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THERMAL DEGRADATION OF NATIVE AND MERCERISED COTTON LINTERS

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ABSTRACT

Differential thermal analysis of native and mercerised Egyptian cotton linters were investigated. The thermal gravimetric behaviour of both samples was studied and the activation energies from the kinetics of weight loss were calculated. Native samples were found to be more stable towards thermal degradation in the range 220–380°C than mercerised samples.

INTRODUCTION

The thermal treatment of cellulose has been extensively studied and much has been learned [1,2]. However, little research has been done on the effect of fibre structure on its thermal behaviour [3,4] and the results obtained are conflicting and difficult to correlate due to differences in experimental conditions, techniques and the history of the treated samples.

In view of the differences between the amount of ordered and non-ordered materials present in Egyptian native and mercerised cotton linters, we have studied the thermal behaviour of both samples and the kinetics of degradation in air. The present study forms part of a more general work investigating the effect of fibre structure on its thermal behaviour.

EXPERIMENTAL

Materials

Egyptian cotton linters were extracted for 6 h using a Soxhlet apparatus (methanol–benzene, 1 : 1) and dried in air. The sample was split into two portions.

(a) For mercerisation using 18% NaOH solution for 1 h at 20°C, washed with distilled water followed by immersion in a 10% solution of acetic acid, and, finally washed again in distilled water and subsequently dried in air.

(b) For direct thermal analysis.

Thermal treatments

Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravimetry (DTG), were run on samples (4 mg) in air on a Shimadzu thermal analyser D.T-30. Fibrous samples were cut into fine pieces and then packed in aluminium pans.

The dynamic gas (air) was passed through the samples at a rate of 40 cm^3 min^{-1}. The temperature of the furnace was raised at a programmed rate of 10° min^{-1}. Loss of weight was indicated on a chart recorder run at 5.4 in. h^{-1}. The chart was ruled in 0.01 units so that the loss in weight could be read off simply as 1/100 part of the original weight taken.

RESULTS AND DISCUSSION

Thermal analysis of native and mercerised cotton linters showed different behaviour. Figure 1 represents the DTA of the experimental samples; both showed a major endothermic decomposition beginning at 308 and 304°C, and peaking at 334 and 339°C, respectively. The thermal decomposition endotherm of the native sample moved to lower temperatures after treatment with NaOH solution of mercerising strength [see Fig. 2(a)]. This slight decrease in the decomposition temperature may be attributed to the increase

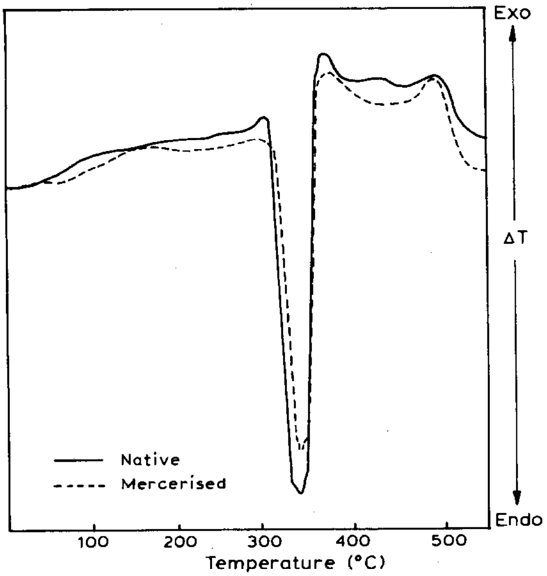

Fig. 1. Differential thermal analysis (DTA) of native and mercerised cotton linters.

