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Comparison of nacre with other ceramic composites

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Mother-of-pearl, the highly filled ceramic composite of mollusc shell, is compared with other, less highly filled, artificial ceramics. Stiffness is fairly simply related to volume fraction of ceramic, but no model seems to be adequate to describe this relationship. Strength, stress-intensity factor and the work of fracture are also dependent on the ceramic content but in a much more complex manner. Nacre has the highest value for all these parameters.

1. Introduction

Mother-of-pearl, or nacre, from mollusc shells is a very unusual composite material. Despite containing 95% by volume $CaCO_3$ in the form of aragonite it can have a work of fracture of up to 3000 times that of pure aragonite [1]. This surprisingly high toughness was thought to be due entirely to the arrangement of the aragonite in staggered layers of interlocking platelets, each platelet being surrounded by the remaining 5% of proteinaceous matrix. Thus when a crack travels through nacre it has to pass around and not through the platelets, and so the much increased path length of the crack leads to an enhanced work of fracture.

More recent work [2, 3] has generally confirmed this view and has shown how the binding of the organic matrix to the surface of the platelets and plasticization of the matrix by water, together serve to augment the energy dissipated in pull-out. Nacre complies with the expectations of standard composite theory; for example, the Young's modulus is fairly accurately predicted by the Padawer–Beecher shear-lag model for platelet composites. This is of interest simply because the standard composite models can only rarely be applied at such extremely high volume fractions, where their validity is unknown.

In this paper we compare nacre with other materials. The first comparison is a very broad one showing how, in absolute terms and on a weight-for-weight basis, the mechanical properties of nacre compare with those of a wide range of other very different materials. In the second comparison the mechanical testing performed on nacre [13] is repeated on four synthetic composites of differing volume fraction of filler. In this way the sort of performance that can be expected from increasing the volume fraction of filler of synthetic particle composites can be readily appreciated. Nacre can be used to indicate the upper limit of performance of such a material.

2. Materials and methods

The flexural Young's modulus, E, flexural strength, σ_f, critical strain energy release rate, G_c, critical stress intensity factor, K_c, slow-propagation work of fracture, R, and filler volume fraction, V_f, have been measured (details of techniques have been described elsewhere [3]) for nacre from *Pinctada* and for four synthetic composites filled with ceramic particles – corian, asterite, occlusin and macro-defect-free (MDF) cement. Their constituents, particle sizes, densities and volume fractions are summarized in Table I. MDF cement is made by mixing the usual chemical ingredients together with a rheological aid which removes large pores, believed to be responsible for the weakness of normal cement. Thus the volume fraction of filler is increased and hence the mechanical performance is improved [4, 5]. The volume fraction is quoted as 85% [6] but this is in fact the volume fraction of all solids as opposed to pores. Consequently, the real volume fraction of ceramic filler will be slightly lower than this. Occlusin is a light-cured filling material for teeth [7]. The rather harsh mechanical environment of the mouth necessitates a high volume fraction of filler with little or no pores. This is achieved by means of a trimodal distribution of filler particles: the small particles fill in the interstices between the large ones. Asterite and corian [8, 9] are composites used to substitute for many indoor household ceramics (e.g. in washbasins). For the sake of reduced cost and ease of moulding, the volume fraction of ceramic filler in these materials is not very high and there are few pores as a result. The synthetic composites were assumed to be essentially isotropic, but for nacre the nomenclature of Currey [1] was used to describe the direction in

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TABLE I The chemical and physical composition of *Pinctada* nacre and the synthetic composites. Data not referred to by reference numbers were obtained by direct observation

	Constituents	Density ($kg\,m^{-3}$)	Volume fraction of filler	Particle size (μm)
Nacre	Aragonite platelets and organic matrix [1]	2.71	95 [1]	4 × 0.5
MDF cement	Calcium silicate, etc., plus polymer [6]	2.52	85 [6]	?
Occlusin	SiO_2, barium aluminoborosilicate plus polyurethane [7]	2.35	70 [7]	trimodal [7] 0.02, 2, 10
Asterite	β-crystobalite, SiO_2 and PMMA [8]	1.82	56 [8]	10
Corian	Al_2O_3 ($3H_2O$) [9] and PMMA	1.8	47 [9]	20

which the sample was tested or the crack propagated. These directions are "across", "along" or "between" the platelets. Some nacre was tested dry (stored at ambient temperature and humidity) and some was tested wet (having been soaked in distilled water for 3 wk). A further set of samples was desiccated by heating for 3 d at 110° C to remove all remaining water.

