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Thermal behaviour of cyanoethylated cellulose

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Abstract

Thermal degradation of cyanoethylated cellulose samples, possessing different degrees of substitution, was investigated using a TGA technique. Pyrolytic degradation of the compounds, except of those of degree of substitution less than 2.0, exhibited three stages. Higher substituted samples passed through four stages. Activation energies, orders of reactions and starting temperatures were estimated for each stage. The introduction of cyanoethyl groups enhances the thermal stability of the cellulosic fibres. Such stability was shown to increase with increase of the degree of substitution. X-Ray diffraction patterns of some selected samples were recorded to show changes in the fibre crystalline structure.

INTRODUCTION

Different polymeric fibres respond quite differently to heat. In the literature numerous investigations have been carried out on the thermogravimetric behaviour of cellulose and some of its derivatives [1–5]. Most of the studies involving the cyanoethylation of cellulosic fabrics aimed at improving their properties for industrial utilization. However, no systematic quantitative investigation was carried out on the thermal behaviour of cyanoethylated cellulose.

The present work deals with the thermogravimetric analysis of differently substituted cyanoethyl celluloses, aiming to investigate the thermal stability and other thermodynamic criteria of some prepared cyanoethyl cellulose samples.

EXPERIMENTAL

Materials

Viscose grade wood pulp was kindly supplied by El-Nasr Co., Bahteem, Egypt. It was found to possess the following specifications: α-cellulose, 94.79%, hemicellulose 4.36%, ash 0.05%, degree of polymerization (DP), 790.

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Acrylonitrile (Merk) was purified according to the method described by Bamford and Jankins [6].

Preparation of cellulosic samples for cyanoethylation

The wood pulp, supplied in the form of sheets, was soaked in water, cut into pieces, shredded in "Emil-Blaschke" type shredder for 30 min, and finally allowed to dry in air.

Cyanoethylation

Native wood pulp was taken as a reference to be compared with the changes occurring in the degree of order and thermal stability upon substitution with cyanoethyl, denoted sample A.

In order to prepare cyanoethylated samples possessing different degrees of substitution, the following procedures were applied:

(i) Shredded wood pulp was soaked at room temperature in 1.5 M NaOH solution at a liquor ratio of 1:100. After 30 min, the sample was squeezed from excess alkali up to one and one half its original weight, transfered into a 100 cm^3 reagent bottle and excess acrylonitrile (1:17) was added. The reaction bottle was shaken at room temperature for 3 h, and the contents were then filtered. The crude product was washed with water until free from alkali, then with ethanol, and finally with ether, and allowed to dry in air. This procedure produces a sample with degree of substitution (DS) 0.63 and was denoted sample B.

(ii) Native sample was pretreated with alkali for a longer period, i.e. 45 min, and interacted with excess acrylonitrile (1:20) under reflux: a product of DS 1.4 was obtained and denoted sample C.

(iii) Samples D and E were obtained upon aging the wood pulp in 1.5 M NaOH solution for 3 days, and reacting with excess acrylonitrile under reflux. The products of such treatment were separated into two components depending on their solubility in acetone. The one which did not dissolve in acetone possesses DS 2.0 and is denoted sample D, while the one which dissolved in acetone and was recovered by evaporation had DS 3.0 and was denoted sample E.

The nitrogen content of the sample was analysed [8] and the degree of substitution calculated from equation [7]

$$\mathrm{DS} = \frac{11.57 \times N}{1 - (3.79 \times N)}$$

where N is the percentage of nitrogen.

In order to account for the variations which occured in the fibre structure of the samples during the course of preparation of the differently

