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The Mechanical Properties of Asbestos

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Stereoscan electron microscope studies and measurements of tensile strength and Young's modulus have been made on chrysotile and five naturally-occurring fibrous amphiboles. The effect of heat on the modulus and fracture mechanism has also been examined. With the exception of tremolite which has a different microstructure from the remaining amphiboles, the moduli and strengths were similar. The loss of strength which occurs when the fibrous amphiboles, and to a lesser extent, chrysotile are heated below their decomposition temperature is shown to be due to an increase in interfibrillar bonding causing the material to become notch-sensitive

1. Introduction

The commercially important fibrous silicates are chrysotile which accounts for 90% of total asbestos production and the amphiboles crocidolite and amosite which make up most of the remainder. Chrysotile, $Mg_3(Si_2O_5)(OH)_4$ has a complex tubular structure which has not been fully resolved whereas the amphiboles, although susceptible to extensive cation substitution, also occur in a non-fibrous form which enabled Warren to determine the structure of tremolite as early as 1930 [1]. It is based on infinite double chains of silicon oxygen tetrahedra, held together by five 6-co-ordinated and two 8-co-ordinated cations per unit cell. Two hydroxyl groups are attached to the central cation of each unit cell and there is a small amount of additional hydrogen, probably as SiOH groups on the peripheral silicate chains. The asbestiform varieties approximate to the following idealised formulae but with extensive interchange of Fe″ and Mg″:

Crocidolite	$Na_2Fe_3''\ Fe_2'''\ Si_8O_{22}(OH)_2$
Amosite	$Mg_2Fe_5''\ Si_8O_{22}(OH)_2$
Actinolite	$Ca_2Fe_5''\ Si_8O_{22}(OH)_2$
Tremolite	$Ca_2Mg_5\ Si_8O_{22}(OH)_2$
Anthophyllite	$Mg_7\ Si_8O_{22}(OH)_2$

They occur as extremely close packed lath-like crystals, which we shall call fibrils, aligned with their c-axes parallel. A bundle containing several hundred such fibrils will be called a fibre. The finest fibre which can be used for X-ray diffraction (about 10 μm thick) gives a photograph with full rotational symmetry so that the fibrils cannot be much more than 0.1 μm thick, nor can they be much less than this as quite sharp spots are obtained [2]. Electron micrographs of chrysotile fibres show them to average about 0.03 μm diameter [2] and to be filled and surrounded by amorphous material of the same composition.

The common structure and closely similar cell parameters of the amphiboles should give rise to fairly similar mechanical properties, but the published data, although conflicting, suggests otherwise. Thus Hodgson [3] reports tensile strengths of 35 000 and 25 000 kg/cm² for crocidolite and amosite but less than 5000 kg/cm² for the remaining amphiboles. Nadgornyi *et al* [4] however found that the strengths of crocidolite and anthophyllite (and chrysotile) were similar but decreased inversely with fibre diameter, in a hyperbolic manner characteristic of whiskers, from 25 000 kg/cm² at a diameter $d = 2$ μm to 5000 kg/cm² at $d = 25$ μm. On the other hand Zukowski and Gaze [5] found a length/strength relationship but no diameter/strength effect so that strengths up to 60 000 kg/cm² (depending on length) were maintained at least up to $d = 30$ μm. Another puzzling feature is the drastic loss of strength which has been found [3] when the amphiboles are heated

to a moderate temperature which is insufficient to cause any change in crystal structure.

The object of the present work was to measure the strength and modulus of chrysotile, the naturally occurring amphiboles and synthetic amphiboles of controlled cation substitution, to determine whether there is any correlation between strength and composition, and also to compare the fracture mechanisms of the natural and heat-treated fibres. There is also need for work on modes of failure of bundles of interacting fibrils.

2. Experimental

The asbestos fibres, supplied by Cape Asbestos Fibres Ltd, were as follows: chrysotile, Thetford, Canada; crocidolite, Koegas, Cape Province; amosite, Penge, Transvaal; anthophyllite, Finland; tremolite, Pakistan and actinolite, Koegas. They were as mined, and consisted of blocks of adherent, closely packed fibrils varying in length from 0.6 cm (actinolite) to 12 cm (amosite)

Standard Tem-Pres hydrothermal equipment was used to synthesise the sodium magnesium amphibole according to the method of Gier *et al* [6].

