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Review

Carbon fibre-reinforced cement

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This review describes fabrication processes for aligned fibre and random fibre carbon-reinforced cement and links important process parameters with composite theory. The way in which the material fits into the general framework of crack constraint and matrix cracking theories is discussed. A broad survey is made of the mechanical properties, durability and dimensional stability of a variety of carbon-reinforced cement composites, and economic constraints on potential applications are considered.

List of symbols

b, breadth of three-point bend specimen
d, depth of three-point bend specimen
E_c, composite Young's modulus
E_f, fibre Young's modulus
E_m, matrix Young's modulus
l, fibre length
l_c, fibre critical transfer length
l_s, specimen span in three-point bend test
m, Weibull modulus
r, fibre radius
P, applied load
V_f, fibre volume fraction
V_m, matrix volume fraction
x', length of fibre needed to transfer load $\sigma_{mu} V_m$
x_d, crack spacing in a composite with short, aligned fibres
ϵ_{fu}, fibre ultimate strain
ϵ_{mu}, matrix ultimate strain
σ_{fu}, fibre ultimate strength
σ_{mu}, matrix ultimate strength
σ_{cu}, composite ultimate strength
σ_{MOR}, modulus of rupture
σ_T, tensile strength
τ, interlaminar shear strength
τ_i, interfacial shear strength
γ_m, matrix work of fracture
γ_F, work of fracture

1. Introduction

The increasing importance of fibre-reinforced cement composites has been recognized recently by the compilation of an excellent comprehensive report by the Concrete Society [1] which covers the whole spectrum of cement composites reinforced by a variety of fine fibres. A further informative review of the general field, with a similar broad scope, was presented to the 1975 RILEM Symposium by Majumdar [2]. Whereas the former made only brief mention of carbon-reinforced cement (CRC), the latter reported work on many of the properties of the material. Because the subject formed only part of a wider review, however, it was not covered in depth.

The pioneering phase of the development of CRC is almost over, and the steady reduction in carbon-fibre prices consequent to increased volume of production, and advances in the technology of production, will make bulk applications attractive. In view of the mounting interest among researchers, consulting engineers and manufacturers which this prospect has stimulated, it is considered that now is an appropriate time to review the work that has been carried out on the development and assessment of CRC.

2. Materials

2.1. Carbon fibres

A range of carbon fibres, with greatly differing mechanical properties, has been used successfully to reinforce cementitious matrices. Most were produced by some variant of the Royal Aircraft Establishment (RAE) process [3] from precursors such as polyacrylonitrile or rayon. The principal factor in the price of these fibres is the cost of the precursor, although another important factor is the cost of heat-treatment, which is higher the greater the treatment temperature. Recently, cheaper fibres, derived from pitch, have entered commercial production.

By variation of the processing conditions fibres with strengths and elastic moduli covering a very wide spectrum may be produced. Using these fibres with widely different characteristics and selecting from a variety of composite fabrication processes, a family of carbon-reinforced cement materials is possible, from which a choice can be made to suit a particular application.

Carbon fibres are made in the form of continuous tows containing, usually, 10^4 discrete filaments 7 to $10\,\mu$m diameter. Their continuity allows their use in processes as diverse as filament-winding and spray-up and, after formation of cloths and mats by modified textile techniques, in conventional hand lay-up operations. For filament-winding applications a manufacturer has developed an open tow fixed by a water soluble binder in the form of a veil [4].

The surfaces of fibres made by the fabrication routes based on textile precursors have turbostratic, fluted structures (Fig. 1) and, particularly after oxidation treatment, may be pitted on a microscopic scale. These surface irregularities are able to key mechanically into a matrix material like cement gel which can conform to the microscopic surface features by micro-crystalline growth during hydration. The quality of the resulting bond has a fundamental influence on the properties of a carbon fibre-reinforced cement composite material, as will be demonstrated later by reference to multiple matrix cracking theories.

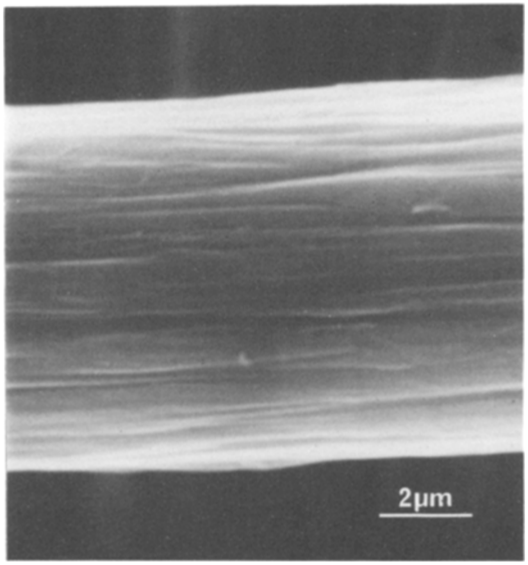

Figure 1 A scanning electron microscope photograph of a PAN-based carbon fibre.

Carbon fibres are, chemically, relatively inert, and are not expected to be attacked by the alkalies in cement. For the same reason they should pose no corrosion problems when exposed to the elements. In principle, therefore, no protective cover for the reinforcement in CRC is necessary, and much thinner, lighter sections are possible with CRC than with conventional reinforced concrete. Another advantage bestowed by their chemical inertness is the possibility of accelerated curing of CRC composites at elevated temperatures without degrading the fibres.

The types of carbon fibre used in the cement-reinforcement studies discussed in this paper, their sources and properties are given in Table I. Although the use of pitch-based fibres in CRC studies has not yet been reported, their properties are included for comparison.

2.2. Cements

In a composite containing expensive fibres such as carbon it is imperative that they should be used as efficiently as possible. To achieve this aim it is necessary to ensure that all the filaments are totally invested with matrix material and uniformly distributed. These requirements are particularly difficult to meet when the matrix is in particulate form and the particles have to be infiltrated between the fibres. For this reason, finely ground cements are preferred, but even the finest cements available contain particles up to $45\,\mu$m diameter, and they create problems when attempts are made to disperse them among the much smaller diameter fibres. The fibre separation to accommodate such particles must be at least $45\,\mu$m and, if the fibres are distributed uniformly, this imposes a theoretical limit of ~5 vol% on the fibre content of a cement matrix reinforced with unidirectional fibres. However, in practice, less than uniform distribution is acceptable, and the finest cements allow the fibre content to be increased to ~12 vol% before infiltration difficulties lead to fibre bundling, higher porosity, and hence lower streng-

TABLE I Types of carbon fibre, their sources and mechanical properties.

Fibre type	Source	Tensile strength (MN m^{-2})	Young's modulus (GN m^{-2})	Reference
Grafil HS	Courtaulds	2800	270	[8]
Grafil HM		2000	380	[8]
Grafil A		1900–2600	190–240	[6, 14, 16, 17]
Modmor I	Morganite	1400–2100	385–455	[1]
Modmor II		2450–3150	245–315	[1]
RAE I	AERE	1800	380	[5]
RAE II	Harwell	2600	230	[5]
Harwell a		1070	80	[5]
Harwell b		270	110	[5]
Pitch-based	Union Carbide	2000	–	[14]

TABLE II Types of cement, their sources and particle sizes

Cement type	Source	Particle size (μm)	Specific surface (m^2 g^{-1})	Reference
OPC RHPC	Blue Circle Group	max. 100 1% < 2	0.35	[8,18]
RHPC		max. 60 2% < 2	0.47	[18]
ERHPC		max. 45 5% < 2	0.78	[5, 6, 11, 14, 16–18]

OPC = ordinary Portland cement; RHPC = rapid hardening Portland cement; ERHPC = extra rapid hardening Portland cement.

ths. Coarser cements may be used, and they provide a cost advantage, but this must be weighed against the disadvantage of greater infiltration problems. Portland cements of all the types available commercially have been used in carbon-reinforced cement studies. Their sources, properties and references are listed in Table II. An advantage of cements with lower specific surface areas is that they require less water to produce a given consistency, and the need to dehydrate a composite can be reduced or eliminated. This is particularly useful in spray techniques.

3. Fabrication processes

3.1. Spray-up

This process, developed at the Building Research Station for the fabrication of glass-reinforced gypsum and glass-reinforced cement panels (see, e.g. [1]) is equally suitable for carbon-reinforced cement [6]. A continuous tow of fibres is fed to a compressed air gun which chops them into predetermined lengths and blows them to impinge simultaneously with a jet of cement slurry on a forming surface. The surface may be a filter under vacuum which reduces the water content of the cement, or the need for water removal may be avoided by use of water-reducing additives in the slurry. An important feature of the process is that it lays down fibres oriented randomly in a plane, giving the resulting composite isotropy of properties in that plane, and maximizing its membrane strength. The response of such a composite structure to tensile stress, assuming elastic stress transfer between fibre and matrix and making allowance for a frictional shear stress between them after the matrix has failed, has received a comprehensive theoretical treatment from Laws *et al.* [7]. Their analysis, which dealt with the case of glass-reinforced gypsum, has general applicability, and has particular relevance to the carbon-reinforced cement case, in which a good frictional bond is to be expected.

Sheets of material produced by the spray process have sufficient tear-strength in the green state to allow them to be bent around formers to produce I-section beams, box girders, cladding panels and permanent formwork [1]. CRC has been thus used to form experimental L-shaped beams [6].

3.2. Slurry press

The slurry-press technique is another process that uses chopped fibres, but in this case they are mixed with cement slurry before being applied to a mould. Great care must be taken over the choice of fibre length and mixing method to avoid balling-up of fibres during mixture. To achieve good consolidation, simultaneous pressing and vacuum dehydration are necessary unless dehydration agents are used in mixing, when simple hand-rolling is adequate. Although the mixing process is conducive to the formation of a fibre array which is random in three dimensions, consolidation has a tendency to cause preferred orientation in a plane perpendicular to the consolidation direction. This results in materials with similar anisotropy of properties to those produced by spraying.

