ELASTICITY OF ISOLATED LIGNIN : YOUNG'S MODULUS BY A CONTINUOUS INDENTATION METHOD

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ABSTRACT

A continuous indentation method has been used to obtain values for the Young's moduli of lignins extracted from **Pinus radiata** D. Don wood by the periodate, Klason, and dioxane processes. The periodate lignin, which is considered to be similar to **in-situ** lignin, was considerably stiffer than the other two lignins at all moisture contents. Values obtained for the Young's modulus of periodate lignin ranged from 6.6×10^9 Pa (at 3.6% moisture content) to 2.8×10^9 Pa (near saturation moisture content).

INTRODUCTION

The elastic moduli of lignin are of considerable importance in theoretical modelling of the wood cell wall. Until recently, however, the only empirical value in common use has been the Young's modulus of high moisture content lignin, which was found by Srinivasan (1941) to be 2.0×10^9 Pa (204 kp/mm^2). Although this value is useful in studies of wood at high moisture contents, it is inapplicable to dry wood because the Young's modulus of lignin varies greatly with moisture content.

Cousins (1976) showed that the value obtained for the Young's modulus of lignin depended not only on the moisture content, but also on the method used for isolating the lignin from the cell wall. In a series of tensile experiments on small rods moulded from lignin powders he found that as the moisture content was increased from 3 to 12% the value for periodate lignin decreased from 6.7×10^9 to 3.1×10^9 Pa, and that for Klason lignin from 4.0×10^9 to 2.3×10^9 Pa. Measurements were not possible at higher and lower moisture contents, however, because the test specimens became too weak to be tested in tension. Attempts to measure the Young's modulus of dioxane lignin were also unsuccessful because of specimen fragility.

Earlier, Cousins, Armstrong and Robinson (1975) had obtained a value for the Young's modulus of dioxane lignin from an experiment in which a spherical steel ball was pressed into the flat surface of the lignin test specimen. They showed that when the indentor ball is rigid in comparison with the test specimen, the classical equation of Hertz (1896) (*see also* Timoshenko and Goodier, 1970) can be simplified to:

$$h_e = (9/8D)^{1/3} \left[(1 - \nu_s^2)/E_s\right]^{2/3} W^{2/3} \quad (1)$$

where h_e is the depth of elastic indentation, ν_s and E_s are respectively the Poisson's ratio and Young's modulus of the specimen, D is the ball diameter, and W the load on the ball. Since ν_s is unknown, a value of $\nu_s = 1/2\sqrt{2}$ can be assumed so as to reduce the uncertainty in E_s due to possible variation in ν_s ($0 \leq \nu_s \leq 0.5$) to $\pm$ 12.5%. Hence, Equation 1 becomes

$$E_s\ (\pm\ 12.5\%) = 0.93\ W/D^{1/2}\ h_e^{3/2} \quad (2)$$

The indentation method has two major advantages over a tensile test for measuring Young's modulus. Firstly, it is a compressive test and the highly stressed region of the specimen is well supported by the remainder of the specimen so that flaw induced failure is unlikely. Secondly, stresses in the specimen decrease rapidly with distance from the region of indentation, and so useful measurements can be made on a small test specimen. Its major disadvantage is that the Poisson's ratio of a specimen must be known before the Young's modulus can be calculated to better than $\pm$ 12.5%. Nevertheless, it is a very useful method for determining the Young's moduli of the small and often fragile specimens moulded from various lignins.

MATERIALS AND METHODS

Three samples of lignin were isolated from extractive-free *Pinus radiata* sawdust by the methods described in the following reports:

(a) Klason lignin: Tappi standard T13m - 54, Lignin in wood,

(b) Dioxane lignin: Rezanowich, Yean & Goring (1963), and

(c) Periodate lignin: Ritchie & Purves (1947).

Small cylindrical test specimens were moulded from the lignin powders by the method of Cousins (1976). They were cut to lengths of 7 mm, conditioned to the desired moisture contents above saturated salt solutions, and glued into blind, close fitting holes in a steel plate in such a way that approximately 0.5 mm of each specimen remained above the surface of the plate after being sanded and polished.

