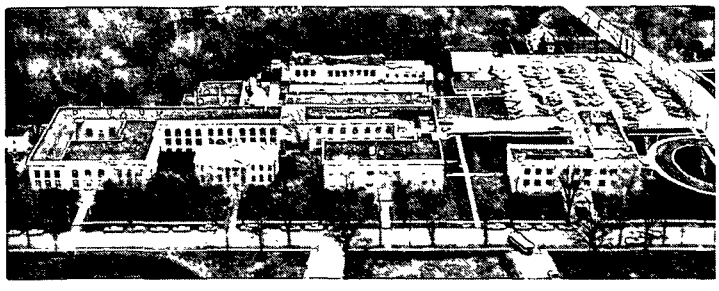

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CELLULOSE: THE INFLUENCE OF ELEVATED TEMPERATURES ON STRUCTURE

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Cellulose: The influence of elevated temperatures on structure

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INTRODUCTION

Since the basic raw material of the Pulp and Paper Industry is green wood, it is important that structural studies focus on the fibers as they exist in the native wood, as well as on the products of exposure to the rather severe conditions typically encountered in pulping. An important consideration, therefore, is the influence of isolation procedure on structure, a question we have addressed extensively. This technical paper describes some representative results and some measures of the effects of exposure to elevated temperatures on a characteristic structural parameter of cellulose fibers.

This has been submitted for publication as a Note in Nature.

Letter to Nature

Cellulose: The influence of elevated temperatures on structure

In the course of our studies we have had reason to question a number of accepted aspects of the phenomenology of cellulose, with respect to both structure[1] and the relative stability of the various polymorphic forms[2]. We report here some recent findings concerning the response of native structure to procedures of isolation from woody tissues; these results are important to understanding the architecture of plant cell walls *in vivo*, as well as to their effective utilization as a resource.

Recent studies have shown that cellulose in its other common polymorph, that is, the mercerized or regenerated form, undergoes substantial increases in crystallinity when it is exposed to elevated temperatures[3,4]. Other polysaccharides have also been reported to crystallize at elevated temperatures in the presence of moisture[5]. These observations suggested questions concerning the effects of elevated temperatures in the course of many of the standard procedures recommended for isolation and purification of cellulose from plant tissue[6-9].

In order to determine the magnitude of such effects in the isolation of native celluloses, we have undertaken a series of experiments wherein the isolation of the cell walls was carried out at low temperatures, and samples were subsequently exposed to elevated temperatures while immersed in relatively inert media. The degree of ordering or crystallization was monitored by x-ray diffractometry. Although we have studied the effect in both angiosperms and gymnosperms, we report here the results of our study of one specie [*Pinus taeda* L.] because they are typical.

The method used for preparation of the cell walls was an adaptation of procedures generally used for the isolation of cell wall polysaccharides other than cellulose, that is the hemicelluloses. Wood from a 1-inch disk cut from a 30-year-old tree, selected to be free of compression wood or tension wood, was cut into small chips approximately 1/4-inch square in cross section. The delignification was carried out by treatment in a solution of sodium chlorite and acetic acid at 60°C for approximately six hours. Some studies were also carried out on wood treated at room temperature for a more extended period. The wood treated in chlorite solution was then extracted with caustic to remove the hemicelluloses, and after neutralization and extensive washing it was lyophilized to prevent collapse of the structure during drying.

The exposure to elevated temperature was carried out in a number of media both protic and aprotic; the following discussion will be confined to samples treated in water at elevated pressures. The temperatures chosen were between 100 and 170°C, for periods up to 4 hours. After the treatment at elevated temperatures the samples were washed and again lyophilized to avoid changes in the structure associated with air drying. Samples of cells exposed to elevated temperatures and unexposed controls were then pressed into pellets in an infrared pellet press at relatively low pressures. The pellets were mounted in the x-ray diffractometer and the reflected scattering scanned.

Although a number of methods of quantifying the crystallinity in cellulose have been described in the literature, for the purposes of the present study only a relative measure was desired. The width at half-height of the 002 peak in the diffractogram of native cellulose was, therefore, used as the primary index of order; it has been found to correlate well with other indices of order described in the literature.

The effect of exposure to elevated temperatures is illustrated in Fig. 1 where the diffractogram of the cells isolated at low temperatures are compared with the diffractogram of cells exposed at 170°C for 4 hours. The width at half-height of the low temperature material is 2.83 degrees while that of the material exposed at 170°C is 2.44 degrees; the relative change of approximately 0.4 degree is very significant for this type of cellulose.

Mats made from both classes of fibrous cells were subjected to a variety of mechanical testing procedures as well as to measurements of their water retention capacity. The results were all consistent with an increase in the crystallinity of the fibers exposed to elevated temperatures; the properties reflected an embrittlement of the cell walls and a reduction of their capacity to absorb moisture. Chemical analyses revealed very little change in saccharide content as a result of the exposure to elevated temperatures.

