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Mechanical Properties of Dry and Swollen *cis*-1,4-Polyisoprene Networks in Simple Tension: Experiment and Comparison with Theory

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ABSTRACT: Results of simple tension experiments on dry and swollen *cis*-1,4-polyisoprene networks are reported. Measurements were performed on various networks with different cross-link densities. To decrease the time of relaxation to equilibrium, the dry samples were swollen and deswollen with a volatile solvent after the application of each load. The dependence of the observed moduli on extension and swelling is well represented by the results of calculations according to the theory of networks with constrained chains presented in the previous paper.

Introduction

Stress–strain experiments in simple tension form a convenient way of characterizing the elastic behavior of amorphous polymeric networks. A significant degree of information on the molecular structure of a network may be obtained from the graphs of reduced force plotted in terms of reciprocal extension. Such plots, commonly referred to as the Mooney–Rivlin graphs, indicate the dependence of the reduced force on the extent of extension or swelling. The reduced force [f^*], which may be identified with the shear modulus of the network, is defined as

$$[f^*] = \frac{f v_2^{1/3}}{A_d(\alpha - \alpha^{-2})} \quad (1)$$

where f is the force acting on the sample, v_2 is the volume fraction of polymer during the experiment, A_d is the cross section of the dry sample, and α is the extension ratio defined as the ratio of the final length along the direction of stretch relative to initial undistorted, swollen length.

The reduced force shows significant decrease with extension and swelling. The observed changes in the reduced force depend also strongly on the degree of cross-linking. In the present study we report results of simple tension experiments performed on *cis*-1,4-polyisoprene (PI) networks in the dry state as well as at different degrees of swelling. We report results on networks of widely different moduli ranging from high to very low degrees of cross-linking.

Results of measurements are interpreted in terms of the molecular theory introduced in the preceding paper,[1] where fluctuations of points along network chains are assumed to be affected by entanglements. The theory is a modification of the Flory theory[2] of the constrained junction model and seems to show satisfactory agreement with the data on polyisoprene networks.

Experimental Section

Samples were generously provided by Manufacture Française des Pneumatiques Michelin. Precursor polymer was an anionic commercial PI (Shell IR 307) with a high *cis*-1,4 configuration (92% cis, 5% trans, 3% 1, 2) and T_g (DSC) = −60 °C. The precursor, with a number-average molecular weight $\bar{M}_n$ = 330 000, was mixed in bulk with several amounts of pure dicumyl peroxide (DCP), molded, and cured. Curing conditions (30 min at 170 °C) were chosen to ensure full decomposition of the peroxide with negligible chain scission during curing.

The thickness t of each isotropic unswollen sample was accurately measured ($t \pm 0.001$ mm) with a Bertin micrometer (2520/D), and the length ($l \pm 0.01$ mm) was determined with a Schlumberger cathetometer (PTI ref 2207-840 9999) by measuring the distance between two points placed approximately 3 cm apart on the surface of the sample in the reference state.

Samples (dimensions ca. 100, 10, 1 mm) were first fixed at the upper clamp for at least 12 h to allow the determination of the swollen unloaded length l_0 in a state as close as possible to equilibrium. Measurements were performed by applying different dead weights at the lower end of the samples and measuring the final length l after at least 5 h. The extension α was calculated for each loading as the ratio of the final length to the initial swollen length. For experiments in the unswollen state, samples were swollen and deswollen with cyclohexane following the application of the dead load. This procedure recommended several years ago by Gee[3] decreases the time required for reaching equilibrium. Dodecane was used as the solvent for other experiments, and the volume fraction of polymer was verified not to change more than

