THE ELASTIC ANISOTROPY OF KERATINOUS SOLIDS

II. THE RIGIDITY CONSTANTS OF RAM'S HORN

By K. RACHEL MAKINSON*

[*Manuscript received November* 30, 1954]

Summary

The rigidity constants of ram's horn have been determined by using a pulse technique to measure the velocities of propagation along the principal axes of transverse elastic waves of frequency 4 Mc/s. The results show that the conclusion, which was drawn previously from measurement of the dilatational constants, that ram's horn is transversely isotropic about the radial direction, is approximately though not exactly correct. The type of anisotropy and the relative magnitudes of the various elastic constants are directly correlated with the histological structure of the horn, which under the conditions of the measurements is more important than the molecular structure in determining the nature of the elastic anisotropy.

Denoting the radial, circumferential, and growth directions of the horn by r, θ, and z respectively, the rigidity constants for shear in the planes θz, zr, and $r\theta$ are $2\cdot4_6$, $2\cdot1_3$, and $2\cdot1_6 \times 10^{10}$ dyn cm^{-2}. The elastic constant which specifies the relation between the tensile stress in the θ direction and the extension in the z direction is about $5\cdot7 \times 10^{10}$ dyn cm^{-2}.

I. INTRODUCTION

In Part I of this series (Makinson 1954) values were reported for the dilatational elastic constants of various forms of keratin at 5 Mc/s; these were obtained by measurement of the velocities of ultrasonic waves in keratin, using a total reflection method with continuous waves. Theoretically, it should be possible to calculate the velocities of shear waves, and hence the rigidity constants, from the data obtained in the course of these experiments. In practice, only very approximate values could be obtained by these calculations, because the results were extremely sensitive to the initial data. Most of the measurements reported here were therefore made by a different method, using a pulse technique.

Throughout this work, the classical theory of elasticity for small strains has been used. Although this theory is not strictly applicable to a material of so complex a structure as keratin, it is adequate to describe the results within the accuracy of the measurements so far made.

II. NOTATION FOR THE ELASTIC CONSTANTS

It is necessary to describe briefly the usual crystallographic representation of the elastic constants of an anisotropic solid, in order to show clearly which constants have been measured and what assumptions or approximations were involved in their measurement. A fuller description is given by Mason (1950).

* Wool Textile Research Laboratories, C.S.I.R.O., Ryde, N.S.W.

In a Cartesian coordinate system with axes x_1, x_2, and x_3, the behaviour of an anisotropic solid is described by 36 constants

$$\left.\begin{matrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\ c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66} \end{matrix}\right\}, \quad .. \quad (\mathbf{1})$$

between which the relations $c_{ij} = c_{ji}$ hold, so that there are at most only 21 different constants. In solids which have sufficiently high crystallographic symmetry with respect to the axes, the matrix (**1**) is simplified by the disappearance of the shear cross-constants c_{ij}, $i \neq j$, i and/or $j > 3$. This is at least approximately the case for ram's horn, and these constants will throughout this paper be equated to zero.

The constants c_{ii} with $i = 1$, 2, or 3 (i.e. c_{11}, c_{22}, and c_{33}) represent the tensile stress in the direction x_i per unit extension in the same direction when all other strains are zero. They determine the velocity of propagation, in an infinite bulk of the solid, of longitudinal elastic waves travelling along the corresponding axes. These constants were measured in the work described in Part I, where they were written c_{rr}, $c_{\theta\theta}$, and c_{zz} respectively.

The constants c_{ii} with $i = 4$, 5, or 6 represent the shear stress in the plane x_2x_3, x_3x_1, or x_1x_2 respectively, per unit shear strain in the same plane, all other strains being zero, i.e. they are the principal moduli of rigidity of the solid; they determine the velocities of shear waves propagated along the principal axes. These are the constants which have been measured in the work described here.

The constants c_{ij} with $i \neq j$ and i, $j = 1$, 2, or 3 are related to the Poisson ratios of the solid; they represent the tensile stress in the x_i direction per unit extension in the x_j direction, all other strains being zero. One of them is evaluated in this paper.

