

Optimized adhesives for strong, lightweight, damage-resistant, nanocomposite materials: new insights from natural materials

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Abstract

From our investigations of natural composite materials such as abalone shell and bone we have learned the following. (1) Nature is frugal with resources: it uses just a few per cent glue, by weight, to glue together composite materials. (2) Nature does not avoid voids. (3) Nature makes optimized glues with sacrificial bonds and hidden length. We discuss how optimized adhesives combined with high specific stiffness/strength structures such as carbon nanotubes or graphene sheets could yield remarkably strong, lightweight, and damage-resistant materials.

1. Introduction

The abalone shell, a composite of calcium carbonate plates sandwiched between organic material, is 3000 times more fracture resistant than a single crystal of the pure mineral [1]. The organic component, comprising just a few per cent of the composite by weight, working together with the structural geometry [2, 3], is thought to hold the key to nacre's fracture toughness [4].

In addition to the details of the structural geometry, one of the main mechanisms that lets a few per cent of 'glue' make such an enormous difference in fracture toughness is the sacrificial bond and hidden length mechanism [4, 5]. By 'glue' in this context we mean polymer adhesive molecules that hold together the hard elements in a composite structure. In the case of biological structures these glues tend to be composed of proteins, proteoglycans, and glycoproteins. The study of such glues is just in its infancy, but so far it appears that one of the key factors is the presence of charged side groups on the biological polymer adhesive molecules that can form sacrificial bonds with other charged groups on the polymers and on the hard elements—sometimes with the help of ions in solution. For example, Ca⁺⁺ ions can help form sacrificial bonds between negatively charged side groups such as phosphate groups.

Sacrificial bonds and hidden length in structural molecules and composites have been found to greatly increase the fracture toughness of biomaterials by providing a reversible, molecular-scale energy-dissipation mechanism. This mechanism relies on the energy, of order 100 eV, needed to reduce entropy and increase enthalpy as molecular segments are stretched after being released by the breaking of weak bonds, called sacrificial bonds. This energy is relatively large compared to the energy needed to break the polymer backbone, of order a few eV. In many biological cases, the breaking of sacrificial bonds has been found to be reversible, thereby additionally providing a 'self-healing' property to the material. Due to the nanoscopic nature of this mechanism, single molecule force spectroscopy [6–8] using an atomic force microscope has been a useful tool to investigate this mechanism [4, 5].

Bone consists of mineralized collagen fibrils and a non-fibrillar organic matrix, which acts as a 'glue' that holds the mineralized fibrils together [9]. Here again the glue is just a few per cent by weight. This glue may resist the separation of mineralized collagen fibrils. As in the case of the abalone shell, in addition to the details of the structural geometry, one of the main mechanisms that lets a few per cent of glue make such an enormous difference in fracture toughness is the sacrificial bond and hidden length mechanism [4, 10]. This mechanism is also used in spider silk [11] and some diatoms, which are

unicellular microalgae with a cell wall consisting of a siliceous skeleton enveloped by an organic case. For some species, such as *Navicula seminulum*, individual diatoms are glued together into tower-like columns that are themselves glued together with a glue that uses the sacrificial bond and hidden length mechanism [12–14].

In the case of bone, the mineralized collagen fibrils occupy only about two-thirds of the volume. The remainder of the space is a solution containing the glue molecules. But again, the glue molecules are just a few per cent by weight. In contrast, in common engineering composite materials the space between the strong elements, for example carbon fibres, is totally filled with ‘glue’, often epoxy. This may not always be desirable. For some applications one does want a composite evaluated on a per volume basis. But for many other applications, including some space applications, one wants a composite evaluated on a per weight basis. For these applications, voids may be not only acceptable, but actually desirable. Further, the density of single walled carbon nanotubes, SWCNTs, and other nanotubes is, of course, a function of their diameter, their packing, and so on. For the applications evaluated on a per weight basis not only voids but also larger diameter nanotubes and novel packing geometries may be acceptable.

2. Discussion

The natural glues in biomaterials have been optimized by evolution. An optimized glue has five characteristics.

