Mechanical Properties and Coordinations of Amorphous Carbons

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The elasticity and hardness of *a*-C and *a*-C:H are related to their mean network coordinations. It is shown that sp^2 sites contribute no rigidity if they form graphitic clusters, as suggested by experiment and electronic structure calculations, despite having coordinations above the critical value 2.4. Hence both sp^2 sites and polymeric $=CH_2$ groups can severely lower the hardness of amorphous carbons.

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Amorphous carbon (*a*-C) and hydrogenated amorphous carbon (*a*-C:H) can form low-friction films which are mechanically hard, chemically inert, and infrared transparent [1-5]. These desirable properties derive from the sp^3 or "diamondlike" component of the film's bonding. Nevertheless, the hardness of *a*-C:H presently reaches only $\simeq 15\%$ of that of diamond itself, essentially because it contains 20%–50% sp^2 carbon and 20–60 at.% hydrogen. A theory relating mechanical properties to chemical bonding is therefore of both fundamental and technological interest.

The bonding of *a*-C was analyzed in detail by Robertson and O'Reilly [5], who showed that a mixture of sp^2 and sp^3 carbon sites will tend to segregate into sp^2-bonded graphitic clusters embedded in a sp^3-bonded matrix. The sp^2 clusters were found to control the electronic properties and it is shown here that the connectivity of the sp^3 matrix largely controls the mechanical properties. The mechanical properties are treated by using the constraint-counting model of Phillips [6] and Thorpe [7] to relate network rigidity to the mean network coordination r. This model finds that r must exceed a value of 2.4 for finite rigidity. The model clearly needs modification to treat carbons and to handle anisotropic bonding, in that graphite, whose coordination is 3, is nevertheless soft along $0z$.

The segregation of sp^3 and sp^2 sites arises from the nonlocal energetics of the π bonding of sp^2 sites [3-5]. The energetics of σ and π bonds are separable, to first order. The stronger σ bonds form the network skeleton and their total energy can be expressed as a sum of the energies of individual two-center bonds. Each energy depends on very short-ranged factors such as bond length and bond angle. The total energy of π states cannot, in general, be so expressed; it is nonlocal because π states can form multicenter (resonant) bonds. The total π energy favors sp^2 sites forming planar sixfold aromatic (benzene) rings and their fusing into clusters, preferably compact (graphitic) rather than elongated (acenic). The σ bond energy is indifferent to clustering so, for a given sp^3-to-sp^2 ratio, π bonding favors a segregation of sp^2 sites into relatively compact graphitic clusters surrounded by a sp^3-bonded matrix.

This suggests a two-phase model of amorphous carbons consisting of π-bonded clusters dispersed in a second phase. In evaporated *a*-C the second phase consists of a rim of sp^3 or defect sites around each cluster. In *a*-C:H it is the majority sp^3-bonded phase, which may be either highly crosslinked as in hard forms of *a*-C:H or mainly $=CH_2$ groups as in softer, more polymeric forms of *a*-C:H. The second phase largely determines the mechanical properties, as will now be shown. The relatively small band gap and the resonant Raman and luminescence spectra strongly support the cluster model for *a*-C:H [2,3]. The clustering is substantial; *a*-C:H with, say, 40% sp^2 sites and a gap $E_g = 1.5$ eV would from

$$E_g = 6M^{-1/2}\,\text{eV} \tag{1}$$

contain clusters of up to $M = 16$ rings [5].

We now consider the mechanical properties, beginning with the most tractable, elasticity and Young's modulus. The elasticity of a random network can be related to its coordination by the constraint-counting model of Phillips [6] and Thorpe [7]. These authors considered a covalent network of N atoms obeying a valence force field of first-neighbor bond-stretching and bond-bending forces. At low coordination there are many ways to deform a network at zero energy cost, i.e., leaving bond lengths and angles unchanged. The number of these deformations or zero-frequency vibration modes is given by the number of degrees of freedom ($3N$) minus the number of linearly independent constraints N_{con}. N_{con} depends on coordination r. There is one constraint associated with each bond (shared between two atoms) and $2r-3$ constraints with the angles of each atom giving a total of

$$N_{\text{con}}(r) = \tfrac{5}{2}r - 3 \tag{2}$$

per site, except for monovalent atoms like hydrogen for which $N_{\text{con}}(1) = \frac{1}{2}$. The fraction of zero-frequency modes is then

$$\begin{aligned} f &= \sum x_r f_r = \sum x_r\left[1 - \tfrac{1}{3}N_{\text{con}}(r)\right] \\ &= \sum_{r>1} x_r\left(2 - \tfrac{5}{6}r\right) = 2 - \tfrac{5}{6}\bar{r}, \end{aligned} \tag{3}$$

where x_r is the concentration of r-fold sites and $\bar{r} = \sum x_r r$ is the mean coordination. Equation (3) defines a percolation threshold

$$r_p = 2.4\,, \tag{4}$$

separating underconstrained floppy networks at $r < r_p$ from overconstrained rigid networks at $r > r_p$. He and Thorpe [8] found the Young's modulus E to vary as

$$E = E_0 \left(\frac{-f}{-f_0} \right)^{1.5} = E_0 \left(\frac{r-2.4}{r_0-2.4} \right)^{1.5} \tag{5}$$

for $r > 2.4$, to reach E_0 at r_0, 4 in our case.

