

Molecular Basis for the Mullins Effect*

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INTRODUCTION

The physical phenomena now widely known as the "Mullins effect" was apparently first studied in detail by Holt¹ in about 1930. He showed that if a vulcanized rubber which contains carbon black is stretched to a relative elongation $\alpha_m = L/L_0$ and released, it will not follow the same stress-strain curve when it is stretched once again to this same elongation. Instead, the rubber appears much softer on the second stretch for elongations below α_m .

Holt examined this behavior in some detail and showed that additional prestretches to α_m softened the rubber further, but to a lesser degree than was observed on the first prestretch. In addition, Holt showed that the rubber regains a portion of its stiffness if allowed to rest in the relaxed state. Although this recovery was very slow at room temperature, up to about 50% recovery was noted after about an hour at 100°C. Similar softening effects were noted in gum stocks at exceedingly high elongations, but the effects were much less marked than in the filled stocks.

This same effect was examined in more detail by Mullins^{2,3} after 1940. His results confirmed and greatly extended the earlier results of Holt. In addition, Mullins speculated about the mechanisms involved but came to no definite conclusion in that regard. Later,³ however, he and Tobin presented a phenomenological theory for the effect wherein they considered the rubber to be composed of hard and soft regions. They showed that their data could be described by assuming that some fraction of the hard regions became soft after a prestretch. No definite molecular basis for this process was proposed by Mullins and Tobin, although they speculated that either the breaking up of filler particle aggregates or the breaking loose of rubber to filler bonds might be involved.

Later work by Blanchard and Parkinson^{4,5} confirmed and extended the data of Holt and

Mullins. Further, these authors concluded that the softening was due to the breaking of rubber to filler bonds. They incorporated this idea into a semiempirical theory which agreed with their experiments. In addition, they obtained what they believed to be a distribution for the strength of the rubber-filler bonds. It will be seen in that which is to follow that their distribution probably does not represent what they thought it did, even though their basic ideas were correct.

MOLECULAR PICTURE

Consider the rubber molecules to be bound to the filler at certain sites on the filler surface. If the surface area of the filler in square centimeters is S per cubic centimeter of rubber compound and the average surface area per chain attachment is σ square centimeters, the number of attached chains will be (S/σ) per cubic centimeter of compound.

When the rubber is stretched to a relative elongation α , the distance between centers of the filler particles will change by the same factors. This means that we assume the positions of the filler particles will undergo an affine deformation. Since the particles are quite large in comparison to atomic dimensions one would expect that even at very large stresses the unbalanced force on any given particle will be unable to move it far through the rubber matrix. Consequently, the assumption of an affine deformation of the filler particle positions should be valid.

Suppose Figure 1 represents three rubber chains

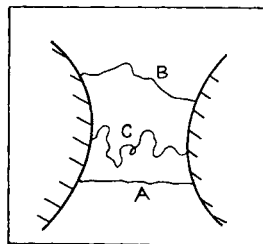


Fig. 1. Three typical chains attached to two adjacent filler particles.

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attached to two filler particles before a force is applied to the rubber. If the rubber is now stretched in the horizontal direction to a relative elongation α , the particles must separate so that the distance between centers is now α times larger than the previous value. If α is appreciable, chain A must rupture. Chain B might rupture if α is sizeable. Chain C will not rupture unless the value of α is quite large. Obviously, the word "rupture" should not be taken to mean that the break occurs in the chain itself. The chain may merely pull loose from the filler surface, instead.

In any event, if the rubber is allowed to retract to its initial value and is restretched, it will appear softer, since the chains which broke are no longer resisting deformation. Consequently, the Mullins effect would be observed. We will show in the quantitative calculation given in this report that this process gives rise to strong enough forces to explain the effect. Even though the number of such chains which break is relatively small, the tremendous force which a chain holds just before it breaks causes the effect of the small number to be easily noticed.

Before proceeding with the computation, it should be explained why a gum stock does not show this effect. The effect depends upon the fact that chains like chain A in Figure 1 must break at very low relative elongations. If chain A were merely tied to two network junction points, as would be the case in a system without filler, the network junctions would be pulled through the rubber matrix so as to keep the forces in A small. In other words, the network junctions do not undergo an affine deformation in the vicinity of a highly strained chain. As a result, chain A need not elongate much, even though the sample is deformed considerably. It will therefore not break until very high deformations are imposed on the sample, and consequently the softening effect will be very small at moderate sample elongations.

