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A molecular theory of adhesive rubber friction

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Abstract. A theory of adhesive rubber friction is proposed where the final expression for the coefficient of friction obeys the Williams-Landel-Ferry transform and correlates with the viscoelastic shear loss modulus, as shown by Grosch and others. Our approach is based on the bead-spring model for polymer chains of Rouse.

1. Introduction

The earlier work on building models of rubber friction (Schallamach 1953, Bartenev 1954) pictured the rubber molecules as entering into, and breaking, bonds with the molecules of the track by thermally surmounting a potential barrier, this barrier being lowered in the direction of motion by an amount proportional to the applied force. These theories were consistent with the data available at the time.

Subsequently, two factors contributing to rubber friction were distinguished:

(a) Hysteresis: rubber is a viscoelastic substance so there will be energy losses in a deformation cycle. If a block of rubber moves over a rough but lubricated surface the energy loss will result in a force resisting the motion. This force is referred to as hysteretic friction (Tabor 1955). Grosch (1963) has shown that the velocity-temperature dependence of this component of friction is that predicted by the WLF (Williams *et al* 1955) transform; in other words it can be regarded as a function only of a single variable $x = Vf(T)$, V being the velocity and T the temperature. The form of $f(T)$ is well approximated by the empirical WLF formula which, with one substance-dependent parameter, holds good for a large class of polymers. One result of this fact is that all curves of $\mu_h(V, T)$, the coefficient of hysteretic friction, against V or T separately can be shown to lie on a master curve $\mu_h = \mu_h(x)$. This is not so surprising since it is to be expected that μ_h will be related to the viscoelastic functions of the material which are well known to have frequency-temperature dependence as given by the WLF equation. In fact, Grosch (1963) quantifies the connection by showing a correlation between the velocity of maximum friction at a given temperature and the frequency at which the loss tangent ($\tan \phi$) is maximum, for the substance in question. The constant of proportionality he found to be a distance of order 10^{-2} cm and is obviously characteristic of the roughness of the track.

(b) Adhesion: this type of friction, regarded as being the primary contributor when a rubber block slides over a smooth unlubricated surface, is usually pictured as being due to molecular bonding between the rubber chains and the molecules of the track. A

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somewhat more surprising result of Grosch (1963) is that $\mu_a(V, T)$, the coefficient of adhesive friction, as a function of V, T also respects the WLF transform; in other words μ_a is a function only of the variable x discussed above. Furthermore, at a given temperature, the maximum of $\mu_a(V)$ correlates with the maximum of the loss modulus $G''(\omega)$ as a function of frequency. Here, the constant of proportionality is a length of molecular dimensions that depends only on the track.

One concludes that the adhesive component of rubber friction, as well as its hysteretic component, is related to the bulk properties of the substance. Of course, this is perhaps not so surprising in view of the cross-linked macromolecular structure of the rubber; because of this structure, a 'tug' at the surface, due to a bond with the track, will excite the cross-linked framework. The object of this paper is to model this effect in a simple way.

Similar results to the above were obtained by Bulgin *et al* (1962) and Bartenev *et al* (1965), although the former correlate the friction coefficient with the loss tangent, and do not distinguish between adhesive and hysteretic friction.

A number of partially successful attempts have been made to build models which predict the results of the last paragraphs. Schallamach (1963) revises his earlier theory concentrating now on adhesive friction and achieves qualitative agreement with experiment, together with, in some sense, a form for μ_a which possesses the WLF property. Rieger (1967) revived a theory of Prandtl (1928), considering a block of rubber sliding over a sinusoidal force with the rubber chains simulated by a Voigt element. This model has certain features in common with the one proposed here.

Lawrentew and Ostreiko (1968) have, from a simple argument based on equilibrium between bond formation and rupture, produced an expression for the friction force as a function of temperature and velocity which qualitatively agrees with experiment.

Kummer (1966) has attempted a unified theory with adhesion and hysteresis treated on the same footing. We mention other interesting theories, Savkooor (1965), Hatfield and Rathman (1956), Ludema and Tabor (1966), and refer to two comprehensive reviews where these are discussed in some detail (Schallamach 1968, Moore 1972).

The object of this paper is to present a model of adhesive friction, using existing mathematical models of polymers. This, to our knowledge, has not been done. Such a theory will be a 'fundamental' theory, at least to the degree that the polymer model we use is a fundamental model.

