Milled fibre reinforced epoxy resin – an engineering polymer composite*

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A milled fibre reinforced epoxy resin composite (MFRE) has been developed for low temperature use. It is resistant to fracture at temperatures down to at least 77 K in direct contact with liquefied gases. It can be used as an adhesive, a gap-filling mastic or a moulding compound for difficult cryogenic applications. The characteristics of the material and some applications are described.

(Keywords: fibre reinforcing; epoxy resin; polymer composite; cryogenic applications)

INTRODUCTION

Epoxy resins and their composites have received considerable attention over the years as structural materials for use at low temperatures. In the aerospace industry, primary and secondary structures, housings for microwave transmitters and receivers and support structures for optical devices constructed with epoxy composites survive the rigours of alternating high and low temperatures. Epoxy resins are used extensively as potting compounds in the construction of superconducting magnets for nuclear physics apparatus; these operate at −250°C or lower.

In the petroleum industry, designs of land tanks[1] for the storage of liquid natural gas (LNG) at −162°C also incorporate glasscloth/epoxy laminates in potential or direct contact with the liquid cargo. In these situations, the laminate is applied onto the surface of, for example, polyurethane foam insulation. The role of the laminate is to reinforce the foam and to prevent or inhibit crack propagation through the insulation layer. Under normal operating conditions the laminate is in a state of biaxial restraint and experiences stresses equivalent to restoring the potential displacements due to thermal contraction.

Where there is a requirement to bond fixtures to a restrained laminate, it is highly desirable to match the zero-strain displacement situation of the laminate with that in the fixture. It is also necessary to ensure that the bonding agent is capable of withstanding the thermally induced stress.

REQUIREMENT FOR A CRYOGENIC ADHESIVE

In a design study for an internally insulated cargo tank of an LNG carrier, a structure suspended from the top of the tank provides support for the submersed pumps, the associated pipework and cables, ladders, etc. This is known as the pipetower. It is necessary to provide additional support at the base of the pipetower to absorb vertical loads and accelerations and, more importantly, the sideways inertia forces induced by the ship's movement and by sloshing of the liquid cargo.

The design considered for this purpose was based upon an invar disc that was to be bonded onto the surface of the glasscloth laminate (see *Figure 1*). Whilst the undersurface of the invar disc could be made planar to a close tolerance, it would be virtually impossible to ensure that the laminate surface was similarly flat. What was required, therefore, was an adhesive medium that could be applied in relatively thick section to accommodate local undulations of the laminate which may have an amplitude of up to, say, 5 mm.

The usual concept for an adhesive requires that the 'glue-line' is kept as thin as possible and this general consideration becomes more important at low temperatures where brittle behaviour becomes more likely. A necessary feature of this adhesive or gap-filling mastic, therefore, was that it should be resistant to brittle fracture.

DEVELOPMENT OF MFRE

The epoxy resin used as the matrix in the glasscloth laminates is basically Epikote 828 modified with a flexibilizer and a thixotropic agent. The use of flexibilizers to improve the resistance of epoxy resins to thermal shock by imparting some degree of ductility has been explored by several workers[2,3]. The thixotropic agent is used to impart the necessary applicational characteristics enabling a laminate to be formed *in-situ* on vertical surfaces and overhead, horizontal surfaces, as well as down-hand.

Nevertheless, this resin still behaves as a brittle material when cast in thick section and used at low temperatures. Some properties are given in *Table 1* in which it is clear that the critical defect size is much less than a millimetre. This is of little consequence when the resin is used at a controlled thickness as a component of a laminate. However, in the proposed application, the critical defect size for a surface or an embedded flaw is between one and two orders of magnitude smaller than the dimension of the projected maximum thickness of adhesive to be employed. Except for the regions in close proximity to the stiff outer layers (the laminate and the invar disc), resin alone, used in bulk to bridge between the laminate and the disc, would be likely to suffer brittle failure following the development of cracks from inherent defects.

