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## Reinforcement of rubber by fractal aggregates

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**Résumé.** — On renforce souvent le caoutchouc avec des agrégats de carbone ou de silice dont la structure a l'invariance par dilatation d'un objet fractal. Les caoutchoucs ainsi renforcés supportent de grandes contraintes qui croissent souvent plus vite que l'élongation. Nous prétendons que, sous élongation forte, cette contrainte apparaît à cause d'une compression latérale des agrégats induite par le module *volumique* important du caoutchouc. Nous établissons une loi de puissance reliant la contrainte et l'élongation  $\lambda$  quand  $\lambda \gg 1$ . Cet exposant  $p$  dépend de la dimension fractale  $D$  et d'un deuxième exposant structural  $C$ . Pour des agrégats dont la cinétique de formation est limitée par diffusion,  $p$  vaut entre 0,9 et 1,1. Si la cinétique est limitée par le soudage local des particules,  $p$  vaut entre 1,8 et 2,4. Sous compression uniaxiale, les puissances homologues valent environ 4. Des caoutchoucs pratiques chargés de tels agrégats devraient approcher des conditions où ces lois d'échelle sont valables.

**Abstract.** — Rubber is commonly reinforced with colloidal aggregates of carbon or silica, whose structure has the scale invariance of a fractal object. Reinforced rubbers support large stresses, which often grow faster than linearly with the strain. We argue that under strong elongation the stress arises through lateral compression of the aggregates, driven by the large *bulk* modulus of the rubber. We derive a power-law relationship between stress and elongation  $\lambda$  when  $\lambda \gg 1$ . The predicted power  $p$  depends on the fractal dimension  $D$  and a second structural scaling exponent  $C$ . For diffusion-controlled aggregates this power  $p$  should lie between 0.9 and 1.1; for reaction-controlled aggregates  $p$  should lie between 1.8 and 2.4. For uniaxial *compression* the analogous powers lie near 4. Practical rubbers filled with fractal aggregates should approach the conditions of validity for these scaling laws.

### Introduction.

It has long been recognized that particulate filler material is more effective in reinforcing rubber when the particles are aggregated or « structured » rather than dispersed [1, 2]. Thus e.g. the stiffness conferred by a given mass of filler is greater when that filler is aggregated. This effect has come to be understood in terms of the « hydrodynamic » point of view, in analogy with the effect of a particulate solute on the viscosity of a suspension [3]. In this picture the anomalous increase in modulus arises from the « occluded rubber » within each

aggregate [4]. This rubber is prevented by the surrounding aggregate from participating in the stress outside it ; as a result strain is concentrated outside each aggregate. The local strain outside the aggregates is amplified beyond the overall average strain ; the result is an increased measured modulus. Nielsen explored the effect of structure in a pioneering study using macroscopic sintered glass beads [5].

However, the most important effects of structured filler occur at large strains : the filler adds substantially to the tearing energy and failure stress ; it can also increase the elongation at break [1]. The composite supports stresses significantly larger than the breaking stress of the rubber. The occluded-rubber picture does not explain this strengthening phenomenon. Instead, it suggests that stress amplification in the non-occluded rubber just outside the aggregates should result in a *reduced* breaking stress. To account for how structured fillers strengthen rubber is thus an important unsolved problem. It seems clear that the deformability of the filler structure plays a crucial role in the strength of the composites, though this deformability is not central to the occluded rubber picture.

In the last decade it has been learned that the random structure within many colloidal aggregates is in fact subject to strong statistical constraints [6, 7] like those that control flexible polymers. When large aggregates are produced under limiting diffusion-controlled or reaction-controlled conditions, the structure that results is that of a tenuous, scale-invariant fractal [7], as shown in figure 1. The size  $R$  of such structures is related to the number of primary particles  $N$  in the structure and to the primary particle size  $a$  through a power law :

$$N \sim (R/a)^D . \quad (1)$$

The « fractal dimension »  $D$  is roughly 1.7 for diffusion-controlled aggregates and 2.1 for reaction-controlled aggregates, independent of the aggregating species and of quantitative

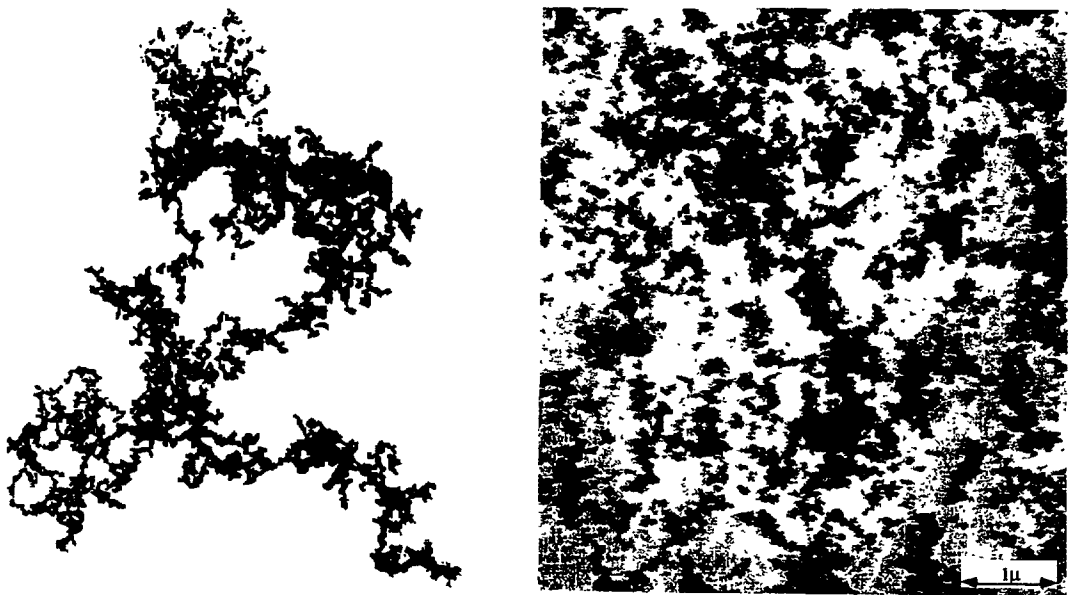


Fig. 1. — Left : Transmission electron micrograph of aggregated particles of colloidal silica, after reference [6]. Aggregates such as this were measured in several ways in order to establish the fractal properties cited in the text. Primary particles are roughly 100 Å in diameter right : A reinforced rubber used for tire treads, after reference [12].

reaction conditions [8, 7]. These aggregates are believed to be branched structures [9], with an essentially unique connecting path between any two particles.

