SHORT-TERM CREEP AS RELATED TO CELL-WALL CRYSTALLINITY

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ABSTRACT

X-ray diffraction technique was utilized to determine the relative degree of crystallinity of some coniferous wood tissues, namely Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) normal and compression wood, and normal wood of Sitka spruce (*Picea sitchensis* (Bong.) Carr.) and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.). Total creep values were available from a previous study for test samples matched with those used for determining degree of crystallinity. Creep response was measured using two constant loads corresponding to predetermined initial strain levels of 3,000 (A) and 6,000 (B) μinches/inch.

The relative degree of cell-wall crystallinity was found to be linearly correlated (inversely) with short-term creep. Results of this investigation also revealed that cell-wall crystallinity contributes up to 67.2 and 51.8% of the total variability in creep response for samples tested at constant loads corresponding to strain levels (A) and (B), respectively. It is suggested that a relatively high degree of crystallinity increases the rigidity of cell wall, which thereby resists excessive creep deformation.

INTRODUCTION

It is generally accepted that individual wood tracheids and composite wood tissues consist of both ordered (crystalline) and disordered (amorphous) regions. Accordingly, it would be expected that varying proportions of each would influence their mechanical behavior. High strength and low extensibility of textile and regenerated fibers have been related to high degrees of crystallinity (Ward 1950; Tripp et al. 1958).

Changes in crystallinity when cellulose fibers are stretched have been a subject of investigation. Such change is based on the hypothesis that fibers undergo a process, during stretching, similar to that experienced with natural rubber samples. A partial conversion of the amorphous into the crystalline state of cellulose fibers has been observed by Berkley and Kerr (1946), Heyn (1965), and Ingersoll (1946). The major difference between cellulose fibers and rubber is that the change is not as reversible as with rubber and is very much less pronounced (Mark 1940), as was observed by Sisson (1938).

Crystallinity as a factor influencing the mechanical behavior of wood and/or wood tissues seems to have been ignored until recently. This was probably due to lack of a technique suitable for determining degree of crystallinity.

The first reported study relating cell-wall crystallinity directly to mechanical response of wood was conducted by Murphey (1963). According to him, crystallinity of yellow birch (*Betula alleghaniensis* Britton) and sugar maple (*Acer saccharum* Marsh.) in-

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creased as a result of tensile strain but, at a given load-causing strain, did not change when the load was sustained for a period of time. In addition, after release of the load inducing the strain, some of the increase in crystallinity remained. Thus, upon application of a tensile load, some increase in molecular lattice perfection appears to take place, causing an increase in cell-wall crystallinity. Part of this increase is retained after removal of load as a result of probable permanent changes in crystallinity. Using Murphey's technique, Ziegler (1969) has found that incremental tensile loads at a given temperature level resulted in increasing crystallinity of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco).

Kouris et al. (1958) examined the effect of various modes of drying upon crystallinity of softwoods, using X-ray diffraction. They did not observe any significant change in crystallinity index when previously undried, pure cellulose fibers were dried from water under a wide range of conditions. On the other hand, they obtained lower values when the fibers were dried from benzene. Crystallinity of early- and latewood of longleaf pine (*Pinus palustris* Mill.) holocellulose pulps was determined by Hill (1967) and Jentzen (1964) as fibers were dried under various axial tensile loads. The authors did not find any change in the degree of crystallinity.

In spite of the increasing knowledge about the influence of cell-wall crystallinity on strength properties of wood and/or wood tissues, virtually nothing is known about the effects that crystallinity might have on time-dependent phenomena of wood tissues. The purpose of this paper is to examine the role that relative degree of cell-wall crystallinity plays in controlling the magnitude of short-term creep response of some coniferous wood tissues.

MATERIALS AND METHODS

The experimental material was carefully chosen from normal wood of single trees of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco), Sitka spruce (*Picea sitchensis* (Bong.) Carr.), and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) and from compression wood of Douglas-fir, available from the University of British Columbia Research Forest, Haney, B.C. Diameters at breast height were 26, 28, 14 and 22 inches outside bark, respectively. One disc was chosen from each tree at breast height. Three tangentially matched blocks (nominal 2.5 inches longitudinally, 1.5 inches radially, and 0.75 inch tangentially) were cut from each disc. One block was used for obtaining material for determining relative degree of crystallinity whereas the others were used for estimating total creep.