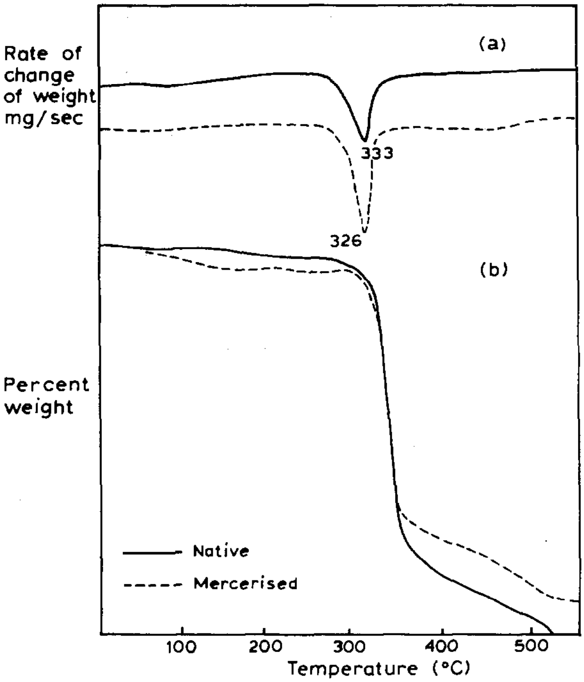

Fig. 2. Thermogravimetric (TG) curves of native and mercerised cotton linters.

in the reducing power; it may also be related to the increase in the amount of the non-ordered fraction since the accessibility of the sample to heat energy will be changed [4]. A similar decrease in the pyrolytic decomposition of non-ordered cellulose has been noted by other workers [5–7].

Experimental TG curves for native and mercerised cotton linters were obtained and are shown in Fig. 2(b). Three distinct regions were detected in each curve; (a) a slight weight decrease after 100°C due to the elimination of physically adsorbed water; (b) a major weight loss in the second region beginning at 220°C for native cotton linters and 230°C for the mercerised sample, due to the rupture of the covalent bonds and disappearance of the fibre structure; and (c) a final loss in weight above 380°C indicating a further reaction involving charring, i.e., pyrolysis.

The weight loss of the mercerised sample in the first stage of heating was higher than for the native sample due to the increased amount of water adsorbed in the non-ordered fraction. The dissimilarity between the behaviour of native and mercerised samples in the third region may be related to the incomplete charring of the mercerised sample in this region. If the amount of ash in the mercerised sample (6.25% calculated from the TG curve) is removed from the system, both samples behave similarly.

In the present work, an attempt was made to calculate the activation energy from the kinetics of weight loss data of native and mercerised cotton linters heated in the temperature region above 220°C, i.e., region (b), which gives the rate of weight loss under isothermal conditions. Plotting $\log_{10}$ $w_0 - w_\infty/w_t - w_\infty$ (where w_t is the weight at time t, w_0 is the initial weight, and w_∞ is the final residue weight) against time, t, for native and mercerised cotton linters gave a good straight line except near the origin, at which a slight curvature occurred due to the initiation of the reaction (see Fig. 3). This indicates that the loss in weight follows a first-order reaction.

Arrhenius [8] pointed out that since the van't Hoff equation for the temperature coefficient of the equilibrium constant (K_c) of the reaction is

$$\frac{\mathrm{d}\log K_c}{\mathrm{d}T} = \frac{-\Delta E}{RT^2}$$

whereas the mass-action law relates the equilibrium constant to a ratio of rate constants [i.e., $K_c = K$ (forward reaction)/K (backward reaction)], a reasonable equation for the variation of the rate constant with temperature is given by