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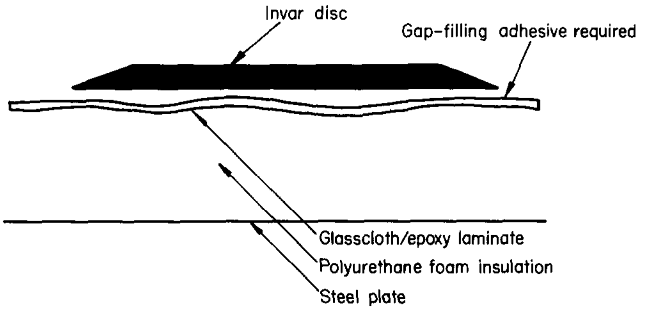

Figure 1 Requirement for bonding pipetower support to surface of internal insulation system

Table 1 Properties of flexibilized epoxy resins at 77 K

Tensile strength	60 MPa
Tensile modulus	5.7 GPa
Coefficient of expansion	$6.0\times10^{-5}\,^{\circ}\mathrm{C}^{-1}$
K_{IC}	$1.8\,\mathrm{MN\,m^{-3/2}}$
Critical surface defect	0.07 mm
Critical embedded defect	0.19 mm

The propagation of a crack would be inhibited by the inclusion of reinforcement. Rubber toughening would only be possible if a material that remained rubbery at the intended service temperature existed. Both particulate fillers and fibres have been considered but it has been shown that for given interfacial properties, whilst microspheres, flakes and fibres can act as crack inhibitors, fibres have the considerable additional advantage of contributing to energy absorption via fibre fracture, debonding and pull-out mechanisms[4].

Fibre reinforcement

The total fracture energy for a fibrous composite, γ_c, can be expressed as the sum of the principal energy absorption processes:

$$\gamma_c = V_f\gamma_f + (1 - V_f)\gamma_m + \gamma_d + \gamma_p \qquad (1)$$

where γ_f and γ_m refer to the fracture energies of the fibre and matrix respectively and V_f is the volume fraction of fibre, γ_d is the work of debonding and γ_p the frictional work of pull-out.

The first term is dependent on the number of fibres present that are of sufficient length to enable the stress to build up to the ultimate value. However, the reported value[5] for γ_f for glass at room temperature is very small ($7\,\mathrm{N\,m^{-1}}$), therefore it is assumed that the contribution to the total fracture energy even at low temperatures can be ignored.

The work of fracture of the matrix may be derived from fracture toughness measurements (K_{IC}) carried out on cast resin specimens:

$$G_{IC} = \frac{K_{IC}^2(1 - \nu^2)}{E} \quad \text{(plain strain)} \qquad (2)$$

Substituting values from *Table 1*, then $G_{IC} = 520\,\mathrm{N\,m^{-1}}$ and since $G = 2\gamma$, $\gamma_m = 260\,\mathrm{N\,m^{-1}}$.

The two remaining terms, γ_d and γ_p for aligned fibre composites are given by[4]:

$$\gamma_d = \frac{V_f\sigma_f^2 y}{4E_f} \qquad (3)$$

where σ_f = ultimate tensile strength of the fibre and
y = debonded length of fibre

and

$$\gamma_p = \frac{V_f\sigma_f l^2}{24 l_c} \quad (l \leqslant l_c) \qquad (4)$$

$$\gamma_p = \frac{V_f\sigma_f l_c^2}{24 l} \quad (l \geqslant l_c) \qquad (5)$$

where l = fibre length, and
l_c = critical fibre length.

In a random fibre composite it may be taken that only a small portion of the fibres are oriented parallel to the fracture plane and therefore the above expressions will still provide a reasonable estimate of the work done[6]. The length of fibre that can debond is clearly related to the strength of the resin-to-glass interface and the transfer and build-up of stress in the fibre is also a function of the bond strength.

Fibre size

The surface treatment (size) applied to glass fibre during the manufacturing process has an effect on (a) the handling and wet-out characteristics, (b) the ease of dispersion in the resin, and (c) the interfacial bond strength. Since the stress transmitted from the matrix to the fibre must traverse the interface, it follows that if the interface is weaker than the matrix, it will have a direct effect on the critical length.

