

# Effect of Cellulose Crystallinity on the Progress of Thermal Oxidative Degradation of Paper

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**ABSTRACT:** Dynamic differential scanning calorimetry (DSC) using paper samples of different compositions has evidenced varying degrees of endothermic activity prior to the exothermic, oxidative decomposition of cellulose under static air. Whereas cotton cellulose papers displayed a significant endothermic activity, wood-pulp papers showed a much less pronounced effect or no activity at all. DSC measurements using microcrystalline cellulose submitted to different extents of milling indicated that the observed endotherm is related to the degree of crystallinity of cellulose. Crystallinity decrease is accompanied by a decrease in the area of the endothermic peak. Thermal disruption of cellulose crystalline domains is therefore believed to be the reason for the appearance of an endotherm in the thermograms of paper. The higher degree of crystallinity of cotton cellulose in comparison to wood-pulp cellulose accounts for the more pronounced endothermic activity observed for cotton papers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 61–66, 2000

**Key words:** paper; cellulose crystallinity; differential scanning calorimetry; thermal oxidative degradation; microcrystalline cellulose

## INTRODUCTION

Cellulose, the basic raw material for papermaking, is the major structural constituent of the wall tissue of most plant cells. It is a linear polysaccharide consisting of D-anhydroglucopyranose units connected by  $\beta$ -1,4-glycosidic bonds. Similar to other polymeric materials, cellulose presents three-dimensional order within molecular aggregates. Cellulose fibers exhibit regions in which the molecules are densely packed in an orderly fashion, and where extensive intermolecular hydrogen bonding is observed. These regions are referred to as crystalline domains, and they impart strength, swelling resistance, and stability to the fiber. Regions where the molecular arrangement is less ordered and compact constitute the amorphous domains of cellulose. Due to a higher

accessibility of amorphous regions, degradative processes of cellulose tend to occur predominantly in those areas.<sup>1–4</sup>

Oxidative reactions accelerate the rate of degradation of cellulose during pyrolysis in air at temperatures up to 300°C.<sup>5</sup> Because oxygen still plays a major role in enhancing the degradation of cellulose at such high temperatures, application of thermal analysis for a comparative investigation of the oxidative stability of cellulose-based materials seems justifiable. Differential thermal analysis (DTA), for instance, has been used to assess the oxidative stability of paper, and the results correlated very well with those of standardized testing methods based on artificial (oven) aging.<sup>6</sup>

Differential scanning calorimetry (DSC) has found wide application in the industry as a fast and simple means of assessing the oxidative stability of synthetic polymers and the effects of antioxidants on their long-term performance. The