3.3. Hand lay-up

A third process leading to the formation of a sheet composite with fibres oriented randomly in two dimensions involves the hand lay-up of chopped fibre mats previously impregnated with cement slurry [8]. The method is particularly useful for the formation of membrane structures with curved surfaces, and draws on skills widely used in the glass-reinforced plastics industry to make, for example, boat hulls.

3.4. Filament-winding

The most elegant of the fibre composite fabrication processes is filament-winding, which allows precise alignment of fibres in the directions of stresses to be supported. In the fabrication of pipes this facility allows the incorporation of reinforcement in appropriate orientations to counter internal pressure or external crushing forces. The process originated in the glass-reinforced plastics field and was adapted for cement-based composites by Biryukovich *et al.* [9]. Briggs *et al.* [5] developed a filament-winding process to make carbon-reinforced cement composites. A continuous, ten thousand filament tow was opened up by a compressed air spreading device and passed through an agitated bath of cement slurry, where it became fully impregnated with cement. Great care was required at this stage to ensure that the fibres were separated sufficiently well for each to be coated with a layer of cement. The coated fibres were then brought together by a profiled roller to form a strand which was fed to a filament-winding mandrel, as shown in the schematic diagram of Fig. 2. By varying the water: cement ratio of the slurry it was possible to control the fibre volume fraction in the resulting composite. An example of the quality of fibre dispersion achieved in a flat plate produced by this technique is given in Fig. 3, which is a micrograph

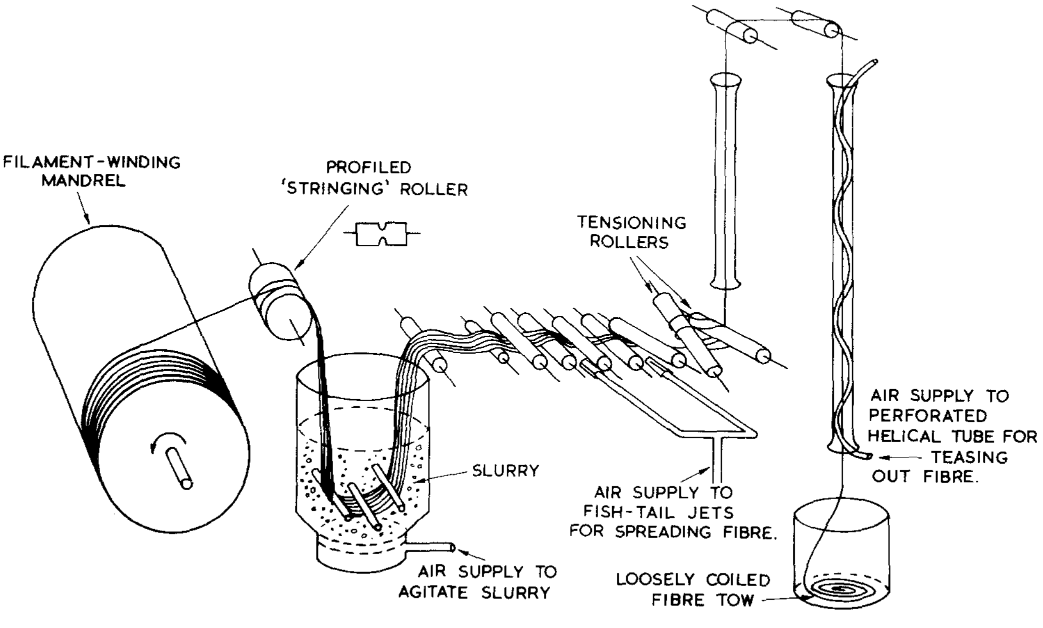

Figure 2 Fibre spreading, impregnation and filament-winding arrangement.

of a polished cross-section of a unidirectional carbon fibre cement composite cut perpendicular to the fibres. The material shown contains 8 vol % fibres, but it is possible to incorporate up to ~ 12 vol % before impregnation difficulties lead to fibre bundling, pore formation and consequently loss of strength. This is illustrated graphically in Fig. 4, taken from a paper by Briggs [10], in which Weibull failure probability plots of the flexural strengths of two carbon fibre cement composites are compared. Both samples contained > 12 vol % fibre and were therefore weaker than the optimum strength. In one case care was taken to disperse the fibres and in the other case no such care was taken. The aim had been to prepare composites with equal fibre contents and fibres in these two conditions of dispersal, but this proved impossible. However, the point is made; the material containing well-dispersed fibres has 50% greater median strength than that containing poorly dispersed fibre, even though the latter contains more fibre.

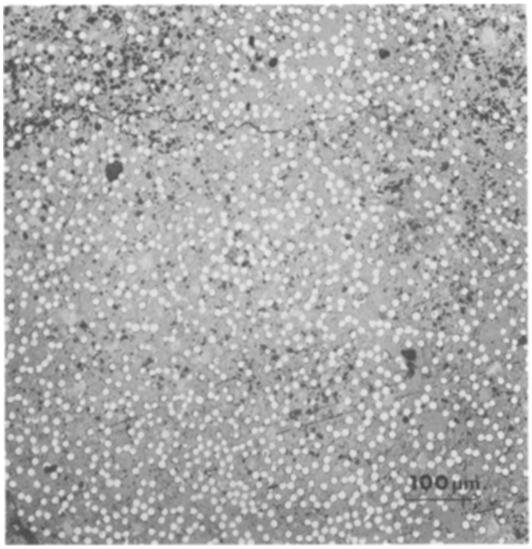

Figure 3 An optical micrograph of a polished section of uniaxial CRC.

A refinement of the above technique obviates the need to separate fibres before impregnation by pre-separation into a continuous veil and fixation with a water-soluble binder. The veil may be stored on a spool and used directly in a filament-winding process. Fibre tows in this condition have also been used to make experimental samples by hand lay-up [4, 6].

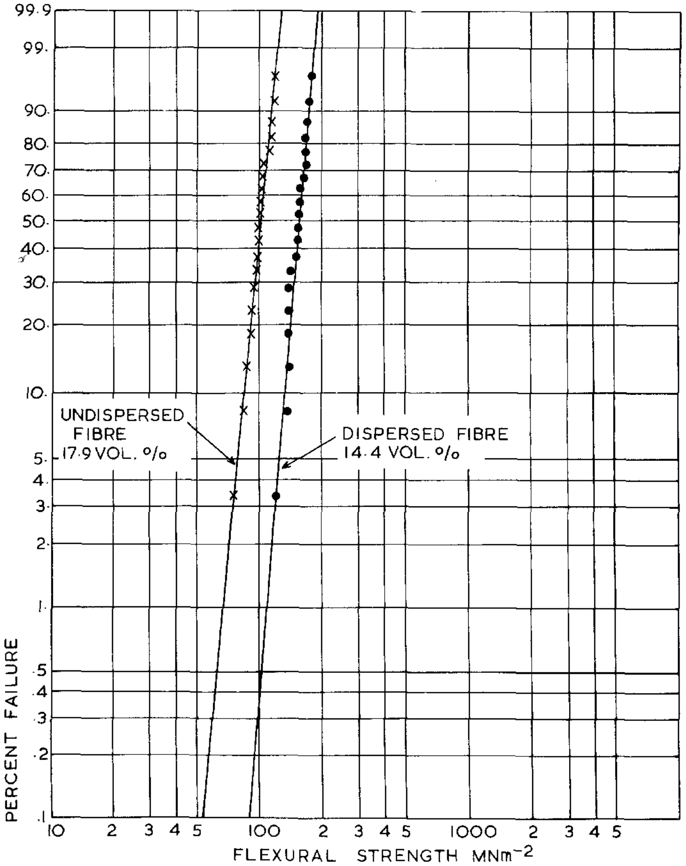

Figure 4 Failure probability as a function of strength for type I carbon fibre-reinforced cement.

3.5. Pull-pressing

A modified version of the filament-winding machine described above was used by Briggs *et al.* [10] to feed slurry-impregnated carbon fibre tows into a variety of moulds to form sheets, planks, beams and trusses. The artefacts were then consolidated and excess water removed by pressing. Fibre contents were again controlled by variation of the water:cement ratio in the cement slurry. Similar processes were described by Biryukovich *et al.* [9], for glass-reinforced cement, and Laws and Spratt [1]. Fig. 5 shows some of the types of structure that can be made by filament-winding or pull-pressing, and demonstrates the versatility of the processes.

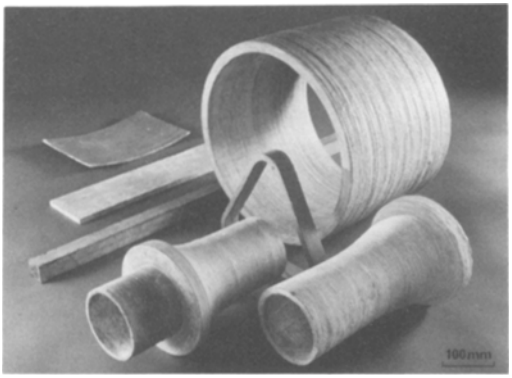

Figure 5 Some types of artefact that can be made in CRC by filament-winding or pull-pressing.

4. Theoretical considerations

Theoretically, the mechanical properties of a fibre composite depend on a number of factors: the dimensions, strength, modulus and stress/strain behaviour of the fibres; the fibre orientation; the nature of the fibre/matrix interface and the type and degree of binding across it; the strength, modulus and stress/strain behaviour of the matrix; the degree of consolidation of the matrix; changes in the properties of fibres or matrix with time and exposure to various environments. In practice, inevitable variations in the properties of constituents, their handling characteristics, process parameters and operator efficiency ensure that theoretical possibilities are seldom achieved. However, deviations from the theoretically possible may be undertood in terms of the microstructure of the composite and the properties of its constituents.

