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Article in *International Journal of Materials Engineering Innovation* · April 2011

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The conch shell as a model for tougher composites

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Abstract: The conch shell is 95% by volume CaCO_3 (chalk), yet its toughness is 10^3 times greater than that of monolithic CaCO_3 . In this review paper we look at how this increase in toughness is achieved and what lessons can be learnt for designing new tough composites. Essentially, we find that the CaCO_3 is finely divided into single crystals whose relevant dimensions are below the Griffith flaw size for the anticipated stresses; thus upon failure intergranular cracking dominates. Furthermore, failure is encouraged to proceed in a controlled way, which frustrates crack growth and maximises crack surface area. This strategy of maximising damage can only be successful in combination with self-healing properties. Examples are given of synthetic analogues, so-called biomimetic materials.

Keywords: nacre; Griffith flaw; self-healing composite; biomimetic; light-weight armour.

Reference to this paper should be made as follows: Williamson, D.M. and Proud, W.G. (2011) 'The conch shell as a model for tougher composites', *Int. J. Materials Engineering Innovation*, Vol. 2, No. 2, pp.149–164.

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This paper is a revised and expanded version of a paper entitled 'The Conch shell as a model for tougher composites' presented at 'LWAG 2009 Conference on Security and Use of Innovative Technologies against Terrorism', Aveiro, Portugal, 18–19 May 2009.

1 Brief introduction to classical fracture

Before we consider what we mean by toughness, it is useful to consider some key results from the field of fracture mechanics.

There are two seemingly different approaches to fracture mechanics, which can be shown to be mathematically equivalent; stress- and energy-based criteria for failure (discussed in following sub-sections).

1.1 The stress-based approach

The first approach to be considered was the stress intensity approach developed by Inglis (1913), who determined that cracks, as the limiting case of sharp ellipses, and sharp corners, weaken a plate of material by magnifying remotely applied stresses to the levels required for bond rupture.

Within a plate, consider an elliptical hole of major axis $2c$ and minor axis $2b$, such that the major axis lies perpendicular to a remote tensile stress σ_L .

In the Inglis analysis the remote tensile stress is magnified by the sharp tips of the ellipse by an amount

$$\sigma(\pm C, 0) = \sigma_L (1 + 2c/b), \quad (1)$$

which in terms of the radius of curvature $\rho = b^2/c$ is

$$\sigma(\pm C, 0) = \sigma_L (1 + 2(c/\rho)^{1/2}). \quad (2)$$

When $b \ll c$ then equation (2) reduces to the approximation

$$\sigma(\pm C, 0) \approx 2\sigma_L (c/\rho)^{1/2}. \quad (3)$$

From equation (1) we conclude that circular hole will magnify a remote stress in ideally brittle materials by a factor of three. Elliptical holes magnify the stresses at either end of their major axes to a greater extent; when the ratio of major to minor axis is equal to 100, the tensile stress is raised 200 times. When the ratio is 1000, the stress is raised 2000 times. Inglis claimed that: “*the ellipse in this latter case would appear as a fine straight crack, and a very small pull applied to the plate the across the crack would set up a tension at the ends sufficient to start a tear in the material. The increase in the length due to the tear exaggerates the stress yet further and the crack continues to spread in the manner characteristic of cracks*”.

Inglis concluded that the dominant cause of stress magnification was not so much the length of the ellipse, but its sharp tip.¹ As such, equation (3) can be used to estimate the stress concentration in many scenarios, where c and ρ represent a characteristic length and radius of curvature.

The Inglis description, whilst doubtlessly insightful, is a mathematical one, of single macroscopic cracks in an idealised elastic material. Whilst his ideas did strongly influence ship design,² it was Griffith (1920) who built upon these ideas, and suggested that the reason real materials did not achieve their theoretical strengths was because of the inherent presence of flaws, each of which magnifies the applied stress in a manner described by the Inglis analysis, leading to premature failure. Later studies showed that flaws are indeed responsible, and that their size populations are governed by statistical functions, e.g. the Weibull distribution (Weibull, 1951). Griffith pointed out that the effective strength of technical materials might be increased many tens of times if these flaws could be eliminated.

1.2 The energy-based approach

Importantly, Griffith also invoked the theorem of minimum energy to describe crack propagation. He stated that: “*the equilibrium state of an elastic solid body, deformed by specified surface forces, is such that the potential energy of the whole system is a minimum. The new criterion of rupture is obtained by adding to this theorem the statement that the equilibrium position, if equilibrium is possible, must be one in which rupture of the solid has occurred, if the system can pass from the unbroken to the broken condition by a process involving a continuous decrease in potential energy*”. Or else, in slightly less precise terms, a stressed body will relieve itself of stored elastic energy by creating new surface energy, if it may do so without increasing its overall potential energy.

