Effect of filler on the mechanical behaviour of elastomers. Relationships between the small strain modulus and the type and concentration of filler

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The relationship between the small strain modulus and the type and concentration of filler is discussed. It is shown that it is possible to represent the modulus–concentration relationship satisfactorily using two empirical equations each of which contain only one parameter; this parameter is determined by the efficiency of packing of the particles. One equation is applicable to nonporous fillers such as glass beads, while the other equation is applicable to porous particles such as the high structure carbon blacks.

INTRODUCTION

It is well known that the presence of inclusions in a matrix generally gives rise to a change in the stiffness or modulus. When the inclusions have a higher modulus than the matrix, the modulus of the composite is greater than that of the matrix; when the inclusions have a lower modulus, the reverse is true. Several attempts have been made to develop analytical expressions which permit the estimation of the elastic modulus of a composite from a knowledge of the properties of the individual components.

These attempts have followed two separate but related approaches. On the one hand, the relative viscosity of a suspension as a function of concentration of suspended particles is calculated from hydrodynamic theory. The basic equations of hydrodynamics and of elasticity can be interconnected. Hence, expressions relating relative viscosity, η_r, of a suspension to the volume fraction of filler, ϕ, can be used directly to calculate the dependence of the relative modulus on ϕ by simply substituting relative modulus for relative viscosity. Solutions based on hydrodynamic theory generally assume constant volume and this one-to-one correspondence between relative viscosity and relative modulus is strictly valid only when Poisson's ratio is one half.

On the other hand, the dependence of the relative modulus on ϕ has been treated directly in terms of elasticity theory. Generally, these calculations assume that the composite is isotropic, macroscopically homogeneous and Hookean. The results obtained from application of elasticity theory are limited to small deformations. However, the elastic solutions do not assume constant volume.

Both the hydrodynamic and elastic solutions are limited, generally, to small particle concentrations in that the two phase system is considered so dilute that particle–particle interaction can be neglected. In addition, with a few exceptions, the particles are assumed to be spherical in shape. A review of these efforts is given in reference 1.

A third approach is based on what may be termed empirical or semi-empirical curve fitting. This approach recognizes that the solution, by either hydrodynamic or elastic theory, for the case of finite ϕ, which is the range of great practical importance, is probably hopelessly complex or impossible. One reason for this is that in the range of finite concentration, where particle–particle interaction occurs, the response of the composite depends not only on the concentration of inclusions but also on their statistical and geometrical distribution within the composite.

Consequently, emphasis here will be on discussion of some of the empricial expressions which have been proposed for relating either the relative viscosity or the relative modulus to the volume concentration of the filler. In particular, it will be shown that a good fit to experimental data can be obtained using an equation of the type first proposed by Eilers and van Dijck[2].

DISCUSSION

Historically, it would appear that more work has been expended on studies of the effect of particle type and concentration on the viscosity of suspensions than on the modulus. Indeed a recent review by Rutgers lists some 200 separate equations which have been proposed over the years for relating particle concentration to the viscosity of suspensions[3]. As has been noted in the Introduction, the relative viscosity can be replaced by the relative modulus, hence it is of some interest to consider some of the concepts and equations which have been found useful for describing the viscosity of suspensions for possible application to the modulus–filler relationship.

In many empirical attempts to describe the viscosity of concentrated suspensions, a theme which recurs frequently

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is based on the concept of the formation of aggregates and the effect of such aggregates on the fraction of fluid which is available for simple viscous flow. Thus, if an aggregate forms by accretion and adhesion of primary particles, then the behaviour of the fluid present in the interstitial space within the aggregate will be of importance to the overall behaviour of the suspension. Thus, there are two simple limiting cases: (1) a 'free draining' aggregate in which the fluid medium can flow through the interstitial space unimpeded within the time scale of the experiment; in this case, the fact that aggregates have formed will have no effect on the behaviour of the suspension, and (2) a 'non-draining' aggregate in which the interstitial fluid cannot flow appreciably within the time scale of the experiment. In this case, since the interstitial fluid does not participate in flow, the fraction of fluid which is 'free' to participate in flow is less than the total quantity of fluid present in the suspension, and hence the formation of aggregates will have an effect on the behaviour of the suspension. An intermediate case which might be considered is that of a partially draining aggregate in which only a portion of the interstitial fluid is immobilized; this intermediate case is probably more realistic than the two limiting cases described above but does not seem to have been as widely used.