Prior to sectioning tangentially on a sliding microtome, blocks were aspirated under vacuum in a vacuum/pressure cylinder until waterlogged (saturated). Each increment preceding the selected one (Number 71, 80, 187, and 60 from the pith for Douglas-fir normal and compression wood, Sitka spruce normal wood, and western hemlock normal wood, respectively) in each block was sectioned and discarded. Once the tangential surface at the chosen position in either early- or latewood had been satisfactorily prepared, one microtome-section (nominal 0.009 to 0.011 inch thick) was cut. Sections were kept in a controlled temperature and humidity (CTH) room maintained at 73 ± 3.5 F and $50 \pm 2\%$ relative humidity. Each section assigned to the creep experiment was punched into strips or replications using a specially machined cutting die fixed to a half-ton arbor press. Matched sections assigned to crystallinity determination were ground for the purpose of making pellets as indicated below.

Determination of cell-wall crystallinity

Preliminary experiments during this investigation showed that thickness of wood samples and orientation of tracheids are extremely important for cell-wall crystallinity determination. Since two different kinds of tissues, early- and latewood, were to be used as experimental material and their specific gravities differ, it was therefore necessary to use the same mass per unit area from each tissue. This was done by grinding each microtome-section, prepared by the method described above, in a Wiley mill. Wood particles that passed through a 20-mesh screen but were retained on the 40-mesh screen were collected. Grinding the material to this size would not affect the diffraction pattern (Nelson and Conrad 1948).

A standard sample of 400 mg was shaped by compression into a thin rectangular pellet (½ × 1¼ inches) at about 1,000 psi in a specially designed die. As a prior step, a drop of dilute glue solution (10 ml Duco cement plus 100 ml amyl acetate) was placed on 400 mg of wood meal after it had been lightly compacted in the die; then the full specified pressure was applied in one to two minutes. It has been indicated by Nelson and Schultz (1963) that the amount of cement used would not affect the diffraction pattern obtained. Because of the limited amount of material available for crystallinity, a maximum of one sample (pellet) was prepared per wood type. On each pellet, two X-ray scans were taken, the average of which was used in the regression analyses.

A Philips X-ray Diffractometer was used for recording the intensity of the predominant peaks of cellulose lattice diffraction, namely (002) and (101 + 10$\bar{1}$). These peaks occur within the range of 6 to 30° (2θ) (Fig. 1). The X-ray beam was generated from a water-cooled copper target. Tests were made at 40 Kv and 15 ma current. Degree of crystallinity was measured by the crystallinity index (*CrI*) proposed by Segal et al. (1959), which expresses the relative degree of crystallinity. The equation used is as follows:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100,$$

where:

I_{002} = the maximum intensity (in arbitrary units) of the (002) lattice diffraction, and

I_{am} = the intensity of diffraction in the same units at $2\theta = 18°$ (approximately).

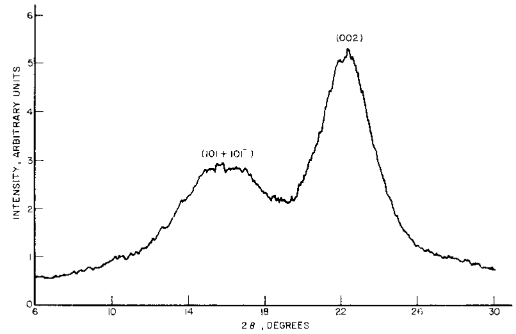


FIG. 1. X-ray diffraction pattern of Douglas-fir latewood (normal wood).

This equation is considered by the writers as the best method available to calculate the relative degree of crystallinity, since the parameters, I_{002} and I_{am} are determined at two points, one most characteristic of the crystalline cellulose and the other most characteristic of the amorphous cellulose, respectively. The same equation has been applied to wood sections and wood fibers by authors such as Jentzen (1964); Hill (1967); and Binotto et al. (1971). However, it must be indicated that this X-ray technique for determining crystallinity is only a relative one and not absolute. Nevertheless, *CrI* as measured herein is a sensitive indication of relative degree of lateral order of cellulose.

