liquid, ϵ', in the present context. Also, it would seem that the temperature dependence of molecular conformations for the polymer liquid and for the "isolated" polymer chain (*i.e.*, in dilute solution under θ conditions) should be different, since the former depends upon ϵ_T and the latter upon ϵ_0.

Conclusions

The present work provides a further insight into the origin of the WLF "iso-free volume" at the glass transition.[25] By eq 1 and 3, at T_g, $\log \eta_g = \log K + 3.4 \log Z + B/(T_g - T_0)$, applying at and above Z_c. But $\log \eta_g = 13$ at Z_c[5] and for vinyl polymers, $\log K \simeq -11.7$ (mean value from Table II) and approximately, $Z_c \simeq 600$.[8,9] Thus, $B/(T_g - T_0) \simeq 15$ and "ϕ_g/b" $= (T_g - T_0)/2.3B \simeq 0.029$, the WLF "free-volume." Even a ± 1 variation in the $B/(T_g - T_0)$ term, arising from a ± 1 variation in $\log K$, produces only a ± 0.002 variation in "ϕ_g/b." In short, the WLF "iso-free volume" constant follows directly from purely kinetic (viscosity) considerations.

Simha and Boyer[26] derived a different "iso-free volume" at the glass transition based on $\Delta\alpha T_g \simeq 0.11$ and shown to be quite constant for a variety of vinyl polymers. However, their definition conflicts with another by which T_0, rather than 0°K, is the zero point for the "free-volume:" $\phi_g' = \Delta\alpha(T_g - T_0) \simeq 0.11 - \Delta\alpha T_0$. Certainly, the last term is not a constant for different vinyl polymers.

We conclude that for vinyl polymers, the Vogel viscosity equation (eq 1) applies and there is no need to invoke a 'hybrid" equation,[8] containing both Arrhenius and "free-volume" terms. Indeed, the "hybrid" equation leads to erratic and, in some cases, unreasonable values for the rotational barriers.[8]

Finally, we offer the following suggestions for extending the Vogel viscosity equation (eq 1) into the non-Newtonian region. Here, both the viscosity and E_T (determined at constant shear rate) decrease with increasing shear rate and approach a second Newtonian region.[27] By restricting the analysis to molecular weights somewhat below M_c, the added complication of "chain entanglements" could be avoided and the effect of shear rate on the rotational energetics (V_0, V_T, ϵ_0, ϵ_T) more readily isolated. High shear rates induce a change in molecular conformation toward a more extended form, as evidenced by (a) the normal stresses produced (*i.e.*, perpendicular to the shear direction) and (b) the "die-swell" effect, *i.e.*, the radical expansion of a polymer melt when rapidly extruded from a capillary die. This change in molecular conformation at the higher shear rates must undoubtedly be associated with a change in the rotational energetics from their normal values at zero shear rate.

Acknowledgment. We appreciate the comments of the referees which were helpful in the revision of this paper.

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Internal Energy Contribution to the Elasticity of Natural Rubber

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ABSTRACT: It has recently been noted by a number of workers that the relative energy contribution, f_e/f, to the elastic stress of rubberlike materials appears to depend on the extension ratio at which thermoelastic measurements were carried out. This apparent strain dependence is in contradiction to the free energy additivity principle of the statistical theory of rubber elasticity. In this paper we resolve this problem by determining f_e/f from the temperature coefficient of shear moduli. The shear moduli were not directly determined from measurements of shear, but calculated from tensile elongation data. This method circumvents the difficulty encountered in directly obtaining the relative energy contribution from stress–temperature data. Both constant length and constant stress thermoelastic measurements were used to obtain f_e/f. A series of natural rubber samples, cross-linked in the presence of various amounts of *n*-hexadecane, were investigated. It is found that the relative energy contribution to the elasticity of natural rubber is 0.18. Changes in intermolecular interactions, brought about by the incorporation of diluents, produce no variation in the value of f_e/f. This observation supports the hypothesis that the energetic stress in rubber elasticity is wholly attributable to intrachain energies of the network chains.

The employment of thermoelastic studies has been instrumental in the development of a molecular interpretation of polymer behavior in the rubbery state. The observation that the stress–temperature coefficient of natural rubber is positive led to the postulate that the elastic force in this material is entropic in origin.[2] Earlier works tended to confirm this postulate, although the possibility that some of the force arose from internal energy change during deformation was considered.[3]

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[1] Department of Chemical Engineering, University of California, Berkeley, California, 94720.

