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Young's Modulus of Hemicellulose as Related to Moisture Content

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Summary. The Young's modulus of hemicellulose extracted from *Pinus radiata* wood has been measured by an indentation method. Values obtained for the modulus varied by almost three orders of magnitude, from 8.0×10^9 Pa in nearly dry hemicellulose to 1.0×10^7 Pa in nearly saturated hemicellulose. The very low value of the modulus at high moisture contents has some interesting implications for models of the mechanical behaviour of the wood cell wall.

Introduction

Much of mechanical behaviour of wood is governed by the properties of the wood cell wall, which in turn can be described in terms of the submicroscopic structure of the wall and the moisture dependent rheology of cellulose, hemicellulose, and lignin. The fine structure of the wood cell wall has received much attention in the past [Mark 1967; Kollmann, Côté 1968; Preston 1974], but little information has been available concerning the elasticity of its components. The only measured data have been values for the Young's modulus of high moisture content lignin [Srinivasan 1941] and the axial Young's modulus of crystalline cellulose [Sakurada, Nukushina, Ito 1962]. Recently, however, Cousins [1976] obtained values for the Young's and shear moduli of isolated lignin over a limited range of moisture contents by using conventional techniques, and later [Cousins 1977] extended the measurements to more extreme moisture contents with a ball indentation method.

The ball indentation test involves pressing a steel ball into the flat surface of the test specimen while continuously measuring the load (W) on the ball and the depth of indentation (h). It was shown [Cousins, Armstrong, Robinson 1975] that when the test specimen is much more compliant than the ball, the depth of elastic indentation (h_e) is given by

$$h_e = [(1 - \nu^2)/E]^{2/3} [9/8\, D]^{1/3} W^{2/3} \quad (1)$$

where D is the diameter of the ball, E the Young's modulus of the test specimen, and ν the Poisson's ratio of the test specimen.

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If the Poisson's ratio is unknown, there is an uncertainty in the value for E, but this can be minimized by assuming that ν is equal to $1/2\sqrt{2}$. Eq. (1) then becomes

$$E^{2/3} (\pm 12\tfrac{1}{2}\%) = (0.95/D^{1/3}) (W^{2/3}/h_e) . \quad (2)$$

A linear relationship between $W^{2/3}$ and h implies that the deformation of the test specimen is elastic, and the Young's modulus can therefore be determined.

The application of the ball indentation method to hemicellulose extracted from *Pinus radiata* wood is now described.

Procedure

Isolation of the test material

The xylan and glucomannan containing fractions of *Pinus radiata* hemicellulose were isolated by the method described by Harwood [1972]. Briefly, the method was as follows: 100 g of 20–80 mesh wood flour was soaked for 6 days in methanol to remove the bulk of the methanol extractives. It was then delignified in 27 % (w/w) sodium chlorite solution. No attempt was made to recover the galactoglucomannan containing fraction (Fraction A), because the amount available would have been too small for physical testing. The xylan containing fraction (Fraction B) was extracted in aqueous 24 % w/w potassium hydroxide solution. A pale yellow powder was obtained in a yield of 11.2 % (w/w) of the original ovendry extractive free wood. Fraction C, the glucomannan containing fraction, was then extracted in a $17\frac{1}{2}$ % aqueous solution of sodium hydroxide to which 4 % (w/w) boric acid had been added. A white powder was obtained in a yield of 6.1 %.

A sample of purified *Pinus radiata* xylan [Harwood 1972] was also obtained.*

Moulding of test specimens

The following procedure was found to give the most durable and uniform specimens. 0.5 g of the hemicellulose powder was conditioned to a moisture content of about 35 % (oven-dry weight) and loosely packed into a 4.8 mm diameter, cylindrical mould. Residual air was evacuated from the mould and the hemicellulose was compressed under a pressure of 2.8×10^8 Pa. No heating was applied.

The hemicellulose coalesced into a uniform, cylindrical rod approximately 10 mm long. Rods manufactured from Fraction B hemicellulose were translucent and tan in colour, while those from Fraction C were translucent and deep orange. They were robust and could be handled freely without fear of damage.

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* The purified xylan was kindly supplied by Dr. V. D. Harwood of the Forest Research Institute, Rotorua, New Zealand.

Because the specimens were translucent, any serious flaws were readily visible. Few of the Fraction B and C rods contained flaws, but all of those manufactured from the purified xylan contained small powdery regions.

Moisture conditioning

Fig. 1 shows the way in which moisture content varied with relative humidity (RH) for the two hemicellulose powders and for three lignins. In most cases equilibrium moisture content was apparently reached after a few days of conditioning at constant RH, but at 92½% RH the hemicellulose B powder, and at 97½% both of the hemicellulose powders showed no signs of reaching equilibrium even after 3 months of conditioning. Over the last two months at 97½% RH the hemicellulose B sample gained moisture at 4 times the rate of the hemicellulose C sample.

