Thermochimica Acta, 191 (1991) 21–27
Elsevier Science Publishers B.V., Amsterdam

Thermal degradation of paper sheets made from wood treated with phenolic resin and bagasse pulps

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(Received 4 February 1991)

Abstract

Phenol–formaldehyde resin of resol and novolac types were precipitated in a predetermined concentration onto wood and bagasse fibres. In addition, use has been made of the residual lignin in bagasse to prepare phenol–lignin–formaldehyde (PLF) inside the fibres. Thermal degradation of paper sheets made from resin-treated as well as untreated wood, and bagasse pulps was carried out by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). A method was developed to evaluate the most reasonable order of reaction for the two thermal degradation processes observed in the TGA profiles.

It has been deduced that neither addition of resin nor in situ formation of PLF affect the order of any of the degradation processes. These were approximately first-order in the first process, and third-order in the second. An increase in the total activation energy was observed on addition of the resin or in situ formation inside the fibres.

INTRODUCTION

The degradation of cellulosic materials is known to proceed through a complex process involving dehydration, depolymerisation, oxidation, hydrolysis, cyclisation and charring. The process may follow two routes: one involves depolymerisation with the formation of combustible volatile fragments which feed the flame (flame combustion); the second involves dehydration and formation of carbonaceous char leading to a slower glowing ignition [1]. Detailed studies by numerous investigators [2–12] have involved the thermal degradation of cellulose and other cellulosic materials. A first-order degradation has been assigned for the whole process [13], which assumed that the rates are dependent only on the amount of reactants remaining in the reactor. Other investigators [14] believe that the degradation process proceeds via successive stages, each with a different order of reaction.

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The presence of resin inside the fibres, either physically adsorbed or chemically incorporated into the bonding system, is expected to affect their thermal behaviour. Thus, the present work describes the results of the thermal degradation behaviour, monitored by DTA and TGA techniques, of paper sheets made from wood with added resol and novolac and from bagasse pulps, as well as those from in situ PLF bagasse pulps.

EXPERIMENTAL

Materials and methods

Paper-grade wood pulp was obtained from the El-Nasr paper making company, Alexandria. Bagasse pulp was delivered from Edfu mill, Upper Egypt. Resol and novolac resins for particle board and resins were purchased from the Mansoura company.

Resins, resol and novolac were added and precipitated onto wood and bagasse fibres according to the method previously described; the concentrations of resins added were those which impart maximum mechanical strength to the sheets [15]. Use has also been made of the residual lignin in bagasse pulp to form phenol–lignin–formaldehyde (PLF) inside the fibre. Two bagasse samples were used: the first, as delivered from the company, has 4.8% lignin; the second, after treatment with sodium chlorite solution, has its lignin content reduced to 1.5%.

Paper sheets were made, according to TAPPI standards, from eight pulp samples: 1, bagasse pulp; 2, bagasse pulp with 0.8% resol; 3, bagasse pulp with 0.6% novolac; 4, wood pulp; 5, wood pulp with 0.2% resol; 6, wood pulp with 0.6% novolac; 7, PLF–bagasse pulp (4.8% lignin); and 8, PLF–bagasse pulp (1.5% lignin).

Thermogravimetric analysis and differential thermal analysis were carried out for the eight samples using a Netzsch thermobalance (Geratebau Gabb. selb. B.N. 3484720). Analyses were performed with a heating rate of $5\,^{\circ}\mathrm{C}\ \mathrm{min}^{-1}$ in the presence of air, and were continued to a constant weight.

RESULTS AND DISCUSSION

Thermogravimetric analysis was carried out on all samples. A representative example is reproduced in Fig. 1; all the other samples yield similar shapes. It has been shown that the degradation of each sample passes through four distinct zones, labelled in the figure as a, b, c, and d. Stage a, which is accompanied by a slight decrease in weight, is ascribed to the evaporation of water and easily volatile materials. The main degradation processes, zones b and c, are attributed to the evaporation of large amounts of pyrolitic products. Zone d denotes the carbonisation of the end products.

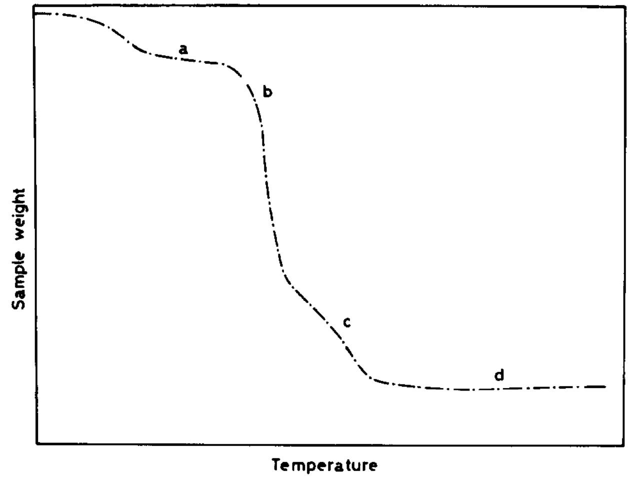

Fig. 1. TGA profile for untreated wood pulp sample.