The classical theory of the dynamics of polymer chains is due largely to Kirkwood (see Kirkwood 1967 for example) and collaborators. His approach provides a rigorous, systematic approach which however is, mathematically, largely intractable. This fact caused a number of authors to look for simplified versions of the theory, but in the same spirit. Rouse (1953) proposed a bead-spring model, which we shall describe and use below. This theory applied to polymer chains in dilute solution and neglected the so called hydrodynamic interaction (Kirkwood 1967, Ferry 1970), ie it held in the free-draining limit. Beuche (1954) considered a similar model but neglected the Brownian motion aspect. Zimm (1956) later introduced the hydrodynamic interaction. A more formal, systematic version of the theory is given by Fixman (1965).

We are not, of course, interested in polymer solutions but in cross-linked polymer frameworks. The Rouse theory can be applied in a limited fashion to this system if we consider the cross-links as fixed points and think of each segment as moving in a medium made up of all the other segments. Mooney (1959) made the necessary adjustment to the Rouse theory to take account of fixed end points. The applicability of the resulting theory is discussed by Ferry (1970).

There are more sophisticated methods of handling cross-linked systems (eg Chompff and Duiser 1966) and more recent work on polymer dynamics (eg Edwards 1974) but our object in this paper is to take the simplest available theory, though it may be of limited applicability, and test our approach for it. Obviously, more sophisticated theories will have to be examined, at a later stage.

In § 2 we describe the model, including our modification of the Rouse theory, treated by Langevin methods rather than the usual approach which uses the Smoluchowski equation (Chandrasekhar 1943). In § 3 we solve the model, giving an expression for μ_a . This is discussed in § 4. We summarize our results in the conclusion.

2. The model

We consider a rubber block (figure 1) sliding over a track with velocity $-V$. For convenience we take a reference axis such that the block is at rest and the track moving with velocity V . The effect of the molecules of the track is summarized by a sinusoidal force acting on the polymer chains in the vicinity. This is, of course, motivated by the experimental correspondence between velocity and frequency, mentioned in § 1. We take the velocity V to be in the x direction and the plane of the track to be the $z = 0$ plane.

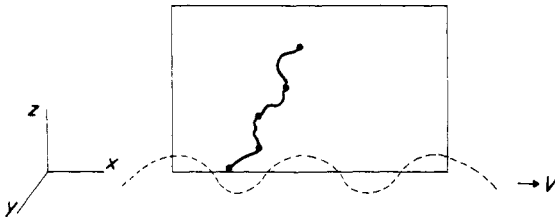


Figure 1.

The polymer chains are assumed to be fixed in the block at one end (cross-linking) and free at the other, where they are subject to the sinusoidal force. They are also taken to be subject to a Brownian force (Kirkwood 1967) due to the medium made up of the rest of the block of rubber, as they move under the influence of the track molecules. The fact that the Brownian force is partly dissipative is the origin of our friction force.

How do we describe the polymer chain? As discussed above we choose the Rouse model, rather than, for example, Kirkwood's, in the interests of mathematical simplicity. Basically Rouse's (1953) approach was to assume that only isolated points on the polymer chain interact with the medium. One then idealizes further, in two ways. One assumes that these points of interaction are equidistant, along the chain; and also that they are far enough apart to allow the Gaussian statistics of the single chain to be applied (Flory 1953, 1969), in other words that distance between adjacent points of interaction obeys a Gaussian distribution. This is undoubtedly the mathematically most tractable way of incorporating the connectivity of the chains into the model.

There are two equivalent approaches to Brownian motion (Chandrasekhar 1943, Wang and Uhlenbeck 1945 for example): (i) the Langevin stochastic differential equation method; and (ii) the Fokker-Planck (or Smoluchowski, if the inertial term is negligible) partial differential equation method. The first has possibly the advantage of offering

greater physical insight though it is not convenient for the calculation of explicit probability distributions; on the other hand it is very convenient for calculating expectation values of physical quantities which is virtually always enough.

In contrast to the bulk of theoretical work in polymers, we will use the first approach here and consider the problem using the second approach, in a subsequent paper. We denote the fixed end of a typical chain as r_0 and the interacting points $r_1, r_2 \dots r_N$. As discussed above we take the equilibrium probability distributions of these points as

$$W(\mathbf{R}_i) d^3 \mathbf{R} = A \exp(-3R_i^2/2b^2) d^3 \mathbf{R}_i \tag{1}$$

where

$$\mathbf{R}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \quad i = 1, 2, \dots N$$

and where b is the average distance between the points. This is equivalent to a temperature-dependent Hookean force between the particles (Zimm 1956) given by