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More recently renewed interest in stress–temperature studies was stimulated by the recognition that the energetic component of the elastic stress is related largely to the conformational energies of network chains.[4] The relative energy contribution to the elastic stress has been shown to reflect the temperature coefficient of unperturbed dimensions of these chains.[5,6] Data from thermoelastic experiments on a number of elastomers have been utilized to correlate with the coefficients calculated on the basis of the rotational isomeric model of polymer chains.[7–9]

More recently, however, a number of investigators[10–12] have found that the value of the relative energetic contribution (f_e/f) obtained from such thermoelastic measurements depends upon the degree of deformation at which the measurement is carried out. Not only does this observation tend to negate the aforementioned correlation with the conformational energies of individual polymer chains, but it also challenges the additivity principle of network free energy, which is one of the basic tenets of the statistical theory of rubber elasticity. In a previous paper,[13] we have proposed a new equation for calculating f_e/f, which was based on the temperature coefficient of shear modulus. Values of f_e/f thus calculated are independent of strain, thus upholding the free energy additivity principle. In this work, we shall provide an alternative, simplified derivation of this equation. Thermoelastic data will be obtained for a series of natural rubber samples preswollen with *n*-hexadecane. Both constant length and constant tension experiments will be performed on these samples and their relative merits compared. If the energy contribution could be attributed to intramolecular interactions alone, values of f_e/f would be unaffected by the presence of diluents which tends to change only the degree of intermolecular interactions.[14] Thus the constancy of f_e/f with respect to diluent content would provide another check on the validity of the free energy additivity principle.

Theoretical Section

According to the current statistical theory, the equation of state for rubber elasticity is[6,15,16]

$$f = GA_0(\lambda - V/V_0\lambda^2) \tag{1}$$

where

$$G = NkT(\bar{r}_0^2/\bar{r}_f^2)/V_0 \tag{2}$$

In eq 1 and 2, A_0 and V_0 and V_0 are the cross-sectional area and volume of the rubber at zero force, zero pressure, and temperature T; V is the volume at force f, pressure P, and temperature T; λ is the extension ratio; N is the number of network chains in the sample; k is Boltzmann constant; $\bar{r}_0^2$ and $\bar{r}_f^2$ are the mean square end-to-end distances of the chain in volume V_0 and in free space, respectively.

At small strains, we can set $\lambda = 1 + \epsilon$ and $V/V_0 = 1$. Substituting these into eq 1 and expanding to first-order terms, we get

$$3G = (f/A_0)/\epsilon \tag{3}$$

The right-hand side of eq 3 is just the definition for the tensile modulus. For rubbers it is well known that the tensile modulus is three times the shear modulus (Poisson's ratio being $^1/_2$). Thus G is the shear modulus. Equation 1 is equivalent to the neo-Hookean equation of continuum theory.[17] It is the statistical theory expression if the shear modulus is defined by eq 2.

The energetic stress is defined as follows[5,6]

$$f_e = f - T(\partial f/\partial T)_{V,L} \tag{4}$$

The stress–temperature coefficient at constant volume and length can be expressed in terms of eq 1 as

$$(\partial f/\partial T)_{V,L} = \frac{f\mathrm{d}G}{G\mathrm{d}T} + f\beta/3 \tag{5}$$

where β is the bulk thermal expansion coefficient of the sample. In eq 5 total differentials for the shear modulus are used since G is not subject to the constraints of constant V and L. Inserting eq 5 into eq 4 and rearranging, one gets the relative energy contribution

$$\frac{f_e}{f} = 1 - \frac{\mathrm{d}\ln G}{\mathrm{d}\ln T} - \beta T/3 \tag{6}$$

which is identical with the expression we have previously obtained by a less direct derivation.[13]

The shear modulus, defined by eq 2, is proportional to $V_0^{-1/3}$, since $\bar{r}_0^2$ is proportional to $V_0^{2/3}$ and all other parameters are independent of volume. But V_0 is the initial volume of the sample at zero force, zero pressure. Thus the shear modulus is independent of the current volume V, and hence independent of any applied hydrostatic pressure. The insensitivity of shear modulus to pressure or volume effects allows us to obtain the temperature coefficient of shear modulus simply by taking the initial slopes of the plots of f/A_0 against $(\lambda - 1/\lambda^2)$ at ambient pressure for a series of temperatures.

The stress–temperature coefficient at constant pressure and length can similarly be obtained from eq 1

$$(\partial f/\partial T)_{P,L} = \frac{f\mathrm{d}G}{G\mathrm{d}T} + \frac{f\beta}{3}\left(\frac{\lambda^3 - 4}{\lambda^3 - 1}\right) \tag{7}$$

We can now combine eq 6 and 7 to yield

$$f_e/f = 1 - (\partial \ln f/\partial \ln T)_{P,L} - \beta T/(\lambda^3 - 1) \tag{8}$$

which is the Flory–Hoeve–Ciferri equation.[5] Equation 8 was utilized in most of the previous works[10–12] in obtaining the relative energy contribution to elastic stress.

