STUDIES ON THE CRYSTALLINITY OF WOOD CELLULOSE FIBRES BY X-RAY METHODS

by

CHI-LONG LEE

B.S.F. Taiwan Prov. Coll. of Agr., China, 1955

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF FORESTRY
in the Faculty
of
Forestry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA
April, 1960
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Forestry

The University of British Columbia,
Vancouver 8, Canada.

Date March 25, 1960
ABSTRACT

It was the purpose of this study to compare pulps prepared from normal, sound wood with those prepared from juvenile wood, compression wood, tension wood and decayed wood with regard to their apparent degree of crystallinity.

The crystallinity index and crystallinity ratio of the pulps prepared from these woods were determined by two different X-ray methods. In method A, the principle of the Debye-Scherrer powder technique was applied and the crystallinity index of the pulp was evaluated from the 002 peak of the X-ray diffraction pattern. In method B a Geiger-counter X-ray spectrometer was used and the crystallinity ratio of holocellulose was evaluated from the (101 + 101) combination peak.

It was found that the apparent crystallinity of wood pulp and holocellulose prepared from normal western hemlock wood increased significantly through successive growth rings from the pith to about 15 years, after which it reached a more or less constant value. The crystallinity of wood pulp and holocellulose of summerwood was significantly higher than that of springwood. The crystallinity of wood pulp and holocellulose of compression wood from Douglas fir was considerably lower than that of normal wood, whereas the crystallinity of tension wood from cottonwood was
significantly higher than that of normal wood. The crystallinity of cottonwood and Douglas fir holocellulose increased significantly during the incipient stage of decay. The rate of increase in crystallinity was very rapid during the incipient stage of decay represented by a six percent weight loss, but became very slow and showed an almost constant value thereafter. The relative value of crystallinity after decay depends mainly on the initial crystallinity rather than the history of decay.
ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to the Faculty of Forestry of the University of British Columbia, and to Dr. R.W. Wellwood under whose direction this study was carried out; to Mr. R.W. Kennedy for his careful review and criticism of the manuscript and for providing some experimental material; to Dr. J.H.G. Smith for suggesting a statistical design; to Dr. L.D. Hayward for discussions in the planning stage; to Dr. J.A.F. Gardner and Mr. W.V. Hancock of the Vancouver Laboratory, Forest Products Laboratories of Canada, Dr. V.G. Griffiths, Dr. E. Teghtsonian, and Mr. Y.I. Ssu of the Department of Mining and Metallurgy at the University of British Columbia and Mr. G.E. Breeze and Mr. R.H. Nilberg of the Department of Physics, British Columbia Research Council for permission to use their equipment and for their kind assistance and cooperation in many ways; and to the National Research Council of Canada for the studentship grant under which this work was completed.
# TABLE OF CONTENTS

| I. INTRODUCTION ........................................ | 1 |
| II. CRYSTALLINE STRUCTURE AND CRYSTALLINITY OF CELLULOSE ................. | 4 |
| A. Chain structure and formation of the crystalline region ............... | 5 |
| B. Lattice structure ........................................ | 7 |
| C. Crystallinity of cellulose .................................. | 11 |
| 1. Concept .................................................. | 11 |
| 2. Determination of crystallinity .................................. | 14 |
| (a) Chemical methods .......................................... | 15 |
| 1) Acid hydrolysis method .................................... | 15 |
| 2) Deuteration method ....................................... | 17 |
| 3) Cellulose derivative method ................................ | 18 |
| 4) Oxidation method .......................................... | 19 |
| 5) Iodine sorption method .................................... | 20 |
| (b) Physical methods .......................................... | 21 |
| 1) X-ray method ............................................. | 21 |
| 2) Moisture regain method .................................... | 25 |
| 3) Infra-red absorption spectroscopy method ........................ | 26 |
| 4) Density method ........................................... | 28 |
| 3. Treatments affecting crystallinity .......................... | 29 |
| (a) Hydrolysis .............................................. | 29 |
| (b) Heat ................................................... | 30 |
(c) Mechanical decrystallization .... 31
(d) Degradation by microorganisms  ... 32
(e) Lattice transition ............. 33
  i) Transition from cellulose I
to cellulose II .......... 33
  ii) Transition from cellulose I
to cellulose III ........ 34
  iii) Transition from cellulose
II and III to cellulose IV . 35
(f) Pulping ..................... 35
(g) Stretching .................. 36

4. Relationship between crystallinity and
   properties of cellulose .......... 36
   (a) Young's modulus .......... 37
   (b) Tensile strength .......... 38
   (c) Elongation ............... 39
   (d) Alpha cellulose content .. 39
   (e) Swelling and dimensional stability .. 40

III. EXPERIMENTAL METHOD ......................... 42
    A. Materials  .................. 42
    B. Statistical design .......... 43
    C. Preparation of samples .... 44
       1. Wood pulp sample .......... 45
       2. Holloccellulose .......... 46
    D. X-ray collimating system and procedure ... 47
1. Method A ............................................. 47
2. Method B ............................................. 50

E. Evaluation of crystallinity ............................... 52
   1. Crystallinity index .................................... 52
   2. Crystallinity ratio .................................... 53

IV. RESULTS AND DISCUSSION ................................. 54

A. Part I: The degree of crystallinity of
   pulp and holocellulose of normal wood .............. 54
   1. Results ............................................. 54
      (a) Tensile strength ................................. 59
      (b) Alpha-cellulose content ......................... 59
      (c) Moisture regain .................................. 60
   2. Probable mechanism of variability of
      crystallinity in wood ................................ 62

B. Part II: The degree of crystallinity of
   pulp and holocellulose of reaction wood as
   compared to normal wood ............................... 63
   1. Results ............................................. 63
   2. Compression wood .................................... 65
   3. Tension wood ........................................ 66

C. Part III: The degree of crystallinity of
   holocellulose of decayed wood ........................ 69
   1. Results ............................................. 69
   2. Biochemical transformation of cellulose ............ 73
   3. Preference of enzymic attack ....................... 75
4. Relationship between lateral order and rate of enzymic attack

V. CONCLUSIONS

VI. BIBLIOGRAPHY
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>TABLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The unit cell structure of cellulose</td>
<td>11</td>
</tr>
<tr>
<td>2. Relationship between alpha-cellulose content and crystallinity</td>
<td>40</td>
</tr>
<tr>
<td>3. Variation in cellulose properties as crystallinity increases</td>
<td>41</td>
</tr>
<tr>
<td>4. Effect of age and season on crystallinity of wood pulp and holocellulose</td>
<td>55</td>
</tr>
<tr>
<td>5. Analysis of variance of crystallinity in Table 4</td>
<td>57</td>
</tr>
<tr>
<td>6. Crystallinity of reaction wood</td>
<td>64</td>
</tr>
<tr>
<td>7. Analysis of variance of crystallinity in Table 6</td>
<td>64</td>
</tr>
<tr>
<td>8. Crystallinity ratio of holocellulose of decayed wood</td>
<td>70</td>
</tr>
<tr>
<td>9. Analysis of variance of crystallinity ratio in Table 8</td>
<td>70</td>
</tr>
<tr>
<td>10. Stepwise biochemical transformation of cellulose</td>
<td>74</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Unit cell of cellulose I</td>
<td>9</td>
</tr>
<tr>
<td>2. Camera arrangement for the Debye-Scherrer powder technique</td>
<td>48</td>
</tr>
<tr>
<td>3. Effect of X-ray exposure time on crystallinity index</td>
<td>48</td>
</tr>
<tr>
<td>4. Wood pulp X-ray diagram</td>
<td>49</td>
</tr>
<tr>
<td>5. Spectrometer geometry</td>
<td>51</td>
</tr>
<tr>
<td>6. X-ray diffraction spectrum</td>
<td>51</td>
</tr>
<tr>
<td>7. Variation of crystallinity with age and season</td>
<td>56</td>
</tr>
<tr>
<td>8. X-ray diffraction spectra of Douglas fir holocellulose</td>
<td>71</td>
</tr>
<tr>
<td>9. Effect of decay and type of wood on crystallinity ratio of holocellulose</td>
<td>72</td>
</tr>
<tr>
<td>10. Schematic lateral order distribution curve and sequence of enzymic attack on the crystalline region</td>
<td>81</td>
</tr>
</tbody>
</table>
INTRODUCTION

The effect of crystallinity on physical and chemical properties of cellulose and its derivatives has been studied extensively during the past few years, particularly during the last decade. Rapid developments in equipment, as well as improvement in precise techniques, have made such kinds of studies fruitful in adding valuable information to knowledge of cellulose chemistry. Most of these works deal with pulp or cotton cellulose, but only a limited number of papers deal with the crystallinity of wood in the light of the results with cotton cellulose, yet it may be one of the important factors which will directly or indirectly affect wood properties and quality.

The main difficulties in studying crystallinity of wood are caused by the complicated chemical composition of wood itself. It is well known that wood contains only about 50 to 60 percent of cellulose. In order to determine the crystallinity quantitatively, the chemical constituents other than cellulose should be removed. Since there is no method which can extract components other than cellulose without degrading cellulose molecular chains, the experimental value of crystallinity determined from such cellulose can hardly be considered the same as that which actually existed in the original wood. However, if the same chemical treatment is applied to different types of wood assuming a uniform degree of degradation of the
cellulose molecular chains during the treatment, it may be possible to compare the relative degree of crystallinity among wood samples.

Based on this premise, studies on crystallinity of wood fibres have been made by various workers. The crystallinity of Cross and Bevan cellulose prepared from wood of different ages was studied by Preston, Hermans, and Weidinger (113) by means of an X-ray method. Results showed that the crystallinity decreased with age. An opposite result was obtained by Taniguchi (142), who found that absolute crystalline cellulose content of Pinus densiflora, as determined by an acid hydrolysis method, increased with age slowly in the early stage of growth. Because of these different results observed, further study was deemed necessary in order to ascertain the variability of crystallinity with age of wood.

Lindgren (77) has pointed out that the summerwood gives a sharper X-ray diagram, which indicates a higher degree of crystallinity as compared with the corresponding springwood. A similar result was observed by Holzer and Lewis (57), who claimed that the summerwood fibres exhibited an unusually high degree of preferred orientation among the crystallites, whereas springwood fibres were found to be much more amorphous. Numerical data were not given by these workers.

The crystallinity of tension wood has been studied thoroughly by Wardrop and Dadswell (154,157). A significantly
high degree of crystallinity of tension wood, as compared with that of normal wood, was found to be due to the existence of an additional layer inside the inner layer of the secondary cell wall. To the writer's knowledge, the crystallinity of the other type of reaction wood, compression wood, has not been studied.

The relationship between crystallinity and microbiological degradation of cellulose has been studied by various workers. Most of these works are confined to pure cellulose which has been treated with enzymes, but little is known about the relationship between crystallinity and wood decay. Crystallinity of decayed wood was first studied by Kohara and Okamoto (71). They found a higher degree of crystallinity in the old timbers taken from ten old Buddhist temples (in use about 300 to 1300 years) as compared with that of new timbers. But the variation in crystallinity of decayed wood as related to the stage of decay still remains unknown.

The purposes of this thesis are to quantitatively study (1) the variation in crystallinity of wood from a young tree with age, (2) the degree of crystallinity of summerwood as compared with that of springwood, (3) the crystallinity of reaction wood as compared with that of normal wood, and (4) the relationship between crystallinity and wood decay.
CRYSTALLINE STRUCTURE AND CRYSTALLINITY OF CELLULOSE

As early as 1913, Nishikawa and Ono (104) showed that the X-ray diagram of cellulose consisted of definite diffraction rings. This discovery led to the concept of crystallinity of fibres. Nishikawa (105) later pointed out that the crystallized areas were not continuous, but separated by more or less disordered material. Extensive research, both physical and chemical, has been carried out since then, but the concept remains the same. Today, it is still considered that cellulose, like other high polymers, will crystallize under proper conditions to form an imperfectly ordered solid, having certain regions possessing a high degree of internal geometrical order known as crystallites. The remainder will possess disordered entangled chain molecules known as amorphous regions.

As the size, shape, and degree of perfection in the crystalline region, or the degree of randomness in the amorphous region, are never constant from sample to sample, the physical and chemical properties of cellulose and its derivatives are correspondingly variable. In order to understand the crystallinity relationships of cellulose, a brief review is necessary of the crystalline structure and crystallinity of cellulose.
A. Chain structure and formation of the crystalline region

To establish the chain structure of cellulose, studies on quantitative yields of glucose units from cellulose were initiated, followed by investigation of the nature of hydroxyl groups and position of hydroxyl groups in cellulose. From these works it was concluded that pure cellulose consisted exclusively of glucose residues (66,93) which contained three hydroxyl groups at the second, third, and sixth carbon atom (27,67), and the basic unit was found to be the anhydroglucose unit (110).