Each lignin specimen was indented with a 6.35 mm diameter steel ball as described in Cousins, Armstrong and Robinson (1975). The load on the ball and the displacement of the crosshead of the testing machine were recorded, as is shown in Fig. 1 for the periodate lignin. The crosshead speed was 50 μm/min.

Deformation of the testing machine was determined separately by pressing a 50.4 mm diameter steel ball into a steel plate, and subtracting the theoretical h_e for steel on steel (Cousins, Armstrong and Robinson, 1975) from the total measured crosshead displacement. There was an apparent excess recovery of the machine on load removal (Fig. 1), but this was an artefact caused by the relatively slow acceleration of the crosshead. Each time the direction of motion of the crosshead was reversed there was a slight pause before the crosshead accelerated to full speed. Since the reversal of the recording chart was instantaneous in comparison, the crosshead motion lagged behind the chart motion and an apparent negative crosshead displacement resulted. This effect can also be seen in each of the lignin curves.

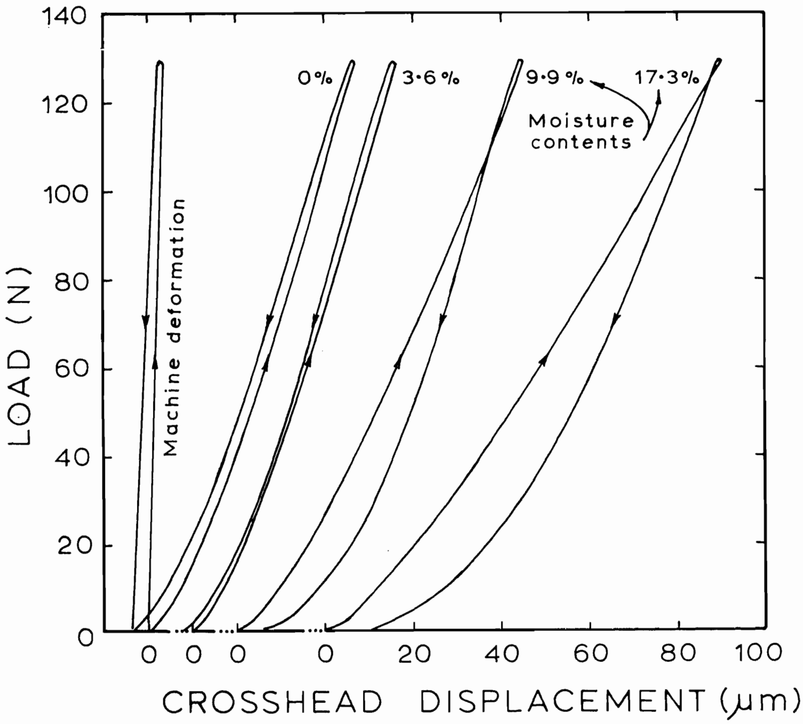

FIG. 1—Load versus crosshead displacement curves for periodate lignin at various moisture contents, and machine deformation. Origins of curves have been offset for clarity.

RESULTS AND DISCUSSION

Subtraction of the machine yielding from the lignin load *versus* crosshead displacement curves gives the $(\text{load})^{2/3}$ *versus* depth of indentation curves shown in Fig. 2. Each curve has an initial linear region indicating elastic deformation, followed by a curved "plastic flow" region. The gradient of the linear portion, and hence the Young's modulus of the lignin, tends to decrease with moisture content. At the same time the permanent deformation and mechanical loss both appear to increase.

Klason lignin showed very similar behaviour to periodate lignin, although it was less stiff at all moisture contents. Dioxane lignin, however, was very different. Its $(\text{load})^{2/3}$ *versus* depth of indentation curves remained essentially linear up to the maximum applied load of 130N. Permanent deformation and mechanical loss were both much smaller than for periodate lignin, and seemed to be independent of moisture content.

The values obtained for the Young's moduli of the lignins are plotted as functions of moisture content in Fig. 3. Included in the diagram are data from the present indentation tests (black symbols), data from Srinivasan (1941), Cousins, Armstrong and Robinson (1975), Cousins (1976), and a value estimated by Mark (1972) (all open symbols). There is good agreement between the tensile measurements of Cousins (1976) and the present indentation results, which gives added confidence in the indentation method.