Tensile strengths and Young's moduli were measured with an "Instron" testing machine. The strain rate was kept roughly constant by varying the cross head speed between 0.01 and 0.1 cm/min according to the length of fibre, although preliminary tests with 3 cm long crocidolite at these two speeds showed that the strength was independent of strain rate within this range. Each fibre was first weighed on a "Cahn" electrobalance [7] and its cross-section obtained from the measured density of the material in the case of the Amphiboles, and the literature value of 2.55 [3] for chrysotile. The fibres were then glued with Araldite to the centres of flats cut in the ends of a pair of 3/16 in. diameter brass rods which were aligned in a jig at the required gauge length. When the glue had set, the rods were inserted into special mountings on the "Instron", fixed in place with set screws and the jig finally removed. Specimens for short term shear tests were set in casting Araldite to prevent splitting, cut to length with a diamond saw and then cleaved to remove the Araldite. The heat-treated crocidolite did not cleave easily, so further machining with a diamond surface grinder was necessary.

Stereoscan samples were coated with 500 Å of gold-palladium alloy.

3. Results

3.1. Tensile Strength and Modulus

The mean tensile strengths (maximum load divided by the original cross-section) and moduli are given in the third and sixth columns of table I. Apart from tremolite the strengths are of the same order, and the moduli the same within the scatter of the results, again with the exception of tremolite. The moduli of actinolite and anthophyllite also appear somewhat lower, although these are less reliable due to the short specimen length and small number (about ten compared with sixty to seventy for the others) of samples tested. Chrysotile loses about one-third of its strength when heated at 500° C (1 h, N_2 atmosphere) whereas crocidolite under the same conditions becomes so brittle that samples invariably break at the glue. Even at 380° C they retain only about one-third of their former strength although the modulus is unaffected.

Fibre cross-sectional areas were in general varied from 5 to 100 $\times$ 10^{-6} cm^2 ($d = 25$ to 114 μm), but were extended down to 5 $\times$ 10^{-7} cm^2 ($d \sim 7$ μm) for chrysotile and crocidolite, and up to 5 $\times$ 10^{-4} cm^2 ($d \sim 250$ μm) for chrysotile and tremolite. To test for any dependence of strength or modulus on cross-section the slope of the line which gave the least squares fit to the data, and its standard deviation were computed. Broadly speaking if the results for all lengths of a given fibre are taken together the only cases where there is a significant (by the criterion that the slope should be at least twice its standard deviation) size dependence are the strength of heated crocidolite and the modulus of natural chrysotile. For all fibres the small size dependence coupled with the scatter of the results preclude anything other than a linear fit to the data down to 7 μm.

The stress/strain curves for the amphiboles were essentially linear up to fracture, which on some occasions occurred suddenly and on others as a series of steps as in fig. 1. As the reduced slope BC corresponds to the reduced cross-section of the fibre remaining unbroken, the final breaking stress can be obtained from the product of the strain and modulus. Comparison with the strengths as originally defined showed that the scatter was reduced and of course the mean strength increased.

The stress/strain curve for chrysotile (fig. 2) is more complex: after an initial linear region (which depends on the ratio of fibre length to diameter) the curve becomes convex, although