Nature of the linkage between these anhydroglucose units was studied by various physical and chemical methods, and finally a spatial model of cellulose was constructed by Meyer and Mark (110). This model had the beta form of Haworth's cellobiose (110) with unit length of 10.3 Å. Distance between carbon atoms was found to be 1.54 Å, whereas that between carbon and oxygen atoms was 1.35 Å. One half of the unit is turned through 180 degrees to fulfill the screw axis requirement which allows the 1,4-linkage.

The molecular chain thus formed by anhydroglucose units is nearly straight, with a degree of polymerization of several thousand glucosidic rings. These extend longitudinally in the direction of the fibre axis, with a small angle of inclination. When all molecular chains extend in this manner, a cross-wise secondary force will be formed. Because of this
interchain force, the molecular chains will attract one another to form a well-ordered region or a crystalline region. Such crystallization cannot take place completely throughout the whole chain. It occurs at the particular region where the intermolecular attraction is strongest, and chain molecules are fitted laterally into a crystal lattice. The other region will remain in a disordered state even though weak secondary attraction forces exist among them. This region is referred to as the amorphous region. It must be pointed out that not only the length of such crystallized portions is variable, but also the interval distance between them is changeable from one type of cellulose to another.

The molecular chains in wood cellulose, which may have a degree of polymerization of more than 3,000 glucose units (145), are approximately $1.5 \times 10^3 \, \AA$ in length, whereas a crystallite has an order of magnitude of $1.4 \times 10^3 \, \AA$ (145). If the amorphous region, on the average, is assumed to be shorter than the crystalline region, then each molecular chain must pass through about ten microphases or, in other words, consists of several crystalline and amorphous regions. This concept was postulated first by Frey-Wyssling (35) and Kratky (74), and led to the fringe micellar theory. As far as the crystalline-amorphous multiple structure is concerned, this theory is considered preferable to the micellar theory, which was accepted before 1930 in order to explain the properties of cellulose.
The micellar theory assumed that molecular chains can never exceed the length of micelles,\(^1\) and amorphous material exists between micelles as a cementing medium which is responsible for swelling of fibres (55). However, the existence of a separate cementing material failed to explain the structure of regenerated cellulose (110). In addition cellulose chains have been shown to be longer than the length of a micelle, by electron microscopic studies and ultracentrifuge and viscosity methods (44,112). For these reasons, the fringe micellar theory is more acceptable.

According to the fringe micellar theory, the crystalline regions alternate with the amorphous regions, with gradual transition from the former to the latter. No clear border exists between two phases, nor correlation between molecular chain length and size of crystallite.

B. Lattice Structure

It follows that cellulosic material has a polycrystalline structure in which the cellulose molecules may traverse several crystalline and amorphous regions. In the crystalline region, the molecular chains form an ordered lattice structure in which lateral intermolecular distance is

---

\(^1\)The terms "micelle" and "crystallite," although generally used interchangeably in scientific papers, are slightly different in nature. The term "micelle" is used to designate a definite concept of a region having distinct boundaries, whereas the term "crystallite" is used without specifying any particular size, shape or nature of the boundary between crystalline regions (110).
kept at a minimum so that an equilibrium is maintained at a minimum potential energy. Mark (85) suggested that the amorphous region should have a higher energy content than the crystalline region. Thus, the intercrystalline area may be considered as highly disordered crystal lattices in which single atoms are shifted considerably from their normal equilibrium positions (100).

The analysis of lattice structure has been rapidly advanced by X-ray diffraction techniques. In the case of the cellulose lattice, the transparent diffraction diagram is generally used for analytical purposes. Since the angle of reflection (2θ) can be calculated from the X-ray diagram and the X-ray system constructed, the interplane spacings can be easily determined by Bragg's Law. The unit cell lattice has been studied on this principle.

The first unit cell was proposed by Polanyi (110), who suggested a rhombic unit cell with dimensions of 7.9x8.45x10.2 Å. A few years later, an orthorhombic unit cell with axis a* = 6.1, b* = 10.25, c* = 5.4 Å, and B* = 88 degrees was suggested by Sponsler (134). Sponsler's suggestion was followed by Meyer and his co-workers (89,90), and finally led to the postulation of a monoclinic unit cell with axis a = 8.35, b = 10.3, and c = 7.9 Å, and B = 84 degrees. The planes of the anhydroglucose unit lie in the a-b plane and the

*The definition of a, b, c, and B are given in Figure 1, page 9.
molecular chains are parallel to the b-axis of the unit cell.

A few years later, Meyer (89) suggested a revised model in which the center chain and corner chains were running in opposite directions, but the dimension of the unit cell remained the same. A model of the unit cell is shown in Figure 1. This structure was supported by Gross and Clark (42) in 1938, and it is still generally accepted.

Figure 1. Unit cell of cellulose I (Meyer and co-workers (110))

As mentioned previously, the formation of the unit cell is attributed to crystallization, which is caused primarily by intermolecular attraction. It has been shown that there are three different types of intermolecular attracting forces acting in three different directions (110, 145). Along the
b-axis, 1,4-glucosidic bonds between carbon and oxygen are connected by primary valence bonding which has a dissociation energy of about 50 kcal. per mole. In the direction of the a-axis, where the distance between the glucosidic ring is approximately 2.5 Å, a strong intermolecular force is present in the form of hydrogen bonds attracting each chain transversely in the a-b plane. The hydrogen bond has an average bond energy of 5 kcal. per mole. In the c-axis, the minimum distance is about 3.1 Å. The only existing attraction is due to van der Waal's forces between the anhydroglucose rings which can be calculated to be 2 to 3 kcal. per mole (110).

The crystalline structure so far discussed belongs to cellulose I or native cellulose. There are three other different crystalline modifications, depending on the type of chemical reagent used to modify the native structure, i.e., cellulose II (hydrate cellulose or mercerized cellulose), cellulose III (ammonia cellulose) and cellulose IV (cellulose T or high-temperature cellulose). Each has a characteristic structure which has been studied by various investigators. The unit cell structure of these four types of cellulose are summarized in Table 1, page 11.
Table 1. The unit cell structure of cellulose (110)

<table>
<thead>
<tr>
<th></th>
<th>Cellulose I</th>
<th>Cellulose II</th>
<th>Cellulose III</th>
<th>Cellulose IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a^*)</td>
<td>8.35</td>
<td>8.1</td>
<td>7.74</td>
<td>8.11</td>
</tr>
<tr>
<td>(b^*)</td>
<td>10.3</td>
<td>10.3</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td>(c^*)</td>
<td>7.9</td>
<td>9.1</td>
<td>9.9</td>
<td>7.9</td>
</tr>
<tr>
<td>B(^**)</td>
<td>84</td>
<td>62</td>
<td>58</td>
<td>90</td>
</tr>
</tbody>
</table>

*unit: Å  
\(^{*}\text{unit: degrees}\)

C. Crystallinity of cellulose

1. Concept

Although a great number of investigations have been made regarding the crystallinity of cellulose, and valuable data have been published, a proper definition of crystallinity has not yet been established. One of the most difficult problems is that there is no borderline which can be drawn between crystalline and amorphous regions. Once this problem is solved, the crystallinity of cellulose can be defined simply as the fraction of cellulose contained in the region in which highly geometric order prevails, with the distance between neighboring molecules governed by strict laws. The amorphous region, accordingly, must be considered to contain all possible intermediate degrees of packing between the liquid and the crystalline state (110).
Various investigators have approached this problem from different points of view by using different definitions of the "crystalline region," which has led to a marked disagreement in absolute values of crystallinity. For instance, those who treat this problem from the physical point of view, define the "crystalline region" as the portion which is in the state of perfect, three dimensional order and which gives rise to selective X-ray diffraction patterns (44). Any portion which fails to produce such diffraction would be defined as an "amorphous region." On the other hand, those who approach this problem by chemical means consider the crystalline region as the portion having extreme resistance to chemical attack, as compared with the rest of the region which is accessible. On treatment with certain chemical reagents under proper conditions, the residue is considered as the crystalline region while the rest is the amorphous region. Because of their different approaches, the results have never coincided. The physical method always gives lower absolute crystallinity than the chemical method. A detailed discussion of the difference in results between these methods will be given later in this thesis.

Since the physical method and the chemical method always give considerably different values of crystallinity, some investigators prefer to use the term "degree of lateral order" (55,84,110) rather than "degree of crystallinity." The concept of degree of lateral order is based on the fringe
micellar theory as described above. That is, the crystalline region in a given cellulose may vary in size, shape and degree of perfection, and is heterogenous rather than homogeneous as far as the order level is concerned. Therefore a complete statistical distribution of degree of perfection of the crystalline region is of greater importance than merely specifying absolute crystallinity. Howsman and Sisson, as cited in Ott et al (110), defined the degree of order by the following equation:

\[
\bar{\theta} = \frac{\text{OH}_C}{\text{OH}_t}
\]

where \(\bar{\theta}\) is a degree of order, \((\text{OH}_C)\) is the total number of hydrogen bonds actually present in the region, and \((\text{OH}_t)\) is the total possible number of hydrogen bonds if all molecules are perfectly crystallized. If it is considered that definite quantities of cellulose \(q_1, q_2, q_3, \ldots, q_n\) can be associated with the order \(\bar{\theta}_1, \bar{\theta}_2, \bar{\theta}_3, \ldots, \bar{\theta}_n\), then a lateral-order distribution curve can be obtained by differentiating the summative mass-order curve in which corresponding values of \(q\) are plotted against \(\bar{\theta}\). A high lateral order in this case corresponds to a high crystallinity.

This idea has practical experimental difficulties as far as the resolution is concerned, since it is dependent on the choice of the original volume element. From the theoretical point of view, sooner or later the distribution curve evaluation will be commonly adopted in the field of structure studies of cellulose.
2. Determination of crystallinity

It has been stated that methods for determination of crystallinity of cellulose can be classified into two groups, chemical and physical. Generally speaking, the chemical methods assume that chemical reagents are unable to penetrate into the crystalline region, thus the reaction takes place very rapidly in the initial stage and finally becomes very slow. The rate of reaction and percentage of cellulose reacted are used as the measure of the accessibility. The physical methods, on the other hand, measure crystallinity on the basis that the crystalline region is assumed to give high X-ray diffraction, high density, or low moisture regain. In the usual case, the chemical method primarily measures the accessible or amorphous fraction, whereas the physical method, in general, measures the crystalline region.

It should be noted that the accessible cellulose is not necessary equivalent to non-crystalline cellulose. This can be demonstrated by the following equation (36):

\[ A = \omega \pm (100 - \alpha) \]

where \( A \) is the percentage of accessible cellulose in the sample, \( \omega \) is the fraction of the cellulose occurring in the surface of the crystalline region, and \( \alpha \) is the percentage of crystalline cellulose in the sample. From the above equation, it immediately follows that \( A \) is dependent upon the size of crystallite as well as the fraction of crystalline cellulose. Since \( \omega \) is not easily determined, most chemical methods do
not make adequate distinction between accessible and non-crystalline cellulose. If an accurate result is required, this equation should be taken into account.

Both chemical and physical methods give the crystallinity in either absolute or relative values. The absolute values do not agree with one another because of the different assumptions involved in the interpretation as noted. The difference is particularly distinct between the acid hydrolysis method and the X-ray method, which will be described in detail in a later section. The relative order of crystallinity for various cellulose preparations as determined by both methods is the same. The order of increasing crystallinity is as follows: high-tenacity rayon, textile rayons, Fortisan, mercerized cotton, wood pulp, and cotton.

The methods for determining crystallinity so far published in the technical literature are described below.

(a) **Chemical methods**

1) **Acid hydrolysis method**

The basis of the acid hydrolysis method is that the intercrystalline chain network is chemically more reactive than is the inaccessible cellulose in the crystalline region. Thus the disordered chain segments are more rapidly attacked by the acid, and the amount of non-crystalline cellulose is estimated from the rate of hydrolysis.
Nickerson was the first to apply the rate of hydrolysis in H Cl - FeCl₃ reagent to evaluate the accessibility of cellulosic materials (96,97,98,101,102,103). The cellulose is first hydrolyzed to glucose, which is then oxidized to CO₂. By comparing the rate of CO₂ evolution with that of glucose oxidized under similar conditions, the rate of hydrolysis is calculated and plotted against the time of hydrolysis. The hydrolysis rate curve thus obtained gives two different rates, being rapid during the first two or three hours of reaction period and then slowing at a later stage. Accessibility is determined by extrapolating the slow rate period to zero time. The reproducibility of this technique was greatly improved by Conrad and Scroggie (22).