$$-M\lambda^2 \mathbf{R}_i = -\frac{3kT}{b^2} \mathbf{R}_i \tag{2}$$

within this formalism. We have denoted the force constant as λ^2 , and the effective mass of each interacting segment as M . The system of equations which we must consider is

$$\ddot{\mathbf{r}}_i + B\dot{\mathbf{r}}_i + \lambda^2(-\mathbf{r}_{i-1} + 2\mathbf{r}_i - \mathbf{r}_{i+1}) = \mathbf{f}_i(\mathbf{r}_i, t) + \mathbf{A}_i(t) \tag{3}$$

where $i = 1, 2, \dots N-1$, remembering that r_0 is fixed and

$$\ddot{\mathbf{r}}_N + B\dot{\mathbf{r}}_N + \lambda^2(-\mathbf{r}_{N-1} + \mathbf{r}_N) = \mathbf{f}_N(\mathbf{r}_N, t) + \mathbf{A}_N(t) \tag{4}$$

where B is the frictional dissipation per unit mass on each particle due to the medium in which it is moving while $\mathbf{A}_i(t)$ is the random force per unit mass due to the medium. These two terms summarize the interaction between the polymer chain and the block of rubber of which it is a part. This splitting into two distinct terms and the properties of the noise term $\mathbf{A}_i(t)$ are discussed at some length by Chandrasekhar (1943). The dot notation in equations (3), (4) denotes differentiation with respect to time, of course. The terms $\mathbf{f}_i(\mathbf{r}_i, t)$ summarize the external sinusoidal force per unit mass on the chain, due to the track. Ideally this should be: (i) the same functional form for all elements; (ii) include a force in the z direction; (iii) the force in the x - y plane should only act on those elements below a certain z value and should be sinusoidal.

The formalism we are describing is capable of treating such a model, at least in some approximation and it is certainly our intention to attempt to work it through, using the general form for $\mathbf{f}_i(\mathbf{r}_i, t)$. However, again in the interests of more immediate mathematical tractability, we will in this paper simplify, by assuming that:

- (i) The particle r_N is fixed in the $z = 0$ plane, ie the plane of the track †.
- (ii) Only this particle experiences the external sinusoidal force.

Assumption (i) is loosely expressed. More precisely we imagine polymer chains becoming bonded with the track, remaining so for a long period and breaking loose again. A long period means one long compared with the other characteristic times in the problem. As a justification for this picture we can only offer the final result. Note that this bond making and breaking refers to the z direction only, corresponding perhaps to a potential barrier, or a lack of tension (at a molecular level) in this direction. This is

† This assumption may be softened slightly by stressing that the N th particle need not be the last in the chain. However, if it is not, we ignore the existence of the subsequent ones.

perhaps the appropriate place to make a related point. Many of the models described in the introduction refer to bond making and breaking in the x direction. Our model is not so different from this concept as might appear at first sight. The sinusoidal force can be viewed as a series of potential barriers; also the thermal barrier breaking formulae are sort of built into the Brownian motion formalism (Chandrasekhar 1943, § 7).

In short, these approximations allow us to ignore the y, z components of the equation and put

$$\begin{aligned} f_i^{(x)}(x_i, t) &= 0, & i &= 1, 2, \dots, N-1 \\ f_N^{(x)}(x_N, t) &= f \cos d(x_N - Vt) \end{aligned} \tag{5}$$

where d is constant. We can summarize our equations in matrix form as

$$\ddot{X} + B\dot{X} + \lambda^2 DX = F(X) + A \tag{6}$$

where the components of the N -dimensional equation are x_i , the x components of the position vectors r_i . The components of F are given by

$$F_1 = \lambda^2 x_0, \tag{7}$$

F_N given by equation (5) and all other components zero. The N vector A is the vector of random forces. The $N \times N$ matrix D is given by

$$D = \begin{bmatrix} 2 & -1 & 0 & 0 & \dots & \dots \\ -1 & 2 & -1 & 0 & \dots & \dots \\ 0 & -1 & 2 & -1 & 0 & \dots & \dots \\ 0 & \dots & \dots & -1 & 2 & -1 \\ 0 & \dots & \dots & 0 & -1 & 1 \end{bmatrix} \tag{8}$$

3. Solution

Our object is to solve equation (6). It is necessary to use an approximation method. First we notice that x_0 can be chosen to be zero, since it is the track that is moving, not the rubber block. Now it is reasonable to assume that F , the friction force, is small compared with other quantities so we use the method of successive approximation as follows. Let $X_0(t)$ be the solution of equation (6) with $F = 0$. It can be found explicitly. The next correction $X_1(t)$ is found by solving

$$\ddot{X}_1 + B\dot{X}_1 + \lambda^2 DX_1 = F(X_0(t)) \tag{9}$$

which can also be solved explicitly. One could continue like this, getting terms of order F^2 but let us neglect these. First the explicit form of $X_0(t)$? Note that this is formally the harmonic oscillator problem treated by Chandrasekhar (1943) except that D is a matrix. However, it commutes with all other quantities in the problem, that is to say, with B which is a scalar. Therefore, we can use Chandrasekhar's formulae, remembering that the functions involved are now matrices.