TABLE I

Material	Length cm	Strength			Young's modulus		
		Mean ± one standard deviation of points from mean kg/cm² × 10⁻⁴	Extrapolated to zero cross-sectional area ± σ* kg/cm² × 10⁻⁴	Slope of strength versus cross-sectional area ± σ* kg/cm² × 10⁻⁷	Mean ± one standard deviation of points from mean kg/cm² × 10⁻⁶	Extrapolated to zero cross-sectional area ± σ* kg/cm² × 10⁻⁶	Slope of modulus versus cross-sectional area ± σ* kg/cm² × 10⁻⁸
Crocidolite	0.3	2.79 ± 0.66	3.03 ± 0.14	6.02 ± 3.0	—	—	—
	3.0	2.04 ± 0.46	2.10 ± 0.08	− 2.04 ± 2.0	1.69 ± 0.19	1.70 ± 0.03	− 1.0 ± 1.5
	5.0	1.68 ± 0.37	1.67 ± 0.07	0.49 ± 2.1	1.78 ± 0.09	1.81 ± 0.02	− 7.3 ± 5.3
Crocidolite after 3 h at 380° C	1.0	1.10 ± 0.25	1.29 ± 0.07	− 5.1 ± 1.9	1.65 ± 0.13	1.69 ± 0.03	− 11.5 ± 9.7
	3.0	0.83 ± 0.21	0.94 ± 0.05	− 3.1 ± 1.1	1.77 ± 0.10	1.77 ± 0.02	− 2.3 ± 5.9
	5.0	0.65 ± 0.28	0.76 ± 0.06	− 4.1 ± 1.9	1.76 ± 0.13	1.77 ± 0.03	− 4.1 ± 9.4
Amosite	0.3	1.55 ± 0.50	1.59 ± 0.18	− 0.55 ± 3.2			
	3.0	1.63 ± 0.40	1.74 ± 0.13	− 2.2 ± 2.4	1.71 ± 0.14	1.77 ± 0.04	− 12.2 ± 7.8
	5.0	1.71 ± 0.42	1.80 ± 0.11	− 2.2 ± 2.3	1.72 ± 0.08	1.76 ± 0.02	− 10.1 ± 4.1
	9.0	1.16 ± 0.41	1.08 ± 0.10	1.9 ± 2.2	1.72 ± 0.07	1.72 ± 0.02	− 1.2 ± 4.1
Tremolite	3.0	0.31 ± 0.13	0.42 ± 0.04	− 0.36 ± 0.11	1.52 ± 0.15	1.49 ± 0.10	1.03 ± 3.8
Actinolite	0.6	1.89 ± 0.47	1.94 ± 0.31	− 1.58 ± 9.03	1.46 ± 0.20	1.59 ± 0.15	− 36.8 ± 40.2
Anthophyllite	0.6	1.35 ± 0.50	1.22 ± 0.46	3.15 ± 4.55	1.54 ± 0.09	1.53 ± 0.09	− 0.31 ± 10.8
Chrysotile	0.3	4.48 ± 1.02	4.59 ± 0.20	− 31.1 ± 24.7			
	3.0	3.06 ± 0.83	3.13 ± 0.18	2.86 ± 5.7	1.60 ± 0.13	1.69 ± 0.04	− 20.5 ± 8.1
Chrysotile after 1 h at 500° C	3.0	2.31 ± 0.45	2.40 ± 0.09	0.87 ± 5.8	1.65 ± 0.06	1.64 ± 0.03	3.1 ± 7.3

σ*is the standard deviation of the line or of its intercept on the strength or modulus axis.

there is no apparent breakage of the fibrils, and on removing the stress it is found that a permanent strain has developed. On further stressing over the range AB, the outer fibrils were seen to be breaking, and at B the fibre either broke completely or as in the case illustrated in fig. 2, the bulk of the fibre pulled out from a sheath of broken fibrils which remained in the glue. As the static friction exceeds the sliding friction a point C (which is at stress zero for some specimens) is reached, where the interfibrillar adhesion is recovered and the curve resumes its original slope from C to D. At D pull-out occurs and the stress falls to zero as this is completed.

Specimens which failed in this way were not included in the data on which table I and fig. 13 are based but are plotted in fig. 3 as σ versus $1/r$. With the assumption that the remaining fibre cross-section is circular, that its cross-sectional area is not significantly less than the original fibre, and that the length bonded to the outside fibrils at pull-out is equal to the length l immersed in the glue; then a rough estimate of the interfibrillar shear strength τ can be made from the pull-out condition:

$$2\pi r l\tau \leqslant \pi r^2\sigma$$

or

$$\sigma = \frac{2\tau l}{r}.$$

The pull-out failures should lie on a line of slope $2l\tau$, and the tensile failures in a region bounded by this line and the maximum tensile strength. Pull-out failures to the right of the line will occur when there is a significant reduction in cross-sectional area on pull-out.

The points in the regions of interest are rather sparse but it does appear that two lines through the origin with significantly different slopes can be drawn for the heated and unheated fibres. The length of fibre embedded in the glue l, was 0.8 cm in each case. The corresponding values of τ are ca 170 and 100 kg/cm² respectively.