Two more independent investigations (80,95) were undertaken in which the resistant residue was used as a means of following the course of hydrolysis. Other hydrolyzing agents, such as sulfuric acid, have also been used instead of hydrochloric acid, but it was found that sulfuric acid was less active as a hydrolyzing agent than hydrochloric acid of equivalent concentration (103).

In general, acid hydrolysis gives considerably lower values of the amorphous fraction as compared with other methods. This is particularly true as compared with the X-ray method. The probable reason for this fact is that the cutting of intercrystalline chain segments removes restraints and allows the loose chain ends freedom to undergo recrystallization.
ii) Deuteration method

Bonhoeffer (12) was the first to observe the reaction of heavy water with the OH group of cellulose. Later Champetier and Viallard (15) claimed that filter paper and lint cellulose were completely accessible to D$_2$O and that exchange was completed in 36 hours at 30°C. Frilette, Hanle and Mark (36) devised a method of digesting pulp in water of high deuterium content. Exchange of H$_2$O and D$_2$O was permitted to occur and the rate of absorption of D$_2$O was determined as a function of time. By using a similar method with improved technique, these investigators obtained a rate curve in which the initial rapid reaction gradually slowed down and became virtually complete in four hours. The fraction which had not reacted after four hours was identified as highly ordered material. This conclusion was further confirmed by Rowen and Plyler's studies by means of infra-red spectroscopy (121).

Quantitative study of deuteration by infra-red spectroscopy was extended by Almin (1), and followed by Mann and Marrinan (83, 87). The latter demonstrated the possibility of distinguishing between the deuteration of the crystalline and that of the amorphous region from the shape of the absorption band in the 3600 to 3000 cm.$^{-1}$ range. They also found that the isotopic exchange reaction between the OH group of cellulose and liquid D$_2$O gave a measure of accessibility and not the crystallinity of cellulose. By deuteration in the vapor phase it was possible to avoid
deuterating crystalline regions, thus an estimate of the percentage of crystallinity was obtained. In this case, the crystallinity of cellulose was defined as the fraction of OH groups which were hydrogen-bonded in a regular crystalline manner. The relative value of crystallinity determined by this method agreed reasonably well with values found by Hermans (83). Since no crystallization takes place during the determination, the value of accessibility is, therefore, much higher than that evaluated by an acid hydrolysis method.

iii) Cellulose derivative method

Determination of accessibility by etherification was illustrated by Assaf, Hass and Purves (7). Cellulose was treated with thallous ethylate to form a thallous derivative, which reacts with methyl iodide to yield thallous iodide and methyl cellulose. Analysis of methyl cellulose for methoxyl content yields a measure of the accessible OH groups. This method can be carried out in a non-aqueous system as well as an aqueous system. The latter system usually gives higher accessibility value than the former one because of swelling due to the medium. The result actually obtained by these workers in a non-aqueous system was the lowest accessibility value ever reported for the chemical method (110).

Tarkow (144) and Nickerson (99) have demonstrated a formic acid esterification procedure for evaluation of accessibility of cellulose. This method is based on the
assumption that the esterification of white dextrin and cellulose are identical chemical processes. The ratio of combined formic acid for cellulose to that of dextrin, under identical conditions, provides an estimate of the accessible fraction of cellulose.

iv) Oxidation method

The oxidation of cellulose with sodium periodate in aqueous solution was studied by Goldfinger, Mark and Siggia (40). The periodate ion is known to attack the second and third position of the glucose anhydride unit by splitting the glycol configuration and converting it to two carbonyl groups. A reaction rate curve similar to that of acid hydrolysis was obtained. By extrapolation of the extremely slow rate curve, the amount of amorphous component was evaluated. Recrystallization probably takes place during the oxidation (110).

Roseveare and Spaulding (120) demonstrated another oxidation method by treating cellulose with nitrogen dioxide in carbon tetrachloride. It has been shown (37,120) that chromic acid acts very largely on the amorphous region while periodic acid acts on the crystalline region as well. Thus Glegg (38) oxidized cellulose with chromium trioxide in acetic acid-acetic anhydride solution and evaluated the accessibility. This method showed a fairly good correlation with the thallous ethylate method over a 200-fold range of accessibility (7).
v) **Iodine sorption method**

In order to know the mercerization effects on cellulose and the degree of mercerization, Schwertassek developed a technique for determination of iodine sorption \(124,125,126,127\). On the basis of his series of experiments, he concluded that iodine sorption could be used as a measure of the amorphous fraction of cellulose. A decrease in iodine sorption is an indication of an increase in crystallinity. The method was applied by Hessler and Power \(59\) in the study of various treatment effects on cotton cellulose. A ratio of the weight of \(I_2\) absorbed by cellulose to that absorbed by methocel gave a value for the amorphous fraction. The crystallinity was obtained by subtracting the percent of amorphous material from 100.

Results were in good agreement with the value obtained by other chemical methods. To apply this method, the temperature at which the adsorption is carried out should be specified, since the adsorption is greatly dependent upon the temperature, as claimed by Chitale \(16\). This method was also criticised by Majury \(82\), who showed that the sorption of iodine by cellulose acetate could not be interpreted solely in terms of sorption by amorphous materials. Thus quantitative application of this method to cellulose fibre may need to be reviewed.
(b) Physical methods

i) X-ray method

Among the physical methods, the X-ray method is the most widely used quantitative method for crystallinity evaluation. Since it is applied in this study, a more detailed description of its principle and procedure is given in this section.

When a fibre sample is exposed to a narrow X-ray beam, the interference corresponding to the crystallographic plane gives rise to selective diffraction which appears on an X-ray diagram as black spots. Generally speaking, cellulose produces three intense interference spots arranged symmetrically along the equator of an X-ray diagram. These three interference spots are diffracted from the 101, 10\bar{1} and 002 plane of the unit cell respectively. For wood fibres, the X-ray diagram shows only two interference spots since the interference caused by the 101 and 10\bar{1} planes are combined. If the randomly oriented fibre specimen is rotated at constant speed during the X-ray exposure, two distinct interference rings appear instead of two interference spots.

A densitometer curve along the equator of the X-ray diagram is usually reproduced from the X-ray diagram. Two interference spots or interference rings will appear as two interference peaks in the densitometer curve. From this curve, the intensity, position, and radial width of the interference
peaks can be measured. These parameters are used to calculate data pertinent to fine structure of cellulose, such as the dimension of a unit cell, orientation of cellulose molecular chains, size of micelles, and degree of crystallinity.

As far as the degree of crystallinity is concerned, the intensity of the interference peaks and the diffuse background are generally taken as a measure of crystallinity. The crystallinity in this case is defined as the fraction of cellulose which gives rise of selective diffraction of X-rays (44). This definition assumes that the crystalline portion of cellulose represents a certain degree of order in the chain system which would reflect itself as X-ray diffraction intensity of a definite magnitude. This assumption is based on the presupposition that the degree of order of the crystalline areas of cellulose is practically constant in all types and crystal modifications of cellulose.

According to the concept of lateral order distribution mentioned in the previous section, this assumption is not always true. Furthermore, the assumption that diffuse background is solely caused by the amorphous fraction, is also doubtful. The surface layer of micelles will also contribute to some extent to the X-ray background scattering as non-crystalline material, because the surface of micelles represents a discontinuity causing some displacement of the chains. This means that decreasing size of the micelles will increase the background scattering. These two points should be
understood before the X-ray method is applied.

X-ray methods so far developed can be summarized below. The first quantitative study of crystallinity by the X-ray method was made by Hermans (46). An X-ray photograph was taken by exposing the fibre specimen in the form of a pellet. The total amount of incident radiation received by one specimen during the exposure was measured by a miniature camera to compare with that of other specimens for the purpose of correction. A radial photometer trace was then taken from one of the exposed quadrants of the X-ray diagram. The integrated intensity of the crystalline interference above the background was considered as a measure of the crystalline fraction, whereas maximum intensity of the background scattering was used as a measure of the fraction of disordered cellulose. A similar assumption was applied later by Kast and Flaschner (31, 69), and Clark and Terford (19). This method has been extensively applied by Hermans and his co-workers in establishing absolute value of crystallinity for different types of cellulose (45, 47, 48, 49, 50, 51, 52, 54).

Although Hermans' method gives an absolute value of crystallinity, it does not necessarily mean that all crystalline regions are completely measured, because of the fact that very small crystalline regions will not contribute to the X-ray maxima. Moreover, this method requires a special type of camera and a rotating sample holder, so that in most cases this method is not easily adopted for routine
purpose. A simple technique with reasonable reproducibility may be much more practical in the case where only relative variation of crystallinity is of interest to the investigator.

Several techniques have been developed during the last few years. These techniques generally use X-ray equipment which is available in most laboratories. The crystallinity is calculated by a simple formula which gives relative rather than absolute crystallinity. Wakelin, Virgin and Crystal (148) have demonstrated an integrated method and a correlation method by using Geiger Counter instrumentation. The result was expressed as a crystallinity index. Ant-Wuorinen (5,6) developed another crystallinity index using the Debye-Scherrer powder technique. The width and height of the 002 peak on the photometer intensity curve were used as a measure of crystallinity. The technique was later improved by Kouris, Ruck and Mason (72,73). The application of an X-ray spectrometer was illustrated by Anker-Rasch and McCarthy (3,4). The intensity of the 10\overline{1} peak was taken as a measure of crystallinity and results were expressed as a crystallinity ratio. Ingersoll (65) also used this peak to evaluate the crystallinity number. Sobue and Minato (133) simply took the area surrounded by the intensity curve (including 101, 10\overline{1} and 002 peaks) and background curve as the crystallinity area for comparison of relative order of crystallinity.
ii) **Moisture regain method**

Hermans was the first to establish the relationship between the sorption ratio \( (SR)^2 \) of cellulose, and amorphous content as estimated by the density or X-ray method \( (43) \). The regression line gave the equation:

\[
SR = 0.07 + 3 (1 - \alpha)
\]

where \( \alpha \) was the fraction of crystalline material. Thus, if the SR is determined experimentally, then the crystallinity is readily calculated from the equation. According to this equation, the sorption ratio of completely amorphous cellulose is 3.07.

Howsmon \( (63) \) also showed that there was an approximately linear relationship between the sorption of cellulose and accessibility to liquid D\(_2\)O-H\(_2\)O mixture. Assuming that the moisture regain was a measure of accessibility, and that Mark's value \( (35) \) for the accessibility of cotton (0.44) was correct, Howsmon obtained the accessibility of other cellulose preparations by multiplying their sorption ratio by 0.44. Later, this value was changed to 0.40 \( (110) \). The relationship between sorption ratio and the fraction of amorphous materials, as measured by Mann and Marrinan \( (83) \), was also illustrated by Valentine \( (147) \) with a regression equation

\(^2\)Sorption ratio (SR) is the ratio of moisture sorption of a specific cellulose to that of cotton under the same conditions \( (146) \). Since the sorption ratio is independent of the temperature and relative humidity over the range of 20 to 70 percent \( (110) \), it is often convenient to use sorption ratio rather than absolute absorption.
SR = 2.6 F_m, where F_m was the amorphous fraction and SR was the sorption ratio.

Magne, Portas and Wakeham (81) calculated the relative amount of frozen water (capillary condensed or solvent water) and unfrozen water (bound water) from calorimetric data. Assuming that three molecules of water were absorbed by each glucose anhydride unit, he was able to calculate the degree of crystallinity. Recently, Preston and Tawde (114) also determined the bound water in fibres, and found a direct correlation between the bound-water ratio (i.e., the bound-water relative to that of cotton) and the sorption ratio. The bound-water ratio of hydrate cellulose (123), which they assumed to be completely amorphous, may be calculated from their data to be 3.2, thus leading to a sorption ratio of the same value.

