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Experiments on the Elasticity of Dry and Swollen Networks: Implications for the Frenkel–Flory–Rehner Hypothesis

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ABSTRACT: Torque and normal force measurements have been performed on cylindrical samples of dicumyl peroxide cross-linked natural rubber with the purpose of obtaining the first derivative of the (elastic) strain energy density function of the dry rubber. Similar rubber samples were swollen to equilibrium in different solvents and tested in uniaxial compression in the swollen state. We find that the dry-state properties can be used to predict the swollen-state properties by assuming, as did Frenkel, Flory, and Rehner, that the elasticity of the swollen network is unaltered by the presence of the solvent other than by (chain) deformation.

Introduction

Frenkel[1] and Flory and Rehner[2] (FFR) assumed that the free energy of mixing and the elastic free energy in swollen networks are additive. Recently, several questions have been raised concerning the validity of this hypothesis and how it should be tested. The FFR hypothesis of the additivity or separability of the free energy is model dependent because specific and rather ideal models of the polymer network are generally introduced at an early stage of the theoretical discussion. Most tests of the hypothesis that have been reported have assumed either that the elastic free energy function can be represented by a specific model of the network elasticity (i.e., phantom, affine, junction constraint, etc.) or that the Flory[3]–Huggins[4] expression for the free energy of mixing is valid. A further assumption that is often made is that the Flory[3]–Huggins[4] interaction parameter is the same in the cross-linked and un-cross-linked systems—an assumption that we have recently shown to be questionable[5] and that we will further question by results presented in this paper.

The use of specific molecular models makes published reports of tests of the validity of the FFR hypothesis suspect. In this paper we intend to test, using measurements of the elasticity of both dry and swollen networks, whether or not the presence of a solvent significantly alters the elasticity of the network—an assumption implicit in the FFR hypothesis. This will be done in a way that is independent of any molecular model, although some assumptions are inevitable. We will endeavor to make our use of these clear.

Thermodynamics of Networks

Swelling. The most common test of the Frenkel[1]–Flory–Rehner[2] hypothesis is that in which the balance of the mixing and elastic contributions to the chemical potential at swelling equilibrium is assumed. This is commonly written as follows:[6]

$$(\mu_1 - \mu^\circ{}_1)_{\text{mix}} = -(\mu_1 - \mu^\circ{}_1)_{\text{el}} \qquad (1)$$

where $(\mu_1 - \mu^\circ{}_1)_{\text{mix}}$ and $(\mu_1 - \mu^\circ{}_1)_{\text{el}}$ are the mixing and elastic contributions to the chemical potential difference between the polymer solvent system and the pure solvent. In terms of the Flory–Huggins expression for the chemical potential and a Valanis–Landel[7] type of elastic free energy function, eq 1 becomes

$$-RT[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 w'(\lambda)/\lambda^2 \qquad (2)$$

where v_2 is the volume fraction of rubber in the swollen state, χ is the Flory–Huggins polymer/solvent interaction parameter, V_1 is the molar volume of the solvent, $w'(\lambda)$ is the derivative of the elastic free energy density per unit volume of dry rubber with respect to the stretch λ ($=\lambda_s = v_2^{-1/3}$ for swelling), and R and T are the gas constant and absolute temperature, respectively. One question commonly asked in testing the FFR hypothesis is whether or not eq 2 is valid. If the value of χ in the cross-linked and un-cross-linked state is the same, then we[5] have shown that eq 2 is not valid. On the other hand if χ is assumed to depend on the cross-link density, eq 2 can be used in conjunction with mechanical and swelling measurements to determine how χ varies with cross-linking. (We have carried out such an analysis recently for swollen natural rubber networks[5] and found a linear relationship between χ and the cross-link density, ν. Also, Freed and Pesci[8] have recently used lattice calculations that involve corrections to the Flory–Huggins mean-field theory that provide a theoretical basis for such a finding. The physical basis of this effect is obvious in hindsight—there can be no random mixing at the cross-link points.) However, when one uses eq 2 to evaluate χ, it is assumed that $w'(\lambda)$ for the dry and swollen rubbers is the same. We investigate this assumption in what follows.

Mechanical Deformations. There is good empirical evidence[9] that the Valanis–Landel[7] propostion that the elastic free energy function of dry rubber networks can be expressed as a separable function in the principal stretches is valid. The assumption that this is true is essential to the analysis of the FFR hypothesis that we will use in this paper.

