would produce complications due to the simultaneously competing reactions (i.e. mullite formation and β' formation) which occur, and to the avaialbility of ammonia at a given reaction site. Thus, a technique which ensures continuous contact of ammonia with all the powder particles such as a fluidized bed would be more appropriate.

Associated with this problem in the thermal decomposition of ammonia, which depends on flow rate and surface area of furnace refractories. At 1400° C substantial decomposition occurs and it is possible that scaling up in the manner suggested would require ammonia flow rates which could not be obtained experimentally.

(2) The kaolin used in the work contains a number of impurities (see Table I). Whether these have any effect on the reaction rate or on the reaction product has yet to be determined. No evidence of any second phase resulting from these impurities has been detected in the reaction products. This, however, does not confirm solid solution of the impurities in the β' phase as the impurity levels are not high enough to be detected by the X-ray and infra-red techniques employed.

(3) One of the most important questions is whether the powders produced by this method will sinter at high temperatures to produce a high density product. No meaningful results on sintering can be obtained until much larger quantities of powder can be produced.

A further programme of work is now in progress with a view to resolving these questions.

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Time-dependent fracture in a unidirectional glass fibre-reinforced epoxy material

The time-dependent fracture behaviour of fibre-reinforced epoxy composites is expected to depend on two factors. The first is the viscoelastic nature of the matrix, and the second is the occurrence of unique fracture processes (namely, debonding and pull-out) typical of the composite system. It is thought that of these two factors the effect of the second is dominant, since fracture in composites is goverened by those processes whose existence is attributed to the composite system, while the normal processes taking place within the individual components are less pronounced.

Results reported in the literature on the time-dependent fracture of fibre-reinforced resins include measurements of the fracture surface energy (γ_I) and the work of fracture (γ_F). For 15% randomly aligned glass fibre composites tested at cross-head speeds ranging from 10^{-7} to 10^{-4} m sec^{-1}, the work of fracture was found to be strain-rate dependent, while the fracture surface energy was time-independent [1]. An increase in γ_F with increasing loading rate in the range 10^{-6} to 1 m sec^{-1} for carbon fibre–epoxy composites is also reported in [2]. Investigation of the dynamic fracture behaviour of 0°/90° carbon fibre–epoxy composites in [3] shows that the crack-initiation energy is essentially independent of temperature and strain-rate, while the fracture propagation energy decreases as strain-rate and temperature increase. The pull-out lengths

of 3% silica fibre-reinforced epoxies are reported by Arridge [4] to decrease as the loading rate increases from 8.5×10^{-7} m sec^{-1} to 8.5×10^{-3} m sec^{-1}. Finally, in a composite system with a more brittle matrix, i.e. carbon fibre-reinforced glass, the work of fracture and the fibre pull-out length are decreased as the rate of loading is increased [5].

It was felt that the data in the literature was inconclusive and could not completely explain the effect of time to fracture on mechanisms such as debonding and pull-out. This was attempted in the present study where we examined the effect of the strain-rate on the values of γ_I and γ_F in longitudinal and transverse fracture of unidirectional glass-epoxy composites over a wide range of fibre volume fraction (V_f). Composites were prepared and tested as described in [6]. The properties measured were γ_I, γ_F, the ultimate strength (σ_F), and Young's modulus (E). Values of the effective crack length (c) were calculated by the method described by Marom [7].

Table I presents the results for the longitudinal testing, and Figs. 1 and 2 demonstrate the trends of the results as functions of the cross-head speed for composites of $V_f = 0.39$. It is seen that E and c are rate independent, while σ_F, γ_I and γ_F increase with increasing strain-rate. The trend of γ_F is in agreement with previous observations which relate the increase in γ_F to the time dependence of the parameter τ_i' defined as the fibre–matrix frictional interfacial shear stress [1, 2, 8]. In these previous studies it is essentially claimed that γ_F, which is determined by the pull-out energy (γ_{po}), obeys

TABLE I The effect of the variation of the cross-head speed on the longitudinal strenth, modulus, fracture energies, and effective crack length

	Cross-head speed (cm min^{-1})			
	0.005	0.1	0.5	5
$V_f = 25\%$				
σ_F(GN m^{-2})	0.33	0.32	0.35	0.32
E(GN m^{-2})	11.5	10.8	11.6	9.7
γ_I(kJ m^{-2})	4.7	6.8	6.2	8.5
γ_F(kJ m^{-2})	12.2	16.8	19.7	24.7
c(μm)	294	449	344	499
$V_f = 39\%$				
σ_F(GN m^{-2})	0.45	0.54	0.54	0.57
E(GN m^{-2})	19.5	20.5	21.5	19.9
γ_I(kJ m^{-2})	13.0	17.3	17.6	20.2
γ_F(kJ m^{-2})	30.4	39.4	46.2	54.7
c(μm)	801	748	800	767
$V_f = 43\%$				
σ_F(GN m^{-2})	0.54	0.54	0.59	0.64
E(GN m^{-2})	21.6	21.1	22.6	23.2
γ_I(kJ m^{-2})	15.0	17.8	18.5	18.8
γ_F(kJ m^{-2})	31.0	37.4	42.2	47.2
c(μm)	709	820	742	667
$V_f = 63\%$				
σ_F(GN m^{-2})	0.64	0.70	0.74	0.77
E(GN m^{-2})	33.4	32.9	32.6	33.4
γ_I(kJ m^{-2})	14.0	17.5	22.4	25.1
γ_F(kJ m^{-2})	61.3	86.1	86.4	104.8
c(μm)	724	736	835	878