Heat of wetting also may be used as a measure of the amorphous fraction of cellulose because highly amorphous cellulose always gives a high value of heat of wetting (151). There is a strong correlation between sorption ratio and heat of wetting, i.e., the higher the heat of wetting, the higher will be the sorption ratio, so that the application of heat of wetting for determination of crystallinity is generally replaced by the sorption ratio or moisture regain method.
iii) **Infra-red absorption spectroscopy method**

The direct application of infra-red absorption spectroscopy into the field of crystallinity studies was ignored until Forziati and Rowen (33,34) demonstrated the spectra of cotton before and after grinding in a vibrating ball mill. They found that the spectra of cellulose I showed sharp and clearly defined absorption bands at 7.0, 7.3, 7.4 and 7.5 micron wave lengths. When the cellulose I is converted into amorphous material by grinding in a vibrating ball mill, these maximum absorption bands merged into a single broad band, and the absorption at 11.2 microns increased.

O'Connor, Dupre and Mitcham (108) made use of this fact and took the relative change of optical density of the absorption bands at 6.9 microns and 11.0 microns as measures of crystallinity. The absorption bands at 6.9 microns and 11.0 microns represented crystalline bands and an amorphous band respectively. The ratio of the absorbance of the band maximum, at about 6.9 microns, to that at about 11.0 microns, was defined as the crystallinity index. The assignment of a crystalline band to a particular wave length is dependent upon types of cellulose under question. Sandeman and Keller (122), for example, assigned absorption bands at 10.7 microns in the spectra of nylon 6, at 10.67 microns in the spectra of nylon 6.6, and at 10.64 microns in the spectra of nylon 6.10, as crystalline bands. For the wood-fibre cellulose
prepared from western hemlock, the writer found that the crystalline band could be assigned at 7.2 microns and the amorphous band at 11.2 microns.\(^3\) Sobue and Fukuhara (132), on the other hand, took the ratio of the optical density at absorption caused by OH stretching (3315 cm.\(^{-1}\) for ramie and 3440 cm.\(^{-1}\) for viscose respectively), to that caused by CH stretching at 2900 cm.\(^{-1}\), as a measure of crystallinity.

\(^{4}\) **Density method**

For a given weight of fibre, the result of a density determination will depend on the extent to which the medium penetrates into the amorphous region, which is the only region allowing the molecules of the medium to penetrate. On this basis, it is logical to presume that the density of packing of fibrous substance provides a reasonable criterion for the quantitative separation of the crystalline and the amorphous portion. Hermans and his co-worker (43,53) estimated the absolute quantity of the crystalline substance by assuming that the difference between the specific volume of the crystalline substance, and that of the amorphous state, are of the same order for cellulose as they are for other organic substances. The results were in good agreement with other physical methods.

It was also suggested that determination of dry density, possibly by the use of a density gradient tube, should

\(^3\) Unpublished data.
provide a convenient method for determining an approximate value of the crystallinity of cellulose fibre (92).

3. Treatments affecting crystallinity

From the foregoing description, it follows that the crystallinities of various cellulosic materials are different from one another, and the absolute value of crystallinity of the same cellulose is also variable depending on the method applied. Furthermore, the initial crystallinity of cellulose can be modified to give higher or lower values by various mechanical and chemical treatments. The purpose of this section is to discuss some major effects of various treatments on crystallinity, and also their significance from the point of view of application to the study of fine structure of cellulosic materials.

(a) Hydrolysis

Meller (88), Ingersoll (65), and Howsmon (63) have shown that the crystallinity of cellulose will be considerably increased after hydrolysis. Both removal of amorphous material by acid attack, and recrystallization of cellulose molecular chains, are responsible for such an effect. The reason is that molecular chains in the amorphous region, once ruptured by acid attack, tend to increase the mobility of the chain end and allow them to rearrange themselves in a much more compact form. The increase in crystallinity by hydrolysis can be shown clearly by X-ray diagrams in which
the intensity of the 002 peak and the 101 + 10\(\bar{1}\) combination peak will increase markedly after hydrolysis.

The fact that the rupture of the chain starts from the amorphous region can be observed from the reaction-rate curve of hydrolysis. During the initial stage of reaction, the chemical reagents penetrate rapidly into the amorphous region. Most of the rupture of the chains takes place at this stage, thus the reaction proceeds at a very rapid rate. As soon as the amorphous region has been destroyed, the reaction will be slowed down because the chemical reagent does not readily penetrate into the crystalline region, but merely attacks the surface of the crystallite. Consequently, the size of the crystallite will gradually decrease as the time of hydrolysis is prolonged (64,11). The percentage of residue recovered will decrease proportionally with time of hydrolysis, but the crystallinity of residue will increase significantly. The rate of increase in crystallinity due to hydrolysis follows a curve similar to the hydrolysis rate curve. The hydrolysis method is generally used to prepare a cellulose standard of high crystallinity (83,87,148).

(b) **Heat**

If the cellulose is dried under heat without a prolonged drying time, its crystallinity is affected to a lesser extent. For instance, very little change in chemical nature takes place when cellulose is heated at a temperature
of 140°C for less than four hours (28). It has been shown (32,39,62,119) that at a sufficiently high temperature, cellulose undergoes both chemical and physical modifications and the molecular chains will be disordered due to a thermal effect.

Hessler and Power (59) observed that surface heat was more effective in opening the crystallite than hot air. Cotton rotated against a hot surface for a few minutes showed a drop in crystallinity from 89 percent to 79 percent as determined by the iodine sorption method. Taniguchi (143) claimed that crystallinity of sulphite pulp decreased on heating with hot air for 1 to 2 hours at 110 to 245°C. The decrease was particularly remarkable as the temperature was increased.

(c) **Mechanical decrystallization**

Grinding and vibrating in a ball mill will cause an appreciable decrystallization (33,34,45,58,72,94,108,136,137). In this case fibres are disintegrated into very fine powder which does not show selective diffraction on an X-ray diagram, but increases the background scattering caused by amorphous particles (72,110). In the infra-red absorption spectrum, this fine powder will show an increased absorption at the amorphous band and decreased absorption at the crystalline band (34,108).
The mechanism for this type of degradation can be explained from the point of view of mechanical impact and stress cycling. If the kinetic energy produced by the impact of the balls on the cellulose fibres is converted directly into molecular vibrational energy, it is sufficient to cause rupture of the primary valence bonds (137). The impact of the balls on the container evolves a considerable amount of heat. By means of the Congo red test, it was shown that the rupture of the cellulose chain was the result of mechanical action rather than a thermal phenomenon (110,137). Mechanical decrystallization is commonly used for the preparation of an amorphous standard in the X-ray method as well as in the infrared absorption spectroscopy method.

(d) Degradation by microorganisms

Decay of cellulosic material is attributed to the enzymes which are secreted by microorganisms. The amorphous regions are loosely compacted and readily available for penetration of enzymes, which, like other chemical reagents, attack the amorphous regions at a relatively rapid rate in the initial stage of decay. The rate of attack will slow rapidly when the enzymes start to attack the crystalline regions.

As a result of such attack, the amorphous materials are dissolved away and the broken chains themselves tend to recrystallize. Hence, during the incipient stage of decay, an appreciable increase in crystallinity could be expected. The
rate of increase in crystallinity is approximately a function of rate of breakdown of cellulose chains by enzymes (110, 131). The rate curve is similar to that of acid hydrolysis. It should be noted, however, that the action of microorganisms is slightly different from that of acid hydrolysis in that the former does not decrease the degree of polymerization (110,151), whereas the latter markedly depolymerizes the cellulose chains (26,163). Some workers claim that enzymatic hydrolysis will also cause considerable depolymerization (30,41,61,76,106,107,159). Thus a controversy still exists on this point.

(e) **Lattice transition**

1) **Transition from cellulose I to cellulose II**

When native cellulose is treated with a certain concentration of sodium hydroxide (mercerization), the lattice structure is changed and cellulose II is formed. Treatment with about 61 percent nitric acid followed by washing also results in the same transition (2). This transition changes not only the dimensions of the lattice unit cell as revealed on the X-ray diffraction pattern, but also the degree of crystallinity of cellulose, which will be decreased due to mercerization (3,54). This is caused mainly by the disordering of the cellulose molecular chains produced by the penetration of sodium hydroxide molecules into the lattice during the mercerization, with the result that the
amorphous region increases at the expense of the crystalline region.

Anker-Rasch and McCarthy (3) made use of this characteristic to study the concentration of sodium hydroxide at which the lattice transition was completed, by following the variation of crystallinity. When the transition took place, the crystallinity decreased rapidly. Higgins (60) also studied the lattice transition by infra-red absorption spectroscopy and found that when lattice transition took place, the absorbency at 7.0 microns decreased, and that at 11.2 microns increased. Since the crystallinity decreases at this point, the relative absorbency at these two wave lengths could be taken as the measure of crystallinity. This gives additional evidence that the assignment of a crystalline band at about 7.0 microns and an amorphous band at about 11.2 microns is acceptable.4

ii) Transition from cellulose I to cellulose III

On treatment of cellulose I with ethylamine, cellulose III is obtained. A decrease in crystallinity is inevitable because of the intracrystalline swelling due to ethylamine (9,18,78,79,128,129). A highly amorphous cellulose, therefore, can be obtained by treating cellulose with ethylamine followed by evaporation of the amine at atmospheric

4See page 28.
pressure. This is sometimes done in order to prepare an amorphous standard for the study of crystallinity (108,148).

iii) **Transition from cellulose II and III to cellulose IV**

When cellulose II or cellulose III is heated at temperatures between 140 to 300°C in water under pressure, in glycerol, or in formamide, cellulose IV is formed (75,91). The crystallinity of cellulose IV is significantly higher than that of cellulose II or cellulose III.

(f) **Pulping**

The effect of pulping on crystallinity of pulp was well demonstrated by Taniguchi's series of experiments. Following the curve of changes in crystalline regions during sulphate pulping, he found that the crystalline region content of bleached pulp and viscosity decreased gradually, and the rate of decomposition increased with the length of pulping time (141). The sulphate pulp was bleached by 2-, 3-, and 5-stage methods and the crystallinity as determined by the hydrolysis method was found to be 91.60, 92.45, and 92.63 percent respectively (138). However, negligible differences in crystallinity of pulp bleached by NaC1O2 and Ca(C1O)2 were observed in his later works (139,140). He also showed that the crystallinity of sulphite pulp increased on heating with water for two hours at 100 to 190°C, but decreased on heating with hot air for 1 to 2 hours at 110 to 245°C. The rate of
decrease in crystallinity increased with temperature (143).

The effect of beating on crystallinity was observed by Wijnman (160). He claimed that when purified cotton fibres were subjected to heavy beating in a Jokro mill, a marked decrease was observed in the degree of polymerization, together with a moderate reduction in the average size of crystallite and a small reduction in crystallinity. Groundwood pulp was found to give high capacity of sulfuric acid sorption (117), which indicates that the groundwood pulp might have a relatively high value of accessibility.

(g) Stretching

Stretching usually causes an increase in crystallinity. For instance, it was estimated that a normal coagulated viscose filament was about 40 percent crystalline and 60 percent amorphous, whereas filaments of the same material after being stretched, appeared to be 70 percent crystalline and 30 percent amorphous (100).

4. Relationship between crystallinity and properties of cellulose

The relationship between crystallinity and chemical reactivity, density, moisture regain, and dye sorption in terms of iodine sorption have been described in detail. The present discussion is confined to the relationship between crystallinity and remaining properties of cellulose.
(a) Young's modulus

It has been pointed out by Mark (161) that uncrystallized and poorly organized chains will exhibit elasticity of the type which has been recently investigated in highly elastic long polymers. Measurements and calculations of various workers (161) also showed that the presence of long flexible chains led to a reversible elasticity, with modulus of about $10^6$ to $10^7$ dynes per sq. cm. and a rather high range of extensibility. On the other hand, if a force is applied to a homopolar covalent bond and the assumption is made that the sample under investigation is made up of infinitely long, uninterrupted, parallel chains, a modulus of elasticity is obtained of about $2 \times 10^{12}$ dynes per sq. cm. This would correspond to a completely crystallized and perfectly oriented material.

Cellulose can be considered as a mixture of crystallized and amorphous regions in which the former have an average elastic modulus of about $10^{11}$, whereas the latter have one of about $10^6$ dynes per sq. cm. (161). Applying this idea, Hermans and co-workers (44), and others (85), explained the long-range, low-modulus, elastic behavior of cellulose by two moduli. The one which corresponded to the crystalline parts had the order of magnitude of $10^{11}$ to $10^{12}$ dynes, and the one which corresponded to the amorphous region had an order of $10^6$ to $10^7$ dynes per sq. cm. In short, from the point of view of a chain model, high modulus is theoretically
understood to be associated with a high degree of crystallinity.