The Valanis–Landel[7] strain energy function can be written as follows:

$$W(\lambda_1,\lambda_2,\lambda_3) = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) \qquad (3)$$

where the $W(\lambda_1,\lambda_2,\lambda_3)$ is the elastic contribution to the free energy of the network and we will refer to $w(\lambda_i)$ as the Valanis–Landel (V–L) function. Importantly, the ability to represent successfully the elastic free energy term as separable in the stretches provides us with a means of obtaining the mechanical response of a network in all deformation geometries from a series of experiments in a limited number of geometries; e.g., we can describe tensile or compression responses from experimental results in torsion. The true stress response to a uniaxial deformation is, for example, written as[7]

$$\sigma_{11} - \sigma_{22} = \lambda w'(\lambda) - \lambda^{-1/2} w'(\lambda^{-1/2}) \qquad (4)$$

where the $w'(\lambda) = \partial w / \partial \lambda$ is the derivative of the V–L function. In addition, we note that often the V–L term is expressed as

$$w(\lambda) = \omega(\lambda) + a \ln \lambda \tag{5}$$

where the logarithmic term has created much discussion[10,11] in the literature but is unimportant[11] in the analysis that will follow.

Kearsley and Zapas[12] have shown how to obtain $w'(\lambda) - w'(1)/\lambda$ from torsion and normal force measurements on cylinders of dry rubber. Here we simply use their result that

$$w'(\lambda) - \frac{w'(1)}{\lambda} = \frac{2}{\lambda}(\lambda^2 - 1)\left[W_1 + \frac{1}{\lambda^2}W_2\right] \tag{6}$$

where the W_i represent the derivatives of the strain energy density function with respect to the ith invariant of the deformation tensor. W_1 and W_2 can be obtained from the torque and normal force measurements at different angular deformations by using the Penn and Kearsley[13] scaling law approach.

Comparison of the Elastic Response in the Dry and Swollen States. The FFR hypothesis is based upon the presumption that the elastic free energy function is the same in the dry state as it is in the swollen one. Flory[14] originally wrote this in terms of the entropy change of the Gaussian network chains upon deformation. Here we take the same approach only we use the V–L form of the strain energy density function. If we define the mechanical deformations imposed on the swollen network as α_i and the deformation relative to the dry network due to the swelling as λ_s, we can write the response expected of the material in the swollen state in terms of the V–L function determined from dry-state measurements. For a uniaxial deformation of a dry rubber we can write

$$\sigma_{11} - \sigma_{22} = \alpha w'(\alpha) - \alpha^{-1/2} w'(\alpha^{-1/2}) \tag{7}$$

where $\sigma_{11} - \sigma_{22}$ is the first principle stress difference. In the swollen state, the swelling deformation is λ_s, the superimposed deformations are the α_i's, and the total deformations become $\alpha_i\lambda_s$. Because $w(\lambda)$ is the strain energy per unit volume in the dry state, we normalize by the volume fraction rubber v_2 in the swollen state. Then the increment in true stress applied to the swollen rubber for a uniaxial deformation α superimposed upon the swollen state can be written[15]

$$\sigma_{11} - \sigma_{22} = [\alpha\lambda_s w'(\alpha\lambda_s) - \alpha^{-1/2}\lambda_s w'(\alpha^{-1/2}\lambda_s)]v_2 \tag{8}$$

and we note that we have assumed that there is no volume change of the swollen rubber upon deformation; i.e., $\alpha_1 = \alpha$, $\alpha_2 = \alpha_3 = \alpha^{-1/2}$.

If eq 8 correctly describes the response of the swollen rubber, one would conclude that the elastic free energy function of the rubber is unchanged by the presence of the solvent. Obviously, lack of agreement would lead to the opposite conclusion. In terms of the reduced stress we would write

$$\sigma_R = \frac{\sigma_{11} - \sigma_{22}}{\alpha^2 - \alpha^{-1}} = \frac{\lambda_s v_2[\alpha w'(\alpha\lambda_s) - \alpha^{-1/2} w'(\alpha^{-1/2}\lambda_s)]}{\alpha^2 - \alpha^{-1}} \tag{9}$$

In the experiments that we have performed we have carried out measurements of $w'(\lambda)$ on the dry rubber. We have performed uniaxial compression experiments on dry rubber and on rubber swollen to equilibrium in an excess of different solvents with the purpose of testing the validity of eq 8 or 9. Our techniques and results and their implications are presented in the sections that follow.