3. Results and discussion

3.1. Comparison with general values from the literature

When the specific mechanical properties of nacre are compared with those of some common engineering and biological materials from the literature (Table II) it is immediately apparent that nacre has only average performance overall. In strength, nacre is more or less normal for its given density, but it is only just superior to the other biological materials in specific modulus and is brittle compared with all except the purer ceramics such as glass. It is also inferior to anisotropic fibre-reinforced composites which possess only half the volume fraction of reinforcement. Clearly, if nacre does conceal an improvement in some mechanical properties over and above what is to be expected from density or volume fraction of filler alone then a much more careful comparison is needed to detect it.

3.2. Comparison with synthetic composites

The results derived in this study for the other ceramic composites (Tables III to VI) are in good agreement with previously published data [7–9]. While there are some slight influences of span-to-depth (S/d) ratio on strength and toughness the results are generally very consistent within any one material.

TABLE II Some specific mechanical properties of nacre and other materials

Material	Specific gravity	σ/ρ (MPa)	E/ρ (GPa)	R/ρ ($kJ\,m^{-2}$)	Reference
Oryx horn	1.3	170	5	28	[10]
Femur bone	2.1	120	7	2	[11]
Bulla bone	2.5	10	13	0.2	[11]
Cervus antler	1.9	100	4	7	[11]
Wood	0.5	200	25	40	[12]
Glass	2.4	70	25	0.005	[12]
Mild steel	7.8	50	25	100	[12]
Aragonite	2.9	30	34	0.0002	[2]
GFRP (V_f = 0.5)	1.5	730	27	3	[13]
Nylon 6,6	1.1	55	3	2	[14]
Nacre	2.7	110	26	0.4	[2]

TABLE III Young's modulus of nacre and synthetic composites

	S/d	Mean Young's modulus (GPa)	Standard deviation	Number of tests
Pinctada nacre				
Across, dry	20	73	9	35
Across, wet	20	64	8	35
Along, dry	35	70	11	19
Along, wet	35	60	10	18
MDF cement	30	45	0.9	10
Occlusin	10	20	1.1	9
Asterite	13	13	0.7	20
Corian	16	10	0.6	20

In Figs 1 to 4, volume fraction of filler is plotted against Young's modulus, flexural strength, G_c and K_c, respectively. It was not possible to cut out large enough specimens of aragonite for mechanical testing so the following data were taken from the literature to serve as limiting values for a 100% ceramic filler: Young's modulus 100 GPa [15], flexural strength 100 MPa [1], surface energy 0.23 J m^{-2} ([16] for calcite).

Normally it is not a wise procedure to plot two variables against each other whilst other variables are not being controlled. Here, the precise constituents, particle shapes and sizes, and the adhesion between ceramic and matrix are all presumably variable for the materials under consideration. Also, it might be justifiably argued that the comparison should be made with bone, antler or fibre-reinforced composites instead of with particulate composites which have no nett orientation of components. But the comparison should be seen as a pragmatic one, to see how nacre compares with some industrial synthetic composites. Also, more importantly, although we have no right to expect any correlation with volume fraction of filler,

TABLE IV *Pinctada* nacre and synthetic composites: flexural strength at different S/d ratios

	S/d	Mean flexural strength (MPa)	Standard deviation	Number of tests
Pinctada nacre				
Across, dry	16	289	33	5
	4	280	83	5
Across, wet	16	309	49	5
	4	252	30	5
Along, dry	4	322	22	5
Along, wet	4	275	48	5
MDF cement	10	155	11	10
	8	147	12	11
	6	153	11	10
	4	160	9	9
Occlusin	10	179	–	1
	4	172	37	5
Asterite	13	108	4	5
	8	116	18	7
	4	121	20	6
Corian	16	60	2	5
	8	63	3	10
	4	69	2	10

