A Simple Theory of Filler Reinforcement in Elastomers Subjected to Shear

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Synopsis

The effects of a filler in an elastomer can be described by means of a theory based on a simple model in which the filler particles are assumed to be of uniform size, of cubic shape, and dispersed in such a manner as to occupy the points of a cubic space lattice. For the case of shear deformation, simple relations can be derived for the increase in the storage modulus G' and the loss modulus, G'' of the bulk material with an increase in filler content. Furthermore, the theory predicts the temperature shift of two points which can be easily determined experimentally: the inflection point of G' and the maximum of G''.

Introduction

Various kinds of fillers are frequently used in elastomers. They are more or less completely dispersed in these materials, e.g., as pigments in plastics or in paint films. In most cases, the filler particles are inorganic and crystalline in nature, having mean dimensions of about 0.1–1 μ. Since the particle size distribution is ordinarily made as narrow as possible, the filler can be considered to consist of particles of approximately uniform size.

Comparatively little is known about the strength of the bond between filler particle and the surrounding viscoelastic material. Although even a chemical bond is conceivable, van der Waals forces are prevailing in most cases, so that the strength of the bond is probably rather poor. One can therefore expect that upon deformation of the bulk material the segments of the macromolecules slide more or less easily along a sufficiently smooth surface of a filler particle. This will obviously not be true if portions of the macromolecules are somehow trapped in crevices or other unevennesses of the filler surface. In practice, both cases should be taken into account unless further details on the bonding conditions are known.

It has often been observed experimentally that the addition of a filler affects the mechanical properties of the bulk elastomer. In the past, theoretical studies on these effects have also been carried out, and have been found for the most part to agree with experimental results. Recent calculations by van der Poel,[1] based on a former approach of Fröhlich and Sack[2] and earlier ones of Bruggeman,[3] have been used to explain the behavior of filled rubber materials, as measured by Schwarzl et al.[4] Another

theoretical treatment of the problem was offered by Guth,[5] who started from Einstein's classical calculation on the rheological effects of small solid spheres in liquids. Lastly, a calculation by Radok and Tai,[6] who make allowance for the bond in the interface between filler particle and viscoelastic environment, must be mentioned.

Although most of these theoretical investigations are highly rigorous, their approach is nevertheless rather lengthy and does not lead to results which can be expressed in convenient form. Moreover, the ideas for the models providing the basis for calculation are by no means as evident as might be expected at a first glance. Although these disadvantages do not in principle diminish the value of the theories mentioned, a simpler approach which facilitates the understanding of the change in the behavior of the material due to the filler might prove useful. The purpose of this paper is to give such an approach; however it must be mentioned from the start that its simplicity necessitates some essential restrictions and idealizations. In the present form the theory proposed below applies to deformation in shear only. However, this is the type of deformation produced, for instance, in the torsion pendulum, which finds frequent application in testing of viscoelastic materials and would provide a good means of comparing theory with experiment here.

Behavior of the Pure Elastomer

First, some preliminary remarks concerning the behavior of the pure elastomer in which the filler is to be imbedded are in order. A crosslinked viscoelastic material can be represented by a three-parameter model.[7] It consists of a spring of shear modulus G_1 connected in series with a Voigt model, i.e., a spring G_2 in parallel with a dashpot η. Both G_1 and G_2 are virtually independent of temperature. The viscosity component η is assumed to obey the Andrade equation for its dependence on temperature T:

$$\eta = \eta_0 \exp\{E/RT\} \tag{1}$$

where η_0 is a constant, R the gas constant, and E the activation energy for the softening process, manifested by higher molecule mobility with increasing temperature. The assumption $G_1 \gg G_2$ can be generally justified. Hence, if the pure elastomer is subjected to an alternating force of angular frequency ω, its shear modulus is expressed in terms of the elements of the three-parameter model as a complex value $G_0 = G_0' + iG_0''$, where the storage modulus G_0' is

$$G_0' = (G_1^2 G_2 + G_1 \omega^2 \eta^2)/(G_1^2 + \omega^2 \eta^2) \tag{2}$$

and the loss modulus G_0''

$$G_0'' = \omega \eta\, G_1/(G_1^2 + \omega^2 \eta^2) \tag{3}$$

Subsequently, both G_0' and G_0'' are temperature-dependent through η, as indicated by eq. (1). It is seen from eq. (2) that at high temperature