Table I
Molecular Masses of Natural Rubber Prepolymer (after Milling) and Molecular Mass between Cross-Links, M_c, of Samples after Cross-Linking with Dicymyl Peroxide

sample	dicumyl peroxide, phr	prepolymer molecular mass[a] M_w	M_w/M_n	M_c,[b] g/mol
APHR1	1	310000	2.8	21800
APHR2	2	310000	2.8	8720
APHR3	3	310000	2.8	5450
APHR5	5	310000	2.8	3115
APHR7.5	7.5	230000	2.4	2020
APHR10	10	310000	2.8	1500
APHR15	15	310000	2.8	550

[a] From size exclusion chromatography in toluene using polystyrene calibration of columns. Universal calibration was used assuming the following Mark–Houwink parameters: polystyrene in toluene, $K = 13.4 \times 10^{-3}$ mL/g, $a = 0.71$; natural rubber in toluene, $K = 50.2 \times 10^{-3}$ mL/g, $a = 0.667$. [b] Calculated from the formula given by Wood:[17] $1/2M_c = 3.6986(f_p - 0.31) \times 10^{-5}$. M_c is the molecular mass between cross-links and f_p is the parts per hundred dicumyl peroxide by mass per 100 parts of rubber. This assumes one dicumyl peroxide molecule reacts to form one cross-link. Because the dicumyl peroxide used contains ≈93% peroxide, f_p is 0.93 times the value in the table.

Experimental Methods

Samples of natural rubber from National Bureau of Standards SRM 385 were mixed with dicumyl peroxide (Di-Cup T; Hercules, Inc.)[16] by milling on a two-roll mill. The samples were then placed in a cylindrical mold 1.27 cm in diameter by 7 cm in length and cured at 149 °C for 2 h. Cross-link density was varied by changing the amount of dicumyl peroxide added during milling. This varied from one part peroxide per hundred parts rubber (phr) to 15 phr. Cross-link density was calculated from Wood's[17] equation relating the amount of decomposed peroxide to the molecular weight between cross-links. The molecular weight of each milled rubber sample was obtained prior to cross-linking by using size exclusion chromatography in toluene. The characteristics of the different samples are presented in Table I.

The cylindrical samples were further machined to final dimensions by using a grinding procedure developed previously,[18,19] which assures flat ends, end surfaces that are perpendicular to the center axis of the cylinder, and for the torsion tests centering of the sample in the test fixtures. For the torsional testing the samples were held to the platens of a Rheometrics RMS-7200[16] rheometer with a cyanoacrylate adhesive. The cylinders were 10–12 mm in diameter by 7–15 mm in height. The actual geometries were measured with a caliper accurate to 0.025 mm. The RMS-7200 configuration used the standard transducer for angular measurements and the 10000 (g cm)/2000 g (1 (N m)/20 N) load cell for torque/normal measurements. The whole is interfaced with a personal computer for data acquisition and control. Single-step stress relaxation experiments were performed by applying a step in torsion and monitoring the torque and normal force responses. All data are reported as 131 s isochronal values for the torque and normal force. The step time was less than 0.5 s.

For compression testing the as-ground samples were tested using a Floor Model Instron[16] mechanically driven test machine. Deformations were obtained by measuring with a cathetometer the length before and after deforming the sample. Forces were measured by using a 100-kg (1000 N) capacity load cell and recording the response on the chart recorder on the test machine. Deformations were applied in less than 30 s. The relaxation response is reported as 131-s isochrones determined as the difference between the total time after the sample loading was begun and half the time required to apply the deformation, i.e., as $t - t_1/2$.[20] Compression testing was carried out in both the dry and swollen states. The tests carried out in the swollen state were performed by first swelling the samples to equilibrium and then testing them in an excess of solvent. Tests in the dry state were performed after placing a silicone oil on the sample ends for lubrication. Barrelling was not observed until large deformations had been applied. Tests for which barrelling did occur were rejected.

