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THERMAL ANALYSIS OF ETHYL CELLULOSE: INFLUENCE OF ATMOSPHERE AND ADDITION OF DIETHYL PHTHALATE AS PLASTICIZER

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ABSTRACT

The influence of atmosphere (inert or oxidizing) and addition of diethyl phthalate as plasticizer on the thermal degradation of ethyl cellulose has been investigated by thermogravimetric, differential thermogravimetric and differential thermal analysis techniques. In the present of an inert atmosphere, the decomposition of ethyl cellulose and plasticized ethyl cellulose occurs in one and two endothermic steps, respectively. In the presence of air, the decomposition of ethyl cellulose with or without plasticization is a very complex process occurring in a number of exothermic stages. In the thermal decomposition, the plasticized ethyl cellulose yields more carbonaceous residue.

INTRODUCTION

Ethyl cellulose has been used extensively as an inhibitor for radial burning double-base rocket propellants [1–3]. This thermoplastic material has a number of other applications. Diethyl phthalate is a plasticizer commonly used for ethyl cellulose to achieve the thermal and mechanical properties required for its application as a thermoplastic material, especially as a rocket-propellant inhibitor. It is therefore of great interest to know the influence of the addition of diethyl phthalate as a plasticizer for ethyl cellulose on its thermal degradation under inert and oxidizing atmospheres. Surprisingly, no study on this matter has been reported in the literature so far. Even the thermooxidative degradation of cellulose is a poorly studied phenomenon [4]. The present investigation was undertaken for the above purpose.

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EXPERIMENTAL

The preparation and characterization of ethyl cellulose (having a specification conforming to CS 2724) and its plasticization have been described previously [3].

The ethyl cellulose (with different concentrations of diethyl phthalate) samples were dried in an air oven at 353 K for 4 h before using them for the thermal analysis.

The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) data on the ethyl cellulose samples were obtained under inert (N_2) and oxidizing (air) atmospheres using an automatic thermal analyser (Netzsch model STA 409). The experimental conditions were: sample size 25 mg; reference compound α-alumina; sample holder platinum crucible; temperature range 303–873 K; heating rate 10 K min^{-1}; atmosphere static air, flowing air (100 cm^3 min^{-1}) and nitrogen (100 cm^3 min^{-1}).

The cylinder gases (nitrogen and air) were of high purity (> 99.99%) and passed over 4A molecular sieves to remove traces of moisture.

RESULTS AND DISCUSSION

Thermal analysis of plasticized ethyl cellulose in inert atmosphere

The thermal curves (TG, DTG and DTA) for ethyl cellulose with and without diethyl phthalate as a plasticizer in the temperature range 303–873 K in an inert atmosphere (maintained by passing oxygen-free nitrogen over the samples at a flow rate of 100 cm^3 min^{-1}) are presented in Fig. 1. The data obtained from the thermal analysis are given in Table 1.

A comparison of the TG, DTG and DTA curves in Fig. 1(a) and 1(b) clearly shows an influence of the addition of diethyl phthalate plasticizer on the thermal degradation of ethyl cellulose. In the absence of plasticizer, the decomposition of ethyl cellulose occurs in a single stage and also the residue remained after the degradation is much lower. Whereas, in presence of the plasticizer, the decomposition occurs in two distinct stages resulting in a larger amount of residue (Table 2). It may be noted that the formation of higher residue (i.e. carbonaceous matter) is beneficial for a better inhibiting action of the ethyl cellulose.

Thermal analysis of plasticized ethyl cellulose in presence of oxidizing atmosphere

The thermal curves for the decomposition of ethyl cellulose containing the plasticizer at different concentrations (0–50 wt.%) in the presence of air

TABLE 1

Data on the thermal analysis of ethyl cellulose containing plasticizer (diethyl phthalate) in different concentrations