Thermodynamic evaluation of the degradation processes

Usually, the rate of a chemical reaction R is expressed by

$$R = -\frac{\mathrm{d}c}{\mathrm{d}t} = kc^n \tag{1}$$

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, c is replaced by the weight of the remaining non-evaporated material at time t, i.e. $W_t - W_\infty$, where W_t is the weight of sample at time t and W_∞ is its value at the end of the process. Thus, eqn. (1) may be written

$$R = -\mathrm{d}W/\mathrm{d}t = k(W_t - W_\infty)^n \tag{2}$$

or

$$k = R/(W_t - W_\infty)^n \tag{3}$$

Recalling the Arrhenius equation [16]

$$\mathrm{d}\ln k/\mathrm{d}T = E_a/RT^2 \tag{4}$$

or

$$\ln k = \ln A - E_a/RT \tag{5}$$

where A is the Arrhenius factor, E_a the activation energy and T the absolute temperature.

From eqns. (3) and (5)

$$\ln R/(W_t - W_\infty)^n = \ln A - E_a/RT \tag{6}$$

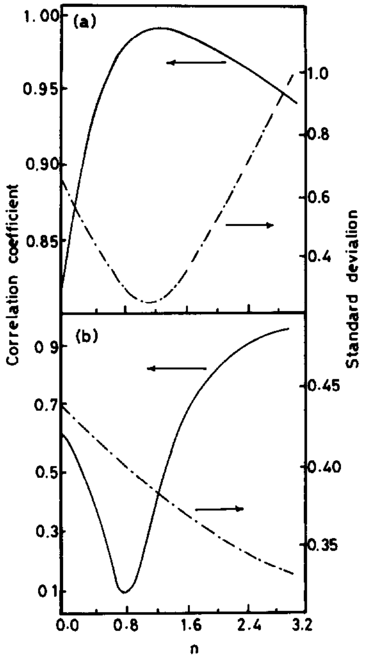

Fig. 2. Statistical determination of n in the thermal degradation of wood pulp sample: (a) first process; (b) second process.

The rate of the reaction, R, is calculated as

$$R = (W_2 - W_1)/(t_2 - t_1) \tag{7}$$

where W_1 and W_2 are the weights of sample remaining after times t_1 and t_2 respectively.

Plotting the values of the left-hand side of eqn. (6) against $1/T$, using various values of n, should give the best straight line with the most appropriate value of n. Thus, when the method of least squares is applied to eqn. (6), taking values of n ranging from 0 to 3 with an increment of 0.1 and calculating the correlation coefficient R_c and standard deviation S_e for each value of n, the best n value is that which gives a maximum R_c and minimum S_e. A computer program was written to calculate R_c and S_e as a function of n, and the results when plotted against n (a representative example is given in Fig. 2) pass through a maximum for R_c and a minimum for S_e at the proper n value. The appropriate values for the orders of reaction calculated this way for samples 1–8 for both degradation processes are given in Table 1. It was found that process b follows nearly a first-order degradation reaction, whereas process c is a third-order reaction.

Returning to eqn. (6), the activation energies, E_a, for both processes and for all samples were calculated from the slope of the lines correlating ln $[R/(W_t - W_\infty)^n]$ with $1/T$ using the previously determined n values; a

TABLE 1

Thermal degradation parameters for paper sheet samples

Sample no.	Process	Order n	E_a (kJ mol^{-1})	Total E_a	Peak temp. T_1, T_2 (K)
1	1	1.2	199	418	612
	2	3.0	219		676
2	1	1.4	185	515	604
	2	2.8	330		664
3	1	1.1	183	592	586
	2	3.0	409		661
4	1	1.1	205	419	596
	2	3.0	214		666
5	1	1.1	223	425	592
	2	3.0	202		667
					677
6	1	1.4	234	444	591
	2	3.0	210		666
					676
7	1	1.1	166	438	581
	2	3.0	272		641
8	1	1.3	190	536	583
	2	3.0	346		663

representative example is illustrated in Fig. 3. The activation energies calculated are included in Table 1.