In the case of carbon fibre-reinforced cement we are concerned with the reinforcement of a weak brittle matrix with a strong brittle fibre whose strain to failure is much greater than that of the matrix. On stressing the composite beyond the strength of the matrix, therefore, if its fibre content is sufficient to support the additional stress thrown onto the fibres, the composite as a whole does not fail, but the matrix cracks. As the stress is increased further, a multiplicity of cracks appears in the matrix until it is broken into a mosaic of blocks. In a seminal series of papers Aveston and his colleagues [4, 11–13] at NPL have established a general theory of multiple matrix cracking in fibre-reinforced cement composites. The ideas developed in those papers were later combined [14] to provide a unified theory of brittle matrix composites covering the two extreme cases when the fibres are elastically bonded or not bonded to the matrix (i.e. when the "bond" is a frictional one). Most fibre-reinforced cement composites are expected to be in the latter category, and even if initially bonded, debonding after cracking is inevitable [14]. In carbon-reinforced cement there is no bond across the interface, but because the rough surface texture of the fibre is intimately penetrated by the cement gel, an exceptionally good frictional bond is produced. This may, indeed, be so good that elastic continuity between fibres and matrix is maintained after cracking.

An important basic principle arising from the NPL theory is the suppression of matrix cracking by fibres, through a constraint effect. This result is equivalent to the Romualdi–Batson theory for crack suppression in wire-reinforced concrete [15], although derived by a different method. As pointed out by Aveston *et al.* [14], however, both theories assume elastic continuity between fibres and matrix, and are therefore invalid for the debonded case. Their theory does predict a smaller but still significant, increase in cracking strain for the case of debonded fibres, and they show experimentally that the effect is greater for carbon fibres than for fine steel wires. Carbon fibre may be a special case. It has a microscopically rough surface, in which the asperities may be larger than any gap produced by a debonding mechanism, and are certainly larger than the Poisson contraction produced by stresses needed to crack the matrix. This could result in a degree of elastic continuity being maintained, and in a situation intermediate between the bonded and debonded cases. A still smaller effect was produced by chopped carbon fibres randomly oriented in a plane. Fig. 6 shows

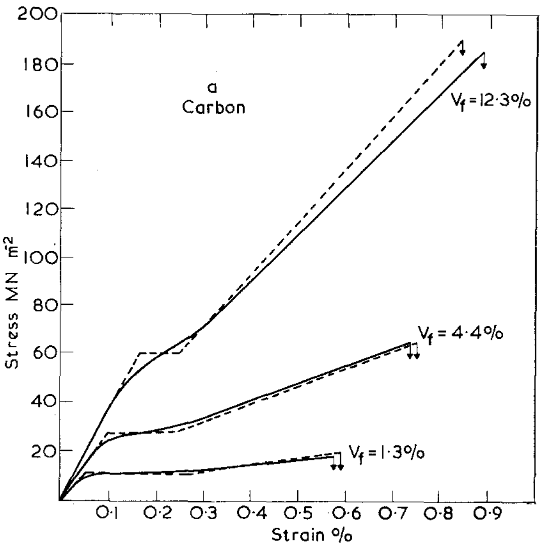

Figure 6 Comparison of theoretical and experimental tensile stress/strain curves for unidirectional and random Grafil fibre CRC, after Aveston *et al.* [14].

the effect of unidirectional carbon fibres as a function of fibre volume fraction compared with theory (the full lines). Aveston *et al.* [14] provide a detailed derivation of the crack constraint theory and also show how it is related to the Griffith theory of crack growth. The outcome of the calculations of Aveston *et al.* [14] for cement reinforced with continuous, unidirectional fibres is the following series of equations.

The matrix will eventually be broken down into a series of blocks of length between x' and $2x'$, where,

$$x' = \frac{V_m}{V_f} \cdot \frac{\sigma_{mu} r}{2\tau_i}\,, \tag{1}$$

and the crack width will be,

$$d = \epsilon_{mu}(1+\alpha)x' \tag{2}$$

where $\alpha = E_m V_m/(E_f V_f)$, and the matrix cracking strain is given by

$$\epsilon_{mu} = \left[\frac{12\tau_i \gamma_m E_f V_f^2}{E_c E_m^2 r V_m}\right]^{1/3}. \tag{3}$$

Aveston *et al.* [14] extend their analysis to the case of short fibres, either aligned or arranged randomly in two or three dimensions, and find that the tensile strength of the composite is,

$$\sigma_{cu} = \left(1 - \frac{l_c}{2l}\right) \sigma_{fu} V_f \tag{4}$$

for the aligned fibres, and $2/\pi$ or $1/2$ of this, respectively for the two- and three-dimensional random fibres, if $l > l_c$. The crack spacing for short, aligned fibres is given by,

$$x_d = \frac{l - (l^2 - 4lx')^{1/2}}{2} \tag{5}$$

x' being the value for continuous fibres.

The theory for the improvement in matrix strain due to the constraint in random fibre composites was not worked out, but for the two- and three-dimensional cases respectively, Aveston *et al.* [14] suggest the application of efficiency factors of $2/\pi$ and $1/2$ to V_f in Equation 3. Laws *et al.* [17] have also treated the stress/strain response of unidirectional and two-dimensional fibre-reinforced brittle matrix composites, with special reference to glass-fibre strands, and obtained results similar to those of Aveston *et al.* [14] for the friction-bonded case.

5. Mechanical properties

5.1. Tensile strength

The measurement of tensile strength poses notoriously difficult experimental problems. Misalignment of the specimen grips or misalignment of the specimen within the grips may introduce bending stresses; stress concentrations within or near the grips may lead to failure there. Both problems can lead to an underestimate of the tensile strength. In spite of the difficulties, a number of workers have carried out tensile tests on carbon-reinforced cement, using a variety of fibres and cements. Most workers experienced problems of fibre dispersion and resorted to hand lay-up techniques to try to overcome them, with varying degrees of success, reflected in the properties of the materials produced. Aveston *et al.* [4], using Grafil A fibre veil fixed in a dispersed form by a water soluble binder, and Swiftcrete cement (water:cement ratio 0.5), produced composites containing 1.3, 4.4 and 12.3 vol% fibres. The stress/strain curves obtained, shown in Fig. 6, have a linear portion, followed by an inflection and an increase in slope, and closely resemble the curves predicted by the Aveston *et al.* multiple matrix cracking model [4]. The curves for the materials with the greater fibre contents also show the Aveston *et al.* constraint effect [11] on the strain at the limit of proportionality, e.g. the tensile cracking strain of reinforced cement paste (2×10^{-4}) is raised to

~ 12×10^{-4} by 12.3 vol% fibre. A remarkable improvement in ultimate tensile strength over that of the unreinforced matrix is also evident; 185 compared with 5 MN m^{-2}.

Sarkar and Bailey [16] used specimens prepared in a similar manner, from similar Grafil A fibre veils and the same matrix, with an identical water:cement ratio. A fibre content of 10 vol% produced an UTS only half that obtained by Aveston *et al.* [4], and the lower strength is probably due to poor fibre dispersion and matrix consolidation. The Sarker and Bailey results also differ from those of Aveston *et al.* in that there is no inflection after the limit of proportionality in their stress/strain curves. The two findings are difficult to reconcile because, if the Sarkar and Bailey specimens indeed had a weaker matrix, its tendency to multiple cracking would be greater, and a more marked inflection in the stress/strain curve would be expected.

Ali *et al.* [8] used Grafil HS (high strength) and HM (high modulus) fibres in unidirectional composites and HM fibres in two-dimensional random mat composites. In all three cases the matrix material was ordinary Portland cement (OPC) with water:cement ratio ranging from 0.30 to 0.35. Fibre dispersion was difficult, due to some extent to the large particle size of the cement. The stress/strain curve for the random mat material showed completely brittle behaviour, whilst the curves for the aligned fibre materials had no inflection after the limit of proportionality, but did exhibit small increases in cracking strain compared with the unreinforced matrix. UTS values for the aligned fibre materials were proportionately even less than those obtained by Sarkar and Bailey [16], and must reflect the greater difficulty of fibre dispersion in coarser cement.

In an attempt to avoid specimen alignment and gripping problems, the author and his colleagues [17] carried out hydraulic burst tests on rings machined from short tubes made by filament winding. Swiftcrete cement-impregnated tows of Harwell type II fibre were used; the winding was circumferential and very good fibre dispersion was achieved by use of a fibre-spreading and impregnation machine developed for the purpose. The fibre content was 9 vol%. The rings, 125 mm i.d.,

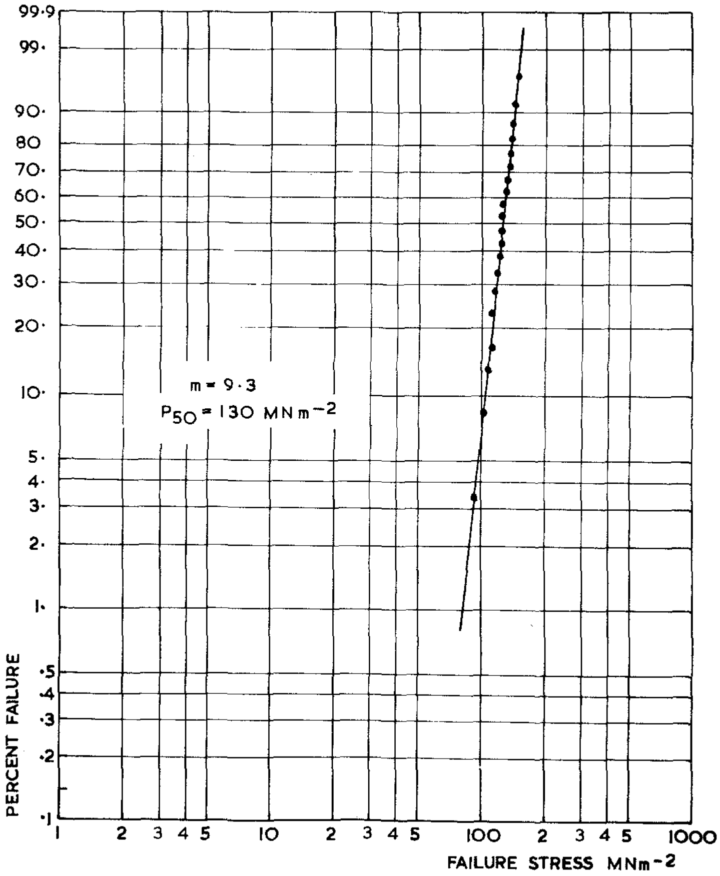

Figure 7 Probability of failure as a function of failure stress for hydraulic burst tests on filament-wound 9 vol% type II fibre CRC.