3.2. Short Beam Shear Tests

When an isotropic brittle material in the form of a beam of span l, breadth b and depth d is subjected to a centrally applied load F, it will fail when the tensile stress at the lower surface σ, given approximately by

$$\sigma = \frac{3Fl}{2bd^2},$$

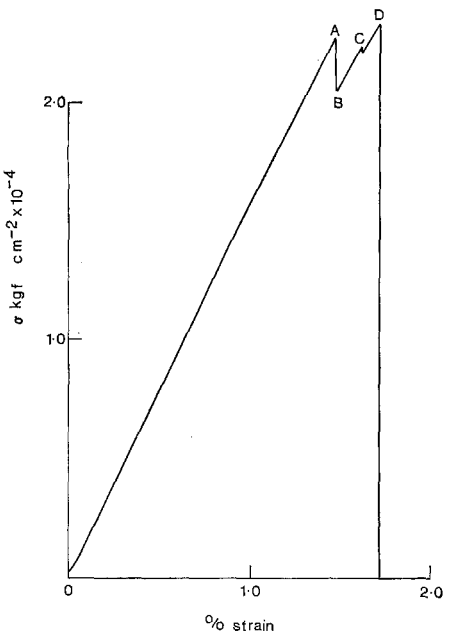

Figure 1 Stress/strain curve for crocidolite fibre with l = 3.0 cm, $d = 38$ μm.

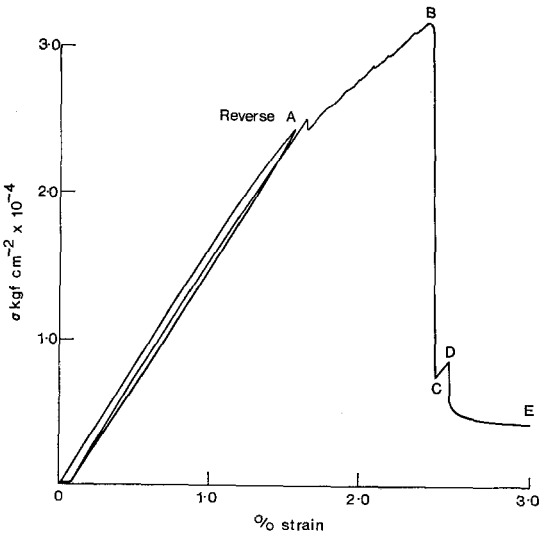

Figure 2 Stress/strain curve for chrysotile fibre with l = 3.0 cm, $d = 41$ μm.

equals the strength of the material. At that point the shear stress τ is approximately

$$\tau = \frac{3F}{4bd} = \frac{d\sigma}{2l}.$$

However, if the material is highly anisotropic with $\tau \ll \sigma$, τ may exceed the shear strength τ_F

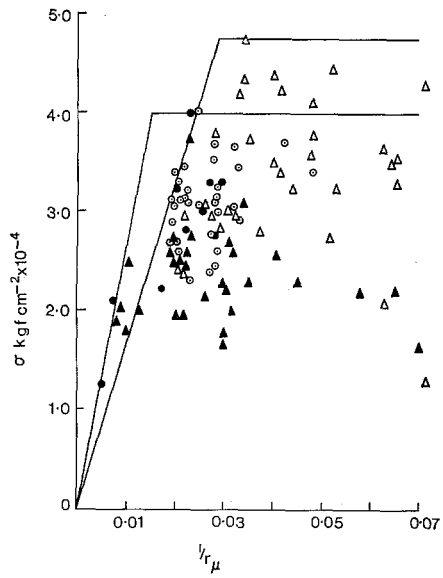

Figure 3 Strength of chrysotile as a function of 1/r. Open symbols represent unheated and solid points heated fibres. Circles correspond to pull-out and triangles to tensile failure.

before $\sigma = \sigma_F$ and the material will then fail repeatedly in shear at constant F to give two beams of depth $d/2$, and so on.

In order to establish the effect of heat on the shear strength of crocidolite, a series of short beam shear tests on the heated and natural material was made. The Instron load traces for typical unheated and heated specimens are illustrated in figs. 4 and 5. The unheated material, invariably failed by shear whereas the specimens heat-treated at 380 and 500° C all failed in tension, usually after the shear stress had exceeded that at which the unheated specimens failed. Although in principle each peak in fig. 4 yields a separate value of τ_F, in practice the computed stress and geometry of the specimens become less well-defined as the deflection and number of cracks increase. A single value of τ_F was therefore computed from each specimen using the first maximum in F and the original specimen dimension. The results are summarised in table II where the figures in parentheses are the computed stresses for the mode other than that in which the specimen failed.