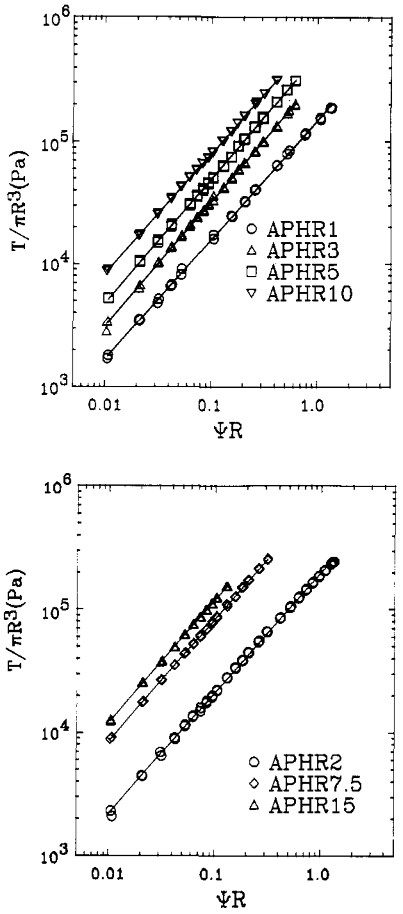

Figure 1. Double-logarithmic representation of torque as $T/\pi R^3$ versus ΨR for dicumyl peroxide cross-linked natural rubber samples. T = 24 ± 1 °C. Data for 131 s isochrones.

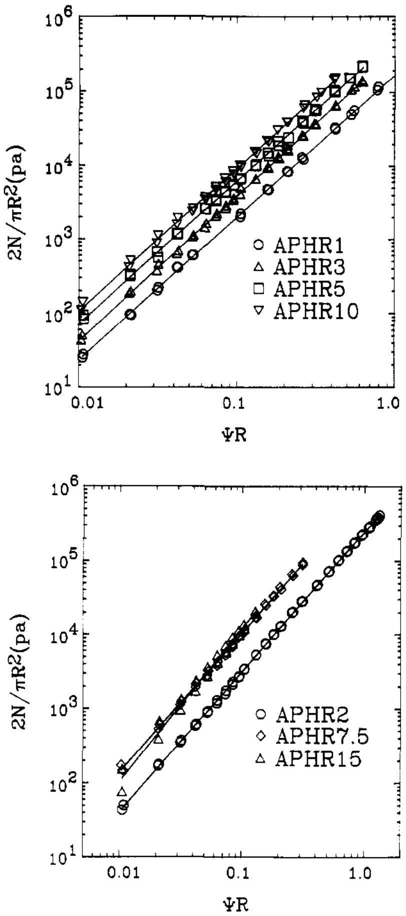

Figure 2. Double-logarithmic representation of normal force as $2N/\pi R^2$ versus ΨR for dicumyl peroxide cross-linked natural rubber samples. T = 24 ± 1 °C. Data are for 131 s isochrones.

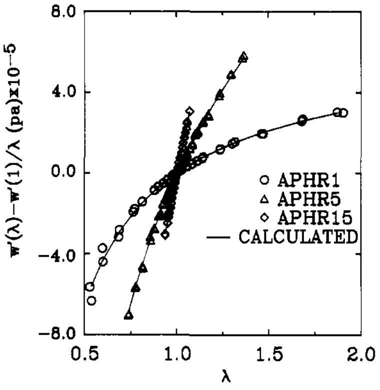

Figure 3. Strain energy function derivative, $w'(\lambda) - w'(1)/\lambda$, versus λ for dicumyl peroxide cross-linked natural rubbers, as indicated. T = 24 ± 1 °C. Points are experimental values. Solid lines represent nonlinear least-squares fits to the data.[21]

All tests were performed at 24 ± 1 °C. The solvents were acetone, methyl ethyl ketone (MEK), n-decane, and benzene, thus covering the range from nonsolvent to good solvent for natural rubber.

Results

Elastic Properties of the Dry Rubber. The elastic properties of the dry rubber were obtained by carrying out torsional tests on the samples of rubber and measuring the torque and normal force responses at increasing angles of twist. The torque results are depicted in Figure 1 in a double-logarithmic representation of $T/\pi R^3$ versus ΨR. The normal force results are shown in Figure 2 in a double-logarithmic representation of $2N/\pi R^2$ versus ΨR. Recall that the data in Figures 1 and 2 are for 131 s isochrones. Although the data are nearly linear on the double-logarithmic plots, there are deviations from linearity at the larger deformations.