These connecting paths themselves appear to obey fractal scaling laws : two particles at geometric distance  $R$  within an aggregate are connected by a path of length  $L$  containing, on average,  $L/a$  particles :

$$L/a \approx (R/a)^C \quad (2)$$

The « connectivity exponent »  $C$  is roughly 1.26 for diffusion-controlled aggregates [10] and is close to 1 for reaction-controlled aggregates [11]. This exponent is variously denoted as  $d_{mn}$  and  $d_{chem}$  in the literature.

Knowledge of these exponents permits us to expand the notion of occluded rubber in a useful way. It has been shown [13] that these aggregates behave hydrodynamically like hard spheres with radii of order  $R$ . Thus the viscosity  $\eta$  of a small volume fraction of aggregates  $\phi$  in a solvent with viscosity  $\eta_s$  is given by

$$\eta = \eta_s(1 + [\eta] \phi + \mathcal{O}(\phi^2)), \quad (3)$$

where  $[\eta] \sim R^3/N \sim R^{3-D}$ . The intrinsic viscosity  $[\eta]$  thus becomes indefinitely larger than 2.5, its value for solid spheres [14]. The modulus of a rubber with a small volume fraction of filler can be expanded in the same way :

$$G = G_0(1 + [G] \phi + \mathcal{O}(\phi^2)), \quad (4)$$

where  $G_0$  is the modulus of the rubber. The intrinsic modulus  $[G]$  must be numerically equal to  $[\eta]$  if the aggregates are sufficiently rigid [3]. (The Stokes equation describing incompressible flow around any object is the same as the equation for equilibrium of an incompressible elastic medium around the same object.)

In practice the aggregates are not infinitely rigid ; indeed, the larger an aggregate grows the less rigid it becomes [15]. Also in practice, aggregates are used in volume fractions far beyond the regime of validity of perturbation equations like equation (4). Under real conditions [16] the aggregates increase the modulus several fold, and the dependence on volume fraction is much stronger than that of equation (4) [16, 17, 11]. Moreover, the dependence of stress on strain is seen to change with the addition of filler [18], as shown in figure 2, curves A and B. The reinforced rubber (like the unfilled rubber) shows a broad regime of upward curvature on the stress-strain plot. This strain-stiffening property is potentially desirable in reducing mechanical failure ; defects in such a material should be less effective in concentrating stress as compared with unfilled material. For contrast, curve C gives an example of a non-reinforcing filler.

In this paper we investigate the origin of this stress-strain characteristic by considering large uniaxial strain in rubber filled with rigid fractal aggregates. The analogous strong-stretching regime of polymer gels was discussed recently by Rabin [9]. In gels, the stress is entirely entropic in origin, whereas for rigid fractals the stress results from solid deformation of the aggregates. In gels the single scaling exponent  $D$  suffices to explain the stress-strain properties ; for branched aggregates a second exponent  $C$  is needed. We find that the rubber matrix may increase the expected stress qualitatively relative to that expected for the aggregates without rubber, even though its shear modulus is much smaller than that of the aggregates. We argue that the aggregates are not deformed affinely along with macroscopic dimensions, but elongate less than the sample as a whole. Then, in uniaxial tension the elastic energy in the aggregates is stored chiefly through lateral compression.

We begin by discussing linear elasticity in aggregate-filled rubbers, describing how strain in

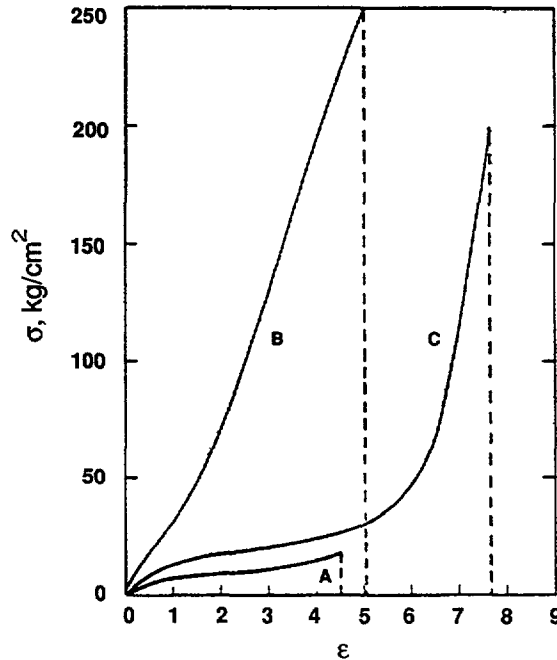


Fig. 2. — Schematic stress-strain curves of an amorphous rubber reinforced with various fillers, redrawn from reference [18]. Elongation factor  $\lambda$  is  $\varepsilon + 1$ . Curve A represents an unfilled vulcanizate of an amorphous rubber. Curve B represents the same rubber reinforced with a highly reinforcing, strongly bonded carbon black. Curve C is characteristic of partially graphitized carbon black, a small-particle, weakly-bonded filler.

the aggregates produces stress in the composite. We then consider conditions of strong elongation and of uniaxial compression and explain why the power-law stress is expected. Finally, we discuss the relevance of our predictions to experiments.

