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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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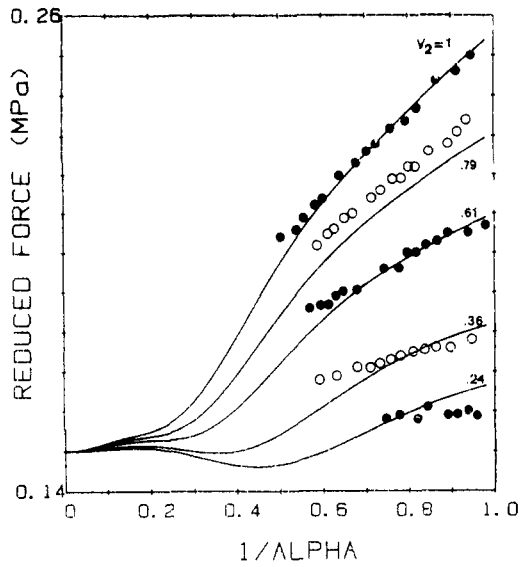

Figure 1. Comparison of the experimental reduced force values[6] for dry and swollen natural rubber networks in simple tension (circles) and the results from the CC model (curves) with $\xi kT/V_d$ = 0.150 MPa and κ_G = 3.0.

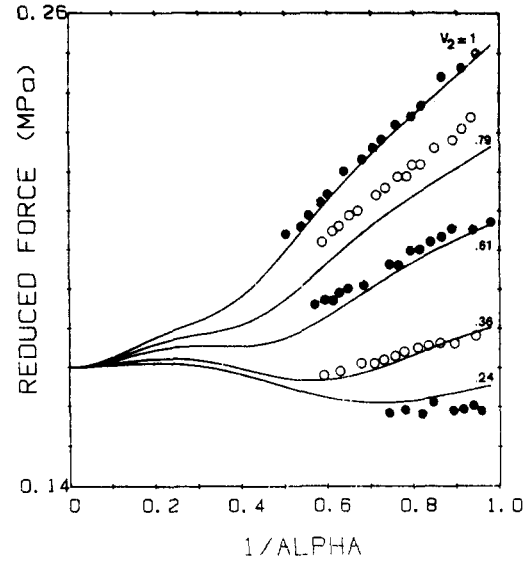

Figure 2. Same experimental data as in Figure 1 with curves obtained according to the MCC theory with $\xi kT/V_d$ = 0.170 MPa and κ_G = 2.0.

three solid curves in Figure 3 are obtained by the CC model with $(\xi kT/V_d)$ = 0.260 MPa and κ_G = 1.5. Same experimental data are used in Figure 4 for comparison with the MCC model. The values $(\xi kT/V_d)$ = 0.275 MPa and κ_G = 1.6 are used in obtaining the curves in Figure 4 for the MCC model. Previous comparison of the experimental data on PEO with results of the constrained junction model by Brotzman and Mark[5] indicated that agreement was possible when the phantom modulus $(\xi kT/V_d)$ and the κ parameter were both chosen to be dependent on v_2. The formulation according to the present model does not require v_2-dependent values of $(\xi kT/V_d)$ and κ_G.

Inasmuch as the networks were prepared by end-linking, the molecular weight of the PEO precursor chains equate to the molecular weight M_c of the network chains between two junctions. The latter is related to the intercept of the reduced force–α^{-1} curve by the relation[9]

$$\frac{\xi kT}{V_d} = \left(1 - \frac{2}{\phi}\right)\frac{\rho RT}{M_c} \qquad (1)$$