When ram's horn is being considered, the axes x_1, x_2, and x_3 will be identified with the axes r, θ, and z, respectively, of Part I. The direction r is the radial direction of the horn, θ is the circumferential direction, and z the grain or growth direction. These are Cartesian, not cylindrical polar, axes.

A type of symmetry which will frequently be referred to in connection with ram's horn is transverse isotropy about x_1, i.e. symmetry such that all directions in any plane perpendicular to x_1 are elastically equivalent. In this case the matrix (**1**) becomes

$$\begin{matrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{22} & c_{23} & 0 & 0 & 0 \\ c_{12} & c_{23} & c_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{55} \end{matrix}$$

with

$$c_{44} = \tfrac{1}{2}(c_{22} - c_{23}).$$

This matrix has only five independent, non-zero constants.

III. Experimental

The specimens used were small parallelepipeds of ram's horn, with thickness between 1 and 3 mm and other dimensions between 5 and 20 mm; the small thickness was necessitated by the high attenuation of transverse waves in the horn. Their edges were aligned as accurately as possible along the principal directions r, θ, z of the horn. Specimens 1 to 6 were cut from one large horn of the pair which had been used for the measurement of the dilatational constants; specimens 7 and 8 were cut from a smaller and less homogeneous horn, in which the sheets of cells described in Part I as lying perpendicular to r were not flat, but were bent into a wavy form in the $r\theta$ plane.

The velocities of shear waves propagated in the direction of the thickness of each specimen were measured by the use of apparatus developed and constructed at the National Physical Laboratory, a modified form of the apparatus described by Bradfield (1950). The specimen was lightly oiled* to establish good acoustic contact and gripped between two steel probes along which was transmitted a pulsed, transverse, elastic wave of frequency 4 Mc/s. The specimen was so orientated that the direction of vibration in the probes was parallel to a principal direction of the horn. The time of transit of the pulse through the specimen and the thickness of the specimen while it was gripped by the probes were measured, and hence the velocity of propagation was calculated.

Some difficulties were encountered in the application of the method to horn. The most serious was that the measured velocity was found to be sensitive to the pressure exerted by the probes on the horn, an effect which had not been encountered with the harder solids for which the apparatus was designed. It was found necessary to adjust the pressure by means of springs to an approximately constant value of about 4×10^8 dyn cm^{-2}.

No correction was applied for end effects due to surface films etc., since these corrections had been found by Bradfield (1950) to be small in this apparatus.

The relative humidity and the temperature were not closely controlled, as they are not important at these frequencies (see Part I). The specimens were stored and used at about 20°C and between 35 and 60 per cent. R.H.

IV. Results

(*a*) *Velocities*

The values of the shear wave velocities determined at a fixed pressure are shown in Table 1 and Figure 1(*a*). The random errors in the individual measurements were small (probable error $\leqslant 0 \cdot 004 \times 10^5$ cm/sec in all but one case, in which it was $0 \cdot 014 \times 10^5$), but duplicate measurements on different specimens differed by a greater amount, owing apparently to inhomogeneity of the horn.

* The present, improved practice in the National Physical Laboratory is to use a solid transfer film, instead of oil, for weak solids; this permits lower pressures between the probes and the specimens.

These data show that most of the principal transverse wave velocities are close to $1 \cdot 3 \times 10^5$ cm/sec, but one is significantly larger: $\omega_{z\theta}$, the velocity of a wave propagated in the z direction with vibration parallel to θ, is $1 \cdot 42 \times 10^5$ cm/sec (range $1 \cdot 40$ to $1 \cdot 44$).

