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Toughness of double elastic networks

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Abstract. – We consider isotropic composites comprising of soft and hard elastic networks. We examine the minimum elastic model of purely elastic, intertwined but energetically independent networks. We obtain toughness enhancement factors in various situations, which may provide guiding principles to make strong composites of soft and hard materials.

Introduction. – Many materials in nature such as timber, teeth and nacre draw their strength from composite structures, which include, quite often, soft and hard elements. Since the soft/hard combination seems crucial (at least empirically) for the strength, it is important to understand the physical reason in a simple way. One of the natural parameters may be the ratio of the hard and soft elastic moduli, $\mu_{\mathrm{h}}/\mu_{\mathrm{s}}$, which is larger than one. In our previous works on nacre [1], which is also a soft/hard composite, we have shown that the fracture energy scales like the square root of $\mu_{\mathrm{h}}/\mu_{\mathrm{s}}$ under certain conditions.

Recently, another type of promising composites are synthesized: double-network (DN) gels comprising of two independently cross-liked networks [2]. They show a remarkable toughness when one network is soft and the other is hard; they have the potential to work as an artificial joint of human being. The DN gels are significantly different from nacre in that they are *isotropic*; nacre is a strongly anisotropic layered system. Actually, anisotropy has been sometimes considered as the essential property of composite materials; most of theories of composites have been developed for anisotropic systems [3].

Inspired by this situation, we propose the minimal model of *isotropic and elastic* composites. We find, for example, that the enhancement factor is simply proportional to $\mu_{\mathrm{h}}/\mu_{\mathrm{s}}$ (see eq. (16) below) under a certain condition, which is different from the anisotropic case. The present work also concerns elastic particle-reinforced composites.

Equal-strain approximation. – Consider a composite comprising of two independent interpenetrated networks "h" and "s". These networks are *symbolically* illustrated in fig. 1. A typical semi-microscopic mesh size is denoted by ξ_i ($i =$ h or s) and, on scales *smaller* than ξ_i, we can consider a *continuum* elastic modulus μ_i. Both networks are assumed to be isotropic and incompressible and so is the composite. *In the decoupling limit* where the two components are energetically independent, the elastic energy per unit volume is given by

$$f = \phi_{\mathrm{h}}\mu_{\mathrm{h}}e_{\mathrm{h}}^2/2 + \phi_{\mathrm{s}}\mu_{\mathrm{s}}e_{\mathrm{s}}^2/2, \qquad (1)$$

where ϕ_i stands for the volume fraction at the level of scaling laws (the factor one-half is merely for convenience); the non-tensorial treatment of strain and modulus is justified later.

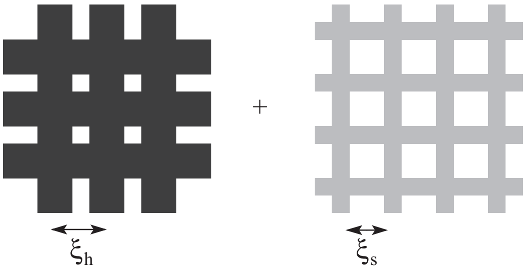

Fig. 1

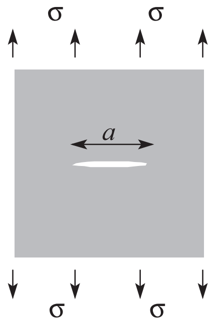

Fig. 2

Fig. 1 – Symbolic representation of two networks. A hard network "h" and a soft network "s" are interpenetrated with each other in the composite.

Fig. 2 – Griffith problem. A through-thickness crack of size a in an infinitely wide plate is subjected to a remote tensile stress σ.