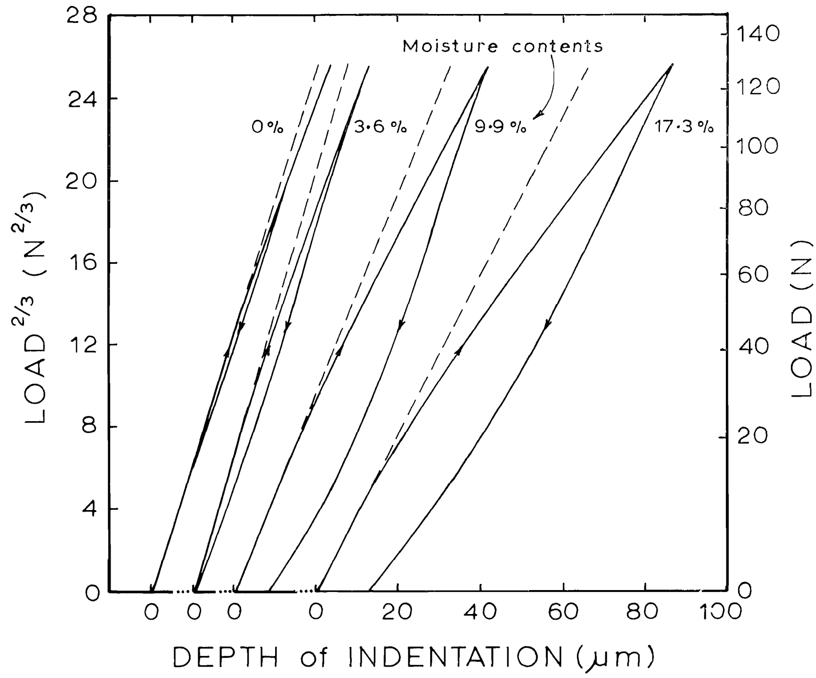

FIG. 2—$(\text{Load})^{2/3}$ **versus** depth of indentation curves for periodate lignin at various moisture contents. Origins of curves have been offset for clarity.

As the moisture content is increased from 0%, the Young's modulus of periodate lignin initially increases to 6.6×10^9 Pa at 3.6%, then decreases, rapidly at first to 3.0×10^9 Pa at 12%, and finally more slowly to 2.8×10^9 Pa at 17.3%. The modulus of Klason lignin behaves in a similar way except that the initial increase does not occur, and the modulus of dioxane lignin reaches its maximum value at 5.4% moisture content. Note that dioxane lignin absorbs much less moisture than periodate and Klason lignins (Cousins, 1976) so that the highest moisture content of the dioxane lignin tested was only 9.2%.

Some difficulties were encountered at zero moisture content. No dioxane lignin specimens were tested because they crumbled during the final stages of drying, and most of the other specimens cracked during testing. This is a possible reason for the large between-specimen variation observed at this moisture content.

In the indentation test, the elastic limit is indicated by the onset of non-linearity in the $(\text{load})^{2/3}$ *versus* depth of indentation curve (Fig. 2). According to Armstrong and Robinson (1974) the mean elastic stress, σ_e, and strain, ε_e, beneath the ball are given by $\sigma_e = 2W/\pi h_e D$ and $\varepsilon_e = (h_e/D)^{1/2}$. Hence it can be shown that the stress at the elastic limit for periodate lignin decreases linearly with moisture content, from $(2.2 \pm 0.1) \times 10^8$ Pa at 0% moisture content to $(0.75 \pm 0.3) \times 10^8$ Pa at 17.3%. The strain at the elastic limit does not vary greatly with moisture content.