In the series of experiments wherein cells isolated at low temperatures were held at different elevated temperatures for varying periods of time, it was observed that most of the change occurred during the first one hour of exposure, and that subsequent change in the width at half-height asymptotically approached a final value dependent on temperature. In Fig. 2 the values of width at half-height, after exposure for six hours, are plotted as a function of temperature; the difference between these values and the asymptotic values are within experimental error. The indication, therefore, is that the final value of the width at half-height of the 002 peak in the diffractogram, is an equilibrium value determined by the temperature of exposure.

Raman spectra were recorded for a number of the samples. Preliminary evaluations of these spectra, which are particularly sensitive to conformational changes

suggest that the increased ordering occurs transverse to the chain direction, rather than as an extension of the order in the direction of the chains.

Perhaps the most significant implication of our observation is that cellulose in cell walls, in vivo, is more flexible than in the cells isolated using most of the well established procedures. From a functional point of view such a structure would minimize development of shear stresses in cell walls and, therefore, enhance the ability of the tissue to withstand stresses arising from mechanical perturbations such as those caused by wind, precipitation, and, under some circumstances, inclination with respect to the gravitational field.

With respect to utilization of the cell walls as a renewable resource by industries based on fiber and forest products as the primary raw materials, the implication of our findings are that commercial processes which involve exposure to elevated temperatures result in a degradation of the physical properties of the fibers. Thus it is clear that the full potential of the fibers is not realized in traditional production processes, and that it may be possible to alter production processes to realize more of the potential mechanical properties of the fibers, and thus further the efforts to conserve forest resources.

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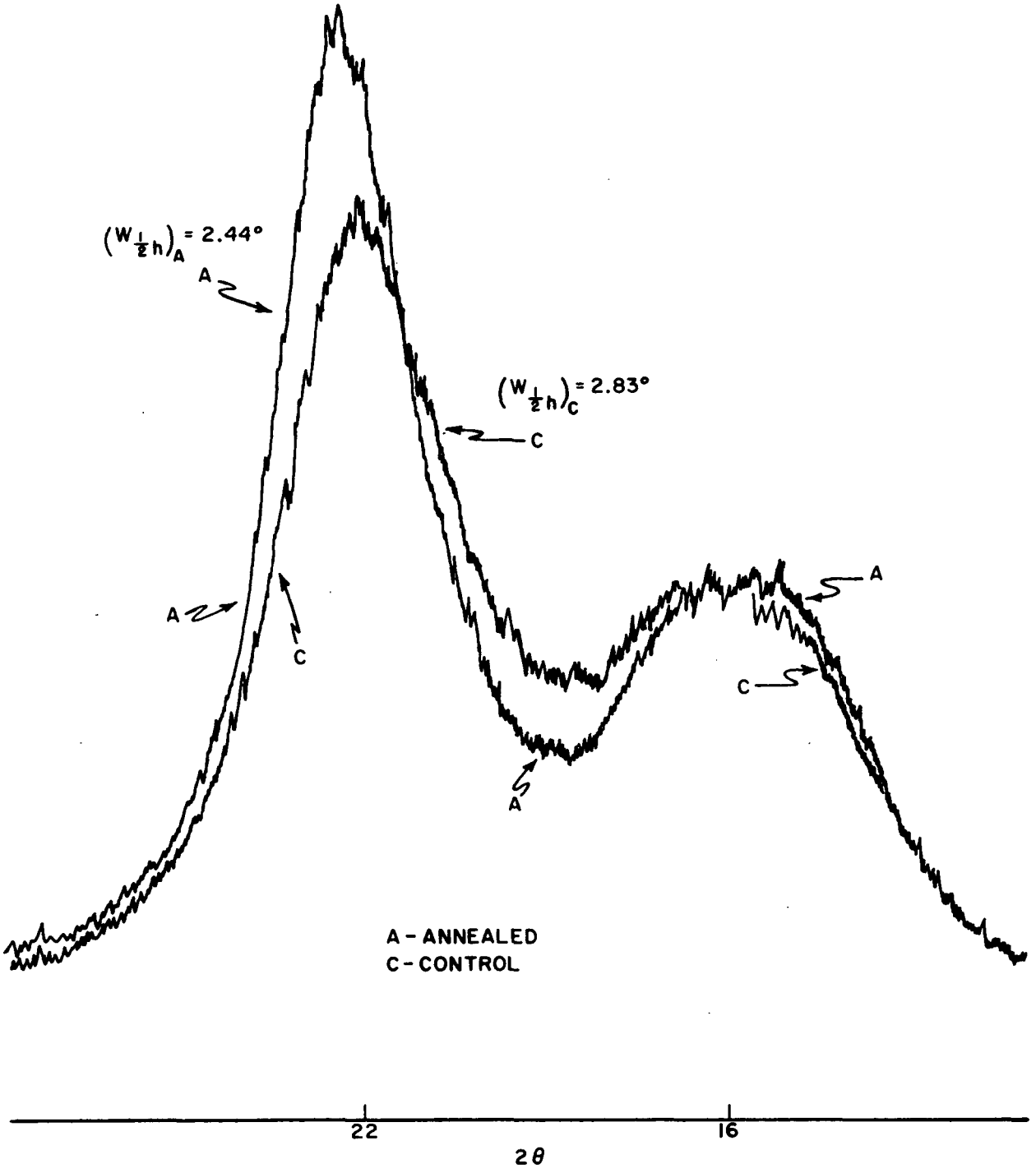