Angus and Jansen [9] found that condition (4) for r_p holds for a hydrogen-containing network if r now represents the C−C coordination, by substituting $r \rightarrow r - x_{1,r}/x_r$ in (2) and $x_r \rightarrow x_r/(1-x_1)$ in (3), where $x_{1,r}$ is the concentration of hydrogen-bonded to r-fold sites:

$$f = \sum_{r>1} \frac{(2-\frac{5}{6}r)x_r + \frac{5}{6}x_{1,r}}{1-x_1}\,. \tag{6}$$

This treats each C−H bond as a broken bond contributing no rigidity. Indeed, all pendant groups like $-CH_3$ contribute no network rigidity.

The constraint model must be modified for π bonding. First, a sp^2 site is planar. While its three bond angles define its planarity, only two are needed to constrain in-plane motions; the third is linearly dependent on these. However, these constraints do not oppose motion out of the bonding plane. This requires an extra four-body puckering force, proportional to the displacement of a sp^2 atom out of the plane of its three neighbors. The net effect is to leave $N_{\mathrm{con}}(3)$ unchanged. Second, a π bond between two sp^2 sites is strongest when their π orbitals are parallel. This effect adds torsional rigidity to the bond and $\frac{1}{2}$ constraint per atom, increasing [10] $N_{\mathrm{con}}(3)$ from 4.5 to 5. In larger systems like graphite, π bonding has a resonant character and gives rise to longer-range forces. Nevertheless, the intralayer lattice modes of graphite are described well by nearest-neighbor force models [11]. The puckering forces now maintain planar layers.

The most important modification to constraint counting concerns graphitic clustering. The problem is not clustering *per se*, but the anisotropy of the bonding. The Phillips-Thorpe [6,7] model is a mean-field theory which assumes a network with no medium-range order. He and Thorpe [8] found that E obeys (5) close to r_p, so mean-field theory itself works well. Therefore, there is no need in general to allow for clustering. However, this is not true if the clustering is graphitic. This is because the model assumes bonding to be isotropic at medium range, whereas a graphite layer uses most of its constraints in only two dimensions and is floppy along 0z, despite being trivalent.

Thorpe [7] showed that clustering was unimportant in three dimensions because the relatively low value of r_p, 2.4, means that there are few small closed rings of bonds (clusters) at r_p. However, clustering effects are much more important in two dimensions. N_{con} is now

$$N_{\mathrm{con}} = \tfrac{3}{2}r - 1 - 3F\,, \tag{7}$$

where F is the number of closed rings per site. This term causes any two-dimensional network of bond stretching and bending forces to be internally rigid [7]. Many of the in-plane angular constraints are now linearly dependent or redundant for $r > 2$. Thus, a planar cluster is internally rigid along x-y in three dimensions. Motions along 0z are separable due to planar symmetry, and the puckering forces of a sp^2 cluster make it internally rigid along 0z. Thus a planar internally rigid cluster of N' sites has $3N'-3$ linearly independent constraints, 3 for each site minus 3 translational degrees of freedom. Joining this cluster to the network at N'' perimeter sites increases N_{con} as if it were an N''-fold coordinated site to give

$$N_{\mathrm{con}}(3) = [(3N'-3) + (\tfrac{5}{2}N''-3)]/N' \tag{8}$$

and

$$f_3 = 1 - \tfrac{1}{3}N_{\mathrm{con}} = \frac{2}{N'} - \frac{5N''}{6N'}\,. \tag{9}$$