Critical length assessment

An estimate for the critical fibre length can be made using the following equation:

$$l_c = \frac{r\sigma_f}{\tau} \qquad (6)$$

where r = radius of fibre,
σ_f = ultimate tensile strength of fibre, and
τ = shear strength of matrix or interface.

For the purpose of assessing the likely range of values for critical length, the maximum shear strength of the matrix may be taken as approximately half of the tensile strength, i.e. 30 MPa. A lower bound for τ, representing a weak interface, may be taken as 15 MPa. The range of tensile strength values for short glass fibres will be in the range 2–3 GPa. Substitution into equation (6) gives l_c in the range 0.4 to 1.3 mm.

Since the critical length probably lies between 0.4 and 1.3 mm, the use of chopped fibres is precluded since these

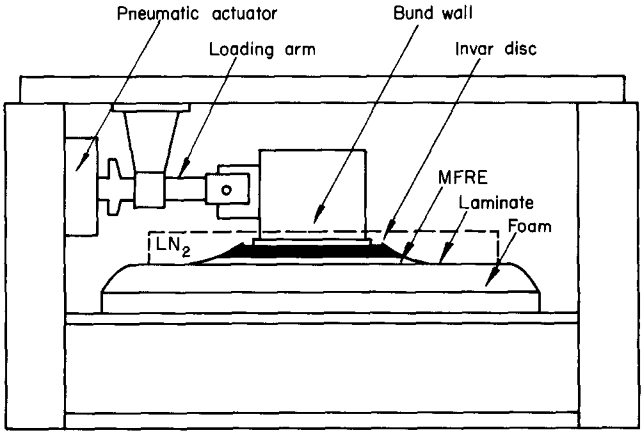

Figure 2 Prototype pipetower support disc test rig

Table 2 Estimates values of K_{IC} for different fibre lengths and critical lengths

($V_f = 0.12$, $\gamma_m = 260\,N\,m^{-1}$, $E_{calc} = 6.5\,GPa$)

l (mm)	l_c (mm)	σ_f (GPa)	γ_d ($N\,m^{-1}$)	γ_p ($kN\,m^{-1}$)	γ_c ($kN\,m^{-1}$)	G_{IC} ($kN\,m^{-1}$)	K_{IC} ($MN\,m^{-3/2}$)
0.35	0.4	2	28	3.1	3.3	6.6	6.9
0.35	1.3	3	64	1.4	1.7	3.4	4.9
0.6	0.4	2	32	2.7	2.9	5.9	6.5
0.6	1.3	3	110	4.2	4.5	9.0	8.0
0.95	0.4	2	32	1.7	1.9	3.9	5.3
0.95	1.3	3	174	10.4	10.8	21.6	12.4

Table 3 Properties of MFRE at 77 K

Tensile strength	49 MPa
Tensile modulus	8.6 GPa
Coefficient of expansion	$3.8 \times 10^{-5}\,°C^{-1}$
K_{IC}	$3.4\,MN\,m^{-3/2}$
Critical surface defect	0.5 mm
Critical embedded defect	1.2 mm

are available only in lengths of 3 mm and upward. On the other hand, milled fibres with lengths ranging from 0.2 mm to ~1 mm are a commercial product. The use of milled fibres would be compatible with the limits imposed by the characteristic dimensions of the final assembly. Using equations (1–5) with appropriate values of σ_f and y to correspond to selected values of l_c, estimates of K_{IC} for composites produced with narrow range milled fibres at $V_f = 0.12$ (25%w) have been made (*Table 2*). Milled fibres of length 0.2–0.5 mm, 0.5–0.7 mm and 0.7–1.2 mm were obtained for evaluation.

The optimum combination of properties, taking into account also the applicational characteristics, was obtained with fibres of length 0.5–0.7 mm. These fibres had been treated to enhance their filamentization and distribution in the resin and this treatment resulted in a relatively weak interface and a critical length of 1.3 mm.