4 mm thick and 6 mm wide, were clamped between rubber rings and water pressure was applied to their inner surfaces through a close-fitting polythene ring. This test geometry allowed the application of almost pure tension (with a slight, superimposed transverse compressive stress). Twenty rings were tested, and the tensile stress at failure is presented in the form of a Weibull failure probability plot in Fig. 7. The median (50% probability) UTS, 130 MN m^{-2}, when adjusted for differences in fibre content, is close to that obtained by Aveston *et al.* with conventional tensile tests on a similar material. The steep slope (m) of the Weibull plot indicates the small scatter in strengths and reflects the uniformity of fibre dispersion in the rings.

5.2. Flexural strength

The flexural strength, known also as bend strength or modulus of rupture, measured by a three- or four-point bending test, and calculated from homogeneous beam theory, is often chosen as an indicator of the load-bearing ability of composites. Such a test simulates the type of loading usually found in practice and is very easily carried out, but its interpretation is not simple in the case of cement-based composites because of the matrix-cracking phenomenon. As pointed out by Aveston *et al.* [4], even for an elastic material the modulus of rupture is usually greater than the tensile strength because of the smaller stressed volume in the bending case. In the case of fibre-reinforced cement undergoing bending, on the tensile side where matrix cracking occurs the material is elastic to a lesser strain than on the compressive side. The stress in a substantial part of the tensile zone may therefore be constant at the cracking stress, and the neutral plane will move towards the compressive face. This results in an increased bending moment and can lead to a modulus of rupture 2 to 3 times the tensile strength. The exact relationship between flexural and tensile strengths for cement composites is derived in Appendix 2 of the paper by Aveston *et al.* [4] and a similar theory has been derived by Allen [18] with similar results. For the case of carbon-reinforced cement, Aveston *et al.* [4] give theoretical, but no experimental results for the relationship between modulus of rupture and tensile strength, but according to their Fig. 12, using appropriate values for α and $\epsilon_{fu}/\epsilon_{mu}$ the ratio σ_{MOR}/σ_T for 9 vol % fibre should be no more than 1.2. This is close to the ratio obtained using the MOR figure for 9 vol % type II fibre composite published by Briggs *et al.* [5] and the figure given above for hydraulic burst tests on similar material. For a composite containing well-dispersed fibre, therefore, the modulus of rupture is ~ 20% greater than the tensile strength.

Waller [6] reported flexural strengths up to 130 MN m^{-2} for Swiftcrete cement reinforced with 7.5 vol % Grafil A fibres. When this figure is adjusted to account for differences in fibre content, and compared with the Aveston *et al.* [4] tensile strength figure for 12.3 vol % Grafil A material the ratio σ_{MOR}/σ_T is 1.15, providing further confirmation of the theory.

Briggs *et al.* [5] measured the modulus of rupture of Swiftcrete cement reinforced with four types of carbon fibre (Harwell types I, II, a and b) covering a range of fibre Young's modulus from 77 to 385 GN m^{-2}. Whatever the fibre modulus, the flexural strength of the composite was roughly proportional to the fibre strength and volume fraction, following a mixtures rule with appropriate efficiency factors to take account of inevitable fibre misalignment and matrix porosity.

Ali *et al.* [8] measured the modulus of rupture of ordinary Portland cement reinforced with 3 to 4 vol % of unidirectional Grafil HS or HM fibre (which type was not specified) and also of material reinforced with two-dimensional random mat, using a three-point bend test. In all three cases the fibres were concentrated in the tensile regions of the specimens. The modulus of rupture was used as a measure of the durability of the composites when stored for periods up to a year in air or water at 18° C, and water at 50° C. No deterioration, but a possible improvement in strength, was found at 18° C whilst a slight decrease in strength occurred at 50° C.

Sarker and Bailey [16] carried out four-point bend tests on Swiftcrete reinforced with 2 to 8 vol % Grafil A fibre. As the fibres were concentrated on the tensile side the results are not comparable with their own results on tensile specimens, which contained more uniformly dispersed fibres, nor with other workers results on cement reinforced with Grafil A. There was little difference between the strengths of their 4, 6 or 8 vol % materials, probably because of fibre dispersion difficulties. True volume fractions in the tensile region would be at least 8, 12 and 16 vol % respectively, and studies have shown that good dispersion of more than 12 vol% of fibres is not possible [10].

5.3. Work of fracture

The three- or four-point bend test for modulus of rupture allows simultaneous measurement of the work of fracture, provided that failure is non-catastrophic and that all the elastic energy stored in the specimen up to the point of fracture is subsequently converted into fracture energy. Cement composites often do fail in a non-catastrophic manner and the work of fracture can then be computed from the area under the load/deflection curve. Only Briggs *et al* [5] have reported work of fracture measurements on carbon reinforced cement. They studied the four types of fibre referred to in Section 5.2 and obtained the results shown in Fig. 8. In the same paper the effect of the degree of matrix consolidation (and hence bond efficiency) on work of fracture was also reported. A progressive reduction in γ_F with increasing consolidation pressure was found, which is probably due to the effect of improved bonding on critical transfer length and hence on fibre pull-out length. Also observed was a significant increase in the number of fibres broken into short lengths when the pressure exceeded 7 MN m^{-2}.

5.4. Young's modulus

The Young's modulus of cement and hence that of cement-based composites is governed by: the degree of hydration of the cement, and therefore its age; the porosity of the hydrated cement, and therefore its initial water:cement ratio and its degree of consolidation. Calculation of the theoretical modulus of a composite from the properties of its constituents must take account of these factors. Several methods are available for the measurement of Young's modulus, and three of them have been applied to carbon-reinforced cement. Two are "static" methods which involve the derivation of the modulus from the initial slope of a stress–strain curve obtained in a tensile or bending test (the so-called tangent methods). The third (dynamic) method calculates the modulus from the resonant frequency of longitudinal vibrations of centrally supported specimens. The tensile method was used by Aveston *et al.* [4] and Sarkar and Bailey [16] for Grafil A/Swiftcrete materials and by Ali *et al.* [8] for HM and HS fibres in OPC. Briggs *et al.* [5] used the bend-test method for a variety of fibres in Swiftcrete and [17] the resonant frequency method for type I fibre/Swiftcrete composites and unrein-

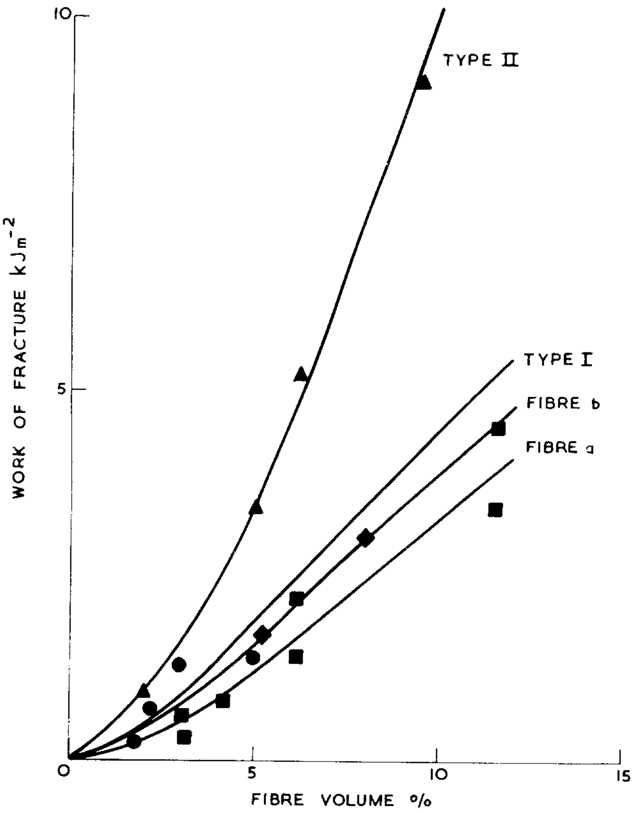

Figure 8 Work of fracture as a function of fibre volume fraction for CRC containing four types of fibre.