Measurement of total creep

Total creep values in tension parallel to grain had been obtained on small wood strips matched with those used for crystallinity determination (El-osta 1971; El-osta and Wellwood 1972). In these studies an experimental technique was devised by which constant loads corresponding to predetermined strain levels of 3,000 (A) and 6,000 (B) μinches/inch were applied to test specimens under CTH room conditions. Briefly, wood strips were glued at both ends between aluminum sheets to facilitate the loading procedure. The assembly was properly aligned in the upper grips of the Instron testing machine. A hooked-end wire was attached to the lower end of the specimen and passed through a hole in the bottom of a bucket resting on the lower crosshead. A 100-g weight was hung at the lower end of the wire to straighten out the wood strip and to facilitate mounting the extensometer on it (Fig. 2). The extensometer was connected to a five-pin adapter feeding directly to the load cell amplifier. Some lead shot, depending on the expected tensile strength of each strip, was then put into the bucket without loading the specimen. After 15 min, during which the zero strain point was suppressed to either 2,600 or 5,600 μinches/inch, the lower crosshead was moved down. More lead shot was immediately poured into the bucket, so that the initial required strain reached levels (A) or (B) on the Instron strip chart recorder, after which the load was kept constant for 60 min. Total creep is defined herein as the amount of plastic deformation occurring above initial strains (A) or (B) over the 60-min period.

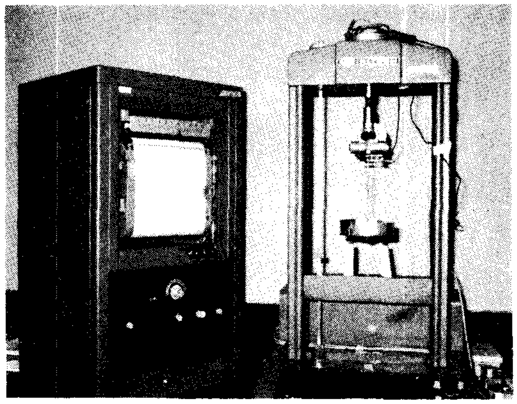


FIG. 2. Creep in tension parallel to the grain set-up.

RESULTS AND DISCUSSION

Values for relative degree of crystallinity, along with total creep values obtained previously, are presented in Table 1. Examination of this table indicates that within one growth increment of the species used, except western hemlock, latewood tissues had higher relative degree of crystallinity than earlywood. These results are in agreement with those reported by Harada and Taniguchi (1971) on *Pseudotsuga japonica*; Holzer and Lewis (1950) on Douglas-fir; and Lindgren (1958) on Swedish spruce.

The variability between earlywood and latewood with regard to the above-noted characteristic might be attributed to:

(1) The higher percentage of lignin of earlywood tissues. Lignin, according to evidence available in the literature, is amorphous material. Its presence would decrease the relative percentage of cell-wall crystallinity. In the present study, lignin content was not determined. However, it has been found by Wilson and Wellwood (1965) that, within one annual increment of the same species, except for western hemlock, earlywood has 2 to 3% higher lignin content than latewood.

(2) The lower alpha-cellulose content of earlywood tissues (Squire 1967).

The relative degree of crystallinity of Douglas-fir compression wood is seen to be lower than that of Douglas-fir normal wood (Table 1). Similar differences have been reported between normal and compression wood of loblolly pine (*Pinus taeda* L.) by Parham (1971). The higher lignin content (Timell 1965), larger microfibril angle, and absence of an S3 layer of compression wood tracheids might be the factors responsible for its lower relative degree of crystallinity. Numerical values are higher than those obtained by Lee (1961). In the present study, averages are 59.4 and 55.1% for Douglas-fir normal and compression wood, whereas those reported by Lee were 54.3 and 46.4%. Instead of using wood meal, Lee subjected his samples to a severe delignification process whereby a reduction in relative degree of crystallinity might have occurred. In addition, the difference might be due to the inherent specimen variation such as that resulting from age (Lee's specimens were from young trees).

