JOURNAL OF MATERIALS SCIENCE 10 (1975) 1655–1658

Young's modulus of lignin from a continuous indentation test

W. J. COUSINS, R. W. ARMSTRONG*, W. H. ROBINSON
Physics and Engineering Laboratory, D.S.I.R., Lower Hutt, New Zealand

The deformation of lignin in a continuous ball indentation test was almost entirely elastic up to a stress of 2.2×10^8 Pa (22 kg mm^{-2}). The load versus depth of indentation curve of the lignin followed closely the classical Hertz equation thus enabling the Young's modulus of lignin to be calculated. From these results a stress–strain curve for lignin was drawn.

1. Introduction

Armstrong and Robinson [1] have demonstrated that the continuous ball indentation test allows measurement of the combined elastic and plastic deformation behaviour of a material. In studies of single crystal KCl it was found that a very small but definite amount of elastic deformation preceded the plastic indentation process. Even after substantial plastic deformation had occured during loading of the indenter, it was found that the unloading curve followed approximately the theoretical elastic loading curve.

Use of the ball indentation test for elasticity measurements is based on the classical analysis of Hertz [2] (see also [3]). According to Hertz the combined ball and specimen elastic deformation h_e is given by

$$h_e = [(1-\nu_b^2)/E_b + (1-\nu_s^2)/E_s]^{\frac{2}{3}}(9/8D)^{\frac{1}{3}}W^{\frac{2}{3}}, \quad (1)$$

where ν_b and ν_s are Poisson's ratios, E_b and E_s are Young's moduli for the ball indenter and specimen, respectively, W is the applied load, and D is the ball diameter.

When a compliant specimen, such as wood lignin, is indented by a relatively rigid ball, say steel, the ball deformation may be considered to be negligible and so the first term in brackets in Equation 1 can be omitted with very little loss of accuracy. Secondly, for an unknown specimen material a value of $\nu_s = 1/2\sqrt{2}$ may be assumed so as to reduce any error in E_s due to the uncertainty in ν_s to ± 12.5%, $(0 \leqslant \nu_s \leqslant 0.5)$. On the basis of these simplifications Equation 1 becomes

$$E_s = 0.93\, W/D^{\frac{1}{2}} h_e^{\frac{3}{2}}. \quad (2)$$

Lignin comprises 50% of the matrix of the fibre-reinforced structure that makes up the wood cell wall. Theoretical investigations of the wood–water–elasticity relationships [4–6] require a knowledge of lignin's elastic constants. Few measurements have, however, been possible because of difficulties involved in the manufacture of test specimens from lignin powder. Lignin is insoluble in most liquids and on heating does not melt but only softens [7]. It is, therefore, difficult to mould defect-free specimens that are large enough for conventional elasticity measurements. An advantage of the ball indentation method is that only a very small region of the test specimen is highly stressed and so small specimens can be used.

2. Specimen preparation

The method of Resanowich *et al.* [8] was followed. 200 g of extractive-free *Pinus radiata* was gently refluxed under nitrogen in 2 litre of a mixture containing 1800 ml dioxane, 160 ml water, 36 ml conc. HCl. After 8 h the mixture was left overnight to cool and then it was filtered through a sintered glass funnel. The residue was washed with 700 ml of fresh dioxane. The combined filtrate and washings were neutralized with excess sodium bicarbonate and allowed to stand for 16 h. The liquid was concentrated at 40° C to a thick syrup using a rotary vacuum evaporator and the lignin was precipitated by forcing the syrup in a thin stream from a syringe

* Visitor from Mechanical Engineering Department, University of Maryland, College Park, Md 20742, USA.

under the surface of a 1% aqueous solution of Na_2SO_4. Further purification was affected by dialysis against distilled water. Finally, the lignin was dried over P_2O_5 in a vacuum desiccator.

Cylindrical test specimens were moulded from the lignin powder by the following method. 0.5 g of lignin powder (containing 3% moisture) was pressed into a 4.8 mm diameter, graphite-lubricated mould with a hand operated press (5000 N maximum load). It was then heated to 210° C while under a pressure of 1.6×10^7 Pa ($1.6\, kg\, mm^{-2}$). Softening occurred at 190° C and was accompanied by a slight decrease in volume. The resulting rods were dark brown in colour. They appeared to be hard and brittle.