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Table I
Structural and Elastic Data

sample	DCP, %	V_{2m}[a]	$10^{-3}M_c$[b] CC	$10^{-3}M_c$[b] MCC	$10^{-3}M_c$[c] CC	$10^{-3}M_c$[c] MCC	$\xi kT/V_d$, MPa CC	$\xi kT/V_d$, MPa MCC	κ_G CC	κ_G MCC
A	1.30	0.197	3.4	3.4	3.5	3.4	0.312	0.325	1.1	0.9
B	0.75	0.165	4.9	4.9	5.0	4.9	0.215	0.220	1.6	1.6
C	0.30	0.133	7.6	7.5	9.0	8.3	0.115	0.125	3.0	2.5
D	0.20	0.112	10.5	10.3	12.1	11.0	0.083	0.092	3.8	3.0
E	0.10	0.081	18.0	18.3	21.4	20.4	0.043	0.045	5.0	6.0

[a] Volume fraction of polymer in swelling equilibrium with benzene at 25 °C. [b] Calculations were performed with corrections for the finite molecular weight of precursor chains as outlined in ref 12. The χ parameter between benzene and PI is taken as $0.39 + 0.04v_{2m}$. [c] From the intercept of the reduced force curves at $\alpha^{-1} = 0$.

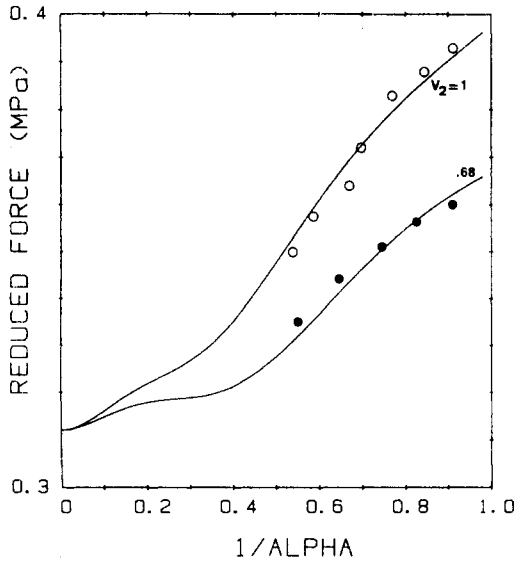

Figure 1. Comparison of experimental data (points) for sample A with results of calculations (curves) for the CC model with $(\xi kT/V_d) = 0.312$ MPa and $\kappa_G = 1.1$. The ordinate represents the reduced force, and the abscisse is the reciprocal extension. The volume fraction of solvent present during experiment is indicated on each curve.

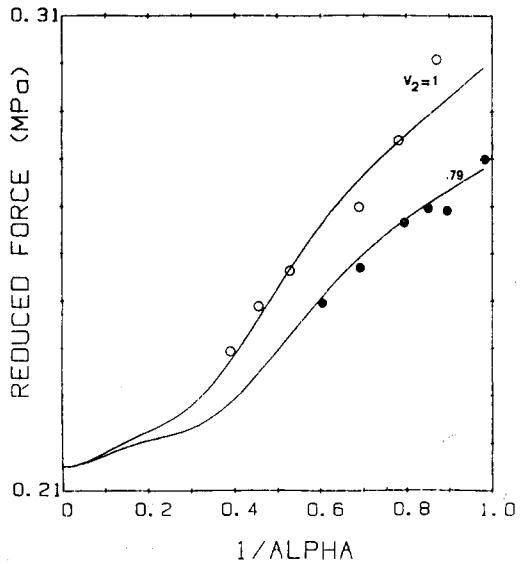

Figure 2. Comparison of experimental data (points) for sample B with results of calculations (curves) for the CC model with $(\xi kT/V_d) = 0.215$ MPa and $\kappa_G = 1.6$.

5% between initial and final states. The reproducibility was observed to be very satisfactory. It is also worth noting that for each cross-link density, measurements in the dry and various swollen states were performed on the same sample to avoid any possible problem with nonhomogeneity of a sheet of polymer.

Structural and elasticity data for the five samples of different cross-link densities are presented in Table I.