- (1) It holds together the strong elements of the composite (e.g. abalone mineral plates or mineralized collagen fibrils in bone).
- (2) It yields just before the strong elements would otherwise break.
- (3) It dissipates large amounts of energy as it yields.
- (4) It self-heals after it yields.
- (5) It takes just a few per cent by weight.

As an example of an optimized glue, consider the glue in bone. If we consider that the strength of bone in tension is roughly 150 MPa [15, 16], then the force per fibril at failure would be $= 150 \times 10^6 \text{ N m}^{-2} \times (10^{-7} \text{ m})^2 = 1.5 \times 10^{-6} \text{ N}$. If we assume a fibril cross sectional area of $(10^{-7} \text{ m})^2$, then the number of glue molecules needed per fibril to supply this force per fibril $= 1.5 \times 10^{-6} \text{ N} / 300 \text{ pN/molecule} = 5000 \text{ molecules}$. The total mass of these 5000 glue molecules, assuming 100 kDa per molecule, is $5000 \times 100 \text{ kDa} \times 1.6 \times 10^{-27} \text{ kg Da}^{-1} = 8 \times 10^{-19} \text{ kg}$. The total mass of the bone over the approximate $5 \mu\text{m}$ length of fibrils observed to pull out in tests of bone to failure in tension [17] is $5 \times 10^{-6} \text{ m} \times (10^{-7} \text{ m})^2 \times 1.9 \times 10^3 \text{ kg m}^{-3} = 1 \times 10^{-16} \text{ kg}$. Thus the fractional mass of glue molecules is less than 1%.

To make the connection to finding optimized glues for strong, lightweight, damage-resistant, composite materials, consider the following thought experiment. Assume that we wanted to join together strong elements consisting of steel bars that had a cross sectional area of $(0.019 \text{ mm} \times 0.003 \text{ mm})$. An optimized glue would be able to transfer the load fully from one steel bar to another. If we assume a strength for failure in tension of 100 MPa for the steel, then the force per bar at

failure would be $100 \times 10^6 \text{ N m}^{-2} \times (0.019 \text{ mm} \times 0.003 \text{ mm}) = 5700 \text{ N}$.

So further assume that we wanted to use magnets as optimized adhesives to glue the bars together and that each magnet could supply a force of 9 N to resist sliding of the bars relative to each other if one end of each bar were pulled in tension. If we wanted the optimized adhesive to fully load, to failure, each bar would need $5700 \text{ N} / 9 \text{ N/magnet} = 630 \text{ magnets}$.

Note: the longer the bars, the smaller the fractional weight of the magnets (the ‘glue’) since the number of magnets is fixed. This is a very important point. It shows that for high modulus materials the longer the strong elements, the lower the percentage, by weight, of the glue for optimum adhesion. Thus the undesirable averaging effect of having so much relatively weak glue that it pulls down the strength of the composite material well below the strength of the strong elements is avoided.

Just to extend this thought experiment, we might actually choose to use fewer magnets, say 500, if toughness were desired at the slight expense of ultimate tension strength. Then, highly loaded bars in a composite material of bars and magnets would slip relative to other bars to redistribute the load rather than having the most highly stressed bars break, which then further loads other bars, which then also fail, leading to global failure of the material. In contrast, if we use fewer magnets, the ability of bars that are locally loaded too heavily to slide relative to other bars to redistribute stress keeps local problems with a few strong elements from propagating into global failure of the composite material.

A dramatic example of some of these effects in a real material is ultra-high-molecular-weight polyethylene. Here the strong elements, the polyethylene chains, are so long that no added glue at all is needed! Just the glue effect of the relatively weak interactions between the polyethylene chains is sufficient [18]. In the same sense, sufficiently long closest-packed carbon nanotubes, or twisted bundles of them [19], might also require no glue.

Now consider a real challenge: to make a composite material with carbon nanotubes (or graphene sheets) that approaches the strength of the carbon nanotubes themselves [18, 20–26].