However in relieving itself of strain-energy, a stressed body below its elastic limit may not simply spontaneously rupture to create new surface where there was none before. Griffith pointed out that to do so would actually increase the potential energy, since work must be done against those attractive forces which act over a small distance, that Griffith described as the ‘*radius of molecular attraction*’, to bind the molecules together. In general the surfaces of a spontaneously formed rupture would not be at a distance greater than the radius of molecular attraction, and the process would not meet the criterion of one involving a continuous decrease in potential energy. An important exception to the above statement is the situation involving the presence of a pre-existing crack, or flaw, within a body whose width is already greater than the radius of molecular attraction. In such a scenario only the tips of the crack are subject to the molecular attractions, and moreover being small, the increase in potential energy associated with driving them forward when the crack propagates is negligible.³ In such a scenario the crack may advance under a state of equilibrium, or else such that the total potential energy is diminished. Or else, once again in slightly less precise terms, an elastically loaded body cannot spontaneously rupture to reduce its potential energy, but a pre-existing flaw or crack may extend under equilibrium conditions, or else act to diminish the overall potential energy by converting stored strain energy into new surface energy.

If we let the U represent the totality of the stored energy of the system, composed of the sum of the work done by applied loads in causing global displacement W_L (which acts to reduce the potential energy), the strain energy U_E and the surface energy U_S , then

$$U = -W_L + U_E + U_S. \quad (4)$$

If c is the length of the crack, then the mathematical expression for the condition of crack advance as described above is given by

$$dU/dc = 0, \quad (5)$$

which is the famous ‘Griffith energy balance’ equation.

It also follows that if equation (5) is satisfied, the strain energy U_E is turned into new surface energy γ :

$$U_E = 2c \gamma. \quad (6)$$

Equation (6) was experimentally verified by Griffith in his 1920 paper by comparing the computed fracture surface energy of glass to that of the surface energy computed by more conventional means, and achieving order of magnitude equality.

To calculate the fracture surface energy, Griffith imagined the scenario of a flaw in a plate, exposed to a remote constant stress σ_L . He then used the Inglis analysis to deduce the strain energy density in the vicinity of the crack tip:

$$U_E = \pi c^2 \sigma_L^2 / E \text{ (plane stress)}. \quad (7)$$

Making use of the fact $W_L = 2U_E$ for such a system, and that $U_S = 4c\gamma$, equation (4) may be written specifically as

$$U = -\pi c^2 \sigma_L^2 / E + 4c\gamma, \quad (8)$$

for which the application of condition (5) allows us to deduce that the critical condition for fracture is

$$\sigma_L = (2E\gamma/\pi c)^{1/2}, \quad (9)$$

which is the famous ‘Griffith flaw’ equation for a 2D plate.⁴ Here for the first time was insight into why large flaws are more detrimental than small ones, an observed phenomenon which had hitherto gone unexplained.

Equation (9) also reveals why materials are weaker than their theoretical strengths. Orowan (1948) pointed out that, on the basis of simple Hookian behaviour up to failure, that we might expect the strengths of perfect materials to be the order of $(2E\gamma/a)^{1/2}$, where a is the inter-atomic spacing. The ratio between Orowan and Griffith strengths is $(c/a)^{1/2}$, which, if we take $c \sim 1 \mu\text{m}$ and $a \sim 1 \text{ \AA}$, is equal to 100; which is to say materials with even micron sized flaws are approximately 100 times weaker than their theoretical strengths.

The equilibrium condition is an inherently unstable one, since once the applied stress exceeds the critical level given by equation (9), the crack is free to propagate without further hindrance. In an extension to the Griffith analysis outlined by Mott (1948), the excess released energy is manifest as kinetic energy. Mott suggested that, in the case of a brittle material, the crack speed will tend to a value of the order of the velocity of sound in the material.⁵

If we let G be the rate of loss of strain energy with crack length

$$G = -\partial U_E / \partial c, \quad (10)$$

then it is clear from equation (6) that the critical energy release rate⁶ G_C is given by

$$G_C = -2\gamma. \quad (11)$$

Equation (11) is simply telling us that the critical condition for crack initiation and propagation is that as the crack extends, sufficient energy must be released to make new surface.