### Linear elasticity.

**RIGIDITY.** — We consider aggregates like those of figure 1 imbedded in rubber. We may treat the rubber as a uniform elastic substance of shear modulus  $G_0$ . This modulus arises from the entropic elasticity of the polymers and is thus much smaller than the bulk modulus. In what follows we shall treat the rubber and the aggregates as incompressible. We shall also assume for simplicity that the rubber completely fills the space around the aggregates, and remains well bonded to the aggregates upon deformation [20]. The equality between the intrinsic modulus [ $G$ ] and the intrinsic viscosity [ $\eta$ ] holds only if the aggregates are sufficiently rigid. The tenuous arms of the aggregate bend slightly in response to the stress. Their response depends on the typical diameter  $a$  of the aggregate arms and on the modulus  $E$  of the aggregate material. The longest arms (of length  $L$ ) will bend the most, with strain  $\gamma_A$ . The elastic energy stored in the aggregate resides chiefly in the few longest arms whose size is of order  $R$  [15]. The arms bend like curved rods of length  $L$  and diameter  $a$ . The well-known equation [21] for the energy stored in a curved rod under an applied force gives the energy  $U_A$  of an aggregate :

$$U_A \sim Ea^3 \frac{a}{L} \gamma_A^2. \quad (5)$$

The modulus  $G_A$  of an aggregate of radius  $R$  is the energy stored per unit volume upon unit strain ( $\gamma_A = 1$ )

$$G_A \approx E (a/R)^3 a/L \approx E (a/R)^{3+C}, \quad (6)$$

where we have used the dependence of arm length  $L$  on aggregate size  $R$  (Eq. (2)). At equilibrium, the stress in the aggregate and in the surrounding rubber should be equal

$$G_A \gamma_A = G_0 \gamma_0,$$

where  $\gamma_0$  is the strain in the rubber. For small aggregates ( $R/a$  small) made out of high modulus material ( $E$  large), the modulus of the aggregate can be much larger than that of rubber  $G_A \gg G_0$ , and then the deformation of the aggregate is small  $\gamma_A \ll \gamma_0$ . The elastic energy is stored primarily in the rubber outside such rigid aggregates

$$U_R \approx G_0 R^3 \gamma_0^2 \gg U_A.$$

The energies stored in the rubber and in the aggregate become comparable  $U_R \approx U_A$  when the effective modulus of the aggregate  $G_A$  is comparable to that of the rubber  $G_0$ .

$$G_0 \approx E (a/R)^{3+C}$$

The aggregates deform substantially when their size  $R$  exceeds a rigidity scale

$$\xi_r \approx a (E/G_0)^{1/(3+C)} \quad (7)$$

Aggregates larger than this scale are relatively ineffective at stiffening the composite, since these would be elastically weaker than the rubber. We shall assume from now on that the aggregates are rigid in the sense  $R \ll \xi_r$ . In the discussion section we shall explore the practical limits of this rigidity.

**AGGREGATE INTERACTION.** — At a volume fraction of order  $\phi^* \equiv [G]^{-1} \approx (R/a)^{D-3}$  the aggregates come into contact: their distance of closest approach becomes much smaller than the typical size of aggregate-free regions [22]. For volume fractions somewhat above  $\phi^*$  stress is transmitted directly by contacts between the aggregates rather than through the rubber. Assuming that the aggregates are well connected by such contacts, these must have a deformation  $\gamma_A$  of the order of the overall deformation  $\gamma$ . Then the stored energy density is  $G_A \gamma^2$ . Since the aggregates are rigid (i.e.,  $R \ll \xi_r$ ), the effective modulus  $G_A$  far exceeds the rubber modulus  $G_0$ . The vast majority of elastic energy is therefore stored in the bending of the aggregates. Thus the modulus  $G$  of the composite is essentially that of the aggregates  $G_A$ . We expect the composite modulus to increase rapidly with aggregate concentration in the vicinity of  $\phi^*$ , from the low levels of order  $G_0$  predicted by equation (4) to the high modulus  $G_A$  of equation (6). This rapid crossover can be described by a percolation model [21]. Above  $\phi^*$  the longest arms of a typical aggregate are pushed up against those of its neighbors. These pressures deflect neighboring arms and allow the aggregate density to increase.

By applying sufficient pressure to a network of aggregates (before cross-linking the rubber) one may increase their concentration far beyond  $\phi^*$ . Then the aggregates must either interpenetrate, compress upon themselves, or break into smaller pieces. For any given  $\phi$  there is a corresponding size  $\xi$  such that aggregates of size  $\xi$  would be just contacting each other and have  $\phi = \phi^*(\xi)$ . In other words

$$\phi \approx (\xi/a)^{D-3} \quad (8)$$

effectively defines  $\xi$ . The situation is perfectly analogous to polymer solutions, where  $\xi$  is called the « blob size » or correlation length [24]. On length scales larger than  $\xi$  the composite is a homogeneous solid which transmits stress uniformly. On length scales smaller than  $\xi$  a given piece of aggregate is only slightly perturbed by neighboring pieces. The modulus is therefore the same as the modulus just above  $\phi^*$ , as given in equation (6) :

$$G = E (a/\xi)^{3+C} = E \phi^{(3+C)\nu(3-D)} \equiv G_{BB} , \quad (9)$$

This formula was previously derived by Ball and Brown [11] in the context of flocculated aggregates. Henceforth we will refer to this Ball-Brown modulus as  $G_{BB}$ . Equation (9) predicts  $G \sim \phi^{3.3}$  for diffusion-controlled aggregates and  $G \sim \phi^{4.4}$  for reaction-controlled aggregates. It appears to account well for their elasticity, as described in the discussion section [17, 16, 25].

### Strong extension.

We have seen that one may readily account for the work to compress aggregates uniformly. The situation is more complicated in an aggregate-filled rubber under tension. In order to show the essential features, we focus on an extreme limiting case. We consider a rubber matrix that retains its linear elasticity for arbitrarily large deformations. We also imagine that the aggregates are very tenuous, and assume that they may be described by a fixed material modulus  $E$ , even for large deformations. We wish to consider the regime where the effective modulus  $G_{BB}$  (Eq. (9)) dominates the rubber modulus  $G_0$ .  $G_{BB} \gg G_0$ . This requirement restricts how tenuous the aggregates can be in practice. These conditions are experimentally attainable, but they are only approximately satisfied in typical aggregate-filled rubbers, as explained in the discussion section.

To maintain constant volume under strong extension, by factor  $\lambda$ , the sample must contract laterally by a factor  $\lambda^{1/2}$ . The volume does not change because the bulk modulus of the rubber dominates the other moduli in the system, including  $G_{BB}$ . In order to find the energy stored by the aggregates under strong extensions, we must know how they deform. A given aggregate is subjected to tensile stress along the extension direction and to compressional stress in the other two directions. Below we analyze both tension and compression and argue that, in a typical composite, the compressional stress plays the dominant role.