(b) **Tensile strength**

If it is assumed that a sample consists of uninterrupted parallel glucosidic chains, a theoretical tenacity of about 400,000 kg. per sq. cm. could be expected (10). In the case of completely parallel, overlapping chains, having an average degree of polymerization of 500 glucose units, this value has been calculated to be 12,500 kg. per sq. cm. (10,90). From the theoretical point of view, the crystallite forms the firm reinforcing part of the structure, whereas the amorphous regions are the actual points of weakness (100). It follows that cellulose of high crystallinity usually has high tensile strength.

On the other hand, both the orientation of micelles and cellulose chain length distribution are also found to be important factors affecting tensile strength (14,21,29,56,86,109,118,135,158). The interactions among these factors are so complicated that one can hardly establish a relationship between crystallinity and tensile strength alone. Ingersoll (65) has shown by a partial linear correlation technique that at a constant wet elongation and orientation, wet tenacity is no longer significantly associated with lateral order. Thus, the degree of crystallinity alone might not be a critical factor which affects the tensile strength.
(c) **Elongation**

Mark (85) has proposed that flexibility and reactivity of cellulose are dependent upon the disordered region of cellulose, whereas the tenacity and elastic modulus are related to the amount of ordered materials. This is confirmed by various experimental data. For example, Ward (151) demonstrated that yarns from cottons of decreased crystallinity did have increased elongation as compared with that of the original cotton. Conrad and Scroggie also found that elongation increased with accessibility (22). Similar results were obtained by Ingersoll (65), who claimed that when orientation and wet tenacity were kept constant by the method of partial linear correlation, the relationship between wet elongation and lateral order remained statistically significant.

(d) **Alpha-cellulose content**

Conrad and Scroggie (22) demonstrated that a decrease in accessibility or an increase in crystallinity, in general, was paralleled by an increase in alpha-cellulose content of the raw material. The decrease in accessibility may arise from somewhat smaller amounts of relatively low-molecular-weight materials such as beta and gamma cellulose in the high-alpha-cellulose material. Actual experimental results (22) showed that xylose and pentosan evolved CO₂ at a rate higher than cellulose or even glucose. An increase in
accessibility should therefore occur when materials of this type are present. The general relation between alpha-cellulose content and crystallinity is shown in Table 2.

Table 2. Relationship between alpha-cellulose content and crystallinity of cellulose (22)

<table>
<thead>
<tr>
<th>Source</th>
<th>Alpha-cellulose content (%)</th>
<th>Accessibility* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood pulp from beech</td>
<td>88.5 - 89.0</td>
<td>11.5</td>
</tr>
<tr>
<td>Wood pulp from southern pine</td>
<td>93.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Wood pulp from western hemlock</td>
<td>91.5</td>
<td>9.0</td>
</tr>
<tr>
<td>High-alpha wood pulp from southern pine</td>
<td>94.5 - 95.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Cotton linters</td>
<td>98.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*Determined by acid hydrolysis method

(e) **Swelling and dimensional stability**

As far as swelling due to water is concerned, it can be considered as the final result of penetration of water molecules into the cellulose inter-molecular chain region, which, in turn, causes an expansion in volume. In order to penetrate between two cellulose molecular chains, a water molecule should have enough energy to overcome the lattice energy or to break the secondary bonds between cellulose molecular chains. This can be done easily in amorphous regions or on the surface of crystallites where the inter-molecular chain bondings are weak, but not in the crystalline region. Therefore, it is reasonable to expect that swelling
will decrease as the crystallinity is increased.

This is confirmed by the fact that swelling decreases as fibre density increases. For example, a rayon which swells 160 percent of its initial volume has a density of 1.503, whereas cotton which swells only 50 percent has a density of 1.534 (100). It should be reemphasized that both degree of crystallinity and size of crystallite play an equally important role in the absorption of moisture and swelling of cellulose.

Based on the characteristic nature of the amorphous and the crystalline region so far discussed, the results shown in Table 3 can be expected if the degree of crystallinity of cellulose is increased.

Table 3. Variation in cellulose properties as crystallinity increases (110)

<table>
<thead>
<tr>
<th>Increase</th>
<th>Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>density</td>
<td>moisture regain</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>dye sorption</td>
</tr>
<tr>
<td>tensile strength</td>
<td>chemical reactivity</td>
</tr>
<tr>
<td>alpha-cellulose content</td>
<td>swelling</td>
</tr>
<tr>
<td>dimensional stability</td>
<td>elongation</td>
</tr>
<tr>
<td>hardness</td>
<td>flexibility</td>
</tr>
<tr>
<td></td>
<td>toughness</td>
</tr>
</tbody>
</table>
EXPERIMENTAL METHOD

A. Materials

The study consists of three parts, as follows:

Part I: Crystallinity of normal wood of various ages and seasons, i.e., summerwood and springwood.

Part II. Crystallinity of reaction wood (compression wood and tension wood.

Part III: Crystallinity of decayed wood.

For part I, a cross-section disc was taken from a 33-year old tree of western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) at a height ten feet above ground. Several small sample blocks were prepared from the 3rd, 9th, 15th and 21st growth ring from the pith at randomized positions within the ring, and separated with a chisel into springwood and summerwood. The innermost portion (about 1 mm. thick) of each ring was taken as the springwood sample and the outmost portion (about 1 mm. thick) of each ring was taken to represent summerwood. Microscopic examination showed that the summerwood sample contained about 50 percent of springwood tracheids. A fibre was considered as a springwood tracheid if the radial width of its cell lumen exceeded twice the cell wall thickness.

The compression wood used in part II was obtained from an 80-year old Douglas fir (*Pseudotsuga menzeisii* (Mirb.))
Franco). The compression wood sample included the 15th to 18th growth rings, whereas the normal wood sample taken from the diametrically opposed position, included from the 13th to 21st growth rings from the pith, which gave the same average age in both cases. For the tension wood sample, a leaning 28-year old northern black cottonwood (*Populus trichocarpa* Torr. and Gray) was sampled. Tension and normal wood samples taken at breast height on opposite sides were of the same age, i.e., 20th to 24th years from the pith.

The decayed wood specimens used in Part III were obtained by treating sample blocks matched to those used in Part II with two brown-rot organisms, *Poria incrassata* and *Poria monticola*. Treatment which caused about 6 percent weight loss due to *Poria incrassata* was designated as stage A, whereas that which resulted in 15 percent weight loss due to *Poria monticola* was designated as stage B.

**B. Statistical design**

In part I, two factors were involved.

Factor A: Four different ages, i.e., the 3rd, 9th, 15th and 21st growth ring from the pith.

Factor B: springwood vs. summerwood.

Since the summerwood sample contained about 50 percent of springwood tracheids, which might have obscured the differences existing in crystallinity between springwood and summerwood, the comparison of differences within factor B
required high efficiency. Therefore, a split plot design was applied in which factor A was assigned as the unit, while factor B was assigned as the sub-unit with three replications for X-ray system A (wood pulp) and two replications for X-ray system B (holocellulose).

In part II, both X-ray method A (wood pulp) and X-ray method B (holocellulose) were used as a randomized block design, with three replications for the former and two for the latter, respectively.

A split plot design was also applied in part III, in order to increase the efficiency for comparison of differences within treatment effects. Thus:

Unit: Four types of wood, i.e., cottonwood tension wood, cottonwood normal wood, Douglas fir compression wood and Douglas fir normal wood.
Sub-unit: Degree of decay, i.e., stage A (approximately 6 percent weight loss), stage B (approximately 15 percent weight loss) and control.

Two replications were found to be sufficient to show differences existing among types of wood and degree of decay.

C. Preparation of samples

Wood pulp and holocellulose samples were prepared for parts I and II of this study, whereas only holocellulose was used for part III. The former was used to prepare a cylinder-type specimen for X-ray method A, while holocellulose
was used to prepare a disc-type specimen for X-ray method B. Procedures for preparation of these samples are given below.

1. **Wood pulp sample**

   The sample blocks were split along the grain into small pieces, placed in test tubes and boiled in water for eight hours. The chips were then treated with a solution containing equal parts of 99.5 percent acetic acid and 30-35 percent hydrogen peroxide. The tubes were submerged in a hot water bath and heated at 100°C. for one hour. The samples were then washed with several runs of water and shaken into individual fibres. The pulp thus obtained was thoroughly washed with water for several days, to remove the last trace of acid, and finally dried at 50°C.

   A cylinder-type specimen, 15 mm. in length and 2 mm. in diameter, was prepared for X-ray exposure. To prepare such a specimen, it was necessary to separate the air-dried pulp into individual fibres by a needle, in order to eliminate the effect of fibre orientation on X-ray diffraction (3,46,65,72). Exactly 50 mg. of separated fibres were weighed and wetted with distilled water. The fibres were put into a glass tube with an inner diameter of 2 mm. A slight pressure was applied until the length of the specimen was reduced to 15 mm. The tube containing the specimen was then dried at 50°C. After two days, the specimen was pushed from the tube and dried in the open air. The specimen thus prepared was perfectly
cylindrical and smooth; otherwise it was rejected.

2. Holocellulose

Wood meal was obtained by grinding the sample blocks with a Wiley mill. Since crystallinity will decrease if the size of particle is too small, only the fraction which passed through a 20 mesh, and was retained on a 35 mesh sieve, was collected.

A modification of the chlorite method of Wise, Murphy and D'Addieco (162), suggested by Dr. A.P. Yundt, was used for preparation of holocellulose. The procedure can be summarized briefly as follows. To 0.7 g. of air-dried wood meal in an Erlenmeyer flask of 60 ml. capacity, were added 10 ml. of stock solution "A" containing 60 g. of acetic acid and 20 g. of sodium hydroxide per liter, and 1 ml. of stock solution "B" containing 200 g. of sodium chlorite per liter. The mixture was well stirred and heated in a hot water bath at 75°C. After .75, 1.5, and 2.5 hours, an additional 1 ml. of the stock solution "B" was added with stirring. After 4 hours heating, the flask was cooled in ice water. Then 15 ml. of ice water was added, and the solution was removed by filtration through mild suction. The residue was washed with 100 ml. of one percent acetic acid solution, followed by two 5 ml. portions of acetone, and dried in the open air.

---

Personal correspondence with Mr. J.M. Jaworsky.
One hundred and fifty mg. of the air-dried hollocellulose were put into a specially designed compression tube, and a gauge pressure of 1000 psi was applied for five minutes, using a laboratory press. The final disc-type specimen had a diameter of 14 mm. and a thickness of approximately 0.75 mm.

D. X-ray collimating system and procedure

1. Method A

The principle of the Debye-Scherrer powder technique was applied, as illustrated in Figure 2, page 48. This technique has been applied by Ant-Wuurinen (5) for determination of the crystallinity of cellulose. The Cu K alpha ray having a wave length of 1.54 Å was monochromized by a nickel filter and passed through a collimator. When this incident ray strikes the specimen rotating at one rpm, it produces symmetrical interference rings on the film. The specimen was set exactly at the center of the camera so that a maximum, constant amount of fibres were exposed to the X-ray. In order to create an unexposed area, the film was covered with a piece of lead foil at the inlet bottom of the collimator. This unexposed area gives a zero reading for the densitometer calibration to be described later.

A Philips X-ray machine (No. 12045) was operated at a voltage of 45 kilovolts and current density of 15 milliamperes. The machine was allowed to warm up for 30 minutes prior to
FIGURE 2. CAMERA ARRANGEMENT FOR THE DEBYE-SCHERRER POWDER TECHNIQUE

A - SOURCE OF X-RAYS
B - NICKEL FILTER
C - LEAD FOIL
D - COLLIMATOR (INLET)
E - ROTATING SPECIMEN
F - COLLIMATOR (OUTLET)
G - FILM
2θ - ANGLE OF REFLECTION

FIGURE 3. EFFECT OF X-RAY EXPOSURE TIME ON CRYSTALLINITY INDEX
introducing the first sample. In order to determine the optimum exposure time, a preliminary experiment was carried out. The results shown in Figure 3, page 48, indicate an optimum exposure time of 20 minutes. Kodak medical safety X-ray film was used. The film was developed by Kodak X-ray developer D-19 for 5 minutes, fixed in Kodak fixer for 10 minutes, and hung up for drying. The X-ray diagram thus obtained is shown in Figure 4.