COMPUTATION

Consider a system of long polymer chains for which the effects of chain ends may be neglected. Imbedded in this polymer is a volume fraction v_f of spherical filler particles with total surface area S per unit volume. There will be certain sites on the filler surface to which a chain unit is attached, the number of such sites being N and the area per site $\sigma = S/N$.

It is necessary to know what the distribution of chain lengths is for chains attached between filler particles. This may be computed in the following

way, provided one assumes gaussian chains for which the root mean square separation of two chain segments n segments apart is $(a^2n)^{1/2}$. We also assume that the primary molecular weight is much larger than the molecular weight between chemical crosslinks.

Suppose first that there are two parallel filler surfaces separated by a distance x . If a certain chain segment is attached to one of these surfaces, the chance that the n th segment along the chain will be within a distance Δx of the other surface is

$$(3/2na^2)^{1/2} \exp \{ -(3x^2/2na^2) \} \Delta x \quad (1)$$

If the chain segments are taken to have a volume near a^3 , then the chance that this segment is attached to the surface will be approximated by letting $\Delta x = a$ and multiplying eq. (1) by a^2/σ . Therefore, the chance that the n th chain segment is bound to the other filler surface is approximately

$$(a^3/\sigma)(3/2na^2)^{1/2} \exp \{ -(3x^2/2na^2) \} \quad (2)$$

It is next necessary to take account of the fact that some segment along the chain closer than the n th may have already been attached to the surface. Since the probability that the p th segment has been attached is given by eq. (2) upon replacing n by p , one has that the chance that no prior segment has attached itself is

$$\prod_{p=1}^{n-1} [1 - (a^3/\sigma)(3/2pa^2)^{1/2} \exp \{ -(3x^2/2pa^2) \}] \quad (3)$$

The probability that the n th segment is the first one along the chain to attach to the opposite surface is the product of expressions (2) and (3). This quantity which will be denoted as $P(n,x)$ is the probability that the chain length between filler surfaces is n when the surfaces are a distance x apart. After expanding and simplifying the product one finds

$$P(n,x) = (a^2/\sigma) (3/2n)^{1/2} \exp \{ -y^2 - (a^2/\sigma)(n)^{1/2} \phi \} \quad (4)$$

where

$$y^2 = 3x^2/2na^2$$

and

$$\phi = (6)^{1/2} \exp \{ (-y) - y(\pi)^{1/2} [1 - E_2(y)] \}$$

with

$$E_2(y) = (4/\pi)^{1/2} \int_y^\infty \exp \{ -t^2 \} dt$$

If the rubber sample of original length L_0 is stretched to length L , the relative elongation α will be L/L_0 . The actual rubber between filler particles

must elongate more than this to compensate for the filler which elongates none at all. It may be shown that the relative elongation α' of the rubber between filler particles in the direction of stretch is related to α in the following way (see Appendix I):

$$\alpha' = (\alpha - v_f^{1/3}) / (1 - v_f^{1/3}) \quad (5)$$

In the remainder of this report, the relative elongations inside the pure rubber will be designated by primes.

The chain which breaks at an extension ratio α_c' will be that for which $n_c a = \alpha_c' x$, where n_c is the value of n for this particular chain. One therefore has that the number of chains which have $n = n_c$ and will break at an extension ratio α_c' is

$$\sum N(x) P(n_{c,x}) \quad (6)$$

where $N(x)$ is the number of chains between surfaces separated by a distance x and the sum extends over all possible separations. It is clear that $N(x)$ will be a complex function involving the average surface separation, size and shape of the particles. We shall approximate it as

$$N(x) = N(\beta/b) \exp \{ -(\beta^2/b^2) (x - b)^2 \} \quad (7)$$

where b is an average surface separation.

The parameter β in eq. (7) determines the sharpness of the distribution. If $\beta = 0$, all separations are equally probable. If $\beta = \infty$, only $x = b$ is allowed. We shall choose β in such a way that $N(a)/N$ gives the proper probability for finding surfaces separated by a distance a , that is, nearly in contact. This particular choice is made since the following portions of the computations are most dependent upon the values at small surface separations. It is easily shown in a qualitative way (see Appendix II) that for spherical particles with radii about 150 A. and for which b/a is about 30, the probability of a separation less than a is of order 10^{-4} . This agrees with eq. (7), provided $\beta = 2.5$. If $\beta = 2.0$, the probability is about ten times larger, and so β is reasonably well determined from even such qualitative considerations.