3. Test procedure

Test specimens of 5 mm height were glued into close fitting holes 4 mm deep, within a steel plate which could be clamped to the base plate of an Instron Testing Machine, model TT-KM (250 KN maximum load). The machine cross-head was fitted with a load cell of type 2511-312 (100 to 5000 N) and a steel ball (diameter = 6.35 mm) indenter assembly was attached directly to the load cell.

Autographic records of the force, W, versus cross-head displacement, h, for loading, and h_u, for unloading, were obtained as shown in Fig. 1. The machine deformation h_m was determined

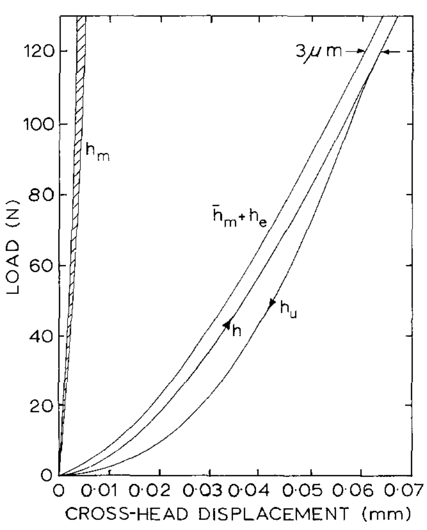

Figure 1 Load versus cross-head displacement for a continuous indentation test of lignin showing the experimental loading and unloading curves, and the calculated loading curve ($\bar{h}_m + h_e$) obtained by adding the calculated value of h_e for lignin to the average machine deformation $\bar{h}_m$.

separately by pressing a 50.8 mm diameter steel ball into a steel plate until a load of 130 N was supported, and subtracting the h_e for steel on steel calculated from Equation 1 from the total measured h value. A range of values of h_m was obtained as shown in Fig. 1.

4. Results

The $W^{\frac{2}{3}}$ versus h curve in Fig. 2 was obtained by subtracting the average machine yielding from selected values of h and h_u. The full line joins the points so obtained. It can be seen that except for an initial region of excessive displacement, the deformation behaviour of lignin was almost entirely elastic, following the Hertz solution to an

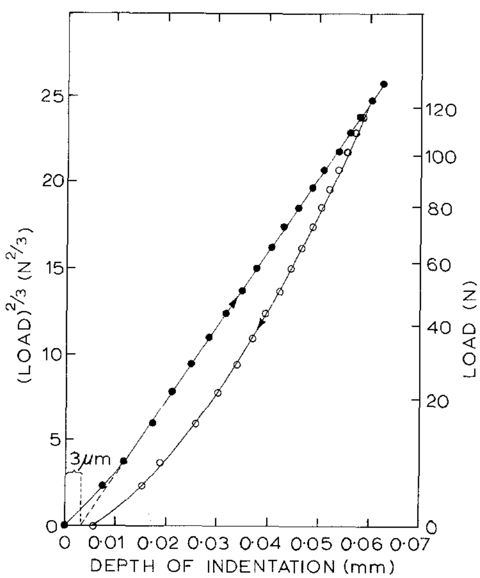

Figure 2 $(\text{Load})^{2/3}$ versus depth of indentation for lignin showing both loading and unloading curves. Extrapolation of the linear portion of the loading curve to zero load (dashed line) shows that an excessive displacement of 3 μm has occurred.

applied load value of 130 N. Of five specimens which were tested only two showed any significant plasticity at large loads. In both of these cases the total (residual) plastic deformation was less than 6 μm as compared with an elastic deformation of 60 to 70 μm. The initial deformation region exhibiting curvature in Fig. 2 was presumed to be due to surface roughness or some other spurious effect, giving an excessive displacement of approximately 3 μm. This occurred in all tests.

The effect of specimen size was investigated by indenting two specimens which were mounted in a "Perspex" (polymethylmethacrylate) plate. Since

Perspex and lignin appear to have about the same values of Young's modulus the lignin–perspex composite was thought to approximate a larger, uniform, lignin specimen. It was found that there were no significant differences between the elastic deformation behaviour of lignin mounted on perspex and lignin mounted on steel. Therefore the specimen size was judged to be adequate for the present tests.

The Young's modulus of lignin was determined from Fig. 2 to be 3.0×10^9 Pa. An average value of $E = 3.3 \times 10^9$ Pa (with a standard deviation of ± 12%) was obtained for the seven specimens. This is higher than the previously reported value of 2.04×10^9 Pa [9] but some difference is to be expected because the lignin used in [9] contained a greater proportion of water than the lignin used in the present tests.