Note that G_C is a material constant, and represents a useful fracture toughness parameter; a material with a high G_C value is more resilient to fracture than a material with a low G_C value.

The Griffith description is one of a reversible process. In general, however, the stresses at the crack-tip will be sufficiently great so as to cause local plastic deformation. As work must be done when the material flows, this represents a dissipative process which is not accounted for in equation (11).

If the plastic zone is small, i.e. diamond fracture, the effect may be neglected, but for many materials the plastic zone cannot be ignored, and nor can the dissipated energy. For such materials both Irwin and Orowan independently extended the Griffith analysis and wrote the more general equation

$$G_C = -2\Gamma, \quad (12)$$

where Γ represents the work of fracture, including dissipative processes, and which reduces to γ for an ideally brittle solid. Thus equation (12) allows us to discriminate between brittle ($\Gamma \approx \gamma$) and tough materials ($\Gamma \gg \gamma$).

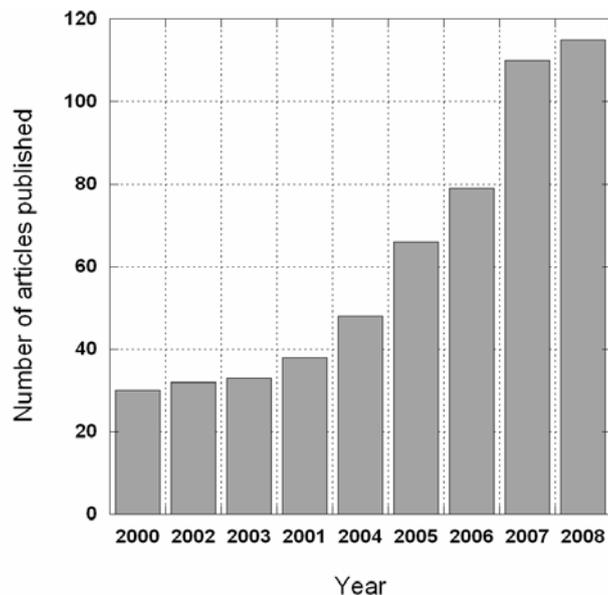
In this review we will be look at how shelled molluscs have adopted methods to maximise this inequality.

2 Why are conch shells interesting?

Conch shells, and the shells of other molluscs, are interesting because they are of the order of 95% by volume CaCO_3 (chalk), yet they can 10^3 times tougher greater than that of monolithic CaCO_3 , that is $\Gamma_{\text{shell}} \approx \gamma_{\text{chalk}} \times 10^3$. The remaining 5% is organic, mostly proteinaceous matter.

Thus they would appear to be good models for the design of high performance composites. And have been heralded as such: Luz and Mano (2009), Munch et al. (2008a, 2008b), Ballarini and Heuer (2007), Darder et al. (2007), Podsiadlo et al. (2007), Mayer (2006, 2005), Mayer and Sarikaya (2002); and this list is certainly not exhaustive – Figure 1 is a graph of data from the ISI database showing the number of nacre-related articles published each year.

Figure 1 Number of nacre related articles published per year (data from ISI database)



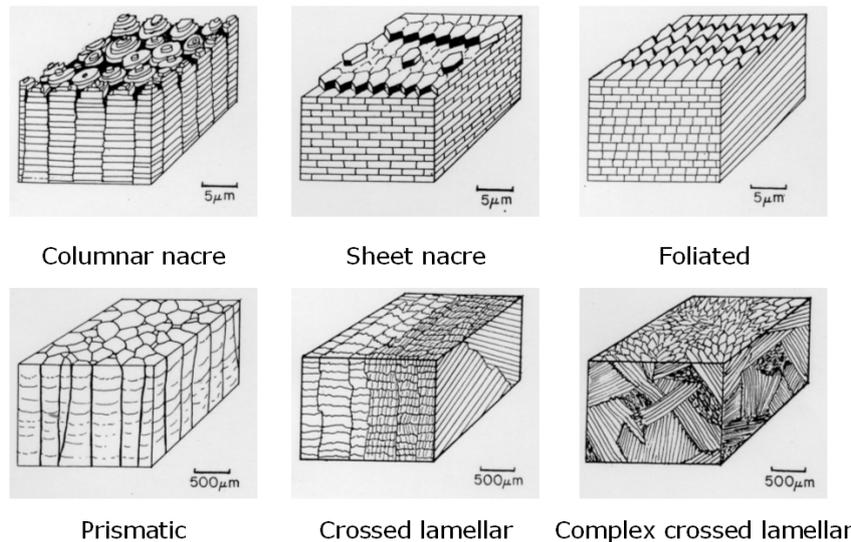
As we shall see molluscan shells are able to achieve their advantage through having evolved a complex architecture on the micro/nano-scale.