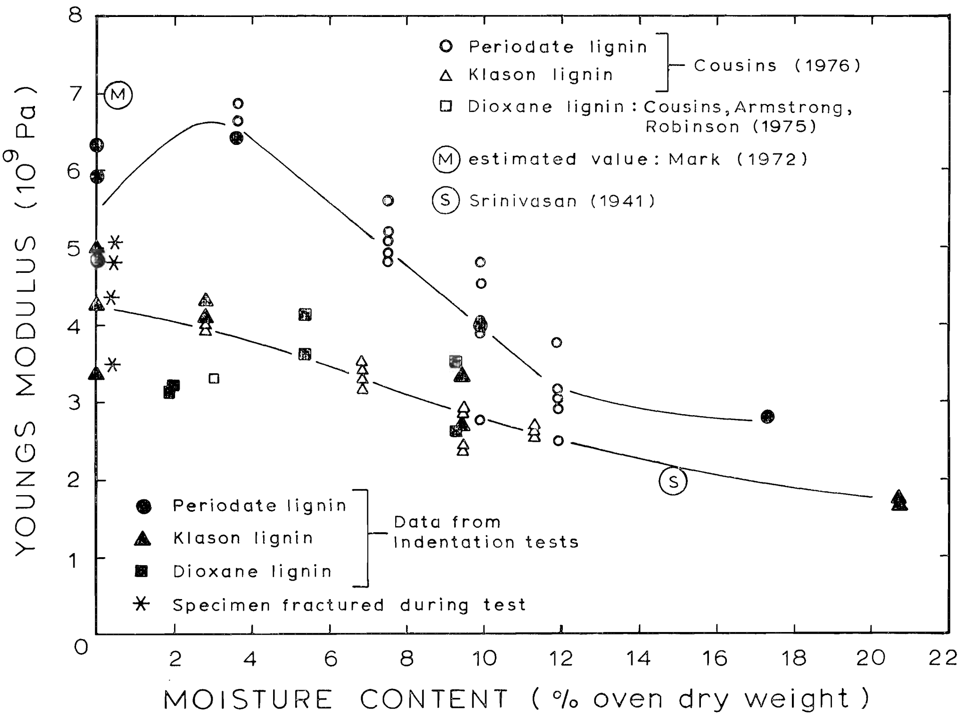

FIG. 3—Variation of Young's modulus with moisture content for periodate, dioxane, and Klason lignins. Data from previous tensile tests are included with the present indentation results.

The above limit stresses are three orders of magnitude higher than the tensile strength of lignin as measured by Gupta, Rezanowich and Goring (1962). A likely reason for the discrepancy is that the pressure used to mould the indentation specimens was three orders of magnitude higher than the pressures used by Gupta *et al.,* thus giving rise to improved internal bonding in the indentation specimens. Stress concentrations at flaws may also have lowered the tensile strengths.

One of the reasons for measuring the elastic constants of lignin is that they may be used in theoretical studies of the rheology of the wood cell wall, and it is necessary, therefore, to decide which of the three lignins tested above best represents *in-situ* lignin. According to Lai and Sarkanen (1971) Klason lignin undergoes more severe chemical degradation during isolation than the other two lignins, while Christensen and Kelsey (1958) state that dioxane lignin is the one most altered in physical structure.

Milled wood lignin also is thought to be relatively little altered chemically during isolation, but was not used in preference to periodate lignin in the above tests because (a) it is dissolved and then reprecipitated during extraction and so is likely to undergo considerable change in physical structure, and (b) it is possibly more representative of lignin from the middle lamella than from the cell wall (Lai and Sarkanen, 1971).

Thus it seems reasonable to suggest that periodate lignin is the most similar to *in-situ* lignin when both the physical and chemical structures are taken into consideration. Indeed, use of the modulus values obtained for periodate lignin in the wood cell wall model described by Cave (1976) leads to realistic predictions for the differential shrinkage and longitudinal Young's modulus of *Pinus radiata* wood. This is a good indication that the elastic behaviour of periodate lignin is reasonably similar to that of *in-situ* lignin.

CONCLUSIONS

The continuous indentation test is a reliable way of measuring the Young's moduli of isolated lignins because there is good agreement between moduli derived from both indentation and tensile techniques.

The elastic properties of periodate, Klason, and dioxane lignins are moisture sensitive. As the moisture content is increased, the Young's modulus of periodate lignin initially increases from an average value of 5.7×10^9 Pa at 0% moisture content to maximum of 6.6×10^9 Pa (average) at approximately 3%, and then decreases to 2.8×10^9 Pa at 17.3%. Klason and dioxane lignins are less stiff than periodate lignin, and the maximum values of their Young's moduli seem to occur at moisture contents of 0 and 5% respectively.

Of the lignins tested, periodate is the least altered during extraction from the cell wall and is likely to be the most similar to *in-situ* lignin so far as elastic properties are concerned. It can be assumed, therefore, that the values of Young's modulus measured for periodate lignin are the best approximations to those of *in-situ* lignin.

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