Robinson[4] was one of the first to assume that aggregates are formed in suspensions by the sticking together of the primary particles. He considers that the total volume of liquid medium present is not the appropriate measure for the true liquid volume because the interstitial fluid is immobilized with the aggregate, i.e. the aggregate is non-draining. The effective volume fraction of filler, ϕ_{eff}, is given by Robinson as

$$\phi_{eff} = \frac{V_p}{V_t - V_v} = \frac{\phi}{(1 - \phi/\phi_m)} \qquad (1)$$

where V_p is the volume of the particles, equal to the weight of the particles divided by the true density, V_t is the total volume of the suspension, V_v is the void volume of the aggregate and ϕ_m is the maximum volume fraction of filler to which the particles can pack. Estimates of ϕ_m can be obtained from sedimentation experiments by measuring the volume occupied by the packed sediment bed. It is interesting to note that when $\phi \rightarrow \phi_m$, $\phi_{eff} \rightarrow \infty$.

Equation (1) assumes that the elementary particles which stick together to form aggregates are not themselves aggregates. For the case when the primary particles are porous or aggregates, the appropriate ϕ_{eff} can be derived as follows: consider the formation of aggregates by the collision and sticking together of primary non-porous particles. If the total volume occupied by the particles is v_t and if the volume of particles contained in the aggregate is v_p, then the volume fraction of particles ϕ_m in the aggregate is

$$\phi_m = \frac{v_p}{v_t} \qquad (2)$$

and the total volume occupied by the aggregates, assuming that they are non-draining, is

$$v_t = \frac{v_p}{\phi_m} \qquad (3)$$

If these aggregates do not form larger aggregates in the suspension, then the effective volume fraction of the dispersed phase is

$$\phi_{eff} = \frac{\dfrac{\phi}{\phi_m}}{\left(1 - \dfrac{\phi}{\phi_m}\right)} \qquad (4)$$

Factors which determine ϕ_m

The parameter ϕ_m occurs in several expressions relating ϕ_{eff} to ϕ, and it is of some interest to consider several of the factors which are known to have an effect on the value of ϕ_m for a system. It has been shown that the apparent value of ϕ_m for a given system depends on several factors such as particle size, shape, surface energy, presence of absorbed materials, polydispersity, etc. It is for this reason that the calculation of ϕ_m from first principles is probably hopeless and hence, estimates of ϕ_m are normally obtained from direct experiment such as the determination of sedimentation volume on the apparent or bulk density[5,6].

The Eilers–van Dijck equation

We have found[1,5,6] that an equation developed by van Dijck[2], and first applied to viscosities of aqueous bitumen suspension by Eilers[2], can be used to fit a wide variety of experiment data. As originally proposed by van Dijck, the dependence of the relative viscosity of the volume fraction of particles in suspension is given by

$$\eta_r = \left(1 + \frac{1.25\phi}{1 - a\phi}\right)^2 \qquad (5)$$

where a is a constant. For bitumen–water suspensions, Eilers found that a good fit to the experimental data was obtained when a was set equal to 1.28. From considerations of packing of particles, Eilers took $a = 1/\phi_m$. Thus a value of $a = 1.28$ corresponded to $\phi_m = 0.78$. Assuming that particle packing takes place on the face-centered cubic lattice, he predicted the value of a to be 1.35 and concluded that the larger value of a required for fitting his aqueous bitumen data implied that the bitumen particles were polydisperse.