In this section, we assume that, at equilibrium, the stress of the hard network σ_h balances with that of soft σ_s because the two networks are locally in contact with each other (this *equal-stress condition* is further discussed later); the stress of the composite σ is given by

$$\sigma = \sigma_i = \mu_i e_i \text{ (no summation)}. \tag{2}$$

Under eq. (2), f can be written as

$$f = \frac{\phi_\mathrm{h}\sigma_\mathrm{h}^2}{2\mu_\mathrm{h}} + \frac{\phi_\mathrm{s}\sigma_\mathrm{s}^2}{2\mu_\mathrm{s}} = \frac{\sigma^2}{2\mu} = \frac{\mu e^2}{2}\,, \tag{3}$$

where the composite modulus μ is given by

$$\frac{1}{\mu} = \frac{\phi_\mathrm{h}}{\mu_\mathrm{h}} + \frac{\phi_\mathrm{s}}{\mu_\mathrm{s}} \tag{4}$$

and the strain of the composite e is defined through

$$e = \frac{\sigma}{\mu} = \frac{\mu_i}{\mu} e_i \text{ (no summation)}. \tag{5}$$

Since the composite is isotropic, on scales *larger* than ξ_i, we can construct the Griffith problem as usual for a crack of length a when $a \gg \xi_i$ (see fig. 2). We start from the potential energy per unit length of the crack front:

$$F \sim \mu \left(\frac{u}{a}\right)^2 a^2/2 - \sigma u a + \gamma a\,, \tag{6}$$

where γ is the fracture energy of the composite. The first term is an elastic energy of strain ($\sim u/a$) localized over a volume ($\sim a^2$) around the crack tip, the second the work done by the external remote stress σ, and the third the surface energy. Minimization with respect to the displacement u leads to the Hooke-type stress-strain relation

$$\sigma \sim \mu u/a \tag{7}$$

and the minimized energy

$$F \sim -\frac{\sigma^2 a^2}{2\mu} + \gamma a\,. \tag{8}$$

The maximum of this quadratic function F of the variable a corresponds to the critical conditions for failure, under which the following relations are satisfied:

$$\sigma \sim \sqrt{\gamma\mu/a}\,, \qquad u \sim \sqrt{\gamma a/\mu}\,, \qquad \sigma u \sim \gamma. \tag{9}$$

The first equation announces the stress distribution near the tip:

$$\sigma(r) = \sqrt{\gamma\mu/r} = \sigma\sqrt{a/r}\,, \tag{10}$$

where r is the distance from the tip. As shown above, the scaling arguments sketched in this paragraph [4] heuristically reproduce the essentials of the linear-elastic fracture mechanics [5].

Equation (10) can be understood as follows. The local stress $\sigma(r)$ should be a function of r and a and approaches the remote value σ at $r \sim a$: $\sigma(r) = \sigma \cdot (r/a)^n$. The exponent n is determined to be $-1/2$ by requiring the scaling property that $\sigma(r)$ becomes independent of a when r is small.

The above continuum theory is valid only when the scale in question (r or a) is larger than the largest mesh size. The maximum stress of our continuum theory is cut off at this size $\xi \equiv \max\{\xi_i\}$; the critical stress can be estimated as

$$\sigma_{\mathrm{m}} \sim \sqrt{\gamma\mu/\xi}\,. \tag{11}$$

On the other hand, the remote failure stress of the non-meshed hard material ($\xi_{\mathrm{h}} = 0$) is expressed as

$$\sigma_{\mathrm{h}} \sim \sqrt{\gamma_{\mathrm{h}}\mu_{\mathrm{h}}/a_{\mathrm{h}}}\,, \tag{12}$$

where γ_{h} is the fracture energy of the non-meshed hard material and a_{h} is a typical microscopic size of defects or Griffith cavities with

$$a_{\mathrm{h}} \ll \xi\,. \tag{13}$$

This *inherent remote failure stress* is appropriate even for the meshed hard network ($\xi_{\mathrm{h}} \neq 0$) on semi-macroscopic scales up to $r \sim \xi$; on scales $r \ll \xi$, the hard network is isotropic and homogeneous except for the cavities ($\sim a_{\mathrm{h}}$).