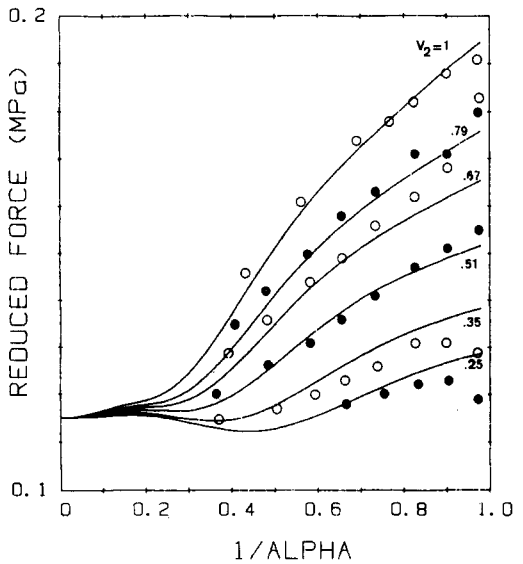

Figure 3. Comparison of experimental data (points) for sample C with results of calculations (curves) for the CC model with $(\xi kT/V_d) = 0.115$ MPa and $\kappa_G = 3.0$.

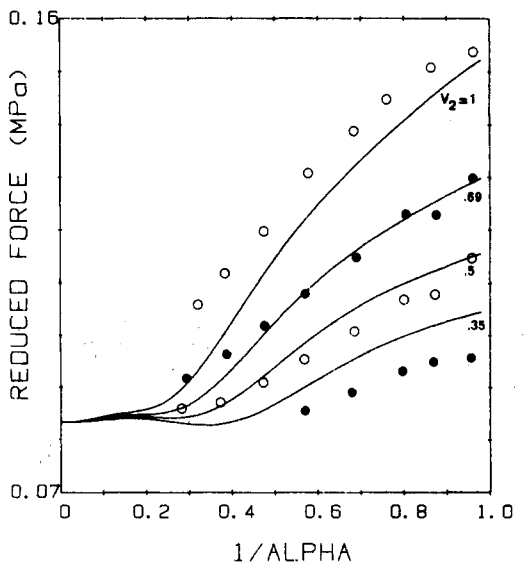

Figure 4. Comparison of experimental data (points) for sample D with results of calculations (curves) for the CC model with $(\xi kT/V_d) = 0.0833$ MPa and $\kappa_G = 3.8$.

Results of Measurements and Comparison with Theory

Results of experiments on the five samples A–E are presented in Figures 1–5. The ordinate in each figure denotes the reduced force and the abscissa the inverse extension ratio. The degree of swelling is given with each set of data. The ordinate values of the data points are calculated from experimental data according to eq 1. The

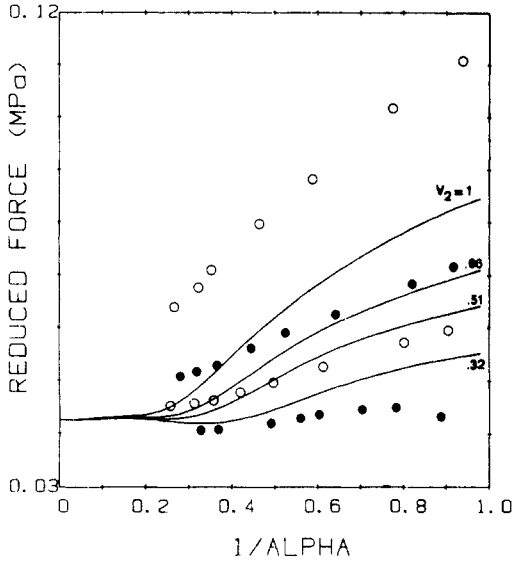

Figure 5. Comparison of experimental data (points) for sample E with results of calculations (curves) for the CC model with $(\xi kT/V_d)$ = 0.0425 MPa and κ_G = 5.0.