Maron and Belner[7] found that the Eilers–van Dijck could be used to describe their experimental data on the viscosity of SBR lattices for ϕ values up to about 0.56. The value of ϕ_m required for fit varied from 0.68 to 0.72 depending on the shear stress range studied. Robinson observed that the equation also could be applied to the viscosity–concentration behaviour of glass bead suspensions[4].

Upon comparing equation (1) with equation (5) and assuming $a = 1/\phi_m$, it may be noticed that the function in the Eilers–van Dijck equation which contains ϕ is identical with Robinson's expression for the effective volume fraction of filler and hence, we can express the Eilers–van Dijck equation more generally as,

$$\eta_r = (1 + 1.25\phi_{eff})^2 \qquad (6)$$

Thus, the appropriate expression for ϕ_{eff} (equations 1 or 4) depending on the nature of the suspended particle, can be used with equation (6).

At this point, it will be convenient to terminate discussions of viscosity and to consider the relationship between modulus and filler type and concentration. Hence, we can rewrite equation (6) in terms of the relative modulus, E_r

$$E_r = (1 + 1.25\phi_{eff})^2 \qquad (7)$$

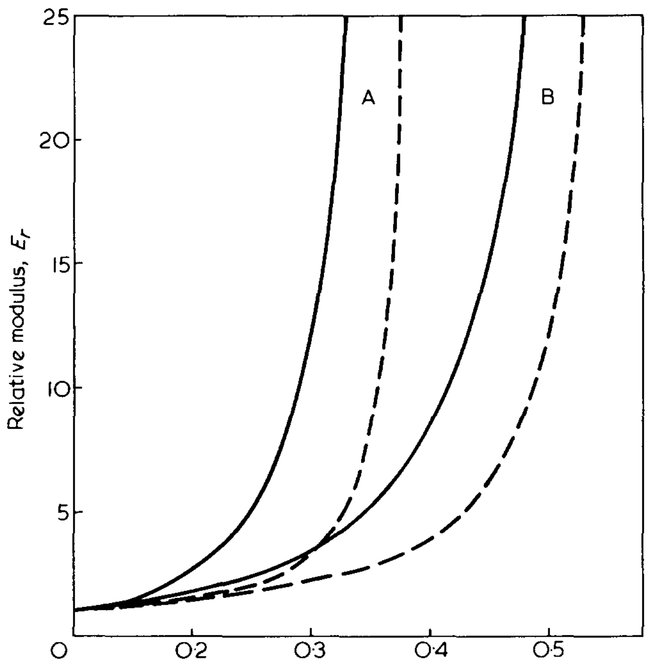

Figure 1 Predicted dependence of relative modulus, E_r on volume fraction of filler for nonporous fillers — — — (equation 8) and a porous filler, —— (equation 9) for $\phi_m = 0.3$ (A); 0.5 (B)

Dependence of the small strain modulus on filler concentration

We have found that the dependence of E_r on ϕ for nonporous fillers is given by

$$E_r = \left(1 + \frac{1.25\phi}{1 - \phi/\phi_m}\right)^2 \quad \text{(nonporous)} \qquad (8)$$

which is similar to the original Eilers–van Dijck equations, while for porous fillers such as the high structure carbon blacks, the relationship is

$$E_r = \left(1 + \frac{1.25\phi}{\phi_m - \phi}\right)^2 \quad \text{(porous)} \qquad (9)$$

which is obtained from equation (7) and the assumption that ϕ_{eff} is properly given by equation (4).

Figure 1 shows the relationships between the relative modulus and filler content for values of ϕ_m of 0.3 and 0.5 for both the nonporous filler, equation (8), shown as the dashed curves and the porous filler, equation (9), shown as the full curves. As may be seen, at any given ϕ_m value, the porous filler leads to a higher relative modulus at any given ϕ value then does the nonporous filler and this is true over the entire range of ϕ. Also evident is the very rapid rise in E_r as ϕ approaches it limiting value, ϕ_m.