TABLE III Young's modulus

Fibre type	Cement type	V_f (%)	Modulus (GN m^{-2})	Stressing mode	Reference
Grafil A 1-D	ERHC	0	19.5	Tensile	[4]
		2	23.5		
		4	27.0		
		6	31.0		
		8	35.0		
		10	38.0		
Grafil A 1-D	ERHC	4	21.4	Tensile	[17]
		6	24.9		
		8	28.4		
		10	30.7		
Grafil HM 1-D	OPC	0	13.8		
		4	26.1		
Grafil HS 1-D	OPC	4	22.1	Tensile	[8]
Grafil HM 2-D random	OPC	3	18.2		
I 1-D	ERHC	0	16.0	Bend	[5]
		2	18.0		
		4	23.5		
		6	30.0		
		8	38.0		
II 1-D	ERHC	2	17.5	Bend	[5]
		4	21.0		
		6	24.5		
		8	29.0		
I 1-D	ERHC	0	5.5	Sonic	[18]
		2	6.5		
		4	7.0		
		6	7.5		
		8	8.0		

forced cement paste. They found that the modulus of the paste was still increasing with consolidation pressure beyond 17.5 MN m^{-2} but that, for a given pressure, it reached an upper limiting value at an age of 30 days. Table III presents the results of all the above workers. Sarkar and Bailey [16] also used the bend-test method for Grafil A in Swiftcrete, but because their fibres were concentrated in the tensile faces of specimens, and poorly dispersed, their results are not comparable with the others. In most cases the Young's modulus derived from static tests was reasonably close to the theoretical value computed from the mixtures rule. The resonant frequency method, however, gave low values and the discrepancy between the methods increased with increasing fibre content. The low resonant frequency results are unexplained, but the relatively small influence of fibres in this method is probably due to a preference of the exciting pulse for travel in the matrix.

5.5. Matrix cracking

Aveston *et al.* [4] published a micrograph of multiple matrix cracks in Swiftcrete reinforced with Grafil A fibres. They measured the mean crack spacing obtained with various volume fractions of fibre and found a linear relationship between x' and ϵ_{mu} (V_m/V_f) which followed closely the prediction of their theory. From the slope of the curve they derived the ratio τ/r, using Equation 1 and substituting $E_m \epsilon_{mu}$ for σ_{mu}. If a radius of 4.5 μm, a typical value for Grafil A fibres, is inserted in τ/r, the figure obtained for the interfacial shear strength, τ, is 2.3 MN m^{-2}. This is a minimum value, as the fibres were not evenly dispersed. The effective fibre radius will therefore be > 4.5 μm and the bond strength τ will be greater.

Briggs *et al.* [17] studied the matrix cracking phenomenon in type II fibre-reinforced Swiftcrete containing 8 vol % fibre. Their specimens,

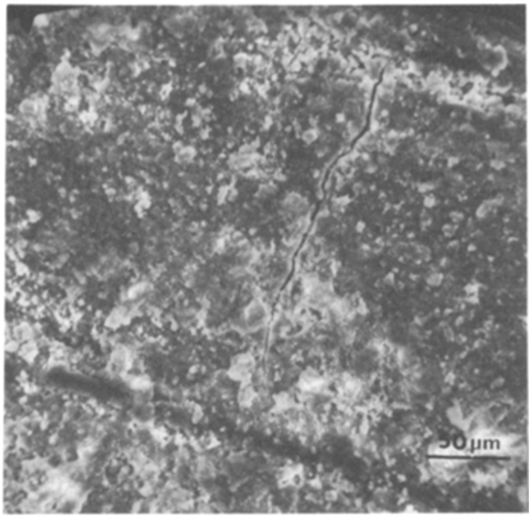

Figure 9 A matrix crack in CRC, stopped at each end by a carbon fibre.

which had been cut from composite boards and surface ground, were found to contain matrix cracks before testing. These cracks were seldom more than one or two inter-fibre distances long, and each end of a crack terminated at a fibre, as shown in Fig. 9. On stressing the specimens beyond the bendover point on their load/deflection curves, no significant increase in the number of cracks and no increase in the surface length of cracks was observed. Crack widening was seen, and this implies growth in crack depth. Limitation of the surface length of the cracks illustrates the effectiveness of carbon fibres as crack stoppers. In [5] Briggs *et al.*, assuming that the bendover point of a load/deflection curve indicated the onset of matrix cracking, plotted cracking stress against fibre volume fraction for four types of carbon fibre in Swiftcrete. In each case the cracking stress was greater than predicted by an expression derived from the mixtures rule by Astbury [19]. The cracking strain was also progressively increased by increasing fibre content [17] and this provides further support for the Aveston *et al.* [14] constraint theory.

5.6. Compressive strength

Measurements of the compressive strength of carbon reinforced cement composites have been reported only by Briggs *et al.* [5]. They cut 10 mm cubes from slabs of Swiftcrete reinforced with aligned type I fibres and tested them with the load parallel to the fibres. Variation of the consolidation pressure on composites containing a fixed 7 vol % fibres showed that maximum compressive strengths were achieved by consolidation at 7 MN m^{-2}. Beyond this pressure fibre breakage caused a reduction in compressive strength. Using the optimum 7 MN m^{-2} pressure, composites with a range of fibre contents were made, and their compressive strengths are shown in Fig. 10. Bajza [20] determined the compressive strength of unreinforced cement paste as a function of porosity, which he varied by varying consolidation pressure. Interpolation on his Fig. 1 indicates that the unreinforced material tested by Briggs *et al.*

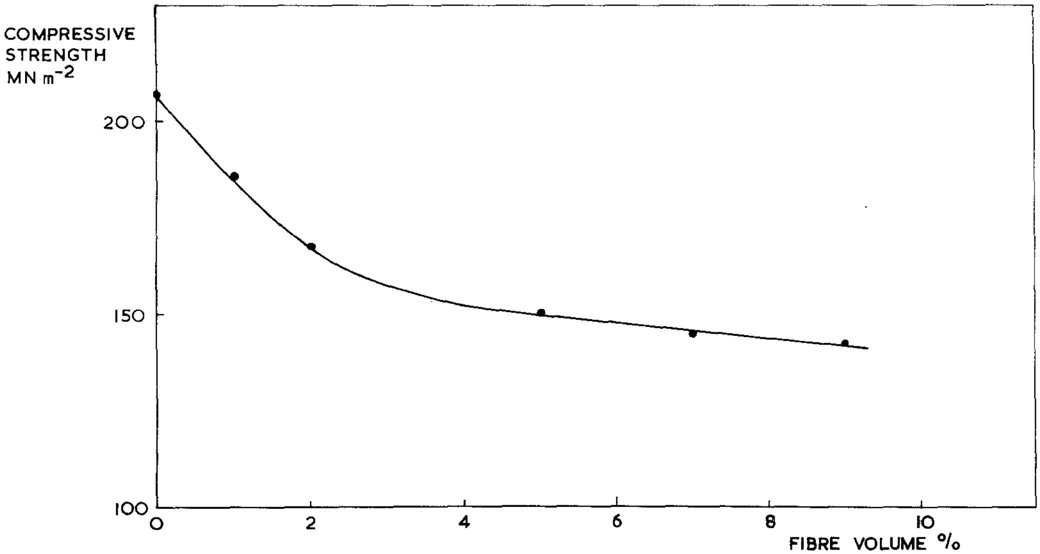

Figure 10 Compressive strength of type I fibre CRC parallel to the fibres, as a function of fibre content.

[5] contained 29% porosity. The compressive strength of their composite material containing, e.g. 9 vol% fibre is equivalent to that of Bajza's unreinforced paste containing 37% porosity, which indicates that, in compression, the fibres behave as though they are extra porosity.

5.7. Interlaminar shear strength

Briggs *et al.* [5] attempted to measure the shear strength of composites reinforced with 2 or 8 vol% type I fibre using a short-beam bend test method. This test is a compromise between the difficulty of achieving a state of pure shear and experimental simplicity. It is based on the premise that, if the maximum shear stress in the specimen exceeds its shear strength before the maximum tensile stress exceeds its tensile strength, failure in shear will be induced. Since the maximum tensile stress in a bending beam is given by,

$$\sigma = \frac{3Pl_s}{2bd^2} \tag{6}$$

and the maximum shear stress by,

$$\tau = \frac{3P}{4bd} \tag{7}$$

then $\sigma/\tau = 2l_s/d$, and it can be seen that the smaller the ratio l_s/d the more likely is the specimen to fail in shear. Work on other composite materials has obtained satisfactory shear failures with $l/d \leqslant 4$ [20]. In the work by Briggs *et al.* [5] specimens with l/d ratios from 2 to 5 were used. In no case was there any indication of neutral plane shear failure. All the 2 vol% specimens failed by transverse cracking; the 8 vol% specimens with $l_s/d > 3$ failed by diagonal cracking and those with $l_s/d < 3$ by crushing under the loading noses. Shear stresses supported by the 2 and 8 vol% material were at least 10 and 16 MN m^{-2} respectively; both values being greater than would be expected from the matrix alone, and much greater than the interfacial shear strength values quoted in Section 5.5. No explanation for the discrepancy was given, but the constraint phenomenon discussed in Section 4 may be responsible for an increase in matrix shear strength.