So $X_0(t)$ is given by (Chandrasekhar 1943)

$$X_0(t) = e^{\mu_1 t} a_1 + e^{\mu_2 t} a_2 + \int_0^t \psi(t, \xi) A(\xi) d\xi \tag{10}$$

where μ_1, μ_2 are the matrix functions

$$-\frac{1}{2}B \pm (\frac{1}{4}B^2 - \lambda^2 D)^{1/2} \tag{11}$$

while $\psi(t, \xi)$ is the matrix function

$$\psi(t, \xi) = \frac{1}{\mu_1 - \mu_2} \{ \exp[\mu_1(t - \xi)] - \exp[\mu_2(t - \xi)] \}. \tag{12}$$

The column vectors a_1, a_2 contain the initial conditions

$$a_1 = -(\mu_2 X_i - U_i) / (\mu_1 - \mu_2) \tag{13}$$

$$a_2 = (\mu_1 X_i - U_i) / (\mu_1 - \mu_2) \tag{14}$$

where we have used X_i for $X_0(t = 0)$ and U_i for $\dot{X}_0(t = 0)$. To get final answers we will of course have to choose coordinates where the matrix D is diagonal, ie normal coordinates.

Now, what we are really interested in is $B \langle \langle \dot{X}_1^T \dot{X}_1 \rangle \rangle$ where we have used standard transpose notation and where the brackets denote averaging over: (i) the distribution of values of the random variable $\dot{X}_1^T \dot{X}_1$ at time t ; and (ii) all possible initial conditions. We will then further average over time to eliminate micro-oscillations. This is then the average rate of dissipation of energy which can be equated to RV where R is the friction force due to this polymer chain. Equation (9) has explicit time dependence on the right so we can once more borrow the formulae of Chandrasekhar (1943) to calculate

$$\dot{X}_1(t) = \sum_{i=1}^2 \mu_i e^{\mu_i t} a_i + \int_0^t \phi(t, \xi) F(X_0(\xi)) d\xi \tag{15}$$

where

$$\phi(t, \xi) = (\mu_1 e^{\mu_1(t-\xi)} - \mu_2 e^{\mu_2(t-\xi)}) / (\mu_1 - \mu_2). \tag{16}$$

We are interested in the steady-state situation which develops for large t , so taking into account equation (11), it is obvious that we can neglect the exponential, or transient, terms in equation (15). Introducing the notation

$$F = F_0 \cos[d(X_{0N}(t) - Vt)] \tag{17}$$

and

$$H(t, \xi_1, \xi_2) = F_0^T \phi^T(t, \xi_1) \phi(t, \xi_2) F_0 \tag{18}$$

we can write (Note: H is a scalar quantity. Also while F_0 has only one nonzero term in our original coordinates, this will not be true in normal coordinates which we will eventually have to switch to.):

$$\dot{X}_1^T(t) \dot{X}_1(t) = \int_0^t d\xi_1 \int_0^t d\xi_2 H(t, \xi_1, \xi_2) \cos(dl(\xi_1)) \cos(dl(\xi_2)) \tag{19}$$

$$= \frac{1}{2} \text{Re} \int_0^t d\xi_1 \int_0^t d\xi_2 H(t, \xi_1, \xi_2) \{ \exp[id(l(\xi_1) + l(\xi_2))] + \exp[id(l(\xi_1) - l(\xi_2))] \} \tag{20}$$

where

$$l(t) = X_{0N}(t) - Vt. \tag{21}$$

We now have to find the expectation value of this quantity. First the average over initial conditions. This refers to the vectors a_1, a_2 given by equations (13), (14) which we claim are multinormal variables. Let the bond be formed at time $t = 0$. Up to this time the chain will not be subject to the force F and will obey the equilibrium distribution for a linked chain, ie the Maxwell–Boltzmann distribution. So the distribution function for X_i, U_i of equations (13), (14) will be (cf equation (1))

$$W(X_i, U_i) = K \exp[-(\frac{1}{2}MU_i^T U_i + \lambda^2 X^T DX)/kT] \tag{22}$$

which is multinormal, with mean zero. It follows that a_1, a_2 are.