Thus the compromise forced by other considerations resulted in a composite with properties as shown in *Table 3*. The critical defect size has improved considerably and the mean inter-filament distance is of the order of 0.07 mm. Thus, referring to *Table 1*, the critical dimension for a surface flaw in the base resin is also 0.07 mm and therefore such a flaw cannot exist in the composite without interacting with one or more reinforcing agents.

SOME APPLICATIONS OF MFRE

The initial use[7] for MFRE was for fixing a prototype pipetower support disc to a laminated foam base. The mixed resin proved easy to apply and the disc was bedded onto the resin and precisely located with minimum effort. A collar of glasscloth and resin was laid into the wet MFRE to close off the edges of the joint and the whole assembly was cured at 40°C.

In order to test the design and components, pneumatic actuators were set up (see *Figure 2*) to apply a cyclic sideways loading of 4 tonnes in a push-pull mode on an 8 s cycle. In the course of each cycle, the stress state at any point in the structure is fully reversed, i.e. tension and compression and direction of shear. More than 5000 cycles were completed at −196°C without failure.

Analogous to the above application, it is envisaged that similar arrangements could be made for attaching fixtures to the cold side of insulation systems in land storage tanks for LNG (see *Figure 3*). This would present a less severe loading condition since although thermal cycling and static loads may be more predominant, the absence of large displacement, cyclic loads would be clearly advantageous.

MFRE has been used as an adhesive for bonding block foam insulation in place. In 1980, a research programme was carried out to study the effects of releasing, instantaneously, large quantities of liquefied hydrocarbon gases onto the surface of the sea[8]. For this purpose a large vessel, some 12 m across and with a capacity of 20 m^3 was specially constructed and insulated (see *Figure 4*). In operation the vessel was designed to sink, under control, on an even keel giving a near instantaneous release of its cryogenic cargo. As a component of the insulation system

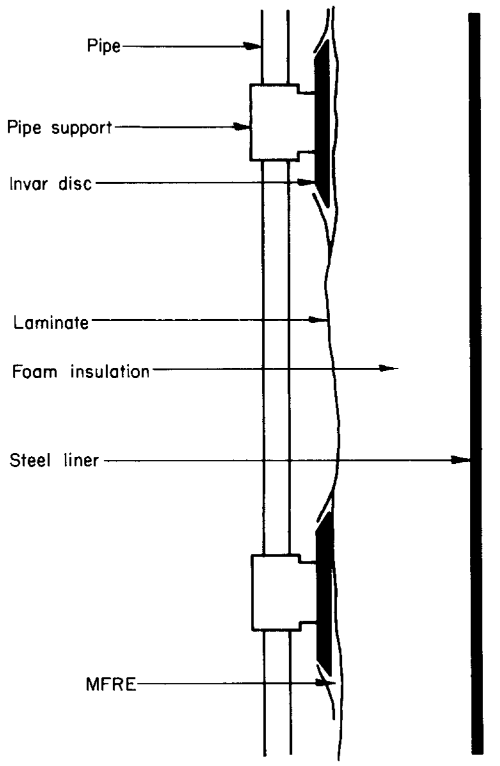

Figure 3 Suggested means of fixing a pipe onto the internal insulation on the wall of an LNG tank