Payne[8] measured the small strain modulus of natural rubber vulcanizates containing various nonporous and essentially spherical fillers such as glass beads, the large size carbon black, P–33, and whiting. His data are shown in *Figure 2* and the prediction of equation (8) with ϕ_m taken equal to 0.63 is shown as the full curve. As can be seen, the fit to the data is satisfactory over the whole concentration range and $\phi_m = 0.63$ is a reasonable value for this parameter for large nonporous particles.

When the filler consists of porous aggregates however, the relative modulus, ϕ data can be satisfactorily described using equation (9). Payne[9] carried out an extensive series of measurements on the dynamic behaviour of filled natural rubber vulcanizates as a function of strain amplitude at a constant frequency of 0.1 Hz. He observed that for very small strains < 0.001%, the dynamic modulus is independent of the strain. In this region, the strain independent dynamic shear modulus is analogous to the limiting shear modulus at zero strain that would be calculated from a static experiment. As the strain amplitude increases, a transition zone is reached, and a rather marked decrease of the modulus is observed. At still higher strain amplitudes, greater than about 10%, the modulus again levels off and becomes independent of the amplitude. The difference between the limiting small strain modulus, G_0, and the limiting large strain modulus, G_∞, is a function of the type and concentration of filler; this difference is essentially zero for a gum vulcanizate.

The G_{0r} and $G_{\infty r}$ data reported by Payne for the system natural rubber–HAF carbon black, a high-structure black, are shown in *Figure 3*. The G_{0r} data are shown as the filled circles and the curve shown is the prediction of equation (9) with ϕ_m taken equal to 0.40. For this carbon black, the dibutyl phthalate absorption (DBP) value leads to an estimate of $\phi_m \geqslant 0.36$ if it is assumed that the total volume of DBP absorbed is equal to the void volume[10]. On the other hand, values of the specific volume[10] lead to an estimate of $\phi_m = 0.43$. Thus, the value required for fitting the data in in reasonable agreement with these two independent estimates of ϕ_m.

As mentioned above, the dynamic modulus which is independent of strain at small dynamic strains, decreases with increasing strain and eventually levels off and reaches another constant value, the large strain value G_∞; this takes place for dynamic strains greater than about 10%. Also shown in *Figure 3* as the unfilled circles is the $G_{\infty r}$ data and the full curve represents the prediction of equation (9) when ϕ_m is set equal to 0.60. It is also possible to fit Payne's data at each strain amplitude using equation (9). The ϕ_m values required for fit increase uniformly with increase in the dy-

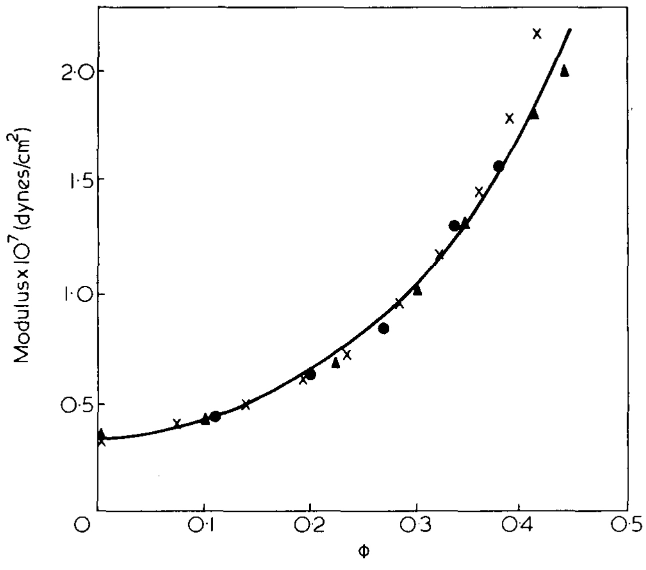

Figure 2 Dependence of the relative modulus of natural rubber vulcanizates containing different types of filler. X, Glass; ●, P-33; ▲, Whiting