AGGREGATES UNDER TENSION. — The undeformed state is as described above : the strongly overlapping aggregates may be regarded as a set of densely packed blobs of size  $\xi_0$ . Four of these blobs are shown in figure 3a. It is useful to define the strain energy  $W(\xi_0)$  of a blob under unit strain. Evidently,

$$W(\xi_0) = G_{BB} \xi_0^3 \simeq E a^3 (a/\xi_0)^C \simeq E a^3 \phi^{C/(3-D)} \quad (10)$$

As a blobs becomes smaller the stiffness of the aggregate within it increases and the strain energy becomes larger. The stress is transmitted across the system through the backbones of the aggregates and through the contacts between these backbones. The behavior of the filled rubber depends on what happens with these contacts upon application of strong stress. For the moment we assume that the blobs are well bonded together, so that the contacts between their backbones survive even large tension. Since the bulk modulus of the rubber is very large, the density of the aggregates does not change ; the side branches are not compressed together. We assume that these side branches bear negligible stress. Thus the energy of deformation is mainly stored in the spanning arms of the blobs. We may readily estimate this energy upon elongation of the system by factor  $\lambda$ . The overall length of a spanning arm  $L \simeq a (\xi_0/a)^C$  is not changed by the deformation.

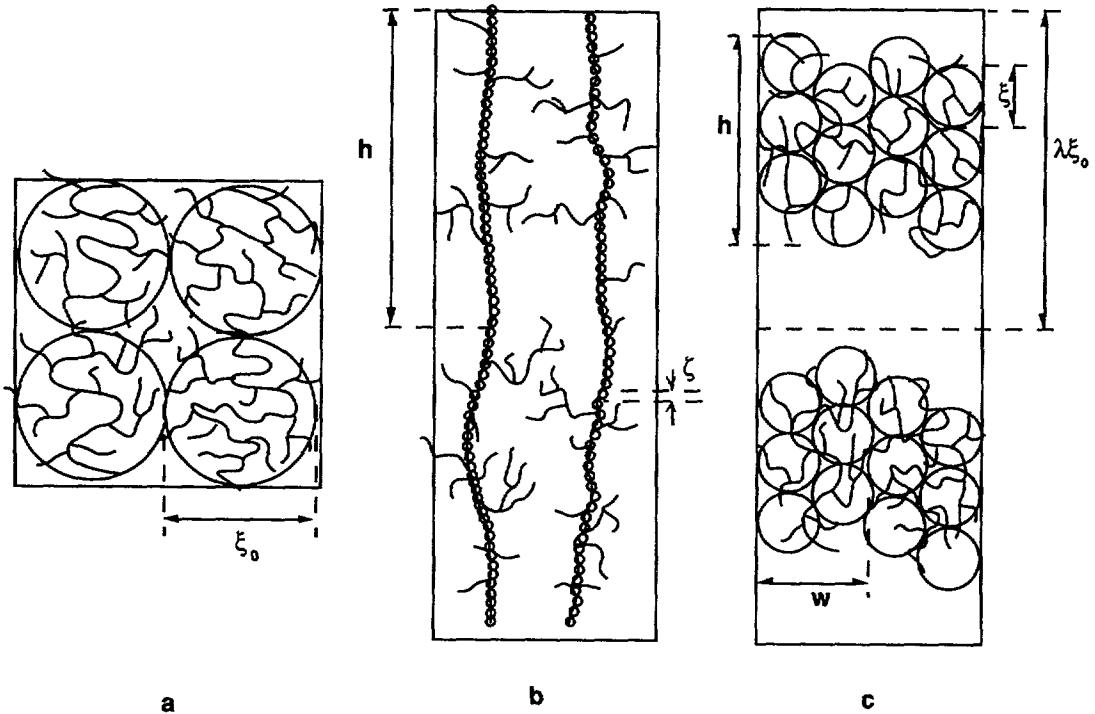


Fig. 3. — Schematic views of strongly elongated aggregates. a) A section of four blobs before deformation. b) Deformation of this section under the assumption that the aggregates are under tension. The backbone of each blob is elongated, but the side branches remain undistorted. The height  $h$  and tensile blob size  $\zeta$  are shown. c) Deformation under the assumption that the aggregates are under lateral compression. Here the height  $h$  of the deformed blob is smaller than the deformed height  $\lambda \xi_0$ . The width  $w$  is also shown.

Clearly the spanning arms are too rigid to be distorted on the shortest length scales. The distortion within a section of an arm becomes larger as one considers larger sections. At some size  $\zeta$  the strain within the section is of order unity : arms of size  $\zeta$  bend a distance of order  $\zeta$ . In analogy with strong stretching of polymers [26] we denote sections of arms of size  $\zeta$  as « tensile blobs » (See Fig. 3). On length scales larger than  $\zeta$  the arm is stretched out in an essentially straight line along the tension direction. On length scales smaller than  $\zeta$  the arm is comparatively unstretched. Thus the length of arm in a  $\zeta$ -sized tensile blob is  $\ell = a(\zeta/a)^C$ . The height  $h$  is evidently the blob size  $\zeta$  times the number of blobs  $L/\ell$  :

$$h = \zeta \frac{L}{\ell} = \zeta (\xi_0/\zeta)^C$$

The deformation  $\lambda$  is given by

$$\lambda = h/\xi_0 = (\xi_0/\zeta)^{C-1}$$

The energy stored in a tensile blob is given by

$$W(\zeta) = W(\xi_0)(\xi_0/\zeta)^C,$$

as in equation (10). The stored energy  $U$  in a spanning arm is the energy in a tensile blob —  $W(\zeta)$  — times the number of blobs,  $L/l = (\xi_0/\xi)^C$ .

$$U = W(\zeta)(\xi_0/\xi)^C = W(\xi_0)(\xi_0/\xi)^{2C} = W(\xi_0) \lambda^{2C/(C-1)}$$

The stress  $\sigma$  is the derivative of the stored elastic energy per unit volume, with respect to the deformation  $\lambda$ . This derivative behaves for scaling purposes as a factor  $\lambda^{-1}$ . Thus,

$$\sigma \approx U/(\xi_0^3 \lambda) \approx \frac{W(\xi_0)}{\xi_0^3} \lambda^{(C+1)/(C-1)} \quad (11)$$

