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Elastic properties of swollen real polymer networks

Song Mingshi, Lin Hangqing, Ni Jianlong*

Department of Polymer Science, Beijing Institute of Chemical Technology, Beijing,
The People's Republic of China

SUMMARY

In this paper a new set of stress-strain relations (uniaxial, equi-biaxial, unequibiaxial extensions and pure shear) for swollen networks were presented. Which are derived from the molecular theory of rubber elasticity with constraints of junctions and trapped entanglements and with crosslinks, trapped entanglements and carbon black-polymer interactions. They successed in relating the elastic equation of state to the volume fraction of polymer in swollen networks by three molecular parameters C'_1, C'_2 and C'_3. The relation of stress-strain for uniaxial extension was verified by experiments. It is shown that this relation can successfully predict the dependence of V_2 on the C'_1, C'_2 and C'_3, and the contribution of modulus for swollen networks from the trapped entanglement which it shows that role of entanglements can only approach to a limited value, never to zero.

INTRODUCTION

It is a simple matter to extened the elementary network theory to the case of a swollen phantom networks. The resulting equation for the work of deformation per unit volume of the swollen phantom networks in pure homogeneous strain is given by Treloar(1)

$$W = \frac{1}{2} NKTV_2^{1/3} (\lambda_{1s}^2 + \lambda_{2s}^2 + \lambda_{3s}^2 - 3) \qquad (1)$$

in which N is the number of chains per unit volume of the swollen networks; T is the absolute temperature; V_2 is the

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* Student of Division of Polymer Physics, Department of Applied Chemistry, China University of Science and Technology

volume fraction of polymer; K is the Boltzmann constant; λ_{1s}, λ_{2s} and λ_{3s} are the principal extension ratios referred to the unstrains (i.e., stress free) swollen dimension. The corresponding relation between the stress(referred to the final strained swollen area) and the extension ratio for simple extension is of the form:

$$f' = G V_2^{1/3} (\lambda_s - \lambda_s^{-2}) , \quad G = NKT \qquad (2)$$

in which f' is the force per unit unstrained swollen area. Experiments show a remarkable deviations from the classical theory, but it may be characterized by the Mooney(2) equation

$$\Phi' = f' V_2^{1/3}/2 (\lambda_s - \lambda_s^{-2}) = C_1' + C_2' V_2^{-2/3} \lambda_s^{-1} = C_1 + C_2 \lambda_s^{-1} \qquad (3)$$

on this basis a plot of Φ'against λ_s^{-1} should yield a straight line with the slope $C_2' V_2^{-2/3}$ and the intercept C_1'. But the experimental data(3) showed that the C_2 falls in a linear manner with increasing V_2.

It is well known that the C_1 and C_2 are only empirical constants, and have no any molecular basis. Thus up to date no generally accepted explanation for the above facts has been put forword. The first theoretical attempts to account for this approximately linear dependence of Φ' on λ_s^{-1} are due to Ronca(4) and Flory(5). The recent molecular theory of Flory and Erman(6) leads to the following expression for tetrafunctional networks

$$\Phi' = (\xi/V_o) RT \{ 1 + [K(\lambda_s^2 V_2^{-2/3}) \lambda_s - \lambda_s^{-2} K(\lambda_s^{-1} V_2^{-2/3})] (\lambda_s - \lambda_s^{-2})^{-1} \} \quad (4)$$

where the function K is defind in ref.6 (equation 37); R is the gas constant; the quantity ξ is the cycle rank and V_o is the volume. It is apparent that the equation of (4) still can not predict the above experimental dependence of C_2 on V_2. Therefore in this paper we will present a new set of stress-strain relations for swollen networks, which was derived from our proposed theory of rubber elasticity(7-8). These relations both can predict successfully the elastic properties of swollen network at moderate degree deformation and explain the dependence of V_2 on the C_1 and C_2.

STORED-ENERGY FUNCTION OF SWOLLEN REAL NETWORKS

In previous papers(7-8) a new molecular theory of rubber elasticity with constraints of junctions and trapped entanglements and with the crosslink, trapped entanglements and carbon black polymer interactions was presented. This investigation is to extend this theory of elasticity to the case of a swollen real networks.