Recalling the analysis section, the determination of the V–L derivative function requires that the data of Figures 1 and 2 be used to calculate W_1 and W_2, the derivatives of the strain energy density function with respect to the invariants of the deformation tensor. This was done by using the scaling law approach of Penn and Kerasley.[13] Then $w'(\lambda) - w'(1)/\lambda$ were obtained from eq 10. The values of $w'(\lambda) - w'(1)/\lambda$ are plotted versus λ in Figures 3 and 4 for the different cross-link density rubbers. In Figure 5 we show the results from compression testing of the dry rubber samples as a plot of reduced stress versus $1/\lambda$. Also depicted are the comparisons of the predictions of the compression behavior calculated from using the data of Figure 3 and 4, which were obtained from the torsion experiments, and eq 7. As can be seen, the agreement is reasonable, supporting the contention that the V–L form of the strain energy function describes well the elastic behavior of dicumyl peroxide cross-linked natural rubber.

Elastic Properties of the Swollen Rubber. In order to test the premise that the elastic free energy function in the swollen state is of the same form as that obtained in the dry state, we carried out compression tests on the swollen rubbers and compared the measured results with those predicted by eq 9 using the values of $w'(\lambda)$ obtained from the torsion measurements on the dry rubber.[21] Thus, in Figures 6–9 we compare the values of reduced stress measured in compression for each network in each of the solvents studied. As can be seen the agreement is good over the entire range of cross-link densities examined,

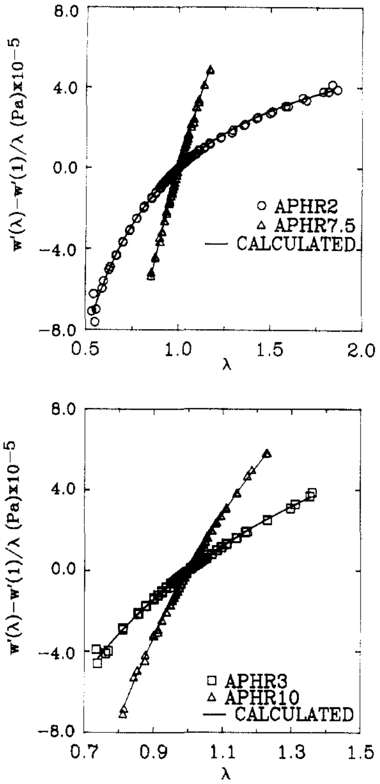

Figure 4. Strain energy function derivative, $w'(\lambda) - w'(1)/\lambda$, versus λ for dicumyl peroxide cross-linked natural rubbers, as indicated. $T = 24 \pm 1$ °C. Points are experimental values. Solid lines represent empirical fits to the data.[21]

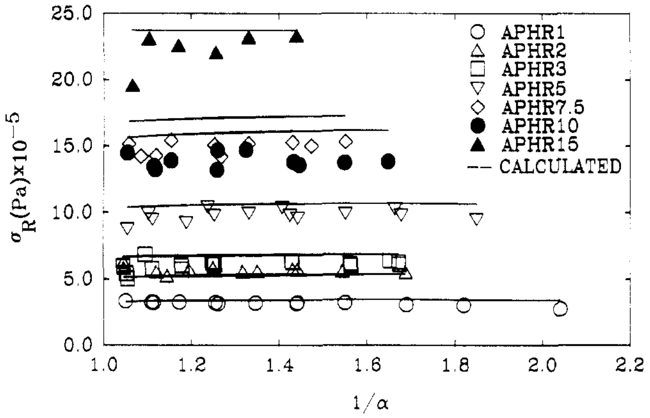

Figure 5. Reduced stress versus $1/\alpha$ for dicumyl peroxide cross-linked (dry) natural rubber in compression. Points are experimental values and lines are calculated from torsional data and eq 4.

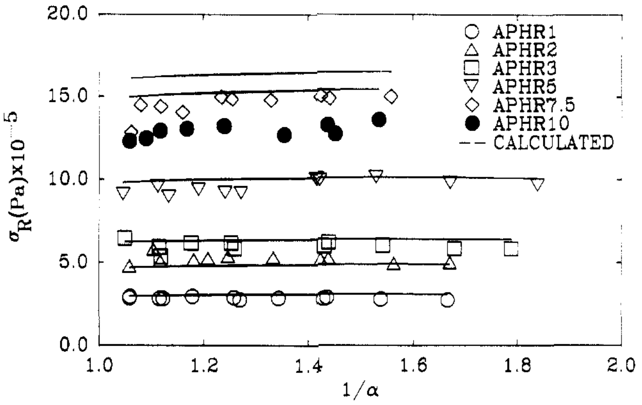

Figure 6. Reduced stress versus $1/\alpha$ for dicumyl peroxide cross-linked natural rubber swollen to equilibrium in acetone and tested in compression. Points are experimental values and lines are calculated from dry rubber properties and eq 9.