Because of the uncertainty of changes that might be induced during any delignification process, a controversial issue is reported in the literature concerning the influence that delignification process might have on the crystallinity of cellulose. For example, a small increase in proportion of

TABLE 1. *Average values of relative degree of crystallinity, and total creep[a] at 3,000 and 6,000 μ inches/inch initial strains*

Species and wood type		Relative degree of crystallinity (%)	Total creep (μinches/inch) At 3,000 μinches/inch	At 6,000 μinches/inch
Douglas-fir				
Normal wood				
Earlywood	1	58.7	324	674
	2		207	607
	3	57.9	197	724
	4		180	610
	5		234	596
	6		214	616
Average		58.3	226.0	637.8
Latewood	1	60.0	200	485
	2	60.9		
Average		60.5		
Compression wood				
Earlywood	1	53.6	370	714
	2		285	787
	3	54.3	255	720
	4		254	767
	5		274	
Average		54.0	287.6	747.0
Latewood	1	56.9	230	636
	2	55.4	190	590
	3		220	610
Average		56.2	213.3	612.0
Sitka spruce				
Normal wood				
Earlywood	1	61.1	140	314
	2		145	327
	3	61.1	130	307
	4		164	293
	5		160	323
	6		110	
Average		61.1	141.5	312.8
Latewood	1		84	270
	2		110	250
	3		107	320
	4	63.7[b]	167	234
	5		104	290
Average			114.4	272.8

[a] Total creep is defined in this study as the amount of plastic deformation occurring above initial elastic strain of 3,000 or 6,000 μinches/inch at the end of the 60-min period.
[b] Based upon one X-ray scan.

TABLE 1. Continued

Species and wood type		Relative degree of crystallinity (%)	Total creep (μinches/inch) At 3,000 μinches/inch	At 6,000 μinches/inch
Western hemlock				
Normal wood				
Earlywood	1		217	427
	2	58.5	182	394
	3	55.8	177	454
	4		167	407
Average		57.2	185.8	420.5
Latewood	1		298	494
	2		254	393
	3	55.4	220	440
	4	54.0	230	480
	5			527
	6			510
Average		54.7	250.5	474.0

crystalline material resulted from stepwise delignification of slash pine wood (*Pinus elliottii* Engelm.) (Nelson 1961). On the other hand, a reduction in the (101) and ($10\bar{1}$) peaks' intensity for Douglas-fir was reported by Chow (1969). Accordingly, it would seem erroneous to state that the delignification process would only increase the degree of lateral order without taking into consideration the possible lattice distortion in the fibrils (Rånby 1958).

It is anticipated that variation in relative degrees of crystallinity of wood tissues would influence the magnitude of creep response. Simple regression analysis with the least squares method fit was conducted to establish a mathematical model that best represents the degree of association between total creep (Y) and the relative degree of cell-wall crystallinity (X), as expressed by crystallinity index. The models are as follows:

(A) Strain level samples:

$$Y = 1159.3 - 16.5\ X \qquad (1)$$
$$SEE = 38.6$$
$$r = 0.82^*$$
$$N = 34$$

(B) Strain level samples:

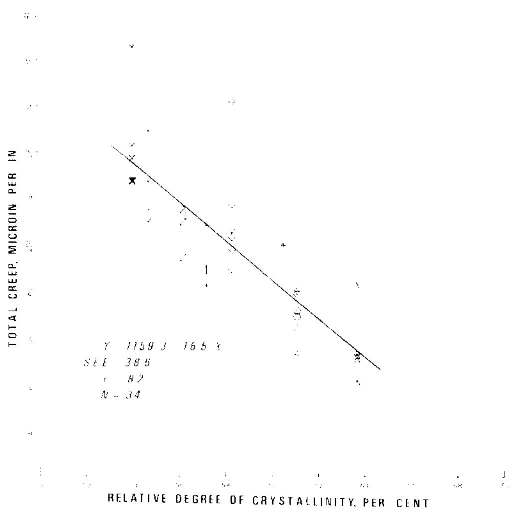
$$Y = 2580.5 - 36.0\ X \qquad (2)$$
$$SEE = 115.4$$
$$r = 0.72^*$$
$$N = 34$$

Equations (1) and (2), along with Figs. 3 and 4, indicate that the magnitude of total creep is inversely related in a linear manner to the relative degree of cell-wall crystallinity.