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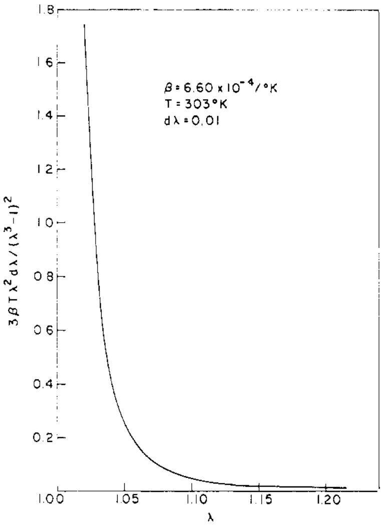

Figure 1. Estimation of error in relative energy contribution due to uncertainties in extension ratio measurements (eq 9).

Equations 6 and 8 are equivalent. However, the former is not as sensitive to the experimental errors normally encountered in thermoelastic measurements. Equation 8 depends on λ to the inverse third power, which magnifies any error in the extension ratios.

We can appreciate this by examining the differential of eq 8

$$\mathrm{d}(f_e/f) = -\mathrm{d}(\partial \ln f/\partial \ln T)_{P,L} + 3\lambda^2\beta T d\lambda/(\lambda^3 - 1)^2 \quad (9)$$

The first term on the right-hand side of eq 9 is normally not too troublesome. The second term, however, is extremely sensitive to errors in λ. We see in Figure 1 that a +1% error in λ would introduce extremely large errors into f_e/f at lower strains. This accounts for the observation that the relative energy contribution of elastomers deviate significantly from the mean value at low extension ratios. Of course, if $\mathrm{d}\lambda = -0.01$ we simply obtain a mirror image of the curve in Figure 1 in the negative quadrant. In this instance, negative deviations for f_e/f will be found, as we shall see later (Figure 6).

It should be mentioned at this point that direct thermoelastic measurements at constant volume were performed by Allen, Bianchi, and Price[18] by means of a pressure balance. In this case eq 4 can be used directly. Unfortunately due to the difficulty involved in such measurements, the scatter in f_e/f data was too great to yield conclusive evidence on the strain dependence of the energy contribution.

An interesting corollary to eq 7 is the thermoelastic inversion point, which can be readily obtained by setting $(\partial f/\partial T)_{P,L} = 0$

$$\lambda_0 = \left[1 + \beta T\left(\frac{\mathrm{d}\ln G}{\mathrm{d}\ln T} + \beta T/3\right)\right]^{1/3} \quad (10)$$

where λ_0 is the extension ratio at which thermoelastic inversion occurs. From eq 6, one finds that the quantity in the parentheses of eq 10 is just $1 - f_e/f$, therefore

$$\lambda_0 = [1 + \beta T/(1 - f_e/f)]^{1/3} \quad (11)$$

which is to be compared with the equation of James and Guth[14]

$$\lambda_0 = (1 + \beta T)^{1/3} \quad (12)$$

and the equation of Oplatka and Katchalsky[19]

$$\lambda_0 = [1 + \beta T/(1 - \beta T/3)]^{1/3} \quad (13)$$

For the special case of ideal rubbers, which have no energy contribution, eq 11 reduces to the equation of James and Guth (eq 12).

Most of the thermoelastic measurements were carried out by keeping the stretched length of the sample constant, and following the changes in the elastic force as the temperature was varied. The alternative procedure is to keep the tension constant, and determine the variations of the sample lengths as a function of temperature. The latter simply corresponds to the condition that the stress–temperature coefficient at constant pressure (but not constant length) vanishes. An explicit expression can be readily obtained by differentiating eq 1 with respect to temperature with the aforementioned constraints

$$\frac{f\mathrm{d}G}{G\mathrm{d}T} + \frac{f\mathrm{d}A_0}{A_0\mathrm{d}T} + GA_0\left[\left(\lambda + \frac{2V}{\lambda^2 V_0}\right)(\beta_L - \beta_L{}^0) - \frac{V}{\lambda^2 V_0}(\beta - \beta^0)\right] = 0 \quad (14)$$

where β_L and $\beta_L{}^0$ are the linear thermal expansion coefficients of the sample in the strained and unstrained states, and β and β^0 are the bulk thermal expansion coefficients in these respective states. It has been shown that the bulk thermal expansion coefficient of natural rubber is unaffected by the application of an uniaxial extension,[18] *i.e.*, $\beta = \beta^0$. Thus the last term in the brackets of eq 14 vanishes. Rearrangement of eq 14 with the aid of eq 1 and setting $V/V_0 = 1$ yields

$$\beta_L = \beta_L{}^0 - \left(\frac{\lambda^3 - 1}{\lambda^3 + 2}\right)\left(\frac{\mathrm{d}\ln G}{\mathrm{d}T} + \frac{2\beta_L{}^0}{3}\right) \quad (15)$$

Therefore knowing the linear thermal expansion coefficient of the rubber at given extension ratios, the temperature coefficient of shear modulus of the sample can be obtained directly. The relative energy contribution can then be determined by means of eq 6.