3.3. Stereoscan Micrographs

The Stereoscan electron micrograph of crocidolite (fig. 6) is typical of all the strong amphiboles

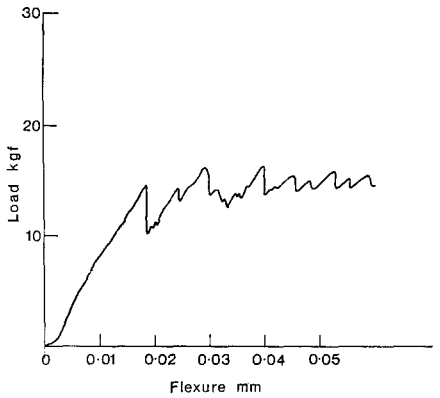

Figure 4 Three point loading test for natural crocidolite specimen 0.30 cm wide × 0.265 cm deep × 2.25 cm span. Sample failed in shear at $\tau = 155$ kg/cm².

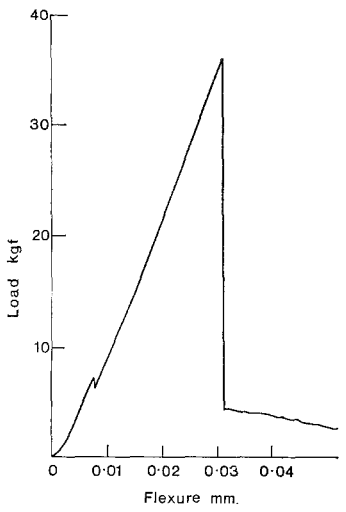

Figure 5 Three point loading test for crocidolite after heating for 4.8 h at 500° cm in a N_2 atmosphere. Specimen 0.40 cm wide = 0.35 cm deep × 2.0 cm span failed in tension at $\sigma = 2230$ kg/cm² at which point the shear stress was 195 kg/cm².

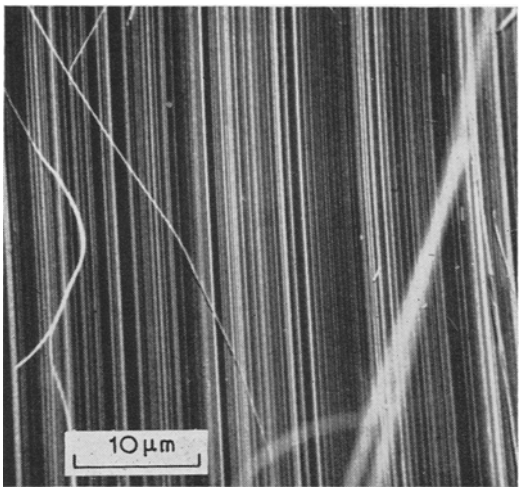

Figure 6 Stereoscan micrograph of natural crocidolite.

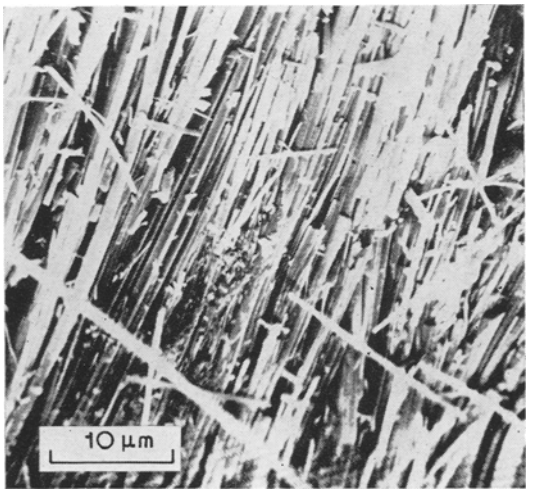

Figure 7 Stereoscan micrograph of tremolite.

TABLE II

Material	Mode of failure	Tensile stress at failure kg/cm²	Shear stress at failure kg/cm²
Natural crocidolite	shear	(2600)	155
	shear	(2860)	153
	shear	(2200)	176
Crocidolite after 4 h at 280° C	shear	(1850)	168
	shear	(1280)	168
Crocidolite after 2 h at 380° C	tensile	2870	(193)
Crocidolite after 5 h at 500° C	tensile	2230	(195)
	tensile	1840	(175)
	tensile	1330	(106)
	tensile	1360	(221)

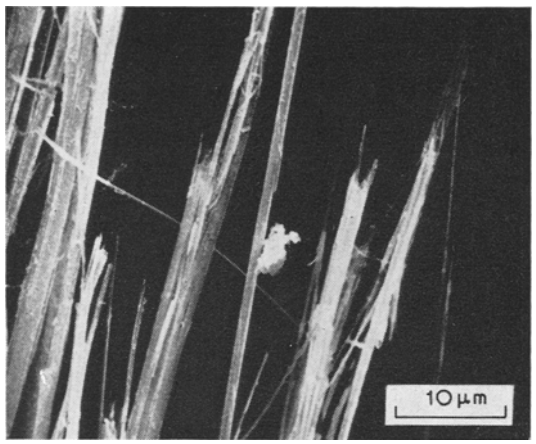

Figure 8 Stereoscan micrograph of fractured natural crocidolite fibre.