According to the generally accepted fringed fibrillar model for the supermolecular arrangement of cellulose chains, microfibrils are considered to be large, imperfect crystals, separated along their peripheries by noncrystalline regions (Hearle 1958, 1963). Consequently, the relative degree of cell-wall crystallinity should logically affect the magnitude of total creep of wood tissues. As a result of this investigation, relative degree of cell-wall crystallinity, as expressed by crystallinity index, is shown above to contribute up to 67.2 and 51.8% (r^2) of the total variability in creep response under strain levels of 3,000 and 6,000 μinches/inch, respectively.

If the well-ordered (crystalline) portion of the cell wall is relatively predominant, wood tissues exhibit high level of resistance to the creep-inducing stresses in tension parallel to grain, thereby minimizing de-

* Significant at the 0.5% level.



LEGEND

- ◈ Douglas-fir earlywood (normal wood)
- ↑ Douglas-fir latewood (normal wood)
- x̄ Douglas-fir earlywood (compression wood)
- Z Douglas-fir latewood (compression wood)
- ⊙ Sitka spruce earlywood
- ◬ Sitka spruce latewood
- \+ Western hemlock earlywood
- × Western hemlock latewood

FIG. 3. Relationship between total creep (Y) and relative degree of crystallinity (X) at a constant load corresponding to initial strain of 3,000 μinches/inch.

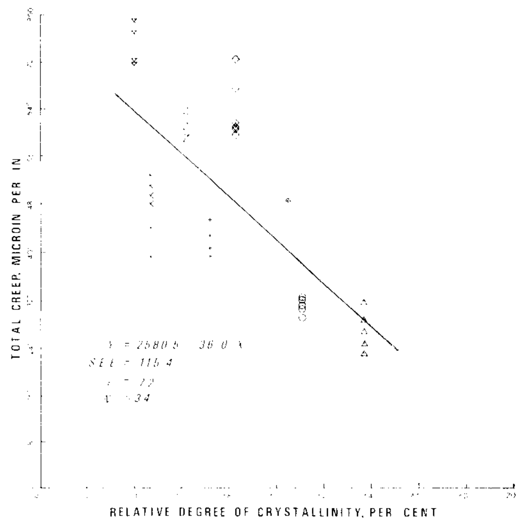


FIG. 4. Relationship between total creep (Y) and relative degree of crystallinity (X) at a constant load corresponding to initial strain of 6,000 μinches/inch. See Fig. 3 for legends.

velopment of excessive creep deformation (Figs. 3 and 4). The dispersion around the regression lines in Figs. 3 and 4 indicates that cell-wall crystallinity is not the only variable affecting creep response of wood tissues. It has been shown by the authors in a previous study that microfibril angle also contributes substantially to variation in total creep (El-osta and Wellwood 1972). In addition, microfibril angle and *CrI* were found to be highly correlated. Other variables tested were specific gravity and extractives content of the cell wall (El-osta 1971).

In developing a regression model that represents the best relationship between creep and the independent variables noted (microfibril angle, *CrI*, specific gravity, and extractives content), it was found that *CrI* could be used in the model instead of microfibril angle but with about 10% reduction in the R^2 values. Detailed statistical treatments of the remaining independent variables, and the regression models including all variables, are now in preparation and will appear in a later publication. Furthermore, the nature of the high correlation between microfibril angle and *CrI* is currently under investigation by the senior author, at the Western Forest Products Laboratory, Vancouver, B.C.

CONCLUSIONS

From the results of this investigation, the following conclusions are warranted:

1. Under constant temperature (73 ± 3.5 F) and relative humidity (50 ± 2%) conditions, total creep response of Douglas-fir normal and compression wood, and normal wood of Sitka spruce and western hemlock is significantly affected by the relative degree of cell-wall crystallinity, as expressed by crystallinity index.
2. Cell-wall crystallinity contributes up to 67.2 and 51.8% of the total variability in creep response under constant load corresponding to a given deformation of 3,000 and 6,000 μinches/inch, respectively.

3. Excessive creep deformation results in part from lower relative degrees of cell-wall crystallinity.

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