Some of the features are comparable to the wavelength of light; this gives the ability to reflect and refract light, and it is this attribute which gives iridescence to nacre, or as it is more commonly known mother-of-pearl.

3 The nature of nacre

Some molluscan architectures are shown in Figure 2, reproduced from Currey and Taylor (1974). These authors pointed out that the crossed lamellar structure is evolutionarily more advanced than the more primitive nacre, yet nacre has better mechanical performance. The answer to this apparent contradiction may be that the crossed lamellar structure is easier to produce, and on balance, this advantage may outweigh the cost of a weaker shell.

Figure 2 Molluscan shell architectures (reproduced from Currey and Taylor, 1974)

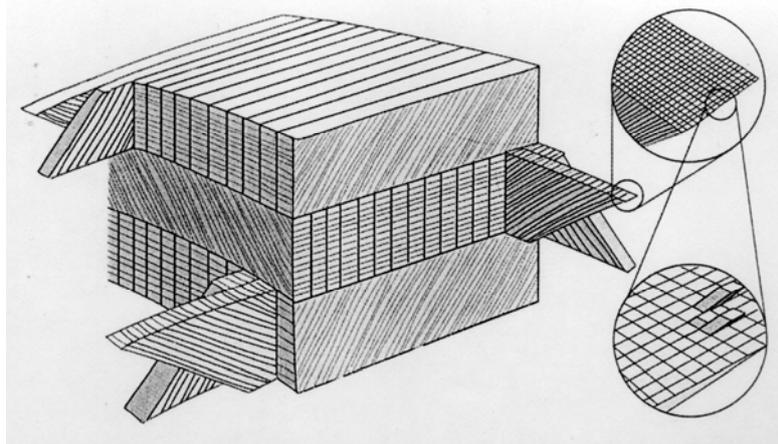


The queen conch (*Strombus gigas*) utilises the crossed lamellar structure. This is given in more detail by [Ballarini and Heuer \(2007\)](#), shown in Figure 3. We see that the structure has a hierarchy of length scales. The coarsest is represented by three layers designated inner, middle and outer in relation to the animal's body. Each layer is made up of smaller first-order lamellar beams, each of which are in turn composed of even smaller second order lamellar beams. A key observation is that at each of these length scales the construction of the structure is cross-ply in nature.

At the smallest length scale are the basic building blocks of the structure: single crystals of aragonite (the orthorhombic polymorph of CaCO_3). Which, according to [Su et al. \(2004\)](#), are of order 60–130 nm thick and 100–380 nm wide, and can be many microns

long. Each crystal is enveloped by a proteinaceous layer 5–10 nm thick. It is these proteins which are thought to dictate CaCO_3 nucleation, polymorph and growth direction, Thomson et al. (2000), Metzler et al. (2007).

Figure 3 The crossed lamellar structure of the conch is more detail (reproduced from Ballarini and Heuer, 2007)



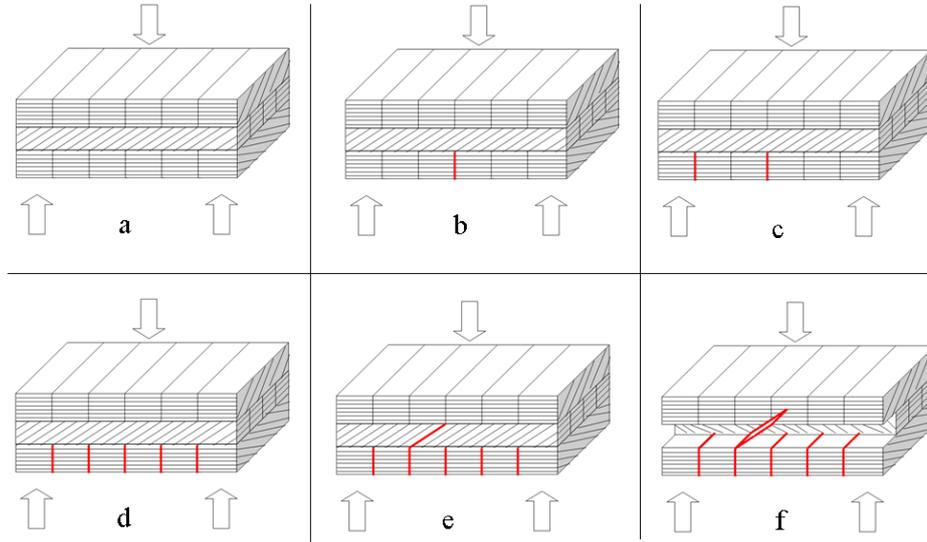
It is the width and thickness of the aragonite crystals which are important from a load bearing perspective. Of critical note is the following, for the global stresses at which these shells fail, equation (9) tells us that these dimensions are below the Griffith flaw size.⁷ Thus they themselves are unlikely to fracture, and this is borne out by experiment, which shows predominantly intergranular failure; Currey (1977).