Figure 4. Wood pulp X-ray diagram

To obtain quantitative data on the intensity of the diffraction pattern, a photovolt electronic densitometer (Model 525) was used. The zero reading of the densitometer was calibrated by the unexposed area of the film and its 100 percent reading, by putting a piece of lead foil on the film. The
film was mounted on a microscope equipped with a stage micrometer which controlled precisely the movement of film. The intensity reading at intervals of 0.2 mm. along the equator of the interference ring was plotted against the angle of reflection ($2\theta$) on graph paper. Since the inner diameter of the powder camera was 114.83 mm., one degree of the $2\theta$ corresponded to one millimeter on the film. The intensity curve thus obtained was the same as that obtained by method B shown in Figure 6, page 51.

2. Method B

A Geiger-counter X-ray spectrometer, type No. 12021, was used in this system. The spectrometer geometry is shown in Figure 5. A specimen was mounted on the glass specimen holder and fitted onto the sample post. The X-ray, which had been collimated by slit 1 (7 mm. x 1.5 mm.), hit the specimen and created an angle of reflection ($2\theta$) as shown in Figure 5. The diffracted ray was then filtered by a nickel filter and passed through slit 2 (4 mm. x 0.5 mm.) into a goniometer. The intensity of the diffracted beam registered by a goniometer was recorded automatically by a Brown Recorder (Model 153). A motor, attached to the end of the goniometer, drove it at a constant speed of $\frac{1}{4}$ rpm from reflection angles of 90° to 0°. The gear arm was set to run through a range of 32° to 10° only. The chart of the recorder was driven by a synchronous motor and could be calibrated directly in degrees per minute. The recorded chart, therefore, furnished a graph containing a
A - SOURCE OF X-RAYS
B - COLLIMATING SLIT NO. 1
C - SPECIMEN
D - NICKEL FILTER
E - COLLIMATING SLIT NO. 2
F - GONIOMETER
G - MOTOR DRIVE
2θ - ANGLE OF REFLECTION

FIGURE 5. SPECTROMETER GEOMETRY

FIGURE 6. X-RAY DIFFRACTION SPECTRUM
B - THE BREADTH OF THE 002 PEAK IN RADIANS
series of peaks proportional to the intensity of the diffracted X-ray beam plotted against the angle of reflection (29).

The X-ray machine was operated from a normal 20 volt, 60 cycle source of supply. The magnification scale on the Brown Recorder was set at 50. The diffraction pattern thus obtained is shown in Figure 5.

E. Evaluation of crystallinity

Since the primary purpose of this study was to compare the relative variation of crystallinity among certain types of samples under test, no attempt was made to evaluate the absolute crystallinity. Crystallinity was evaluated as a crystallinity index in X-ray method A (wood pulp), and crystallinity ratio in X-ray method B (holocellulose). The formulae applied are shown below.

1. Crystallinity index

Crystallinity index (Cr. I.) = \(1 - \frac{100 B}{I_{002} - I_{\text{min}}}\) 100,

where \(B\) is the breadth of the 002 peak expressed in radians, \(I_{002}\) is the maximum intensity of the 002 peak in arbitrary units, and \(I_{\text{min}}\) is the minimum intensity between the 002 peak and the (101 + 10\(\bar{1}\)) peak in the same arbitrary units. This formula was developed by Ant-Wuorinen (5) and has been applied in studies of relative transition of crystallinity due to various treatments (72). Because of the limited accuracy in
the measurement of intensity by the densitometer, the index was reported to one decimal only.

2. **Crystallinity ratio**

\[
\text{Crystallinity ratio (Cr. R.)} = \frac{I_{(10\bar{1} + 10\bar{1})}}{I_{(10\bar{1} + 10\bar{1})} + I_{\text{min}}} \times 100,
\]

where \(I_{(10\bar{1} + 10\bar{1})}\) is the maximum intensity of the combined \((10\bar{1} + 10\bar{1})\) peak, and \(I_{\text{min}}\) is the minimum intensity between the 002 peak and the \((10\bar{1} + 10\bar{1})\) peak in arbitrary units.

The intensity should be corrected by subtracting background intensity, if the claim of Anker-Rasch and McCarthy (3) is valid. Since the nature of the specimen holder used in their experiment was different from that used in this experiment, it was necessary to determine whether a background correction was necessary.

To do this, two diffraction intensity charts were prepared, one with both specimen and sample holder, the other, with the specimen only. Comparison of these two charts showed that the former gave a slightly higher intensity on the average due to some reflection caused by a specimen holder, but the difference was so small that it could be neglected. Accordingly, the intensity was corrected by subtracting the initial reading from the \(I_{(10\bar{1} + 10\bar{1})}\) and \(I_{\text{min}}\) reading on the intensity chart. The crystallinity ratio thus calculated was reported to the nearest hundredth.
RESULTS AND DISCUSSION

A. Part I: The degree of crystallinity of pulp and holocellulose of normal wood

1. Results

The results shown in Table 4, page 55, and Figure 7, page 56, indicate that crystallinity of both wood pulp and holocellulose increases with age from pith for about 15 years, then reaches a more or less constant value. The crystallinity of summerwood pulp and of holocellulose, is also higher than that of the comparable springwood specimens. These differences in crystallinity are found to be clearly significant on analysis of variance, as shown in Table 5, page 57. Further analysis shows that the difference in crystallinity between the 15th and the 21st growth rings is non-significant. This implies that the crystallinity of juvenile wood tracheids increases with age, whereas that of mature wood tracheids is more constant, exhibiting negligible variation. Maturity in this case is defined as the age at which the curve of crystallinity vs age flattens.

The numerical value of crystallinity index and crystallinity ratio obtained in this study is considerably lower than those obtained by other workers. The range of crystallinity index of wood pulp in the present result is
Table 4. Effect of age and season on crystallinity of wood pulp and holocellulose

<table>
<thead>
<tr>
<th>Season</th>
<th>Specimen</th>
<th>Crystallinity index -X-ray method A- (wood pulp)</th>
<th>Crystallinity ratio -X-ray method B- (holocellulose)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3* 9 15 21</td>
<td>3 9 15 21</td>
</tr>
<tr>
<td>Summer-wood</td>
<td>1</td>
<td>53.4 55.4 56.3 58.1</td>
<td>54.56 54.88 55.51 55.52</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>53.3 54.2 57.5 58.0</td>
<td>54.31 54.73 55.28 55.63</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>53.0 54.9 57.3 56.9</td>
<td>54.44 54.81 55.40 55.58</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>53.2 54.8 57.0 57.7</td>
<td>54.44 54.81 55.40 55.58</td>
</tr>
<tr>
<td>Spring-wood</td>
<td>1</td>
<td>53.1 55.0 57.0 56.5</td>
<td>54.31 54.65 55.06 54.89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>52.0 54.4 56.3 56.4</td>
<td>54.21 54.76 55.00 55.05</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>52.2 54.6 56.4 56.2</td>
<td>54.26 54.71 55.03 54.97</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>52.4 54.7 56.6 56.4</td>
<td>54.26 54.71 55.03 54.97</td>
</tr>
</tbody>
</table>

*Age from pith, years.

52.0 to 58.1, whereas that obtained by Ant-Wuorinen (5) is 63.0 (bleached sulphite wood pulp), and that by Kouris, Ruck and Mason (72) is 70.6 (softwood dissolving wood pulp). The range of crystallinity ratio of holocellulose obtained in the present result is 54.21 to 55.63, whereas that obtained by Anker-Rasch and McCarthy (3) is about 64.5 (bleached sulphite cellulose containing 96.7 percent alpha-cellulose) to 65.0 (bleached kraft cellulose containing 93.4 percent alpha-cellulose). These are mainly due to the different types of cellulose examined.

The increase in crystallinity of wood tracheids during the immature stage (from the pith to the 15th growth stage...
**Figure 7. Variation of Crystallinity with Age and Season in Normal Wood**

(A) Wood Pulp - Crystallinity Index

(B) Holocellulose - Crystallinity Ratio
Table 5. Analysis of variance of crystallinity in Table 4

(A) Crystallinity index (wood pulp)

<table>
<thead>
<tr>
<th>Source of variance</th>
<th>D. F.</th>
<th>S. S.</th>
<th>M. S.</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>replication</td>
<td>2</td>
<td>0.77</td>
<td>0.385</td>
<td>1.774</td>
</tr>
<tr>
<td>age</td>
<td>3</td>
<td>69.44</td>
<td>23.147</td>
<td>106.668</td>
</tr>
<tr>
<td>error</td>
<td>6</td>
<td>1.30</td>
<td>0.217</td>
<td></td>
</tr>
<tr>
<td>Subunit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>season</td>
<td>1</td>
<td>2.80</td>
<td>2.800</td>
<td>13.462</td>
</tr>
<tr>
<td>AxS</td>
<td>3</td>
<td>1.07</td>
<td>0.357</td>
<td>1.716</td>
</tr>
<tr>
<td>error</td>
<td>8</td>
<td>1.66</td>
<td>0.208</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>23</td>
<td>77.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** Significant at 1 percent level
*** Significant at 0.1 percent level
N.S. Non-significant

(B) Crystallinity ratio (holocellulose)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>D. F.</th>
<th>S. S.</th>
<th>M. S.</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>replication</td>
<td>1</td>
<td>0.011</td>
<td>0.011</td>
<td>0.550</td>
</tr>
<tr>
<td>age</td>
<td>3</td>
<td>2.251</td>
<td>0.750</td>
<td>37.500</td>
</tr>
<tr>
<td>error</td>
<td>3</td>
<td>0.059</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>Subunit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>season</td>
<td>1</td>
<td>0.388</td>
<td>0.388</td>
<td>48.500</td>
</tr>
<tr>
<td>AxS</td>
<td>3</td>
<td>0.152</td>
<td>0.051</td>
<td>6.375</td>
</tr>
<tr>
<td>error</td>
<td>4</td>
<td>0.030</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>15</td>
<td>2.891</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** Significant at 1 percent level
N.S. Non-significant
ring) seems to follow a constant increment. This means that the apparent degree of crystallinity might be correlated with age, if the influence of prepared fibre orientation in the samples could be discounted. Such preferred orientation of fibre has been found to give rise to unpredictable changes in relative intensity of the corresponding interference pattern (46). Neglect of this effect during the X-ray exposure will cause a misleading interpretation in the experimental results (3,46,65,72).

The orientation effect was minimized in method A by careful preparation of sample, and rotation of specimen during the X-ray exposure. In method B, no rotation was applied during the X-ray exposure, so that only two-dimensional randomness of fibre was achieved rather than a three-dimensional one. A slight orientation effect was apparently inevitable in both X-ray methods. Since the present results are in good agreement with those obtained by Taniguchi (142), in which the orientation effect may be completely ruled out by the acid hydrolysis method, the results can hardly be considered as solely attributable to the orientation effect. It could be assumed that difference in crystallinity might actually exist among ages in the juvenile wood. Evidence supporting this point of view is shown below.
(a) **Tensile strength**

Wardrop (152) has illustrated that tensile strength of tracheids increases with tree age. Since an increase in tensile strength is usually accompanied by an increase in crystallinity, it is theoretically acceptable that the crystallinity increases with age. But this does not necessarily mean that an increase in tensile strength is solely attributable to an increase in crystallinity. Fibril angle and cellulose molecular chain length distribution are also important in this respect.

(b) **Alpha-cellulose content**

It has been shown that Cross and Bevan cellulose content (70,152), or holocellulose content (164), increases with age for a given period in certain species. Since there is a strong positive correlation between alpha-cellulose content and holocellulose content (164), as well as the Cross and Bevan cellulose content (70), it may be assumed that the alpha-cellulose content increases with age. If this is true, then the crystallinity can be expected to increase with age, since a cellulose of high alpha-cellulose content always gives a high degree of crystallinity (22).

---

6 cf. page 38.
(c) **Moisture regain**

The higher the crystallinity, the lower the moisture regain will be.\(^7\) Moisture regain data obtained by Wardrop (152) showed it to decrease with age. This indicates the following two possibilities:

i) Crystallinity might increase with age so that moisture regain would decrease with age.

ii) The hemicellulose fraction could decrease with age. In this instance, moisture regain would also decrease with age.

It has been noted by Ranby (11) that the lower lattice order of wood cellulose, as compared with that of cotton cellulose, should be due to the presence of other monosaccharides in the cellulose chains. Conrad and Scroggie (22) also claimed that an increase in accessibility will occur when relatively low-molecular-weight materials such as beta and gamma cellulose are present. If these workers are correct, then holocellulose near the pith, which contains higher hemicellulose as revealed by Zobel *et al* (165), should give lower crystallinity. This is in good agreement with the present results. Thus both of the above mentioned possibilities are theoretically acceptable.

