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Observations on regenerated chitin films

I. JOFFE*, H. R. HEPBURN†
*Department of Physics, †Department of Physiology, University of the Witwatersrand, Johannesburg, South Africa

Chitin films regenerated from shrimp shell waste were studied in order to determine stress-strain behaviour and tensile strengths as related to preferential chain orientation.

Plastic deformation of the chitin films was observed to cause a decrease in the transmission of visible light and the stress-strain behaviour could be described approximately by a linear Bingham model incorporating work-hardening.

The properties of chitin films were observed to deteriorate both in strength and dyestuff affinity over a 30-year period.

1. Introduction

Chitin (poly-*N*-acetyl-*D*-glucoseamine), a common structural polymer of insects, crustaceans, and fungi, has long been of interest to biologists and a number of studies have been made on its physical properties as related to structure [1]. It is of interest to note that chitin was also extensively studied by industrial chemists during the 1920 – 1940 period as the possible basis of regenerated polymers [2]. The subsequent development of synthetic polymers diverted attention from this material until only recently when it is again being investigated as a possible basis for natural polymeric material. The present account reports on some mechanical and chemical properties of regenerated chitin films.

2. Experimental procedure

2.1. Materials

A film of regenerated chitin, 25 μm thick, prepared from a chitin xanthate dispersion of shrimp shell waste was used for tensile testing. The material tested was a portion of a film originally made by C. J. B. Thor around 1940 [3].

The occurrence of form birefringence as observed in a polarizing microscope indicated the presence of preferential orientation of the chitin polymer chains in the sheet. On immersion of the film in water, anisotropic swelling occurred, confirming this and allowing the direction of the preferential orientation to be unambiguously determined.

Because Thor's preparation technique used glycerol as a softener [3], the possibility existed that this contaminant was still present in the sheet supplied. Consequently the specimens were soaked for 2 h in distilled water to extract any residual glycerol present and then allowed to dry in air.

2.2. Tensile testing

Specimens for tensile testing having conventional dumb-bell shapes were punched from the chitin sheet in such a way that, when tested, the tensile stresses could be applied either perpendicular or parallel to the preferential axis of the sheet. In all tests an extensometer designed for use with small samples was used [4]. Specimen guage lengths ranged from 3.2 to 7.2 mm and testing was performed at constant rates of elongation, up to 33 μm min^{-1}. These corresponded to strain rates of up to about 1% min^{-1}. Testing was performed at room temperature.

2.3. Dyestuff affinity

Offcuts from tensile specimen preparation were used to test the dyestuff affinity of this material. A series of tests for affinity to acidic (fast green, orange G and Biebrich scarlet, Heidenhain's haematoxylin, and Evans blue) and basic (acridine orange, methylene blue, basic fuchsin, and toluidine blue) dyes was performed by

immersion dyeing for 1 h at room temperature followed by a wash in water for several hours. No mordants were used.

3. Results

3.1. Mechanical properties

For both orientations it was found that the stress-strain curves of the regenerated chitin sheet consisted essentially of two linear regions for the rates of elongation used. The elastic region was Hookean and the linearity was preserved up to strains of about 1%. The transition point from the elastic to the plastic region was not sharply delineated (Figs. 1 and 2) and no evidence was found for anelastic behaviour.

Fig. 1 is a stress-strain curve representing the average behaviour of nine samples tested with the tensile stress parallel to the preferred axis of the specimens. The elastic modulus had a value of

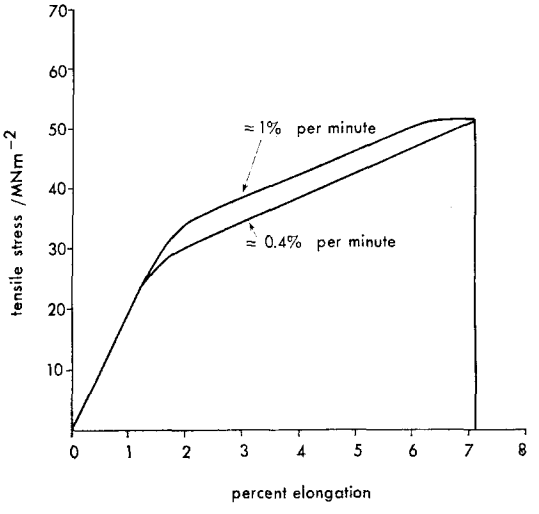

Figure 1 Average stress-elongation curves for regenerated chitin. Tensile stress applied parallel to the preferred orientation of the specimen.