where ϕ is the functionality (ϕ = 3 for the PEO networks),

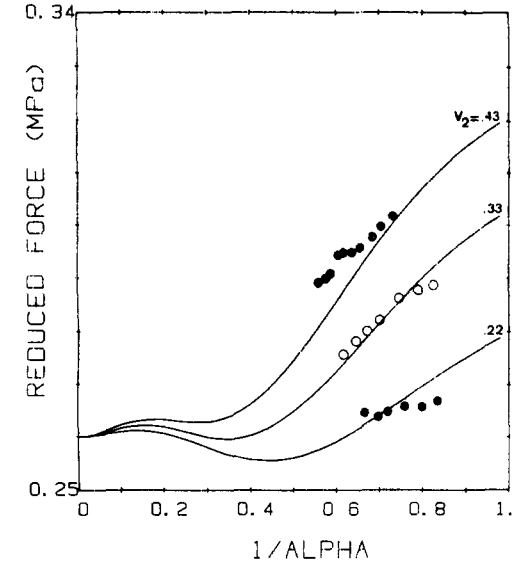

Figure 3. Comparison of the experimental reduced force values[8] of swollen poly(ethylene oxide) networks in simple tension (circles) and the results from the CC model (curves) with $\xi kT/V_d$ = 0.260 MPa and κ_G = 1.5.

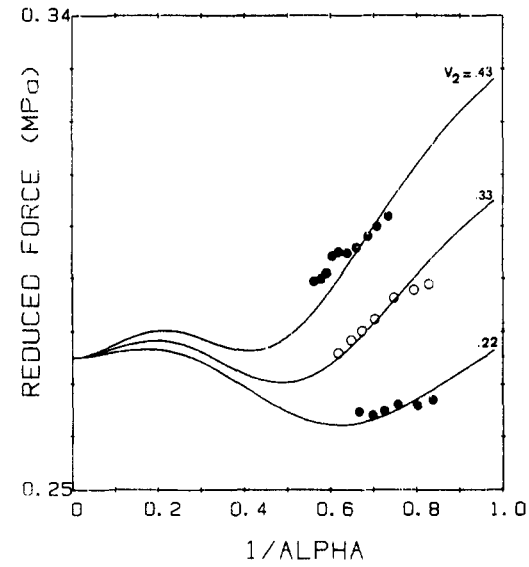

Figure 4. Same experimental data as in Figure 3 with curves obtained according to the MCC theory with $\xi kT/V_d$ = 0.275 MPa and κ_G = 1.6.

ρ is the density (ρ = 1.12 g cm^{-3}), and R is the gas constant. Using the reported value of $M_c = 3.25 \times 10^3$ g mol^{-1}, the value of $(\xi kT/V_d)$ is calculated from eq 1 to be 0.285 MPa at room temperature. This result is in satisfactory agreement with the values of 0.260–0.275 MPa obtained from the stress–strain data.

Polybutadiene. Experimental values[10] of the reduced force for PBD are presented in Figure 5 as a function of reciprocal extension α^{-1} for a wide range of swelling. The networks were prepared by cross-linking high molecular weight, 94% *cis*-1,4-PBD chains with sulfur. The swelling agent used was 1,2,4-trichlorobenzene. The curves in Figure 5 are obtained by the CC model with $(\xi kT/V_d)$ = 0.235 MPa and κ_G = 2.0. The dependence of the reduced force on extension and swelling is approximately predicted by the theory for the data on swollen samples. However, the measured values of the reduced force for the dry sample remain above the theoretically obtained curve. Use of the MCC model shown in Figure 6 for the same network (with $(\xi kT/V_d)$ = 0.235 MPa and κ_G = 2.6) does not result in better agreement. Additionally, the concentration de-

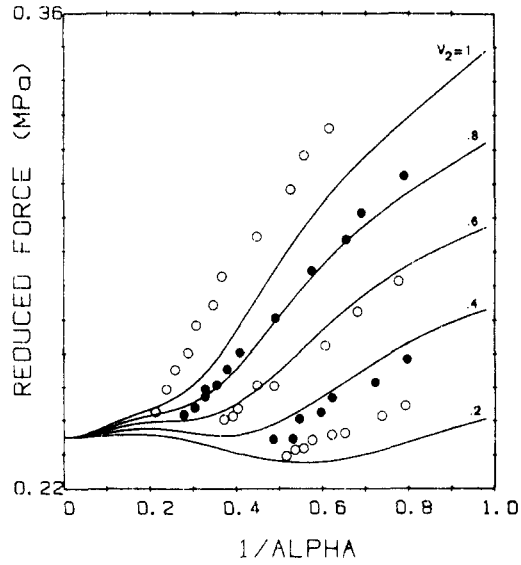

Figure 5. Comparison of the experimental reduced force values[10] for dry and swollen polybutadiene networks in simple tension (circles) and the results from the CC model (curves) with $\xi kT/V_d$ = 0.235 MPa and κ_G = 2.0.