For realistic values of  $C$  this represents a very rapid increase of stress with elongation. For diffusion-controlled aggregates ( $C = 1.26$ ), it implies a stress varying as the ninth power of the elongation. Reaction-controlled aggregates, with  $C$  closer to 1, would have an even stronger dependence. (A fractal with  $C = 1$ , such as a semicircular wire, can only elongate by a finite factor (viz.  $\pi$ ) by the bending mechanism considered here. Thus arbitrarily large extensions  $\lambda$  cannot be attained with finite stress.) This stress includes only the arms of original length  $\xi_0$ ; any deformation of shorter arms would only increase this stress. This stress-strain relationship is much stronger than those seen in practice. And it implies a great concentration of stress in the stretched arms as they progressively straighten with increasing elongation. It seems likely that in actual aggregates, such tensile contacts would simply fail rather than supporting such stresses. Thus we turn to an alternative picture of stress within the aggregates that allows the inter-aggregate contacts to fail.

**AGGREGATE UNDER LATERAL COMPRESSION.** — In the case treated above we assumed that the contacts between aggregates were sufficiently strong to support the applied tensile stress. We now abandon this assumption. We assume further that the aggregates are at an initial concentration of order  $\phi^*$ . Now when the sample is elongated, contacts between aggregates in the elongation direction are free simply to separate, as illustrated in figure 3c. Still, the aggregates are deformed by lateral compression. The lateral width goes from an initial value  $\xi_0$  to a final value  $\xi_0 \lambda^{-1/2}$ . This compression in general changes the density within the aggregate from  $\phi^*$  to some higher value  $\phi$  with associated correlation length  $\xi$ . The energy per blob increases from  $W(\xi_0)$  to

$$W(\xi) = W(\xi_0)(\xi_0/\xi)^C$$

The aggregate of original size  $\xi_0$  is divided into  $(\xi_0/\xi)^D$  blobs of size  $\xi$ . The energy stored in this aggregate is

$$U = W(\xi)(\xi_0/\xi)^D = W(\xi_0)(\xi_0/\xi)^{C+D} \quad (12)$$

In order to find the blob size  $\xi$  and the energy  $U$ , it is necessary to know how far the aggregate extends in height  $h$ . The height increases in order to reduce the density and thus the energy of compression. This increase in height also requires elongational energy, as calculated above. The aggregates elongate to a height that minimizes the sum of elongational and compressional energies. At this height the two energies must be comparable. This occurs if each blob of size  $\xi$  also is elongated so that its tensile blob size  $\zeta$  is about equal to  $\xi$ . Then clearly the energy of compression and that of elongation are both of order  $W(\xi)$  per blob; this leads to the situation depicted in figure 3c.

Under this equal-energy condition, the height  $h$  of the aggregate is determined by the extensibility of the spanning arm of the original aggregate of size  $\xi_0$ . As in the previous



subsection, this spanning arm is divided into  $h/\xi$  blobs :

$$h/\xi = (\xi_0/\xi)^C \quad (13)$$

The width  $w$  of the aggregate is determined by the overall extension  $\lambda$  of the whole system (of both the aggregates and the rubber)

$$w = \xi_0 \lambda^{-1/2} \quad (14)$$

We shall find that the aggregates occupy only part of the original volume  $\xi_0^3$  (the rest is filled by rubber). The volume occupied by the deformed aggregate is packed with  $(\xi_0/\xi)^D$  blobs of volume  $\xi^3$  each :

$$hw^2 = (\xi_0/\xi)^D \xi^3 \quad (15)$$

Substituting the aggregate height  $h$  and width  $w$  from equations (13) and (14) in equation (15) we find the decrease in blob size  $\xi_0/\xi$  as a function of composite elongation  $\lambda$  :

$$\xi_0/\xi = \lambda^{1/(C-D+2)}$$

The stress energy stored in volume  $\xi_0^3$  (neglecting the energy stored in the rubber) is calculated from equation (12) :

$$U = W(\xi_0) \lambda^{(C+D)/(C-D+2)}$$

The stress in the system is given by

$$\sigma = U/(\lambda \xi_0^3) = [W(\xi_0)/\xi_0^3] \lambda^p, \quad (16)$$

with  $p = 2(D-1)/(C-D+2)$ . For diffusion-controlled aggregates, with  $C \approx 1.26$  and  $D \approx 1.7$ , the exponent  $p \approx 0.9$ ; the elasticity is nearly linear. For reaction-controlled aggregates, with  $C \approx 1$  and  $D \approx 2.1$ ,  $p \approx 2.4$ ; there is a strong stiffening under elongation.

### Strong uniaxial compression.

We may extend the approach developed above for lateral compression to treat strong *uniaxial* compression. The approach of this section would also apply to such systems as aerogels, flocculated suspensions, colloidal dispersions, etc., where fractal aggregates are not surrounded by rubber, but rather permeated by solvent. Uniaxial compression occurs, for example, when aggregates are crushed onto a surface by capillary forces. The result depends strongly on whether the fractal dimension  $D$  of the aggregate is larger than twice its connectivity exponent  $C$  (the fractal dimension of its spanning arms).

We first consider the case  $D > 2C$ , as in reaction-controlled aggregates. The aggregate under compression is expected to expand laterally to a width  $w$  controlled by the elasticity of its spanning arms, as shown in figure 4. Like the height under strong extension, this width may be decomposed into tensile blobs of size  $\zeta$  :

$$w/\zeta = (\xi_0/\zeta)^C \quad (17)$$

The height of the aggregate is determined by the deformation ratio  $\lambda$  (now much *smaller* than 1) :