$$\frac{\mathrm{d}\log_e K}{\mathrm{d}T} = \frac{-E_a}{RT^2}$$

by integration

$$\log_e K = \frac{-E_a}{RT} + \log_e A$$

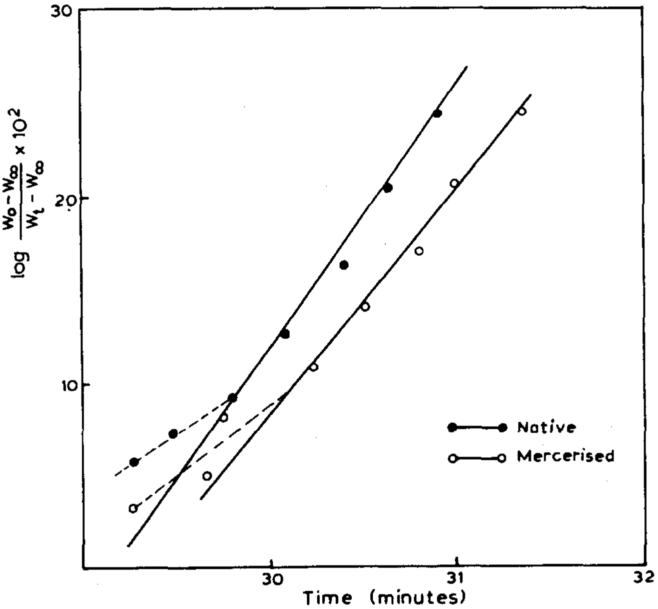

Fig. 3. Relations between low $w_0 - w_\infty/w_t - w_\infty \times 10^2$ against time for native and mercerised cotton linters.

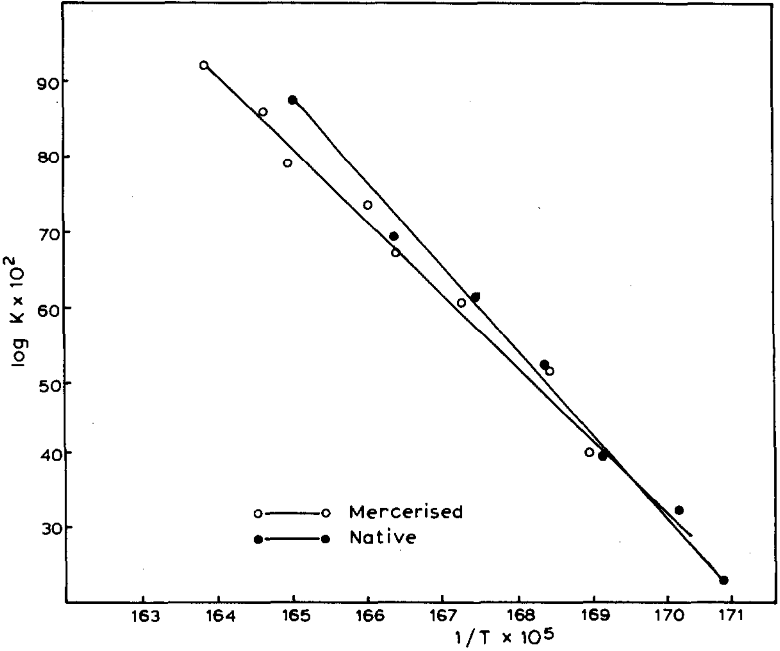

Fig. 4. Arrhenius plot of the first-order reaction of native and mercerised cotton linters heated in air.

Thus, a plot of $\log_{10} K$ against the reciprocal of the temperature should give a straight line of slope $-E_a/2.303R$ where E_a is the activation energy and R is the gas constant. Figure 4 shows the plot of $\log_{10} K$ against $1/T$ for both native and mercerised cotton linters and the activation energy values are 209.08 and 184.96 kJ mol^{-1} for native and mercerised samples, respectively, in the range of 250–380°C.

These values indicate that native samples are somewhat more stable towards thermal treatment than mercerised cotton within the experimental temperature range. It should be noted that the values obtained in the present work are much higher than those obtained from the kinetics of strength loss for samples heated at 220°C [9]. It should also be pointed out that more covalent bonds are expected to breakdown in weight-loss kinetics, a phenomenon which does not or only slightly occurs in strength-loss kinetics. Moreover, a loss in strength occurred below 220°C, i.e., less energy being needed, whereas weight loss occurred above 220°C, i.e., more energy is involved.

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