1). Stored-Energy Function of Real Networks

The approximate expression of stored-energy function for real network in second order is given by the following equation$^{(7-8)}$

$$W = F_{tt} = 1/2\,KT\{[\xi_c B_c + \xi_e B_e + \xi_{cf} B_{cf} + \xi_{ef} B_{ef}](I_1 - 3) + (\xi_c D_c + \xi_{cf} D_{cf}) \ln(I_3) + [\xi_e D_e + \xi_{ef} D_{ef}] \ln[I_1/3] + [\xi_e C_e + \xi_c C_c + \xi_{cf} C_{cf} + \xi_{ef} C_{ef}](I_1^2 - 3^2)\} \quad (5)$$

where $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$; $I_3 = \lambda_1 \cdot \lambda_2 \cdot \lambda_3$. $\xi_c B_c$, $\xi_e B_e$, $\xi_{cf} B_{cf}$ and $\xi_{ef} B_{ef}$ are the number of elastically active long chains in the crosslinked, trapped entanglement and carbon black-polymer networks; $\xi_c D_c$ and $\xi_{cf} D_{cf}$ are the number of elastically active chains in connexion with changing volume; $\xi_e D_e$ and $\xi_{ef} D_{ef}$ are the number of elastically active entanglement chains in the trapped entanglement and carbon black-polymer networks; $\xi_e C_e$, $\xi_c C_c$, $\xi_{cf} C_{cf}$ and $\xi_{ef} C_{ef}$ are the number of elastically active short chains in crosslinked, trapped entanglement, and carbon black-polymer networks. For incompressible networks the equation of (5) reduce to

$$W = F_{tt} = C_{100}(I_1 - 3) + C_{020} \ln(I_1/3) + C_{200}(I_1^2 + 3^2) \quad (5')$$

where $C_{100} = C_{100c} + C_{100cf} + C_{100e} + C_{100ef}$, $C_{020} = C_{020e} + C_{020ef}$, $C_{200} = C_{200c} + C_{200e} + C_{200cf} + C_{200ef}$, λ_1, λ_2, and λ_3 are the principle extension ratios referred to unswollen state.

2). Stored-Energy Function of Swollen Real Networks

Let us consider the original unit cube swollen in the ratio of $1/V_2$ and subsequently deformed to the dimension l_1, l_2, and l_3 by principal stress τ_1, τ_2 and τ_3. According our proposed theory$^{(7-8)}$ the total change in the network free energy, $\Delta F_0'$, in passing from the unstrained unswollen state to the strained swollen state is given by equation

$$\Delta F_0' = C_{100}(l_1^2+l_2^2+l_3^2-3)+C_{020}\ln[1/3(l_1^2+l_2^2+l_3^2)] + C_{001}\ln(l_1 l_2 l_3)+C_{200}[(l_1^2+l_2^2+l_3^2)^2-9] \tag{6}$$

the change in free energy, ΔF_0, due to the isotropic swelling in the ratio $\lambda_0 = 1/V_2^{1/3}$ and in absence of stress is

$$\Delta F_0 = C_{100}(3\lambda_0^2-3)+C_{020}\ln[1/3(3\lambda_0^2)]+C_{001}\ln(\lambda_0^3)+C_{200}[(3\lambda_0^2)^2-9] \tag{7}$$

the required free energy of deformation of swollen networks, $\Delta F'$, is the difference between these two quantities, which is given by

$$\Delta F' = \Delta F_0' - \Delta F_0 = C_{100}(l_1^2+l_2^2+l_3^2-3V_2^{-2/3})+C_{020}\ln\left(\frac{l_1^2+l_2^2+l_3^2}{3V_2^{-2/3}}\right) + C_{001}\ln\left(\frac{l_1 l_2 l_3}{V_2^{-1}}\right)+C_{200}[(l_1^2+l_2^2+l_3^2)^2-9V^{-4/3}] \tag{8}$$

for an incompressible swollen networks the term of $C_{001}\ln\left(\frac{l_1 l_2 l_3}{V_2^{-1}}\right)$ is equal to zero, therefore the above equation reduces to

$$\Delta F' = C_{100}(l_1^2+l_2^3+l_3^2-3V_2^{-2/3})+C_{020}\ln\frac{l_1^2+l_2^2+l_3^2}{3V_2^{2/3}}+C_{200}[(l_1^2+l_2^2+l_3^2)^2-9V_2^{-4/3}] \tag{9}$$

This may be more conveniently expressed in term of the extension ratios $\lambda_{1s}, \lambda_{2s}$ and λ_{3s}, referred to the swollen unstrained state by writing $l_1 = \lambda_{1s}/V_2^{1/3}$, $l_2 = \lambda_{2s}/V_2^{1/3}$ and $l_3 = \lambda_{3s}/V_2^{1/3}$, namely

$$\Delta F' = C_{100}V_2^{-2/3}(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2-3)+C_{020}\ln[\tfrac{1}{3}(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)]+C_{200}V^{-4/3}[(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)^2-9] \tag{10}$$

this is the free energy of deformation per unit volume, measured in the unswollen state. To obtain the stored-energy function per unit volume we require the free energy of deformation per unit volume, measured in the swollen state. Denoting this by ΔF, we have