($\omega\eta \ll G_1$) the storage modulus approaches G_2, characteristic of the entropy-elastic state of the material, and at low temperature ($\omega\eta \gg G_1$), it approaches G_1, characteristic of the energy-elastic state. In both cases, the loss modulus G_0'' vanishes.

Two features of the model will be mentioned here in view of experimental verification, to be dealt with below: (1) the loss modulus assumes a maximum for $\omega\eta = G_1$, in which case both G_0' and G_0'' have the same value, $G_1/2$; (2) the storage modulus has an inflection point for $\omega\eta = G_1/\sqrt{3}$, for which G_0' and G_0'' become $G_1/4$ and $\sqrt{3}\,G_1/4$, respectively.

In the following analysis the angular frequency is to be considered as constant. It is determined by the experimental arrangement, for example, the torsion pendulum mentioned.

Model of the Filled Material

It is assumed that the filler consists of particles which have the shape of small cubes, all of the same size. Although in reality the particles are randomly dispersed throughout the bulk material, they will be considered as located on sites equidistant from one another, as is the case when they occupy the points of a cubic space lattice. Furthermore, the edges of the particle cubes will all be considered parallel to the three main axes of the lattice. The bulk material therefore consists of identical cubic elementary cells, to each of which a particle cube is assigned. The particle cube may rest in any of the corners of the cell. It does not matter which corner is selected for that purpose, but it must be the same corner in all elementary cells. Finally, the forces acting upon the bulk material may be such as to produce a shear deformation of the elementary cell, as depicted schematically in Figure 1. The cell is divided in different regions, of which regions 1, 2, and 3 are pure elastomer (modulus G_0), while region 4 represents the filler cube (shear modulus G_F).

The various regions ($i = 1,2,3,4$) experience deformations of different magnitude under the influence of the forces F_i, which act in the directions
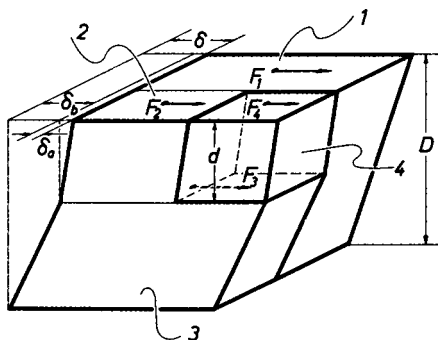

Fig. 1. Diagrammatic representation of the elementary cell of the filled elastomer in the deformed state: (regions 1, 2, 3) pure elastomer; (region 4) filler cube.

indicated in Fig. 1. The following four equations determine the relations between forces and deformations:

$$F_1 = G_0 D(D - d)(\delta/D) \tag{4a}$$

$$F_2 = G_0 d(D - d)(\delta_a/D) \tag{4b}$$

$$F_3 = G_0 dD[\delta_b/(D - d)] \tag{4c}$$

$$F_4 = G_F d^2(\delta_a/d) \tag{4d}$$

Moreover, because of continuity, $F_3 = F_2 + F_4$. The total displacement δ of the top face of the cell and the total force F acting upon that face and producing the deformation are obviously:

$$\delta = \delta_a + \delta_b \tag{5}$$

and

$$F = F_1 + F_2 + F_4 \tag{6}$$

The shear strain is then given by δ/D and the shear stress by F/D^2, both of which are found from the last seven equations. The ratio of stress and strain yields the shear modulus of the elementary cell as a whole, i.e., of the filled material, in the form:

$$G = fG_0 \tag{7}$$

where the factor f, which is complex since it incorporates G_0, takes account of the reinforcement of the bulk material by the filler addition. It is also a function of G_F and of the geometrical dimensions of the cell. The ratio of the length of filler cube edge to that of the elementary cell is denoted by $x = d/D$. Thus the factor f turns out to be:

$$f = 1 + x^3/[x - x^2 + (G_0/G_F)] \tag{8}$$

where the approximation $|G_0|/G_F \ll 1$ has been used. It is the quantity x which introduces the effect of the filler content; its relation to the filler volume concentration p is simply $x = \sqrt[3]{p}$.