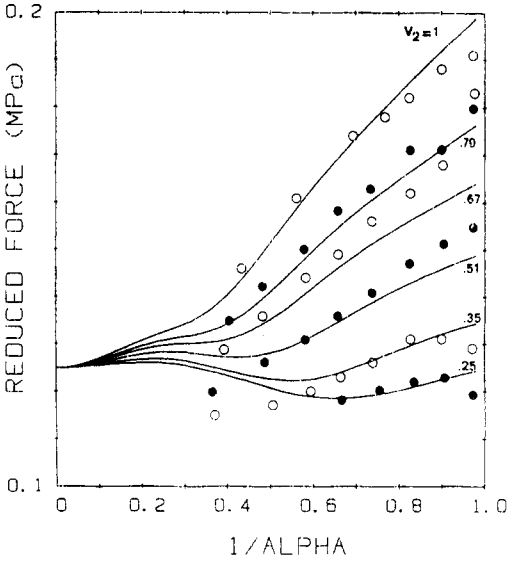

Figure 6. Comparison of experimental data (points) for sample C with results of calculations (curves) for the MCC model with $(\xi kT/V_d)$ = 0.125 MPa and κ_G = 2.5.

solid curves through the data points are calculated according to the theory presented in the preceding paper.[1] To reduce cross referencing, we rewrite eq 4 of ref 1 corresponding to the present case of tetrafunctional networks cross-linked in the bulk state:

$$[f^*] = (\xi kT/V_d)\{1 + (1 - 2/\phi)^{-1}[\alpha K(\lambda_1^2) - \alpha^{-2}K(\lambda_2^2)] \times (\alpha - \alpha^{-2})^{-1}\} \quad (2)$$

where ξ is the cycle rank, V_d is the volume of the dry network, $\xi kT/V_d$ is the shear modulus of the phantom network model, ϕ is the junction functionality, and λ_1 and λ_2 are respectively the longitudinal and lateral deformation ratio related to α by

$$\lambda_1 = v_2^{-1/3}\alpha \qquad \lambda_2 = v_2^{-1/3}\alpha^{-1/2} \quad (3)$$

The function $K(\lambda^2)$ appearing in eq 2 is obtained according to the theory as

$$K(\lambda^2) = \frac{B\dot{B}}{1+B} + \frac{D\dot{D}}{1+D}$$

$$B = \frac{h(\lambda)^2(\lambda^2 - 1)}{[\lambda^2 + h(\lambda)]^2}$$

$$D = \lambda^2 B/h(\lambda)$$

$$h(\lambda) = \kappa_G[1 + (\lambda^2 - 1)\Phi]^{-1}$$

$$\dot{B} = \partial B/\partial\lambda^2$$

$$\dot{D} = \partial D/\partial\lambda^2 \quad (4)$$

In ref 1, parameter Φ was derived for two different pictures of the phantom network. According to one, the fluctuations of all points along the chain in a phantom network are independent of macroscopic strain. This picture of the phantom network was first treated by Pearson[4] and Ullman.[5] The theory of constraints based on this model of the phantom network is referred to as the constrained chain (CC) scheme.[1] According to the second, fluctuations of points along the chain in a phantom network are taken to depend on macroscopic strain. Only those of the junctions are invariant to strain. This was derived in a recent work by Erman et al.[6] The theory of constrained networks based on this modified picture of the phantom network model is referred to as the modified constrained chain (MCC) scheme. For sufficiently long network chains, the parameter Φ takes the following form for the CC and MCC schemes:[1]