5.8. Dynamic fatigue

Fatigue-in-bending tests on materials containing 8 vol% type I or type II fibre were carried out by Briggs *et al.* [5] using an Instron machine cycling 30 times a minute for high stress–short life tests (up to 10^4 cycles) and an Amsler Vibrophore cycling 2000 times per minute for lower stress–longer life tests. In each test a small minimum load was applied to the specimen to keep it in place, cycling between that load and the desired test load begun, and the number of cycles to failure recorded. Fig. 11 shows the failure stress plotted against the number of cycles to failure for both materials. Data points carrying arrows pointing to the right represent specimens that had not failed when a test was stopped. The point with an arrow pointing left represents a specimen which failed in an unknown number of cycles < 1000. The single-cycle results were obtained from modulus of rupture tests. Low-frequency and high-frequency results for the type I material lie, within the limits of experimental error, on the same curve, which indicates that increasing the frequency had no extra effect on the fatigue strength. The tendency of the curve to level off around 10^8

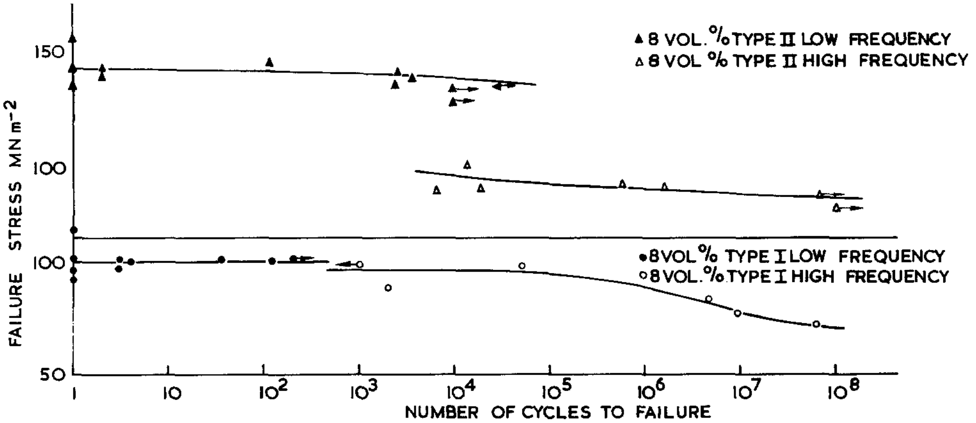

Figure 11 Failure stress as a function of number of stress cycles to failure.

cycles suggests that the material has a fatigue limit ~ 70 MN m^{-2}. Cycling at high frequency had a different effect on type II material, apparently causing fatigue damage at much lower stresses than low-frequency cycling. This can probably be attributed to the greater deflection of the lower modulus type II material, which would increase the fretting experienced by the fibres where they crossed matrix cracks. The type II material had a more distinct fatigue limit which occurred at a greater stress (~ 80 MN m^{-2}) than that found for the type I material. In both it is notable that the fatigue limits occurred at stresses much greater than the respective matrix cracking stresses, which suggests that such cracking is not deleterious to the performance of the materials under cyclic stresses less than their fatigue limits.

5.9. Impact resistance

Davidge and Phillips [22] discussed the significance of impact data for composites in terms of their material properties and the test conditions. They concluded that the impact strength of a tough composite may be controlled by its work of fracture, but that the more brittle the material the more its impact strength would depend on the elastic energy stored at the instant of fracture initiation. The difficulty of interpretation of results from the commonly used impact test was emphasized and the authors recommended that impact should be correlated with other properties, such as work of fracture, strength and Young's modulus.

Briggs *et al.* [17] measured the Izod impact strength of continuous uniaxial and continuous cross-ply fibre CRC containing various fibre types and Swiftcrete cement, and also measured the flexural strength and work of fracture of specimens taken from the same sample boards. In [5] results for two types of uniaxial fibre are given and they show that the impact fracture energy is 2.5 to 3 times the slow bend work of fracture (when allowance is made for two fracture faces in the impact figures). In [17] cross-ply fibre composites containing three types of fibre required 2 to 3.5 times the slow bend fracture energy for impact fracture, as shown in Fig. 12. The difference in the energy involved in the two types of test can probably be accounted for by the different failure modes. Whereas in the bend test, failure was often by simple transverse cracking, in the impact test the failure was often complex, involving compression and delamination modes. As pointed out by Kelly [23] an important factor in impact resistance is the interfacial bond strength between fibres and matrix, which determines the degree of fibre pull-out and hence the energy absorbed during fracture. Similar considerations

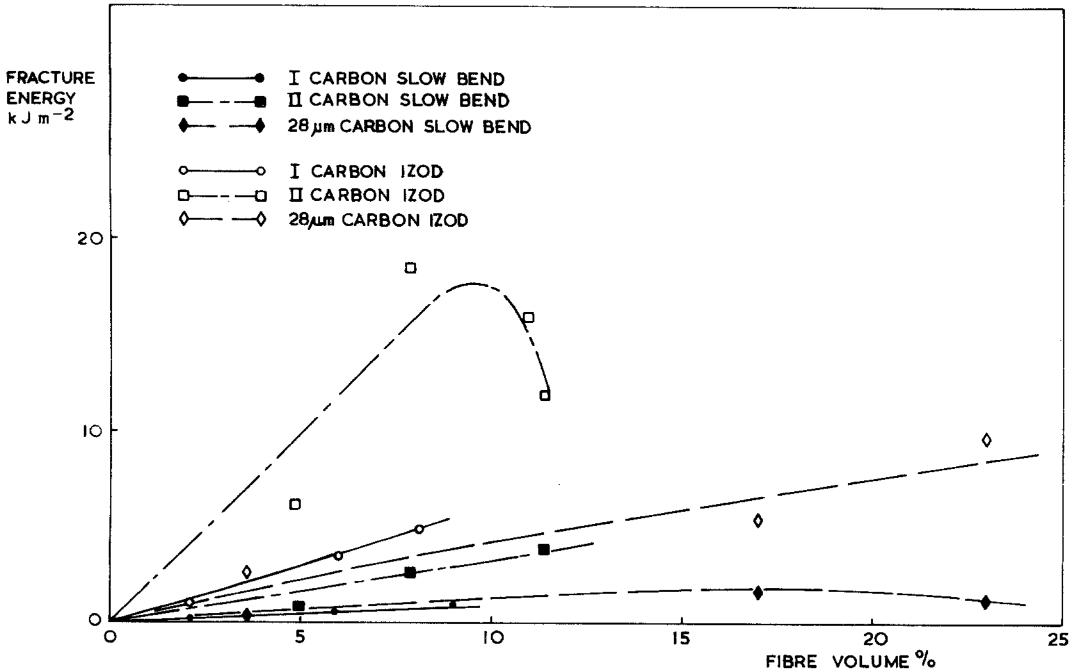

Figure 12 Izod and slow-bend fracture energies for cross-ply composites containing three types of fibre.

also apply to the work of fracture. The bond strength is therefore governed by (among other factors) the degree of compaction of the matrix, and this was demonstrated by Briggs *et al.* [5], who found a great inverse dependence of γ_F on the consolidation pressure.

The only other published work on the impact resistance of CRC was by Ali *et al.* [8], who carried out Izod tests on composites containing 3.7 vol% uniaxial HM fibre, 4.0% uniaxial HS fibre and 3.0% random mat HM fibre in a matrix of ordinary Portland cement. Similar improvements were produced by the two uniaxial fibres, but the impact resistance of the random mat composite was no better than that of the unreinforced matrix. They compared the performance of CRC and GRC containing rather more (5 vol%) random glass fibre and found that the latter gave an order of magnitude greater impact resistance. A suggestion was made that more work is necessary on the nature of the interfacial bond in CRC in order to understand its different behaviour in impact tests.

Glass fibres have smooth surfaces, are normally coated with an organic size to prevent abrasion damage, and are used in integrated strands. For these reasons no bonding except a small degree of frictional bonding between fibre and matrix is possible until, as the composite ages, chemical bonding and infiltration of the strand by cement hydrates can occur. Until this happens, fibre pull-out is easy, and consequently the material has good impact resistance. Carbon fibres, on the other hand, are unsized, discrete filaments, and they have turbostratic, pitted surfaces which are replicated by the hydrating matrix, producing an intimate, strong bond by mechanical keying. In this case fibre pull-out is not easy and the impact fracture energy is correspondingly small, whereas flexural and shear strengths may be increased, relative to those of comparable GRC composites.

5.10. Creep resistance

All materials containing Portland cement as a major constituent are expected to reflect the known creep properties of cement gel to some degree. An extensive literature exists on the creep of cement paste and concrete which shows that the magnitude and rate of creep deflection depend on cement content and stress [24]; the humidity gradient between the gel and its environment [25]; the degree of hydration and amount of uncombined water present in the gel at the start of loading and whilst under load [26]. Most of the phenomena observed may be explained by the water diffusion theory due to Powers [27] and Ishai [28].

Little work on the influence of fine fibres on the creep resistance of cement paste has been published, however, and only Briggs *et al.* [5] have reported work on carbon-reinforced cement. They studied the effects of fibre content, stress and humidity on the creep behaviour of composites containing aligned type I fibre. Specimens 200 mm × 10 mm × 5 mm supported on a 150 mm span were dead-loaded in the middle and their mid-point deflections measured by capacitance transducer. To examine the effect of fibre content on creep, water-soaked specimens of unreinforced cement and composites containing 2 and 9.3 vol% fibre were subjected to a bending stress of 4.7 MN m^{-2}, whilst maintained wet. In each case there was an initial rapid, but diminishing, creep rate followed by a slower, constant rate. The creep deflection was followed until, after ~ 240 h a constant creep rate was established. The load was then removed and the creep recovery followed until a constant recovery rate was established (after a further 100 h). Fig. 13 shows the deflection after 240 h and the recovery after 100 h as functions of fibre content. The presence of fibres, even in concentrations as low as 2 vol%, had a profound influence on creep, reducing the deflection under a given load by a factor 6. 9 vol% fibre reduced the creep deflection by a factor 40, and the steady creep rate by a factor 5. Creep recovery after removal of the load, as a proportion of the creep deflection, increased as the fibre content increased. For example, the 9 vol% material recovered two thirds of its original creep deflection, compared with the one sixth recovery of the unreinforced matrix material. Such effects on creep and recovery indicate a strong mechanical interaction between fibres and matrix. The fibres are left with a residual stress as a result of the creep, and impose a restoring force on the composite after the load is removed. In effect, the matrix becomes pre-stressed.

The effect of stress on creep, for material containing 9.3 vol% type I fibre, at 40% relative humidity, is shown in Fig. 14. Except at high stresses the creep deflection is proportional to the stress, and this is consistent with the observations of a number of workers on concrete.