The number of chains having $n = n_c$ is obtained by substituting from eqs. (4) and (7) into eq. (6) and replacing the summation by an integral over x . In carrying out this integration it must be remembered that $n_c = \alpha_c' x/a$. The integral is not easily carried out without approximation. We have evaluated it by expanding the exponential, retaining only two terms of the expansion, and then expanding ϕ in series form. The resulting series is then integrated term by term after ignoring the small variation of the factors in front of the exponentials.

The final result is a rather involved series. To avoid working with such a cumbersome expression, we have replaced it by the following one which fits it within the range of interest to a few per cent. The number of chains having $n = n_c$ is found to be

$$NP(n_c) = 4.75 \times 10^{-3} N(a/b)^{1/2} (a^2/\sigma) \exp \{ 4.7(a\alpha_c'/b)^{1/2} \} \quad (8)$$

where β has been given the value of 2.5 suggested above. The factor 4.75×10^{-3} varies inversely as β^9 and the factor 4.7 varies directly as β^2 to a good approximation for $2 \leq \beta \leq 4$.

The number of chains within range dn_c is $NP(n_c) dn_c$. It is of more interest to know the number of chains which break within the range $d\alpha_c'$. Since the average value of n_c is obtained by replacing x by b one has $n_c = \alpha_c'(b/a)$ from which $dn_c = (b/a)d\alpha_c'$. One therefore finds that the number of chains which break in the extension range $d\alpha_c'$ is

$$4.75 \times 10^{-3} N(a/b)^{1/2} (a^2/\sigma) \exp \{ 4.7(a\alpha_c'/b)^{1/2} \} d\alpha_c' \quad (9)$$

If one is interested in the contribution of such chains to the retractive force in the rubber when the extension of the rubber is α_c' , it is necessary to determine the way in which the tension in a chain varies as a function of α'/α_c' . The correct expression for the tension F in a chain which is extended to a fraction r/na of its maximum length is⁹

$$r/na = \coth(aF/kT) - (kT/aF) \quad (10)$$

This expression may be approximated in such a way that, if F_c is the tension in the chain at break, the tension at any elongation is given by

$$F = F_c(\alpha'/\alpha_c') / [(\gamma + 1) - \gamma(\alpha'/\alpha_c')] \quad (11)$$

where $\gamma = F_c a/kT$. This expression is exact at $F = F_c$ and becomes a progressively poorer approximation as F becomes smaller and as γ is decreased. For $\gamma = 100$ the correct value for $F/F_c = 0.093$ at $\alpha'/\alpha_c' = 0.90$, while eq. (11) gives $F/F_c = 0.082$. Since γ will usually be larger than 100, as will be seen later, eq. (11) should be satisfactory for the present purposes.

Not all of the N chains should be counted in computing the load being held by the sample. This is the result of the fact that only the number of chains acting across a given cross section of the sample hold the load. The remainder of the chains are essentially in series with these chains and should not be counted. Considering a sample in the form of a unit cube, any cross section will have $(1/\sigma)$

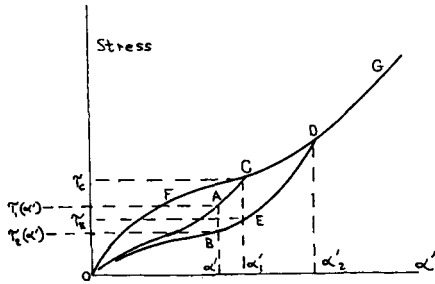


Fig. 2. A schematic set of stress-strain curves illustrating the Mullins effect.

filler bound chains crossing it. Therefore, N in eq. (9) should be replaced by $(1/\sigma)$ if one is interested in the tensile forces held by the filler bound chains.

Refer to Figure 2. If a filled rubber is stretched for the first time to an elongation α_1' , it will follow the stress-strain curve OFC. Upon a second stretch it will follow the curve OACD. If, after reaching point D on this curve, the rubber is again allowed to retract, it will follow the curve OBEDG on the next stretch. Using the equations derived here, we can now write down an expression for the softening effect due to prestressing. In particular one can write an expression for $\tau_1(\alpha') - \tau_2(\alpha')$ where these quantities are defined in Figure 2.