Concentration of plasticizer (wt.%)	DTG peak temperature (K)				DTA peak temperature (K)				Weight loss (%) (temperature range, K)		
	1	2	3	4	1	2	3	4	Stage I	Stage II	Stage III
Decomposition in N_2 (flow rate 100 cm^3 min^{-1})											
0	629	–	–	–	619 (broad)	–	–	–	90.30 (455–765)	–	–
23	492	603	–	–	461	597	–	–	23.86 (406–553)	84.60 (553–884)	
Decomposition in presence of air (flow rate 100 cm^3 min^{-1})											
0	454	586	702	–	442	596	697	–	3.80 (436–466)	85.96 (466–639)	96.76 (639–733)
6	436	580	723	–	430	511	585	718	6.50 (391–454)	82.50 (454–612)	95.50 (612–796)
10	435	492 (hump)	581	723	417	489	584	712	8.17 (384–454)	83.44 (454–634)	95.90 (634–728)
23	442	502	580	723	424	496	586	718	5.60 (385–448)	83.62 (448–650)	94.80 (650–733)
42	423 (hump)	501	581	722	410	495	591	717	40.95 (377–513)	86.64 (513–634)	95.00 (634–743)
50	501	574	723	–	472	577	712	–	62.10 (357–530)	88.65 (530–639)	95.00 (639–743)

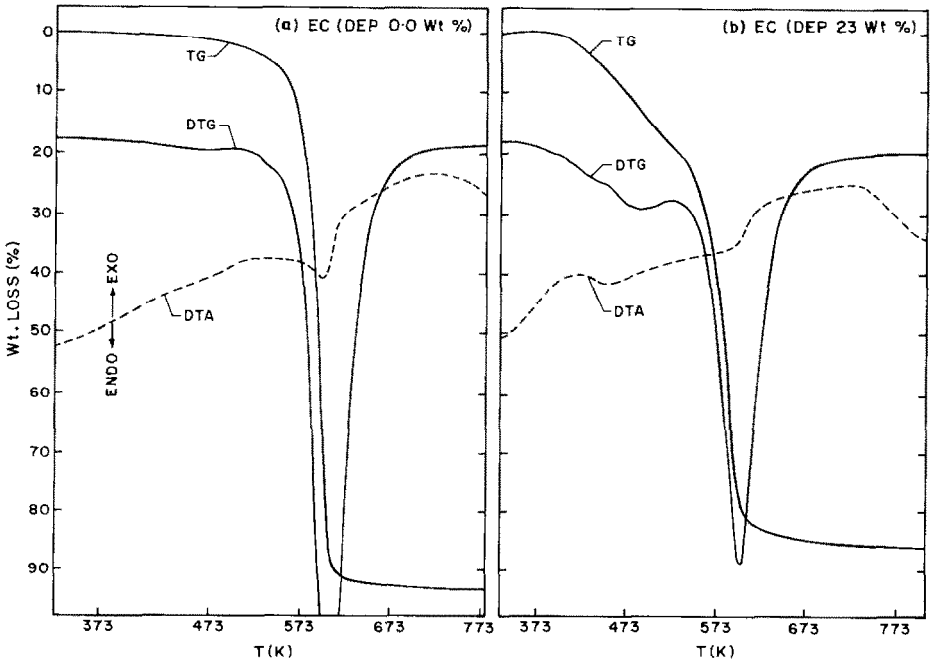

Fig. 1. The TG, DTG and DTA curves for the thermal decomposition of ethyl cellulose (EC) with and without plasticizer (DEP) in the presence of nitrogen (flow rate 100 cm^3 min^{-1}).

flowing over the sample (air flow rate 100 cm^3 min^{-1}) are presented in Fig. 2. The data obtained from the thermal analysis are given in Tables 1 and 2.

The results (Fig. 2 and Table 1) show that the decomposition of ethyl cellulose with or without plasticization is an exothermic process (as indicated by the maxima in the DTA curve) and occurs in a number of stages. The results in Table 2 reveal that the carbonaceous residue obtained after

TABLE 2

Carbonaceous residue obtained after the thermal analysis of ethyl cellulose with or without plasticizer

Concentration of plasticizer in ethyl cellulose (wt.%)	Carbonaceous residue (wt.%)	
	Decomposition in air	Decomposition in N_2
0.0	3.4	9.7
6.0	4.5	–
10.0	5.0	–
23.0	5.2	15.4
42.0	5.0	–
50.0	5.0	–