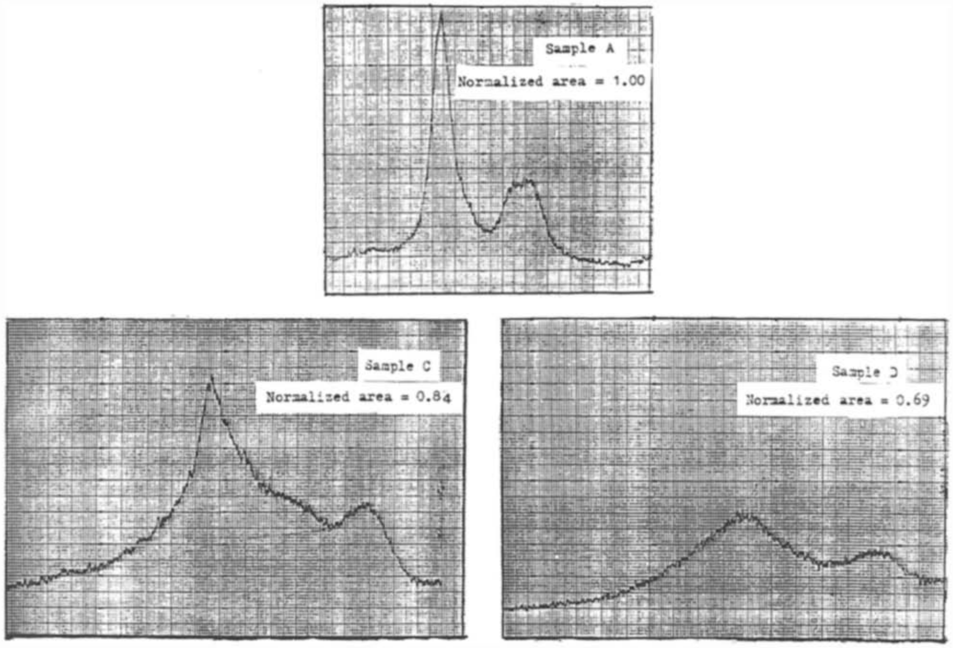

Fig. 1. Diffraction patterns of the samples A, C and D.

substituted cyanoethyl celluloses. X-ray diffraction was recorded for selected samples, namely A, C and D having DS 0, 1.4 and 2.0, respectively, using a Philips diffractometer operated at 40 kV and 25 mA. The diffraction patterns of the three samples are illustrated in Fig. 1.

Thermal analysis of the prepared samples

Thermogravimetric analysis (TGA) of the native sample (sample A) and of the cyanoethylated ones (samples B–E) having DS of 0.63, 1.4, 2.0 and 3.0 respectively, were carried out using a Shimadzu TGA 30 thermobalance. A linear rate of heating (10 K min^{-1}) was applied and the measurements were undertaken in an atmosphere of nitrogen, from ambient temperature up to 973 K.

RESULTS AND DISCUSSION

In order to prepare cyanoethylated cellulose with DS varying from 0 up to 3.0, various conditions in the treatment of the native cellulose were applied. Among these conditions are the concentration of alkali, time of alkali pretreatment, and time and temperature of reaction between acrylonitrile and alkali pretreated cellulose. Such variations would result in products of varying DS and differing also in the degree of polymerization (DP), degree of order, proportion of smaller molecules and the number of substituted cyanoethyl groups with their heterogeneous distribution throughout the cellulose chains; such differences will definitely be reflected in the thermal behaviour of the final product.

Thermogravimetric behaviour of samples A–E

Variation in the shape of the thermogram

The TGA curves of samples A–C, having DS values of 0, 0.63 and 1.4 respectively, exhibit three stages, denoted in Fig. 2 as stages a, b and c. However, the first degradation step (stage a) in samples A–C, appears to be split into two substages, denoted as a and a′ in samples D and E which have DS values of 2.0 and 3.0, respectively.

Furthermore, one notices from Fig. 2, that complete degradation occurs in sample A, while upon substitution with cyanoethyl groups, the degradation becomes incomplete as indicated by the increase in the mass remaining at the end of the degradation process. This residual mass progressively increased as the DS of samples increased.

It seems possible to postulate that the mass loss observed in the first

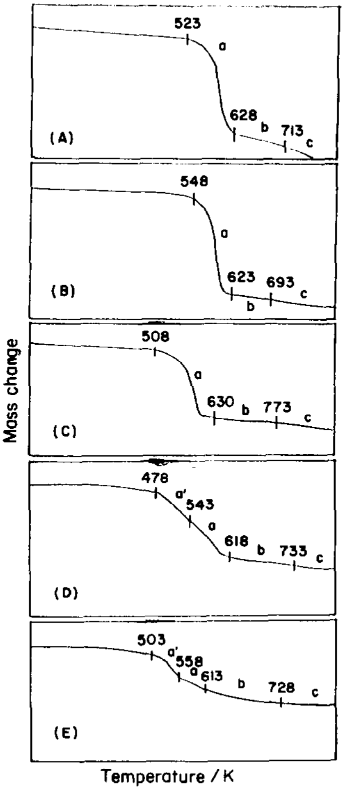

Fig. 2. TG curves of samples A–E.