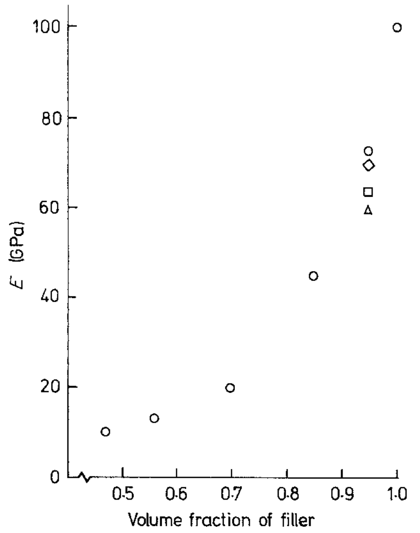

Figure 1 Mean Young's modulus plotted against volume fraction of filler for nacre, aragonite and synthetic composites. For all figures the materials can be identified at the following volume fractions: corian (0.47), asterite (0.56), occlusin (0.7), MDF cement (0.85), nacre (0.95) and aragonite (1.0). The different test conditions and orientation of nacre: (○) across, dry; (□) across, wet; (◇) along, dry; (△) along, wet. Error bars have been omitted for clarity.

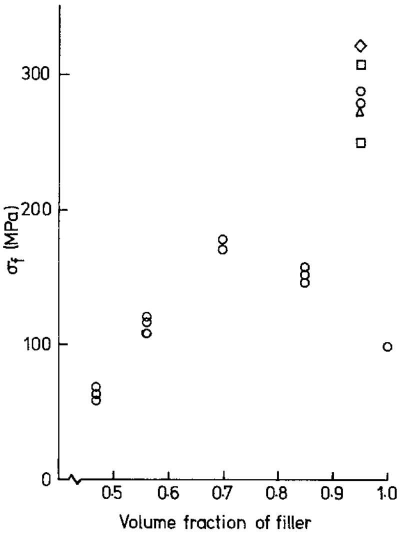

Figure 2 Mean flexural strength plotted against volume fraction of filler for nacre, aragonite and synthetic composites. Repeated points are for different S/d ratios. Other details as in Fig. 1.

the comparison does provide a useful check on the extent of its influence on mechanical properties. Obviously only a positive result would be interesting: a negative result (i.e. no correlation) would prove nothing, for this would imply that the effect of volume fraction was being masked by the greater effect of the other variables. But by having a platelet aspect ratio of only 8, nacre approximates more closely to a randomly filled, isotropic composite with particles of aspect ratio = 1 than it does to a fibre-reinforced composite with fibre aspect ratios in excess of 100. So it is fairer to compare nacre with materials like MDF cement and occlusin than with those such as bone and antler. Fig. 1 shows nacre to be the stiffest composite. It achieves this status by its high ceramic content and because the modulus is measured at low strains where interfacial properties are not important. The good correlation of the Young's modulus with volume fraction of filler shows that adhesion between particles and matrix, alignment of the particles, etc., are of minor importance. A similar non-linear increase of modulus with volume fraction of ceramic filler has already been observed for bone [17, 18] and for synthetic composites (e.g. [19, 20]).

The flexural strength of nacre (Fig. 2) is in agreement with a linear trend extrapolated from the first three synthetic composites (corian, asterite and occlusin) but is far in excess of what MDF cement and aragonite might lead us to believe is the expected strength. However, nacre is behaving as we would expect given its composition [2, 3]. How many other materials manage to achieve the necessary structural organization so as to realize the full theoretical strength? MDF cement and aragonite certainly do not! A high volume fraction

TABLE V *Pinctada* nacre and synthetic composites: three-point bend, unstable fracture toughness results, at different S/d ratios; x = mean, S.D. = standard deviation, n = number of tests

