Graded cross-links for stronger nanomaterials

Cross-links are nowadays recognized to play a key role in the overall mechanical strength of buckypapers, nanotube or graphene based materials; material scientists or chemists are thus developing new nanomaterials with denser and stronger cross-links in order to maximize their mechanical strength. However, in spite of some fascinating achievements of material science and chemistry today, we are evidently far from an optimal result; the reported mechanical strength of a buckypaper, for example, is comparable to that of a classical sheet of paper. In this concept article we try to solve the paradox showing that the cross-link stiffness, a parameter still ignored in the literature, governs (more than its strength) the overall mechanical strength. New strategies for the experimentalists, e.g. the use of graded cross-links, are consequently suggested.

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An explosion of interest in the scaling-up of buckypapers, nanotube bundles and graphene sheets is taking place in contemporary material science. If nanostructures are mainly useful as electronic components insofar as, they can be assembled (or well dispersed in a matrix) in order to produce new strong materials and structures. Recently, macroscopic buckypapers[1-5], nanotube bundles[5-12] and graphene sheets[13-16] have been realized. In spite of these fascinating achievements of the contemporary material science and chemistry we are evidently far from an optimal result. The reported mechanical strength of buckypapers and graphene sheets, for example, are comparable to that of a classical sheet of paper, see Fig. 1, and macroscopic nanotube bundles have a strength still comparable to that of steel. Why? Can the scaling-up frustration be mitigated? How?

Regarding the first question three answers are possible. The first is that in the scaling-up procedure the probability of introducing

ISSN:1369 7021 © Elsevier Ltd 2010

Fig. 1 A buckypaper over a sheet of paper, which is the strongest? Buckypaper produced at the Florida State University by the Kroto group, courtesy of Nobel Laureate H. Kroto (Picture taken by M. C. Alessio).

defects in nanotubes or graphene sheets is also scaled-up, and since the strength is dictated by the most critical (often the largest) defect, larger is necessarily weaker[17]. Even if this argument can be invoked to justify the observed strength of nanotube bundles[18,19], it is alone insufficient for quantitatively justifying the weakness of bukypapers or graphene sheet composites. The second possibility is that the weakest link is the most critical cross-link; cross-links are in fact needed for load transfer between different nanotubes or sheets, or as interconnections with a matrix in a composite. This scenario could quantitatively explain the observations. The third and last possibility is intermediate, even if substantially similar to the previous one, i.e. that the weakest link is at the interface between the cross-link and the related nanotube or sheet, or matrix. Material scientists and chemists are aware of the "weakest-cross-link" concept and are adopting new techniques for increasing the number and strength of the cross-links[4]. But how we can optimize them?

In order to transfer the load between nanotubes, e.g. in bundles, buckypapers or nanocomposites, nanotubes must be functionalized by cross-links. The strength of the connection is related to the strength and number of the involved cross-links, but also and especially to their stiffness, a parameter still ignored in this context. To convince the reader, we have calculated the exact force distribution, according to discrete elasticity, in a given number of cross-links, placed at different locations and having different stiffness. The calculation demonstrates that the force distribution can be very inhomogeneous: the maximum transmissible total force is thus much lower than the breaking force of a single cross-link times their number; this result is fully intuitive. More importantly and less intuitively, in order to increase the total transmissible force, an optimal distribution of their location/stiffness emerges (including the limiting case of infinitely compliant cross-links).

The results of our analysis could be useful for maximizing the load transfer between functionalized nanotubes or graphene sheets, e.g. in bundles, buckypapers or nanocomposites, or to predict their strength and breakage mechanisms, including the stability of the process, and thus suggest new experimental strategies for producing stronger nanomaterials.