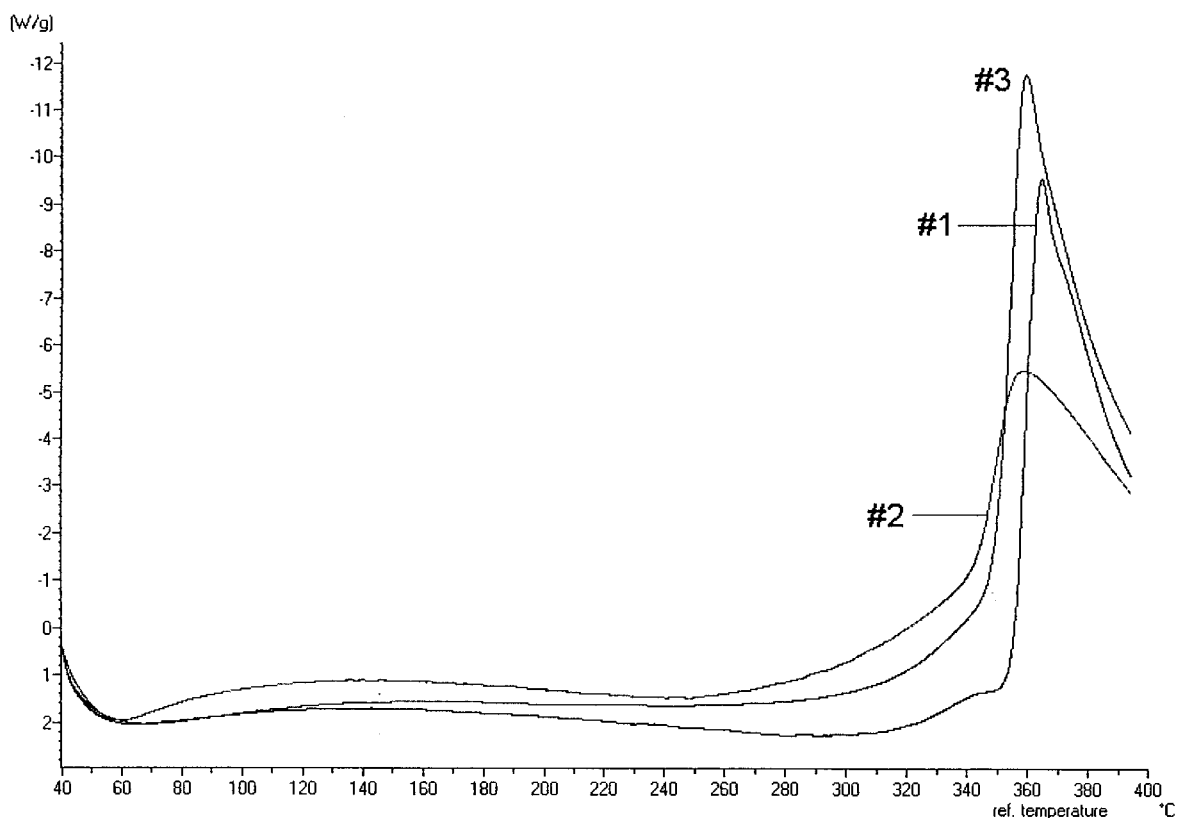
**Table I Investigated Paper Samples**

Sample	Fiber Furnish	Sizing/Fillers
1	Bleached sulphite softwood cellulose	None
2	Groundwood + bleached sulphite softwood cellulose	Alum-rosin
3	Bleached softwood/hardwood chemical pulp	Alkaline / CaCO <sub>3</sub>
4	Cotton linters cellulose	None
5	Cotton cellulose	Alum-rosin
6	Cotton cellulose	None

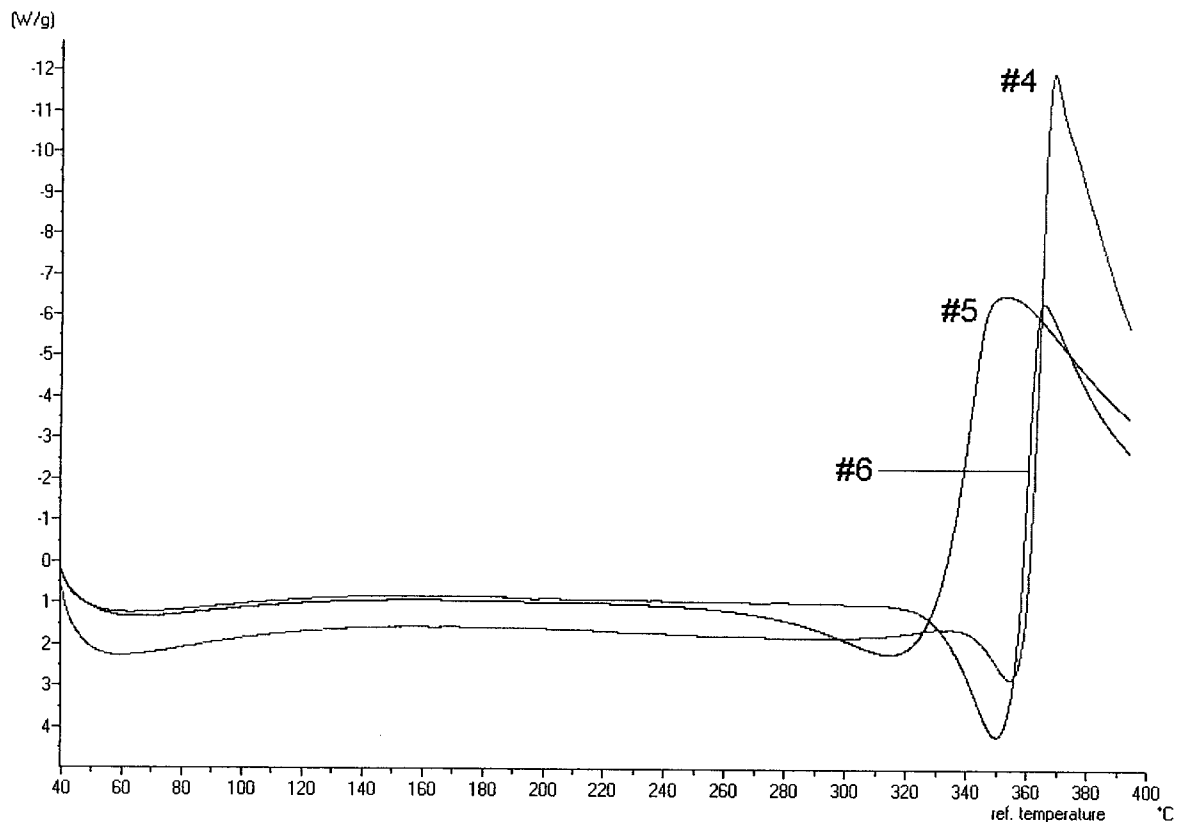
possibility of using DSC analysis to investigate the influence of different factors on the oxidative stability of paper would offer a practical tool to those concerned with paper permanence. While assessing the applicability of dynamic DSC to compare the oxidative stability of different papers, a major dissimilarity between the thermograms of cotton papers and those of wood-pulp