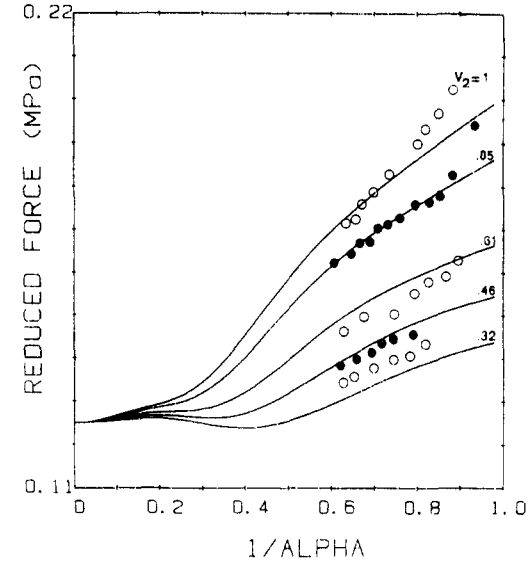

Figure 7. Comparison of the experimental reduced force values[12] for dry and swollen poly(dimethylsiloxane) networks in simple tension (circles) and the results from the CC model (curves) with $\xi kT/V_d$ = 0.125 MPa and κ_G = 2.5.

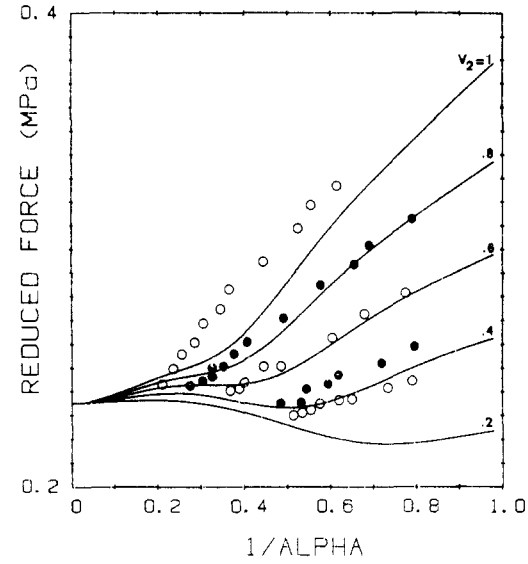

Figure 6. Same experimental data as in Figure 5 with curves obtained according to the MCC theory with $\xi kT/V_d$ = 0.235 MPa and κ_G = 2.6.

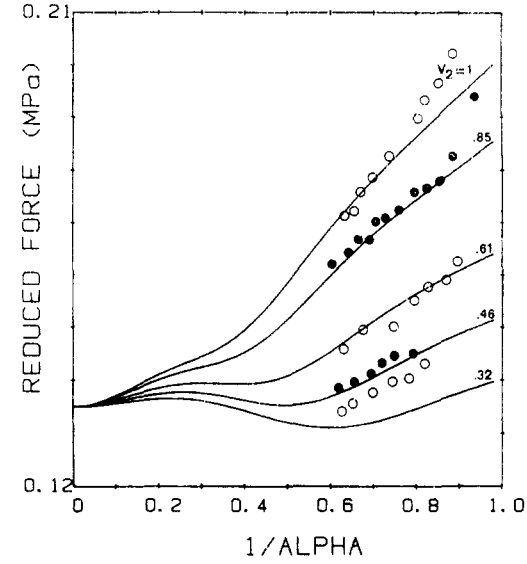

Figure 8. Same experimental data as in Figure 7 with curves obtained according to the MCC theory with $\xi kT/V_d$ = 0.135 MPa and κ_G = 2.0.

pendence of the reduced force from the MCC model appears to be stronger than that suggested by experimental data on PBD.

Previous comparison of the data for the PBD network with the constrained junction model[5] showed that ($\xi kT/V_d$) and κ values should be dependent on v_2 for a quantitative agreement between theory and experiment. The present comparison with the constrained chain model in Figure 5 indicates that such concentration dependence of the parameters is not required—with the exception of the data set for the dry sample. Results of experiments performed on PBD networks[11] indicate, in general, larger reduced force values in the dry state than the predictions of any of the theories. Data in the swollen state appear to be in better agreement with theory.