The curve in Fig. 1 representing load versus calculated cross-head displacement (W versus $\bar{h}_m + h_e$) was obtained by adding the average machine displacement $\bar{h}_m$ to the h_e value obtained from Equation 1 with $E_s = 3.0 \times 10^9$ Pa. Except for the initial 3 μm of excessive displacement the agreement between the calculated and experimental load versus cross-head displacement curves is good.

Because the material deformation behaviour appears to be essentially elastic in these experiments, the Hertz theory can be carried a step further to describe an elastic stress–strain behaviour for the material. The mean stress at the surface of contact between the ball and the specimen surface is given [1] as

$$\sigma_e = W/(\pi h_e D/2). \quad (3)$$

From Equation 1 and neglecting the elastic deformation of the steel ball, σ_e may then be expressed as

$$\sigma_e = (4\sqrt{2}/3\pi)(E_s/(1-\nu_s^2))(h_e/D)^{\frac{1}{2}}. \quad (4)$$

A plot of σ_e against the strain ϵ_e where $\epsilon_e = (h_e/D)^{\frac{1}{2}}$ is shown in Fig. 3. To determine h_e so that this graph could be produced the initial excessive displacement (3 μm) was subtracted from the experimental results shown in Fig. 2. With the exception of one point the results follow Equation 4 extremely well further confirming the Hertz solution. The lower-most point in Fig. 3 deviates from the theoretical line because the corresponding point in Fig. 2 lies in the region of excessive displacement.

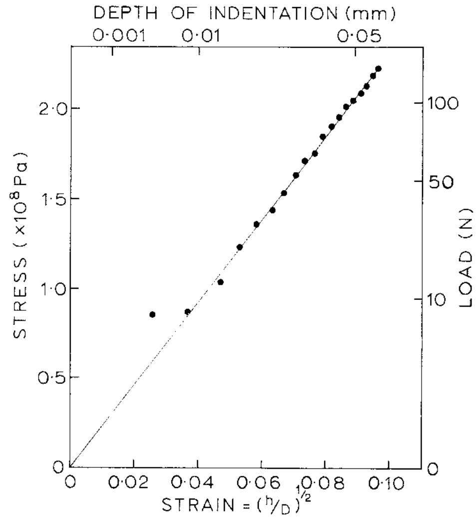

Figure 3 Stress–strain curve on loading for lignin; experimental points from Equation 3 and theoretical line from Equation 4.

5. Conclusions

The continuous ball indentation test is a satisfactory method of determining the Young's modulus of lignin because the deformation behaviour of lignin in this test is almost completely elastic. The Young's modulus of dioxane lignin at 3% moisture content is 3.3 (± 0.4) × 10^9 Pa, assuming that the Poissons ratio of lignin is $1/2\sqrt{2}$.

(1) The fact that $(\text{load})^{2/3}$ is proportional to the depth of indentation confirms the Hertz solution.

(2) It is possible to draw a stress–strain curve for lignin.

Acknowledgement

The authors are grateful to the New Zealand–United States Educational Foundation for the award of a Senior Fullbright-Hays Fellowship (to R.W.A.) during whose tenure this research has been accomplished.

References

1. R. W. ARMSTRONG and W. H. ROBINSON, *N.Z.J. Sci.* 17 (1974) 429.
2. H. R. HERTZ, "Miscellaneous Papers" (Macmillan, London, 1896) Chs. 5, 6.
3. S. P. TIMOSHENKO and J. N. GOODIER, "Theory of Elasticity" (McGraw-Hill, New York, 1970).
4. I. D. CAVE, *Wood Sci. and Tech.* 3 (1969) 40.
5. *Idem, ibid* 6 (1972) 157.

6. R. E. MARK, in "Theory and Design of Wood and Fibre Composite Materials," edited by B. A. Jayne (Syracuse University Press, Syracuse, New York, 1972).
7. D. A. I. GORING, *Pulp and Paper Mag. Canada,* **64** (1963) T517.
8. A. RESANOWICH, W. Q. YEAN and D. A. I. GORING, *Svensk Paperstidning* **66** (5) (1963) 141.
9. P. S. SRINIVASAN, *Q. J. Indian Inst. Sci.* **4** (1941) 222.

Received 21 March and accepted 14 April 1975.