

drop through water with their flat sides normal to the direction of fall is incorrect and disproved by countless examples of dropstones piercing with their sharp edges or corners through the underlying lamination<sup>3-5</sup>. Even small dropstones penetrate the host rock lamination in this fashion; that has been demonstrated to Schermerhorn on a visit to the Numees Formation.

Schermerhorn and Stanton<sup>8</sup> state that "deposition of the tilloids was thus a type of geosynclinal turbidite sedimentation" and "... a subaqueous mudflow ... even becomes a turbidity current". Also "The beds of quartzite (intercalated in mixtite—A.K.) must have arrived as turbidity currents".

The mixtites extend for more than 800 km in the West Congo Basin and no mechanism can explain this distribution satisfactorily by mudflow deposition.

The association of mixtites with carbonates is characteristic of most late Precambrian glaciogenic deposits<sup>9</sup> but, contrary to Schermerhorn's belief, it is not evidence against glacial deposition. The Numees tillite<sup>3-5</sup> and the Bthaat Ergil Group in, Mauritania<sup>10</sup>, to cite only two well documented examples, are both undisputably related to ancient glaciation but, nevertheless, contain carbonate beds.

Dr Schermerhorn claims boldly but incorrectly that the Angolan mixtites are the best documented of all such sediments in Africa or in the Southern Hemisphere, though only one publication had appeared about them before ours. If it were true, the argument about their origin would long have been settled in favour of glacial deposition.

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## Work of fracture of natural cellulose

THE work of fracture (that is, the energy needed in order to form a fracture surface roughly at right angles to the grain direction) is, for timber, exceptionally high in relation to other mechanical properties and density. It compares well, on a weight basis, with that of ductile metals. Our tests on air dry (12% moisture content) pitchpine (*Pseudotsuga taxifolia*) for instance, give a mean value of  $0.92 \times 10^4 \text{ J m}^{-2}$ . That is far higher than the energy needed to break the interatomic bonds in any given cross section of timber (which can hardly exceed  $2 \text{ J m}^{-2}$ ). It also seems to be noticeably higher than the energy that is likely to be absorbed by the fibre pull-out mechanisms which operate in conventional, artificial fibre composites<sup>1</sup>. There is reason therefore to suspect the existence of a special energy absorbing mechanism during fracture in trees and presumably, in other, plants.

Air dry timber has normally a macroscopic breaking strain in tension along the grain of about 1.0%, which is not very different from that of the cellulose fibrillae of which it is principally composed. Such a low breaking strain is not obviously compatible with the absorption of so much energy at fracture.

Cowdrey and Preston<sup>2</sup> have shown, however, that in the cell walls of timber the cellulose fibrillae are disposed in a preponderantly helical manner, making an angle which may vary between 6° and 30° in different cells but which always has the same sense in any one tree.

Page *et al.*<sup>3</sup> have shown that when an individual cellulose cell is detached from its surroundings and pulled in tension, the walls buckle into the lumen in such a way that total longitudinal extensions of the cell of between 15% and 20% are possible. Page, however, was concerned with paper fibres and not with the fracture energy of timber.

We have made large (~ 2 mm diameter) model cellulose fibres by winding glass and carbon fibres into hollow helices with resin. When tested individually in tension, such tubes behave elastically up to a well defined yield point. Beyond that point the tube wall buckles and the equivalent of plastic yield takes place, enabling the tube to extend irreversibly by 10–20%, and thus to absorb a great deal of energy. We have made composite models resembling timber, by glueing together a number of parallel tubes of this type, and these exhibit experimental works of fracture up to about  $40 \times 10^4 \text{ J m}^{-2}$ , which may be higher than any value previously recorded for a non-metallic material.

We have observed that the fracture behaviour of timber, watched under the optical microscope, much resembles that of our fibre-composite models. The first irreversible event to be observed is the lateral separation of many of the cells in the immediate neighbourhood of the fracture (see ref. 4). That enables the walls of the cells in that region to buckle, and the cells themselves to elongate. Thus, although the elastic strain in the timber as a whole seldom much exceeds 1.0%, the cells close to the fracture surface typically extend 15–20% before breaking, absorbing much energy as they do so.

The adoption of a helical arrangement of reinforcing fibrillae naturally, involves some reduction in the maximum attainable value of longitudinal Young's Modulus. By calculation this reduction seems to be proportional to the square of the cosine of the helical fibre angle. That is equivalent to the loss of about 1% for a 6° helix, increasing to 25% for a 30° helix. Such a loss of stiffness may well be regarded as an acceptable price to pay for the acquisition of so much fracture toughness.