Optimized graded cross-links

To make a complex problem simple, let us consider the scheme reported in Fig. 2. A force F is applied at one nanotube end and is transmitted to the substrate/matrix by cross-links; each of these is defined by the relative position z_i, the distance from the next cross-link, and by the shear stiffness k_i. What are the unknown forces X_i transmitted by the cross-link chain? The exact elastic solution can be determined assuming a constitutive law for the nanotube. Here we assume, as experimentally well documented for nanotubes, linear elasticity. The nanotube cross-sectional area is A and its Young's modulus is E. The key for solving the problem is imposing the compatibility of the displacements. In order words, imagine that we remove the cross-links and in their stead impose on the nanotube the unknown forces X_i. The forces X_i result in an elastic axial displacement of the nanotube; the displacements of the points of the nanotube where we had the cross-links must be equal (compatible) with the elastic displacements $-X_i/k_i$ of the related cross-links (since nanotube and cross-links are in contact without sliding). To produce a more compact system of linear algebraic equations we equivalently impose the compatibility of the increment in length Δz_i of each nanotube segment, between two adjacent cross-links. Accordingly, the following equations must hold:

$$\frac{z_i}{EA}\left(F-\sum_{j=1}^{i}X_j\right)=\frac{X_i}{k_i}-\frac{X_{i+1}}{k_{i+1}}, \quad i=1,\ldots,N-1 \qquad (1)$$

or, equivalently:

$$\sum_{j=1}^{i}X_j+c_iX_i-\lambda_{i+1}c_{i+1}X_{i+1}=F, \quad c_i=\frac{EA}{z_ik_i}, \quad \lambda_i=\frac{z_i}{z_{i-1}} \qquad (2)$$

where N is the number of cross-links. The missing equation is the equilibrium equation:

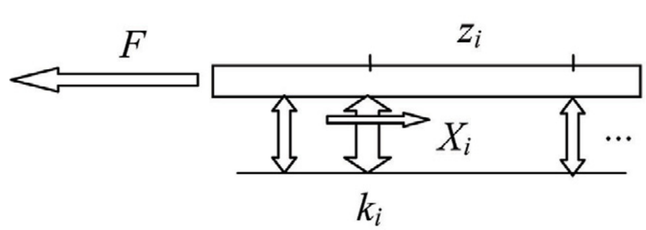

Fig. 2 Load transfer by cross-links between a single stretched nanotube and a substrate/matrix.

$$\sum_{j=1}^{N} X_j = F \tag{3}$$

Thus, the problem can be formulated as:

$$[K]\{X\}=\{F\} \tag{4}$$

where:

$$[K]=\begin{bmatrix} 1+c_1 & -\lambda_2 c_2 & 0 & 0 & 0 & 0 & 0 & \dots & \dots & 0 \\ 1 & 1+c_2 & -\lambda_3 c_3 & 0 & 0 & 0 & 0 & \dots & \dots & 0 \\ 1 & 1 & 1+c_3 & -\lambda_4 c_4 & 0 & 0 & 0 & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & 1 & 1 & 1 & \dots & 1+c_i & -\lambda_{i+i} c_{i+1} & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & \dots & 1+c_{N-1} & -\lambda_N c_N \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & \dots & 1 & 1 \end{bmatrix}$$

$$\{X\}_i = X_i$$

$$\{F\}_i = F$$

and admits the following solution for the forces transmitted by the cross-links:

$$\{X\} = [K]^{-1}\{F\} \tag{5}$$

The failure of the cross-links takes place for an external force $F_c \le Nf$, where f is the mean cross-link strength, when in the most solicited cross-link a force equal to its strength f_i is reached, namely:

$$F_c\text{: } \max|X_i| = f_i \tag{6}$$

The evolution and stability of the chain breakage mechanism could be analyzed by setting to zero the stiffness of the most solicited (now broken) cross-link and repeating the analysis up to the failure of the last cross-link.

The forces X_i in the cross-links are in general different, thus the load transfer is not optimized. In order to optimize it, we impose in the compatibility equations the optimal force distribution $X_i = F/N$ (trivially deduced from $X_i = const$ in the equilibrium equation). We accordingly derive the following general condition for the optimal load transfer:

$$c_i - \lambda_{i+1} c_{i+1} = N - i \tag{7}$$

which physically corresponds, for uniformly spaced cross-links ($\lambda_i = 1$), to having relative compliances c_i decreasing in subsequent cross-links ($\Delta c = c_{i+1} - c_i = i - N < 0$) or, equivalently, for identical cross-links ($c_i = c$) to have a decreasing spacing ($\lambda_i \equiv \frac{z_i}{z_{i-1}} = 1 - \frac{N-i}{c} < 1$). Note that the optimal condition of eq. (7) mathematically includes the case of perfectly compliant cross-links ($c_i = \infty$).