The discrepancy between experiment and theory for the dry samples may be attributed, in part, to the formation of multifunctional junctions (ϕ in excess of 4) during the cross-linking of PBD.

Poly(dimethylsiloxane). Experimental values of the reduced force for PDMS are presented in Figure 7 as a function of reciprocal extension α^{-1} for a wide range of swelling. The data were obtained[12] on PDMS networks cross-linked with electron radiation. The networks were swollen with benzene and were maintained at fixed activities. The curves in Figure 7 are obtained by the CC model with ($\xi kT/V_d$) = 0.125 MPa and κ_G = 2.5. The extent of decrease of the reduced force with swelling and extension seems to be well predicted by the model. Previous comparison of the same data with the constrained junction model required ($\xi kT/V_d$) = 0.138 MPa, κ = 6, and ζ = 0.12.

The same experimental data are compared in Figure 8 with predictions of the MCC model. Values of the parameters for best fit are ($\xi kT/V_d$) = 0.135 MPa and κ_G = 2.0. Results of comparison according to this model seem to be not significantly different from those for the CC model.

Discussion

The theory of rubber elasticity based on the constrained chain model[1] is applied to the analysis of simple tension

data on four different polymeric networks. The strong dependence of the reduced force on extension and swelling, observed in all the experiments, seems to be well characterized by the constrained chain model in which the effects of constraints along the network chains are taken into account explicitly in the formulation. In this respect, the model may be regarded as an improvement over the constrained junction model where the effects of entanglements were assumed to be concentrated at the junctions only.

The quantitative agreement between the strain- and swelling-dependent part of the data and of the theory is achieved by adjusting only the parameter κ_G. The values of this parameter range between 1.5 and 3.0 for the four networks. A similar range of values is obtained from the analysis of polyisoprene networks.[2] Following the same arguments[7] for the relationship of κ to $(\xi kT/V_d)$, the parameter κ_G may be related to the degree of cross-linking as given in the previous study,[2] i.e., by a relation of the form

$$\kappa_G = C(\xi kT/V_d)^{-m} \tag{2}$$

where the coefficient of proportionality C should reflect the molecular constitution of the polymeric system chosen.[7] If such a relationship holds, then κ_G may be evaluated by the knowledge of the cross-link density of the network. Accepting the relation between $(\xi kT/V_d)$ and molecular weight M_c, given by eq 1, and assuming that M_c is known then lead to the conclusion that no adjustable parameter remains in the theory. The complete stress–strain–swelling behavior may then be determined by the knowledge of two structural parameters, M_c and ϕ.

Description of network behavior without any adjustable parameters, as outlined in the preceding paragraph, is one of the basic aims of a consistent statistical theory. However, several features of the scheme outlined in the preceding paragraph are yet uncertain. In the first place, acceptance of eq 1 implies that trapped entanglements do not contribute to the phantom modulus, which is still a subject of significant controversy (it should be noted that the result obtained in this work for PEO is an example favoring the absence of trapped entanglements). Second, the relationship given by eq 2 still remains conjectural. According to the analysis given in ref 7, m should equate to $^1/_2$. This is supported by recent experimental evidence.[13,14] However, subsequent computer simulations[15] have led to a value of unit for m, and there is yet no conclusive experimental evidence favoring one or the other.

Results of calculations shown by the curves in Figures 1–8 indicate that the reduced force exhibits both a minimum and a maximum at smaller values of v_2. The minima and maxima become more pronounced as v_2 is decreased. Results according to the MCC model exhibit the effect more strongly than those for the CC model. The presence of maxima and minima is also seen, to a lesser extent, in the results of the constrained junction model.[4]

As a general concluding remark, it should be noted that it is insufficient to test elasticity theories by simple tension experiments on dry samples only. Experiments on samples swollen to various degrees by suitable solvents are requisite for a better test of a theory. Further work along these lines on well-characterized networks is necessary. In particular, studies performed on model networks with known molecular weights of chains between junctions are most desirable. Such experiments would lead to the direct calculations of ξ from data, leaving only one adjustable parameter, κ_G.

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