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DIFFERENTIAL SCANNING CALORIMETRIC STUDY OF SOME IRAQI PAPERS

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ABSTRACT

Differential scanning calorimetry was used to study the thermal degradation of various types of Iraqi papers under oxygen and nitrogen atmospheres between room temperature and 500 °C. A massive exothermic peak due to oxidative degradation was recorded under oxygen atmosphere, while two endothermic peaks were recorded under nitrogen atmosphere, one at 130–150 °C due to loss of sorbed moisture, and a major peak between 300 and 400 °C indicating massive decomposition.

Thermal and physio-chemical data of the papers are presented and discussed. Significant correlation was indicated between the enthalpy, ΔH, involved in the major endothermic decomposition and the percentage ash content of the papers studied.

INTRODUCTION

Thermoanalytical techniques such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), including differential thermogravimetry (DTG) have been used extensively in recent years for the characterization and study of the thermal stability of polymers, petroleum products, and various organic and inorganic compounds [1].

Considerable work has also been carried out with DTA on the characterization of wood and the components of wood, various types of fibres, and sundry organic materials [2–6]. Work involving papers and modified cellulose materials using the DTA technique has also been reported in the literature [7]. Two main endothermic peaks were observed, the first, occurring between 75 and 150 °C, has been ascribed to loss of moisture and other adsorbed substances, and the second main decomposition endotherm, which occurs between 300 and 380 °C under an inert atmosphere, is associated with the formation of tar consisting mainly of levoglucosan.

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DSC has been defined as a technique for recording the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [8].

In this study DSC traces were obtained for various locally manufactured Iraqi papers. Data on the thermal behaviour and degradation processes they underwent were collected and correlated with some of their physio-chemical properties.

EXPERIMENTAL

Apparatus

The DSC measurements were carried out in a Heraeus TA 500 thermal analyser. Samples were heated at a rate of 10 °C min^{-1} in an aluminium crucible under nitrogen or oxygen atmosphere flowing at 10 l h^{-1}. Dried aluminium oxide powder was placed in a similar reference cell.

Materials

Various types of Iraqi papers were obtained from different sources. Data on the properties of these products are described in Table 1. Standard benzoic acid and pure tin were used in calibrating the instrument.

Procedure

Paper samples weighing 5–10 mg were cut into small discs (6-mm diameter) in order to be placed into the aluminium crucible.

TABLE 1

Data on papers

Type of paper	Basis wt. ($g\ m^{-2}$)	Thickness (mm)	Ash %	pH, hot
Eucalyptus commaldunensis	60	0.097	7.48	9.2
Date palm leaf (25% leaflets + 75% midrib)	60	0.170	9.50	9.6
Date palm leaf, bleached	65	0.204	2.19	10.1
Recycled waste paper	50	0.229	1.85	8.2
Mixed rags	110	0.442	3.22	9.6
Paper of 25% waste + 75% rags	60	0.228	3.91	9.5
Bleached tamarix	61	0.118	3.25	7.1

RESULTS AND DISCUSSION

Typical DSC traces under oxygen and nitrogen atmospheres for seven commercial papers manufactured locally from different sources are shown in Fig. 1.

It is apparent that under oxygen atmosphere a massive exothermic peak due to oxidative degradation starts at about 140 °C and increases in intensity with an increase in temperature. However, when the experiment was performed under nitrogen atmosphere an endothermic peak occurred near 130–150 °C which is usually associated with the loss of absorbed moisture. A major second endothermic peak exhibiting a massive decomposition process is recorded between 300 and 400 °C. The initial temperature of decomposition, T_i, maximum temperature, T_m, final temperature of decomposition, T_f, and the enthalpy, ΔH, of this transition are presented in Table 2.

There was no logical pattern to the thermal data presented with respect to the composition of the papers. Tamarix showed the lowest T_m value of 340 °C, while the sample composed of 25% waste paper and 75% rags exhibited the highest T_m value of 375 °C. All other types of paper exhibited a T_m value ranging between 360 and 370 °C. It is clear from the same Table, that the recycled waste paper exhibited the highest value for the enthalpy involved in the major endothermic decomposition ($\Delta H = -31.5$ J g^{-1}) while the date palm leaf paper made of 25% leaflets and 75% midrib possessed the lowest ΔH value of -16.2 J g^{-1}.

It is obvious that the composition parameter of the various types of papers does not play a major role in determining the maximum temperature of the endothermic transition (T_m) nor in the ΔH values of the transformations.

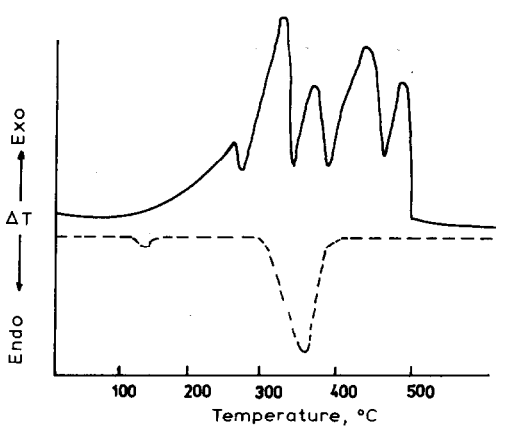

Fig. 1. Typical DSC traces of papers, under oxygen (————), and nitrogen (— — —) atmospheres.