Assume that the soft network is very soft (and almost like a liquid),

$$\mu_{\mathrm{h}} \gg \mu_{\mathrm{s}}\,, \tag{14}$$

but persistent (the hard network breaks before the soft one). Then, a criterion of failure may be that the maximum stress of the composite, σ_{m}, reaches the inherent failure stress σ_{h}. Note that σ_{h} is a "remote" stress and the scale $r \sim \xi$ is already "remote" on the cavity scale a_{h}. This condition ($\sigma_{\mathrm{m}} \sim \sigma_{\mathrm{h}}$) results in

$$\gamma \sim \frac{\xi}{a_{\mathrm{h}}} \cdot \frac{\mu_{\mathrm{h}}}{\mu}\gamma_{\mathrm{h}} \equiv \lambda\gamma_{\mathrm{h}}\,, \tag{15}$$

where the enhancement factor of the fracture energy can be rewritten as

$$\lambda = \frac{\xi}{a_{\mathrm{h}}}\left(\phi_{\mathrm{h}} + \phi_{\mathrm{s}}\frac{\mu_{\mathrm{h}}}{\mu_{\mathrm{s}}}\right) \sim \phi_{\mathrm{s}}\frac{\xi}{a_{\mathrm{h}}}\frac{\mu_{\mathrm{h}}}{\mu_{\mathrm{s}}}\,. \tag{16}$$

Under eqs. (13) and (14), this λ is large.

Although we are mainly concerned with the work of fracture, the *macroscopic* fracture stress and strain (*i.e.*, in the presence of a macroscopic fracture with size a, where $a \gg \xi$) can also be derived as in the following example: the remote fracture stress σ_{F} of the composite can be expressed as $\sigma_{\mathrm{F}} \sim \sqrt{\gamma\mu/a}$, while that of the non-meshed hard material is given by $\sigma_{\mathrm{h,F}} \sim \sqrt{\gamma_{\mathrm{h}}\mu_{\mathrm{h}}/a}$; the comparison of these two stresses results in a large stress enhancement factor:

$$\lambda_\sigma \equiv \sigma_{\mathrm{F}}/\sigma_{\mathrm{h,F}} = \sqrt{\mu\lambda/\mu_{\mathrm{h}}} = \sqrt{\xi_{\mathrm{h}}/a}\,. \tag{17}$$

Equal-strain approximation. – In this section, we assume the equal-strain condition ($e_{\mathrm{h}} \sim e_{\mathrm{s}}$). Then, eq. (4) is replaced by

$$\mu = \phi_{\mathrm{h}}\mu_{\mathrm{h}} + \phi_{\mathrm{s}}\mu_{\mathrm{s}}\,. \tag{18}$$

In this case a failure criterion for the composite is set not for stress but for strain because it is the strain that is common to the two networks; we compare the maximum strain of the composite,

$$e_{\mathrm{m}} \sim \sqrt{\frac{\gamma}{\mu\xi}}\,, \tag{19}$$

with the *inherent* failure strain of the *non-meshed* hard material,

$$e_{\mathrm{h}} \sim \sqrt{\frac{\gamma_{\mathrm{h}}}{\mu_{\mathrm{h}}a_{\mathrm{h}}}}\,. \tag{20}$$

Matching of these stresses leads to another energy enhancement factor:

$$\lambda = \frac{\xi}{a_{\mathrm{h}}} \cdot \frac{\phi_{\mathrm{h}}\mu_{\mathrm{h}} + \phi_{\mathrm{s}}\mu_{\mathrm{s}}}{\mu_{\mathrm{h}}} \sim \phi_{\mathrm{h}}\frac{\xi}{a_{\mathrm{h}}}\,. \tag{21}$$

