RELATIONSHIPS BETWEEN CELL-WALL COMPOSITION AND CELL-WALL DENSITY¹

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ABSTRACT

The alpha-cellulose content, holocellulose content and crystallinity index were measured for thirteen hardwood and five softwood samples, for which both cell-wall substance and cell-wall densities had been measured in an earlier study. Direct relationships were found between crystallinity index, alpha-cellulose content, and cell-wall density. A simple method of mixtures was used to relate the constituent densities to the cell-wall substance density. Attempts to rationalize the difference between these calculated densities and the measured cell-wall substance densities suggested that the density of one or more of the cell-wall constituents is appreciably different, *in situ*, than that measured on the material removed from the cell wall.

Additional keywords: Alpha-cellulose, holocellulose, crystallinity index, hemicellulose, cellwall substance, hardwoods, softwoods, density, cell-wall density, chemical composition.

INTRODUCTION

Variations in cell-wall density of dry wood may result from differences in either the proportion, densities, or arrangement of the basic cell-wall substances or in the amount of voids within the wall. Wilfong (1966) suggested that the void volume in the dry cell wall would not exceed 5%. This opinion was supported by Kellogg and Wangaard (1969) whose measurements on 18 species of hardwoods and softwoods indicated a range of void volumes from 1.64 to 4.76%.

Wilfong (1966) attributed variability in wood substance density of unextracted material to differences in extractive content and, to some degree, to relative holocellulose and lignin content. Stamm and Sanders (1966) have shown that wood substance density is related to the relative holocellulose-lignin composition and the component

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substance densities, provided the measurements are made on the same material. Beall (1972) determined the density of various hemicellulose components of both hardwood and softwood species. He used these values, together with available estimates of cellulose and lignin densities from Stamm (1964, 1969) to calculate wood substance density. Beall used a constant value for cellulose density of 1.52 g/cm3, but recognized that densities for cellulose may range from 1.47 to 1.59 g/cm³ for unordered to ordered cellulose (Treiber 1957). Thus, one would anticipate that variations in cellulose crystallinity would be reflected in a change in both cell wall and cell-wall substance density.

Kellogg and Wangaard (1969) implied such a relationship in relating cell-wall density to strain-dependent mechanical properties. In a recent study on the relationships between cellulose crystallinity and various wood properties, Wellwood et al. (1974) also implied a strong relationship to cellwall density, but to our knowledge no one has attempted to directly relate these two properties. Others have reported relation-

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FIG. 1. Relationships between cell-wall density and crystallinity index.

ships between the mechanical behavior of wood and crystallinity (Murphey 1963; Elosta and Wellwood 1972).

The objectives of this work were, first, to directly evaluate the influence of variations in cellulose crystallinity on cell-wall density and, second, to evaluate the accuracy of determining cell-wall substance density based on the densities of the scparate constituents and their relative proportions.

MATERIALS AND METHODS

Material from the thirteen hardwoods and five softwoods was still available from the earlier study of cell-wall density by Kellogg and Wangaard (1969) and this provided essentially all the experimental material, as well as cell-wall density values, for the present investigation. All measurements were made on extractive-free material. Relative crystallinity expressed as crystallinity index was determined on wood meal samples from all 18 species following the X-ray technique described by El-osta and Wellwood (1972). The constituent proportions of the major chemical components were also determined on matchstick size splinters. Peracetic acid holocellulose was obtained employing the technique used by Leopold (1961), part of which was further reduced to alpha-cellulose following TAPPI Standard T203 OS-61 method (1961) scaled to accommodate micro-amounts of material.

RESULTS AND DISCUSSION

The values of cell-wall density, crystallinity index, holocellulose yield, and alphacellulose yield are shown in Table 1 for all 18 species. Regression analysis revealed a highly significant correlation ($\mathbf{r} = 0.838$) between cell-wall density and crystallinity index, as shown in Fig. 1. Considering the number of factors outlined earlier that will contribute to variations in cell-wall density, the effect of cellulose crystallinity is clearly evident.