papers has been observed. Significant endothermic activity prior to the exothermic, oxidative degradation of cellulose was noted for all cotton papers. Contrarily, wood-pulp papers showed little or no such activity.

Endothermic activity observed in a DTA thermogram of paper analyzed under air has been attributed to oxygen insufficiency in the reaction site.<sup>6</sup> Changing the atmosphere to pure oxygen caused the endotherm to disappear. Shafizadeh and Bradbury explained the appearance of such endotherm in the DTA thermogram of cotton cellulose linters as a result of formation and evaporation of volatile pyrolysis products.<sup>5</sup> Because the composition of paper seems to influence the progress of its thermal oxidative degradation concerning the occurrence of endothermic activity prior to the exothermic degradation of cellulose, it was decided to assess the effect of cellulose crystallinity on this particular phenomenon. Bertran and Dale have already shown the influence of cellulose crystallinity on the shape of paper DSC thermograms in the region of loss of absorbed water.<sup>7</sup> Its effect in the region of thermal decom-



**Figure 1** Thermograms of paper samples 1-3 (exotherm upward). Heating rate: 20°C/min.



**Figure 2** Thermograms of paper samples 4–6 (exotherm upward). Heating rate: 20°C/min.

position of cellulose, however, has not yet been studied.

In the present work the crystallinity of microcrystalline cellulose has been reduced by vibrating milling, and samples milled to varying extents have been submitted to dynamic DSC analysis to verify the dependence of endothermic activity prior to oxidation on the degree of crystallinity of cellulose. Microcrystalline cellulose is a well-defined substrate, and its use was aimed at eliminating the influence of morphological features of papermaking fibers other than the crystallinity of cellulose.

## MATERIALS AND METHODS

### Paper Samples

Paper samples used in this study are listed in Table I.