TABLE 1

Values of activation energies, and the onset temperatures of the samples A–E

Sample	DS[a]	Stage a′ ΔE_a[b]/ kJ mol^{-1}	T[c]/ K	Stage a ΔE_a[b]/ kJ mol^{-1}	T[c]/ K	Stage b ΔE_a[b]/ kJ mol^{-1}	T[c]/ K	Stage c ΔE_a[b]/ kJ mol^{-1}	T[c]/ K
A	0.00			177	523	230	628	329	713
B	0.63			223	548	268	623	274	693
C	1.43			109	508	226	630	146	773
D	2.00	139	478	119	543	254	618	132	733
E	3.00	112	503	282	558	124	613	103	728

[a] Degree of substitution. [b] Activation energy. [c] Onset temperature.

degradation step of samples D and E is due to the decrease in the degree of order (Fig. 1) accompanied by the formation of small molecules during the course of cyanoethylation [9]; this is reflected by the decrease in the starting temperature. However, the slight increase in the starting temperature observed in sample E (see Table 1) may be related to a slight recrystallization occurring at higher temperatures. Furthermore, due to the heterogeneous distribution of substituents throughout the cellulosic chains, the products are more easily degradable during the first degradation stage, through their highly substituted glucose rings. This is manifested by stage a′ in samples D and E which facilitates degradation at lower threshold temperatures.

Variation in the thermal stability of the samples

In order to account for the effect of substitution on the thermal resistivity of the samples towards degradation at temperatures higher than 600 K, the percentage mass loss in the five samples are plotted as a function of temperature in Fig. 3. It is clear that the increase in the number of cyanoethyl groups per anhydroglucose unit results in a sample of higher stability. This may be ascribed to the increased probability, at elevated temperatures, of cross link formation through the cyanoethyl groups. The percentage mass losses at 773 K are 99, 89, 70, 65 and 50 for samples A–E respectively.

Variation in the onset degradation temperatures

The onset degradation temperatures for stages a–c (and a′ in samples D and E) are given in Table 1. It is clear that the main degradation step starts at about 523 K for the native sample. Upon substitution the onset temperature increases to 548 K for sample B (DS 0.63). The inclusion of polar cyanoethyl groups leads to an increase in the bonding strength between fibre chains, and consequently more energy is needed for

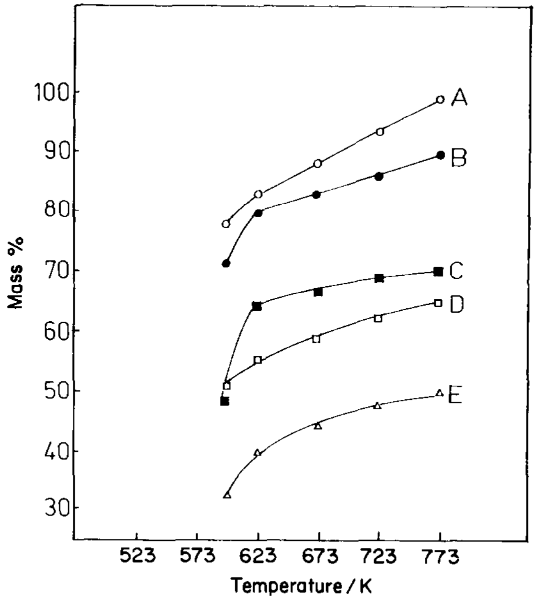

Fig. 3. Relation between the mass loss in % and temperature.

decomposition. Furthermore the dissolution of the low fractions in sample B upon treatment with 1.5 M NaOH results in an increased crystallinity as manifested by X-ray diffraction. With increasing DS the samples start to lose their fibre structure, as indicated in Fig. 1, and consequently the onset temperature of the main degradation process is expected to decrease slightly, as observed in sample C (DS 1.4). The increase in the degradation temperature observed in samples D (DS 2.0) and E (DS 3.0) may be explained in terms such that the possible increase in the destruction of the fibre structure may be compensated for by the increase in the number of polar cyanoethyl groups. However, the dipole association of side groups and the formation of cross links between the cyanoethyl cellulose molecules, may lead to an increase in the onset degradation temperatures of the above samples. The formation of easily degradable molecules, even in a small ratios, in the case of highly substituted samples, may be ascribed to the occurrence of an earlier degradation stage, stage a′, in samples D and E. The increased stability of sample E over sample D, as indicated by the increase of the starting temperature from 543 to 558 K, may be attributed to the increase in the number of the polar cyanoethyl groups from 2.0 to 3.0 per anhydroglucose unit, in addition to the slight improvement in the degree of order occurring in some crystallographic directions.