Combinations of failure points of constituting networks. – The above results are modified depending on the combination of the inherent failure stress σ_i^{F} and strain e_i^{F} of the non-meshed soft and hard materials. The criterion employed in the equal-stress assumes $\sigma_{\mathrm{h}}^{\mathrm{F}} < \sigma_{\mathrm{s}}^{\mathrm{F}}$ and thus $e_{\mathrm{h}}^{\mathrm{F}} < e_{\mathrm{s}}^{\mathrm{F}}$: the hard network breaks before the soft one (the soft network is persistent); otherwise, an extra energy cannot be stored efficiently in the soft network to increase the work of fracture. This situation is illustrated in fig. 3a. In this case, $\gamma_{\mathrm{s}} > \gamma_{\mathrm{h}}$ (the hatched area is proportional to γ_{s}). The criterion employed in the equal-strain implies $e_{\mathrm{h}}^{\mathrm{F}} < e_{\mathrm{s}}^{\mathrm{F}}$. This case includes both situations in fig. 3a ($\gamma_{\mathrm{s}} > \gamma_{\mathrm{h}}$) and b ($\gamma_{\mathrm{s}} < \gamma_{\mathrm{h}}$): no restriction between the magnitudes of γ_{h} and γ_{s}.

Let us consider the opposite case where the soft component breaks first. Even in this case, since it is the hard element that supports the shape of the composite, failure is achieved only when the hard network breaks down. But this time the soft network is virtually absent at the moment of failure; $\phi_{\mathrm{s}} = 0$ in eq. (1). Then, the enhancement factor is given by the final expression in eq. (21), regardless of the equal-strain or equal-stress condition.

Particle-reinforced composites. – As symbolically illustrated in fig. 4, consider the elastic matrix combined with elastic particles. Even if the particles are not spheres but the directions are randomly distributed, the system should become isotropic from a macroscopic continuum view if the scale in question is large enough.

When hard particles of size ξ_{h} are embedded in the soft matrix, failure of the composite is accomplished when the soft matrix breaks down (this time, the matrix is the softer component

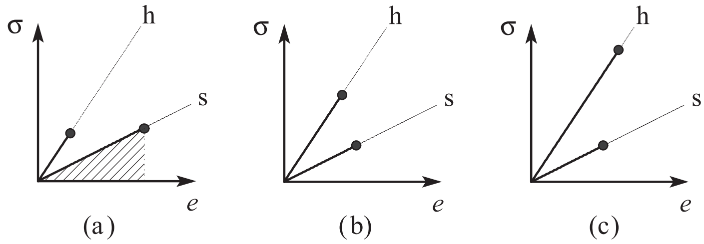

Fig. 3

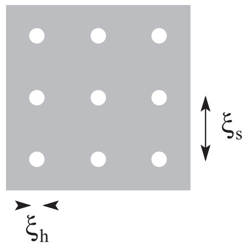

Fig. 4

Fig. 3 – Failure points of ideal networks in strain-stress curve. The dots stand for (microscopic) failure points of each network where the upper line corresponds to the hard material ($\mu_{\rm h} > \mu_{\rm s}$).

Fig. 4 – Particle-reinforced composite. Elastic particles of size $\xi_{\rm h}$ are distributed in an elastic plate with interparticle distances $\xi_{\rm s}$.

and thus it cannot be truly like a liquid). Under the equal-strain condition, the enhancement factor in eq. (21) is replaced with

$$\lambda = \frac{\xi}{a_{\rm s}} \cdot \frac{\phi_{\rm h}\mu_{\rm h} + \phi_{\rm s}\mu_{\rm s}}{\mu_{\rm s}} \sim \frac{\xi}{a_{\rm s}} \cdot \frac{\phi_{\rm h}\mu_{\rm h}}{\mu_{\rm s}}\,, \tag{22}$$

where λ is defined such that $\gamma = \lambda\gamma_{\rm s}$; this factor stands for enhancement not from $\gamma_{\rm h}$ but from $\gamma_{\rm s}$. In the above, we have assumed that hard components (or particles) break after the matrix, that is, $\gamma_{\rm h} > \gamma_{\rm s}$ (see fig. 3c); otherwise, the above factor is replaced with $\lambda = \phi_{\rm s}\xi/a_{\rm s}$ because the hard component is virtually nonexistent. Under the equal-stress condition, we find, instead,

$$\lambda = \frac{\xi}{a_{\rm s}} \cdot \left(\phi_{\rm s} + \phi_{\rm h}\frac{\mu_{\rm s}}{\mu_{\rm h}}\right) \sim \phi_{\rm s}\frac{\xi}{a_{\rm s}}\,. \tag{23}$$

In this case, even if particles break apart after the matrix, the enhancement factor is given by $\lambda = \phi_{\rm s}\xi/a_{\rm s}$.