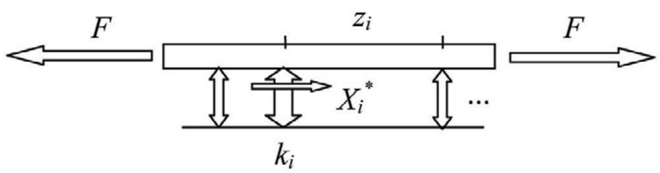

Fig. 3 Load transfer by cross-links between a doubly stretched nanotube and a substrate/matrix.

The developed procedure can be straightforwardly extended for the case of two opposite forces F applied at both the nanotube ends, Fig. 3; in fact, the linearity of the problem allow us to invoke the superposition principle; thus, thanks to the symmetry of the geometry, the forces X_i^* in the cross-links would be:

$$X_i^* = X_i - X_{N+1-i} \tag{8}$$

(where X_i denote the solution of the previous problem, Fig. 2).

We can also treat soft substrates, e.g. for modelling the interaction between different nanotubes in a network. For such a case, the shear stiffness of the cross-link k_i must be formally substituted with the equivalent shear stiffness k_i^* of the cross-link/substrate system, according to:

$$\frac{1}{k_i^*} = \frac{1}{k_i} + \frac{1}{K_i} \tag{9}$$

in which K_i is the shear stiffness of the substrate at the position of the cross-link i.†

The two discussed modifications can be directly coupled, considering both X^*_i and k^*_i, e.g. for modelling a stretched nanotube network.

† For example, if the upper nanotube is attached by the cross-link i to the middle position of an orthogonal bent nanotube segment of length y_i, we have $K_i = \alpha EI/y_i^3$, where I is the moment of inertia of the lower nanotube (having Young's modulus E) and α is a geometrical constant (e.g. 48 for clamped-like junctions). Accordingly, for a nanotube network having mails of size $z_i \times y_i$, the previous analysis has to be applied substituting c_i with $c_i^* = c_i + \alpha s_i^2$, where s_i is the slenderness of the mail, defined as $s_i = Az_i^3/(Iy_i)$.

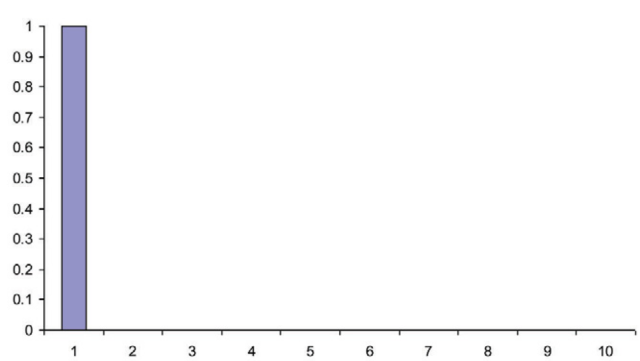

Fig. 4 Forces X_i in the cross-links $i = 1 - 10$, for $\lambda_i = 1$ (constant spacing) and $c_i = 0$ (perfectly rigid cross-links). Only the first cross-link is solicited and the failure force is minimal and equal to $F_c = f$.

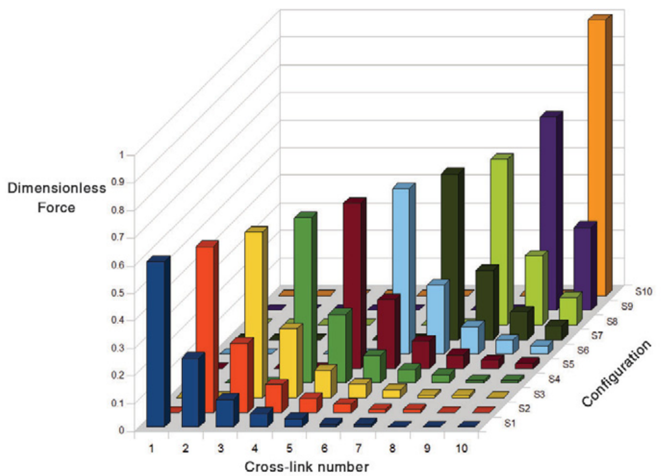

Fig. 5 Dimensionless forces X_i in the cross-links $i = 1 - 10$, for $\lambda_i = 1$ (constant spacing) and $c_i = 1$ (rigid cross-links). All 10 cross-links are solicited in the configuration S1, and the maximum transmissible load is $F_c \approx 1.67f$. Then, cross-link 1 is broken ($c_1 = \infty$) and a new force distribution takes place, see configuration S2, and so on up to configuration S10, where only the last cross-link is surviving and the transmissible load is $F_c = f$. As can be easily evinced, the breakage propagation is here weakly unstable up to the failure of cross-link n. 8 and then becomes abruptly unstable.