4 How to win at failing

Failure is observed to occur as debonding of the proteinaceous layer from the aragonite or else as a cohesive failure of the proteinaceous layer, in either case passing around the periphery of the aragonite crystals. In general, toughness can be increased by maximising true surface area generated per nominal fracture plane. In the conch case this is achieved by virtue of the cross-ply construction.

Apparently, the major threat to conches comes from the mouths of turtles and the claws of crabs, and the bending moments that they can introduce; the basic failure behaviour of the crossed lamellar structure in bending was documented by Currey and Kohn (1976), and can be found in more detail in later articles, e.g. Kamat et al. (2004). In a three point bending scenario cracks are observed to progress in the manner illustrated in Figure 4. Cracks are initiated at the bottom layer between lamella (b), but are arrested at the interface with the middle layer. The crack density increases (c) → (d). A crack propagates through an inner layer lamella (e), note the crack plane is orientated 90° to adjacent lamella of the same layer (f).

Figure 4 How failure is observed to progress in a three point bending scenario; (a) initial crack in bottom layer; (b) crack density in inner layer increases; (c) → (d) crack through inner layer lamella; (e) note this is 90° to adjacent lamella; (f) crack can now propagate into top layer, but will result in crack bridging (see online version for colours)



Ideally, this will result in alternate cracking, Figure 5a, and bridging of the inner layer lamella, Figure 5b. Second-order, in-plane, crack-bridging can also be observed, Figure 6.

Figure 5 (a-left) Alternate cracking of middle-layer lamella (reproduced from Ballarini and Heuer, 2007); (b-right) a good illustration of the primary crack-bridging phenomena that results (reproduced from Kamat et al., 2004)

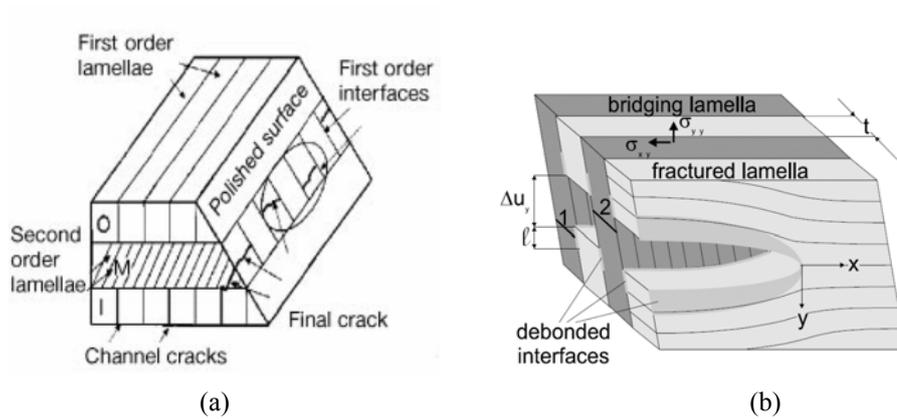
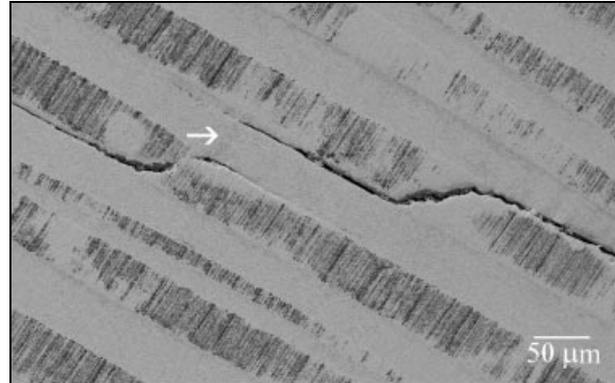


Figure 6 Secondary crack bridging (reproduced from Kamat et al., 2000)

The bridging lamella pin the would-be crack faces together. The pull-out and differential sliding of neighbouring aragonite crystals associate with further loading is performed against a background of a viscous matrix which itself will expend energy when sheared. In fact many authors suggest it is the transfer of strain energy to the viscous matrix which expends the most energy.