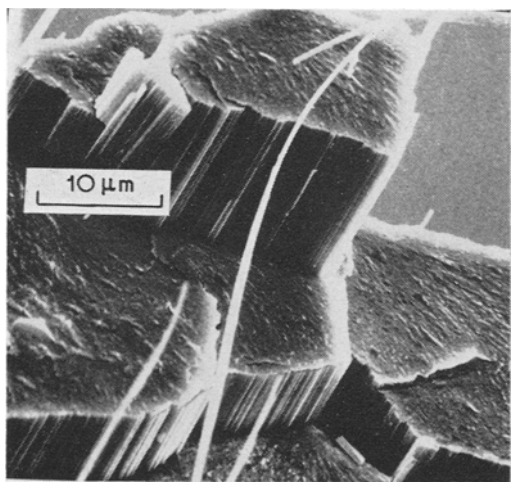

Figure 9 Stereoscan micrograph of fractured surface of crocidolite fibre which had been heated for 1.5 h at 500° in a N_2 atmosphere.

in revealing a close-packed bundle of well-aligned fibrils 0.1 to 0.2 μm across which appeared to be continuous along the whole length of the specimen. The corresponding micrographs of the heated fibres are identical. In contrast, tremolite (fig. 7) contains short, less well-aligned fibrils. Although the micrographs of the sides of the natural and heat-treated crocidolites are indistinguishable from each other, the fracture surfaces are strikingly different. The natural fibre (fig. 8) is almost completely divided at the extreme ends into the component fibrils, whereas in the heat-treated material (fig. 9) the crack has travelled normal to the principal tensile stress over large areas of the fracture surface.

The surface of chrysotile which had been carefully freed from fine material appeared similar to crocidolite, except that the fibrils were finer. However, some of the fine tangled material which had been peeled from the main block and bent through an acute angle in the process, or any fibre which had been drawn over a sharp edge such as a razor blade, assumed the curious kinked or spiral configuration shown in fig. 10.

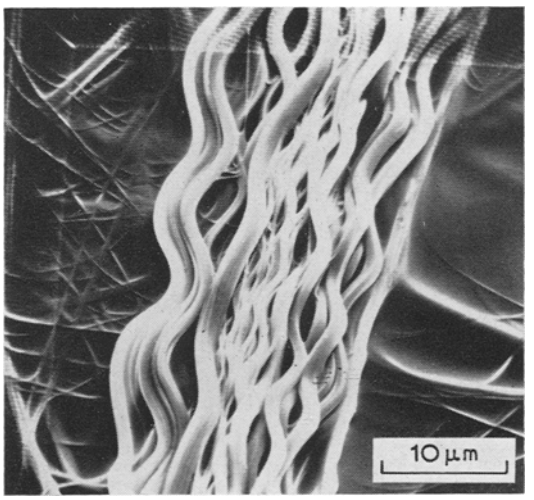

Figure 10 Stereoscan micrograph of "kinked" chrysotile fibre.

3.4. Synthetic Amphiboles

Gier *et al* [6] have shown that under extreme hydrothermal conditions (3000 atm, 700° C) it is possible to synthesise fibrous amphiboles of controlled cation content. We have been unable to do more than confirm their results: the product always consisted of a wadding-like mass of densely intertangled fibres (fig. 11) which was quite unsuitable for tensile measurements. However, it was clear from the tests on the natural fibres reported above that there was unlikely to be any direct correlation between mechanical properties and chemical composition.

