Determination of crosslinking density of polymer networks by mechanical data in simple extension and by swelling degree at equilibrium

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A large amount of experimental data published by several laboratories has been reanalysed to determine the average molecular weight between crosslinks (M_c) for natural rubbers. The values of M_c determined using swelling measurements have been compared with those estimated using stress–strain data. Good agreement is found between $M_c(S1)$ and $M_c(G_e)$ obtained, respectively, from swelling degree at equilibrium through classical Flory–Rehner theory and from mechanical data through a new stress–strain relationship.

INTRODUCTION

Measurements of stress–strain response offer the simplest method of characterizing the crosslink density of polymer networks. According to the kinetic theories of rubber elasticity, the stress–strain–crosslink density relationship in simple extension is given by[1,2]

$$\sigma = A_\phi \rho R T M_c^{-1}(\lambda^2 - \lambda^{-1}) = G_n(\lambda^2 - \lambda^{-1}) \qquad (1)$$

where σ is the true stress, λ the extension ratio, ρ the density of the rubber, M_c the average molecular weight between crosslinks, R the gas constant, T the absolute temperature, A_ϕ a prefactor depending on the theory considered and G_n the well known neo-Hookean modulus.

However, most experimental data show a significant deviation from the kinetic theories. A semi-empirical equation suggested by Mooney[3] and Rivlin[4] with two constants, $2C_1$ and $2C_2$, allows a satisfactory description of stress–strain data in the moderate strain region:

$$\sigma = (2C_1 + 2C_2/\lambda)(\lambda^2 - \lambda^{-1}) \qquad (2)$$

Comparison of equation (2) with equation (1) led many authors[1] to assume that the average molecular weight between crosslinks M_c can be estimated from the low strain modulus $(2C_1 + 2C_2)$:

$$M_c(2C_1 + 2C_2) = A_\phi \rho R T/(2C_1 + 2C_2) \qquad (3)$$

Others[5,6] suggested that M_c should instead be estimated from the parameter $2C_1$:

$$M_c(2C_1) = A_\phi \rho R T/2C_1 \qquad (4)$$

Recently, it has been shown that the true stress in simple extension can be considered as a sum of two contributions[7,8]:

$$\sigma = \sigma_0(\lambda) + G_e(\lambda^2 - \lambda^{-1}) \qquad (5)$$

The first term, $\sigma_0(\lambda)$, rapidly reaches a constant value σ_0. The value of σ_0 depends on the chemical nature of the rubber considered, but not on the crosslink density[7]. Parameter G_e depends on the degree of crosslinking. By analogy with equations (3) and (4) the average molecular weight between crosslinks M_c can be estimated from the value of G_e:

$$M_c(G_e) = A_\phi \rho R T/G_e \qquad (6)$$

On the other hand, swelling by a suitable low molecular weight liquid provides another simple method for characterizing polymer networks. According to the theory of Flory and Rehner[1,2], the average molecular weight between crosslinks M_c is related to the swelling degree at equilibrium v_2:

$$M_c(S1) = A_\phi \rho V_1 v_2^{1/3}/\{\ln(1 - v_2) - v_2 - \chi v_2^2\} \qquad (7)$$

where V_1 is the molar volume of the swelling liquid, v_2 is the volume fraction of the rubber in the swollen state and χ is the polymer–solvent interaction parameter. $M_c(S1)$ stands for the molecular weight between crosslinks determined from equation (7), whereas $M_c(S2)$ is the same quantity determined from the following expression, obtained by Flory[2] through modification of equation (7):

$$M_c(S2) = A_\phi \rho V_1 (v_2^{1/3} - v_2/2)/\{\ln(1 - v_2) - v_2 - \chi v_2^2\} \qquad (8)$$

In the present study, the average molecular weight between crosslinks M_c has been estimated from both mechanical and swelling data[9–12] using the classical relationships (3), (4), (7) and (8) together with the new proposed relation (6). The analysis focused on the mechanical response of natural rubbers and their swelling behaviour in benzene since the polymer–solvent interaction parameter χ is a constant independent of polymer concentration for the natural rubber–benzene system. Our aim is to correlate the values of M_c determined from mechanical measurements $(M_c(2C_1), M_c(2C_1 + 2C_2)$ and $M_c(G_e))$ with those determined from swelling experiments $M_c(S1)$ and $M_c(S2)$.

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DATA ANALYSIS

As already mentioned in the introduction, most of the stress–strain data in simple extension can be described by the Mooney–Rivlin equation. It is interesting to note that the same data can also be described by equation (5).