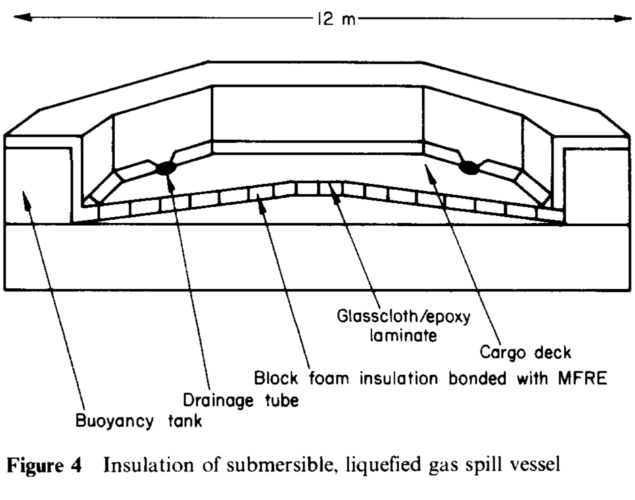

Figure 4 Insulation of submersible, liquefied gas spill vessel

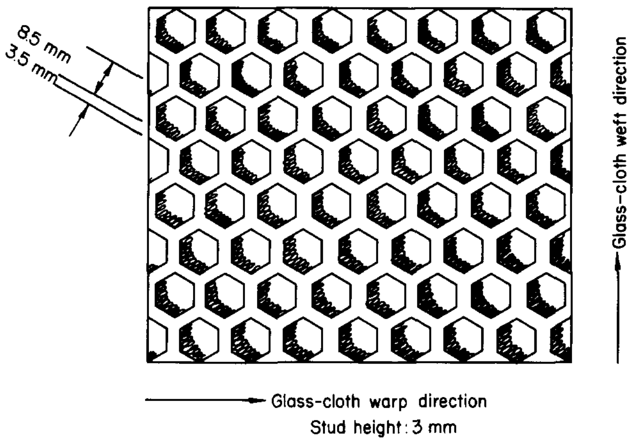

Figure 5 Configuration of MFRE studs in channelled laminate

the MFRE performed well in contact with the liquefied gases.

A version of MFRE has been used in the production of a channelled laminate that was designed to be part of a continuous leak detection facility for an LNG internal insulation system[9]. The laminate consisted of two glass-cloth layers separated by hexagonal studs moulded from MFRE. The laminate therefore had an interlinked network of passages through which a purge gas could circulate and carry any methane to a remote detector.

Figure 5 shows the configuration of the studs. The individual studs were formed by filling a silicone rubber mould with MFRE. A layer of glasscloth laid into the wet MFRE provided a flexible backing when the MFRE had cured. The backing cloth was impregnated with resin to fix the laminatè in position and a similar cloth was laid, *in-situ*, to form the closing layer.

Finally, the use of MFRE as a component of an insulation system[10] has been further explored in the construction of a test tank consisting of foam blocks bonded together with MFRE (see *Figure 6*). This mode of construction reduces the thermal stress developed in the bulk of the MFRE and limits the cold regions essentially to line contact at the edges of the blocks. The particular tank illustrated has experienced many shock-cooling cycles with liquid nitrogen and has not suffered any ill-effects.

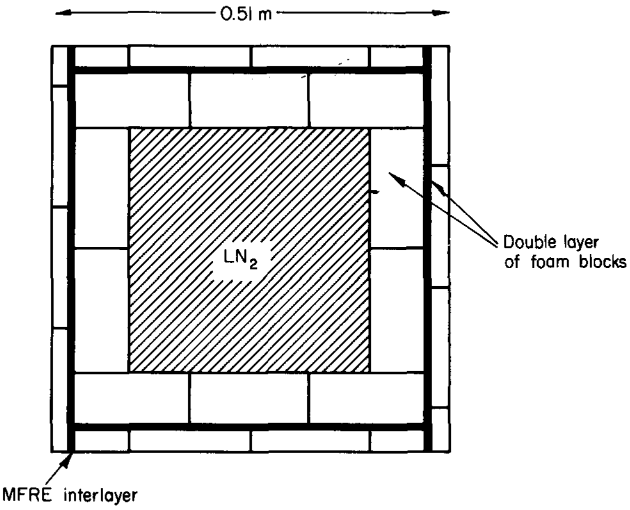

Figure 6 Test tank constructed of foam blocks and MFRE

CONCLUSIONS

A composite that is resistant to fracture at low temperatures has been formulated on the basis of fracture mechanics considerations using a flexibilized epoxy resin and milled glass fibres.

It has been used successfully as an adhesive in thick sections, which is contrary to the normal concept of an adhesive layer. It has also been used as a structural component, in the role of an adhesive and a moulding compound, in insulation systems that operate in direct contact with the cryogen.

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