The softening represented by the quantity $\tau_1(\alpha') - \tau_2(\alpha')$ is the result of the breaking of filler-chain bonds as the rubber was stretched from C to D during the second stretching cycle. To compute this quantity one replaces N by $(1/\sigma)$ in eq. (9), multiplies eq. (9) by eq. (11), and integrates the result, $\alpha_1' \leq \alpha_c' \leq \alpha_2'$. This process merely adds up the forces which are caused at an extension α' by filler attached chains which will subsequently break at extensions between α_1' and α_2' . Of course, if one takes α_2' to be very large and $\alpha_1' = \alpha'$, one will obtain the amount by which the rubber is stiffened at any elongation α' by the action of the rubber-filler attached chains. In practice α' should never be taken larger than the ultimate elongation in a nonfilled rubber of comparable structure, since such values of α_2' are physically impossible.

If one carries out the integration indicated one finds, upon neglecting the relatively slow variation of the exponential in eq. (9),

$$\begin{aligned} \tau_1(\alpha') - \tau_2(\alpha') = & 4.75 \times 10^{-3} F_c (a/b)^{1/2} (a/\sigma)^2 (\gamma + 1)^{-1} \\ & \exp \left\{ 4.7 (a\alpha_1'/b)^{1/2} \right\} \left\{ \alpha' \ln \left[\frac{\alpha_2' (1 + \gamma^{-1}) - \alpha'}{\alpha_1' (1 + \gamma^{-1}) - \alpha'} \right] \right. \\ & \left. - \ln \left[\frac{\alpha_2' (1 + \gamma^{-1}) - 1}{\alpha_1' (1 + \gamma^{-1}) - 1} \right] \right\} \quad (12) \end{aligned}$$

The second logarithm in the brackets in eq. (12) is a correction term (usually small) needed to make $\tau_1(1) - \tau_2(1) = 0$ as it must be. It is made necessary by the fact that no provision had been made in previous equations for the fact that all internal chain forces must balance out to zero when $\alpha' = 1$.

APPLICATION TO SBR

Equation (12), which should be applicable to any rubber-filler system, contains four molecular parameters, a , F_c , σ , and b . However, since the segment length a never occurs alone, the equation is completely determined by three parameters, aF_c , b/a , and σ/a . The parameter a may be evaluated from the stress-strain curve of the vulcanized unfilled rubber if so desired. This is done for the case of SBR in Appendix III, where it is found that $a = 4.3 \text{ \AA}$. In any case, its value is not needed for the application of eq. (12).

The constants listed above may be obtained from a set of experimental curves such as those shown in Figure 2. In particular, the two curves OAC and OBD allow one to determine $\gamma = aF_c/kT$. This is done as follows.

The ratio $R = (\tau_1 - \tau_2)/(\tau_1 - \tau_E)$ may be computed from the experimental data. This ratio may also be obtained from eq. (12) by dividing eq. (12) by a similar equation in which α' is replaced by α_1' . All the unknown constants except γ disappear from this ratio, and so comparison of the experimental value for R with the theoretical value will give a numerical value for γ . It is more accurate, however, to compute R from the experimental data at various α' values and plot these values of R as a function of α' . Assuming a value for γ , one can also plot a theoretical curve for the variation of R with α' . The value of γ which gives rise to the best agreement with experiment is the correct value.

This has been done for some data of Mullins³ for SBR containing 50 parts of MPC black. The values $\alpha_1' = 8.5$ and $\alpha_2' = 13.5$ were used. These values correspond to α_1 and α_2 values of 4 and 6, respectively. The results are shown in Figure 3, where the points are from the experimental data. It is clear that the agreement between the experimental and theoretical curves leaves something to be desired. However, the upper portion of the experimental curve shown there is extremely sensitive to a small amount of permanent set which plagues this type of measurement. In addition, the upper portion of the curve will be lowered somewhat by a second extension to α_1 and so the exact experimental values in this region are in doubt. It appears that γ should be taken to be about 200,

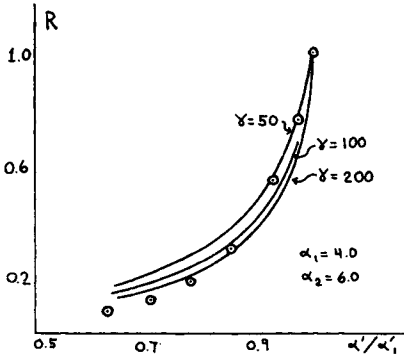


Fig. 3. Comparison of experiment (points) and theory for the determination of γ at the γ values indicated on the curves.

although it might possibly be as low as 100 or as high as 300. Fortunately, its exact value is not extremely critical in determining the overall shapes of the experimental curves.