$$h = \lambda \xi_0. \quad (18)$$

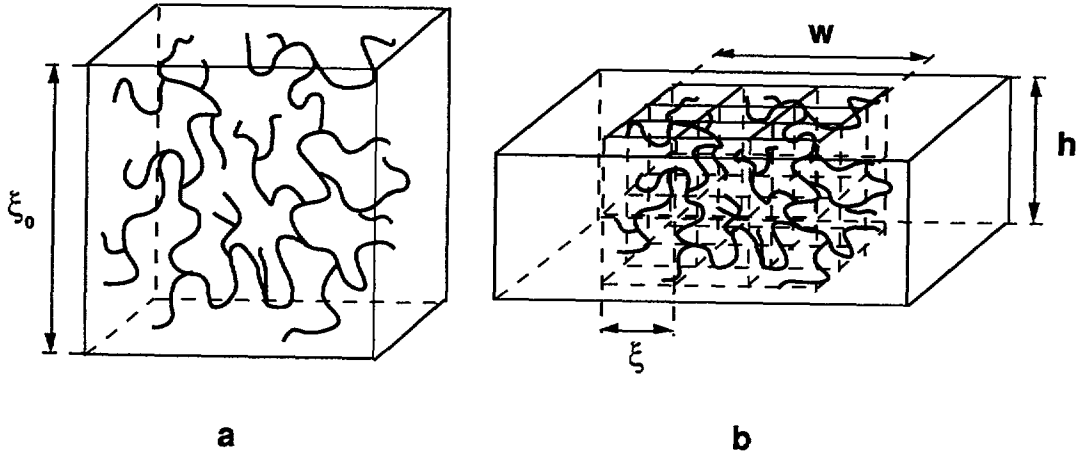


Fig. 4. — Schematic view of uniaxial compression of an aggregate with  $D > 2C$ . a) Before compression ; b) after compression.

The volume of the aggregate is densely filled by blobs of size  $\xi$  (Fig. 4b), as in the lateral compression case (Eq. (15)). Again, since the energy of extension should be comparable to that of compression, the tensile blob size  $\zeta$  should be the same as the compressional blob size  $\xi$ . Here again the occluded rubber or solvent is pushed out of the aggregate and occupies the remaining volume of the system, so that  $hw^2 < \xi_0^3$ . Combining equations (17), (15) and (18), we find the dependence of the reduction of the blob size  $\xi_0/\xi$  on the compression ratio  $\lambda$  :

$$\xi_0/\xi \approx \lambda^{-1/(2C-D+1)} \quad (19)$$

The compression energy  $U$  of the aggregate can be determined from equations (12) and (19) :

$$U \approx W(\xi_0) \lambda^{-(C+D)/(2C-D+1)}$$

This energy is stored in volume  $\xi_0^3$ . If we again neglect any energy stored in rubber, the stress is given by

$$\sigma \approx U/(\lambda \xi_0^3) \approx [W(\xi_0)/\xi_0^3] \lambda^{-(3C+1)/(2C-D+1)} \quad (20)$$

For reaction-controlled aggregates, this stress  $\sigma$  grows faster than the fourth power of the compression factor  $\lambda$  :  $\sigma \sim \lambda^{-4.4}$ .

For diffusion-controlled aggregates, with  $D < 2C$ , the above picture is not applicable. This is immediately clear by examining the number of layers of blobs

$$h/\xi \approx (\xi_0/\xi)^{D-2C},$$

obtained from equations (18) and (19). It suggests that for  $D < 2C$  the blob size  $\xi$  exceeds the height  $h$ , so that the blobs are larger than the compressed object ! The reason for this difference is that for aggregates with larger connectivity exponent  $C$ , the spanning arms are very elastic and these no longer limit the lateral spreading [27]. The blob size  $\xi$  is now the compressed height  $h$  of the aggregate as shown in figure 5, leading to a

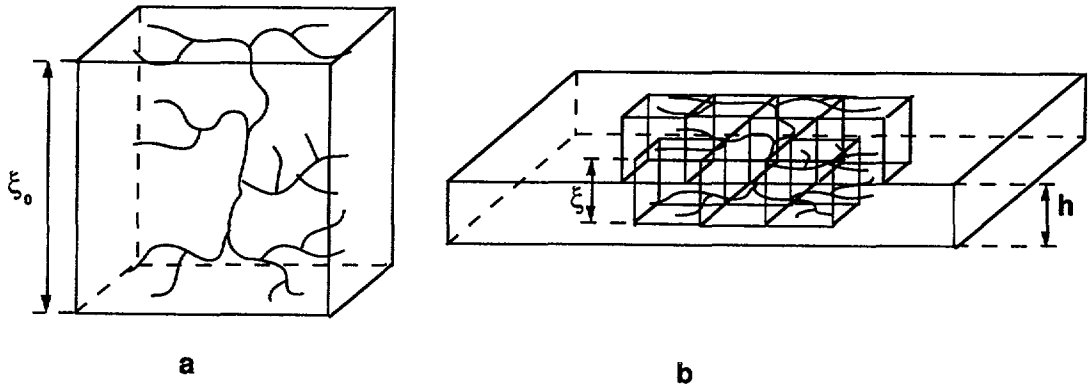


Fig. 5. — Schematic view of uniaxial compression of an aggregate with  $D < 2C$ . a) Before compression ; b) After compression.

compression factor

$$\lambda = (\xi_0/\xi)^{-1} \tag{21}$$

The energy stored in the aggregate is obtained from equations (12) and (21) :

$$U \approx W(\xi_0) \lambda^{-(C+D)}$$

leading to a stress in the composite

$$\sigma \approx U/(\lambda \xi_0^3) \approx [W(\xi_0)/\xi_0^3] \lambda^{-(C+D+1)} \tag{22}$$

For diffusion-controlled aggregates, this stress  $\sigma$  grows roughly as the fourth power of the compression factor  $\lambda$  :  $\sigma \sim \lambda^{-4.0}$ . Our results for the stress-strain power laws for the cases considered above are summarized in table I, which shows the effect of experimental uncertainties in  $D$  and  $C$ .

Table I. — Summary of stress-strain exponents.

$\sigma \sim \lambda^p$	Strong Extension controlled by		Strong Uniaxial Compression	
	lateral compression	tension (strong contacts between aggregates)	$D < 2C$	$D > 2C$
Exponent $p$	$2(D-1)/(C-D+2)$	$(C+1)/(C-1)$	$-(C+D+1)$	$-(3C+1)/(2C-D+1)$
Diffusion Controlled $D = 1.7-1.8$ $C = 1.2-1.3$	0.9-1.1	8-11	$(-3.9)-(-4.1)$	—
Reaction Controlled $D = 2.0-2.1$ $C = 1.0-1.1$	1.8-2.4	$> 21$	—	$(-4)-(-4.4)$

### Discussion.

The development of the last section suggests implications for stress-strain relationships, and also for other observable properties of highly deformed composites. Here we explore these implications and discuss the limitations of our predictions for real experiments. Finally, we compare the predictions with available data.