A potential weakness of materials optimised against threats from a specific direction is built-in anisotropy. Indeed, Currey (1977) showed an order of magnitude difference in the work of fracture across the grain compared to along it.

5 Measuring up

Jackson and Vincent (1990) list properties normalised by the specific gravity of nacre and some other common materials. These authors point out an ‘average’ overall performance, and state ‘clearly, if nacre does conceal an improvement in some mechanical properties over and above what is to be expected from density or volume fracture of filler alone then a much more careful comparison is needed to detect it’.

Table 1 Comparison of material properties (data from Jackson and Vincent, 1990). σ is flexural strength, E flexural Young’s modulus, R is work of fracture

Material	Specific gravity (ρ)	σ/ρ (MPa)	E/ρ (GPa)	R/ρ (kJ m ⁻²)
Oryx Horn	1.3	170	5	28
Femur bone	2.1	120	7	2
Wood	0.5	200	25	40
Glass	2.4	70	25	0.005
Mild steel	7.8	50	25	100
Aragonite	2.9	30	34	0.0002
Nacre	2.7	110	26	0.4
GFRP ($V_f=0.5$)	1.5	730	27	3

It is worth pointing out, as do [Menig et al. \(2001\)](#), that comparing nacre (and indeed other bio-materials) is very difficult. Some researchers go to pains to use fresh samples which have been kept in salt water, others use dusty dried up specimens from zoological collections. This is important because as [Jackson et al. \(1988\)](#) point out, water does have a significant effect, acting to plasticise the proteinaceous layer and increase its tenacity.

Similarly, very few researchers appear to discriminate between quasi-static and dynamic experiments, although [Menig et al. \(2001\)](#) did address just this issue, showing an approximately 50% increase in compressive strength in the dynamic case.

But it is the 10^3 increase in work of fracture that nacre possesses over aragonite which captures the attention most researchers. The question arises as to whether modern composites can achieve the same performance.

At this point is worth noting the attributes which make nacre and other molluscan shell materials desirable. The first, which is often overlooked, is the ability to self-heal. Clearly if the strategy of survival depends not upon resilience in the sense of emerging from an encounter unscathed, but rather on allowing damage to occur in a extensive yet controlled manner which maximises energy expenditure, it is crucial that self-healing can occur between encounters to prevent cumulative damage.

As we have seen, having filler particles less than the Griffith flaw size for the anticipated stress is key to tough material behaviour; this forces the cracks to follow the microstructural contours of the materials, which can be torturous, maximising the real surface area generated. Otherwise cracks will have a tendency to follow geometric paths of highest tension, and the crack surface area will be relatively small in comparison. This necessitates that the binder adhesion/cohesion should be the weakest link; but only just so if we want to maximise the overall strength.

The binding matrix itself should be viscoelastic such that it can dissipate energy when sheared. Ideally, the glass transition condition would be made to coincide with the anticipated environmental temperatures and strain rates. However, [Kamat et al. \(2004\)](#) reported a glass transition temperature of $+180^{\circ}\text{C}$, which would imply brittle behaviour at ambient temperatures; it may well be worth repeating these experiments to confirm this value.

A final point, which ties in with the last, is a high degree of perfection is required. Since imperfections such as voids are *the* classic Griffith flaw.

6 Laboratory analogues

This section of the paper is only meant as a brief introduction to the topics covered.

6.1 Self-healing composites

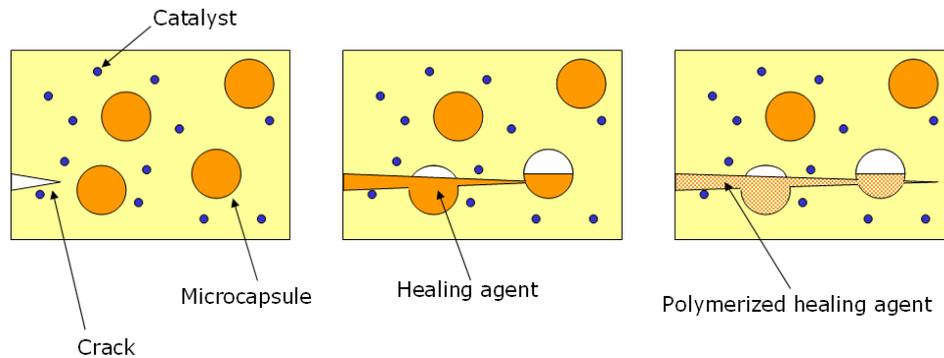
A good overview of self-healing in polymer-based concepts is given by Yuan et al. (2008). In it materials are classified as either intrinsically or extrinsically self-healing; the former are able to heal on their own, the latter use a pre-embedded healing agent.