	S/d	G_c (J m^{-2})			K_c (MN m$^{-3/2}$)		
		x	S.D.	n	x	S.D.	n
Pinctada nacre							
Across, desiccated	4	264	138	9	2.9	0.5	9
Across, dry	16	352	130	14	4.6	0.8	14
	4	464	143	8	3.3	0.3	8
Across, wet	16	587	189	14	4.5	0.4	14
	4	1240	778	9	3.7	0.6	9
Along, dry	11	328	32	10	5.0	0.2	10
	4	439	142	9	3.7	0.5	9
Along, wet	4	788	252	7	5.0	0.9	7
Between, dry	4	–	–	–	2.1	0.3	15
MDF cement	10	198	31	11	3.8	0.2	11
	8	138	24	12	2.4	0.2	12
	6	241	80	12	2.5	0.2	12
	4	186	94	12	2.0	0.2	12
Occlusin	10	201	34	8	2.1	0.2	8
	4	308	76	8	2.2	0.5	8
Asterite	13	262	78	15	1.6	0.3	15
	8	332	49	12	1.9	0.2	12
	4	324	58	11	1.7	0.2	11
Corian	16	154	45	15	1.1	0.1	15
	8	198	25	12	1.3	0.1	12
	4	276	42	12	1.4	0.2	12

TABLE VI *Pinctada* nacre and synthetic composites: single-edge-notch, three-point bend, stable fracture

Method	Material	Mean work of fracture (J m^{-2})	S.D. (J m^{-2})	Number of tests
Continuous propagation	*Pinctada* nacre			
	Across, dry	437	141	11
	Across, wet	1034	272	12
	Along, dry	250	68	9
	Along, wet	553	167	11
	MDF cement	114	9	4
	Occlusin	153	29	2
	Asterite	287	27	6
	Corian	238	11	8
Loading–unloading*	*Pinctada* nacre			
	Across, wet	889	493	20
	Asterite	278	125	55
	Corian	174	63	45

*Segmental work areas pooled from 14 specimens of Asterite, 17 specimens of Corian and 4 specimens of nacre.

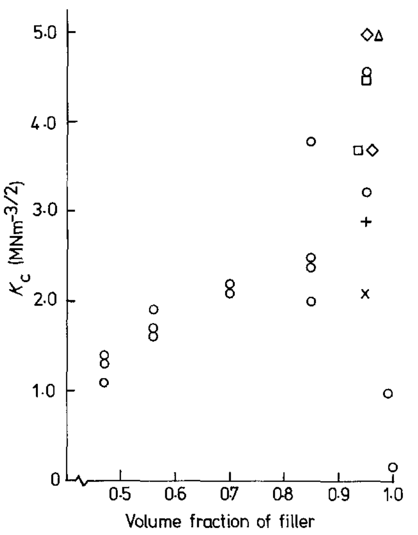

Figure 3 Mean critical stress intensity factor (K_c) plotted against volume fraction of filler for nacre, aragonite, homogeneous mollusc shell material and synthetic composites. Repeated points are for different S/d ratios. For key see Fig. 1, also for nacre, (+) across, desiccated, (×) between, dry (diagonal cross); homogeneous shell material has a filler volume fraction of 0.99.

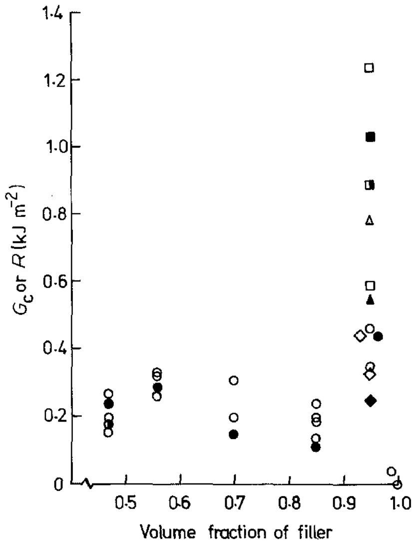

Figure 4 Mean critical strain energy release rate, G_C, or work of fracture, R, plotted against volume fraction for nacreous and homogeneous shell material, aragonite and synthetic composites measured in single-edge-notch, three-point bend tests. (○, □, △, ◇) unstable fracture; (●, ■, ▲, ◆) stable continuous fracture; (◑, ◨) stable, loading/unloading fracture. Other details as for Figs 1 and 3.