Experimental Section

n-Hexadecane, purchased from the Eastman Organic Chemicals, was milled into pale crepe, and the resulting mixture cured in the presence of 1.5 parts dicumyl peroxide per hundred parts of rubber at 145° for approximately 40 min. Samples with 0, 11, 25, and 43 parts of hexadecane per hundred parts of rubber were made. Densities of these samples were measured by displacement method. Glycerine was used as the confining fluid, since it has been shown not to swell natural rubber.[20] These density data were then used to calculate the actual amount of *n*-hexadecane in the rubber

$$V_r = (\rho_r - \rho)/(\rho_r - \rho_h) \quad (16)$$

samples by where V_r is the swelling ratio, ρ is the density, and subscripts r and h refer to rubber and hexadecane, respec-

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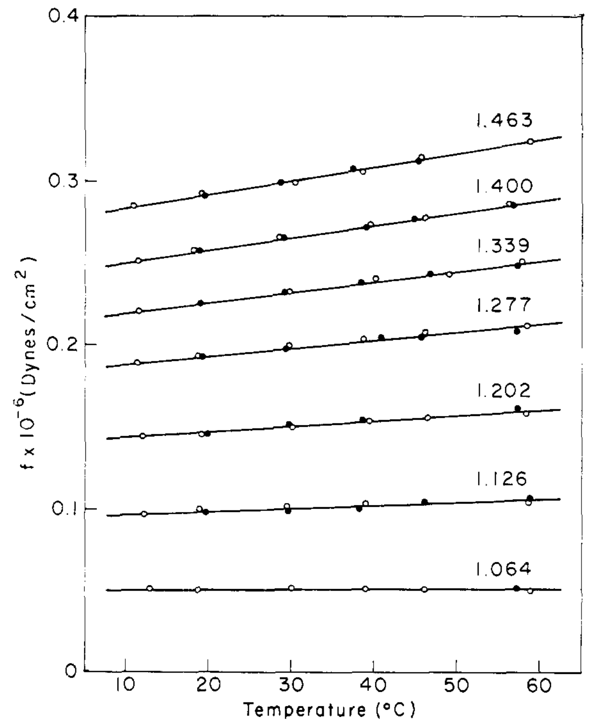

Figure 2. Stress–temperature curves of natural rubber preswollen with 33.6% *n*-hexadecane. Numerals on the right indicate the extension ratios at 30°.

tively. From the bulk thermal expansion coefficient[19] of natural rubber, $\beta_r = 6.60 \times 10^{-4}$ cc/cc °K, and *n*-hexadecane, $\beta_h = 8.88 \times 10^{-4}$ cc/cc °K, the bulk thermal expansion coefficients of the swollen samples were calculated by assuming that they are additive

$$\beta = [\beta_r + (V_r - 1)\beta_h]/V_r \qquad (17)$$

These data are summarized in Table I.

Table I
Characterization of Rubber Samples

Hexadecane per hundred parts of rubber	Density, g/cc	% hexadecane	β^a cc/cc °C × 10^4
0	0.9199	0	6.60
11	0.9058	9.6	6.80
25	0.8999	13.7	6.87
43	0.8834	25.3	7.06
75	0.8713	33.6	7.17

^{a} Calculated from eq 17.

Strips of the approximate dimension of 0.25 × 0.25 × 10 cm^3 were cut by a high-speed rotating blade. Ends of these sample strips were first degreased by dipping into dilute sulfuric acid for a few seconds and then glued to two small Invar blocks. Specially constructed racks were used to keep the samples in stretched state. They were then stored in an evacuated desiccator to allow stress–relaxation to take place for at least 2 weeks. After this period of time the sample was transferred to the relaxometer, which has been described previously,[11] for the constant length measurements. The sample was allowed to stand at 60° for at least 2 more days to ensure that no further stress–relaxation takes place. Temperature was then changed between 10 and 60° at 10° intervals. Two hours were allowed to elapse at each temperature to ascertain the achievement of thermal equilibrium. After the temperature cycle was complete, the extension ratio was changed to the next lower value and the cycle repeated. Figure 2 shows the stress–temperature data for natural rubber preswollen with 33.6% *n*-hexadecane. Experimental points taken during heating and cooling cycles all fall on good straight lines, indicating that the equilibrium condition prevailed. To minimize chemical effects, the experiment was conducted in ultrapure nitrogen atmosphere.[11]