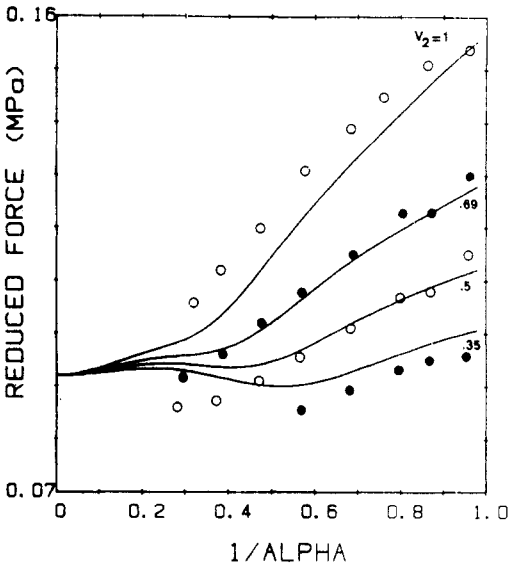

Figure 7. Comparison of experimental data (points) for sample D with results of calculations (curves) for the MCC model with $(\xi kT/V_d)$ = 0.092 MPa and κ_G = 3.0.

$$\Phi = (1 - 2/\phi)^2/3 \quad \text{(CC)}$$

$$\Phi = (1 - 2/\phi)^2 \quad \text{(MCC)} \quad (5)$$

Differences between the constrained network results formulated according to the CC and MCC schemes are pointed out in the previous paper.[1] The parameter κ_G appearing in eq 4 represents the degree of constraints operating on the fluctuations of a chain in the real network. The curves through the data points are obtained by trial and error, where the phantom modulus $\xi kT/V_d$ in eq 2 and the κ_G parameter in eq 4 are varied. Better agreement between experimental data was observed for the CC scheme of the phantom network model. The highly sensitive dependence of the modulus on elongation and swelling as suggested by the MCC scheme is not observed in the present results. Nevertheless, both schemes are considered in evaluation of the data for the purpose of comparison. In Figures 1–5, data are compared with re-

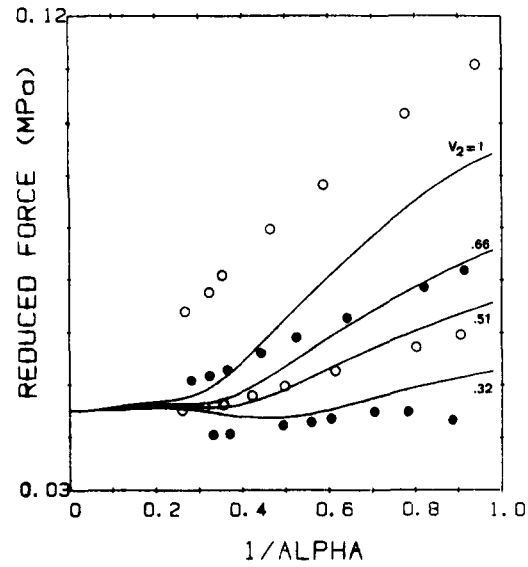

Figure 8. Comparison of experimental data (points) for sample E with results of calculations (curves) for the MCC model with $(\xi kT/V_d)$ = 0.045 MPa and κ_G = 6.0.

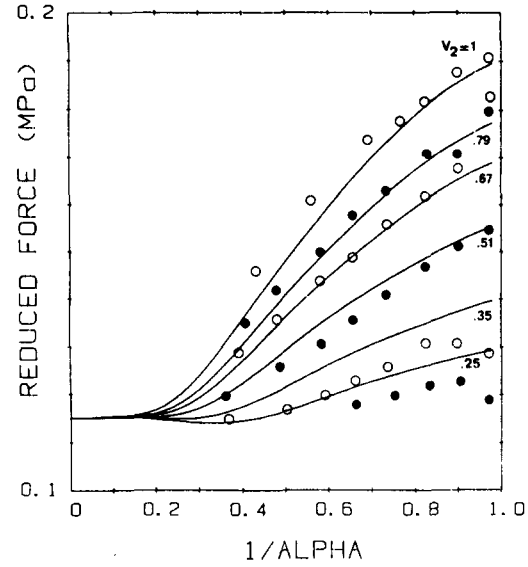

Figure 9. Comparison of experimental data (points) for sample C with results of calculations (curves) for the constrained junction model with $(\xi kT/V_d)$ = 0.115 MPA, κ = 10, and ζ = 0.05.

sults from the CC formulation. In Figures 6–8 comparison of data for samples C, D, and E with results of MCC scheme are presented. The parameters used in the theory are summarized in Table I.