As $N'' \ll N'$ for compact clusters [$N'' = \pi(N'/2)^{1/2}$ by geometry for large circular clusters and one finds $N'' \simeq 2.5(N')^{1/2}$ by counting for typical compact clusters]

$$f_3 \simeq \frac{2}{N'} - \frac{2.1}{(N')^{1/2}}\,. \tag{10}$$

This shows that clustering has the effect of raising r_p for sp^2 sites and making graphite itself borderline floppy. As clusters tend to be large, we take $N' \rightarrow \infty$ and

$$f_3 \simeq 0 \tag{11}$$

to first order. Also, if the hydrogens bonded to sp^2 sites are spread evenly across a cluster, only those on the perimeter affect network rigidity and their concentration is

$$x'_{1,3} = x_{1,3}(N''/N') \rightarrow 0 \tag{12}$$

as $N' \rightarrow \infty$. Thus (6) finally simplifies to

$$-f \simeq -\frac{x_4}{1-x_1} f_4 = \frac{\frac{4}{3}x_4 - \frac{5}{6}x_{1,4}}{1-x_1}\,. \tag{13}$$

This shows that both the graphitic and polymeric bonding components contribute no network rigidity. Thus in the two-phase model, the network of *a*-C:H consists of graphitic clusters which control the band gap embedded in a sp^3 matrix whose C−C coordination alone controls the rigidity.

The lack of rigidity from graphitic bonding can be confirmed by considering E of glassy carbon (Table I). Its E is seen to be only about $\frac{1}{20}$ of that of the in-plane E of graphite. This is consistent with an E derived only from its interlayer cross-links, occurring every $L_a \simeq 20$ rings apart, the observed in-plane correlation length [3].

The graphitic clustering of sp^2 sites reduces the num-

TABLE I. Comparison of Young's modulus E, Poissons ratio ν, hardness H, and yield stress Y.

	E (GPa)	ν	H (GPa)	Y (GPa)	Reference
Diamond	1050	0.104	103	59	[12,13]
Graphite $\parallel a$	686				[12]
Polythene	0.3		0.03	0.015	
Glassy C, GC20	32	0.17	2.2	0.73	[14,15]
PD a-C:H $V_b=100$ V	143	0.4	17.0	10.6	[16]
PD a-C:H $V_b=1$ kV	55	0.2	6.4	3.1	[16]
MSIB a-C			20–110	12–65	[23]
Si	130	0.278	10.4	5.0	[12,19]
a-Si:1% H	100	0.32	10.0	4.9	[20]

ber of useful constraints in a network. This increases the minimum sp^3 content and r_p needed to form a rigid network, as seen in Fig. 1.

The present model can be tested by considering the Young's modulus of plasma-deposited a-C:H. Its properties depend strongly on deposition parameters such as bias voltage V_b. The material is soft for $V_b < 100$ V due to a high concentration of $=CH_2$ groups. Its H content drops rapidly and its sp^2 content rises gradually with bias (with the substrate negative) so that $\equiv CH$ and $=C=$ groups predominate at intermediate bias and sp^2 sites predominate at high bias. Figure 2 compares the Young's modulus of methane-deposited a-C:H measured by Jiang *et al.* [16] to that calculated from coordination data of a-C:H films deposited under very similar conditions by Tamor, Vassell, and Carduner [17]. Coordinations are very difficult to measure reliably in a-C:H. For instance, coordinations deduced from C—H vibrational bands [18] neglect unhydrogenated sites. Recently, reliable concentrations and hydrogenations of both sp^2 and sp^3 sites have been measured by nuclear magnetic resonance (NMR) [17]. However, the degree of hydrogenation of sp^3 sites (CH_y) is not given by NMR and is taken here to vary as $y=2-0.000857\ V_b$ rather than as $y=2$ as in Tamor [17], so as to give a $\equiv CH/=CH_2$ ratio of 1.5 at $V_b=700$ V as found by infrared [2]. The moduli in Fig. 2 were calculated for both clustered and dispersed sp^2 sites using Eqs. (5), (13), and (6) and $E_0=E$ (diamond). The bias dependence of the coordination data was slightly smoothed to simplify the figure.

The experimental moduli are seen to have a magnitude and bias dependence very similar to those calculated for clustered sp^2 sites. Note that dispersed sp^2 sites give a much higher E than that observed, particularly at high bias where sp^2 contents are highest and clustering most likely. Indeed, the decrease in E at higher biases can only be reproduced if clustering is included. Interestingly, E lies above the clustered limit and towards the

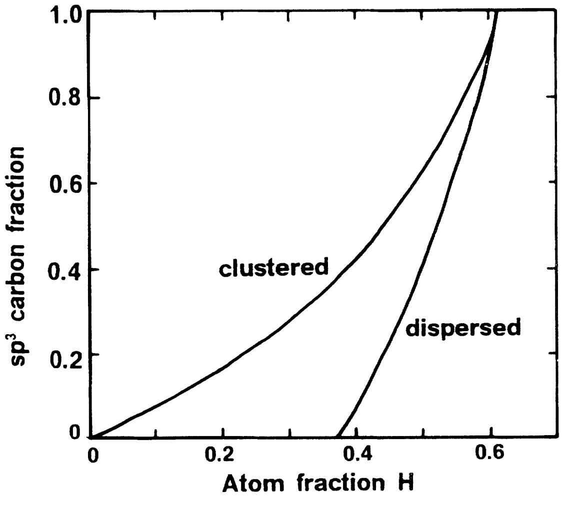

FIG. 1. Comparison of H and sp^3 contents for the critical coordination for network rigidity r_p of a-C:H for clustered and dispersed sp^2 sites.