Fig. 1. Diffractograms of treated (A) and control (C) samples recorded with Ni filtered Cu K(α) source

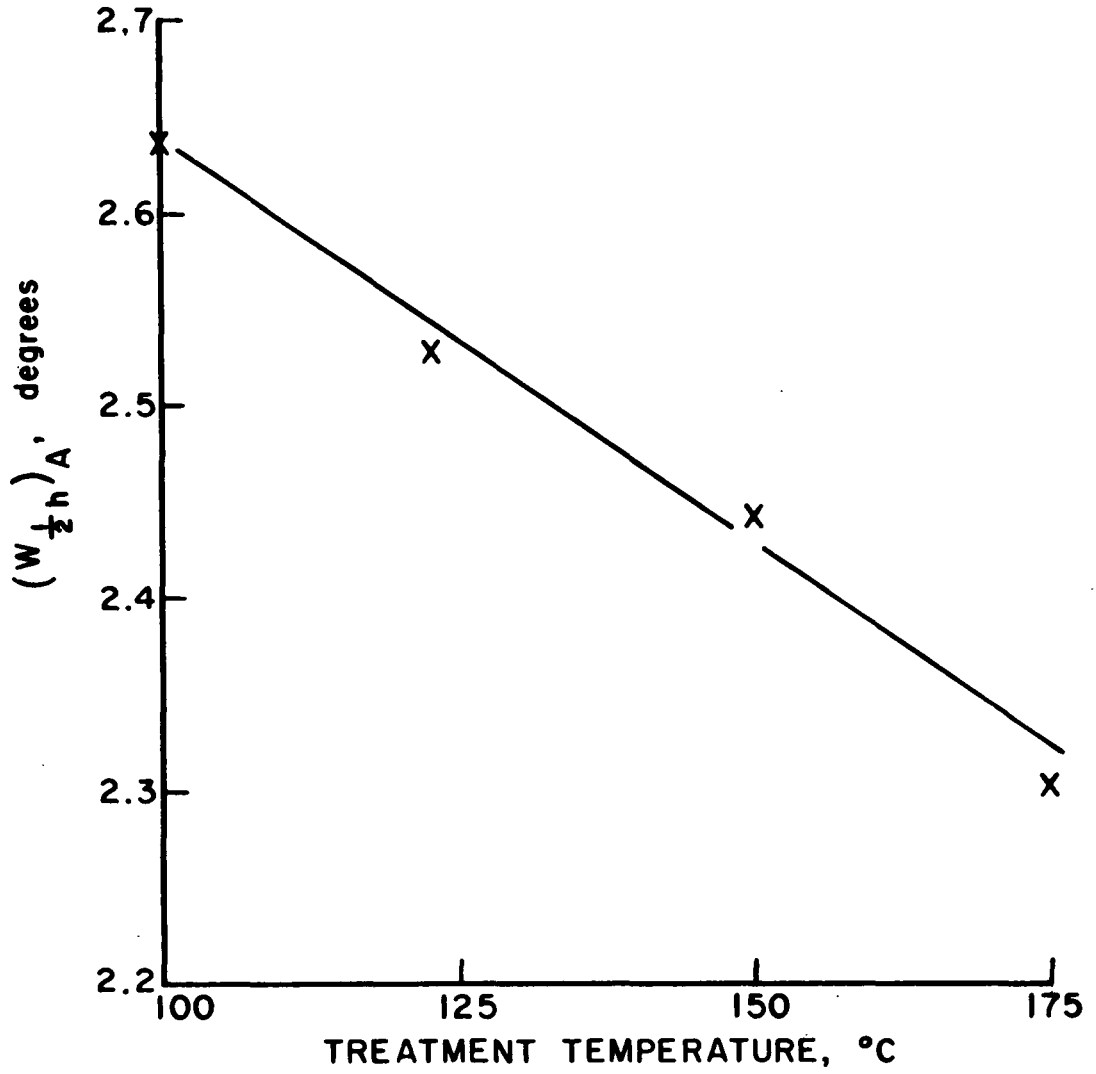

Fig. 2. Width at half-height of the 002 peaks after treatment for 6 hours at different temperatures