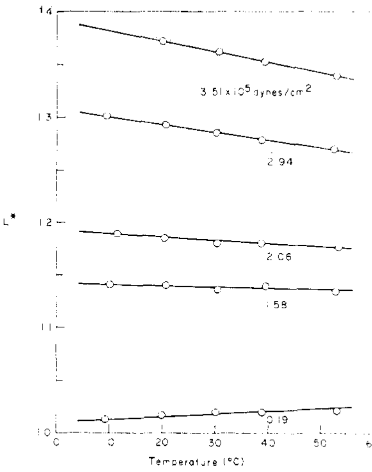

Figure 3. Length–temperature curves of natural rubber preswollen with 33.6% *n*-hexadecane. Numerals on the right indicate the loads on the rubber sample. L^* is the length of the sample reduced by the unstrained sample length at 30°.

For the constant stress measurements, the sample was similarly glued to two metal blocks. One end was attached to a pan on which known weights can be placed. The rubber–weight assembly was then suspended inside a glass flask. The flask was repeatedly evacuated and purged with nitrogen. The sample was then allowed to reach its equilibrium length at 60° under the highest load to be used in the experiment. After no further creep was observed between measurements on successive days, the temperature was varied as in constant length experiments. Changes in lengths as a function of temperature were determined by a cathetometer accurate to ±0.1 mm. After this temperature cycle, part of the load was removed. The sample was left standing overnight before the next length–temperature measurements were initiated. Figure 3 illustrates the length–temperature data for natural rubber preswollen with 33.6% *n*-hexadecane. From Figure 3 linear thermal expansion coefficients at various extension ratios can be readily obtained for use in subsequent f_e/f calculations.

Results and Discussion

1. Effect of Strain. The relative energy contribution, f_e/f, can be readily calculated from eq 6 by obtaining the shear moduli, G, at a series of temperatures. It should be noted, however, that G's were obtained in this work not from direct measurements of shear, but rather were calculated from tensile–elongation experiments. From eq 1, G is defined as the slope of the straight line in a f/A_0 *vs.* $(\lambda - 1/\lambda^2)$ plot, as shown in Figure 4 for natural rubber preswollen with 33.6% *n*-hexadecane. In order to obtain the "best" value for the slope, we used a least-square program "forced" through the origin on an Autonetics Recomp III computer. Figure 5 shows the shear moduli obtained for the series of rubber samples preswollen by *n*-hexadecane. Here the slope dG/dT can again be calculated on

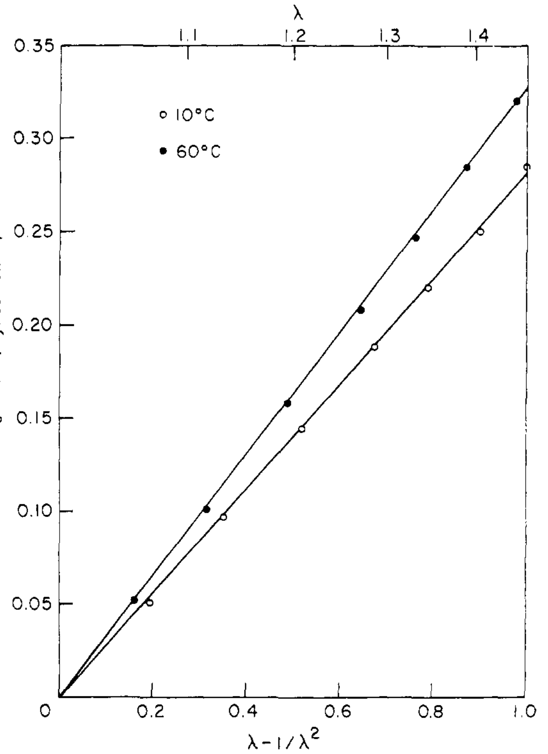

Figure 4. Determination of shear moduli of natural rubber preswollen with 33.6% *n*-hexadecane according to eq 3.

the computer by another least-square program. These data are summarized in Table II.

TABLE II
RELATIVE ENERGY CONTRIBUTION CALCULATED FROM STRESS-TEMPERATURE DATA OF NATURAL RUBBER PRESWOLLEN WITH N-HEXADECANE[a]

No.	% diluent	G, dyn/cm² × 10⁻⁶	dG/dT, dyn/cm² °C × 10⁻³	$\beta T/3$	f_e/f
1	0	1.94	5.97	0.067	0.15
2	9.6	1.08	3.31	0.069	0.15
3	13.7	0.76	2.43	0.070	0.18
4	25.3	0.46	1.45	0.071	0.12
5	33.6	0.30	0.99	0.072	0.08

[a] Reference temperature = 30°.