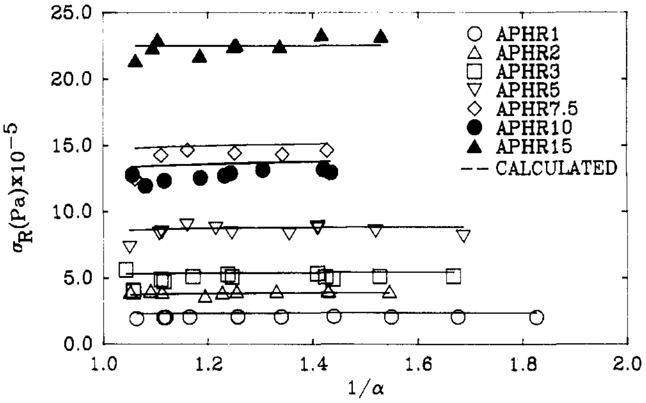

Figure 7. Reduced stress versus $1/\alpha$ for dicumyl peroxide cross-linked natural rubber swollen to equilibrium in methyl ethyl ketone and tested in compression. Points are experimental values and lines are calculated from dry rubber properties and eq 9.

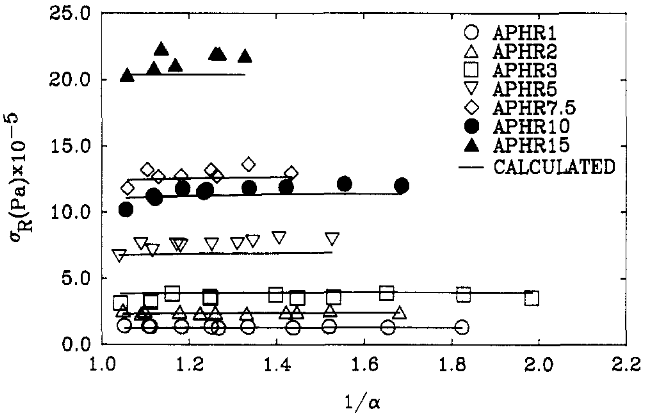

Figure 8. Reduced stress versus $1/\alpha$ for dicumyl peroxide cross-linked natural rubber swollen to equilibrium in normal decane and tested in compression. Points are experimental values and lines are calculated from dry rubber properties and eq 9.

although deviations appear at the highest degrees of cross-linking. These results suggest strongly that for lightly to moderately cross-linked rubbers the elastic free energy function that describes the behavior of the dry rubber is not significantly different from that for the rubber in the swollen state. Another way of looking at the data is to plot σ_R versus λ_s for the different cross-link density rubbers, noting that λ_s varies due to changing solvent quality. Because σ_R was independent of deformation (the response looks neohookean) we used the average σ_R from measurements at all deformations. This is done in Figure 10. Again, we see that the agreement between the calculated and the experimental values is quite good. Again, we do note deviations at the highest degrees of cross-linking, where the swelling dependence of the experimentally observed values of σ_R is less than that predicted. If this is a real effect, and it is just outside our estimated experimental uncertainty, it is perhaps not surprising as the molecular weight between cross-links is quite low for these rubbers ($M_c \simeq 1500$ for the APHR10 rubber).

Discussion

Validity of the FFR Hypothesis. As stated at the beginning of this paper, one of the presumptions of the FFR hypothesis is that the form of the elastic component of the free energy function is not affected by the presence of solvent molecules. The changes in elastic properties of the swollen rubber are then attributed to changes in chain conformation alone.[2,14,23] The results presented above for

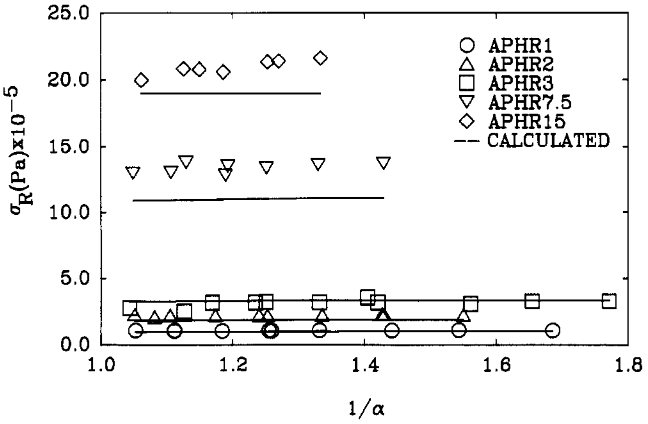

Figure 9. Reduced stress versus $1/\alpha$ for dicumyl peroxide cross-linked natural rubber swollen to equilibrium in benzene and tested in compression. Points are experimental values and lines are calculated from dry rubber properties and eq 9.