The agreement between theory and experiment may be regarded as satisfactory when the wide range of cross-linking degrees and swelling are considered. The largest discrepancy between theory and experiment occurs in Figures 5 and 8 for sample E, with the lowest cross-link density. The two parameters $\xi kT/V_d$ and κ_G were chosen for this sample to obtain better agreement for the data on swollen samples. The largest discrepancy between theory and data is then observed for the dry sample, where the prediction of the theory falls ca. 15–25% below experimental data in the small strain region. An alternate approach to curve fitting to experimental data in Figures 5 and 8 would be to match the theory with results on dry samples. This would then result in a discrepancy of theory and experiment for the swollen networks.

Discussion

Predictions of the theory presented in the preceding paper compare favorably with results of experiments on *cis*-1,4-polyisoprene networks. It should be pointed out that the complete set of data is matched by theory in which only two parameters, the phantom modulus and the κ_G parameter, are adjusted. Previous comparison of similar data with the constrained junction theory[7] has indicated that an additional parameter, ζ, was required for quantitative agreement. In Figure 9, data for sample C is compared with results of the constrained junction theory. Best fit is obtained by trial and error. The curves shown are for κ = 10 and ζ = 0.05. Without the ζ parameter, the reduced force values from the constrained junction model did not show sufficient decrease with extension and swelling. The necessity of the ζ parameter was subsequently shown for various other systems.[8,9] The present work shows that such an additional parameter is not necessary when constraints along the chain contour are considered.

The two parameters $\xi kT/V_d$ and κ are not independent of each other in the constrained junction theory,[7] according to which κ varies as the inverse square root of $\xi kT/V_d$. This relation results from the assumption that κ is proportional to the number of junctions in the domain pervaded by a network chain. Computer simulation of Adolf and Curro[10] on networks with constrained junctions indicate, on the other hand, that κ should be proportional to the inverse of $\xi kT/V_d$. Inasmuch as κ and κ_G pertain to similar physical models, the same arguments may be adopted for the latter. The relationship may, in general, be represented by

$$\kappa_G = C(\xi kT/V_d)^{-m} \tag{6}$$

where C is a function of network constitution, i.e., of the characteristic ratio of network chains, polymer density, and junction functionality. Results of calculations for the five samples of the present work indicate that m = 0.78 for the CC scheme and 0.93 for the MCC scheme. These values of m lie close to the findings to Adolf and Curro. Further experimental work, similar to the present one, on other polymeric systems would be invaluable for a definitive evaluation of the exponent m.

Finally, it should be indicated that values of κ_G obtained according to the present model seem to be smaller than those obtained by the constrained junction theory. Recently, neutron-scattering experiments were performed on junction-labeled PDMS networks of $\bar{M}_w$ = 5500 by Ewen et al.[11] in which the radius of the junction fluctuation domain was measured to be in the range 23–28 Å. The corresponding radius in a phantom network would be 35 Å. This leads to a value of about unity for the κ parameter of the constrained junction model. Similar experiments on chain-labeled networks would lead to information on the magnitude of κ_G of the present treatment. A direct measurement of the κ_G parameter based on the fluctuations of points along the chain by neutron scattering would therefore be invaluable for the test of the present theoretical model.

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Stress–Strain–Swelling Behavior of Amorphous Polymeric Networks: Comparison of Experimental Data with Theory

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ABSTRACT: Results of the theory of elasticity of amorphous polymeric networks with constrained chains are compared with results of simple tension experiments on dry and swollen natural rubber, poly(ethylene oxide), polybutadiene, and poly(dimethylsiloxane) networks. The strong decrease in the modulus of the networks by elongation and by swelling is satisfactorily represented by the theory.