**LIMITATIONS.** — In order to discuss asymptotic properties for large deformation, we restricted our system in certain artificial ways. First, we assumed that the aggregates were rigid relative to the rubber matrix. The aggregates in practical composites are made of rigid solids like silica or amorphous carbon. These are intrinsically some  $10^4$  times stiffer than a typical unfilled rubber with low crosslink density. Still, as we have seen, the effective rigidity of fractal aggregates falls off rapidly as their size increases. Using equation (7), we estimate that aggregates more than about ten particles across are effectively not rigid. Such aggregates, having  $D = 2$  would have of the order of a hundred particles. This corresponds roughly to the size of aggregates actually used in reinforcing composites, as shown in figure 1. This suggests that there is no empirical advantage in using aggregates larger than the rigidity limit.

But the small size of these real fractals limits their scaling behavior. Since they are so small, we can only expect qualitative scaling of the elastic behavior over a limited range of deformation  $\lambda$ . Another factor limits the attainable range of  $\lambda$ : the rubber matrix itself reaches its elastic limit for  $\lambda \leq 6$ . This problem may be mitigated by using larger aggregates, like that of figure 1a and a rubber matrix of lower modulus. The modulus could be reduced by weakly cross-linking a polymer solution near its overlap concentration  $\phi^*$ , and then removing the solvent. The bulk modulus of the matrix is then much larger than the shear modulus, as assumed in the theory. This procedure produces an unentangled rubber, which should have both the needed deformability and low modulus [28]. Such a composite, while interesting for testing the predictions above, would be a weak, deformable material, not suitable for most purposes. It is important that the matrix not be weakened by added solvent. For then, its bulk and shear moduli become comparable, and the rubber becomes incapable of laterally compressing the aggregates.

Even under these ideal conditions there are uncertainties in our conclusions. These arise chiefly from our ignorance of how the aggregates transmit forces across their contacts. Because of this ignorance we were obliged to calculate the stress under two alternate assumptions. In the first, we assumed that the aggregates could transmit tensile stress so that any contacts in the initial state held up under deformation. This assumption seems unpalatable for practical composites. When aggregates like those of figure 1 form, their particles are believed to be bonded together by strong primary bonds; contacts between aggregates are believed to form relatively weak secondary bonds [17]. Empirically, flocs of these aggregates precipitated from a solvent are notoriously fragile [29]. Thus it seems unlikely that the aggregates could support appreciable tensile stress on their own.

Our alternative assumption was that there are no tensile contacts between aggregates. Here we were obliged to assume that the initial concentration was near overlap:  $\phi = \phi^*$ . Practical composites like those of figure 1 appear to be near overlap in this way. In this case, the problem of how the aggregates deform is nontrivial. We argued that a given aggregate achieves a uniform internal density with a uniform stress even though each aggregate becomes arbitrarily long and narrow. It is not clear whether branched aggregates will allow this uniform stress and uniform density to be achieved simultaneously. But it seems clear that our assumption gives a lower limit on the energetic cost of lateral compression, and thence on the exponent  $p$  of equation (16).

NONUNIFORMITY. — Under this assumption of lateral compression, we deduced a power-law dependence of stress on strain. But a consequence of this result was that the aggregates must elongate less than the sample as a whole. Large-scale nonuniformity in the sample must result. The structure of this nonuniformity is an open question. If the aggregates were simply arranged on a cubic lattice, gaps of pure rubber would open up between planes of aggregates. Then clearly the stress could not be found without knowing the extensional modulus of the rubber. But if the structure were more disordered like that of figure 6, the tension could be supported by lateral contact between the aggregates. In either case, strain should increase the nonuniformity on the scale of the aggregates or larger. This nonuniformity should be readily observable in scattering. This is an important test of our assumption that the aggregates do not maintain longitudinal contact. In addition, scattering would give insight about the structure of the actual nonuniformity. It is not clear that our assumption of uniform lateral stress on each aggregate can remain qualitatively valid at large elongation.

EXPERIMENTS. — There is some confirmation that fractal aggregates under *isotropic* compression behave as predicted by the Ball-Brown formula equation (9). The predicted

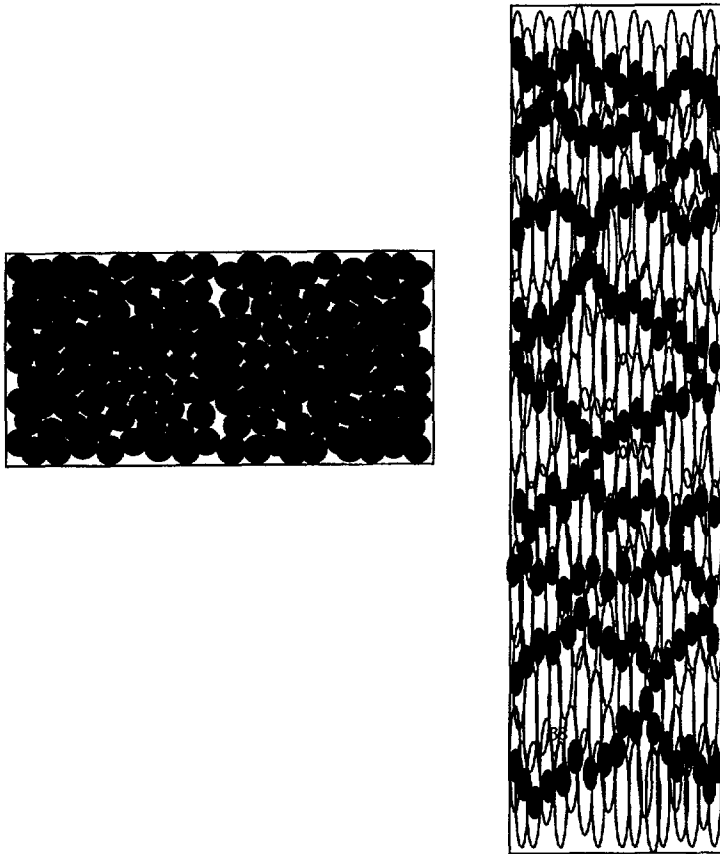


Fig. 6. — Sketch showing how nonuniformity might appear in an elongated composite with  $\lambda \approx 4$ . In the initial state (left) the aggregates are represented as circles. These compress laterally by a factor  $\lambda^{1/2} \approx 2$ . Aggregates can maintain lateral contact upon extension (right). Unfilled ovals suggest the deformation of the rubber near each aggregate.

power law was observed in flocculated aggregates, as noted above [17]. This law also appears consistent with the measured moduli of fumed aggregates and aerogels at various concentrations [16, 25], as shown in figure 7. The Brown-Ball picture also has implications for scattering. In X-ray or neutron scattering the compressed aggregates should show a correlation length comparable to the blob size  $\xi \sim \phi^{1/(D-3)}$ . This is consistent with the neutron scattering data of Sinha *et al.* [30].