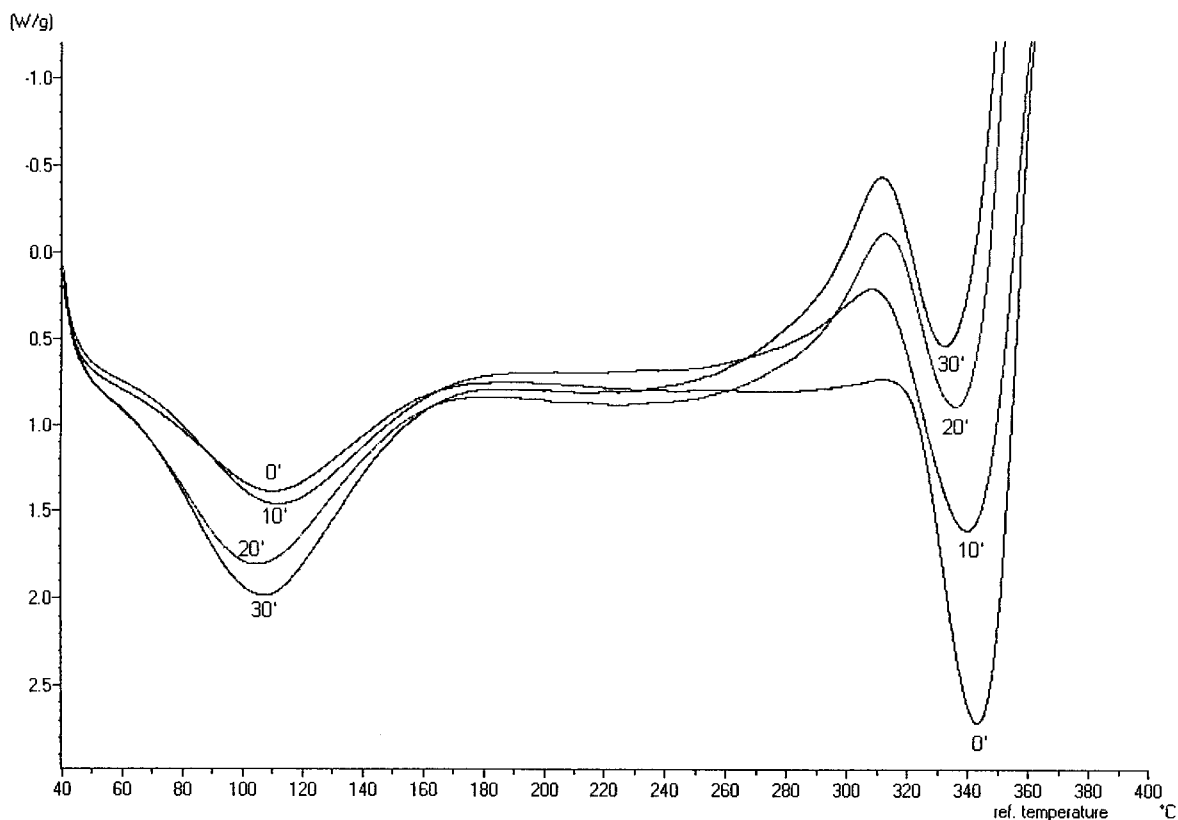
### Microcrystalline Cellulose

Microcrystalline cellulose (Lamers and Indemans, S-Hertogenbosch, The Netherlands; aver-

age particle size: 140  $\mu\text{m}$ ) was milled in a Perkin-Elmer vibrating mill for time intervals of 10, 20, and 30 min before submitted to DSC analysis. To confirm the decrease in crystallinity of microcrystalline cellulose caused by vibrating milling action, X-ray diffractometry was carried out by using a Philips PW3710 Diffractometer (Cu tube anode; generator tension: 36 kV; generator current: 24 mA).

### DSC Analysis

DSC analysis was carried out by using a Mettler DSC 12E unit. Paper discs ( $\Phi = 5$  mm) were prepared by using a paper puncher. The discs were inserted in standard aluminum crucibles (40  $\mu\text{L}$ ) where they fitted precisely. Optimum contact was obtained between the samples and the bottom of the crucibles. Measurements were performed in static air with open crucibles. Conditions of heat transfer and material transport within the test specimen are considered the same for all paper samples. For the analysis of microcrystalline cellulose, sealed standard aluminum crucibles with perforated lids were used. Mea-



**Figure 3** Thermograms of microcrystalline cellulose submitted to different extents of vibrating milling (exotherm upward). Heating rate: 20°C/min.

measurements were also carried out under static air. Dynamic DSC experiments were performed by heating the test samples up to 400°C at a heating rate of 20°C/min. All measurements were duplicated.