alone is clearly not enough, otherwise pure ceramics such as aragonite would not be so weak in tension. To restrict the propagation of potentially exploitable flaws, the brittle ceramic must be finely subdivided and separated by a less stiff matrix. For the same reason, porosity must be kept to a minimum. Unfortunately, it is practically impossible to envelop each particle of ceramic without introducing either too much matrix, too many pores or too many coagulated particles. This explains why the flexural strength of synthetic composites deteriorates at a volume fraction of about 70%: the absence of large pores in MDF cement does indeed provide an improvement in strength over conventional Portland cement but the presence of smaller pores (which reduce the effective volume fraction of filler and cause some degree of stress concentration) together with contiguities of ceramic particles (which contain large flaws) still prevents the ideal strength being reached. Only by laying down its platelets slowly, by excluding all pores, and by wrapping each platelet in a tenuous matrix does nacre achieve the so-called "normal" or "expected" strength. An interesting parallel to this work is that of Currey who found a relationship between the strength of bone and the mass fraction of ash which it contains [11, 17, 18]. The bone of the tympanic bulla of the whale has a very high mass fraction of ash but is much weaker than it should be if one extrapolates from the low mass fractions. Like aragonite and MDF cement, this may be attributed to the presence of large volumes of ceramic filler which contain critical Griffith flaws.

As the apparent strength of a material is dependent on its fracture toughness, it is not surprising to find a similar decline in K_c and G_c above a certain volume fraction. This volume fraction is greater for K_c (Fig. 3) than it is for G_c (Fig. 4). With few exceptions (e.g. "between" nacre and desiccated nacre) the toughnesses measured for nacre are larger than those of any of the synthetic ceramic composites, and are much larger than those of homogeneous shell and pure aragonite. Although less convincing, the majority of K_c values for nacre also lie well above the empirically expected level of toughness for a 95% volume fraction (especially when wet), and are even higher when correlated for embedded crack length. Thus, nacre is not as good as it was originally claimed to be [1] but is still better than examples of what man has achieved with the same kind of starting materials. Nacre has also been found to exceed many synthetic composites and pure ceramics in Knoop hardness [21]. Analogies have been made between the performance of nacre and that of MDF cement [5]. What these results show is that while MDF cement is indeed an improvement over conventional cements, it still has some way to go before matching nacre.

3.3. Theoretical modelling of the Young's modulus

The simplest and most obvious way to start modelling the Young's modulus of any composite is to set the limits dictated by either a completely parallel (Voigt) or a completely series (Reuss) arrangement of filler and matrix, assuming that they are bonded perfectly together. In the former (Voigt) model, each component experiences the same strain and the overall composite Young's modulus is given by

$$E_c = V_f E_f + (1 - V_f) E_m$$

This is the familiar "rule of mixtures" equation, where V, E, f, m and c stand for volume fraction, Young's modulus, filler, matrix and composite, respectively. In the Reuss model, filler and matrix are stressed rather than strained equally and the composite Young's modulus is expressed by a reciprocal rule of mixtures

$$1/E_c = V_f/E_f + (1 - V_f)/E_m$$

By taking the moduli of the components from the

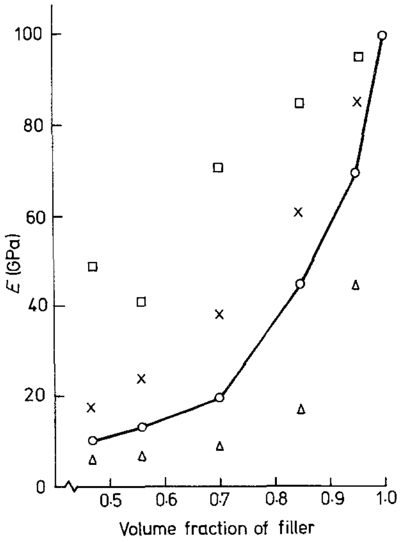

Figure 5 Experimentally determined Young's modulus of nacre, aragonite and synthetic composites (○) compared with theoretical values determined using the Voigt model (□), Reuss model (△) or the phenomenological model of Braem *et al.* (×). The materials can be identified using the information given with Fig. 1.