4. Discussions

According to Hodgson [3] asbestos fibres are built up from a series of overlapping fibrils of various lengths which are held together in the crystal by hydrogen bonding. He showed that over the temperature range (200 to 500° C) in

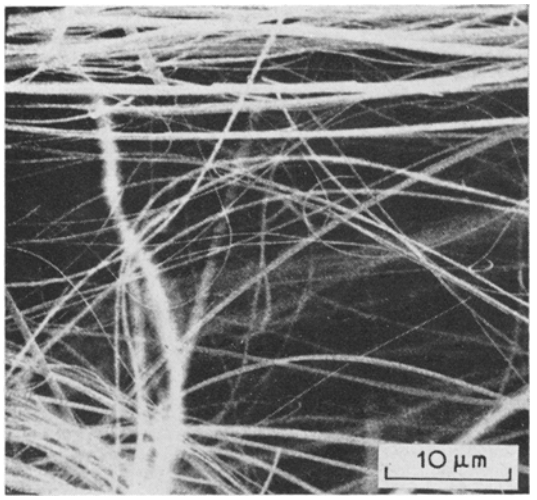

Figure 11 Stereoscan micrograph of sodium magnesium amphibole synthesised at 700° C/3000 atm.

which virtually all the strength is lost, the amphibole fibres lose only a small amount of so-called physically combined water, which is not associated with any crystallographic change in the fibrils, and suggested that the corresponding decrease in hydrogen bonding so weakens the adhesion between the fibrils that they are pulled apart on fracture.

The Stereoscan micrograph of tremolite (fig. 7) is consistent with this model and the low strength of tremolite could well be due to some of the fibrils pulling out on fracture. However, the micrographs of all the strong amphiboles, of which crocidolite (fig. 6) is typical, show that the fibrils are essentially continuous. If this were not so – for example if some fibrils were less than 1 mm – then the chance of seeing the end of a fibril in fig. 6 would be about 1/20, whereas apart from some surface debris all the 200 or so fibrils appear continuous.

Moreover, the shear strengths reported in section 3.2 show that far from there being a decrease in interfibrillar adhesion on heating there is actually an increase. Admittedly if the heat-treated (380 and 500° C) specimens had failed in shear at the stresses given in parentheses in table II then the increase in shear strength would be insignificant, but it must be emphasised that all of them failed in tension and that judging from the difficulty experienced in cleaving these specimens the actual shear strengths were greatly in excess of these values. The shear strength of chrysotile on the other hand was so low that it was not possible to prepare three-point loading specimens of adequate dimensions and with the ends free from splits.

We therefore propose a structure for asbestos which is based on bundles of *continuous* fibrils in which the interfibrillar adhesion is low for chrysotile, somewhat higher for the amphiboles, and *much* higher for the heat-treated amphiboles. As the strongest fibres break at a stress of ca E/30 compared to the theoretical value for a perfect brittle material of ca E/10 the component fibrils are assumed to contain stress-concentrating flaws, such as growth steps, distributed randomly throughout the fibrils. It then follows that the strength of the bundle or fibre will be the average of a large number of units arranged in parallel and thus independent of fibre diameter. However, unless the fibre has completely uniform properties a length-dependent strength must arise. In practice, fibres of length l/n with strength distribution $f(x)$ were cut from fibres of length l. The combined probability that any one of the n fibres will have a strength between x and $(x + dx)$ and that the remaining $(n - 1)$ will have a strength greater than x (i.e. that the fibre of length l will fail between x and $(x + dx)$ is given by

$$nf(x)\left[\int_x^\infty f(x)\,dx\right]^{(n-1)} dx$$

and hence the strength distribution for fibres of length l if they break at the weakest point is given by

$$y = nf(x)\left[\int_x^\infty f(x)\,dx\right]^{(n-1)}.$$

This function, computed by assuming that the underlying strength distribution of the shortest (0.3 cm) fibres is normal, is drawn on the strength histograms of crocidolite and chrysotile in figs. 12 and 13. If the component fibrils were completely independent over their entire length, then each would break at its weakest point and the strength of the fibres would be less than that computed on the weakest link basis. Therefore as the strengths of the chrysotile and crocidolite fibres fit the computed curves reasonably well it appears that the fibrils are coupled to the extent that the fracture region is restricted to less than 0.3 cm, although over shorter distances the fibre

must eventually behave more as a parallel bundle in order to account for the appearance of the fracture surface in fig. 8 and the absence of a strength diameter effect.