TABLE 1

VELOCITIES OF TRANSVERSE WAVES, $\times 10^{-5}$ CM SEC^{-1}, AT FIXED PRESSURE

Direction of progagation		r	r	θ	θ	z	z
Direction of vibration		z	θ	z	r	r	θ
Specimen	Thickness (cm)						
1*	0·308						
2	0·223			1·33	1·31		
3	0·259	1·29	1·26				
4	0·200	1·32	1·29				
5	0·258					1·25	1·40
6	0·112					1·25	1·44±0·03
Means		$1 \cdot 30_5$	$1 \cdot 27_5$	1·33	1·31	1·25	1·42

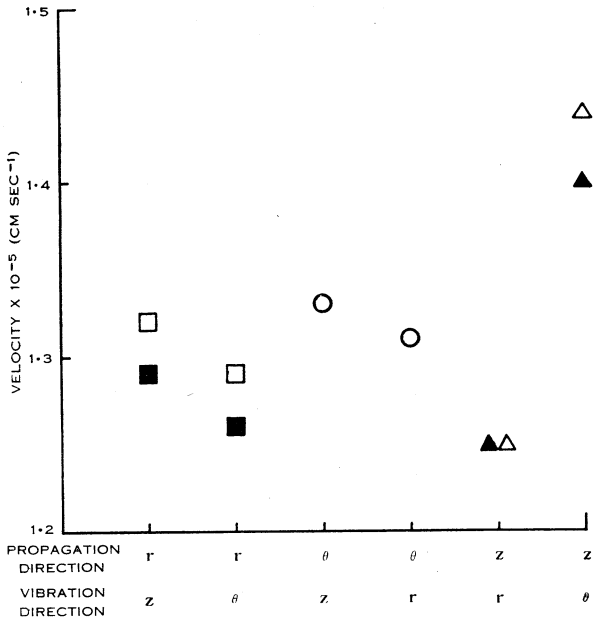
Error (1 in 20 level) for each individual measurement was $\leqslant 0 \cdot 01 \times 10^{-5}$ cm sec^{-1} except where otherwise indicated.

* Specimen 1 was damaged before measurement.

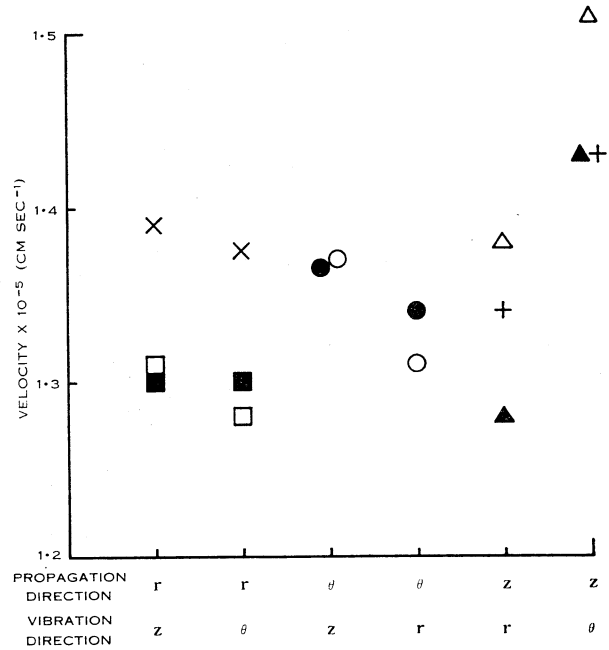
Three other sets of measurements confirm that $\omega_{z\theta}$ is greater than the other velocities; these are: (i) the less accurate measurements on specimens 1 to 6 which are shown in Figure 1(b). These were made without standardizing the pressure or correcting for compression of the horn; (ii) some approximate measurements on specimens 7 and 8, which are also shown in Figure 1(b). These were preliminary measurements made by a different observer, Dr. G. Bradfield, of the National Physical Laboratory, on specimens cut from a different horn, one which had a poorly oriented structure (see last section); (iii) calculation from the observations made during measurement of the dilatational velocities, which gave $\omega_{z\theta}$ about $1 \cdot 6 \times 10^5$ cm/sec as against about $1 \cdot 3$ or $1 \cdot 4 \times 10^5$ cm/sec for the other velocities. In this case there was no static pressure.

In none of these three sets of measurements can much significance be attached to the absolute values of the velocities, but their relative values, which are more accurate, confirm that $\omega_{z\theta}$ is higher than the other velocities.