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## Imparting strength and toughness to brittle composites

HIGH strength and high toughness are usually mutually exclusive in composites which have brittle filaments in a brittle matrix. The high tensile strength characteristic of strong interfacial filament-matrix bonding can, however, be combined with the high fracture toughness of weak interfacial bonding if the filaments are arranged to have alternate sections of high and low shear stress (and low and high toughness). Such weak and strong areas can be achieved by appropriate intermittent

coating of the fibres. The strong regions ensure that the filament strength is picked up. Randomly positioned weak areas effectively blunt running cracks by the Cook-Gordon mechanism<sup>1</sup>, which in turn produces long pull-out lengths with an associated large contribution to toughness. Boron-epoxy composites of volume fraction 0.20–0.25 have been made in this way; they have fracture toughnesses of over  $200 \text{ kJ m}^{-2}$ , and they retain rule of mixtures tensile strengths ( $\sim 650 \text{ MN m}^{-2}$ ). At the volume fractions used, that apparently represents  $K_{IC}$  values greater than  $100 \text{ MN m}^{-3/2}$ .

When the interfacial bond between fibre and matrix is strong in composites which have brittle filaments and a brittle matrix, fracture is often caused by rapid matrix cracks which break through all filaments in their paths. The toughness of such composites is low because, in general, the critical transfer length associated with strong interfacial bonding is small, which limits the various components of the total toughness—the ‘surfaces’ component, Piggott-Fitz-Randolph stress redistribution and Cottrell-Kelly pull-out (see, for example, ref. 2). The critical length is given by  $l_{crit} = \sigma_f d / 2\tau$ , where  $\sigma_f$  is the filament strength,  $d$  the filament diameter, and  $\tau$  the interfacial shear strength.

A general increase of  $l_{crit}$  by lowering the filament-matrix shear bond will increase the toughness, and a relationship between rule of mixtures (ROM) strength,  $\sigma$ , and total composite toughness,  $R$ , may be developed by recognising that in, general terms,  $R \propto l/\tau$ . Weak interfaces throughout the composite, however, reduce the tensile strength quite significantly. The question that presents itself is whether there are means by which the ROM tensile strength can be maintained along with high toughness values.

Marston<sup>3</sup> suggested that, providing there were ‘sufficient’ regions of high interfacial shear stress to ensure that the ROM strength was picked up, the rest of the composite could have quite weak interfacial bonds. Were such a composite to be laid up randomly with respect to weak and strong regions, both high strength and high toughness should be produced simultaneously. Then, if the lengths of the strongly bonded regions were greater than the critical length associated with the strong interfacial  $\tau$ , the filament strength should be attained. At the same time, those weak interfaces situated randomly ahead of running cracks would serve to blunt the cracks by debonding.

Weakly and strongly bonded interfaces can be achieved by coating intermittently the filaments with some suitable substance before composite lay up. Experiments with silicon vacuum grease (SVG) and polyurethane varnish (PUV) coatings are described here; the uncoated regions have high interfacial shear stress and the coated regions are ‘weak’. Tensile strength and toughness specimens were made from layers of intermittently bonded, epoxy composite tape, manufactured on a drum apparatus with a device for coating the filaments before lay up (A.G.A., unpublished). The tape (similar to Avco Rigidite, Prepreg tape) consisted of a  $250 \mu\text{m}$  monolayer of B/W filaments in EPON 828 epoxy, backed, for ease of handling, on  $760 \text{ mm}$  wide nylon scrim cloth about  $50 \mu\text{m}$  thick. The tensile strength specimens consisted of 2 layers of the tape, in  $100 \text{ mm} \times 6 \text{ mm}$  strips, with end tabs reinforced by additional layers. Most toughness measurements were made on flat sheet edge-crack specimens, similar to American Society for Testing and Materials ‘compact tension’ specimens in profile. These consisted of 10 layers of tape in panels  $76 \text{ mm} \times 76 \text{ mm}$ . To prevent the composite arms above the crack from shearing off under load, two outside layers of tape were arranged on each side of the specimens, with the filaments parallel to the crack. The central core of the specimen thus consisted of six unidirectional filaments perpendicular to the starter crack, where, within the limitations of the specimen and tape preparation method, the coated and uncoated layers occurred randomly, relative to each filament. Fracture toughness in the edge-crack specimens was measured for increments of crack area, using Gurney’s sector area technique<sup>4</sup>.