Cell-wall density was also found to be correlated to a slightly lesser degree (r = 0.745) with alpha-cellulose yield. As the alpha-cellulose content increases, it is pos-



FIG. 2. Relationships between cell-wall density and holocellulose yield.

sible for the proportion of higher density crystalline cellulose to increase. Figure 2 shows the relationship between cell-wall density and holocellulose vield, in which there is a distinct difference between the hardwoods and softwoods. This is unlike the relationship between cell-wall density and either crystallinity index or alpha-cellulose yield which showed a continuum of behavior. At a given holocellulose content, the softwoods have a markedly greater cellwall density than the hardwood species. Within the hardwoods there is, however, a highly significant correlation between cellwall density and holocellulose yield. A similar trend exists within the softwoods, but the correlation does not attain formal statistical significance. We must look to the distinct differences in the composition of the cell walls of hardwoods and softwoods for an explanation of this behavior. Since the relationship with alpha-cellulose content is a continuum, and that with holocellulose content is not, one obvious possibility is the nature of the hemicellulose fraction.

Beall (1972) has reported substance densities for two hardwood and five softwood hemicelluloses. The softwood hemicellulose densities were markedly greater than the hardwood hemicelluloses as a group. He also calculated wood-substance densities from a consideration of the constituent fractions of the chemical components and their respective densities, and compared his values with the cell-wall densities reported (Kellogg and Wangaard 1969) for these same seven species. The difference between these values was found to be less than 1%. Expression of the difference as a percentage is somewhat misleading. If the possible range in values is small relative to the mean value, then poor estimates of an expected value will appear as a small percentage error. In this case, the average error in Beall's estimate is only 1/2% compared to a range of measured cell-wall density of

	\$pecies	Cell-wall substance density ¹ (g/cm ³)	Cell-wall density ¹ (g/cm ³)	Crystallinity index ² (%)	Holocellulose yield ² (%)	Alpha- cellulose yield ² (%)	Calculated cell-wall substance density (g/cm ³)	Calculated cell-wall density (g/cm ³)
1.	Basswood	1 515	1 /01	53 7	70.8	44 0	1 466	1 443
2.	Eastern cottonwood	1.010	1.491	22.7	//.0	44.0	1,400	1.445
	(Populus deltoides Bartr.)	1.517	1.480	47.8	79.0	42.8	1.465	1.431
з.	White ash							
	(Fraxinus americana L.)	1.497	1.433	44.2	73.4	41.4	1.459	1.399
4.	Yellow poplar (Liviodendron tulipifera L.)) 1.510	1.472	49.7	77.7	45.6	1.465	1.431
5.	Black cherry							- 101
ć	(Prunus serotina Ehrh.)	1.508	1.451	46.5	74.0	43.4	1.461	1,406
0.	(Acer sacchamum Marsh.)	1.508	1 451	47.5	77.3	43.0	1.463	1.410
7.	Red maple	2.000	11/01	47.5	····	4310		11/1-1
	(Acer rubrum L.)	1.517	1.459	47.6	76.9	41.3	1.462	1.408
8.	Beech							
~	(Fague grandifolia Ehrh.)	1.504	1.468	48.3	77.0	42.8	1.463	1.429
9.	(Batula nonumifona March)	1 510	1 472	50 4	80.0	66 3	1 467	1 /33
10	Red oak	1.510	1.472	50.4	00.9	44.1	1.407	T*433
10.	(Quercus rubra L.)	1.513	1.458	44.5	76.5	41.9	1.462	1.410
11.	Yellow birch		20.000					
	(Betula alleghaniensis							
	Britton)	1.511	1.458	43.6	79.0	41.0	1.464	1.414
12.	White oak				7/ 5		1 // 0	
1.2	(Querous alba L.)	1.513	1.440	44.4	74.5	41.4	1.460	1.393
10.	[Carria opata (Mill) K. Koch	1 1 508	1 442	45 1	74 5	40.5	1.459	1.399
14.	Eastern white pine	.] 1.500	1.442	40.1	74.5	40.2	1.435	1.377
	(Pinus strobus L.)	1.524	1,494	51.0	72.2	43.0	1.514	1.486
15.	Red spruce							
	(Picea rubens Sarg.)	1.529	1.498	51.6	71.9	45.3	1.510	1.479
16.	Eastern hemlock							
	(Isuga canadensis (L.)	1 517	1 / 80	4 9 0	70.0	43 3	1 507	1.470
17.	Spruce pine	1,017	1.400	43.0	/0.0	40.0	1,507	1,470
11.	(Pinus glabra Walt.)	1.529	1.499	48.7	74.9	44.8	1.520	1.490
18.	Loblolly pine							
	(Pinus taeda L.)	1.529	1.500	51.8	71.5	44.5	1,510	1.481