For unswollen natural rubber f_e/f is 0.15, which is close to the average value of 0.18 in the literature calculated from eq 8. The advantage of eq 6 is that it averages out the experimental errors by first obtaining the shear moduli. Thus values of f_e/f are necessarily independent of the extension ratios. On the other hand, the use of eq 8 to calculate relative energy contribution from the same set of data would give rise to significant deviations from the average value at lower strains. This is amply documented in the literature,[10-12] and is illustrated in Figure 6 for both the unswollen natural rubber and that preswollen with 33.6% *n*-hexadecane. Note that both positive and negative deviations are observed, depending on whether the error in extension ratios is positive or negative (see eq 9 and Figure 1). The apparent strain dependence of values f_e/f is of great concern because it appears to contradict one of the basic tenets of the statistical theory of rubber elasticity. In the derivation of this theory, the number of configurations available to an individual polymer chain is given by the Gaussian distribution function. The configurational free energy of a network of such chains is then assumed to be just the sum of free energies of these network chains. In order for this assumption to be valid, it is necessary that configurations of the individual chain are unaffected by the presence of other chains in the network. Thus deformation of the rubber network must not produce any change in interchain interactions. Customarily the energetic contribution to the elastic stress of rubbers is attributed to *intra*chain energies, such as the thermodynamic potential energy difference affecting rotations along the hydrocarbon chain backbone. These intrachain energies can certainly not be expected to depend on the degree of deformation of the rubber network. Thus the dependence of f_e/f on λ raises the question whether the *inter*chain energies are indeed absent, as required by the statistical theory. The question is, of course, now resolved by using eq 6 to calculate f_e/f. The apparent strain-dependence of the relative energy contribution

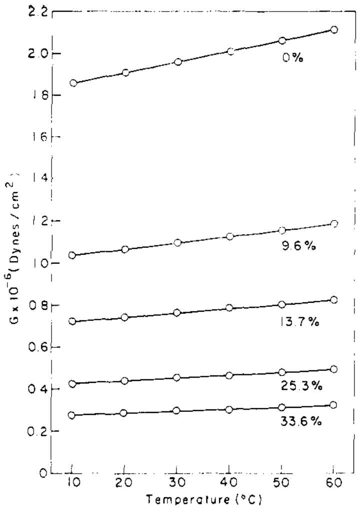

Figure 5. Shear moduli-temperature curves of natural rubber preswollen with *n*-hexadecane. Degrees of swelling are indicated on the right.

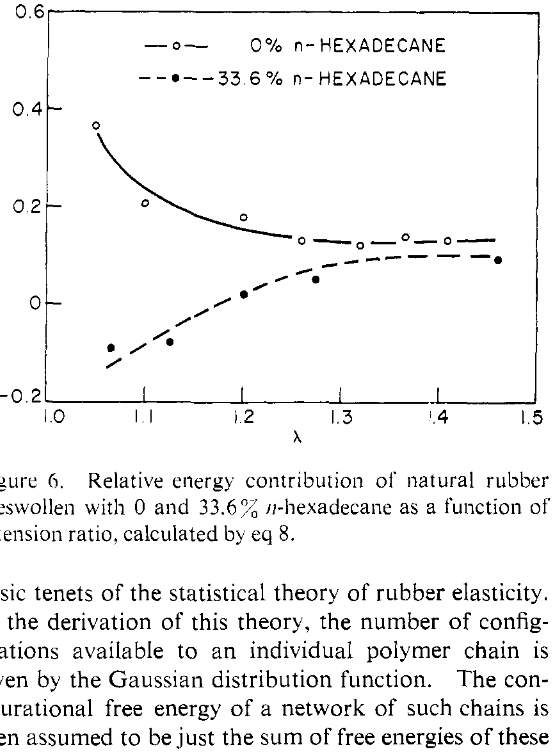

Figure 6. Relative energy contribution of natural rubber preswollen with 0 and 33.6% *n*-hexadecane as a function of extension ratio, calculated by eq 8.

calculated by eq 8 is just the result of the sensitivity of the term $\beta T/(\lambda^3 - 1)$ to experimental errors in λ (see Figure 1). The use of eq 6, which we have shown to be equivalent to eq 8, would circumvent this difficulty to yield values of f_e/f that are independent of strain. This is, of course, just what the basic assumption of the statistical theory of rubber elasticity requires. Thus the additivity principle of network free energy is vindicated.