literature or by guessing them (for occlusin and MDF cement), the Voigt and Reuss models can be applied to nacre and the synthetic ceramic composites (Table VII). Initially (Fig. 5) the Reuss model is in fairly good agreement with the data, but as the volume fraction of ceramic increases the experimental points move to approximately half way between each model. The composites can, of course, be considered as a combination of the two models, as has been done for bone [22], but to do this is merely to describe, rather than to explain, their behaviour. Having said that, it is still useful to apply an intermediate model as a means of quantifying the proportion of parallel (equal strain) to series (equal stress) elements; if indeed such a combination really does explain why the data lie between the extreme models. It is not correct to argue that if a composite has a modulus half way between the Voigt and Reuss estimates that it therefore contains 50% Voigt and 50% Reuss elements; in Cartesian space, the non-linear approach to the Reuss model must be taken into consideration. This was done in the model of Hirsch [23]. On simplifying his equations, we have

$$1/E_c = x[1/(V_f E_f + V_m E_m)] + (1 - x)[(V_f/E_f) + (V_m/E_m)]$$

where x and $(1 - x)$ are the relative proportions of material conforming to the upper and lower bound solutions. The values of x for nacre and the synthetic composites are also listed in Table VII. At first sight, corian seems to be predicted more accurately by the Reuss extreme rather than the Voigt extreme but, contrary to expectation, the value of $x = 0.5$ indicates that the modulus of corian is attained by a roughly equal contribution from Reuss and Voigt elements. As the volume fraction of filler increases the rate of increase of the x values exceeds the rate at which the points in Fig. 5 approach the Voigt curve. In other words, what seems to be an equal approximation to both models is in fact a much closer agreement with the Voigt model (i.e. $x = 0.7$ as opposed to a half-way separation of the points). Beyond simple comparisons, the value of x for nacre is difficult to comment upon. It is not too dissimilar from the synthetic ceramics and from concrete ($x = 0.5$ [23]) but it is a lot lower than bone ($x = 0.925$ [22]).

TABLE VII Young's modulus of nacre and synthetic composites compared with the predictions of the Voigt (V) and Reuss (R) models. x is a term from the Hirsch model which describes the proportion conforming to the upper and lower bound solutions

	V_f	E_P	E_M	E_C	E_V	E_R	x
Nacre	0.95	100*	4*	70	95	45	0.68
MDF cement	0.85	100*	3*	45	85	17	0.77
Occlusin	0.7	100*	3*	20	71	9	0.63
Asterite	0.56	70 [12]	3 [14]	13	41	7	0.56
Corian	0.47	100*	3 [14]	10	49	6	0.51

*Estimated values

There are, of course, many improvements and modifications of the simple Voigt and Reuss extremes but most suffer to some extent, like the Hirsch model, in being only semi-empirical.

More recently a phenomenological model to predict the elastic modulus has been proposed [24]. The Young's modulus then shows exponential dependence on volume of filler. This can be interpreted as a generalization of the Voigt model, but where there is linear mixing of the logarithms of the modulus of the two phases

$$\ln(E_c) = V_f \ln(E_f) + (1 - V_f) \ln E_m$$

or

$$E_c = (E_f)^{V_f}(E_m)^{(1-V_f)}$$

In our case, taking E_f as 100 and E_m as 4 produces the curve shown in Fig. 5. The model over-estimates the experimental results but is a much better prediction than the Voigt extreme. In fact, by using more exact values, i.e. $E_f = 77$ for the silica in occlusin, realizes values of 31.7 and 38 which are closer still to the measured value of 20.

A tighter set of bounds to Voigt and Reuss can be applied using an approximation of Hashin and Shtrikman [25] as discussed by Katz [26]. Here the calculation involves obtaining upper and lower bounds of the bulk modulus (K) and shear modulus (G) of the composite from which E can be derived. The determination of the parameter for filler and resin and of Poisson ratio, however, requires further estimation and is outside the scope of this paper.

For the synthetic composites containing spherical filler particles or randomly orientated particles of any shape, there is no need to consider the distribution of stress along the length of the filler particle. But for a perfectly aligned platelet composite such as nacre it could cause a substantial reduction. This has been considered in detail [3] where a "shear-lag" analysis with simplifying idealizations leads to two models due to Padawar and Beecher [27] and Riley [28] which successfully predict the measured modulus.