Intrinsic self-healing can be either physical or chemically based. Physical self-healing occurs when thermoplastics are heated above their glass transition temperatures and slight pressure is applied. Under such conditions inter-diffusion of polymer chains can occur across the intimate crack surfaces, the degree of recovery can be quite respectable. Importantly

for armour applications some polymers can heal through melting caused by frictional heating, for example during ballistic penetration. Chemically based self-healing is based upon thermally reversible cross-linking behaviour; at temperatures above ambient the cross-linking is ‘undone’ and is restored upon cooling, this allows for healing if the crack faces are in intimate contact, Liu and Chen (2007).

Extrinsic self-healing polymers carry either enclosed tubes or capsules of healing agent. The concept is that a crack will break through capsules of polymer precursor, which will spread via capillary action through the crack and react with embedded catalyst in order to crosslink and heal the sample, Figure 7. In the example given by [White et al. \(2001\)](#), the authors claim 75% recovery of the original toughness.

Figure 7 Concept of a extrinsically self-healing polymer based on embedded microcapsules of healing agent (based on a figure from White et al., 2001). From left to right: microstructure with embedded catalyst and microcapsules of healing agent (polymer precursor), crack ruptures microcapsules and healing agent coats crack surfaces via capillary action, catalyst cross-links healing agent (see online version for colours)



6.2 Microstructured composites

A group at Lawrence Berkley National Laboratory has been pursuing a technique called ice-templating to form composite structures, taking bio-materials as their inspiration ([Deville et al., 2006](#); [Deville et al., 2007](#); [Munch 2008a](#); [Munch, 2008b](#)). In their latest publication (2008b) the fabrication process of ($\text{Al}_2\text{O}_3/\text{PMMA}$) composites is described thus; ceramic alumina powder suspensions in water are frozen using directional freezing. This creates a ceramic scaffold which is lamella like in structure. This can be further crushed and sintered to form a *nacre-like* ‘brick and mortar’ scaffold, Figure 8. The thicknesses of the layers are of order unit microns. The ice is then removed by sublimation and the remaining void infiltrated with PMMA.

Similar to nacre, the authors claim a greatly enhances fracture toughness over monolithic alumina, >300. A very important observation is that an unstructured homogeneous mixture of alumina particles dispersed in PMMA shows negligible increase in toughness; the advantage is strongly dependant on the architecture, Figure 9.

Figure 8 Structure of ice-templated materials. The scale bar in each is 100 μm (reproduced from Munch et al., 2008a, 2008b)

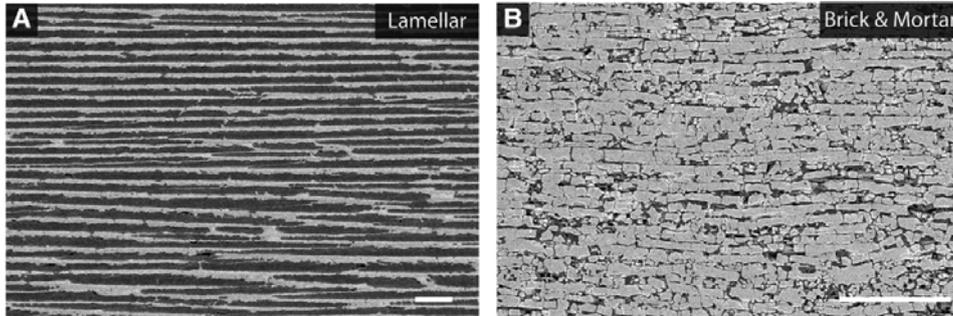
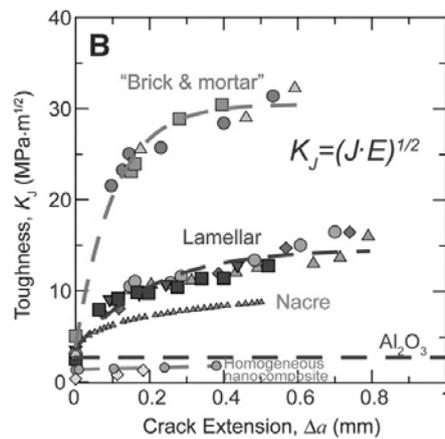


Figure 9 Crack resistance curves for ice-templated materials, nacre and a homogeneous dispersion of alumina in PMMA, note the latter show no advantage (reproduced from Munch et al., 2008a, 2008b)



6.3 Defect-free composites

Here we give the example of so-called Macro Defect Free cement (MDF-cement). An article by [Kendal et al. \(1983\)](#) makes clear the febleness of cement (compared to its theoretical strength) is due to the voids created when the water is removed.