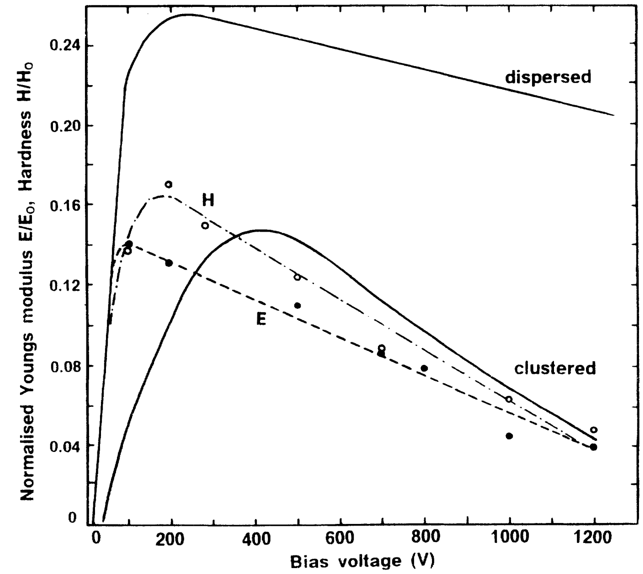

FIG. 2. Young's modulus and hardness of a-C:H after Jiang *et al.* [16] normalized to diamond, compared with those calculated for clustered and dispersed arrangements of sp^2 sites. E and H fall to low values at $V_b=0$ V.

dispersed limit below 200 V where sp^2 contents are lower and clustering is less likely. Overall, the agreement is very satisfactory considering the remaining uncertainties in the coordination data. Indeed, the comparison is probably a sterner test of the coordination data than of our model, e.g., retaining $y=2$ at 1000 V reduces E/E_0 from 0.069 to 0.022 for clustered sites.

The moduli for $V_b=100$ V and 1 kV films in Table I can be used with (5) to deduce C—C coordinations of $r=2.83$ and 2.63, respectively. These coordinations are well below the ideal value of 4 but well above $r_p=2.4$. Angus and Hayman [1] argued that the H and sp^2 contents of a-C:H vary during deposition to give $\bar{r}\simeq r_p$, as this allows the energy gain from increased bond density to balance the higher network strain energy. Our analysis emphasizes that coordinations must exceed r_p to give a finite rigidity and hardness. Luckily, for the sake of forming hard carbons, they do. Nevertheless, the low E of a-C:H compared to that of diamond serves to emphasize that its C—C coordination is relatively low, whereas E of fully tetrahedral a-Si:H are close to those of c-Si [20].

Hardness is the parameter of most technical interest in diamondlike carbons. It is measured by indentation and we restrict interest to data in which the indent depth is much less than the film thickness. It is empirically related to the yield stress Y by [21,22]

$$H/Y\simeq 0.07+0.6\ln(E/Y)\simeq -0.04+0.77\ln(E/H)\simeq 1.8 \tag{14}$$

for materials with low E/Y ratios like diamond and a-C:H (much lower than $H/Y=3$ typically used for metals). The form of this equation is supported by continuum elasticity theory for an indent [21].

The yield stress of a metal is controlled by dislocation flow, but it is close to the cleavage stress for covalent materials in which dislocation flow is very difficult, like diamond and a-C:H. The cleavage stress is the stress needed to separate two adjacent planes of atoms of the solid. This can be related to the Young's modulus by the Orowan approximation taking the interplanar force as a sine function and equating E to the initial slope to give [12] $Y\simeq E/\pi$. However, Table I shows that a factor of 6 gives a better fit for diamond so, with (14), this gives

$$H/E\simeq 0.1\,. \tag{15}$$

Hardness data for a-C:H follow Eq. (15) quite well, as seen in Table I and Fig. 2 where the normalized H and E have a similar bias dependence. Hence the present theory can describe the elasticity and hardness of a-C:H in terms of its network coordination using parameters taken only from diamond. Hardnesses have also been measured for a-C deposited from mass-selected ion beams. They reach values similar to that of diamond [23], consistent with the high sp^3 content of this material [24] and showing that techniques do exist for preparing a-C with hardness close to that of diamond.

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