$$\Delta F = V_2\Delta F' = C_{100}V_2^{1/3}(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2-3)+C_{020}V_2\ln[1/3(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)] + C_{200}V_2^{-1/3}[(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)^2-9] \tag{11}$$

the corresponding stored-energy function thus becomes

$$W = \Delta F = C_{100}V_2^{1/3}(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)+C_{020}V_2\ln[\tfrac{1}{3}(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)] + C_{200}V_2^{-1/3}[(\lambda_{1s}^2+\lambda_{2s}^2+\lambda_{3s}^2)^2-9] \tag{12}$$

comparison with (5') shows that this is of the same form as the stored-energy function for the unswollen rubber, except for the factor $V_2^{1/3}$, V_2 and $V_2^{-1/3}$ in the corresponding C_{100}, C_{020} and C_{200}.

RELATION OF STRESS TO STRAIN AND EQUILIBRIUM MODULI FOR SWOLLEN NETWORK

A). Relation of stress to strain

The relationships of stress to strain for four types deformation at constant volume were derived from equation of (12) by the relation $\tau_i = (\frac{\partial W}{\partial \lambda_i})$. They are given by the following equations:

1). Uniaxial extension ($\tau_s = f/A_{os}$, f-force, A_{os}-the initial cross section)

$$\tau_s = 2(\lambda_s - \lambda_s^{-2})[C_{100}V_2^{1/3} + C_{020}V_2/(\lambda_s^2 + 2/\lambda_s) + 2C_{200}V_2^{-1/3}(\lambda_s^2 + 2/\lambda_s)] \quad (13)$$

$$\tau_s = 2(\lambda_s - \lambda_s^{-2})[C_{100}V_2^{1/3} + C_{020}V_2/(\lambda_s^2 + 2/\lambda_s)] \quad (13')$$

2). Unequi-biaxial extension ($\tau_{1s} = f/A_{1s}$, $\tau_{2s} = f/A_{2s}$, $\tau_{1s} \neq \tau_{2s}$)

$$(\tau_{1s} - \tau_{2s}) = 2(\lambda_{1s}^2 - \lambda_{2s}^2)[C_{100}V_2^{1/3} + C_{020}V_2/(\lambda_{1s}^2 + \lambda_{2s}^2 + \lambda_{1s}^{-2} \cdot \lambda_{2s}^{-2})] \quad (14)$$

3). Equi-biaxial extension ($\tau_{1s} = \tau_{2s} = \tau_3$, $\tau_{3s} = 0$)

$$\tau_s = 2(2 + \lambda_s^3)(\lambda_s - \lambda_s^{-5})[C_{100}V_2^{1/3} + C_{020}V_2/(2\lambda_s^2 + \lambda_s^{-4})] \quad (15)$$

4). Pure shear ($\lambda_{3s} = 1$, $\tau_{1s} = \tau_s$, $\tau_{2s} = 0$)

$$\tau_s = 2(1 + \lambda_s^2)(\lambda_s - \lambda_s^{-3})[C_{100}V_2^{1/3} + C_{020}V_2/(\lambda_s^2 + \lambda_s^{-2} + 1)] \quad (16)$$

B). Equilibrium moduli

The equilibrium mudulus can be obtained from the following relation $\frac{1}{3}(\frac{dW}{d\lambda})_{\lambda-1} = G_{sh}$ (8), they are given in equatuon of (17)

$$(G_{sh})_s = 2C_{100} \cdot V_2^{1/3} + \frac{2}{3}V_2 \cdot C_{020} + 12V_2^{-1/3} \cdot C_{200} \quad (17)$$

The equation of (13) can be rewritten in the following form

$$\Phi'' = [\frac{\tau_s V_2^{-1/3}}{2(\lambda_s - \lambda_s^{-2})} - C_{100}]/V^{-2/3}(\lambda_s^2 + \frac{2}{\lambda_s}) = 2C_{200} + C_{020}\frac{V_2^{4/3}}{(\lambda_s^2 + 2/\lambda_s)^2} \quad (18)$$

where ϕ'' and λ_s are referred to the unstrained swollen area and extension ratio.