the relationship

$$\gamma_F = \gamma_{po} = V_f \sigma_f l_c/24 = V_f \tau_i' l_c^2/12d \quad (1)$$

where σ_f, d and l_c are the ultimate strength, diameter, and critical length of the fibre, respectively. It is then stated that τ_i' is time-dependent because of the viscoelastic nature of the matrix

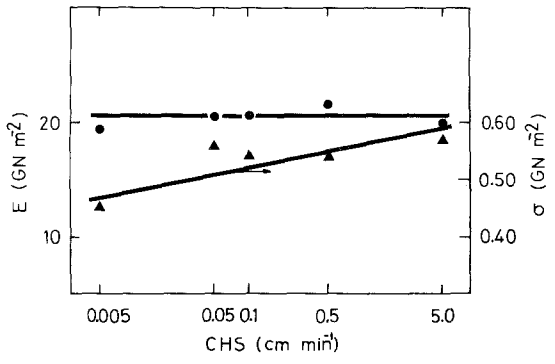

Figure 1 Values of the longitudinal modulus and ultimate strength as functions of the cross-head speed (CHS). The results at 0.05 cm min^{-1} are taken from [6], and $V_f = 0.39\%$.

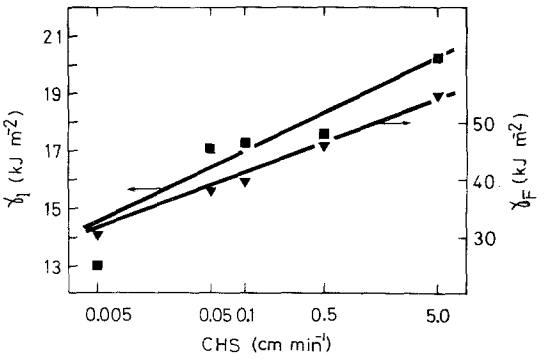

Figure 2 Values of the longitudinal fracture surface energy and work of fracture as functions of the cross-head speed (CHS). The results at 0.05 cm min^{-1} are taken from [6], and $V_f = 0.39\%$.

and that τ_i' will increase with the strain-rate [1, 2]. However, it seems to us that if τ_i' is time-dependent, then τ_i, the interfacial shear stress, will also be so. Thus l_c, which is determined by $\tau_i (l_c = \sigma_f d/2\tau_i)$, will be time-dependent, and Equation 1 cannot, therefore, be used for explaining the time-dependence of γ_F. Moreover, since τ_i' is really the interfacial shear stress after the debonding, it can only be marginally affected by the viscoelastic nature of the matrix. We believe that γ_{po} can be more meaningfully expressed by Equation 2 as follows [6]:

$$\gamma_{po} = V_f \sigma_f^2 d/48\tau_i'. \quad (2)$$

We also think that τ_i' may simply be considered as the fibre–matrix friction stress, and thus it depends on the coefficient of sliding friction, itself being a decreasing function of the velocity [9]. Since we did not observe a significant change in the pull-out length as a function of the cross-head speed, and also since the calculated value of c corresponding to the diameter of the debonding zone [7] is rate-independent, it is maintained that Arridge's [4] observations are not applicable to practical composites of high fibre contents. Furthermore, the observation of the time-dependence of the pull-out length in the carbon fibre-reinforced glass composites [5] can be attributed to the fact that in this system the glass matrix is more brittle than the fibres. A decrease in the mean pull-out length $(\bar{x})$ with increasing strain-rate is expected to result in a more brittle mode of fracture, and hence in lower γ_F values. This result which contradicts the present case as well as other experimental findings [1, 2, 8] can be seen clearly by substituting $l_c = 4\bar{x}$ [6] in the relationship $\gamma_{po} = V_f \sigma_f l_c/24$.

The value of γ_I in longitudinal fracture is determined by the surfaces formation mechanism which includes debonding [6]. With c and E being independent of the strain-rate, it seems (Table I) that the increase in γ_I with the strain-rate corresponds with the increase in σ_F according to the Griffith equation $(\gamma_I \propto \sigma_F^2)$. Since σ_F of either glass or plastics is expected to increase with the strain-rate [10], γ_I is also expected to increase concomitantly. Thus despite this increase in γ_I it is thought that the debonding mechanism which partly determines γ_I is not time-dependent.