In *Figure 1*, experimental results of Smith *et al.*[12] for natural rubber NN-6 have been plotted according to the Mooney–Rivlin equation. Here the values of the true stress have been calculated from the nominal stress τ (available in Table 3 of Reference 12) according to $\sigma = \lambda \times \tau$. In *Figure 2*, the true stress σ has been plotted as a function of $\lambda^2 - 1/\lambda$. The open squares represent the same data as in *Figure 1*; the filled symbols correspond to the true stress calculated according to equation (3), using the Mooney–Rivlin constants $2C_1$ and $2C_2$ given in *Table 1*. Obviously, one obtains a series of straight lines which allow us to determine the values of the two parameters σ_0 and G_e. The same analysis has also been made on experimental data of Bristow[9], Ciferri and Flory[10] and Gumbrell *et al.*[11]. The values of σ_0 and G_e obtained in this way, as well as the values of $2C_1$, $2C_2$ and v_2 (in benzene), for all the samples analysed are listed in *Table 1*.

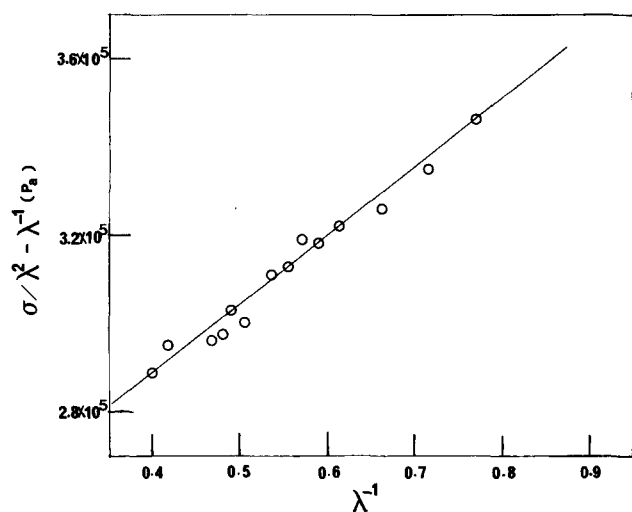Since the values of $2C_1$, $2C_2$, G_e and v_2 are known,

the average molecular weight between crosslinks can be estimated from mechanical characterization through equations (3), (4) and (6), and from swelling degree at equilibrium through equations (7) and (8). In this study, the prefactor A_ϕ in equations (3), (4) and (6) and in equations (7) and (8) was assumed to be equal to 1.

In *Figure 3*, $\log M_c(S1)$ (filled symbols) and $\log M_c(S2)$ (open symbols) have been plotted as a function of $\log M_c(G_e)$. It can be seen clearly that a satisfactory agreement between $M_c(S1)$ (filled symbols) and $M_c(G_e)$ is obtained. However, when we compare $M_c(2C_1 + 2C_2)$ and $M_c(2C_1)$ with $M_c(S1)$ and $M_c(S2)$, as known classically, $M_c(2C_1 + 2C_2)$ is too small and $M_c(2C_1)$ is too high with respect to M_c estimated from swelling measurements.
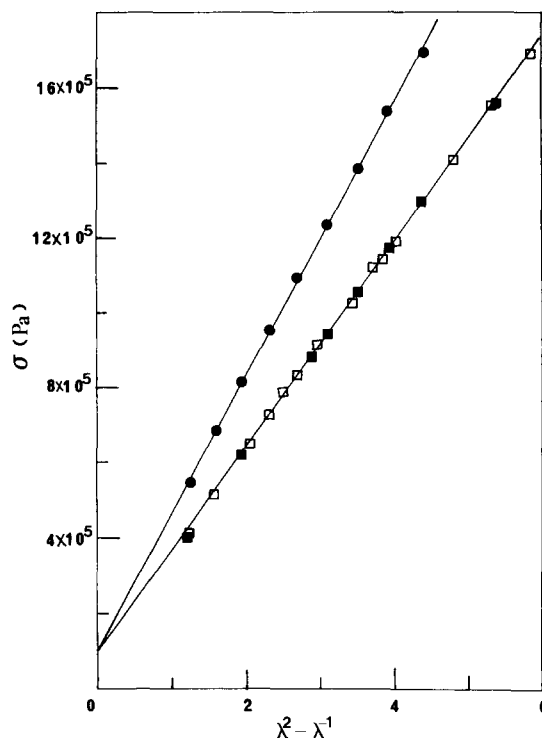

Figure 1 Ratio of true stress to the strain function $\sigma/(\lambda^2 - 1/\lambda)$ *versus* $1/\lambda$ for natural rubber[12]

Figure 2 True stress σ as a function of $(\lambda^2 - 1/\lambda)$ for natural rubbers: $\square$, calculated according to $\sigma = \lambda \times \tau$; $\blacksquare$, $\bullet$, calculated according to the Mooney–Rivlin equation using $2C_1$ and $2C_1$[12]