The data of Figures 1(a) and 1(b) show a small difference between $\omega_{r\theta}$ and ω_{rz}, to which significance must be attached since the compared velocities were measured on the same specimens, so excluding the effect of variation of the horn.



(a)



(b)

Fig. 1.—The velocities of transverse waves in ram's horn: (*a*) at fixed pressure of 4×10^8 dyn cm^{-2}; (*b*) less accurate values obtained without standardizing the pressure. Specimens 1 to 6 cut from one horn, specimens 7 and 8 from another, of inferior orientation.

Specimen	1	2	3	4	5	6	7	8
Symbol	●	○	■	□	▲	△	×	+

The small differences shown in Figure 1(*a*) between ω_{zr} and ω_{rz}, and between $\omega_{r\theta}$ and $\omega_{\theta r}$, cannot be considered significant, as the compared measurements were made on different specimens. It was not possible in the time for which the apparatus was available to make a thorough statistical test of these differences.

(*b*) *Elastic Constants*

In order to calculate the elastic constants it is necessary to know the crystallographic symmetry of the horn. This is discussed in the next section, where it is shown that it is a reasonable approximation to put the shear cross-constants equal to zero, and to calculate the rigidity constants from the equations

$$c_{44} = \rho\left(\frac{\omega_{\theta z} + \omega_{z\theta}}{2}\right)^2; \quad c_{55} = \rho\left(\frac{\omega_{zr} + \omega_{rz}}{2}\right)^2; \quad c_{66} = \rho\left(\frac{\omega_{r\theta} + \omega_{\theta r}}{2}\right)^2,$$

where ρ is the density of the horn, taken as $1 \cdot 30 \pm 0 \cdot 02$ gm cm^{-3} (see Part I). The values so calculated are shown in Table 2. It is clear that c_{55} and c_{66} are equal within the accuracy of the data, and less than c_{44}.

It will be shown in the next section that ram's horn is approximately transversely isotropic about r, so that the constant c_{23} $(= c_{\theta z})$ can be calculated approximately from the relation

$$c_{44} = \tfrac{1}{2}(c_{22} - c_{23}).$$

TABLE 2

THE PRINCIPAL RIGIDITY CONSTANTS OF RAM'S HORN

Calculated with the assumption of transverse isotropy about radial direction

Constant	Shear Plane	Value of Constant $\times 10^{-10}$ (dyn cm^{-2})
c_{44}	θz	$2 \cdot 46 \pm 0 \cdot 2$
c_{55}	zr	$2 \cdot 13 \pm 0 \cdot 1$
c_{66}	$r\theta$	$2 \cdot 16 \pm 0 \cdot 1$

The limits given correspond to the range of the observations at fixed pressure.

Values of c_{22} $(= c_{\theta\theta})$ have been determined by both pulse and continuous wave techniques (see Part I); it is appropriate to use the former value, $c_{22} \doteq (1 \cdot 05 \pm 0 \cdot 01) \times 10^{11}$ dyn cm^{-2}, since the conditions under which this value was obtained were similar to those of the transverse wave measurements, although the static pressure was not as high. This value of c_{22} gives $c_{23} = (5 \cdot 6_5 \pm 0 \cdot 1) \times 10^{10}$ dyn cm^{-2}. In view of the approximations of the argument and the sensitivity of c_{23} to the value adopted for c_{22}, which itself depends on pressure, this value of c_{23} should be treated with some reserve; e.g. adoption of the continuous wave value $c_{22} = 1 \cdot 01 \times 10^{11}$ dyn cm^{-2}, determined under zero static pressure, would have given $c_{23} = 5 \cdot 2 \times 10^{10}$ dyn cm^{-2}. It seems probable that c_{23} under a static pressure of about 4×10^8 dyn cm^{-2} lies in the range $(5 \cdot 7 \pm 0 \cdot 5) \times 10^{10}$ dyn cm^{-2}.