$(1.97 \pm 0.07) \times 10^9$ Nm^{-2} and the tensile strength of the material was $(5.10 \pm 0.19) \times 10^7$ Nm^{-2}. The quoted uncertainties have been calculated for 95% confidence intervals. Similar values were obtained for some specimens which had not been glycerol-extracted. For this specimen orientation, rupture occurred for elongations of about 7.1%, whereas the proportional limit was found approximately at 1.2% elongation. The second linear region, occurring in the domain of plastic deformation, had a slope of $(4.08 \pm 0.08) \times 10^8$ Nm^{-2}. Thus, the material work-hardened in proportion to the amount of plastic deformation. For specimens tested with the stress applied perpendicular to the preferred axis, the stress-strain behaviour was as is shown in Fig. 2. In this orientation, for nine samples, the elastic modulus was $(2.13 \pm 0.06) \times 10^9$ N m^{-2} and the tensile strength was $(4.38 \pm 0.44) \times 10^7$ N m^{-2}. Elongation at rupture was about 14% (double the previous value) and the proportional limit decreased. Work-hardening was considerably less rapid, the slope of the second linear region having decreased to $(1.44 \pm 0.14) \times 10^8$ N m^{-2}.

From Figs. 1 and 2 it will be seen that for both orientations an increase in the strain rate (within the restricted range of elongation rates used) produced almost no change in the elastic behaviour of the material. However, more rapid deformation had the effect of shifting the second linear region of the curves towards higher stresses while keeping the slope reasonably constant.

3.2. Fracture behaviour

It was observed visually that the regenerated chitin films became opaque as the degree of elongation increased to relatively large values. This effect was not observed in the elastic region of the curves and after rupture the material remained opaque. Thus, the decrease in optical transmission is associated with irreversible plastic deformation and the occurrence of localized opacity during testing was taken as evidence of local plastic deformation.

Fracture propagation was studied using notched specimens. Right-angled triangular notches were cut to a depth of about 55 μm and the notch characteristics were such that crack propagation began at an average stress of $(4.8 \pm 0.3) \times 10^7$ N m^{-2} when applied parallel to the preferred axis and $(4.0 \pm 0.3) \times 10^7$ N m^{-2} when perpendicular to the axis. Under these circumstances, crack propagation was slow in both orientations and appeared to be driven by the continuing extension of the sample. Stopping the extensometer with the crack only partially through the material had the effect of allowing the crack to propagate slightly further as the elastic strains relaxed, after which crack motion ceased. This observation of the stress-strain behaviour with the observed strain-rate dependence strongly suggests the occurrence of viscous flow in the deformation mechanism.

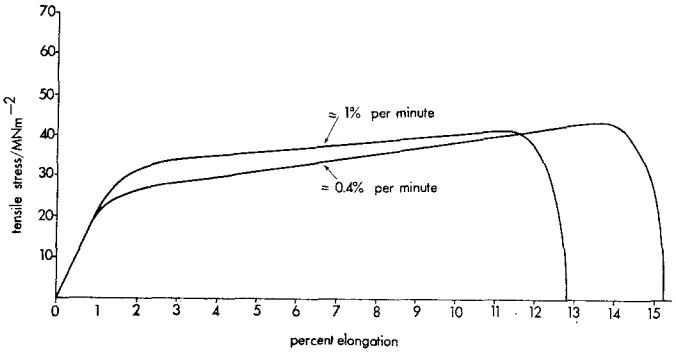

Figure 2 Averaged stress-elongation curves for regenerated chitin. Tensile stress applied perpendicular to the preferred orientation of the specimen.

For both orientations studied, the cracks travelled horizontally across the specimens, indicating fracture in a pure tensile mode both parallel and perpendicular to the preferred orientation direction. Opacity ahead of the crack tip supplied evidence that fracture was accompanied by extensive plastic deformation, consequently any theoretical treatment of the fracture of this material should take the energetics of this process into consideration.

3.3. Dyestuff affinity

In view of the fact that regenerated chitin has been used in the manufacture of both washable wall-papers and coloured fabrics resistant to laundering [2], dye retention is an important quality of this material. It was originally reported for this same sheet [3] that acid dyestuffs were retained but that basic dyestuffs were not. In the present study both acidic and basic dyes were equally well retained.