The determination of a/b is best made by examining the curve OFCDG of Figure 2. From eq. (12) it is seen that, if $\phi(\alpha_1')$ is the function

$$\left\{ \alpha' \ln \left[\frac{\alpha_2'(1 + \gamma^{-1}) - \alpha'}{\alpha_1'(1 + \gamma^{-1}) - \alpha'} \right] - \ln \left[\frac{\alpha_2'(1 + \gamma^{-1}) - 1}{\alpha_1'(1 + \gamma^{-1}) - 1} \right] \right\}$$

in eq. (12), then a plot of $\ln Q = \ln [(\tau_c - \tau_E)/\phi(\alpha_1')]$ vs. $(\alpha_1')^{1/2}$ will give a straight line of slope $4.7(a/b)^{1/2}$. The values of $\tau_c - \tau_E$ are obtained from the experimental curves OFD and OBED and the values of $\phi(\alpha_1')$ are obtained by setting $\alpha' = \alpha_1'$ and using $\gamma = 200$. Making use of the same experimental data as before, one obtains the straight line shown in Figure 4. The slope of this line gives a value for b/a of 29.

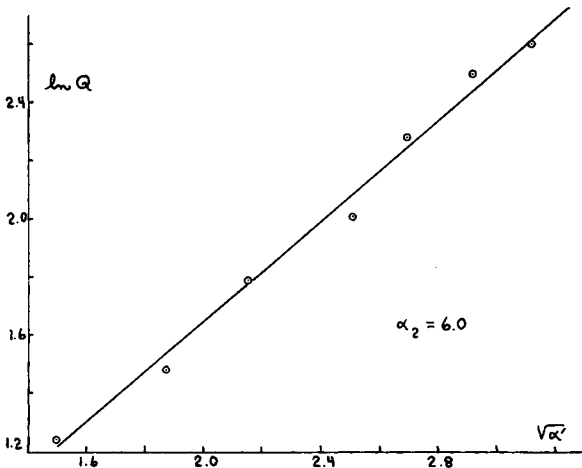


Fig. 4. Comparison of theory (points) and experiment showing the Mullins effect in SBR loaded with 50 parts of MPC black.

Finally, the value of (a/σ^2) is chosen so that eq. (12) gives the experimental value for $\tau_1 - \tau_2$ at some arbitrary value of $\alpha' = \alpha_1'$. For the greatest accuracy, one should probably determine (a/σ^2) for the data at a rather large value of α' . In the present case, the theoretical curve fits the experimental so well that the value of (a/σ^2) does not vary more than 6%, no matter which value of α' is selected for its evaluation. One finds that $(\sigma/a) = 10 \times 10^{-8}$ cm.

DISCUSSION

Having determined the constants γ , (b/a) , and σ/a , one can use eq. (12) to plot any set of curves such as those in Figure 2 for this rubber-filler system. To test the equation, the curves of Figure 5 have been plotted. The full curves are those found from experiment by Mullins.² The points were obtained from eq. (12) by use of the constants found in the previous section. It is clear that substantial agreement is obtained. Furthermore, this agreement is not just a fortuitous coincidence which occurs because of our choice of the three parameters. Variation of these parameters within their limits of error does not seriously harm the agreement found in Figure 5. Moreover, we will next show that these constants are entirely reasonable in magnitude.

First, consider the ratio b/a . If a is given the value found in Appendix II, 4.3 A., then b will equal 130 A. If one pictures the MPC black particles to be spherical with radius 125 A. and placed on a cubic lattice in the rubber, the distance between their centers will be about 330 A. It would therefore

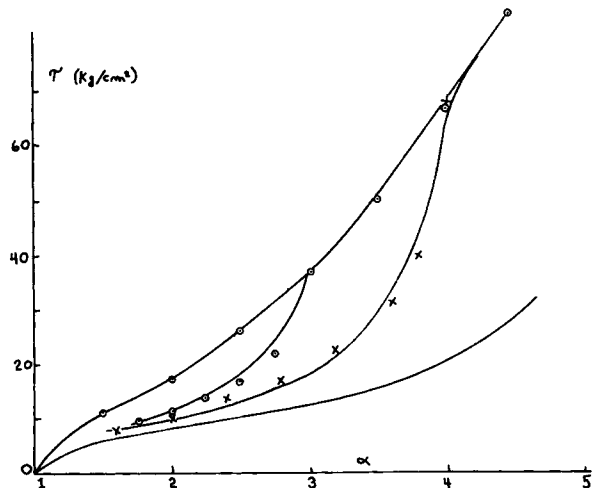


Fig. 5. A plot of the experimental data in a form useable for the determination of b/a .

appear that the value found for b , the average distance between surfaces in any one direction in the matrix, is not unreasonable.