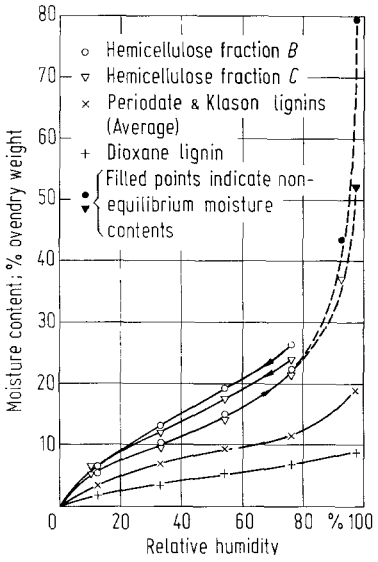

Fig. 1. Sorption of moisture by hemicelluloses and lignins

The solid hemicellulose rods generally behaved in the same way as the powders, although the time taken by the rods to reach equilibrium weight was somewhat longer. Abnormal behaviour occurred at RH's of 0 and 12%, where the rods still contained excess moisture after 3 months of conditioning. The rate of moisture loss after 3 months was so low however, that a quasi-equilibrium state seemed to have been reached and there seemed to be no reasons for not carrying out the mechanical tests with the specimens at the "high" moisture contents. To obtain measurements at lower moisture contents some replicate specimens were ovendried at 105 °C for 72 hours.

The rods conditioned at the very high RH's were still gaining moisture at the time of testing and so will probably have contained moisture gradients, especially the hemi-

cellulose B rods. Consequently the effective moisture contents in the outer regions of the specimens near the points of contact with the ball indenter will have been higher than the measured average values. Although this situation is clearly undesirable, it was necessary to test the specimens without delay as they were beginning to grow mould.

Test procedure

The apparatus and test procedure used were as described by Cousins, Armstrong and Robinson [1975]. Specimens were indented with a 6.35 mm diameter steel ball which was fitted to the load cell of an Instron testing machine.

Results

The load-displacement behaviour of the hemicelluloses was very similar to that of periodate lignin [Cousins 1977]. At all moisture contents a plot of $W^{2/3}$ versus h was linear for low values of h, but became nonlinear for high values. The gradient of the linear portion, and hence the Young's modulus of the specimen, decreased with moisture content, while in the non-linear region the permanent deformation and mechanical loss both appeared to increase with moisture content.

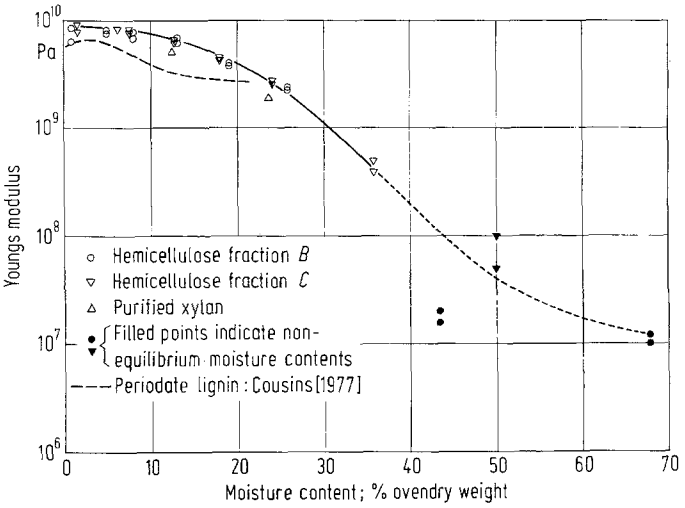

Fig. 2. Young's modulus of hemicellulose fractions B and C at various moisture contents

Young's modulus calculated according to Eq. (2) is plotted as a function of moisture content in Fig. 2, and for comparison the modulus of periodate lignin is also shown. The relationship between modulus and moisture content is generally well defined and seems to be almost identical for hemicellulose Fractions B and C.

The variability between individual values at moisture contents below 2 % is not surprising because of the severity of the drying method that had to be used. This is indicated by other specimens which when dried to even lower moisture contents developed many cracks during the drying process and were obviously not suitable for testing.

At moisture contents above 40 % there is apparently considerable scatter in the modulus values, but much of this is probably due to uncertainties in the moisture contents. The moisture content values used in the diagram were the average values measured for the test specimens, whereas the effective moisture contents will have been higher, especially for the hemicellulose B specimens.

The modulus values obtained for the purified xylan are lower than those for the Fractions B and C, but this is probably due to the presence of flaws in the xylan test specimens.