As opposed to the meshed networks, here, we do not have the freedom to set the volume fraction independent of ξ_i; at the level of scaling relations, $\phi_{\rm h} \sim \xi_{\rm h}^3/\xi_{\rm s}^3$ and $\phi_{\rm s} \sim \xi_{\rm s}^3/\xi_{\rm h}^3$. When the particles are sparsely embedded ($\xi = \xi_{\rm s} > \xi_{\rm h}$), the enhancement factor in the equal-strain and -stress cases is given by

$$\lambda \sim \frac{\xi_{\rm h}}{a_{\rm s}} \cdot \left(\frac{\xi_{\rm h}}{\xi}\right)^2 \cdot \frac{\mu_{\rm h}}{\mu_{\rm s}} \qquad \text{and} \qquad \frac{\xi}{a_{\rm s}} \cdot \left(\frac{\xi}{\xi_{\rm h}}\right)^3, \tag{24}$$

respectively. The second expression implies that an increase in the particles fraction $\phi_{\rm h}$ (*i.e.*, a decrease in ξ) will result in a decreased toughness. Such a decrease in toughness with increased filler content is observed in many particle-reinforced composites. We note that λ can be less than one in some cases (λ does not always imply an enhancement): for example, the second factor in the first expression in eq. (24) contains the ratio $\xi_{\rm h}/\xi$, which is less than one.

If the particles are densely spread, we may set $\xi \simeq \xi_{\rm h} \simeq \xi_{\rm s}$ to find

$$\lambda \sim \frac{\xi}{a_{\rm s}} \cdot \frac{\mu_{\rm h}}{\mu_{\rm s}} \qquad \text{and} \qquad \frac{\xi_{\rm s}}{a_{\rm s}}\,. \tag{25}$$

As above, these expressions provide guiding principles to develop strong particle-reinforced composites.

Tensor properties. – We have ignored the tensor characters of our elastic problem. In this section, we consider this point in the case of equal stress; the equal-strain case can be treated in a similar way. In the tensor form, the stress-strain relation is described by Hooke's law:

$$\sigma^{(i)} = E^{(i)} e^{(i)}, \tag{26}$$

where $i = 1$ or 2 stands for the 1st or 2nd networks. Here, the stress $\sigma^{(i)}$ and strain $e^{(i)}$ are both second-rank tensors, while the elastic modulus $E^{(i)}$ is a four-rank tensor whose typical magnitude of the non-zero elements corresponds to μ_i in the above. The energy of the composite material per unit volume *in the decoupling limit* is given by

$$f = \frac{\phi_1}{2} \operatorname{Tr}\left(\sigma^{(1)} e^{(1)}\right) + \frac{\phi_2}{2} \operatorname{Tr}\left(\sigma^{(2)} e^{(2)}\right). \tag{27}$$

The tensorial equal-stress condition, $\sigma = \sigma^{(1)} = \sigma^{(2)}$, leads to the expression

$$f = \frac{1}{2} \operatorname{Tr}(\sigma e) \tag{28}$$

with tensor relations

$$e = \phi_1 e^{(1)} + \phi_2 e^{(2)}, \tag{29}$$

$$\sigma = E e, \tag{30}$$

where the inverse of the four-rank tensor E is given by

$$E^{-1} = \phi_1 \left[E^{(1)}\right]^{-1} + \phi_2 \left[E^{(2)}\right]^{-1}. \tag{31}$$

Equations (29) and (31) are rules of mixtures of composite materials in *tensor forms*. Note that the conventional rules of mixtures of composite materials have been constructed from the anisotropic slab model and they are for a specific component of a tensor [3].

