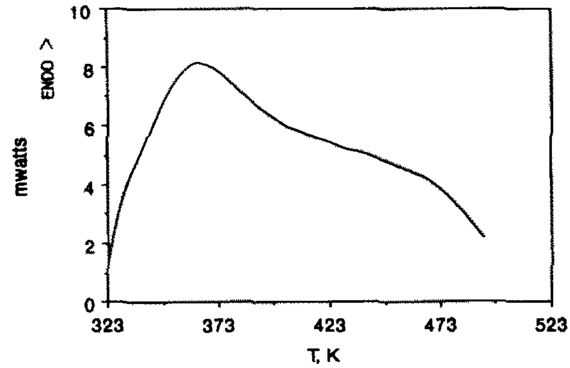

Fig. 2. Dynamic DSC curve of HA; scanning rate, 20 K min^{-1}.

RESULTS

The DSC curve of MAO (Fig. 1) shows a very large but well-defined endothermic peak from 386 to 465 K with a maximum at 427 K. The ΔH

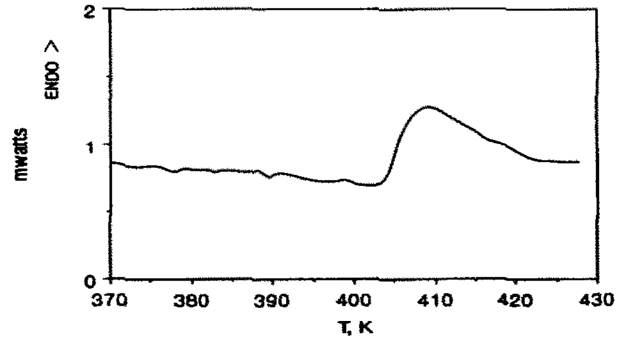

Fig. 3. The first dynamic DSC curve of FA; scanning rate, 20 K min^{-1}.

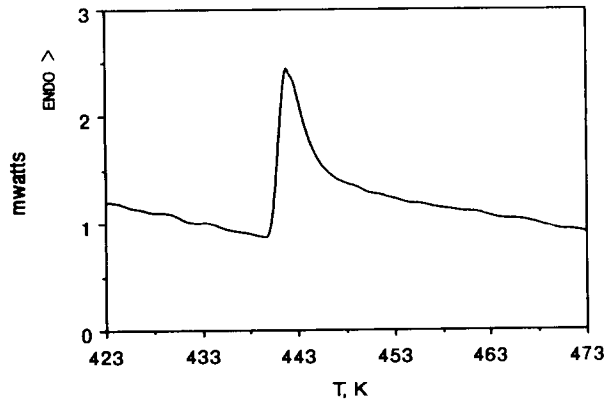

Fig. 4. The second dynamic DSC curve of the FA sample from the first dynamic test, after cooling; scanning rate, 20 K min^{-1}.

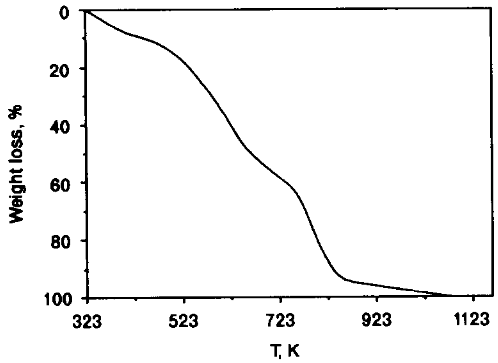

Fig. 5. Thermogravimetric curve under nitrogen of FA; scanning rate, 20 K min^{-1}.

value is 211.4 J g^{-1}. This peak probably corresponds to a phase transition of the oligomer. The curve indicates that a decomposition phenomenon starts from about 493 K. Figure 2 shows the DSC curve obtained with HA. In this case a very large endothermic peak is also observed; it ranges from 332 to

TABLE 2

Thermal stability of MAO, FA and HA under air and nitrogen

Sample	*T* (K) corresponding to 10% weight loss		*T* (K) corresponding to 50% weight loss		Residue (%) at 1223 K	
	Air	Nitrogen	Air	Nitrogen	Air	Nitrogen
MAO	423	438	563	588	0	0
FA	423	443	563	663	0	0
HA	488	513	743	803	15	11