Let us assume that the nanotubes have a strength of 100 GPa [27–31] and a cross sectional area of one nanometre squared. Then each nanotube would need to carry a load of $100 \times 10^9 \text{ N m}^{-2} \times (10^{-9} \text{ m})^2 = 10^{-7} \text{ N}$. To fully transfer a load of 10^{-7} N , assuming that each glue molecule could transfer a load of 300 pN [9] we would need $10^{-7} \text{ N} / 300 \text{ pN/molecule} = 300 \text{ molecules}$. If we further assume 1 kDa per molecule, then these 300 molecules would weigh $300 \times 1 \text{ kDa} \times 1.6 \times 10^{-27} \text{ kg Da}^{-1} = 5 \times 10^{-22} \text{ kg}$. In comparison, the total mass of the nanotube (for a nanotube that is $50 \mu\text{m}$ long) would be $5 \times 10^{-5} \text{ m} \times (10^{-9} \text{ m})^2 \times 1.3 \times 10^3 \text{ kg m}^{-3} = 6.5 \times 10^{-20} \text{ kg}$. Thus, for nanotubes $50 \mu\text{m}$ long and glue molecules of molecular weight 1 kDa or less, the fractional mass of glue molecules would be <1%.

There is, however, one major problem with this simple analysis. The implicit assumption that the strength of nanotubes is independent of their length is not a valid assumption for other materials. The typical situation is that one

needs to consider the statistical nature of defects that results in a decrease of strength with length or size for conventional materials; this can perhaps be mitigated, and perhaps even eliminated, by future developments in fabrication techniques for the nanotubes. One must however appreciate the challenge of synthesizing carbon nanotubes that are completely defect free, and there is no evidence that such defect free CNTs have been produced to date. If one accepts that the CNTs will have some defects that reduce their strength, then a real optimized adhesive must be chosen as a compromise between the benefits of longer strong elements, such as a lower percentage of the weaker glue, with the disadvantage that longer strong elements may themselves be weaker! It is thus of interest to consider the types of defects that have the largest impact on strength of CNTs—namely point defects or clusters of missing atoms (in short, holes) [27–29, 32, 33]. Indeed, even a few missing atoms and thus small holes in the tube structure can cause a significant reduction in strength, as is discussed in detail elsewhere [27]. In this regard, it is possible that graphene sheets, if extracted from ‘high quality’ graphite, might contain both smaller, and also fewer, critical defects. On the other hand, synthetic approaches which yield essentially perfect (defect-free) carbon nanotubes may yet be found.

3. Summary

The concept of an optimized adhesive is based on using only enough adhesive to fully transfer the desired load to the strong elements in a composite material. This full transfer will require a fixed number of adhesive molecules—independent of the length of the strong element. Thus, the longer the strong elements, the less the fractional weight of the glue in the composite material. Fractional weights as small as a few per cent are found in natural materials such as abalone shells and bone.

Making synthetic composite materials with just a few per cent of glue remains a challenge for the future. Nature gives us some hints to help. For example, it is not important to avoid microscopic voids. In fact it is better to have microscopic voids than to fill them with excess glue molecules because these can actually weaken the material. Moreover, it is useful to use entropic elasticity or friction to dissipate energy in the glue molecules rather than in breaking strong bonds if we want a tough material. Finally, it is useful to focus on having the only bonds that are broken during energy dissipation be weak bonds that can be reformed, such as Coulomb or van der Waals or hydrogen bonds if we want a self-healing material.