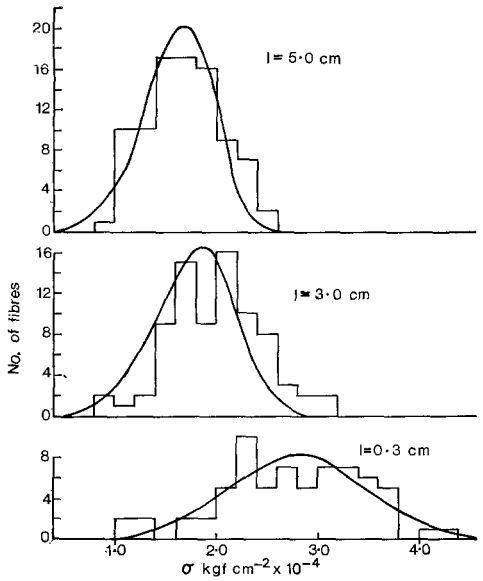

Figure 12 Histogram of crocidolite strength. Curve for 3 mm fibre is normal with the values of the mean and standard deviation given in table I. Other curves are computed from this on a "weakest link" hypothesis.

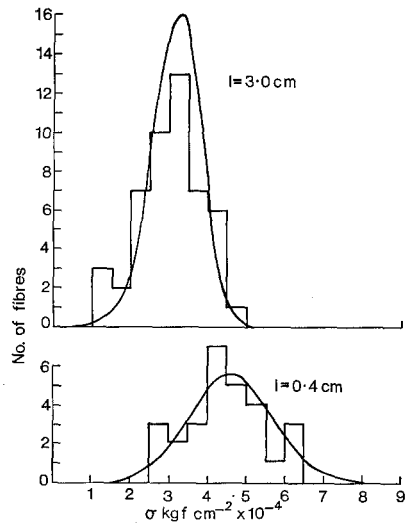

Figure 13 As fig. 12 but for chrysotile.

On heating crocidolite fibres it is suggested that the adhesion between the fibrils reaches the point where the stress concentration at the tip of a surface crack can no longer be relieved by a secondary crack propagating perpendicularly in a plane of weakness according to the mechanism suggested by Cook and Gordon [8]. The onset of a strength/diameter relationship for crocidolite which had been heated at 380° C and the fracture surface of the heat-treated (500° C) crocidolite (fig. 9) are consistent with this increase in notch sensitivity as the interfibrillar adhesion increases.

Many of the properties of chrysotile may be similarly interpreted in terms of adhesion between the fibrils. The pull-out data in fig. 3 suggest a moderate increase in interfibrillar adhesion on heating which is consistent with the low (relative to crocidolite) loss of strength and also with the decreased curvature of the stress/strain curves for the heated fibres. The permanent strain developed in the thicker chrysotile fibres (fig. 2) results from the more highly stressed outer fibrils undergoing a permanent displacement relative to those at the centre, so that they remain in tension when the strain is removed. Similarly, when a fibre is bent through an acute angle the outer fibrils are displaced, and if the adhesion can be recovered – and the stress/strain curve (fig. 2) provides some evidence for this – then the fibre will assume the spiral configuration shown in fig. 10.

The strength of asbestos, which is inferior only to pristine glass fibres and whiskers is not exploited commercially in unreinforced products such as cloth and paper, which fail by the short fibres pulling apart, or in reinforced plastics where the problem is one of alignment and where the above results could be significant. Current alignment methods involve the extrusion of a suspension of the dispersed fibre through a hole or slot. With the amphiboles the process is straightforward, but they have other disadvantages as a reinforcing material. Chrysotile, on the other hand, disperses to a tangled mass of fine fibres and it is necessary to pre-treat the material with hot phosphoric acid [9]. It was found in the present work that the increase in interfibrillar adhesions in the heat-treated material was sufficient to prevent complete dispersion and that a product of fine whisker-like fibres resulted.

In conclusion it must be admitted that no single piece of evidence for the hypothesis that the strength of asbestos is determined largely by the interfibrillar adhesion is sufficient in itself. To prove a direct correlation it would be

necessary to make more accurate measurements of shear strength encompassing several varieties of asbestos both before and after heating, but the material is such that it is difficult to devise such experiments to give an unambiguous answer. The discrepancies between the strengths of the less common amphiboles reported here and those in the literature, further emphasise the problems associated with obtaining a representative sample of a natural product. However, when taken together, the evidence from the stereoscan micrographs the shear tests, the shape of the stress/strain curves, the strength/diameter relationship for the heated (but not the unheated) crocidolite fibres and the pull-out data for chrysotile, are considered reasonably convincing.

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