V. The Symmetry of Ram's Horn

The values of the dilatational elastic constants reported in Part I indicated that ram's horn is transversely isotropic about the radial (r) direction. If this were strictly true, the "transverse" waves in the principal directions would be strictly transverse, and their velocities would satisfy the relations

$$\omega_{rz} = \omega_{zr} = \omega_{r\theta} = \omega_{\theta r}\,;\ \omega_{\theta z} = \omega_{z\theta},$$

where ω_{ij} is the velocity of a wave propogated along the x_i-axis with vibration direction parallel to x_j.

The results quoted in the last section show that $\omega_{\theta z} \neq \omega_{z\theta}$ and $\omega_{rz} \neq \omega_{r\theta}$. It is highly improbable that these inequalities are due merely to misalignment of the specimens, since they have been found for different specimens and, in the former case, by different methods of measurement. The most probable explanation is that the symmetry of ram's horn is rather low, being that of a crystal system for which the shear cross-constants are not all zero.

In order to calculate the rigidity constants from the measured velocities, the approximation has been made of putting the shear cross-constants equal to zero, which would entail $\omega_{ij} = \omega_{ji}$, and using the mean of ω_{ij} and ω_{ji} in the calculations. Since the differences between ω_{ij} and ω_{ji} are not large, the error introduced by this approximation should be small, as may be seen by comparison with a rather similar problem considered by Fein and Smith (1950). There would be little point in attempting to improve the estimates of the rigidity constants at present, as the horn itself is so variable.

The data of Table 2 show that within the accuracy of this approximation ram's horn is transversely isotropic about r, as was concluded from measurement of the dilatational constants.

VI. Correlation of the Elastic Anisotropy with the Structure

It was shown in Part I that if the elastic anisotropy of ram's horn was primarily determined by its molecular structure, its symmetry would approximate to transverse isotropy about the growth direction z, whereas if it were determined by the histological structure the symmetry would approximate to transverse isotropy about the radial direction r; the latter was observed. This observation is confirmed by the data on the shear wave velocities presented here.

The small departure from strict transverse isotropy about r does not contradict the conclusion that the anisotropy is determined primarily by the histological structure; it is to be expected that the spiral manner of growth of ram's horn will introduce some small departure of the crystallographic axes from orthogonality.

The correlation of the anisotropy with the histological structure can be carried a little further. The structure of ram's horn, described in Part I, approximates to a pile of sheets of keratin lying perpendicular to r, comparatively weakly joined together along r. Since the molecular chains lie in the plane of the sheets, the constant $c^h{}_{rr}$ will be less than $c^h{}_{\theta\theta}$ or $c^h{}_{zz}$, where the superscript h refers to the material of the sheets. All three constants for the pile of sheets will be reduced by the lamination of the structure, but it can easily be shown

that c_{rr} will be reduced more than $c_{\theta\theta}$ or c_{zz}. Hence, for the horn as a whole, c_{rr} should be less than $c_{\theta\theta}$ and c_{zz}, as is in fact observed.

In the case of the rigidity constants it is not possible to say with certainty which of the constants $c^h{}_{44}$, $c^h{}_{55}$, and $c^h{}_{66}$ would be greatest, but it is probable that $c^h{}_{44}$ would be, since the crossed or dispersed molecular chains lie in planes perpendicular to r. It can be shown that c_{55} and c_{66} will be reduced by the lamination of the structure more than c_{44}, so it is very probable that for the horn as a whole c_{44} would be greater than c_{55} and c_{66}, as is in fact observed.

VII. Comparison with Results Obtained by Other Workers

Very few measurements have been made of the rigidity constants of keratin. All previous ones have been made on wool or hair fibres at frequencies of the order of 0·1 c/s, and only the torsional rigidity about the fibre axis (c_{44}) has been determined. The weight of the evidence (Auerbach 1923 (after correction); Peirce 1923; Herzog 1928; Speakman 1929; Ray 1947; Lochner 1949; Meredith 1954) is that under these conditions and at 20°-25°C, c_{44} for keratin fibres is about $1{\cdot}8 \times 10^{10}$ dyn cm^{-2} in the completely dry state and $1{\cdot}0 \times 10^{10}$ dyn cm^{-2} at a relative humidity of 65 per cent.