Since each elementary cell is sheared in exactly the same way, no voids are generated in the bulk material in the course of the deformation process. Although such an idealized deformation is conceivable—at least in principle—it is nevertheless rather artificial. It involves an unhampered sliding of the elastomer portions of region 1 past the other regions 2 and 3 along their common interface as well as along those faces of the filler cube in contact with region 1. On the other hand, sufficient adhesion is assumed to exist between the surfaces of the filler cube adjacent to elastomer regions 2 and 3 to prevent such sliding; for it would otherwise hardly be conceivable how the deformation of the filler cube could be brought about at all. The relative simplicity of the form of the reinforcement factor f outweighs the shortcomings of this idealized model. Two features of the reinforcing effect are worth mentioning. (1) The effect depends only

upon filler volume concentration (through x). Obviously the absolute dimensions of the filler particle do not play an essential part, as d does not explicitly enter the expression for f. (2) Whenever the elementary cell is sheared, the filler cube blocks a certain amount of the deformation of the elastomer (represented by region 2), to the same extent as the cube itself is deformed. The counterpart to this blocking effect appears as a stronger deformation of other elastomer portions of the elementary cell (represented by region 3). It is evident that this simple picture will fail for too small or too large a filler cube, for in either case the region 2 loses its shape as a parallelepiped with edges of equal order of magnitude. This assumption on the form of that region seems to provide the only reasonable basis for the concept of the blocking effect. Consequently, the model is certainly not applicable for, say, $d < 0.2D$ and $d > 0.8D$, i.e., not for filler volume concentrations below 0.8%, corresponding to practically unfilled material, and above 50%, the latter being the more important restriction.

Consequences of the Model

The complex reinforcement factor f can be separated into its real and imaginary parts:

$$\operatorname{Re}(f) = A(x) = 1 + [x^2/(1 - x)] \tag{9}$$

$$\operatorname{Im}(f) = -(G_0''/G_F)B(x) = -(G_0''/G_F) [x/(1 - 2x + x^2)] \tag{10}$$

where all those summands containing the ratios (G_0'/G_F) and (G_0''/G_F) and their higher powers have been neglected. In most cases, these expressions are used in further calculations in order to avoid an undue complication. The parts of the shear modulus of the filled material are in conjunction with eq. (7):

$$G' = G_0' \operatorname{Re}(f) - G_0''\operatorname{Im}(f) \tag{11}$$

$$G'' = G_0''\operatorname{Re}(f) + G_0'\operatorname{Im}(f) \tag{12}$$

For the purpose of experimental verification some modifications are useful. The reinforcing effect on the storage modulus G' can best be observed in either the entropy-elastic or energy-elastic region, where G_0'' vanishes. In these regions, eq. (11) simplifies to:

$$G' = A(x)G_0' \tag{13}$$

Here, the factor $A(x)$ makes allowance for only the influence of the concentration of the filler but not for the filler modulus. This latter quantity entered the original eq. (8) for f in the form of the ratio G_0/G_F. In the entropy-elastic region, where $G_0' \approx G_2$ and $G_0'' \approx 0$, this ratio becomes G_2/G_F, which is so small that it can always be neglected. The reinforcement factor f then simplifies directly to $A(x)$ in eq. (9); as a result, this equation should indeed be applicable in the entropy-elastic state.