The present results disagree with those obtained by Preston, Hermans and Weidinger (113), who found that the

\(^7\)cf. Table 3.
crystalline-non-crystalline ratio decreased with age. The samples used in their study were Cross and Bevan cellulose. According to the standard procedure for preparing the Cross and Bevan cellulose, the sample should be delignified until an end-point reached. The time of delignification required to reach this end-point for various samples is variable. If a sample taken near the pith is assumed to have a higher lignin content than one near the bark, then the time of delignification for the former should be relatively long, and the duration of recrystallization of cellulose chains during the delignification would be considerably prolonged. Consequently, the cellulose thus prepared might give higher crystallinity as compared with the one near the bark, even though the initial crystallinity was identical for both samples.

In both the present experiment and that of Taniguchi (142), time of delignification was kept constant. The final lignin content of each sample might therefore be variable since no end-point technique was applied. Thus the lower value of crystallinity observed near the pith may be due to a slightly higher lignin content in the pulp sample. The variation of extractive content may also affect the final result since it will influence the rate of penetration of chemicals, which in turn gives different degrees of delignification. If it is assumed that extractive content is higher near the pith, then its delignification would be
poorer than that near the bark when the time of delignification is kept constant for both samples. It is apparent that the method of sample preparation will critically affect the final results and will lead to different interpretations.

The observation that summerwood has higher crystallinity than springwood is in good agreement with Holzer and Lewis (57), and Lindgren (77). The difference in crystallinity between summerwood and springwood is smaller than was expected. This might be due to the fact that the summerwood sample contained about 50 percent of springwood tracheids because of inaccuracy in dissection and to the anatomical characteristics of a wood such as western hemlock. Using the same argument of the previous paragraph, one might expect summerwood to be of higher crystallinity, since it contains a lower proportion of lignin than springwood. Thus at the end of a given time of delignification, less lignin might have been removed from the relatively lignin-rich springwood.

2. Probable mechanism of variability of crystallinity in wood

The mechanism of variability of crystallinity with age and season is unknown, because of the inadequate information available about the mechanism of the formation of cellulose crystallites and fibrils of the cell wall. Wardrop (153) has proposed that crystallization of cellulose is facilitated by the absence of lignin, based on the fact that
cellulose displays its highest crystallinity value when the lignin content is low. If this hypothesis is correct, summerwood cellulose should be more highly crystallized than springwood cellulose because the proportion of cellulose in the summerwood has been found to be higher than that of springwood, while the proportion of lignin in summerwood is lower than that of springwood (116,161). Crystallinity might also increase with age in juvenile wood, since the cellulose content has been shown to increase with age for given periods in certain species (70,152,164). The hypothesis proposed by Wardrop remains to be proved.

B. Part II: The degree of crystallinity of pulp and holocellulose from reaction wood as compared to normal wood

1. Results

The crystallinities of pulp and holocellulose of reaction wood as compared to those of normal wood are shown in Table 6, page 64. Analysis of variance (Table 7, page 64) shows that crystallinity of compression wood fibres and holocellulose is significantly lower than that of normal wood, while crystallinity of tension wood is significantly higher than that of normal wood in the form of both pulp and holocellulose. These are discussed separately below.
Table 6. Crystallinities of reaction wood

<table>
<thead>
<tr>
<th>Replication</th>
<th>C-T</th>
<th>C-N</th>
<th>D-N</th>
<th>D-C</th>
<th>C-T</th>
<th>C-N</th>
<th>D-N</th>
<th>D-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.8</td>
<td>55.4</td>
<td>54.9</td>
<td>47.5</td>
<td>57.74</td>
<td>54.55</td>
<td>53.84</td>
<td>52.86</td>
</tr>
<tr>
<td>2</td>
<td>66.2</td>
<td>54.8</td>
<td>54.1</td>
<td>46.5</td>
<td>57.71</td>
<td>54.35</td>
<td>53.79</td>
<td>52.41</td>
</tr>
<tr>
<td>3</td>
<td>65.8</td>
<td>54.8</td>
<td>53.9</td>
<td>45.2</td>
<td>57.73</td>
<td>54.45</td>
<td>53.82</td>
<td>52.64</td>
</tr>
<tr>
<td>av.</td>
<td>66.6</td>
<td>55.0</td>
<td>54.3</td>
<td>46.4</td>
<td>57.73</td>
<td>54.45</td>
<td>53.82</td>
<td>52.64</td>
</tr>
</tbody>
</table>

*C-T represents cottonwood tension wood
C-N represents cottonwood normal wood
D-N represents Douglas fir normal wood
D-C represents Douglas fir compression wood

Table 7. Analysis of variance of crystallinity in Table 6

(A) Crystallinity index (wood pulp)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>D. F.</th>
<th>S. S.</th>
<th>M. S.</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replication</td>
<td>2</td>
<td>4.535</td>
<td>2.264</td>
<td>11.691**</td>
</tr>
<tr>
<td>Type of wood</td>
<td>3</td>
<td>623.062</td>
<td>207.687</td>
<td>1070.552***</td>
</tr>
<tr>
<td>Error</td>
<td>6</td>
<td>1.165</td>
<td>0.194</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>628.762</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Significant at 1 percent level
***Significant at 0.1 percent level

(B) Crystallinity ratio (holocellulose)

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>D. F.</th>
<th>S. S.</th>
<th>M. S.</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replication</td>
<td>1</td>
<td>0.067</td>
<td>0.067</td>
<td>3.526 N.S.</td>
</tr>
<tr>
<td>Type of wood</td>
<td>3</td>
<td>28.506</td>
<td>9.502</td>
<td>500.114 ***</td>
</tr>
<tr>
<td>Error</td>
<td>3</td>
<td>0.056</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7</td>
<td>28.629</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*** Significant at 0.1 percent level
N.S. Non-significant
2. Compression wood

The present results might be expected in view of the lower alpha-cellulose content, higher longitudinal shrinkage and lower strength values observed in compression wood. The correlation of these three properties to low degree of crystallinity has been discussed previously. The present discussion will be confined to the problem as to why the crystallinity in compression wood should be low.

In compression wood, the decreased tracheid length is usually accompanied by an increase in fibril angle. These attributes are associated with an increased number of oblique anticlinal divisions in the cambium, occasioned by the increased radial growth rate (156). It has been pointed out that vigorous radial growth is achieved by periclinal division of the fusiform initials of the cambium (111). Thus, if rapid periclinal division is accompanied by an increased number of oblique anticlinal divisions, then a wider growth ring will produce shorter tracheids (155). This implies that fibril angle as well as fibre length are simply a function of rate of change of growth in circumference.

Since the same relationships are found in the juvenile wood, it follows that the relationship of fibril angle and fibre length to growth rate holds for both normal wood and compression wood. Accordingly, there would be no

8cf. Table 3.
appreciable differences in fibril angle between two tracheids as long as they are formed in a ring of the same growth rate, irrespective of age or wood condition. This is confirmed by Wardrop and Dadswell (155), who claimed that compression wood tracheids are apparently no different from normal wood tracheids of the same length so far as the fibril angle of the layer S2 is concerned. From this point of view, compression wood may be considered more juvenile than adjacent wood of the same age.

The properties of compression and juvenile wood compared to normal, mature wood show that both juvenile wood and compression wood have lower cellulose content, tracheid length, tensile strength, and higher fibril angle, longitudinal shrinkage and lignin content. Consequently, the previous assumption that compression wood can be regarded more juvenile than adjacent normal wood seems acceptable. Under this assumption, compression wood should, theoretically, give lower crystallinity as observed in the present study.

3. **Tension wood**

The high degree of crystallinity of cellulose found in tension wood as compared with normal wood is in good agreement with the work of Wardrop and Dadswell (11,153,154, 157).\(^9\) The structure of tension wood has been well established by means of polarizing microscopy and X-ray diffraction

\(^9\)No numerical data were given in their results.
(154,157). In brief, there exists a thick inner gelatinous layer in addition to the layers S1, S2 and S3, or the S3 layer, or both S2 and S3 layers, may be lacking. The fibril angle in this additional layer has been shown to be approximately $5^\circ$ with respect to the longitudinal axis of fibre. Further evidence has shown that this layer is un lignified and that its cellulose is in a highly crystalline state.

On reviewing characteristics of tension wood, the question may be raised as to whether the high crystallinity of cellulose in tension wood is attributable to all layers of the secondary wall or solely to the additional gelatinous layer. Wardrop and Dadswell (157) have studied this problem from the point of view of equilibrium moisture content, density, and sharpness of an X-ray diffraction pattern. They finally concluded that the high degree of crystallinity of cellulose in tension wood was solely attributable to a greater degree of lateral order in the crystalline region of the gelatinous layer, whereas the paracrystalline phase (or the amorphous phase) of the rest of the layers was similar in both normal and tension wood.

Since tension wood consists of cellulose of high crystallinity, it should possess all the characteristics of highly crystalline cellulose given in Table 2. There are several deviations from this theoretical expectation however: abnormally high longitudinal shrinkage (17,20,24,154), low
strength values for fibre stress at the proportional limit of bending, modulus of rupture, modulus of elasticity, work to the proportional limit, work to ultimate load and longitudinal shear (13). Tension wood does not decrease the toughness (19), which is supposed to be lower if crystallinity of cellulose is high.10 Several workers (17,19,154) have suggested possible explanations, but further investigations are required.

Even some chemical properties of tension wood are at variance with those expected. For instance, the alpha-cellulose content of tension wood is significantly higher than that of normal wood, whereas the pentosan content is lower (17). Thus some workers pointed out that the cellulose in tension wood was of longer molecular chain than the cellulose in normal wood (17). Nevertheless, the degree of polymerization found in the holocellulose of tension wood was reported to be lower than that of normal wood (11).

It is clear now that a single factor such as crystallinity, which is found to be strongly correlated with physical and chemical properties of cellulose and wood under normal conditions, cannot be applied to explain the behavior of reaction wood without considering the effects of some other factors. Gross anatomical structure also has a role as important as fine structure.

10A similar abnormality can also be found in compression wood, which has a lower crystallinity accompanied by a very low value of toughness.
C. Part III: The degree of crystallinity of holocellulose of decayed wood

1. Results

Some of the X-ray spectra of decayed wood holocellulose are shown in Figure 8, page 71. The variation in the crystallinity ratio of wood holocellulose due to decay is shown in Table 8, page 70, and Figure 9, page 72. Analysis of variance (Table 9, page 70) indicates that both decay and type of wood are clearly significant at 0.1 percent level. Further analysis shows the following:

(a) Crystallinity of holocellulose is greatly increased due to decay in both normal and reaction wood.

(b) The relative magnitude of increase in crystallinity is approximately identical for each type of wood. Thus the order of decreasing crystallinity after decay remains the same as that of the controls. The order of crystallinity of different types of decayed wood depends mainly on the initial crystallinity of wood rather than on the history of decay.