Comparison of the activation energies of samples 1–6 shows that for the first process, the activation energies calculated for bagasse samples with added resin are lower than that observed for untreated pulp. The reverse was true for wood pulp samples. For the second degradation process, addition of resin increases the activation energies of bagasse pulp, while no trend is observed in the case of wood pulp.

For in situ PLF bagasse samples 7 and 8, the activation energies for the first process decrease, whereas those of the second process increase. The formation of PLF inside the fibres reduces the thermal stability of sheets made from bagasse pulp, based on process b. This deterioration in stability does not depend on the amount of lignin present in the pulp. However, the mechanism of degradation (indicated by the order of reaction) remains the same.

Differential thermal analysis

As can be observed from the DTA profiles of the samples investigated, thermal degradation proceeds via two exothermic processes with peak values at temperatures T_1 and T_2, respectively, see Table 1. An example of the DTA profiles is given in Fig. 4. In addition, the DTA profiles of wood pulps

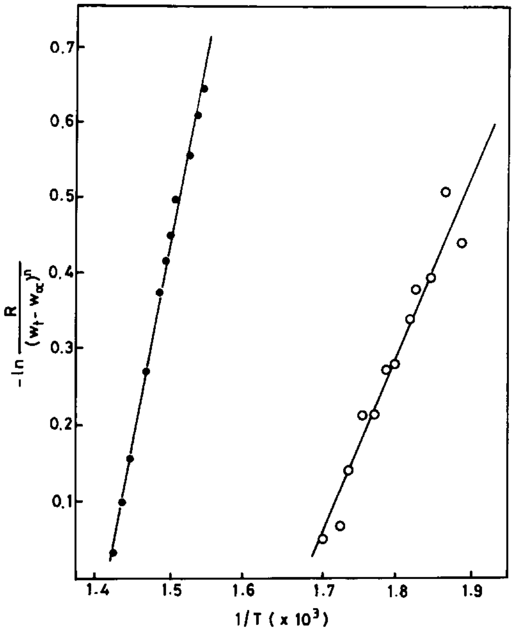

Fig. 3. Variation of $\ln[R/(W_t - W_\infty)^n]$ with $1/T$ for the thermal degradation processes for wood pulp: ○, first process; ●, second process.

with added resin show small shoulders at 677 and 676 K in resol-added and novolac-added wood pulp samples which may be ascribed to the degradation of physically adsorbed resins on the wood pulp fibres. The absence of

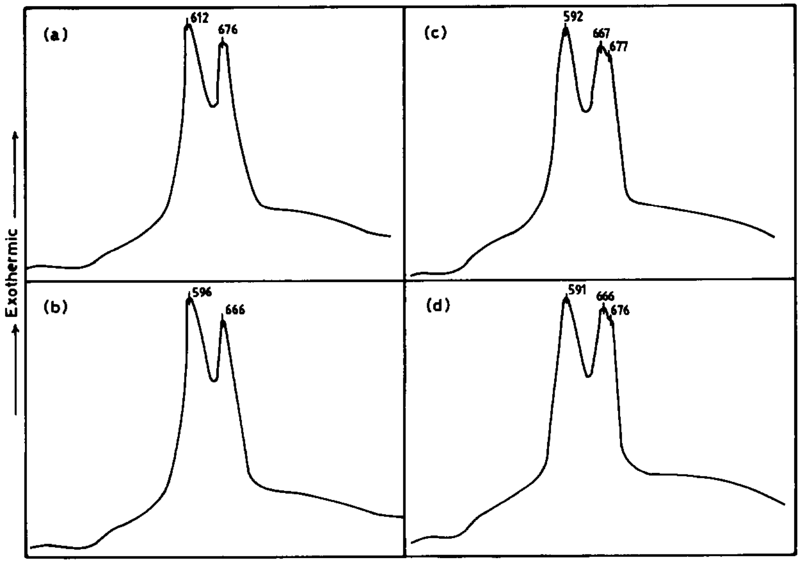

Fig. 4. DTA of paper sheets made from: (a) bagasse pulp; (b) wood pulp; (c) wood pulp with 0.2% resol; and (d) wood pulp with 0.6% novolac.

such shoulders in untreated wood and bagasse pulps as well as in resin-added bagasse pulps, indicate that the resin is bound chemically with the residual lignin present in the bagasse pulp.

Comparison of the peak temperatures determined for samples 1–8 reveals that resin-treated samples have lower degradation temperatures, T_1, than those of untreated samples, indicating a lowering of stability following resin treatment. The second process was found to be less affected by the addition of resin.

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