If the model is isotropic and incompressible, eq. (30) reduces to $\sigma_{ij} = \mu e_{ij}$, where μ is a scalar modulus, and eqs. (28) and (31) reduce to eqs. (3) and (4) under the interpretation $\operatorname{Tr} e^2 \sim e^2$, etc.

Discussion. – 1) Physical interpretation of toughness.

The enhanced toughness in the double elastic network comes from a cut-off factor ξ/a_i and/or a modulus factor $\mu_\mathrm{h}/\mu_\mathrm{s}$, in addition to the volume fraction ϕ_i. This situation makes a good contrast with our previous treatment of nacre in that the analytical dependence on these parameters is not the same [1].

The cut-off factor ξ/a_h, for example, in eq. (16), can be understood as reduction (or cut-off) of the stress concentration (stress concentration occurs only for *sharp* cracks). Even when the second network is absent, we can expect this factor: *the meshed structure strengthens toughness* if the fracture size is larger than the largest mesh size. Note that this cut-off factor appears under either the equal-stress or equal-strain condition.

The modulus factor μ_h/μ with ϕ_s in eq. (16) suggests that a large extra work is required to attain the same stress-strain state for the hard network when combined with the soft network, which implies a larger work of fracture for the composite; when the stress is applied to the two networks, the soft network stores larger amount of energy ($\sigma^2/\mu_\mathrm{s} \gg \sigma^2/\mu_\mathrm{h}$ when $\mu_\mathrm{h} \gg \mu_\mathrm{s}$). The modulus factor $\mu_\mathrm{h}/\mu_\mathrm{s}$ with ϕ_h in eq. (22) has a meaning different from this; failure is judged not by the stress but by the strain, and the strain threshold can be large: an extra large elastic energy due to the hard network is required.

The failure criterion invoked in this article, for example to derive eq. (15), comes from the matching of a macroscopic continuum stress $\sigma(r)$, which is valid only down to $r \sim \xi$, with a semi-macroscopic stress σ_{h}, which is valid only up to $r \sim \xi$, at the moment of failure at the mesh size. This is similar in spirit to the criterion first employed in (a) of [1]; there we balanced a macroscopic stress with an inherent failure stress of an aragonite plate at the cut-off length.

2) Equal-stress and equal-strain assumptions.

When the composite is pulled in one direction it is compressed in perpendicular directions to preserve the volume, and then the compression may tend to adjust two networks to keep the equal stress for the two networks at the cost of strain mismatch. This consideration is in favor of the equal-stress condition. On the other hand, we can think of other factors favorable to the equal-stress approximation. Detailed structures behind the simplified view in fig. 1 may determine a certain stress-strain state (equal-strain, equal-stress or other states). Specific cases will be discussed elsewhere.

3) Comparison with real double-network gels.

The experimental data given in [2] demonstrate that both networks are highly *nonlinear* even from an elastic point of view, and there viscoelasticity may come into play. In addition, we should be careful with how to map or coarse-grain hydrogel networks to the present model. Depending on the real interpenetrated structure, one may or may not consider the water volume fraction, $1 - \phi_{\mathrm{h}} - \phi_{\mathrm{s}}$, explicitly and associate μ_i with a single chain or with a locally developed hydrogel (chains + water). These points require a separate work.

Conclusion. – We constructed the minimum theory for isotropic composites comprising of soft and hard elastomers, including particle-reinforced materials in the two limiting situations: equal-strain and equal-stress conditions. We obtain expressions for the toughness enhancement factor in various situations, which provide guiding principles to develop strong composite materials. We find that, in general, the ratio of the two elastic moduli and the mesh sizes, in addition to the volume fraction of each element, are especially important in controlling toughness. Our result implies also that even a meshed structure possesses a larger fracture energy than the non-meshed counterpart when the crack size is larger than ξ; this particular result does not depend on the equal-stress or equal-strain condition.

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