The starting temperatures of the second degradation step, stage b, showed no significant difference between the first three samples A–C and decreased slightly in the case of samples D and E due to the loss of the fibre structure. However, the diversity in the onset temperatures of stage c may be related to cross-link formation (see Table 1).

Kinetics of degradation processes

Generally the rate of a chemical reaction k is expressed by

$$k = -\mathrm{d}c/\mathrm{d}t = Kc^n \tag{1}$$

where c represents the concentration of the reactants at time t, K is the specific rate constant and n is the order of reaction. In a thermogravimetric analysis the concentration c is replaced by the mass of the remaining, non-evaporated, materials at time t for each process, i.e. $w_t - w_\infty$, where w_t represents the mass of the sample at time t, and w_∞ is its value at the end of the process. In such a case eqn. (1) may be rewritten as

$$k = -\mathrm{d}w/\mathrm{d}t = K(w_t - w_\infty)^n \tag{2}$$

Applying Arrhenius equation [10] we obtain

$$\ln K = \ln(\mathrm{d}w/\mathrm{d}t)/(w_t - w_\infty)^n = \ln A - \Delta E_a/RT \tag{3}$$

The rate of reaction $(-\mathrm{d}w/\mathrm{d}t)$ is calculated as

$$-\mathrm{d}w/\mathrm{d}t = -(w_2 - w_1)/(t_2 - t_1) \tag{4}$$

where w_1 and w_2 are the masses of samples remaining after times t_1 and t_2 respectively.

Thus, plotting the left-hand side values of eqn. (3), i.e. $\ln K$, versus $1/T$, using various values of n should give the best straight line with the most appropriate order of reaction n. If the method of least squares is applied, using eqn. (3) and taking values of n ranging from 0 to 3 with increments of 0.1, then calculating for each value of n the correlation coefficient, R_c, and the standard deviation, S, the appropriate n value is that which would give maximum R_c and minimum S.

The activation energies are then calculated making use of eqn. (3) and applying the appropriate n values for all processes of all samples. Figure 4,

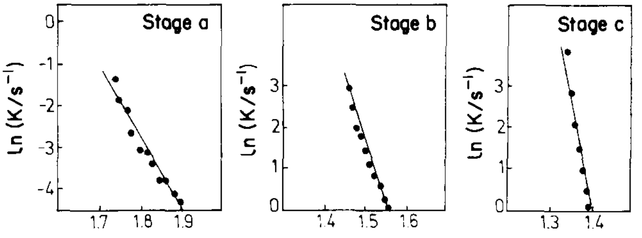

Fig. 4. Representative plots of $\ln K$ versus $1/T$ for the untreated sample A.

as an example, represents the variation of $\ln K$ as a function of $1/T$ for the three stages observed for the pyrolytic degradation of viscose wood pulp (sample A). The activation energies are calculated from the slopes of similar plots for all processes of all samples and the results are included in Table 1.

Changes occurring in the order of pyrolytic degradation reaction

In all samples investigated the order n of stage a of the reaction was unity, i.e. in the early stage of the degradation process the order of reaction does not depend on the degree of substitution, indicating a similar mechanism for the decomposition at this stage whatever the degree of substitution.

As the thermal degradation proceeded, the reaction proved to be third order for the next steps in all samples investigated. This may be ascribed to splitting of the molecule into smaller ones accompanied by their recombination at high temperatures.

Changes occurring in the activation energy values

The activation energy values calculated for the three steps of degradation of all samples showed similar behaviour for the starting temperatures. However the diversity of some calculated values may be ascribed to several factors amongst which are, (i) random splitting of the molecules and their recombination; (ii) formation of easily degradable molecules and differences occurring in their ratio to less easily degradable molecules; (iii) the possible increase in the degree of order upon thermal treatment (recrystallization) especially the more highly substituted samples.

It should be noted that the values of the activation energy calculated for sample E, for example, are obtained as a result of nearly 50% mass loss, whilst those calculated for the untreated sample result from nearly 100% mass loss.

CONCLUSIONS

From the above results it can be concluded that,

(1) cyanoethylation of cellulosic fibres render them thermally stable: the stability increases with increases of the degree of substitution;

(2) pyrolytic degradation of cyanoethyl cellulose proceeds via three stages (a–c) except for the highly substituted samples. The first stage of degradation follows a first order rate equation and does not depend on the degree of substitution, whilst the other stages follow a third order rate equation;

(3) the diversity in the activation values calculated for the samples are explained and related to several factors.

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