Introduction

The effects of constraints on the fluctuations of points along chains in amorphous polymeric networks are formulated in the first of the preceding two papers in this series.[1] The results of calculations based on this formulation, which we call the constrained chain model, are compared with experimental data on *cis*-1,4-polyisoprene networks in the second paper.[2] The analysis of experimental data in terms of the constrained chain model and the previously introduced constrained junction model[3,4] showed that three parameters, ξ, κ, and ζ, are required for a quantitative description of data with the constrained junction model, whereas only two parameters, ξ and κ_G, are sufficient when the constrained chain model is used. In this respect the constrained chain model seems to be more attractive for the interpretation of stress–strain–swelling data on amorphous polymeric networks.

Further comparison of the constrained junction theory with various dry and swollen polymeric network systems by Brotzman and Mark[5] indicated that the values of the κ parameter showed some dependence on the degree of swelling of the networks. In general, lower values of κ were required for describing the behavior of the networks at higher degrees of swelling. This indicates that the values of the reduced force depend on swelling more strongly than predicted by the constrained junction theory. Results of the recently proposed constrained chain model exhibit this stronger dependence of the modulus on swelling and also on strain.

As a further quantitative check of this feature of the constrained chain model, we have compared the theory with previous stress–strain–swelling data on different systems. The comparison is performed for natural rubber (NR), poly(ethylene oxide) (PEO), polybutadiene (PBD), and poly(dimethylsiloxane) (PDMS) networks. For comparative purposes we have adopted the two versions of the proposed constrained chain model,[1] which are termed as the constrained chain model (CC) and the modified constrained chain model (MCC). For the interest of brevity, the formulation is not repeated in the present paper and the reader is referred to ref 1 and 2.

Comparison of Experimental Data and the Constrained Chain Model Predictions

Natural Rubber. Experimental values of the reduced force for NR are presented in Figure 1 as a function of reciprocal extension α^{-1} for various values of swelling indicated by the volume fraction v_2 of polymer. The data are taken from the work of Allen et al.[6] Natural rubber was cross-linked thermally with dicumyl peroxide, and experiments were performed on samples swollen with *n*-decane. The volume fraction of polymer is shown on each curve in Figure 1. The curves are obtained with the CC model with the choice of $(\xi kT/V_d) = 0.150$ MPa and $\kappa_G = 3.0$. The curves are obtained by trial and error, by choosing a pair of values for $(\xi kT/V_d)$ and κ_G and repeating calculations with different values of these two parameters until a best fit was obtained. There are thus two adjustable parameters in the theory, the $\xi kT/V_d$ value, which is the $\alpha^{-1} = 0$ intercept, and κ_G. The former, being the modulus of the phantom network, locates the position of the curves on the vertical scale. The strain and swelling dependence of the data is then obtained by the only adjustable parameter, κ_G. The experimental reduced force values are well represented by the calculations based on the CC model. Previous treatment of the same data by the constrained junction model[7] showed similar agreement by using three adjustable parameters, $(\xi kT/V_d) = 0.167$ MPa, $\kappa = 8$, and $\zeta = 0.12$.

In Figure 2, the same experimental data are compared with the modified constrained chain model. Values of the parameters that give the best fit are $(\xi kT/V_d) = 0.170$ MPa and $\kappa_G = 2.0$. Comparison of Figures 1 and 2 shows that the MCC model gives slightly better agreement with data than the CC model, especially in the higher levels of extension.

Poly(ethylene oxide). Experimental values of the reduced force for PEO are presented in Figure 3 as a function of reciprocal extension α^{-1} for three degrees of swelling. The networks were prepared[8] by end-linking hydroxyl-terminated chains with an aromatic triisocyanate, thus leading to trifunctional junctions. The swelling agent used in the stress–strain experiments was phenyl acetate. The

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