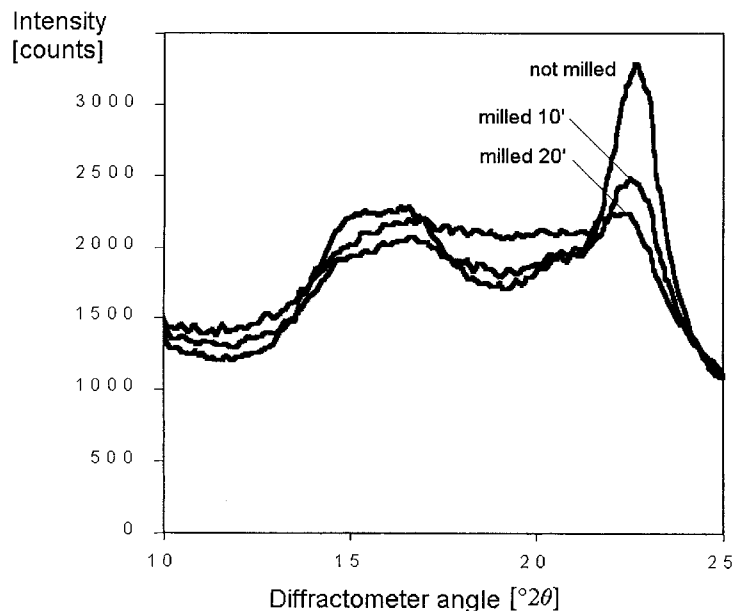
## RESULTS AND DISCUSSION

Thermograms of the paper samples are shown in Figures 1 and 2. Typical features of the DSC traces are the endotherm due to loss of absorbed water within the range of 40–100°C, the steep exotherm arising from the oxidation of cellulose pyrolysis products (330–360°C), and an endothermic peak prior to that exotherm. The latter is only present in the thermograms of samples 4–6, and with less intensity in that of sample 1.

The degree of crystallinity of cellulose has been shown to influence the shape of thermograms in thermogravimetric analysis of pulps, where a cotton linter pulp exhibited a higher onset temperature of weight loss than several wood pulps.<sup>8</sup> Such initially high thermal stability has been attrib-

uted to the higher crystallinity of cotton cellulose. Initiation of thermal decomposition reactions is probably inhibited by a greater extent of hydrogen bonding and of van der Waals' interactions, and by the absence of irregularities (sites with higher reactivity) within the crystalline domains of cellulose. It can be expected, therefore, that this additional thermal stability imparted by the crystalline structure of cellulose would also be evidenced in DSC thermograms of cellulosic materials.

Figure 3 shows the decrease in the area of the endothermic peak occurring prior to the oxidation exotherm in the thermogram of microcrystalline cellulose caused by increasing milling time. Milling action reduces the crystallinity of cellulose, which is shown by the X-ray diffractograms in Figure 4. An estimate of the decrease in crystallinity can be obtained according to the procedure of Segal et al.<sup>9</sup> Table II lists the crystallinity index calculated from the diffractograms and the amount of heat absorbed prior to oxidative degradation (integrated area of the endothermic peak in the DSC thermograms) for the analyzed micro-



**Figure 4** Diffractometer traces showing the decrease in crystallinity of microcrystalline cellulose due to vibrating milling action.

crystalline cellulose samples. Although a linear relationship between absorbed heat and crystallinity index cannot be verified, it seems clear that there is a dependence of the former on the latter. Energy must be supplied to the system to disrupt the crystalline structure of cellulose before oxidative decomposition occurs.

Simultaneous to the decrease in endothermic activity prior to the oxidation exotherm due to milling action, there is an increase in the endothermic peak centered at ca. 110°C, which is due to loss of absorbed water. As the crystalline domains of cellulose are converted into amorphous areas by milling, the equilibrium moisture content of the sample becomes higher and more heat is required to remove absorbed water. It is also of

interest to note the development of an exothermic peak centered at ca. 310°C with increasing milling time. This could also be attributed to the generation of less thermally stable amorphous phases within the milled sample.

## CONCLUSION

The endothermic activity evidenced in DSC thermograms of paper samples prior to the exothermic oxidation of volatile cellulose pyrolysis products in air is related to energy absorption required to disrupt crystalline domains of cellulose. The higher endothermic activity observed for cotton papers in comparison to that of wood-pulp papers is a result of the higher crystallinity of cotton cellulose compared to wood-pulp cellulose. Although there is an obvious qualitative dependence of heat absorption on cellulose crystallinity, a linear relationship between absorbed heat and the X-ray crystallinity of cellulose could not be verified by DSC measurements using microcrystalline cellulose milled to different extents.

**Table II Crystallinity Index and Absorbed Heat Prior to Oxidative Decomposition for Microcrystalline Cellulose Milled to Different Extents**

Milling Time (min)	Crystallinity Index <sup>a</sup> (%)	Absorbed Heat (J · g <sup>-1</sup> )
0	43	139.0
10	22	116.0
20	7	61.3
30	—	58.3

<sup>a</sup> According to Segal et al.<sup>9</sup>

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