4. Discussion

The value originally obtained by Thor and Henderson [3] for the tensile strength of regenerated chitin was 9.31×10^7 N m^{-2} which is about 1.8 times greater than the values recorded in the present work for the same sheet tested more than 30 years later. Great care was taken to avoid inadvertent notches in the specimens, and it is concluded that regenerated chitin, exposed to the atmosphere for long periods, degenerates in time. However, in view of past consumer applications of regenerated chitin this need not detract seriously from its use.

The similarity of the values obtained for the elastic modulus parallel and perpendicular to the preferred orientation axis of the chitin indicates relatively strong cross-linking of the polymer chains. This must be responsible, to some extent, for the observed viscous damping of the plastic flow. The mechanism of fracture of the film is of interest since, while the ultimate tensile strengths of the two orientations were not greatly different, the fractional elongations at failure differed by a factor of 2. This probably results from different deformation mechanisms operating for the two orientations, also producing different rates of work-hardening.

The origin of the opacity induced by plastic deformation is somewhat obscure. It could be due, possibly, to the microscopic fracture of individual polymer chains or alternatively, to strain-induced enhancement of molecular alignment. This could produce opacity in a similar way to that in which nematic liquid crystals become opaque with increasing order. Both of these mechanisms would be consistent with the observed mechanical properties.

It would seem that the above points are crucial to an understanding of the behaviour of regenerated chitin and only direct evidence, such as might be obtained from X-ray diffraction observations, will enable the deformation mechanisms to be unequivocally established.

The general nature of the stress-strain curves suggests the presence of viscous damping which is borne out by the strain-rate dependence seen in Figs. 1 and 2. The linearity of the elastic regions and the regions of plastic deformation enables a naive phenomenological model of the mechanical behaviour of this material to be constructed. This is based on the linear Bingham model [5], modified to take account of work-

hardening which is assumed proportional to the degree of plastic deformation. The model is shown schematically in Fig. 3 in which the work-hardening is introduced by making the weight of the Saint-Venant body linearly dependent upon the position. If the applied stress is σ and the yield stress is μ, a solution of this model yields

$$\sigma = KX_0\epsilon, \quad \sigma < \mu$$

$$\sigma = \mu + \frac{KX_0\epsilon}{\left(\frac{K}{\mu a} + 1\right)} + \frac{\eta RK^2 X_0}{(K + \mu a)^2}\left[1 - \exp\left\{-\left(\frac{K + \mu a}{\eta R}\right)\epsilon\right\}\right],$$

for $\sigma \geqslant \mu$, where ϵ = strain, X_0 = gauge length, KX_0 = elastic modulus, a = fractional rate of work-hardening, R = strain rate, and η = linear coefficient of viscous drag.

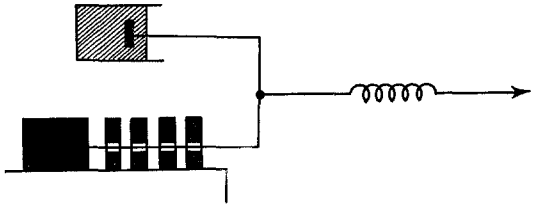

Figure 3 Linear Bingham model modified to include a work-hardening element. For the Saint-Venant element $\sigma = \mu(1 + ax)$ where x = plastic extension.

This model qualitatively describes the observed stress-strain curves. Despite the fact that this approach is purely an analogue, it might nevertheless provide a starting point for a formal theory of the deformation properties of such polymeric materials which work-harden at a rate proportional to the amount of true plastic deformation. It might also be of interest to study the behaviour of this material in uniaxial compression subsequent to plastic tensile straining.

5. Summary

Regenerated chitin films were tested in a tensile mode with the stress applied both perpendicular and parallel to the preferred molecular orientation of the test specimens. For relatively low rates of elongation, it was found that the two orientations differed strongly with respect to breaking strains and only to a lesser extent with respect to the elastic modulus, breaking strength, elastic limit and rate of work-hardening. At large strains, the material becomes irreversibly opaque as the degree of plastic deformation increases. The stress-strain behaviour of these polymeric materials can be approximately described in terms of a modified linear Bingham model incorporating work-hardening. Both the mechanical and chemical properties of regenerated chitin were observed to deteriorate considerably over a 30-year time span.

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