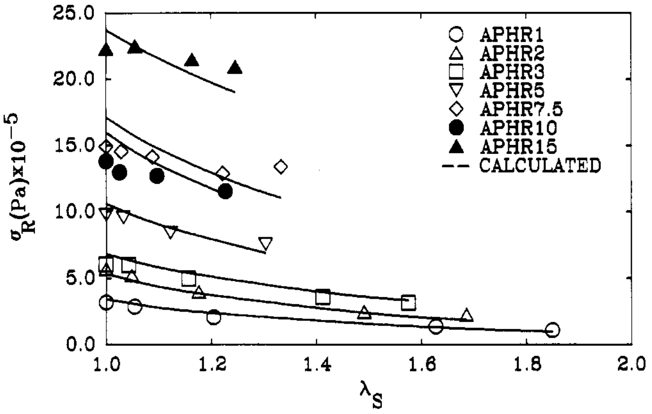

Figure 10. Reduced stress versus swelling deformation $\lambda_s = v_2^{-1/3}$ for dicumyl peroxide cross-linked natural rubber samples. Points are for data obtained from compression tests on samples swollen to different degrees by swelling in an excess of various solvents. Solid lines represent response calculated from eq 9 based on dry-state properties of the rubbers obtained from torsion and normal force measurements.

the lightly to moderately cross-linked rubbers strongly support this assumption. Thus, we can state in a strong fashion that the elastic free energy function of these rubber networks is unaffected, at least to first order, by the presence of solvent.[24] This appears to be true over the entire range of swelling deformations and solvent qualities examined. It is important to note that the definition here of "light to moderate cross-linking" is for molecular weights between cross-links of greater than approximately 1500 g/mol.

Even if we accept that the presence of the solvent does not greatly affect the elastic contribution to the free energy of the network (other than through network deformation), we must still add that the work presented here does not validate the full FFR hypothesis. Rather it suggests that reported violations of the FFR hypothesis by changes in the elasticity of the networks due to the presence of the solvent should be reevaluated.[25,26] We suggest that possible sources of difficulty may arise from the assumed equality of the Flory–Huggins χ parameter in cross-linked and un-cross-linked rubber,[27,28] changes in the thermodynamics of mixing due to chain deformation,[29] etc. Obviously these possibilities must now be explored.[30]

Summary

Experimental comparisons have been made of the elastic free energy function of dicumyl peroxide cross-linked natural rubber networks in both the dry and swollen states. The results show that, except for extremely high cross-link densities, the elastic contribution to the free energy function is unaffected by the presence of the solvent other than through network deformation.[25] This is consistent with one of the fundamental premises of the Frenkel[1]–Flory–Rehner[2] hypothesis that the free energy of mixing and the elastic free energy of swollen networks are simply additive. The results presented here show that recent discussions of the failure of the FFR hypothesis based upon the presumption that the elastic free energy is changed by the presence of the solvent need to be reassessed.

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(15) We note that this equation is unchanged whether $w'(1) = 0$ or not since the terms $w'(1)/\alpha\lambda_s$ and $w'(1)/\alpha^{-1/2}\lambda_s$ cancel.
(16) Certain commercial materials and equipment are identified in this paper to specify the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or that the materials and equipment identified are necessarily the best available for the purpose.
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havior in swelling required extrapolation of the values of $w'(\lambda) - w'(1)/\lambda$, we used the Gaylord–Douglas[22] model as empirically fit to our data to objectively carry out the extrapolations. The form of $w'(\lambda)$ in this case is $w'(\lambda) = A(\lambda - 1/\lambda) + B(1 - 1/\lambda)$. As seen by the lines in Figures 3 and 4 the model fits the data very well. Furthermore, the extrapolations were not large, and we found little difference between the use of this equation and a simple graphical extrapolation by hand.

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(24) Another possibility here is that the value of $w'(1)$ in the strain energy function changes as a function of the solvent or swelling deformation. We are not pleased with this prospect and are in the process of carrying out experiments to measure the elastic properties of rubber swollen to different amounts at different vapor pressures (isopiestically) rather than in different solvents to assess this problem We prefer to think that in the undistorted configuration ($\lambda_1 = \lambda_2 = \lambda_3 = 1$) the elastic free energy function is at a minimum, which would require $w'(1) = 0$ for the isotropic (swelling) deformation.