Using the same value for a , one finds that the surface area per attachment, σ is about 44 A.². This again is a reasonable value. Although Frisch et al.⁶ have found an area of about 900 A.² for solution adsorption of polystyrene on carbon black, and others^{7,8} have found similar values for adsorption of rubbers from solution, not too much importance should be given to these values, since there is no real reason to believe that the rubber-filler bonds discussed here are the same as in the case of solution adsorption.

The value of the strength of the weakest point in the chain may be found from the fact that $\gamma = (F_c a/kT) = 200$. This gives a value for F_c of about 2×10^{-4} dynes. It is not known what force the C—C bond can hold for an appreciable time, and so one is unable to say from this information alone whether the chain breaks loose at the filler particle or whether it breaks along the chain. The answer to this question may be determined in the following way.

Equation (10) gives the chain end displacement, r , in terms of the force applied to it. The energy stored in the chain at break is obtained by multiplying dr by F and integrating over r from $r = 0$ to the value of r at the breaking point. This is easily done, and the result for the elastic energy stored in the chain at break is

$$nkT[\ln(\gamma/\sinh \gamma) + \gamma \operatorname{ctnh} \gamma - 1] \quad (13)$$

The elastic energy per bond E_e is then

$$E_e = kT[\ln(\gamma/\sinh \gamma) + \gamma \operatorname{ctnh} \gamma - 1] \quad (14) \\ \cong kT[\ln(2\gamma) - 1]$$

where the approximate form is accurate to better than a few per cent for $\gamma > 10$. With $\gamma = 200$ one finds $E_e/kT = 5.0$. This is a relatively small amount of energy compared to that needed to break a C—C bond, about 60 kcal./mole, and so the effect of thermal energy must also be considered.

If a bond is to break at a temperature T in a reasonable length of time, say 10^2 sec., then the product of the bond vibration frequency, about 10^{12} , by the factor $\exp\{-E_e/kT\}$ must be about 0.01, where E_e is the thermal energy needed to break the bond. We therefore have

$$\exp\{-E_e/kT\} \cong 10^{-14}$$

from which

$$E_e/kT \cong 32$$

One therefore has that the bond concerned here requires an energy E to break, which is given by

$$E/kT \leq (E_i/kT) + (E_e/kT) \cong 37 \quad (15)$$

Therefore E is about 22 kcal./mole. This is to be compared with the C—C bond energy of about 60 kcal./mole.

The above result indicates that the weak link is the attachment at the filler surface. An examination of eq. (14) shows that any reasonable value of γ will not alter the above result by much. In addition, the assumption that the elastic energy is evenly distributed along the chain is not a critical factor. It would therefore appear quite certain that the chain itself does not break but that the break occurs at the point of attachment.

The energy of the filler-rubber bond is not accurately given by the above computation, however. This is a result of the fact that eq. (14) was derived only for the rubber chain, and the bond at the filler surface will certainly not comply with eq. (10). About all one can say is that the energy needed to break this bond is greater than 20 kcal./mole or it would break by itself at room temperature. Temperature variation studies of the Mullins effect will be needed to place an upper limit on this value as well as to raise the lower limit.

At first thought it seems possible to determine the strength of the filler-rubber bond from the enclosed area of loops such as OACDEO in Figure 2, since this area is a measure of the energy lost by breaking bonds along the portion of the curve CD in Figure 2. This process is not as simple as it seems, however. Although one can easily calculate the number of chains which are torn loose from the filler, the energy loss due to these chains is not simple to interpret. First, the energy per chain is stored in the total n bonds of the chain plus the bonds at the filler surface. Although one can show that the elastic plus thermal energy per bond is less than 60 kcal., it is impossible to obtain the exact energy one should assign to the filler-rubber bond. One is therefore no better off than with the previous method of calculation. In fact, it turns out that the result obtained from the loop area is much more sensitive to the exact value of γ than was the previous method. It therefore appears that the filled-rubber bond energy is not obtainable from the present data taken only at one temperature.