Table 1 Numerical values of $2C_1$, $2C_2$, σ_0, G_e and v_2 for natural rubbers

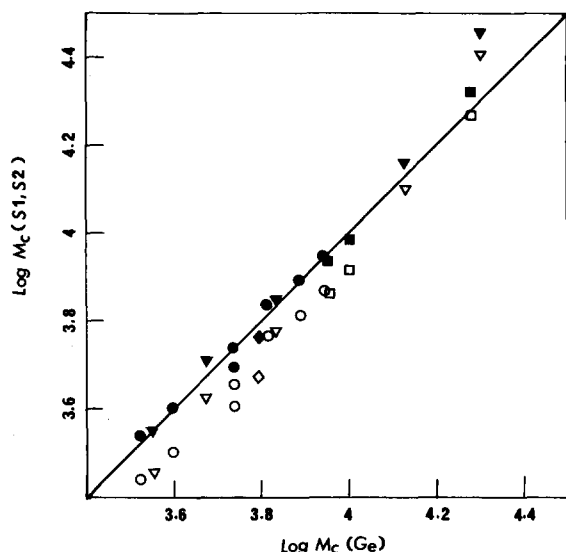| Samples	Temperature (°C)	v_2 in benzene	$2C_1$ (10^5 Pa)	$2C_2$ (10^5 Pa)	σ_0 (10^5 Pa)	G_e (10^5 Pa)
Natural rubber[9]	25	0.1021	0.76	1.28	1.0	1.13
		0.1426	1.29	1.45	1.0	1.71
		0.1993	2.86	1.59	0.9	3.36
		0.2309	4.15	1.72	0.9	4.84
Cis-polyisoprene[9]		0.2700	6.27	1.49	0.9	6.80
NR-1[10]	34	0.119	0.88	1.39	1.0	1.24
NR-3[10]		0.173	1.88	1.57	1.0	2.35
NR-6[10]		0.183	1.96	1.96	1.0	2.61
A[11]	25	0.192	2.29	1.96	1.0	2.96
B[11]		0.181	1.96	1.96	1.0	2.61
C[11]		0.202	2.81	2.02	1.0	3.52
D[11]		0.235	3.39	2.06	1.0	4.16
E[11]		0.223	3.43	2.06	1.0	4.18
F[11]		0.257	4.99	2.04	0.9	5.76
G[11]		0.272	6.04	2.00	0.9	6.86
NN-6[12]	50		2.26	1.60	1.0	2.72
N-6[12]	30	0.22	2.85	2.25	1.0	3.68

Figure 3 Log $M_c(S1)$ (filled symbols) and log $M_c(S2)$ (open symbols) as a function of log $M_c(G_e)$ for natural rubbers. ▼, ▽, Reference 9; ■, □, Reference 10; ●, ○, Reference 11; ◆, ◇, Reference 12

DISCUSSION AND CONCLUSIONS

Starting from the classical kinetic theory of rubber elasticity and the lattice model of dilute polymer solution, good agreement is found between the average molecular weight between crosslinks estimated from mechanical characterization (through equations (5) and (6)) and that determined from swelling degree at equilibrium (through equation (7)). As already seen, the kinetic theory neglects a contribution represented by σ_0 and is therefore inadequate to describe the mechanical properties of rubbers. However, the modulus G_e defined by equation (5) seems to be identical to the neo-Hookean modulus G_n predicted by the kinetic theory. Concerning the use of the Flory–Huggins theory of dilute polymer solution, we are aware of the criticism that the theory is inadequate to account for solution properties since the interaction parameter χ depends on concentration for most polymer–solvent systems[2,13]. Here, we use it as a simple tool to estimate the variation of free energy due to mixture. Furthermore, we note that the parameter χ is almost independent of

composition for natural rubber–benzene systems in the concentration range analysed $(0.1 < v_2 < 0.3)$[14,15].

In summary, a large amount of experimental data obtained by different authors has been reanalysed. Good agreement was found between the elastic modulus estimated from swelling degree at equilibrium $(M_c(S1))$ and the value G_e obtained from rheological measurements through equation (5). This result seems to support the assumption that the tensile force is the sum of a conformational entropy contribution represented by $G_e(\lambda^2 - 1/\lambda)$ and a further contribution indicated by σ_0. Further studies on the physical meaning of the parameter σ_0 and the zero shear modulus are currently underway.

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15 See, for example, Eichinger, B. E. and Flory, P. J. *Trans. Faraday Soc.* 1968, **64**, 2035, Figure 3