COMPARISON WITH EXPERIMENTS

The observations of Gee(9) have shown that the deviation of force-extension curve for vulcanized rubber from the form predicted by classical theory becomes progressively less noticeable as the degree of swelling is increased. This effect has been reexamined in more detail by Gumbrell, Mullins and Rivilin(3) for a number of different swelling liquids. Their experimental stress to strain data were treated with equation of (13') derived from our proposed theory of rubber elasticity. The reduced force ($\Phi' = \tau_s/2(\lambda_s-\lambda_s^{-2})$) is plotted against $(\lambda_s^2+2/\lambda_s)^{-1}$. A series of lines with different volume fraction of rubber was obtained. They are given in Fig. 1. The $C_1' = C_{100}V_2^{1/3}$ and

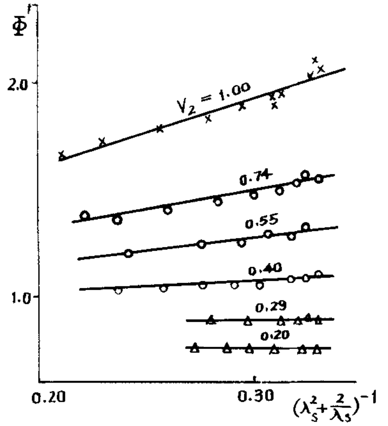

Fig. 1. Relation of stress to strain for uniaxial extension(3) with equ.(13').

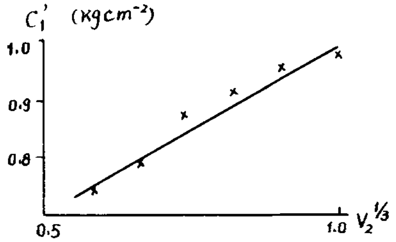

Fig. 2. Dependence of C_1' on V_2

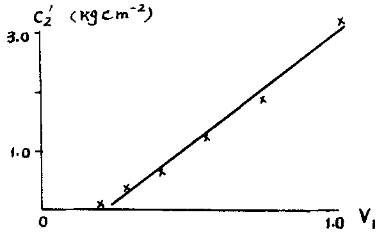

Fig. 3. Dependence of C_2' on V_2

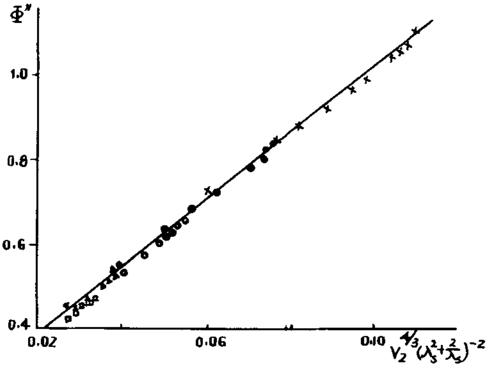

Fig. 4. Relations of stress to strain for uniaxial extension(10) with equ. (18);
V_2 =1.00; 0.753; 0.585
0.455; 0.407.

$C_2' = C_{020}\,V_2$ were determined from the intercept and slope by least square method. Then the C_1' and C_2' are plotted against V_2 and V_2 respectively. Two predicted lines are obtained and given in Fig. 2 and 3. The values of C_{100} and C_{020} determined from the slope are in agreement with the other from the unswollen state very well.

For the larger deformation of swollen networks the Mullins' experimental data(10) was treated by equation of (18). The Φ'' is plotted against $V_2^{4/3}(\lambda_s^2 + 2/\lambda_s)^{-2}$. A predicted composite line was obtained. It is given in Fig. 4. The C_{200} and C_{020} were obtained from the slope and intercept by least square method. Their values are in agreement with the other obtained from the unswollen state very well.

These above results once again show that our proposed molecular theory of rubber elasticity is in agreements with experiments very well; and offer same evidence, that the contribution of equilibrium moduli for swollen networks from the trapped entanglements can only approach to a limited value, never to zero. It is due to that in experiments the value of volume fraction for polymer in swollen networks with pure solvents can never take the value of zero. The equilibrium moduli of swollen networks with different volume fraction V_2 of polymer was calculated by the equation of (17). Their values are given in Table 1.

Table 1. The molecular parameters of swollen networks with different volume fraction of polymer

V_2	1.00	0.753	0.585	0.455	0.407
G_{sh} ($Kgcm^{-2}$)	5.46	4.56	4.01	3.65	3.54
C_{100}(")	$-5.45\ 10^{-5}$				
C_{020}(")	$7.14\ 10^{-4}$ $(7.87\ 10^{-4})$*				
C_{200}(")	$0.15\ 10^{-4}$ $(0.12\ 10^{-4})$*				

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*Obtained from slope and intercept.

CONCLUSION

A new set of stress-strain relations (uniaxial, equi-biaxial, unequi-biaxial extension and pure shear) was presented. Which are derived from the molecular theory of rubber elasticity with constraints of junctions and trapped entanglements and with crosslinks, trapped entanglements and carbon black-polymer interactions. They succeeded in relating the elastic equation of state to the volume fraction of polymer V_2 in swollen networks by three molecular parameters C_1', C_2' and C_3' .

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