The present theory provides a basis for a fruitful experimental approach to the problem of rubber reinforcement. It should be possible to characterize accurately the filler-rubber bond by the

two constants F_c , the force needed to break it, and σ , the area per attachment. For poor reinforcing fillers, F_c should be smaller and σ larger than the values found for MPC black. In addition, the temperature variation of σ and F_c may possibly allow one to compute the energy of the rubber-filler bond. The quantity b is a measure of the distance between filler particles. For a given filler size and loading, b should increase as the filler dispersion becomes better.

APPENDIX I

Consider the two filler particles shown in Figure 6. Although it is not necessary to do so, we assume them to be cubical in shape and to be dispersed uniformly through the rubber. Suppose the rubber is stretched so that the centers of the two particles separate a distance ΔL . Using the definition of α , α' and the distances L_0 and L_0' shown in Figure 6, one has

$$\Delta L = (1 - \alpha)L_0$$

and

$$\Delta L = (1 - \alpha')L_0'$$

But since $L_0' = L_0(1 - \nu_f^{1/3})$, one can equate the expressions for ΔL and cancel out the distance L_0 . The resulting equation can be solved for α' to give eq. (5) in the text.

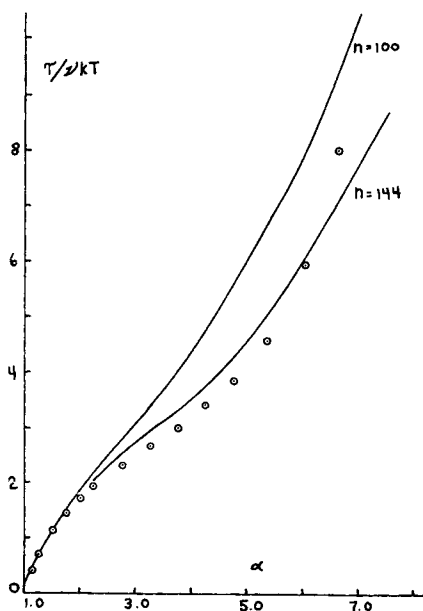


Fig. 6. A schematic diagram for the computation carried out in Appendix I.

APPENDIX II

Consider two filler particles with radii r . Suppose that their separation may have any value between zero and $2b$ with equal probability. It is desired to find the probability that a point on the surface of one of the spheres is within a distance a of a point on the other sphere. This may be done qualitatively as follows.

The probability that the two spheres are within a distance a of touching is $a/2b$. The surface area of one sphere which is within a distance a of the surface of the other sphere when the spheres are touching is $2\pi ra$. When the spheres have separated to a distance a , none of the area is within a distance a of the other sphere. As an approximation, say that an area πra of one sphere is within a distance a of the other sphere when the sphere separation is a or less. It will be zero when the separation is greater than a .

When any area at all of one sphere is within a distance a of the other sphere, the fraction of the hemispherical area within a distance a will be $(\pi ra/2\pi r^2)$. This fraction, when multiplied by the probability that the sphere separation is a or less, will give the desired probability. It is $(a^2/4rb)$. If a is taken to be 4 A. and b and r to be 150 A. this probability is given to be 1.8×10^{-4} .

APPENDIX III

The segment length, a , can be found from a consideration of the stress-strain curve for SBR. Treloar⁹ has shown that the James-Guth equation for the tensile stress in a gum vulcanizate can be written to good approximation as

$$\tau/\nu kT = (1/3K) [\mathcal{L}^{-1}(\alpha K) - (3K/\alpha^2)] \quad (16)$$

with $K = (1/n)^{1/2}$. The quantity n is the number of segments per network chain and ν is the effective number of network chains in unit volume.

If one plots eq. (16) in the form $\tau/\nu kT$ vs. α for various values of K , the resultant curves can be compared with actual experimental data plotted in the form $\tau/(\text{const.})$ vs. α . The constant in the experimental plot is chosen so as to fit the theoretical

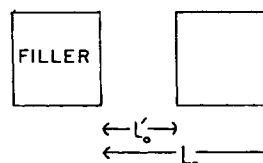


Fig. 7. Comparison of the experimental stress-strain curve for SBR gum stock (points) with the James-Guth equation.

curves at low α values where all the curves must coincide. By comparing the experimental curve with the theoretical curves, one can choose the proper value of K to obtain the best fit. This value of K , in turn, yields a value for the number n of segments per network chain in the rubber upon which measurements were taken. These plots are shown in Figure 7. The experimental data are those of Treloar⁹ for SBR gum stock.