With respect to the other averaging, it is well known (Chandrasekhar 1943) that the random force term of equation (10) is multinormal. It follows that $X_{0N}(t)$, being a sum of normal variables is normal. Its mean is also zero. Remembering the definition of the characteristic function of a distribution and its form, in the Gaussian case, we deduce that

$$\begin{aligned} \langle \dot{X}_1^T \dot{X}_1 \rangle &= \frac{1}{2} \text{Re} \int_0^t d\xi_1 \int_0^t d\xi_2 H(t, \xi_1, \xi_2) \left[\exp\left(-\frac{d^2\sigma_1^2}{2} - idV(\xi_1 + \xi_2)\right) \right. \\ &\quad \left. + \exp\left(-\frac{d^2\sigma_2^2}{2} - idV(\xi_1 - \xi_2)\right) \right] \end{aligned} \tag{23}$$

where

$$\sigma_1^2 = \langle (X_{0N}(\xi_1) + X_{0N}(\xi_2))^2 \rangle \tag{24}$$

$$\sigma_2^2 = \langle (X_{0N}(\xi_1) - X_{0N}(\xi_2))^2 \rangle. \tag{25}$$

These quantities can be calculated as explicit functions of ξ_1, ξ_2 by going over to normal coordinates. The expressions are long; they also make explicit evaluation, in closed form, impossible. It is straightforward to show that they are sums of exponentials and constant terms. By expanding the exponentials of exponentials in infinite series, it is straightforward, though tedious, to show that most of these are negligible in the limit of large t , which is what we are interested in. The remaining terms are the constants and certain of the cross terms resulting from averaging the product of two noise functions. The neglect of these involves, in the large B limit (see below, eg (35)), neglecting d^2b^2 . This could be understood as saying that the chain is confined to a region small compared with the wavelength of the force, which may well be true in real rubbers where the density of chains and other ingredients is large. Implicit in this statement is the view that the essentially artificial parameter b is determined by the effects of the medium as well as by the chain itself. In this paper we neglect d^2b^2 . Averaging over oscillations kills the first term in equation (23). So, our final expression is

$$B \langle \dot{X}_1^T \dot{X}_1 \rangle = \frac{1}{2} \text{Re} \int_0^t d\xi_1 \int_0^t d\xi_2 H(t, \xi_1, \xi_2) \exp[-i\omega(\xi_1 - \xi_2)] \tag{26}$$

where

$$\omega = dV. \tag{27}$$

To evaluate this, we go over to normal coordinates where the matrix D is diagonal, with eigenvalues $\gamma_i, i = 1, 2, \dots N$. Let Q be the matrix that diagonalizes D , ie

$$(QDQ^T)_{ij} = \delta_{ij}\gamma_i. \tag{28}$$

Of course Q is orthogonal. In the appendix it is shown that

$$Q_{rs} = \left(\frac{4}{2N+1} \right)^{1/2} \sin \left(\frac{2\pi s(r-\frac{1}{2})}{2N+1} \right) \quad r, s = 1, 2, \dots N \quad (29)$$

$$\gamma_r = 4 \sin^2 \left(\frac{\pi(r-\frac{1}{2})}{2N+1} \right) \quad r = 1, 2, \dots N. \quad (30)$$

Introducing the notation

$$\lambda_i^2 = \lambda^2 \gamma_i \quad (31)$$

and $\phi_i(t, \xi)$ for the function defined by equation (16) except that γ_i replaces D in the quantities μ_1, μ_2 , we get

$$B \langle \dot{X}_1^T \dot{X}_1 \rangle = \frac{1}{2} B \operatorname{Re} \int_0^t d\xi_1 \int_0^t d\xi_2 f^2 \exp[-i\omega(\xi_1 - \xi_2)] \sum_{i=1}^N Q_{iN}^2 \phi_i(t, \xi_1) \phi_i(t, \xi_2) \quad (32)$$

$$= \frac{1}{2} f^2 \sum_{i=1}^N \frac{\omega^2 B Q_{iN}^2}{(\lambda_i^2 - \omega^2)^2 + \omega^2 B^2}. \quad (33)$$