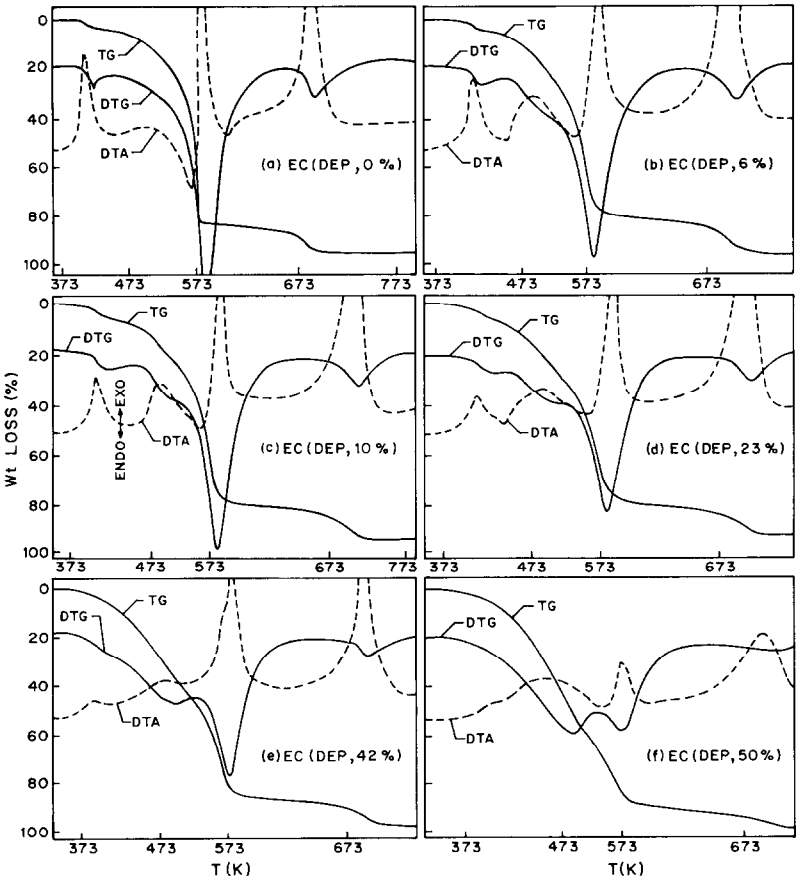

Fig. 2. The TG, DTG and DTA curves for the thermal decomposition of ethyl cellulose (EC) containing plasticizer (DEP) at different concentrations in the presence of air (flow rate 100 $cm^3\ min^{-1}$).

the oxidative degradation is increased significantly because of the addition of the plasticizer.

The weight loss at the lower temperature (< 460 K) is expected to be mostly due to the evaporation of volatile matter contained in the interstices of ethyl cellulose. The corresponding exothermic DTA peak indicates that the evaporated matter is oxidized. It may be noted that the weight loss due to the desorption and subsequent oxidation is decreased with the increase in the concentration of the plasticizer. The weight loss at the higher temperature (> 460 K) is due to an oxidative degradation of the ethyl cellulose and the plasticizer therein, as indicated by the exothermic DTA peaks. The overall oxidative decomposition of ethyl cellulose with or without the plasticizer is a very complex process and may involve a number of degradation and oxidative reactions [4].

CONCLUSIONS

The thermal analysis of ethyl cellulose with or without plasticization by diethyl phthalate under an inert or oxidizing atmosphere leads to the following conclusions. In presence of an inert atmosphere, a thermal decomposition of ethyl cellulose occurs in a single endothermic step; whereas, the decomposition of plasticized ethyl cellulose occurs in two endothermic steps and results in a larger amount of carbonaceous residue. In presence of air, the thermal decomposition of ethyl cellulose with and without plasticization by diethyl phthalate is a very complex process occurring in a number of exothermic steps. The plasticization results in more carbonaceous residue in the oxidative decomposition.

REFERENCES

1 R.E. Kirk and D.F. Othmer, Encyclopedia of Chemical Technology, Vol. 5, Wiley-Interscience, New York, 3rd edn., 1979, p. 143.
2 C.G. Lawson, ERDE, U.K. Technical Memorandum No. 14/M/65, 1965.
3 A. Chakrabarti and J.P. Agrawal, Ind. J. Technol., 24 (1986) 600.
4 R.T. Conley, Thermal Stability of Polymers, Vol. 1, M. Dekker, New York, 1970, p. 523.