The appropriate value of n appears to be about 140. In addition, νkT , the constant needed for the experimental curve, is about 4.3×10^6 dynes/cm². If one assumes that the original gum stock had a number average molecular weight of 35,000, one can then compute the molecular weight of a network chain M_c from the value of ν . This yields a value of about 4800 for M_c . It is therefore known that a chain of this molecular weight contains about 140 segments.

To find a , one makes use of the fact¹⁰ that the mean square end-to-end distance of nearly all common polymers is known experimentally to conform with the relation $R^2 \cong (7.5 \times 10^{-9})^2 M$. Since one also has that $R^2 = na^2$, one can equate these two expressions for R^2 and replace n and M by the values found above. One then finds that a is about 4.3 Å.

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Synopsis

A molecular theory for the softening of filled rubbers which is caused by prestressing is presented. It is based upon the assumption that the centers of the filler particles are displaced in an affine manner during deformation of the rubber. Those network chains which are fastened at both ends to filler particles will break when the filler particles have separated enough to stretch the chains to near full

elongation. The loss of these chains causes a prestressed rubber to exhibit a much lower modulus than did the original rubber. Equations are derived to describe this phenomena and are tested by comparing with data for black filled synthetic rubber. Good agreement is found if the filler surface area per chain attachment is taken as 44 Å² and if the strength of the chain is 2×10^{-4} dynes. It is shown that the chains break loose from the filler particle rather than breaking at C—C bonds along the chain. The theory appears to offer a convenient tool for systematic studies of rubber-filler interactions.

Résumé

On présente une théorie moléculaire de l'amollissement des caoutchoucs contenant des charges par suite d'une extension préalable. Elle se base sur la supposition que les particules de remplissage se déplacent d'une manière progressive au cours de la déformation du caoutchouc. Ce réseau de chaînes qui sont liées à chaque extrémité à des particules de remplissage rompront lorsque ces particules de remplissage se sont séparées suffisamment que pour étendre les chaînes tout près de leur élongation maximum. La perte de ces chaînes provoque l'apparition dans un caoutchouc étiré d'un module beaucoup plus faible que celui observé le caoutchouc initial. On déduit des équations pour décrire ce phénomène et on les contrôle avec les résultats obtenus sur du caoutchouc synthétique chargé au noir animal. On trouve un bon accord si on prend pour surface de la charge rattachée à la chaîne 44 Å² et si la tension de la chaîne est de 2×10^{-4} dynes. On montre que la chaîne rompt plutôt à la hauteur d'une particule de remplissage plutôt qu'à la hauteur d'une liaison C—C de la chaîne. La théorie semble pouvoir constituer un outil adéquat pour l'étude systématique des interactions caoutchouc-particules de charge.

Zusammenfassung

Eine molekulare Theorie für die Erweichung von gefülltem Kautschuk durch Spannungsvorbehandlung wird entwickelt. Sie beruht auf der Annahme, dass die Zentren der Teilchen des Füllstoffes während der Verformung des Kautschuks eine affine Verschiebung erfahren. Diejenigen Netzketten, die an beiden Enden an Füllstoffteilchen verankert sind, werden zerreißen, sobald die Füllstoffteilchen weit genug voneinander entfernt wurden, um die Ketten nahezu auf volle Elongation zu strecken. Der Verlust dieser Ketten führt dazu, dass ein Spannungsvorbehandelter Kautschuk einen viel niedrigeren Modul aufweist als der ursprüngliche Kautschuk. Gleichungen zur Beschreibung dieser Erscheinung werden abgeleitet und durch Vergleich mit Ergebnissen an russgefülltem, synthetischen Kautschuk überprüft. Gute Übereinstimmung wird unter der Annahme gefunden, dass die Füllstoffoberfläche pro Kettenhaftstelle 44 Å² beträgt und die Festigkeit der Kette 2×10^{-4} dyn ist. Es wird gezeigt, dass die Ketten von den Füllstoffteilchen abgetrennt werden, eher als dass C—C-Bindungen in der Kette gespalten werden. Die Theorie scheint ein brauchbares Werkzeug für eine systematische Untersuchung der Wechselwirkung zwischen Kautschuk und Füllstoff zu liefern.

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