On the other hand, in the energy-elastic region one finds that the ratio G_0/G_F becomes approximately G_1/G_F. The quantity G_1 is smaller than

G_F by only, say, one order of magnitude. Thus, one must retain it in the factor f, which is real (for once again $G_0'' \approx 0$), and which is equal to:

$$A_1(x) = 1 + x^3/[x - x^2 + (G_1/G_F)] \tag{14}$$

This expression replaces $A(x)$ in eq. (13). One should expect A_1 to be a better approximation than A for the representation of the reinforcing effect in the energy-elastic state, since it now contains the modulus of the filler.

The maximum of the loss modulus can also readily be observed experimentally. Making use of the fact that G_0' and G_0'' are both equal to $G_1/2$ there, one finds from eq. (12)

$$G_{max}'' = (G_1/2)A(x) [1 - C(x)(G_1/G_F)] \tag{15}$$

where $C(x)$ is a combination of the quantities $A(x)$ and $B(x)$ of eqs. (9) and (10) defined by $C = A/2B$.

Temperature Shifts

The filler can also cause a shift in the position of the maximum of G'' and of the inflection point of G', both considered as functions of $\omega\eta$. Let $\omega\eta_0$ represent the unshifted position; then the new, shifted position is approximately:

$$\omega\eta = \omega\eta_0[1 - C(x)(G_1/G_F)] \tag{16}$$

In deriving this expression, one retains only terms linear in (G_1/G_F).

A shift with $\omega\eta$ actually implies a shift with temperature T. If one defines $\eta_0 = \exp\{E/RT_0\}$, in accordance with eq. (1), where T_0 is the temperature of the maximum of G_0'' or of the inflection point of G_0', respectively, one finds from eqs. (1) and (16) by taking logarithms on both sides:

$$(1/T) - (1/T_0) = (R/E)\cdot\ln[1 - C(x)(G_1/G_F)] \tag{17}$$

Expansion of the logarithm up to the first power finally leads to:

$$T = T_0[1 + C(x)(G_1/G_F)(RT_0/E)] \tag{18}$$

for the temperature where the points in consideration appear. The factor in brackets is greater than unity and originates from a binomial expansion of its reciprocal, higher powers than the first being omitted.

It is noteworthy that the temperature shift appears as a consequence of the slight deformability of the filler; for if the shear modulus G_F were too great with respect to the storage modulus G_1 of the elastomer in the energy-elastic state, such a shift should not be observable. Evidently, the inflection point exhibits not only a temperature shift but also a change in magnitude. It can be shown that this increase is governed by the factor $A(x)$ of eq. (9).

Comparison with Experimental Results

The results of Schwarzl et al.,[4] who studied the effects of filling polyurethane rubber with sodium chloride, may serve as an example for such a comparison. Although van der Poel's theory was used by the authors to describe their results with sufficient accuracy, the pertinent relations in
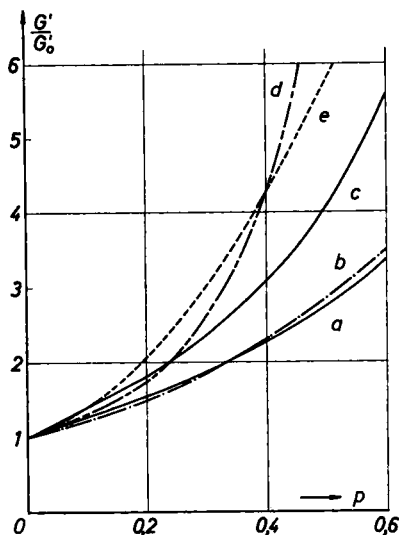
Fig. 2. Increase of the storage modulus, expressed by (G'/G_0'), vs. filler volume concentration p. Theoretical curves: (a) function A_1 of eq. (14) with $G_1/G_F = 0.123$, (c) function A of eq. (9), (e) Guth's relation; experimental curves: (b) at $-70°C.$, (d) at $80°C.$

this theory do not appear in explicit form and their employment is therefore somewhat complicated. The value of the shear modulus of pure polyurethane rubber in the energy-elastic region was determined to be $G_1 = 1.60 \times 10^9 N/m^2$. The shear modulus of sodium chloride is $G_F = 1.31 \times 10^{10} N/m^2$. In Figure 2 the functions A and A_1, the latter being calculated with these values for G_1 and G_F, are shown by the solid curves a and c, respectively. Curve b represents the experimental results in the energy-elastic region at $-70°C.$ and curve d those in the entropy-elastic region at $80°C.$