A case study is numerically treated in Figs. 4-7, considering N=10, F=1 and $f_i = f$, for the basic scheme of Fig. 2. Note that the related force-displacement curves could be easily generated. Fig. 4 shows that, for perfectly rigid cross-links, only the first one is solicited, resulting in the worst load transfer and thus minimal failure force ($F_c = f$). Fig. 5 (configuration S1, rigid cross-links, $F_c \approx 1.67\,f$) and Figure 6 (compliant cross-links, $F_c \approx 3.33f$) show that the force distribution is decreasing in subsequent cross-links. The breakage mechanics is also analysed in Fig. 5, resulting in an initially weakly and then abruptly unstable global failure. Fig. 7 shows the best load transfer, in optimized cross-links; they carry the same force, the failure force is maximal (theoretical value $F_c = 10f$) and the process is metastable.‡

‡ It is clear that the chain failure could also be stable. For example, considering a chain composed of M perfectly rigid cross-links and subsequently $N-M$ perfectly compliant ones, would occur at a force $F = f$ for the first M cross-links; in order to reach the global failure we must increase the force up to a value of $F_c = (N - M)f$. Also, an intermediate cross-link and not just the first one, e.g. with a large intrinsic strength f_i, could break.

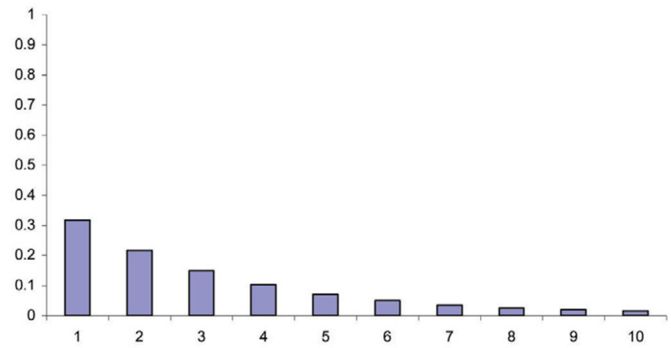

Fig. 6 Forces X_i in the cross-links $i = 1 - 10$, for $\lambda_i = 1$ (constant spacing) and $c_i = 10$ (compliant cross-links). A more uniform distribution is achieved and the maximum transmissible load is $F_c \approx 3.33f$. The chain breakage mechanisms is similar to that discussed in Figs. 5.

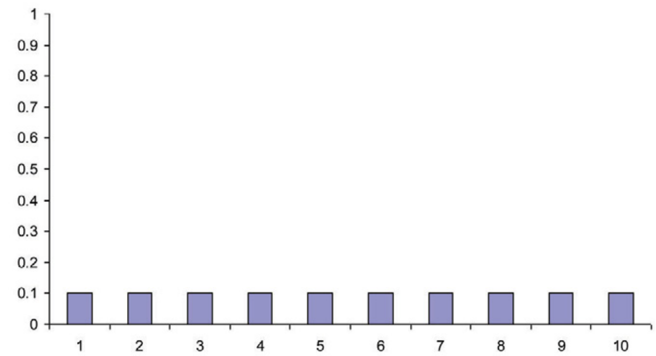

Fig. 7 Forces X_i in the cross-links $i = 1 - 10$, for optimized cross-link (graded solution, eq. (7)). A perfectly uniform distribution is achieved and the failure force is maximal, i.e. $F_c = 10f$, corresponding to the metastable failure of the cross-link chain.

Conclusions

The analysis demonstrates the validity of the following bio-inspired concept (biological materials are often graded): functionally grading the cross-links, theoretically (even if the reality is much more complex than our theory) according to eq. (7), e.g. using strong but flexible molecules, will result in stronger nanomaterials also at the macroscopic scale. Graded cross-links are a current challenge of material science and chemistry and could be the solution to our scaling-up frustration. mt

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