We equate this quantity to RV where R is the friction force due to this chain and V is the velocity. So finally we have

$$R = \frac{1}{2} f^2 d \sum_{i=1}^N \frac{\omega B Q_{iN}^2}{(\lambda_i^2 - \omega^2)^2 + \omega^2 B^2} \quad (34)$$

where $\lambda_i^2 = \lambda^2 \gamma_i$ is temperature-dependent, since $\lambda^2 = 3kT/Mb^2$ as also is B in general. The denominators in equation (34) are all of the classical form associated with resonance phenomena. In fact our answer is what one would get from the entirely trivial model assuming that the end of the chain is subject to a time-dependent, space-independent, oscillating force, of frequency $\omega = Vd$, and forgetting all about random forces. This is the first, most simple-minded model that one could build, and it is interesting, though not entirely unexpected, that the above, presumably more realistic, model reduces to it, in first approximation.

In this context, it is always justified to neglect the acceleration term. This corresponds to B and λ_i^2 becoming large in such a way that

$$B^2 \gg \lambda_i^2 \gg \omega^2. \quad (35)$$

So, in this limit equation (34) becomes

$$R = \frac{1}{2} f^2 d \sum_{i=1}^N \left(\frac{Q_{iN}^2}{\lambda_i^2} \right) \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (36)$$

where

$$\tau_i = B/\lambda_i^2 \quad (37)$$

identifiable as relaxation times of the polymer chain. Equation (36) is therefore the

friction force due to a single polymer chain, in contact with the track. This must be multiplied by n the average number of chains bonded at a given time. A more general version of our present approach might very well be capable of predicting an expression for this number, but here we satisfy ourselves with a rather crude argument to derive the temperature dependence of n which is what we are really interested in. Consider the dynamics of our chain in the z direction. Let the force due to the track, in this direction, be independent of time, ie non-oscillatory. We then expect that, after a sufficiently long time, the distribution of particles at z_1, z_2 etc will be the Maxwell-Boltzmann distribution. Concentrating on z_n one sees that it will be subject to a Gaussian force due to the fact that z_0 is fixed. This will be temperature-independent. Also z_n will be subject to a potential barrier due to the track which we approximate, in the region of interest by a quadratic function. Let us assume that this region of interest is small enough to allow us to neglect the Gaussian force due to the connectivity of the chain and the fact that z_0 is fixed. So the probability distribution of z_N can be approximated by a Gaussian of the form

$$P(z_N) dz_N = A \exp[-c(z_N - a)^2/kT] \quad (38)$$

where a is the equilibrium point of the potential, c is the other shape parameter and A is a normalization constant. The important point is that the variance is proportional to kT . The above form corresponds to an attractive force above and a repulsive force below a , which is broadly in agreement with the usual models of Van der Waals type forces. Now we take it that the number of bonds will be proportional to the number of particles that find themselves well below a , out on the tail of the Gaussian, which number will be proportional to $(kT)^{1/2}$ by standard arguments. It will also be proportional to the number of track molecules in the 'interaction region'; we take it that a similar argument applies to these, and that we get another factor $(kT)^{1/2}$, giving in all a factor kT . The remaining temperature dependence will be very weak and is neglected.

The load dependence of n is also of interest; we bypass the issue here and take it to be linear in the load with, possibly, other weaker load dependence to take account of experimental results indicating deviations from Amontons' law.

Taking into account the factor kT in n , and absorbing all unknown constants into one unitless parameter we finally get the coefficient of adhesive friction

$$\mu_a = C \sum_{r=1}^N \left(\frac{Q_{rN}^2}{\gamma_r} \right) \frac{\omega\tau_r}{1 + \omega^2\tau_r^2} \quad (39)$$

where equation (31) has been used. The constant C has no temperature dependence. Note that we have taken N to be the same for all chains in interaction with the track. More realistically it can be regarded as an average value.

By equations (29), (30) one sees that

$$\mu_a = C_N \sum_{i=1}^N \frac{\rho_r \omega\tau_r}{1 + \omega^2\tau_r^2} \quad (40)$$

where

$$C_N = C/(2N + 1) \quad (41)$$

$$\rho_r = \cot^2 \left(\frac{(r - \frac{1}{2})\pi}{2N + 1} \right). \quad (42)$$

4. Discussion

The expression (39) will obviously have the Williams–Landel–Ferry property since, in each term, the velocity and temperature dependence are totally contained in the combination

$$x = \omega B/\lambda^2 \quad (43)$$

$$= \frac{MdVBb^2}{3kT}. \quad (44)$$

Furthermore, in any bead–spring model, the viscoelastic functions are functions of the combination given by equation (43). This is equivalent to saying that our shifting factor will be the same as that found in viscoelastic experiments, which is in agreement with the experimental results of Grosch (1963).