2. Effect of Diluent. Another way to test the validity of neglecting interchain energies is to change the intermolecular interactions by introducing diluents into the rubber network.[14] If diluents were incorporated during cross-linking, the network chains would still be in a relaxed state and the equation of state of rubber elasticity (eq 1) can be used without modification.[21,22] Table II summarizes the f_e/f values for natural rubber preswollen by *n*-hexadecane. Should the energy contribution be attributable to intrachain forces alone, values of f_e/f should remain invariant with the degree of swelling. Here we see that for natural rubber with 0–25.3% *n*-hexadecane, $f_e/f = 0.15 \pm 0.3$. The value of f_e/f for natural rubber with 33.6% *n*-hexadecane appears to be lower than the average.

We now turn to our length–temperature data for the same series of rubber samples. Figure 7 shows the plot of the linear thermal expansion coefficient (in the direction of stretch) as function $(\lambda^3 - 1)/(\lambda^3 + 2)$, as suggested by eq 15. The intercept should correspond to the linear thermal expansion coefficient of the rubber in the unstrained state. For unswollen natural rubber, $\beta_L{}^0 = 2.2 \times 10^{-4}$ deg^{-1}, which is borne out in our data. From the slope of this plot, one can readily obtain the value of the temperature coefficient of shear modulus, d ln G/dT. In Figure 7 we included the data for all the samples used in this work. We see that the incorporation of *n*-hexadecane produces no effect on the temperature coefficient of shear modulus for natural rubber. From least-square fitting, we obtain d ln G/d$T = 2.48 \times 10^{-3}$ deg^{-1}. Use of this value in eq 6 yields $f_e/f = 0.18$ for natural rubber preswollen to various degrees by *n*-hexadecane. In arriving at this number we have neglected the small differences in the linear thermal expansion coefficients of the samples in the unstrained state, which varies from 2.2 to 2.4 $\times 10^{-4}$ deg^{-1}. The data embodied in Figure 7 convincingly demonstrate the absence of diluent effects in the thermoelastic behavior of natural rubber. Owing to its very simplicity in experimentation, we feel that the length–temperature data are probably more accurate than the stress–temperature data on the same samples. Thus we tend to regard the low value of 0.08 for the f_e/f of natural rubber preswollen with 33.6% *n*-hexadecane determined from stress–temperature measurements as a result of experimental errors. From both constant length and constant stress experiments, data support the prediction of invariance of energy contribution with changes in intermolecular interaction brought about by swelling.

3. Pressure Dependence of the Shear Modulus. We shall now return to examine the validity of asserting the insensitivity of shear modulus to the application of pressure in the Theoretical Section. In the derivation of the statistical theory of rubber elasticity, the Helmholtz free energy of the rubber network can be written as[6,23]

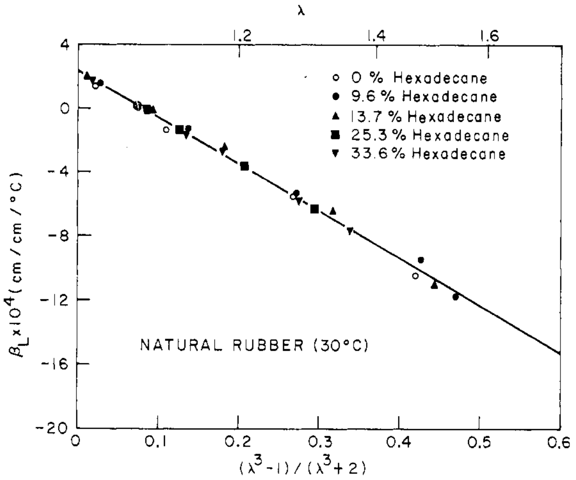

Figure 7. Linear thermal expansion coefficients or natural rubber preswollen with *n*-hexadecane plotted against $(\lambda^3 - 1)/(\lambda^3 + 2)$ (eq 15).

$$F(T, V) = F_0(T, V) + kT\sum_{i=1}^{N} b_i{}^2\overline{r}_i{}^2 \qquad (18)$$

where $b_i{}^2$ is $(^3/_2)\ {}_{i,f}{}^2$, $\overline{r}_{i,f}{}^2$ being the end-to-end mean square distance of the *i*th chain in free space. However, $b_i{}^2$ conforms to this definition only if the network was formed under ideal conditions. Equation 1 was obtained assuming such ideal conditions by differentiating the free energy expression with respect to sample length at constant temperature and volume. However, the condition of constant volume is not strictly valid due to the strain-induced volume dilation. To handle this properly we imagine that the sample is subjected to varying pressures that keep the volume constant, including negative pressures if necessary. The current statistical theory assumes that $b_i{}^2$ would be unaffected by such pressures, since it is related to the equivalent network chain in free space. However, it is just conceivable that the statistically equivalent random chain[3] representing the network chain at ambient pressure may not be the same as that under these hydrostatic pressures. In other words, $b_i{}^2$ might be affected by the changes in intermolecular forces brought about by the volume contractions due to the applied pressure. In this case the equation of state must be modified to read[23]

$$f = G'A_0(\lambda - V/V_0\lambda^2) \qquad (19)$$

where the shear modulus G' is now volume dependent

$$G' = G(V/V_0)^{\gamma} \qquad (20)$$

γ being an empirical parameter. For the current statistical theory (eq 1 and 2), $\gamma = 0$. Experimentally there appears to be some evidence that γ is not zero,[23–25] but