The structure of keratin fibres is different from that of ram's horn, and they would be expected to be transversely isotropic about the fibre axis, so that this modulus is not exactly comparable with any of the values $c_{44} = 2{\cdot}4_6$, $c_{55} = c_{66} = 2{\cdot}1_5 \times 10^{10}$ dyn cm^{-2} found here for ram's horn. However, they should not differ much under the same conditions, as the anisotropy is not marked in either case. The large difference observed is to be ascribed to the very large difference in the frequency of the measurements, relaxation processes which occur in the keratin at low frequency being unable to follow the high frequency. Such dispersion of the elastic constants is common in high polymers, and is also shown by the dilatational constants of keratin (see Part I). These relaxation processes in keratin can also be blocked to some extent by a decrease of regain, as is shown by the steep increase in the low-frequency elastic constants with decrease in regain. Under completely dry conditions, c_{44} for the fibres at 0·1 c/s ($1{\cdot}8 \times 10^{10}$ dyn cm^{-2}) is approaching the value of c_{55} or c_{66} ($2{\cdot}1 \times 10^{10}$ dyn cm^{-2}) determined for ram's horn at 4 Mc/s.

It is not possible to make any comparison of the constant c_{23} determined here with the value of the Poisson ratio $\sigma_{z\theta}$ which was measured by Warburton (1948) for horn, since $\sigma_{z\theta}$ cannot be calculated from c_{23} until the remaining constant c_{12} has been measured independently.

VIII. Conclusions

The measurements of the dilatational elastic constants of various forms of keratin at 4 and 5 Mc/s, which were reported in Part I, led to the conclusion that the elastic anisotropy of keratin in the region of small strains depended at least as much on its histological as on its molecular structure. The measurements of the rigidity constants of ram's horn reported here support this conclusion. The elastic behaviour again approximates to transverse isotropy about

the radial direction, which is histologically unique, rather than about the growth direction, which is molecularly unique. There is a small departure from strict transverse isotropy, which is to be expected in view of the spiral structure of ram's horn. The relative magnitudes of both the three dilatational and the three rigidity constants are such as would be expected in view of the histological structure of ram's horn.

The rigidity constants of ram's horn are: $c_{44} = (2\cdot46 \pm 0\cdot2) \times 10^{10}$; $c_{55} = (2\cdot13 \pm 0\cdot1) \times 10^{10}$; $c_{66} = (2\cdot16 \pm 0\cdot1) \times 10^{10}$ dyn cm^{-2}; these constants refer to shear in the θz, zr, and $r\theta$ planes respectively, and have been determined at a frequency of 4 Mc/s, a temperature of about 20°C, and relative humidities between 35 and 60 per cent., under a static pressure of 4×10^8 dyn cm^{-2}. They have been calculated by making the approximation that the shear cross-constants are zero. The limits quoted correspond to the range of the observations.

These values are higher by a factor of two than the values, determined by other workers, of the torsional rigidities of wool and other keratin fibres about the fibre axis at frequencies of the order of 10^{-1} c/s and at about 65 per cent. R.H.; this is ascribed to the blocking of relaxation processes at the higher frequency.

The elastic constant c_{23}, which measures the tensile stress in the x_2 or θ direction per unit extension in the x_3 or z direction, has been roughly evaluated by making the approximation that ram's horn is transversely isotropic about x_1 or r. It probably lies in the range of $5\cdot2$ to $6\cdot2 \times 10^{10}$ dyn cm^{-2}.

No estimate can be made from these data of the remaining constant c_{12}.

IX. Acknowledgments

The bulk of this work was carried out while the author held an I.C.I. Research Fellowship in the Electrical Engineering Department of the University of Leeds. The author wishes to thank the University and the Department for the Fellowship and for the facilities provided. She is also deeply indebted to Dr. G. Bradfield for allowing her to use for most of the measurements an apparatus designed and constructed at the National Physical Laboratory, and to both Dr. Bradfield and Mr. R. F. Pulfer, of the same laboratory, for their help. She also wishes to thank Dr. K. M. Rudall, of the University of Leeds, for several helpful discussions on structure.

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