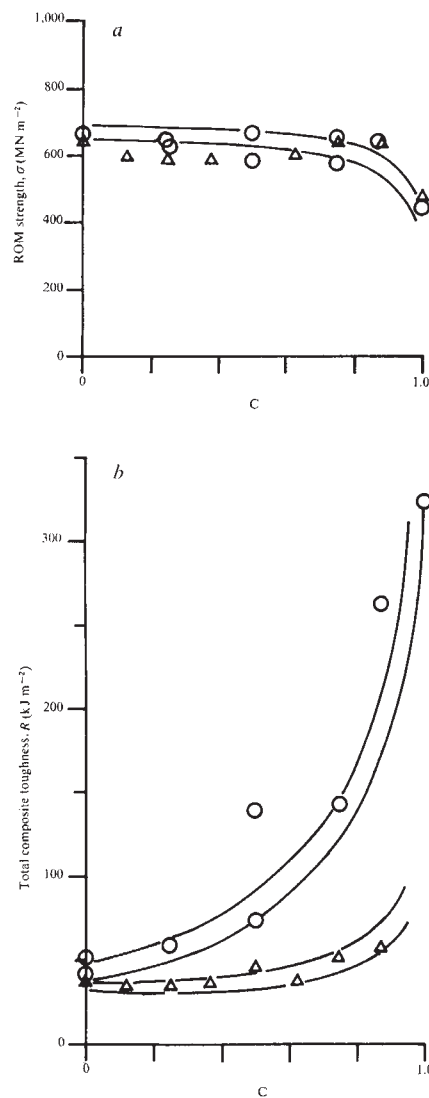


Fig. 1 Tensile strength (a) and edge-crack fracture toughness (b) plotted against the percentage coating,  $C = l_c / (l_c + l_{uc})$ ; where  $l_c$  is the coated length,  $l_{uc}$  the uncoated length, and  $(l_c + l_{uc})$  is the repeat distance of the coating pattern along the filaments.  $\circ$ , Results with PUV coating;  $\triangle$ , results with SVG coating.

Tensile strength and edge-crack fracture toughness, for both SVG and PUV coatings, have been plotted against  $C$ , the ‘percentage coating’ (Fig. 1a, b). The tensile data remain at or about the ROM value until  $C$  becomes greater than 0.8. In the same range of  $C$ , the toughness with SVG coating, shows a modest increase over the initial ( $C=0$ ) case. In contrast, the PUV coatings give marked improvements in toughness when the percentage of coating is increased (Fig. 1a, b): in the edge-crack specimens, with  $V_f=0.25$ , toughnesses of about  $100 \text{ kJ m}^{-2}$  are produced for  $C=0.5$ , and values over  $200 \text{ kJ m}^{-2}$  occur at large  $C$ .

Superimposed on the figures are the predictions of analyses for  $\sigma$  and  $R$ , details of which are to be presented elsewhere. Both coating materials maintain tensile strengths of the order of the ROM values up to large  $C$ , which suggests that both produce similar coated interfacial shear-strengths. Their effects on toughness are, however, different, which suggests that interfacial shear-strength may not be the controlling parameter for toughness. With PUV it seems that Cook-Gordon debonding takes place (average pull-out lengths of

$l_{crit}/4$  being augmented by additional debonding), but it is apparently absent in the case of SVG.

The Cook-Gordon mechanism itself seems to be only a small toughness sink, but the extra debond lengths markedly increase the pull-out contribution to toughness. The manner in which interfacial properties, other than shear strength, are affected by the coating procedure is therefore both interesting and important, because it is probably the 'toughness' of the interface that is of ultimate concern, rather than the 'strength'. Tensile debonding ahead of a crack, envisaged by Cook and Gordon, is Mode I fracture in the nomenclature of fracture mechanics; the shear debonding implicit in the Outwater-Murphy debonding analysis<sup>5</sup> for toughness, is in the 'forward sliding' Mode II. Each mode has its own toughness, with explicit relationships with interfacial tensile and shear strengths, which are not obvious.

Further information on the intermittent bond concept is to be presented elsewhere.

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## Effect of temperature on recombination luminescence and electron tunnelling

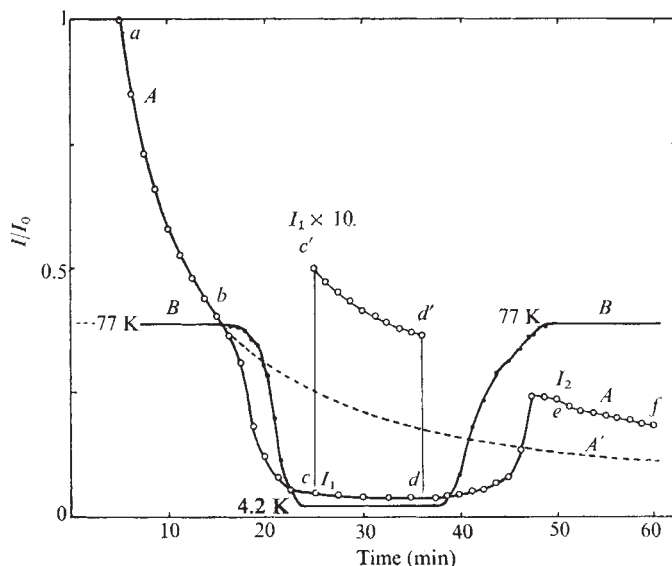
RECOMBINATION luminescence which occurs in alkaline glass after  $\gamma$  irradiation at 77 K, decreases in intensity when the glass is cooled. Between 60 K and 4 K the activation energy is probably about zero. This seems to be direct proof of a tunnelling mechanism.