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is a small number of the order of 10^{-1}. The relative energy contribution on the basis of eq 19 and 20 is

$$\frac{f_e}{f} = 1 - \frac{\mathrm{d}\ln G}{\mathrm{d}\ln T} - \frac{\beta T}{3} + \gamma\beta T \qquad (21)$$

which differs from eq 6 by the term $\gamma\beta T$. If γ were 0.1, then for natural rubber at room temperature (T = 300°K, $\beta = 6.6 \times 10^{-4}$ deg^{-1}) $\gamma\beta T = 0.02$. However, there is at present as yet insufficient data to establish unequivocally the nonzero nature of the γ parameter. Thus within the framework of the current statistical theory ($\gamma = 0$), shear modulus is independent of the application of hydrostatic pressure.

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Effect of Fillers on the Photooxidative Stabilization of Polyethylene

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ABSTRACT: The influence of fillers on the morphology of the polymer matrix is shown to be as important as light shielding in the photooxidative stabilization of polyethylene. High surface energy fillers (*i.e.*, diamond and graphite) which generate a highly structured polymer matrix and are effective light shields enhance the photodegradative process. Low surface energy fillers (*i.e.*, polytetrafluoroethylene and polychlorotrifluoroethylene) which are not effective light shields and do not influence the morphology of the matrix are moderately effective photostabilizers. It is proposed that the stabilization of the carbon black filled polyethylene is due not only to its light shielding capability but also to its moderately low surface energy. Our experiments indicate that light shielding in combination with a low surface energy filler promote protection to photooxidative degradation.

The photooxidative protection of polyethylene afforded by fillers, such as carbon black, is believed to be due to its light shielding properties and, in some cases, to its action as a synergistic agent for the antioxidant.[1] However, it is recognized that fillers have a considerable influence on the morphology and physical properties of the polymer in a polymer–filler composite.[2,3] In this paper, we shall demonstrate the effect of fillers on the morphology of polyethylene matrices and how this, in turn, contributes to the photooxidation resistance of the polymer. This effect has not been studied to any extent.

Previous studies[4] have shown that thin polyethylene films (1 mil), when nucleated and crystallized in contact with a high surface energy substrate, produce a transcrystalline region in the polymer which differs in both morphology and mechanical properties from that found in the normal spherulitic structure. Since one of the controlling factors in the oxidative stability of polyethylene is related to its morphology,[1] it was believed probable that the photooxidative resistance of a "polyethylene-plus-filler" composite may be affected by the nature of the filler surface.

To investigate this possibility, we exposed a series of polyethylene films containing different types of high and low surface energy fillers to photooxidative conditions and followed the oxidation process in each film by infrared spectroscopy. We report here the results of that study.

Experimental Section

A low density (0.919 g/cc) finely powdered polyethylene containing no antioxidants and identified as DKPC (Union Carbide Co.) was used throughout this study. A series of "PE + filler" samples was prepared containing 3% (w/w) of the following powdered fillers: carbon black (Kosmos BB), polychlorotrifluoroethylene (CTFE), polytetrafluoroethylene (PTFE), KBr, diamond, and graphite. The choice of filler was governed by surface free energy considerations which are related to the nucleating ability of the filler material. Table I lists the various fillers and pertinent data.

TABLE I
SURFACE AND BULK PROPERTIES OF FILLERS

Filler	Density (ρ), g/cm^3	Particle size	Surface free energy, ergs/cm^2
Diamond	3.51	0.5–1.0 μ	>1000[a]
Potassium bromide	2.1	<0.1 μ	~200[b]
Graphite	2.2	<0.1 μ	~110[c]
Carbon black	1.9	180 Å	~50[c]
Polychlorotrifluoroethylene	2.1	<0.1 μ	31[d]
Polytetrafluoroethylene	2.2	<0.1 μ	18.5[d]

[a] Calculated from B. V. Belogurov, *Russ. J. Phys. Chem.*, **34,** 206 (1960). [b] Extrapolated melt surface tension. [c] Estimated from heat of wetting and wettability: A. C. Zettylmoyer, *J. Colloid Interfac. Sci.*, **28,** 343 (1968). [d] Critical surface tension of wetting.

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