(c) The rate of increase in crystallinity is very rapid in the earlier stage of decay, represented by a 6 percent weight loss, but it levels to almost constant crystallinity thereafter except in compression wood, where crystallinity is still increasing to stage B, but at a slower rate. In this latter case, the increase is statistically significant.
Table 8. Crystallinity ratio of holocellulose of decayed wood

<table>
<thead>
<tr>
<th>Type of wood</th>
<th>Replication</th>
<th>Control</th>
<th>Decay stage A</th>
<th>Decay stage B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cottonwood tension wood</td>
<td>1</td>
<td>57.74</td>
<td>59.70</td>
<td>59.56</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>57.71</td>
<td>59.50</td>
<td>59.70</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>57.73</td>
<td>59.60</td>
<td>59.63</td>
</tr>
<tr>
<td>Cottonwood normal wood</td>
<td>1</td>
<td>54.35</td>
<td>55.95</td>
<td>55.90</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>54.55</td>
<td>55.83</td>
<td>56.17</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>54.45</td>
<td>55.89</td>
<td>56.04</td>
</tr>
<tr>
<td>Douglas fir normal wood</td>
<td>1</td>
<td>53.84</td>
<td>54.50</td>
<td>54.65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>53.79</td>
<td>54.71</td>
<td>54.59</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>53.82</td>
<td>54.61</td>
<td>54.62</td>
</tr>
<tr>
<td>Douglas fir compression wood</td>
<td>1</td>
<td>52.41</td>
<td>53.17</td>
<td>53.77</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>52.86</td>
<td>53.46</td>
<td>53.88</td>
</tr>
<tr>
<td></td>
<td>av.</td>
<td>52.64</td>
<td>53.32</td>
<td>53.83</td>
</tr>
</tbody>
</table>

Table 9. Analysis of variance of crystallinity ratio in Table 8

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>D. F.</th>
<th>S. S.</th>
<th>M. S.</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>replication</td>
<td>1</td>
<td>0.061</td>
<td>0.061</td>
<td>2.179 N.S.</td>
</tr>
<tr>
<td>type of wood</td>
<td>3</td>
<td>111.009</td>
<td>37.003</td>
<td>13215.000 ***</td>
</tr>
<tr>
<td>error</td>
<td>3</td>
<td>0.083</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>Subunit:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>treatment</td>
<td>2</td>
<td>8.911</td>
<td>4.456</td>
<td>278.500 ***</td>
</tr>
<tr>
<td>t x w</td>
<td>6</td>
<td>1.198</td>
<td>0.200</td>
<td>12.500 **</td>
</tr>
<tr>
<td>error</td>
<td>8</td>
<td>0.125</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>23</td>
<td>121.387</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** Significant at 1 percent level
*** Significant at 0.1 percent level
N.S. Non-significant
FIGURE 8. X-RAY DIFFRACTION SPECTRA OF DOUGLAS FIR HOLOCELLULOSE
A. DECAYED NORMAL WOOD, STAGE B
B. DECAYED COMPRESSION WOOD, STAGE B
C. COMPRESSION WOOD, CONTROL
FIGURE 9. EFFECT OF DECAY AND TYPE OF WOOD ON CRYSTALLINITY RATIO OF HOLOCELLULOSE

C-T COTTONWOOD TENSION WOOD
C-N COTTONWOOD NORMAL WOOD
D-N DOUGLAS FIR NORMAL WOOD
D-C DOUGLAS FIR COMPRESSION WOOD
In order to understand the probable mechanism behind these experimental results, the biochemical transformation of cellulose and wood which may occur during decay should be reviewed.

2. Biochemical transformation of cellulose

Though much has been learned regarding the enzymatic degradation of cotton and modified cellulose, enzymatic breakdown of whole wood is less well understood. This is due to the relative complexity of wood compared to other cellulosic materials, and the inadequacy of present knowledge of the chemical structure of wood, in particular of the lignin. The following presentation is based primarily on enzymatic degradation of cellulose rather than wood.

The energy that hyphae require for growth is derived from that available in glucose. This energy is made available to hyphae by the physiological oxidation, in which one mole of glucose provides a theoretical amount of energy equivalent to $676.6$ kcal. (131).

$$C_6H_{12}O_6 + 6 \text{O}_2 \rightarrow 6 \text{H}_2\text{O} + 6 \text{CO}_2 \quad \Delta F = -676.6 \text{kcal}.$$  

In order for this reaction to proceed, cellulose must be transformed to glucose. The biochemical transformation of cellulose into glucose includes two major steps.

Step 1: Transformation of the native cellulose into individual linear cellulose molecules by splitting of the three-dimensional cross-linkage.

Step 2: Breakdown of the linear cellulose chains into glucose.
Both of these reactions are carried out by enzymes secreted by hyphae. Recent studies (76,115) have shown that there are at least two types of enzymes which are responsible for the biochemical transformation of cellulose molecules. The first type of enzyme is responsible for making cellulose molecules available for reaction, corresponding to step 1, while the second type of enzyme is responsible for hydrolysis of the linear polysaccharide into sugars, corresponding to step 2. The former type is known as cellulase (130), whereas the latter is named Cx (115). The condensed stepwise transformation is illustrated in Table 10.

Table 10. Stepwise biochemical transformation of cellulose into glucose (131)

<table>
<thead>
<tr>
<th>Native cellulose (cotton)</th>
<th>crystalline region</th>
<th>amorphous region</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(slow)</td>
<td>(rapid)</td>
</tr>
</tbody>
</table>

... rupture of H-bonds, van der Waals forces, by cellulase

Linear Polysaccharide

... Polysaccharidase enzyme, Cx, acting

Cellobiose

... Cellobiase acting

Absorption into organism
In the case of wood, only restricted groups of fungi are able to utilize it for food. The nature of the association between cellulose and lignin of wood is primarily responsible for such restriction. It has been suggested that the biochemical transformation of wood cellulose into linear polysaccharides is carried out by an unknown factor "X" presumably enzymatic, possessed only by fungi adapted to this type of substance (23). The symbol "X" has been used to identify the as-yet-unknown enzymes responsible for this transformation. Absence of this factor accounts for the inability of non-wood-destroying fungi to utilize wood for food. The transformation from linear polysaccharides to glucose is the same as that of native cotton (23).

3. Preference of enzymic attack

Evidence indicates that the enzymic degradation of cellulose starts preferably from the amorphous region rather than randomly. On the basis of a differential energy requirement, the amorphous region is preferable to the crystalline region because much less energy will be required to dislodge a cellulose chain in the former (131). Assuming that the action of the enzymes is similar to that of dilute mineral acid as described previously, it is reasonable to presume that the reaction starts in the amorphous region and extends gradually into the crystalline region. Several workers (106,107,149) have demonstrated the similarity of acid and enzymatic hydrolysis by comparing the rate of hydrolysis. Walseth (150)
made use of this characteristic to determine the accessibility of cellulose, and his results were in good agreement with those obtained by acid hydrolysis. Norkrans and Rånby (106,107) also claimed that the enzymatic degradation apparently occurred in easily accessible regions of the cellulose aggregates, leaving more resistant particles, and therefore better crystallized cellulose, as a residue.

It has been shown (8) that there are certain wood-destroying fungi whose hyphae advance by producing helically oriented cavities within the thick secondary wall of fibres. Such cavities are of two principal geometric forms. They may be biconical or cylindrical, with conical ends, and are oriented parallel to the long axis of the fibril. In some cases they may be oriented at an angle of 20 to 25 degrees to the axis of the fibril. These cavities were found to be the result of hydrolysis of cellulose through enzymatic activity. The reaction takes place in the amorphous region first, and leaves the crystalline region entirely intact, so that the external shape of the microfibril and fibril is maintained.

It is now clear that the initial enzymatic reaction starts from the amorphous region. This preference is believed to be the most probable factor resulting in the rapid increase in crystallinity during the earlier stage of decay observed in this study. The increase in crystallinity may be attributed to either or both of the following factors:
(a) Removal of the amorphous materials.
(b) Recrystallization during preparation of the cellulose specimen used for determination of crystallinity. Recrystallization is quite possible because the free ends of the broken chain on the surface of the crystallite always tend to arrange themselves for recrystallization. Since there is no possible way to show whether or not recrystallization actually took place, probably both recrystallization and removal of amorphous materials are responsible for an increase in crystallinity after decay.

As the decay progresses, the enzymes will gradually reach the crystalline region which is relatively inaccessible to chemical reaction, and highly resistant to enzymatic hydrolysis.

The rate of increase in crystallinity will slow down and finally level off, as shown in stage B, Figure 9. In other words, an increased degree of crystallinity will give rise to greater resistance to enzymatic hydrolysis. This is in good agreement with results of other workers (68,106,149,150).

4. **Relationship between lateral order and rate of enzymatic attack**

The present result shows that crystallinity of decayed-wood holocellulose depends largely on crystallinity of sound wood. This might be attributed to the following two points:
(a) During the early stage of decay, the enzymes attack the amorphous regions at almost the same rate for various types of wood.

(b) The degree of perfection of the lattice structure in the crystalline regions is heterogeneous rather than homogeneous. There must be a statistical distribution of degree of lateral order.

Two mechanisms have thus far been postulated in order to explain the breakdown of cellulose chains by enzymes. One is a random cleavage mechanism and the other, an endwise attack mechanism (107). Since the former is thought to be much more probable (131), it is assumed that the enzymes randomly attack cellulose chains at the surface of the crystallite. Thus both width and length of crystallite will decrease simultaneously as the decay advances.

As shown in part II, the order of decreasing crystallinity of holocellulose from various types of wood is tension wood, normal wood and compression wood. These differences in crystallinity can be represented by the schematic lateral-order distribution curve illustrated by Howsmon and Sisson (110).\textsuperscript{11} Postulated curves obtained in this way are shown in Figure 10A, page 81. The high crystallinity of tension wood is characterized by a negatively skewed distribution curve, whereas the low

\textsuperscript{11}cf. page 13.
crystallinity of compression wood is characterized by a positively skewed distribution curve. In order to correlate the sequence of enzymatic attack to the variation of crystallinity, the lateral order distribution curves are transformed to two-dimensional diagrams as shown in Figure 10B. The lateral order is assumed to be highest at the central portion of the crystalline region, and to gradually decrease toward the surface of the crystallite. Thus the highly crystalline tension wood possesses a larger area of high lateral order at the center of the crystallite, while the weakly crystalline compression wood has a larger area of low lateral order at the surface of the crystallite. No definite borderline actually exists between each phase of lateral order, so that the transition of lateral order should be regarded as continuous.

As enzymatic hydrolysis begins, the outermost area of low lateral order, which corresponds to the amorphous region, will be dissolved away quickly to leave the relatively high lateral order portion (see Figure 10C). Consequently the degree of crystallinity of cellulose increases rapidly at this stage, as shown in Figure 9. Since the relative area of the high lateral-order portion is not changed through successive stages of decay, as shown in Figure 10D, the order of degree of crystallinity can be expected to remain the same as in the control.
When all readily accessible cellulose is dissolved and decay advances from stage A to B, enzymatic attack still proceeds, but presumably at slow rate, and only at the surface of the crystallite (150). Hence the rate of increase in crystallinity will be negligible at this stage, as demonstrated by the experimental results summarized in (c) page 69.

As mentioned previously, crystallinity of compression wood holocellulose increased continuously throughout stage B. This can be explained by its abnormally low lateral order as illustrated in Figure 10B. At stage A, there is still a considerable amount of relatively low lateral-order material left on the crystallite surface of compression wood (see Figure 10C). The enzymatic attack continues to proceed at a fast rate, allowing the crystallinity to increase as shown in Figure 10D, and Figure 9.
FIGURE 10. SCHEMATIC LATERAL ORDER DISTRIBUTION CURVE AND SEQUENCE OF ENZYMATIC ATTACK ON THE CRYS TALLINE REGION

A. SCHEMATIC LATERAL ORDER DISTRIBUTION CURVE
\[ \frac{dq}{do} = \text{QUANTITY OF CELLULOSE BELONGING TO A} \]
\[ \text{PARTICULAR ORDER} \]

B. CROSS SECTION OF THE CRYS TALLINE REGION OF THE CONTROL

C. DECAY STAGE A (APPROX. 6 PERCENT WT. LOSS)

D. DECAY STAGE B (APPROX. 15 PERCENT WT. LOSS)

LATERAL ORDER

\[ \text{[Schematic representation of lateral order]} \]
CONCLUSIONS

1. Crystallinity of wood pulp and holocellulose of the normal western hemlock wood sampled increases significantly through successive growth rings from the pith to about 15 years, after which it reaches a more or less constant value.

2. Crystallinity of wood pulp and holocellulose of summer-wood from the western hemlock sampled is significantly higher than that of springwood.

3. Crystallinity of wood pulp and holocellulose of the Douglas fir compression wood specimens is considerably lower than that of normal wood, whereas crystallinity of wood pulp and holocellulose of the tension wood samples of cottonwood is significantly higher than that of normal wood.

4. The abnormal physical and chemical properties of reaction wood suggest that crystallinity is not the only factor which affects reaction wood properties. There must be other factors responsible for the properties of reaction wood.

5. Crystallinity of cottonwood and Douglas fir wood holocellulose increases significantly during decay caused by the brown-rot fungi, *Poria incrassata* and *Poria monticola*. 
6. The rate of increase in crystallinity due to decay is very rapid during the incipient stage of decay represented by 6 percent weight loss, but becomes very slow and shows almost a constant value of crystallinity thereafter. In the case of compression wood, the crystallinity increases through the stage of decay represented by 15 percent weight loss, but at a rate slightly lower than that of the earlier stage of decay.

7. The order of degree of crystallinity for various woods after decay is the same as the controls, i.e., tension wood exhibits the highest and compression wood the lowest value of crystallinity. The relative value of crystallinity after decay depends mainly upon the initial crystallinity rather than the history of decay.
BIBLIOGRAPHY


100. ____. 1951. The relative crystallinity of cellulosi. Adv. in Carbohydrate Chem. 5:103-126.