We next examine what our model says about the correlation of the maxima of $\mu_a(V)$ and $G''(\omega)$, as found by Grosch (1963). The Rouse theory predicts, for the loss modulus (eg Ferry 1970, chap 10)

$$G''(\omega) = K \sum_{r=1}^N \frac{\omega\tau_r'}{1 + \omega^2\tau_r'^2} \quad (45)$$

where K is linear in temperature and the τ_r' are the relaxation times appropriate to chains with two fixed ends. These are well known and can be derived as indicated in the appendix. Now, both G'' and μ_a are functions of the variable x (equation (43)) and purely numerical factors. Both functions have simple maxima. A plot of μ_a is given in figure 2; G'' has a similar structure. Now this maximum will be at x equal to some numerical factor, different in each case, though this is irrelevant. Remembering the definition of x (equation (43)) and equation (27) we see that Grosch's result follows trivially, if one keeps in mind the function B is the same in both functions; ie the constant of proportionality between the two maximum points will be a numerical factor times d and so will be independent of the rubber parameters, since the N dependence is negligible.

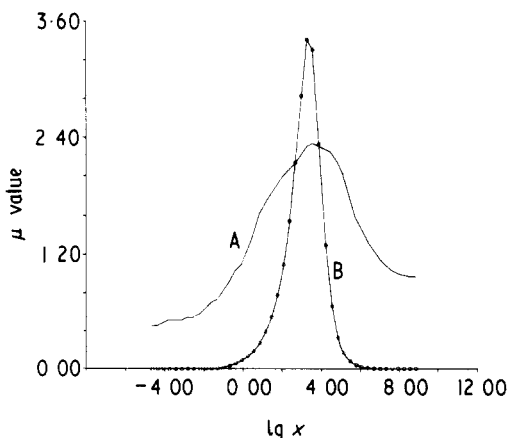


Figure 2. Least-squares fit of the model to Grosch's master curve (A) for the isomerized natural rubber E on clean silicon carbide, reference temperature $T_0 = 20^\circ\text{C}$. Our curve (B) is the one with open circles on it.

It remains to actually fit our prediction to the experimental curve. Grosch (1963) gives a master curve of $\lg Va_T$ against μ_a (see figure 2) where a_T is the shift function (more correctly, its logarithm is) and, in our model, is given by

$$a_T = \frac{(\tau_1)T}{(\tau_1)T_s} \quad (46)$$

where T_s is the standard reference temperature. The variable that occurs in our expressions, namely $\omega B/\lambda^2$, will be proportional to Va_T but with the proportionality constant not readily evaluable, so we fit the function,

$$\mu_a = C_N \sum_{r=1}^N \rho_r \frac{Kx\gamma_r}{1 + K^2x^2\gamma_r^2} \quad (47)$$

where

$$x = Va_T \quad (48)$$

and C_N, K are adjustable parameters, to Grosch's curve for the isomerized natural rubber E on clean silicon carbide using a reference temperature 20° C. The best least-squares fit is shown, for $N = 100$ in figure 2: our curve is the one with the open circles. Note that this is a logarithmic plot and extends over a huge range of values. While our curve has the same general shape as the experimental curve it is not wide enough to fit it well; the point should be made however that it would be extraordinary if such a simple model did fit such a huge range of data, with only two parameters (or three if one includes N). The fit was not substantially improved by changing the value of N . The best values of our parameters for this curve were

$$C_N = 0.088/(2N + 1) \quad (49)$$

$$\lg K = -7. \quad (50)$$

It should be stressed that we could easily choose C_N so that the maximum points of both curves agree. The width, however, presents a real problem.

5. Conclusion

From a very simple polymer model we have deduced an expression for the coefficient of adhesive friction which, in agreement with experiment, has the WLF temperature dependence, is correlated with the loss modulus and has the same general structure as the experimental curves; however, with two parameters, our fit to Grosch's experimental curve is not so good. This weakness is, no doubt, attributable to our many simplifying assumptions, which we restate briefly, here.

Let us take the point of view, without discussion, that the diffusion model is a correct physical description of polymer dynamics. Then our model is an approximation in the sense that it used the idealization of Rouse and fixed points to simulate cross-links. Also, we picture the force due to the track as acting on only one element of the chain rather than a z dependent force acting on all elements. Obviously, our sinusoidal force is an idealization, with some validity if the track is crystalline in structure but which otherwise must be improved upon. Our use of perturbation theory possibly needs to be justified slightly more though it is an extremely reasonable assumption that the interaction between chains and track is very weak compared with the other forces on the chains.