TABLE 1. Density, crystallinity index, and yield of carbohydrate fractions for 18 species

¹ Data from Kellogg and Wangaard (1969).

Average based on two measurements, uncorrected for lignin.

2.8%, or 20% of the possible range. Expressed in this way, the agreement between the values is not as dramatic.

However, encouraged by Beall's observations, the cell-wall substance density for each of the 18 species was estimated using the constituent densities assumed by Beall as shown in Table 2 and the constituent fractions calculated from our determinations of chemical composition. These values are shown in Table 1. The hemicellulose content was taken as the difference between holocellulose and alpha-cellulose yield, while the lignin content was estimated by subtracting the holocellulose yield from unity. Figure 3 shows a plot of the relationship between calculated cell-wall substance density and measured cell-wall density. Although a strong relationship exists for the hardwood species, it is clear from the distinct difference between the slope of the relationship and the line of equivalency that these are not equivalent parameters as Beall has suggested. The apparent similarity he found between these same parameters was fortuitous. The four hardwoods he worked with had measured cellwall densities close to the average value for the hardwoods (1.460) and therefore, as seen in Fig. 3, will differ little from the calculated cell-wall substance densities.

The cell-wall substance densities that had been calculated were next corrected for the cell-wall void volumes estimated for this same experimental material by Kellogg and Wangaard (1969) in order to obtain esti-



FIG. 3. Relationships between calculated cellwall substance density and measured cell-wall density. Line of equivalency is shown,

mates of the dry cell-wall densities listed in Table 1. Figure 4 is a plot of these calculated cell-wall densities against the measured cell-wall densities. Statistical analyses revealed that the slopes of the separate relationships for the hardwood species and softwood species did not differ significantly from the slope of the line of equivalency. Thus, it would appear that the concept of void volume in dry cell walls is supported and that this is the correct comparison of parameters to make. It is also obvious that the calculated cell-wall densities are too

TABLE 2. Assumed values for constituent densities

Constituents	Constituent density, g/cm ³				
	Hardwoods	Sof twoods			
Alpha-cellulose	1.520	1.520			
Hemicellulose	1.457	1.666			
Lignin	1.366	1.347			

Source: Beall 1972. All values determined by a suspension method.



FIG. 4. Relationships between calculated cellwall density and measured cell-wall density. Line of equivalency is shown.

low, particularly for the hardwoods. A comparison of calculated and measured cellwall substance densities, as shown in Fig. 5, reveals the same discrepancies. These differences may result from several sources of error. One or more of the constituent substance densities may be in error, the constituent proportions may be incorrect, or the physical state of the constituents, *in situ*, may be different from that when physically separated from the cell wall. We will now consider the possibilities for each of these sources of error in turn.