Table II presents the results of the transverse case. Here γ_F is the only property which exhibits a clearly consistent increase with the strain-rate, although γ_I also seems to behave similarly; c seems to be rate independent. Earlier investigations of transverse fracture in such composites pointed out the crucial dependence of γ_F on the fracture of misaligned fibres [11, 12]. It is thus maintained that the transverse γ_F case is analogous to the longitudinal one. Also, the value of γ_I in transverse fracture is given by a "rule of mixtures" [11], and therefore the time-dependence of γ_I is again attributed to this dependence of σ_F.

TABLE II The effect of the variation of the cross-head speed on the transverse strength, modulus, fracture energies, and effective crack length

	Cross-head speed (cm min^{-1})		
	0.005	0.5	5
$V_f = 22\%$			
σ_F (MN m^{-2})	33.4	39.1	31.7
E (GN m^{-2})	3.0	3.2	2.7
γ_I (kJ m^{-2})	0.21	0.21	0.35
γ_F (kJ m^{-2})	0.20	0.36	0.45
c (μm)	326	254	579
$V_f = 39\%$			
σ_F (MN m^{-2})	30.0	32.0	28.3
E (GN m^{-2})	4.3	4.7	3.4
γ_I (kJ m^{-2})	0.12	0.12	0.16
γ_F (kJ m^{-2})	0.22	0.27	0.45
c (μm)	356	313	423
$V_f = 43\%$			
σ_F (MN m^{-2})	27.8	31.8	24.5
E (GN m^{-2})	3.7	4.5	3.3
γ_I (kJ m^{-2})	0.097	0.099	0.088
γ_F (kJ m^{-2})	0.15	0.21	0.30
c (μm)	273	258	281

It is concluded from our work on unidirectional glass fibre-reinforced composite materials that whereas the pull-out mechanism is time-dependent, the surfaces formation mechanism which includes debonding is not. Since σ_F and γ_I are related by the Griffith equation, the strain-rate dependence of γ_I in both the longitudinal and transverse configurations is determined by the time-dependence of σ_F.

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Structure of a sea urchin tooth

Markel and Gorny in 1973 pointed out [1] the remarkably similar appearance of the central region of a sea urchin tooth and a glass fibre-reinforced plastic. We thought it might be of interest to materials scientists to describe this structure briefly in a journal more accessible to them.

The common British sea urchin *Psammechinus miliaris* feeds on plant material. It has five ever-growing teeth with which it scrapes and triturates its food. The major part of the tooth is like the rest of the sea urchin's skeleton, being made of substantial crystals of calcite which, because of the influence of the living tissues surrounding them, do not look like crystals but have smoothly rounded outlines and are pierced by a series of interconnected holes.

The central region is different. Its appearance is shown in Fig. 1 and 2. The fibres are single crystals of calcite; the matrix is probably amorphous calcium carbonate. The aspect ratio of the fibres is extremely large. Indeed, since the fibres are 1 mm or more in length and about 6 μm in diameter, they can be considered to be effectively continuous. Two other features of interest can be seen in Fig. 2: the packing of the fibres is very regular, and their volume fraction is high, about 55% in the part of the tooth shown here. The central region

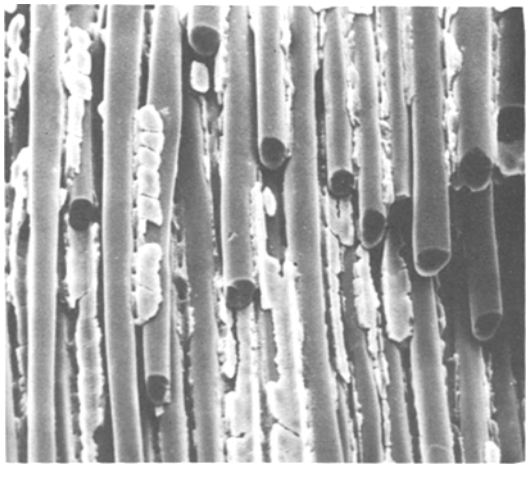

Figure 1 Scanning electron micrograph of the central region of the tooth of *Psammechinus miliaris.* The tooth was fractured and then vibrated in an ultrasonic bath for 2 min. The fibres are about 6 μm in diameter.

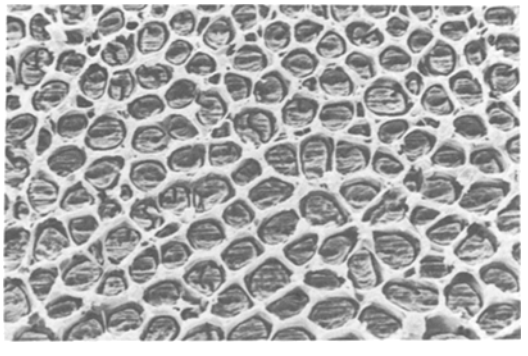

Figure 2 Scanning electron micrograph of the central region of the tooth of *Psammechinus miliaris.* The tooth was embedded in resin, ground down to a plane normal to the long axis of the fibres, polished and etched briefly in dilute hydrochloric acid. The mean diameter of the fibres is about 6 μm. Note the parallel lines on the etched surfaces of the fibres. These show that the fibres have all essentially the same crystallographic orientation.