Implicit however in this assumption is our neglect of strong adsorption of monomers of the chain by the track. Finally, there is our neglect of d^2b^2 .

Given the strong approximations we have made, the model is an undoubted success and certainly warrants further sophistication with the aim of achieving precise quantitative agreement with experiment. A relevant final point is that Grosch's curve may include effects other than adhesive friction in the narrow sense that we are using it here and that this is the cause of at least some of the discrepancy.

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Appendix

Our object is to find the eigenvalues of the matrix D , given by equation (8) and the transformation which diagonalizes it. This involves finding its eigenvectors. Our method owes a lot to a paper by Synge (1973). The basic problem is the evaluation of the determinant

$$\Delta'_N = \begin{vmatrix} \alpha & -1 & 0 & & & & \\ -1 & \alpha & -1 & 0 & & & \\ 0 & -1 & \alpha & -1 & 0 & & \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & & & 0 & -1 & \alpha & -1 \\ 0 & & & 0 & 0 & -1 & \alpha_1 \end{vmatrix} \tag{A.1}$$

where we put

$$\alpha_1 = \alpha + \epsilon \tag{A.2}$$

and where we are interested in the case $\epsilon = -1$. We also use the notation

$$\Delta_N = \Delta'_N(\epsilon = 0). \tag{A.3}$$

Now, it is easy to show that Δ_N obeys the difference equation

$$\Delta_N = \alpha\Delta_{N-1} - \Delta_{N-2} \tag{A.4}$$

and that a particular solution of (A.4) is Z^N where (Synge 1973)

$$Z = \frac{1}{2}\alpha \pm [(\frac{1}{2}\alpha)^2 - 1]^{1/2}. \tag{A.5}$$

The general solution is a linear sum of these two solutions. By fitting initial conditions, ie values for Δ_1, Δ_2 , it is easy to show that

$$\Delta_N = \frac{(Z^{N+1} - (1/Z)^{N+1})}{Z - (1/Z)} \tag{A.6}$$

where Z can be taken as one of the solutions (A.5) say the one with plus sign and $1/Z$ the other. By putting

$$Z = \exp(i\theta) \quad (\text{A.7})$$

the usual normal-coordinate formulae for fixed ends follow easily from equation (A.6). Now

$$\Delta'_N = \alpha\Delta_{N-1} - \Delta_{N-2} + \epsilon\Delta_{N-1} \quad (\text{A.8})$$

$$= \frac{\sin(N+1)\theta + \epsilon \sin N\theta}{\sin \theta} \quad (\text{A.9})$$

by equation (A.7). For eigenvalues, we want the zeros of Δ'_N . These are easy to find for our case $\epsilon = -1$ and also for $\epsilon = 0, 1$. We specialize to the case $\epsilon = -1$ and find that the zeros are given by

$$\theta_r = \frac{2\pi(r - \frac{1}{2})}{2N+1}, \quad r = 1, 2, \dots, N \quad (\text{A.10})$$

or from equations (A.7), (A.5)

$$\alpha_r = 2 \cos\left(\frac{2\pi(r - \frac{1}{2})}{2N+1}\right) \quad (\text{A.11})$$

so that our eigenvalues are

$$\gamma_r = 4 \sin^2\left(\frac{\pi(r - \frac{1}{2})}{2N+1}\right). \quad (\text{A.12})$$

The solution of the eigenvector equation can easily be shown to be

$$x_s^{(r)} = \Delta_{s-1}^{(r)} x_1 \quad (\text{A.13})$$

where the value of $\Delta_{s-1}^{(r)}$ will depend on the eigenvalue in question. To get the transformation matrix we need normalized eigenvectors; to find the normalization constant we need to evaluate the sum of squares of Δ_s given by equation (A.6). It is elementary to prove the following identity:

$$\sum_{s=1}^N \left(Z^s - \frac{1}{Z^s}\right)^2 = \frac{Z^{2N+1} - (1/Z^{2N+1})}{Z - (1/Z)} - (2N+1). \quad (\text{A.14})$$

One deduces that the normalized eigenvectors, and the elements of the transformation matrix Q are given by

$$x_s^{(r)} = Q_{rs} = \left(\frac{4}{2N+1}\right)^{1/2} \sin\left(\frac{2\pi s(r - \frac{1}{2})}{2N+1}\right). \quad (\text{A.15})$$

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