The agreement in the energy-elastic region is rather good, even up to relatively high values for the filler volume concentration p. This indicates that the application of A_1 in the place of A in eq. (13) was indeed necessary. For the function A, presumed primarily to represent the behavior of the material in the entropy-elastic region, the agreement with experiments is less satisfying, but it reflects the steeply ascending nature of the experimental curve, at least qualitatively. Guth's[5] relation, occasionally used in the past for the description of the reinforcing effect because of its simplicity, is lastly shown as curve e in the diagram. It seems to give a somewhat better representation of the experimental results for the higher values of p than does A, but the latter is obviously more accurate through the range of $p \lesssim 0.2$.

The temperature shift of the inflection point can also be checked. In order to obtain the activation energy E appearing in eq. (18), the parameters of eq. (2) must be so chosen as to provide the best fit of the storage modulus of pure polyurethane rubber G_0', given by that equation, to the

experimental data.   This S-shaped curve for the dependence of G_0' on $\omega\eta$, in other words on T, can be rather exactly described with $G_2 = 1.30 \times 10^6$ N/m^2, $\omega\eta_0 = 2.82 \times 10^{-6} N/m^2$, and $E = 15.2$ kcal./mole.   Substituting the latter in eq. (18) one finds a temperature shift of 1.9°C. for $p = 0.5$. The experimental value was 7.1°C. for the same filler concentration.

The direction of the temperature shift is thus given correctly by the theory.   However, in view of the various idealizations involved in the conception of the model, one can hardly expect more than an agreement in the order of magnitude of the effect, as indeed revealed by comparison with experiment.   Furthermore, it must be mentioned that the Andrade equation used in deriving the relations for the temperature shift is itself only a relative crude approximation.   In conclusion, it can however be stated that several features of the effect of a filler added to an elastomer find a fairly good verification in the relations developed on the base of the assumed model, at least in as far as the order of magnitudes and the tendencies are concerned.   Further tests on the theory, including the study of the filler effects on G'' and its temperature shift, are being prepared.

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Résumé

Les effets d'une matière de remplissage dans des substances viscoélastiques peuvent être décrits sur la base d'un modèle simple, dont on suppose que les particules de cette matière aient une grandeur uniforme, une forme cubique, et soient dispersées d'une manière qu'elles occupent les points d'un réseau spatial cubique.   Dans le cas où la matière remplie est soumise à une déformation par cisaillage, des rélations simples peuvent être dérivées qui indiquent pour cette matière l'augmentation des modules de stockage (G') et de perte (G'') avec la concentration de la matière de remplissage.   De plus, la théorie prédit le déplacement de température de deux points qui peuvent être déterminés facilement par des essais: le point d'inflexion de G' et le maximum de G''.

Zusammenfassung

Die Einflüsse eines Füllstoffes in viskoelastischen Materialien können auf der Basis eines einfachen Modells beschrieben werden, bei dem angenommen wird, dass die Füllstoff-Teilchen eine einheitliche Grösse und würfelförmige Gestalt haben und derart verteilt sind, dass sie die Punkte eines kubischen Raumgitters einnehmen.   Für den Fall, dass das gefüllte Material einer Scherbeanspruchung unterworfen wird, lassen sich relativ einfache Beziehungen ableiten, die für dieses Material die Erhöhung des Speicher-Moduls (G') und des Verlust-Moduls (G'') mit der Füllstoffkonzentration angeben. Darüber hinaus gibt die Theorie eine Voraussage über die Temperaturverschiebung von zwei Punkten, die leicht experimentell bestimmt werden können: den Wendepunkt von G' und das Maximum von G''.