TABLE 2

Thermal data on papers [a]

Type of paper	T_i (°C)	T_m (°C)	T_f (°C)	ΔH [b] (J g^{-1})
Eucalyptus commaldunensis	330	362	380	19
Date palm leaf (25% leaflets + 75% midrib)	330	362	387	16.2
Date palm leaf, bleached	320	362	378	29.4
Recycled waste paper	320	367	395	31.5
Mixed rags	335	370	395	26.4
Paper of 25% waste + 75% rags	325	375	395	25.2
Bleached tamarix	308	340	375	25

[a] Average of three determinations.

[b] Determined by evaluating the peak area of the major endothermic curve followed by conversion to enthalpy ΔH.

From Tables 1 and 2, it is also evident that the bleached date palm leaf paper had the highest value for the pH of hot water extraction, while the Tamarix bleached paper had the lowest pH value of 7.1. However, no significant correlation was found upon plotting the pH values of the hot water extraction against T_m or ΔH values as shown in Figs. 2 and 3, respectively.

The plots of the percentage ash by weight of the various types of papers against the T_m and ΔH values again indicated a non-linear relationship for the former, as shown in Figs. 4 and 5. However, a significant correlation is observed between the percentage ash content and the ΔH of the major endothermic transition under nitrogen atmosphere. Samples with the lowest ash content had the highest ΔH value of transition, and vice versa (i.e., recycled waste paper had a ΔH value of -31.5 J g^{-1} and a percentage ash content of 1.85, while the date palm leaf paper made of 25% leaflets and 75%

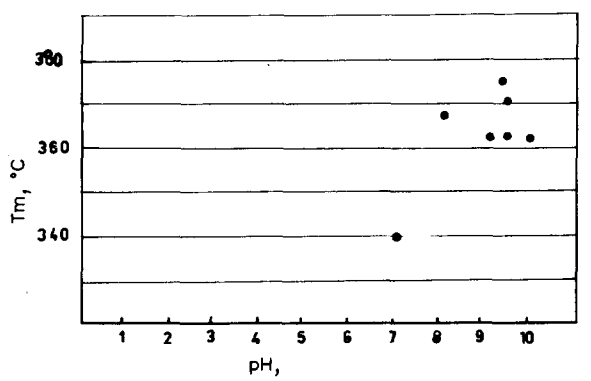

Fig. 2. Variation of DSC maximum temperature of the major decomposition endotherm with hot extraction pH.

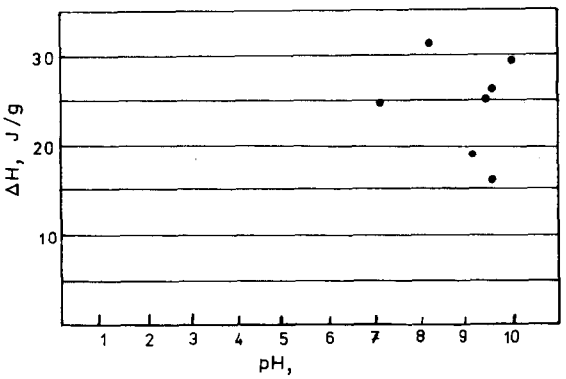

Fig. 3. Variation of ΔH of the major decomposition endotherm with hot extraction pH.

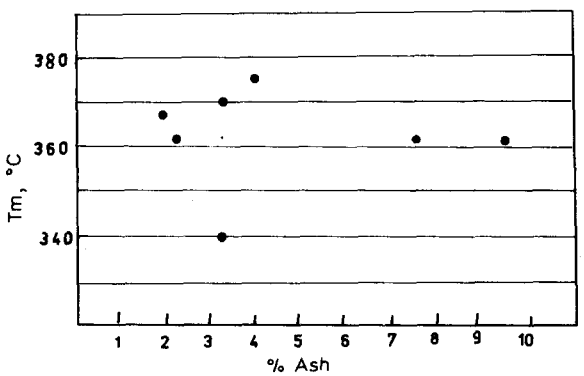

Fig. 4. Variation of DSC maximum temperature of the major decomposition endotherm with % ash content.

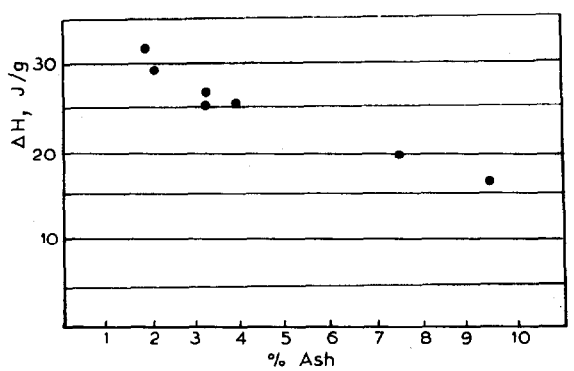

Fig. 5. Relationship between ΔH of the major decomposition endotherm and % ash content.

midrib possessed a ΔH value of $-16.2\ J\ g^{-1}$ and a percentage ash content of 9.5).

It can be concluded that differential scanning calorimetry proved to be a potential method in evaluating the thermal degradation process of the

various types of paper. Although the parameters presented showed no correlation to the thermal stability of the papers studied, a close relationship was exhibited between the enthalpy involved in the major thermal transition and the percentage ash content which is a result of the chemical changes occurring during thermal degradation.

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