First, let us consider the possibility that the density of one or more constituents is in error. Beall guestioned the accuracy of the density value he used for the alpha-cellulose constituent. If we use the theoretical maximum value of pure crystalline alpha-cellulose (1.585 g/cm³—Stamm 1964), the relationship between calculated and measured cell-wall density appears as shown in Fig. 6. The agreement between the data points and line of equivalency is considerably improved, but even with the use of the maximum value the calculated hardwood cellwall densities are still consistently lower than the measured values. As a further check on the suitability of the accepted density value for alpha-cellulose, densities



FIG. 5. Relationships between calculated cell-wall substance density and measured cell-wall substance density. Line of equivalency is shown.

were determined for the available alphacellulose for two softwoods (spruce pine and loblolly pine) and four hardwoods (basswood, hickory, red oak, white ash) using the liquid-suspension method described by Beall (1972). The average density of the alpha-cellulose for these six species was found to be 1.515 g/cm³. Since this value is essentially the same as that (1.520 g/cm³) used in our calculations, it is clear that an error in the accepted density value for alpha-cellulose is not the cause of the observed discrepancy.

In considering the possibility of error in the density values assumed for hemicellulose, we note that Beall (1972) reported a markedly lower density value for the acetylated hardwood hemicellulose (1.457 g/cm³) compared with the average softwood hemicellulose value (1.666 g/cm³). Since no other observations could be found in the literature to support or refute the low value for the hardwoods, verification was carried out on a sample of the identical birch 0-acetyl-4-0-methylglucuronoxylan¹. The density value obtained for this material (1.450 g/cm³) was virtually identical to that reported by Beall. Native hemicellulose was then prepared from the holocellu-

¹Obtained through the courtesy of Dr. T. E. Timmell, S.U.N.Y., Syracuse.



FIG. 6. Relationships between calculated cell-wall density and measured cell-wall density. Alpha-cellulose density assumed to be 1.585 g/cm³. Line of equivalency is shown.

lose material of white ash and basswood. The method used was a dimethyl sulfoxide extraction described by Bouveng and Lindberg (1965). After extraction, the hemicellulose was precipitated in ethanol. After several washings with ethanol, the hemicellulose was brought through an ethanolcarbon tetrachloride series to pure CCl₄ from which the density measurements were initiated. The density values obtained for replicated samples of these native xylans were 1.344 g/cm³ and 1.308 g/cm³ for white ash and basswood, respectively. The hemicellulose samples were then evaporated to the dry state, dissolved in water, and freezedried. The freeze-dried samples were saturated in CCl₄ and their densities re-determined. In this case, the replicated values were 1.416 g/cm³ and 1.413 g/cm³, respectively. Obviously the method of preparation affects the density value obtained, but there is no evidence that the discrepancy in the results can be explained on the basis of an erroneously low native hemicellulose density value.

No attempt was made to verify the density values used for the hardwood or softwood lignins.

In considering the second possible source of error, there is little chance that errors in the constituent proportion values used could account for the discrepancy in the results. The values obtained are within the range expected for these substances. Even if the values were altered by as much as 20%, the effect on the calculated cell-wall substance density would be small relative to the discrepancy of the calculated value from the measured value.

The final possibility seems to be the most logical conclusion to draw. That is, the density of one or more of the cell-wall constituents is appreciably different, *in situ*, from that measured using a flotation method on material removed through chemical isolation from the cell wall.

The general assumption that seems to have been made in the literature is that the densities of cell-wall constituents should be additive. It is accepted that this is not the case in the mixtures of certain liquidsi.e. water and sulphuric acid-and in certain solid-liquid interactions-i.e. cellulosewater. Our work and that of others have shown that the method of isolation markedly affects the density of the cell-wall constituents. Perhaps it is reasonable to expect that these solid substances, formed in an aqueous solution, and in many cases capable of developing strong chemical interactions, would not demonstrate an additivity of their separate densities.

CONCLUSIONS

Crystallinity index and alpha-cellulose content both have been shown to be directly related to cell-wall density. A simple method of mixtures was used to relate the constituent densities to cell-wall substance densities. Attempts to rationalize the difference between these calculated densities and the measured cell-wall substance densities suggest that the density of one or more of the cell-wall constituents is appreciably different *in situ* than that measured on the material removed from the cell wall. The method of preparation markedly affects the density of hardwood native xylans.

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