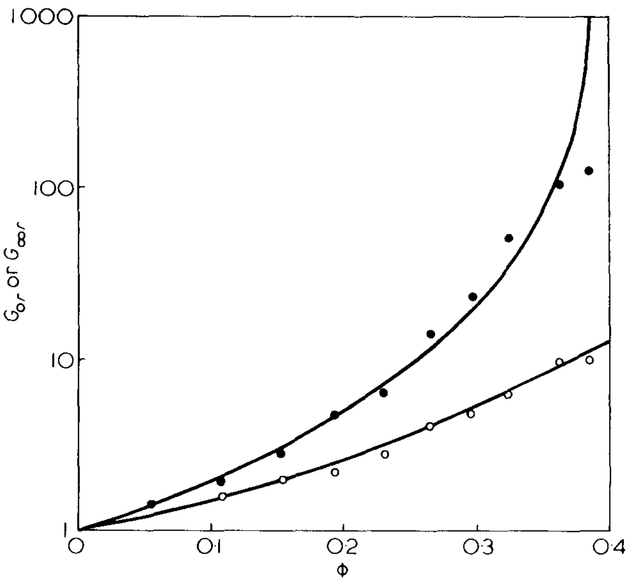

Figure 3 Dependence of the limiting relative shear modulus at small strains, G_{0r}, ●, and at large strains, $G_{\infty r}$, ○, on volume fraction of HAF for natural rubber vulcanizates

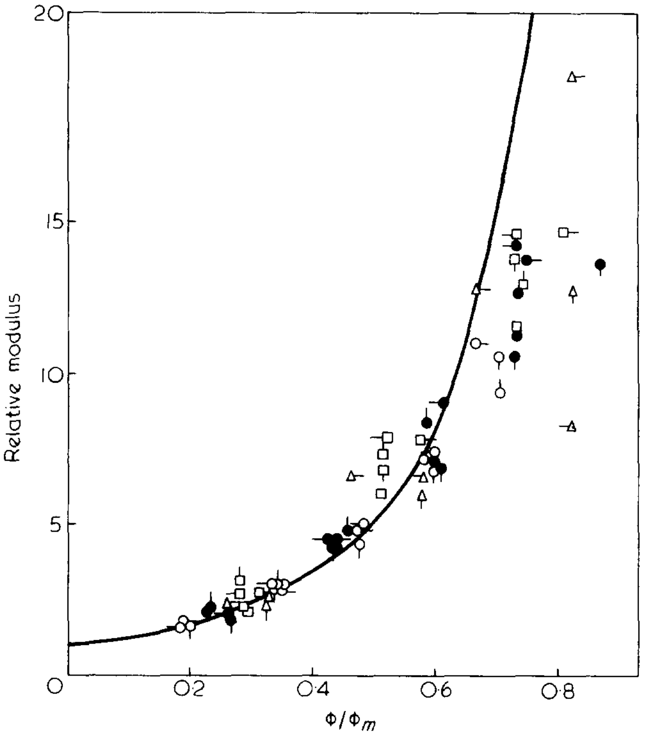

Figure 4 Dependence of the relative modulus at 300% for SBR containing different HAF carbon blacks on the concentration of black for various degrees of crosslinking. These symbols correspond to the symbols used in reference 13

namic strain. Thus, for the limiting small strain modulus, $\phi_m = 0.40$, for a strain of 0.01, $\phi_m = 0.41$, for a strain of 0.1, $\phi_m = 0.48$ and for the limiting large strain modulus, $\phi_m = 0.60$.