4. Conclusions

Part of the reason for studying natural materials is to discover the basis of their often outstanding mechanical properties, shown both in the present paper and in [29]. Nacre is stiffer, stronger and tougher than four examples of synthetic, lightly filled, ceramic composites. Their properties appear to be dependent largely upon the volume fraction of filler despite their structural differences. Nacre, with platelets of aspect ratio of only 8, approximates more closely to a random isotropic composite with isometric plates than it does to long-fibre-reinforced composite with aspect ratio from 100 to infinity. The question arises – is it worth modelling such materials in any aspect in order to develop advanced materials?

References

1. J. D. CURREY, *Proc. Roy. Soc. Lond. B* **196** (1977) 443.
2. A. P. JACKSON, J. F. V. VINCENT, D. BRIGGS, R. A. CRICK, S. F. DAVIES, M. J. HEARN and R. M. TURNER, *J. Mater. Sci. Lett.* **5** (1987) 975.
3. A. K. JACKSON, J. F. V. VINCENT and R. M. TURNER, *Proc. Roy. Soc. B* **234** (1988) 415.
4. J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, *Nature Lond.* **289** (1981) 388.
5. J. D. BIRCHALL, *Phil. Trans. Roy. Soc. Lond. A* **310** (1983) 31.
6. N. McN. ALFORD, J. D. BIRCHALL, A. J. HOWARD and K. KENDALL, in Proceedings of the 1st Conference in Materials Engineering, University of Leeds (1984) p. 73.
7. Occlusin brochure, ICI Dental, ICI Pharmaceuticals, Macclesfield.
8. ICI, Asterite brochure.
9. du Pont, Corian brochure.
10. A. C. KITCHENER, PhD thesis, University of Reading (1985).
11. J. D. CURREY, *J. Biomech.* **12** (1979) 313.
12. J. E. GORDON, "Structures, or why things don't fall down" (Penguin, Harmondsworth, 1979).
13. D. HULL, "An Introduction to Composite Materials" (The University Press, Cambridge, 1981).
14. A. G. ATKINS and Y.-W. MAI, "Elastic and Plastic Fracture: Metals, Polymers, Ceramics, Composites, Biological Materials" (Ellis-Horwood, Chichester, 1985).
15. R. F. S. HEARMON, *Rev. Mod. Phys.* **18** (1946) 409.
16. J. J. GILMAN, *J. Appl. Phys.* **31** (1960) 2208.
17. J. D. CURREY, *Phil. Trans. Roy. Soc. B* **304** (1984) 509.
18. *Idem*, *J. Biomech.* **21** (1988) 131.
19. S. YALVAC and J. H. HAND, *J. Amer. Ceram. Soc.* **67** (1984) 155.
20. S. McGEE and R. L. McCULLOUGH, *Polym. Comp.* **2** (1981) 149.
21. A. K. ABELL, M. A. CRENSHAW and D. T. TURNER, in "Biomedical and Dental Applications of Polymers", edited by F. K. Koblitz (University Press, Oxford, 1981) p. 347.
22. K. PIEKARSKI, *Int. J. Engng Sci.* **11** (1973) 557.
23. T. J. HIRSCH, *Proc. Amer. Concr. Inst.* **59** (1962) 427.
24. M. BRAEM, V. E. VAN DOREN, P. LAMBRECHTS and G. VANHERLE, *J. Mater. Sci.* **22** (1987) 2037.
25. Z. HASHIN and S. SHTRIKMAN, *J. Mech. Phys. Solids* **11** (1963) 127.
26. J. L. KATZ, *J. Mater. Sci. Lett.* **7** (1988) 131.
27. G. E. PADAWER and N. BEECHER, *Polym. Engng Sci.* **10** (1970) 185.
28. V. R. RILEY, *J. Comp. Mater.* **2** (1968) 436.
29. A. K. JACKSON, J. F. V. VINCENT and R. M. TURNER, *Comp. Sci. Tech.* **36** (1989) 255.

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