Electron stabilisation occurs in deep intermolecular traps (2-3 eV) during low-temperature radiolysis of polar glasses<sup>1</sup>. After  $\gamma$  irradiation, at 77 K, of aqueous alkaline glasses containing efficient electron scavengers ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ), a long range electron transfer occurred, apparently by a tunnelling mechanism<sup>1,2</sup>. The observation and kinetic study of prolonged isothermal luminescence (ITL) in glassy organic matrices<sup>3,4</sup> and in alkaline glass<sup>3</sup> at 4 K and 77 K, which results from the recombination of trapped electrons ( $e^-_t$ ) and positive ions, confirms the validity of this mechanism; it also shows that the phenomenon is general in glassy materials.

Our aim was to study the temperature effect on recombination kinetics, using the ITL technique in the range between 77 K and 4 K, where electron tunnelling is apparently the predominant mechanism.

Sodium hydroxide glass (10 mol  $\text{dm}^{-3}$ ) containing phenol (0.03-0.3 mol  $\text{dm}^{-3}$ ) was used because ITL intensity is increased by the presence of phenol<sup>3</sup>. Irradiations were carried out at 77 K with a cobalt-60 source at a dose rate of 5 krad  $\text{min}^{-1}$  for periods of 5-15 min. After recording the ITL decay for about 10 min, liquid helium was transferred into the cryostat, whilst monitoring of the luminescence continued.

Following  $\gamma$  irradiation of NaOH glass, whether pure or with phenol, at 4 K or 77 K, ITL can be observed for up to several hours<sup>3</sup>. The kinetics of the decay, just as in the



**Fig. 1** Recombination luminescence in NaOH glass (10 mol  $\text{dm}^{-3}$ ) containing phenol (0.03 mol  $\text{dm}^{-3}$ ), irradiated with  $\gamma$  rays (dose: 50 krad) at 77 K. *A*, Luminescence intensity (relative units): sections *ab* and *cd*, ITL at 77 K and 4 K (*c'd'* enlarged 10 times); sections *bc* and *de*, luminescence intensity during cooling to 4 K and warm up to 77 K; section *ef*, ITL at 77 K after cooling and warm up cycle. *A'*: extrapolation of the initial ITL decay at 77 K based on the linear plot of  $I/I_0$  against time, according to equation (1). *B*, Temperatures corresponding to light intensities of *A*.

case of organic glasses<sup>4,6</sup>, can be described by the relationship

$$I_0/I = 1 + k(t - t_0) \quad (1)$$

in which  $I_0$  and  $I$  are ITL intensities at the beginning of the observation  $t_0$  and at time  $t$ ; and  $k$  is a coefficient (with the dimension of a rate constant) depending on the duration of  $\gamma$  irradiation, but independent of dose and dose rate. Under identical experimental conditions, the kinetics observed at 4 K and 77 K coincide. The intensity of ITL after irradiation at 4 K is, however, approximately five times larger than after irradiation at 77 K.

Figure 1 shows the change of luminescence intensity with temperature in alkaline glass irradiated at 77 K. The decrease in temperature (Fig. 1, section *bc*) brings about a reduction of luminescence intensity by a factor of about five. Thus, the ITL intensity after irradiation at 4 K is actually about 25 times that after irradiation at 77 K and subsequent cooling to 4 K.

When the temperature is raised again (section *de*), the luminescence intensity increases and reaches a value higher than the normal ITL curve at 77 K (curve *A'*). The kinetics of ITL decay in the sections *ab* (77 K), *cd* (4 K) and *ef* (77 K) can all be represented linearly by equation (1). This indicates that the same recombination mechanism must be predominant under the experimental conditions of these luminescence decays.

This temperature effect is reproducible and can be repeated on the same luminescence decay curve, as long as there is sufficient light intensity.

Because the luminescence intensity at any moment is proportional to the reaction rate of recombination, it can be considered to be proportional to the rate constant when temperature is the only parameter which changes. Therefore, the fivefold decrease in luminescence intensity observed during cooling from 77 K to 4 K suggests an exceedingly low activation energy. In fact, there is practically no change between 60 K and 4 K.