An increase in ϕ_m from 0.40 to 0.60 with increasing strain could imply that the packing of the HAF aggregates is becoming more efficient, i.e. the asymmetry of the particles is decreasing with strain. This mechanism for the change in modulus with strain amplitude has been proposed by Voet and Cook[11] who observed that the decrease in modulus with increasing strain is a reversible process. It is more likely, however, that this effect is due to dewetting, i.e., separation of the rubber from a portion of the filler particle.

In another study Kraus[12,13] showed that the stress at 300% strain for SBR vulcanizates containing different concentrations of four carbon blacks which differed in the extent of structure alone, could be superposed by using a reduced volume fraction of filler, $a\phi$. Here, a is a shift factor, independent of the strain for strains less than about 400%, whose value is related to the DBP absorption value by

$$a = \frac{24 + A}{24 + A_0} \tag{10}$$

where A is the DBP absorption value for one type of black and A_0 is the corresponding value for one black chosen as reference.

These same data of Kraus have been replotted and are shown in *Figure 4* using the same symbols used by Kraus[13]. These data represent the variation in structure of the black, filler concentration and network chain concentration. The value of the stress at 300% strain for the gums was not reported but was estimated from the reported network chain concentration as calculated from equilibrium swelling measurements in conjunction with

$$\sigma_{300} = 3.94\nu_e RT \tag{11}$$

where R is the gas constant, and T is the temperature. The data are plotted as the relative modulus at 300% strain versus the reduced volume fraction of filler, ϕ/ϕ_m. The full curve is the prediction of equation (9). When plotted in this manner, all the data, regardless of the nature of the filler, the filler content, or the degree of crosslinking, should fall on one curve. As can be seen, the fit is satisfactory for ϕ/ϕ_m values less than about 0.6. For larger values of the ratio, the experimental data fall below the predicted response and this may be a reflection of the fact that some dewetting is occurring. The relationship between the ϕ_m required for fitting the data and the measured DBP absorption

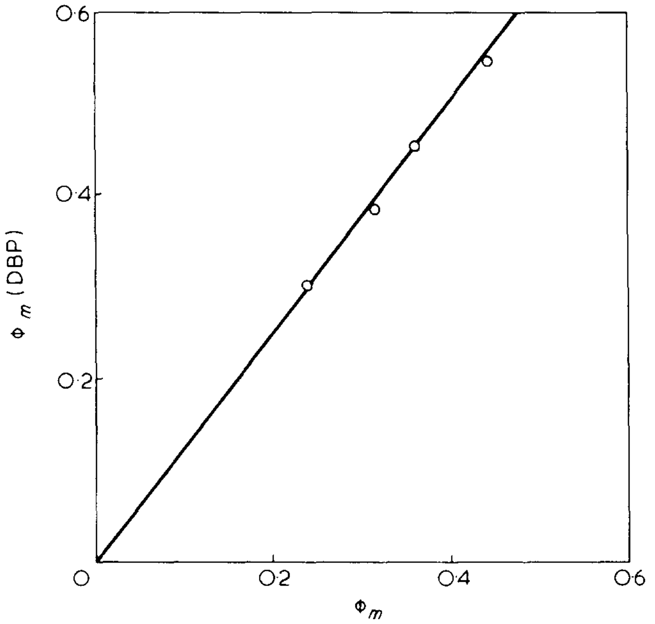

Figure 5 Dependence of ϕ_m required for the fit shown in *Figure 4* on dibutyl phthalate absorption values of the filler