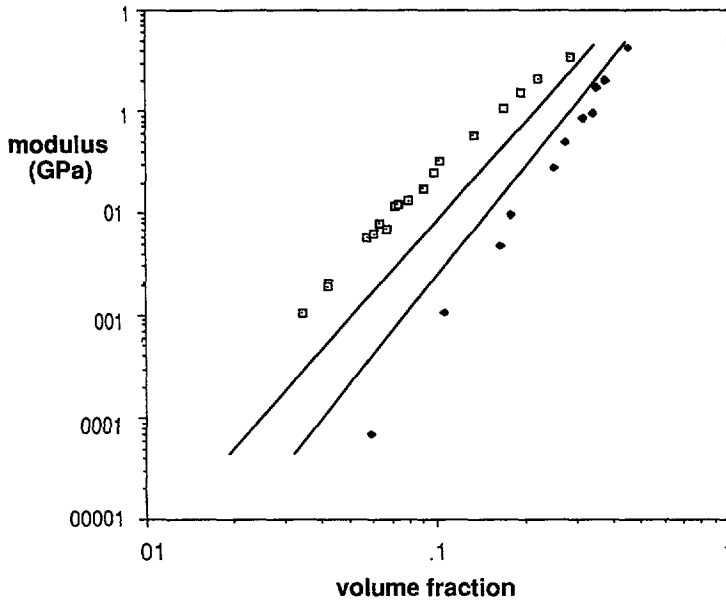


Fig. 7. — Modulus vs. concentration in two different aggregate materials, after reference [31] (silica aerogel, filled dots) and reference [25], (fumed silica, open rectangles). These experiments approach the percolation threshold at low concentrations ; this is expected to depress the moduli below the predicted power-law. The straight lines, with slopes 3.2 and 3.55, indicate the power law predicted by the Ball-Brown formula for diffusion-controlled aggregates, equation (9), including the experimental uncertainties in  $D$  and  $C$  indicated in table I.

The analogous behavior for *uniaxial* extension has not been measured, to our knowledge. But we believe that such experiments would be feasible, in a model rubber-fractal composite like that discussed above. The theory could be tested in another way by uniaxial compression. Here a rubber matrix is not necessary. Our theory may also be relevant for existing uniaxial compression experiments on flocs and aerogels [32]. Stress under uniaxial elongation is widely studied in practical composites [2, 33]. There one may approach elongations  $\lambda$  of order three or four, as illustrated in figure 2. The filler results in a marked increase in stress for a given elongation. At large elongation this stress exceeds the failure stress in the pure rubber. This is consistent with our picture in which most of the strain energy is stored in the aggregates rather than in the rubber. Qualitatively, the stress-to-strain ratio increases with elongation, as predicted in our model.

In our model the elongation of the sample pushes the aggregates laterally against one another. They can be pressed into contact even if they are initially separated. This agrees with the dramatic rise in electrical conductivity seen when carbon-black filled rubber is stretched [34]. Another consequence of our compression-driven model for strong extension is that the

rubber phase is required to supply considerable compressional stress through its bulk modulus. This would mean that the rubber within the aggregates was under strong negative pressure. In the right conditions one might expect the material to fail by cavitation in the rubber caused by this pressure. This prediction is in qualitative agreement with observations that addition of small amounts of solvent like ammonia gas can induce apparent debonding of the rubber from the filler material. Such cavitation and debonding have been invoked to explain the well-known softening of filled rubbers upon repeated application of stress [35]. One could study this effect much more thoroughly by using solvents with well-established cavitation properties in bulk rubber. The incipient cavitation would be readily observable by scattering. Recent scattering studies of stretched rubbers and gels [36] have shown remarkable large-scale structure even without filler. This is thought to be due [37, 38] to inhomogeneity in the moduli of the rubber. With the strong inhomogeneity present in filled rubber, these scattering effects ought to be even more pronounced.

**ALTERNATIVE EXPLANATIONS.** — Our aim in this study has been to understand how filler with apparent fractal structure strengthens rubber. We have argued that the interconnections among the aggregates permit large stresses to be transmitted and may give rise to the mild stiffening seen in composites as strain increases. It is not clear though whether our scheme gives the correct account of this toughening. It could be instead that the fractal structure of reinforcing filler is irrelevant ; this structure may be a mere by product in filler with the proper surface interactions. Or again, the connectivity between aggregates may be irrelevant ; instead, the filler may simply act to increase the allowable stress in the rubber matrix. We believe that the theory proposed above can help to choose between these alternative explanations of rubber reinforcement.

### **Conclusion.**

We have presented a model for the stress-strain properties of rubbers filled with fractal aggregates. In tension we find that lateral compression of the aggregates allows them to bear the vast majority of the stress, resulting in increased strength. Our mechanism results in increasing nonuniformity with increasing extension, as the rubber is squeezed out of the aggregates. This picture may offer some insight into the irregular macroscopic tearing morphology observed in aggregate-filled rubbers [39]. This inhibited tearing is another facet of the toughness of reinforced rubber. The microscopic heterogeneity we predict should easily be observed in scattering experiments ; these would constitute an important preliminary test of our ideas. Another test is to compare the stress-strain relationship of reaction-limited and diffusion-limited aggregates ; the theory predicts substantially more strain stiffening in the reaction-limited case. By using model composites it seems feasible to test both the validity of our theory and its relevance to practical composites.

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