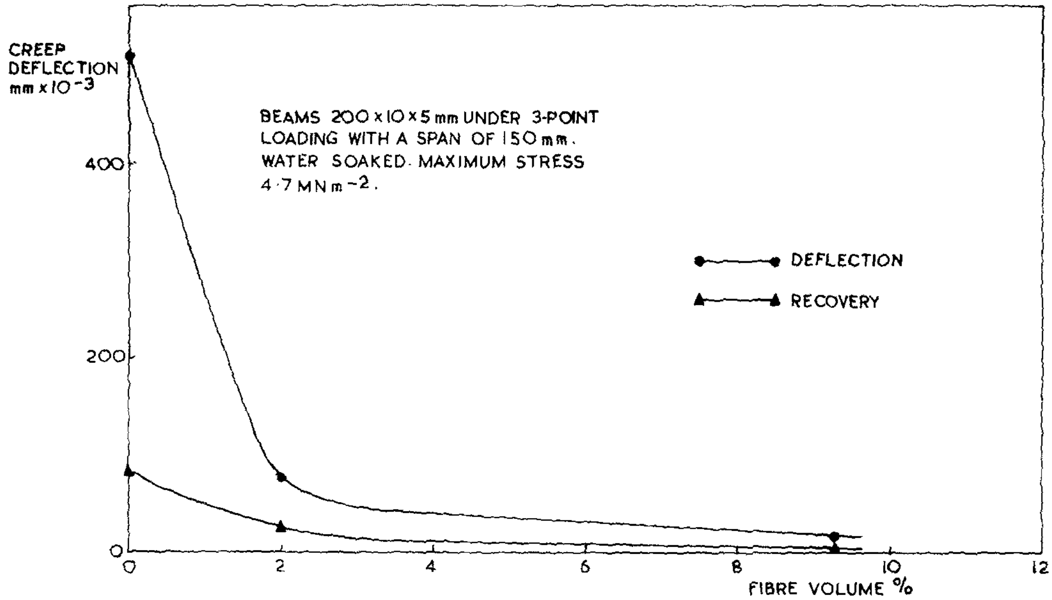

Figure 13 Creep deflection after 240 h and recovery after 100 h as functions of fibre content, for type I fibre CRC.

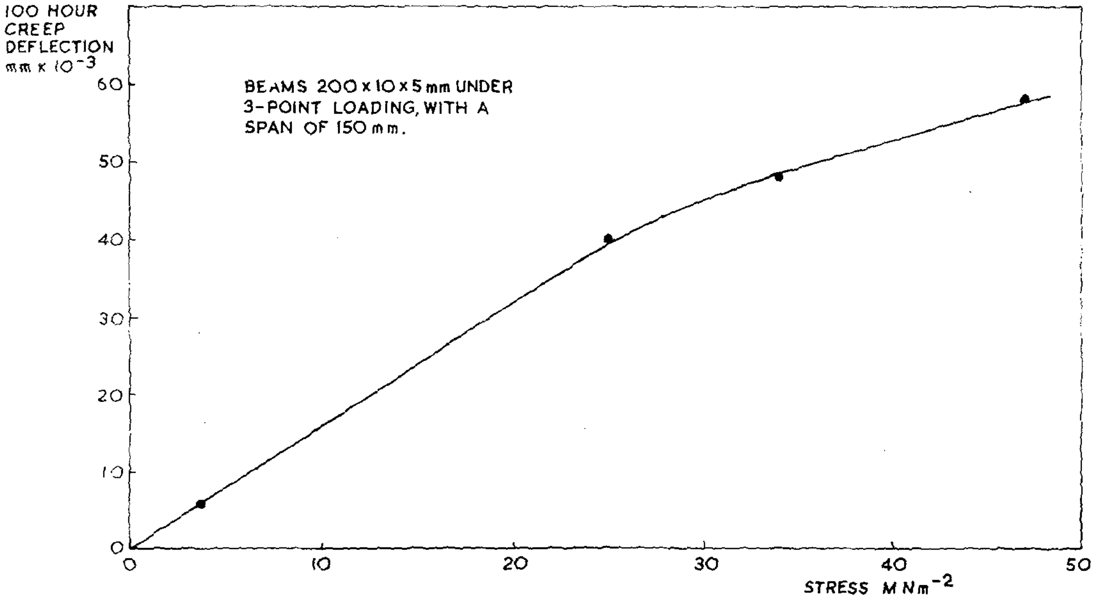

Figure 14 Creep deflection after 100 h as a function of stress for 9.3 vol% type I fibre CRC.

The effects of moisture and moisture gradient on creep are illustrated in Fig. 15, which compares the creep curves of specimens containing 9.3 vol% type I fibre under the same stress (47 MN m^{-2}) one soaked with water and the other "dried" at 40% r.h. It is clear that soaking in water causes a great increase in initial creep rate and deflection, although eventually the creep rates of wet and "dry" materials settle down to about the same value. After the steady creep rate of the soaked specimen had been established it was exposed to a 40% r.h. environment to create a moisture gradient. This produced a twenty-fold increase in creep rate which then diminished to a steady value 1.5 times that of the initially "dry" specimen at 40% r.h. The marked increase in creep rate supports the moisture diffusion theory of Powers [27] and Ishai [28].

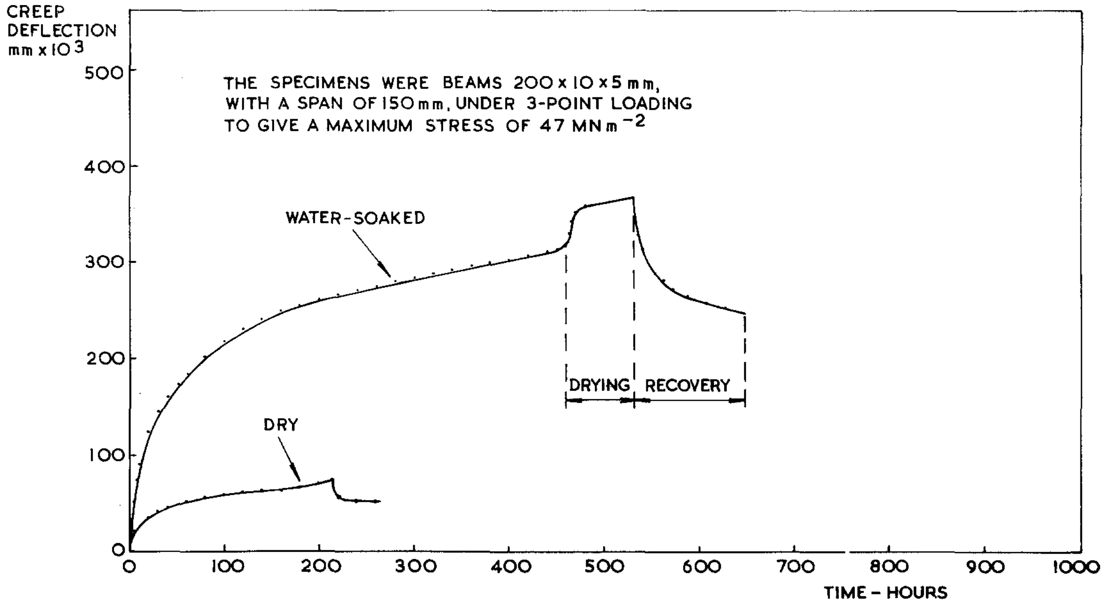

Figure 15 Creep deflection and recovery as functions of time for 9 vol% type I fibre CRC.

6. Durability

An important consideration in the assessment of the suitability of new materials for structural or semi-structural applications is their long-term durability. In wet conditions Portland cement produces a highly alkaline solution of calcium hydroxide, whose pH over the years may reach values >12 [8]. Such an environment can cause severe degradation and loss of strength in some reinforcing fibres. It is, therefore, necessary to study the long-term durability of new fibre-reinforced cement composites in wet conditions. Two groups of workers have assessed the durability of carbon-reinforced cement in a variety of environments, using the flexural strength after exposure as a measure of the resistance to attack.

The tests of Ali *et al.* [8] were carried out on uniaxial and two-dimensional mat reinforced OPC specimens in which the reinforcement was concentrated in the tension face, and on random mat specimens. There was no loss of strength by any specimen stored in air or water at 18° C for periods up to 1 year (Fig. 16). Indeed, there was some indication that strengths increased. Uniaxial specimens subjected to the much more severe test of storage in water at 50° C suffered a slight loss of strength after exposure for a year, as shown in Fig. 17. This accelerated test is probably equivalent to exposure under normal ambient conditions for 20 years.

Briggs *et al.* [5] examined the durability of type I fibre reinforced Swiftcrete in five environ-

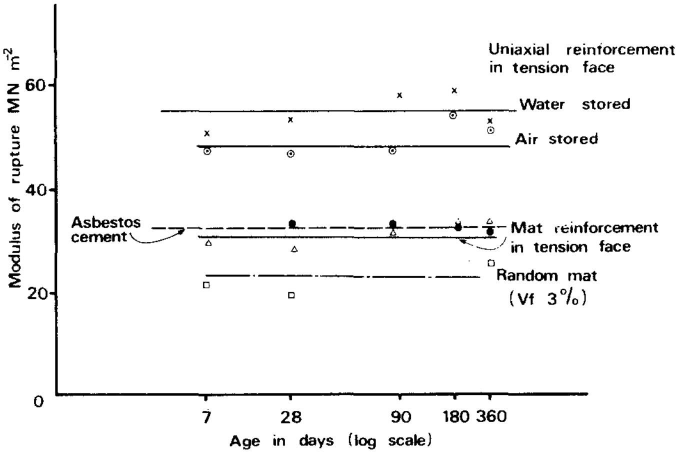

Figure 16 Flexural strength as a function of exposure time for uniaxial and random-mat CRC stored in air or water at 18° C, after Ali *et al.* [8].