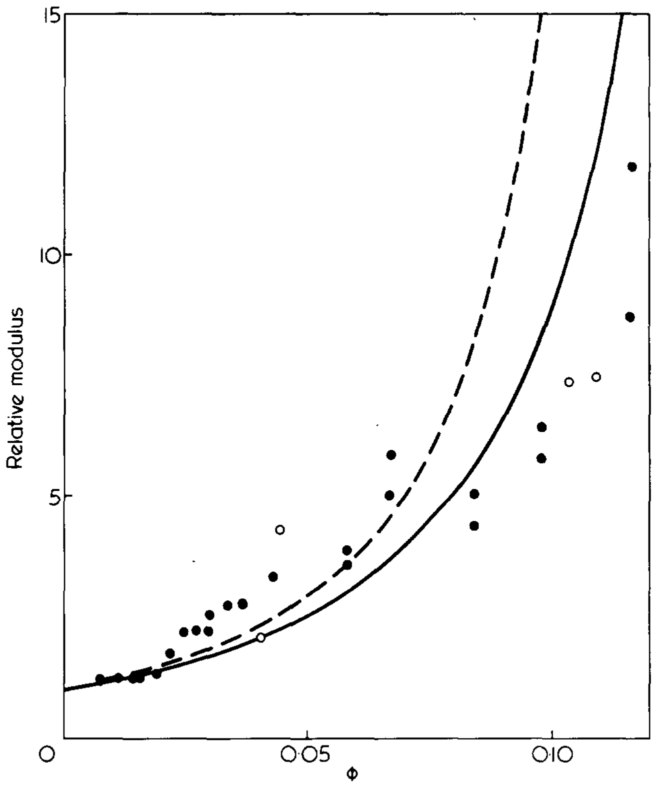

Figure 6 Dependence of relative modulus on volume fraction of filler for natural rubber-phenyl beta naphthylamine vulcanizates

value is shown in *Figure 5*. The slope of the linear relationship is 1.25. The remaining data reported by Kraus[13] for other elastomers such as EPDM and for other types of black could also be described using equation (9).

As another example, consider the interesting data reported by Linning, Parks and Stiehler[14] on the stiffening effect of phenyl beta naphthylamine (PBNA) on vulcanized rubber. They observed that PBNA, when introduced into vulcanizates by absorption from a solvent caused a very marked increase in modulus compared to that of the crosslinked gum. No appreciable effect on modulus however, was observed when the PBNA was introduced by normal milling. Stiffening was also observed when PBNA was incorporated by milling provided that the vulcanizates were heated above the melting point of PBNA and then permitted to cool. The modulus values were calculated from the measured strain after one minute under a load of 5 kg/cm^2 using the stress–strain equation of Martin, Roth and Stiehler[15]. Payne[16] also measured the dynamic properties of similar vulcanizates with the PBNA being introduced by swelling. The results of Payne are remarkably similar to the behaviour obtained with natural rubber containing highly reinforcing carbon blacks such as HAF except that the stiffening effect of PBNA was even greater than that of the black.

Figure 6 shows the data of Linning as the full circles and the limiting small strain dynamic modulus data of Payne as the unfilled circles. The best overall fit to these data was obtained by assuming that equation (9) is applicable and the dashed curve represents the fit when $\phi_m = 0.14$, while the full curve is the fit when $\phi_m = 0.16$. Although the scatter is relatively great, due, no doubt, in large measure to the difficulty of reproducing the same PBNA crystallization conditions, the fit is satisfactory for ϕ values less than about 0.07. The rather small value of ϕ_m must mean that the PBNA recrystallizes in the form of highly asymmetric particles for it is known that asymmetric particles pack less efficiently than do symmetric particles, i.e., a random heap of toothpicks occupies much more volume than a random heap of marbles. Hence, the results in *Figure 6* suggest that the highly stiffening effect of PBNA, when it is permitted to crystallize *in situ*, is a reflection of the highly asymmetric nature of the crystallites.

A similar effect was observed previously with propellants containing ammonium perchlorate as the filler[17]. It was observed that the small strain modulus of such composites increased markedly if they were first permitted to absorb moisture for several days and then dried. The dried specimens were much stiffer than the original and microscopic examination showed that some of the initially roughly spherical ammonium perchlorate particles first dissolve in the absorbed moisture and then recrystallize in the form of highly asymmetric dendritic crystals.

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