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(27) Richard Gaylord of the University of Illinois considered this possibility and talked with us about it in March, 1988. It implies that the dilatational modulus[25,26] S is written as

$$S = \lambda_s \ln a_c/a_u = (\chi_c - \chi_u)\lambda_s^{-5} + \frac{V_1 w'(\lambda_s)}{RT\lambda_s}$$

where a is the activity, χ is the Flory–Huggins interaction parameter, the subscripts c and u refer to the cross-linked and un-cross-linked rubbers, respectively, and the other symbols are as defined in the text. Then, if $w'(1) = 0$ as postulated in ref 24, the fact that S is not zero at zero swelling is indicative that $\chi_c \neq \chi_u$.

(28) Arndt, K. F.; Hahn, I. *Acta Polym.* **1988**, *39*, 560.

(29) Deloche, B.; Samulski, E. T. *Macromolecules* **1988**, *21*, 3107.

(30) **Note Added in Proof:** We have recently found that simple application of eq 8 or 9 to predict the tensile response of the swollen rubber is not as successful as the predictions observed here for the compressive behavior. This is being explored in detail and will be reported upon in a future publication.

Effects on the Cloud Point of Aqueous Poly(ethylene glycol) Solutions upon Addition of Low Molecular Weight Saccharides

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ABSTRACT: Cloud point measurements are reported for aqueous poly(ethylene glycol) solutions with an added third component. The added third component is in all cases a saccharide with glucose as the monomer. The following saccharides have been investigated: glucose, maltose, cellobiose, isomaltose, maltotriose, isomaltotriose, and β-cyclodextrin. All saccharides except cyclodextrin are found to decrease the cloud point in the poly(ethylene glycol) solution. The phase diagram of a mixture of glucose with PEG20000 and water is also studied. Both the phase diagram and the cloud point curve are reasonably well described by a recently presented mean-field theory. Finally a tentative explanation is given for the differences between the saccharides in their ability to decrease the cloud point in aqueous poly(ethylene glycol) solutions.

Introduction

The use of aqueous two-phase polymer systems for purification and partitioning purposes in biochemistry has long been an established and generally used method.[1] Since systems suitable for laboratory use were developed at an early stage (usually being those with dextran and poly(ethylene glycol)), there has been relatively little work done to explain and understand the fundamental mechanisms that cause polymer incompatibility. With today's advances within biotechnology, there is great interest in finding separation methods that are suitable for large-scale applications with respect to both performance and economy. One separation method that shows great promise for large-scale applications is the use of aqueous two-phase polymer systems, if the cost problem could be solved. There is thus great interest in finding new phase systems that are both cheap and effective.[2] This work would of course be facilitated if basic physical knowledge concerning phase separations in aqueous polymer systems was available. Consequently, we have initiated a project, financed by grants from the National Swedish Board for Technical Development (STU), with the aim of studying the fundamental molecular mechanisms leading to polymer incompatibility in aqueous systems. In previous work we concluded that the basic mechanisms for incompatibility in aqueous polymer systems are well described with a modified Flory–Huggins model.[3-5] This means that the explanation of phase separation is not to be found in some specific property of the solvent but is rather to be found in the molecular interactions between the different monomer segments of the polymers. As we have pointed out earlier, a crucial point in this analysis is that the molecular interactions between the different polymer segments are well understood. In order to understand these interactions we have in an earlier work studied the temperature dependence of the phase equilibria in the system poly(ethylene glycol)/dextran/water.[5] In the present work we have continued from a preliminary report[6] and have studied how the cloud point temperature for an aqueous poly(ethylene glycol) (PEG) solution changes when small amounts of low molecular weight saccharides are added. Our studies show that the different saccharides show large differences in how they effect the PEG solutions. Further the cloud point changes and the phase diagram are well described with model calculations for the system poly(ethylene glycol)/glucose/water.

Materials and Methods

Poly(ethylene glycol) (trade name PEG20000) with a molecular weight of 17 000–20 000 and all the saccharides were obtained from Serva, Heidelberg, FRG. Before stock solutions were prepared, the polymer was completely dried over phosphorous pentoxide in a vaccum desiccator for at least one week. All samples were prepared with Millipore purified water.

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