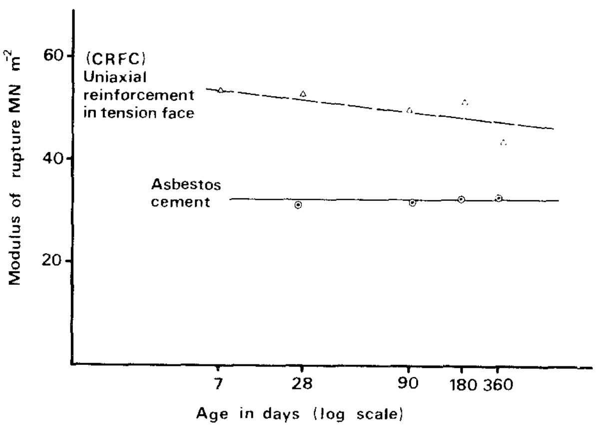

Figure 17 Flexural strength as a function of exposure time for uniaxial CRC stored in water at 50° C.

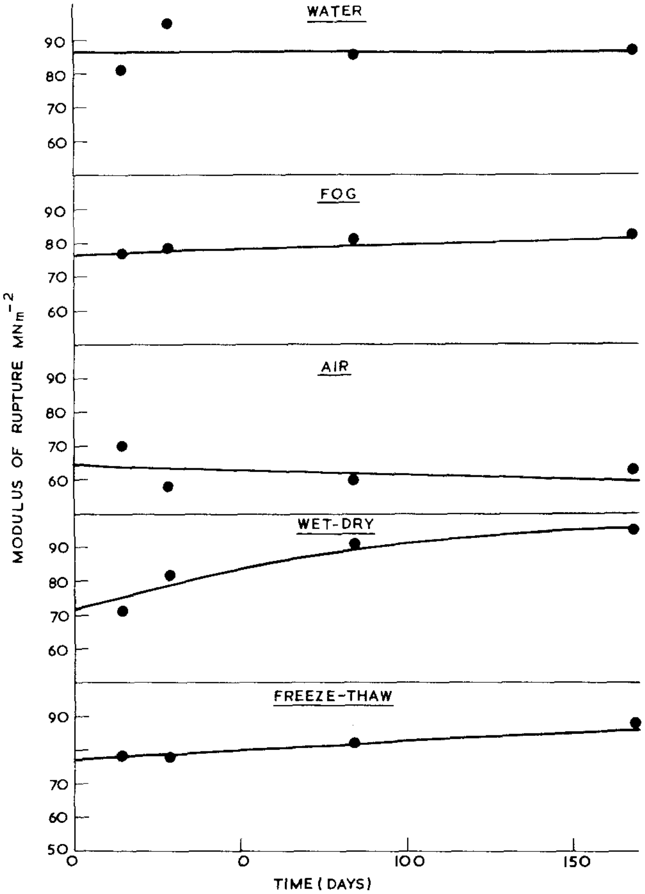

Figure 18 Flexural strength as a function of exposure time for uniaxial type I fibre CRC stored in various environments.

ments for periods up to 6 months. The conditions were:

(a) water at 19° C;

(b) fog at 19° C;

(c) air at 22° C and 45% r.h.;

(d) wet/dry cycling (water at 19° C for 12 h, followed by air drying at 20° C and 45% r.h. for 12 h);

(e) freeze/thaw cycling (air freezing to − 15° C for 12 h, followed by water spraying at 15° C for 12 h).

As shown in Fig. 18, there was little or no change in strength produced by water, fog or air storage, and a marked increase in strength caused by wet/dry and freeze/thaw cycling. The last two conditions both cause alternate expansion and contraction of the matrix with respect to the fibres. In each case the matrix expansion coincides with the wet phase of the cycle. Further cement hydration can then fill in the interface gaps produced and lead to progressive strengthening of the composite by improved bonding.

7. Dimensional stability

Expansions and contractions in hardened cement paste due to moisture movement caused by wetting or drying respectively can produce sufficiently high stresses to crack the material. Thorough drying invariably produces craze-cracking in surfaces. However, there is reason to believe that, if fine, strong fibres, with high elastic modulus, could be well-dispersed in the cement and intimately bonded to it, both shrinkage and expansion should be restrained. To test this hypothesis Briggs *et al.* [5] prepared samples containing 5.6 vol % type I fibre which were fitted, after hardening, with mechanical strain-gauge reference studs. The samples were exposed, together with unreinforced control specimens, in air at 20° C and 60% r.h. or in water at 20° C, and the shrinkage or expansion measured at intervals up to 6 months. The results in Fig. 19 show clearly that both shrinkage and expansion were markedly reduced by the presence of carbon fibres, and indicate that the fibres were just as effective in compression as in tension.

8. Economic considerations

The foregoing review of fabrication methods and properties demonstrates the feasibility and technical excellence of carbon-reinforced cement composites. Over-riding the technical aspects, however, and determining whether the materials will be used, is their cost. This hinges on the price of carbon fibres, which depends on two main factors:

(a) The scale of production. Economies of scale are expected to result in substantial price reductions, but the production levels required to achieve these economies are, themselves, dependent on the creation of bulk markets. This is unlikely unless carbon fibres become sufficiently cheap to be attractive to the building and construction industries, which brings us back to the need for economies of scale.

(b) Cheaper production methods. To break out of the circular "scale of production-price-scale of usage" situation radical changes in the technology of production of carbon fibres are necessary. The most promising approach appears to be the substitution of expensive textile precursors by pitch which is expected to reduce the costs of large-scale production to such an extent that the price is less than £2.50/kg. Comparable polyacrylonitrile-based fibres have a projected price of £5/kg for 100 tonne quantities [29].

9. Applications

The availability of carbon fibres at the prices quoted above will make possible their use in a variety of CRC applications, particularly those in which the special properties of the composite are exploited, e.g. its strength, stiffness and low

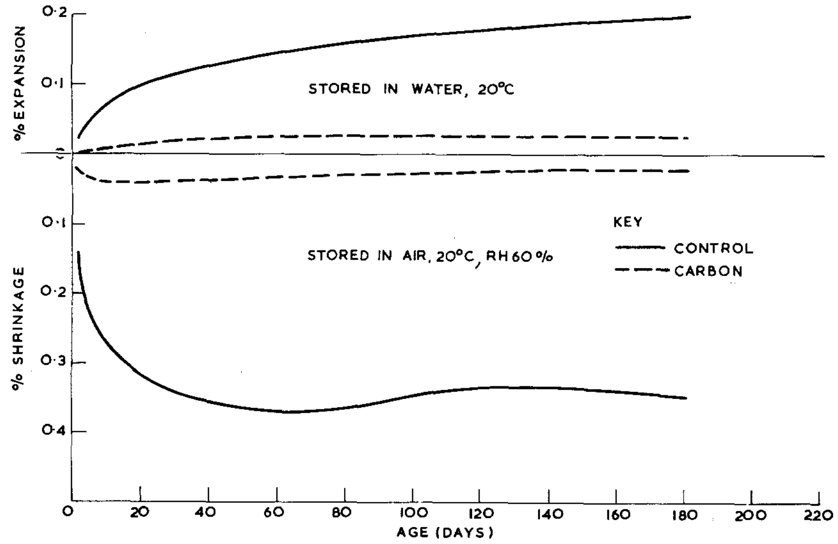

Figure 19 Expansion and shrinkage of 5.6 vol % uniaxial type I fibre CRC as functions of storage time in water and dry air.

density, which make it an ideal material for membrane structures [6]. Fowler [29] has considered various applications involving membrane action, including hollow planks, shells and pre-cast flooring units. He carried out detailed costing for a CRC floor plank and obtained a finished floor price of £6.90/m^2 (at 1972 prices, using a fibre price of £4.50/kg), compared with £6 to £7 for conventional pre-cast floors. An important indirect effect pointed out by Fowler, due to the reduced self-weight of a building with CRC floors, would be reduced building costs, which would be particularly significant for a multi-storey structure.

Briggs [10] examined the application of filament-wound CRC in pressure pipes and found that, on strength grounds, CRC would be in direct competition with asbestos cement. In order to compete economically the cost of the carbon fibre must be less than £2/kg. The author [10] also considered the case of CRC as a timber substitute, selecting the example of scaffold boards for detailed costing. For this application, which requires a composite containing only 4 vol% fibre, a fibre price of £3/kg could be tolerated. As the prices of timber imports escalate, other applications, which have traditionally been the preserve of timber, will become possible, e.g. domestic house roof trusses and joists, containers, transportation pallets.

10. Conclusions

(1) Carbon-reinforced cement composites can be fabricated by a variety of industrially applicable processes ranging in sophistication from hand lay-up to filament-winding.

(2) By selection of the types of carbon fibre used it is possible to make a family of composite materials, covering a wide spectrum of mechanical properties.

(3) The mechanical properties of the materials obtained may be understood in terms of current theories of brittle matrix composites.

(4) The durability of some of the composites in a variety of environments in the short term has been established, and in the long term may be predicted from accelerated tests.

(5) Potential applications of the materials are in structures exploiting their stiffness and resistance to membrane forces, and as substitutes for structural and semi-structural timber.

(6) Application of carbon-reinforced cement in any of these fields is contingent upon the availability of fibres at a sufficiently low price. This, in turn, requires bulk manufacture and radical developments in fibre production technology. Since bulk manufacture can be justified only if bulk markets are available, an impasse exists, which may be broken if cheaper production routes can be developed. The most promising approach to the production of cheaper fibres appears to be the introduction of pitch precursors.

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