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References

- [1] Jackson A P, Vincent J F V and Turner R M 1988 *Proc. R. Soc. B* **234** 415
- [2] Abdala A A, Milius D L, Adamson D H, Aksay I A and Prudhomme R K 2004 *Am. Chem. Soc.* **227** U525 (Abstracts of papers)
- [3] Evans A G, Suo Z, Wang R Z, Aksay I A, He M Y and Hutchinson J W 2001 *J. Mater. Res.* **16** 2475
- [4] Smith B L, Schaffer T E, Viani M, Thompson J B, Frederick N A, Kindt J, Belcher A, Stucky G D, Morse D E and Hansma P K 1999 *Nature* **399** 761
- [5] Fantner G E *et al* 2006 *Biophys. J.* **90** 1411
- [6] Rief M, Gautel M, Oesterhelt F, Fernandez J M and Gaub H E 1997 *Science* **276** 1109
- [7] Rief M, Fernandez J M and Gaub H E 1998 *Phys. Rev. Lett.* **81** 4764
- [8] Rief M, Gautel M, Schemmel A and Gaub H E 1998 *Biophys. J.* **75** 3008
- [9] Fantner G E *et al* 2005 *Nat. Mater.* **4** 612
- [10] Fantner G E *et al* 2006 *Biophys. J. BIOFAST* **90** 1411–8
- [11] Becker N, Oroudjev E, Mutz S, Cleveland J P, Hansma P K, Hayashi C Y, Makarov D E and Hansma H G 2003 *Nat. Mater.* **2** 278
- [12] Gebeshuber I C, Kindt J H, Thompson J B, Del Amo Y, Stachelberger H, Brzezinski M, Stucky G D, Morse D E and Hansma P K 2004 *J. Microsc.-Oxford* **214** 101
- [13] Gebeshuber I C, Kindt J H, Thompson J B, Del Amo Y, Stachelberger H, Brzezinski M A, Stucky G D, Morse D E and Hansma P K 2003 *J. Microsc.-Oxford* **212** 292
- [14] Gebeshuber I C, Kindt J H, Thompson J B, Del Amo Y, Stachelberger H, Brzezinski M, Stucky G D, Morse D E and Hansma P K 2000 *Biophys. J.* **78** 10a
- [15] Reilly D T and Burstein A H 1975 *J. Biomech.* **8** 393
- [16] Cezayirlioglu H, Bahniuk E, Davy D T and Heiple K G 1985 *J. Biomech.* **18** 61
- [17] Braidotti P, Branca F P and Stagni L 1997 *J. Biomech.* **30** 155
- [18] Crist B 1995 *Annu. Rev. Mater. Sci.* **25** 295
- [19] Qian D, Liu W K and Ruoff R S 2003 *Compos. Sci. Technol.* **63** 1561
- [20] Zhang S L, Mielke S L, Khare R, Troya D, Ruoff R S, Schatz G C and Belytschko T 2005 *Phys. Rev. B* **71** 115403
- [21] Ruoff R S, Calabri L, Ding W and Pugno N M 2005 *Rev. Adv. Mater. Sci.* **10** 110
- [22] Ruoff R S and Lorents D C 1995 *Carbon* **33** 925
- [23] Ruoff R S, Tersoff J, Lorents D C, Subramoney S and Chan B 1993 *Nature* **364** 514
- [24] Ramanathan T, Liu H and Brinson L C 2005 *J. Polym. Sci. B* **43** 2269
- [25] Zhang Y C and Wang X 2005 *Int. J. Solids Struct.* **42** 5399
- [26] Moulton S E, Minett A I, Murphy R, Ryan K P, McCarthy D, Coleman J N, Blau W J and Wallace G G 2005 *Carbon* **43** 1879
- [27] Pugno N M and Ruoff R S 2004 *Phil. Mag.* **84** 2829
- [28] Mielke S L, Troya D, Zhang S, Li J L, Xiao S P, Car R, Ruoff R S, Schatz G C and Belytschko T 2004 *Chem. Phys. Lett.* **390** 413
- [29] Belytschko T, Xiao S P, Schatz G C and Ruoff R S 2002 *Phys. Rev. B* **65** 235430
- [30] Dumitrica T, Hua M and Yakobson B I 2006 *Proc. Natl Acad. Sci. USA* **103** 6105
- [31] Ruoff R S 2006 *Proc. Natl Acad. Sci. USA* **103** 6779
- [32] Yu M F, Lourie O, Dyer M J, Moloni K, Kelly T F and Ruoff R S 2000 *Science* **287** 637
- [33] Yu M F, Files B S, Arepalli S and Ruoff R S 2000 *Phys. Rev. Lett.* **84** 5552