Variation in the moisture content of the hemicellulose seems, therefore, to be the main cause of variation in the data while differences in the chemical composition are of little importance. From 0 to 10 % moisture content the variation in modulus is small, but from 10 % the modulus decreases by nearly three orders of magnitude, from 8×10^9 Pa to about 1×10^8 Pa at 50 % (for Fraction C) and then 1×10^7 Pa at 68 % moisture content (for Fraction B). A comparison with the behaviour of periodate lignin is very interesting. Apart from an initial increase in value, the Young's modulus of periodate lignin also decreases with moisture content but not to the same extent. The minimum value for the lignin seems to be 2.8×10^9 Pa which is only 60 % below the maximum lignin value and is two orders of magnitude higher than the smallest hemicellulose value.

Discussion

Elasticity measurements on isolated hemicellulose and lignin may have some direct applications to isolated materials, but will mostly be used in the study of whole wood or paper. Accordingly, the question that must be answered is "how applicable to the *in situ* materials are the moduli of isolated hemicellulose and lignin?".

There are three main problems associated with current extraction procedures. They are (1) the possibility of changes in chemical structure, (2) changes in physical structure, and (3) the isolation of non-representative samples. In the case of lignin it is well recognized [Lai, Sarkanen, 1971] that alterations do occur during isolation. Acid, periodate, and dioxane lignins are changed chemically, dioxane, methanol and milled wood lignins suffer changes in physical structure, and methanol and milled wood lignins are possibly not representative of whole lignin. Taking all possible changes into consideration, periodate lignin is the one most likely to resemble *in situ* lignin so far as elastic properties are concerned.

With hemicelluloses there generally seems to be an implicit assumption that there is little chemical degradation during isolation. There are, however, almost certainly

some alterations in physical structure or arrangement. X-ray diffraction studies of the hemicellulose rods showed that there were no preferred molecular orientations, but there is some evidence for alignment in wood. Liang et al. [1960] suggest that both the xylan and glucomannan molecules, though not necessarily crystalline, tend to be aligned with the cellulose microfibrils. Since there appears to be no evidence for significant anisotropy in the transverse plane the assumption of transverse isotropy for the *in situ* hemicellulose seems to be realistic. The longitudinal Young's modulus for *in situ* hemicellulose would then have a greater value than the transverse modulus and an isotropic sample of isolated hemicellulose would have a modulus value between the two. Assuming that this is true, the very low value of the modulus near saturation moisture content has some interesting implications for models of the wood cell wall. For example, according to the "interrupted lamella" model of Kerr and Goring [1975] approximately one third of the hemicellulose forms a coating on the broad tangential faces of the cellulose fibrils, while the remaining two thirds is distributed throughout the amorphous lignin matrix. At high moisture contents the hemicellulose will contribute very little to the stiffness of the matrix and the stiff cellulose fibrils will tend to be decoupled from the matrix. Transverse loads on the wood cell will, therefore, be carried mainly by the lignin and the favourably oriented microfibrils of the P and S1 layers.

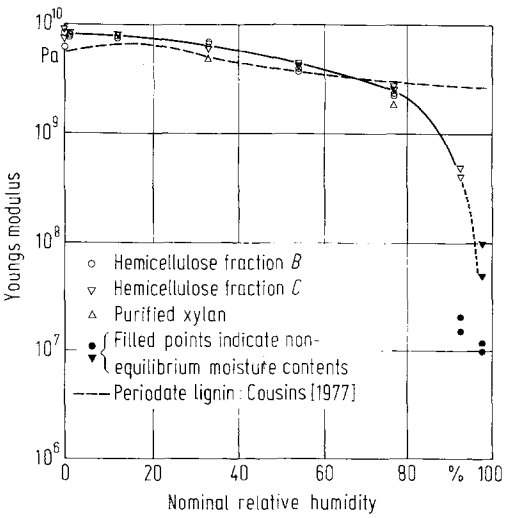

Fig. 3. Young's modulus of hemicellulose as a function of relative humidity

Although changing moisture content is likely to be the primary cause of the observed variations in the modulus values of hemicellulose and lignin, the relationship between the two moduli is governed by RH. For example, when the wall components are intimately mixed as in a cell wall, they will experience the same relative humidity and each will absorb moisture according to its sorptive capacity (Fig. 1). Thus the correct relationship between the moduli of the *in situ* components is best

illustrated if they are plotted as functions of relative humidity as shown in Fig. 3. The dominance of the lignin at moisture contents near saturation is then apparent.

Conclusions

Variation in the Young's modulus of hemicellulose is primarily due to variation in moisture content, and chemical differences between the xylan and glucomannan containing fractions seem to have little effect. The modulus varies from a value of 8×10^9 Pa at low moisture contents (0 to 10%) to 1×10^7 Pa at moisture contents near saturation (70%). In contrast the modulus of periodate lignin has a minimum value of 2.8×10^9 Pa, or more than 100 times that of the hemicellulose, near saturation moisture content.

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