The more water is used, the greater the porosity and the weaker the resultant material, which goes back to Feret's Law (1897). Since 1 cm^3 of Portland cement, on full hydration, converts to 2.2 cm^3 of hydrate, itself 28% porous, it follows for every 1 cm^3 of water used $\sim 0.5 \text{ cm}^3$ of porous volume is created.

The authors were able to show that the weakness could be reconciled by Griffith theory as applied to the pores resulting from the above process.

Large pores were removed by the addition of plasticisers, since when using them it was found that (a) less water was required in the first place, and (b) the resulting dough had its entrained air more readily squeezed out by application of external pressure. In doing so the strengths could be dramatically increased, Table 2.

Table 2 Improved properties of MDF cement compared with ordinary cement (reproduced from Kendal et al., 1983)

<i>Property</i>	<i>Ordinary cement</i>	<i>MDF cement</i>
Flex strength/MPa	10	40–150
Young modulus/GPa	20	35–50
Compressive strength/MPa	40	100–300
Fracture energy/J m ⁻²	20	40–200

In this case the strength limiting flaw size became correlated with the solid particle loading size. Adding sand grains of increasing size progressively dropped the strength, which went some way to confirming this hypothesis.

7 Summary and conclusions

Through controlling the architecture of composite materials it is possible to make them orders of magnitude tougher than their constituents. Molluscan shells are an excellent example of this in nature; nacre is often cited as a ‘gold standard’. The following attributes are deemed necessary:

- A high degree of architectural perfection is required; flaws must be smaller than the filler particles in order to prevent premature failure.
- The filler particles should be smaller than the Griffith flaw size for the anticipated stress regime; this forces cracking to be confined to either debonding the filler particles or else cohesive failure within the matrix.
- The filler particles must be arranged in such a way that as much true surface area is generated per nominal fracture plane as possible. Crack bridging by filler particles is desirable as this promotes shear strains in the matrix. In the crossed lamellar structure this is achieved by hierarchical cross-plying of lamella at multiple length scales. A limitation of materials which are optimised to such to meet a single threat is their anisotropic properties.
- The nature of the matrix should be viscoelastic, such that induced shear strains dissipate as much energy as possible. This could be achieved by tailoring the glass transition condition to coincide with the anticipated strain-rate/temperature regime. For a synthetic analogue polycarbonate would be a good off-the-shelf candidate material for ballistic conditions.
- If one accepts the philosophy of maximising damage, in a controlled way, so as to dissipate as much energy as possible, the ability to self-heal becomes very desirable to prevent cumulative damage occurring.
- Finally, it is important to treat these bio-materials as sources of inspiration, rather than prototypes to be replicated in exquisite detail. After all, if nature had access to materials like TiB₂, would seashells look the same as they do now?

Acknowledgements

Dr. Leslie Payne is foremost acknowledged for suggesting such an interesting title. AWE are thanked for their continued funding of the authors.

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Notes

- Note that absolute size does not enter in the description of stresses around ellipses; a small circular hole has just as detrimental an effect as a large one.
- Although is questionable as to how much attention was paid; the catastrophic failure of some of the subsequent US Liberty ships, due in part to stress concentrations caused by square hatches, could have been avoided if Inglis' results had been applied.
- In a 2D scenario this quantity is zero, but in general a crack or flaw is a 3D entity, and advance will necessitate an increase in the perimeter subject to the molecular attractions.

- 4 The corresponding 3D result was deduced by [Sack \(1946\)](#), and represents ~50% increase in the required critical stress: $\sigma_L = (\pi E \gamma / 2c)^{1/2}$.
- 5 This has since been proven not to be the upper bound it was once thought to be.
- 6 Note this is a spatial derivative, not a time derivative.
- 7 Using an aragonite surface energy of 0.58 J m^{-2} , modulus of 98.6 GPa (from [Jackson and Vincent, 1990](#)) (see Table 1), and a tensile failure stress of 75 MPa ([Currey and Taylor, 1974](#)) the critical flaw size is calculated to be $\sim 5 \mu\text{m}$.