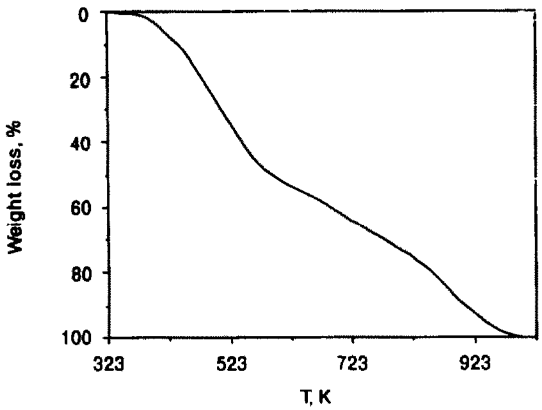

Fig. 6. Thermogravimetric curve under nitrogen of MAO; scanning rate, 20 K min^{-1}.

413 K, with a maximum at 363 K and a ΔH value of 98.2 J g^{-1}. FA (Fig. 3) shows a DSC curve characterized by an endothermic peak in the range from 400 to 420 K (maximum at 407 K) having a ΔH value of 137.5 J g^{-1}. After cooling, the same sample, subjected to a second dynamic test, yields a very sharp endothermic peak (from 439 to 452 K, maximum at 441 K) (Fig. 4) which is quite like the melting curve of a crystalline substance. The ΔH value of this peak is 230.5 J g^{-1}. In the case of MAO, the DSC curve obtained from the sample previously heated to 473 K shows a peak which is still very large.

The thermal stability of these products has been studied by means of thermogravimetric measurements under both air and nitrogen. Table 2 shows some relevant data for the substances studied in this paper. Figures 5 and 6 show the thermogravimetric curves under nitrogen of FA and MAO respectively.

Neither FA nor MAO left a residue. Under nitrogen, MAO leaves no residue starting from 1000 K; while under air, the decomposition is already complete at 823 K. Under nitrogen, FA decomposes completely, starting from 1103 K; while under air, decomposition is already complete at 753 K. At 1223 K HA gives a 15% residue under air and an 11% residue under nitrogen.

DISCUSSION

The data reported in Table 2 indicate that the decomposition of the three acids occurs more rapidly under air, according to the temperature at which 50% of the starting material has decomposed.

The results indicate a similarity in the thermal behaviour of MAO and FA, as seen by the temperatures at which the weight losses are 10 and 50%

(Table 2). Subsequently, the behaviour becomes different, as indicated by the temperature at which the decomposition is complete.

On the same basis it can be concluded that the FA structure is less stable to thermal stress than the HA structure. This conclusion agrees with other data found in the literature [8].

The degradation probably starts with the decarboxylation of the carboxyl sequences which are certainly present in MAO [9] and that have been assumed to be also present in FA on the basis of mass spectrometry measurements [5].

Recently, ^{13}C NMR investigations have indicated the presence of carbohydrates, together with carboxyl sequences, in FA [10–12]. The presence of interactive carboxyl and hydroxyl groups can explain the ready crystallizability of FA demonstrated by the appearance of a very sharp melting peak in the DSC curve. It is interesting to observe that the maxima of the transition peaks of MAO and FA are adjacent (MAO, 427 K; FA, 441 K), whilst HA shows a maximum at 363 K.

CONCLUSION

FA and MAO show similar thermal behaviour. The DSC curves indicate that FA has a melting point, while for MAO the transition is much less sharp and may correspond to a glass transition. In the case of FA, the presence of molecular sequences capable of polar interactions which promote the crystallizability of the system can be assumed.

The thermogravimetric measurements confirm similarity between FA and MAO; in fact the data indicate that, under nitrogen, a 50% weight loss takes place at the same temperature for both FA and MAO.

It is clear that neither the DSC nor the TG results for HA are comparable with the corresponding data obtained for FA and MAO.

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