Experimental tests of entanglement models of rubber elasticity: 1. Uniaxial extension-compression

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The predictions of several entanglement models of rubber elasticity for the uniaxial stress–strain response of crosslinked polymer networks are examined. It is found that the Gaylord tube model and the Flory constrained junction fluctuation model both agree well with the experimental data.

Keywords Rubber elasticity; polymer networks; tube model; uniaxial stress–strain; junction fluctuation model

INTRODUCTION

A number of theoretical models have recently been proposed to account for entanglement effects in crosslinked polymer networks. These models can be grouped into four types of approaches (see the original papers for specific model details): tube models[1–7] in which each network chain is confined within a tube; sliplink models[8,9] in which each network chain threads its way through a number of small rings; primitive path models[4,9] in which the chain segments lie either along the shortest path between chain ends that does not violate topological restrictions or in loops from the path, and constrained junction fluctuation models[10,11] in which each network junction is subjected to a domain of constraint.

There are several criteria to be considered in choosing between these theoretical approaches, including: the reasonableness of the underlying physical concepts (e.g., are entanglements discrete and specific, do entanglements act exclusively on junctions, can chain segments be divided into distinct categories); the simplicity and ease of usage of the mathematical expressions; the degree of organic unity, and; the agreement between the theoretical predictions and the experimental data. It is this latter test to which we will turn our attention herein.

COMPARISON TO DATA

To test the ability of the different models to describe the stress response of real networks to uniaxial strain, two sets of experimental data were chosen: (1) Rivlin and Saunders' data[12] for natural rubber vulcanized with sulphur; (2) data obtained by Pak and Flory[13] for poly(dimethyl siloxane) crosslinked by 3% dicumyl peroxide. These particular sets were chosen because of their relatively large range of strain, a feature rarely encountered in most works. In both cases, compression data were obtained by inflation of a sheet and extension data were measured on a strip cut out from the same sheet used in the compression experiment. We note that despite the careful experimental procedure followed in both studies, there is a large amount of scatter in the data. In addition, the measurements on the natural rubber samples may have resulted in overestimated reduced stress values at both extremities of the strain range as a result of stress induced crystallization and the measurements on the PDMS samples showed hysteresis effects, possibly due to stress relaxation.

The predictions of the Edwards[4] (E), Marrucci[6] (M), and Gaylord[7] (G) tube models, the Doi–Edwards–Marrucci–Graessley[8,9] (D) sliplink model and the Flory[11] (F) constrained junction fluctuation model were compared to these two sets of data.

The functional forms of the reduced stress expressions of the models are given in *Table 1*. Of the five models, three (M, G, D) are two parameter models, but two (E, F) are three parameter models which require information on the network structure in order to estimate *a priori* the value of one of the parameters. For all five models, the least-sum-of-squares criterion was used to determine the values of the *two* parameters which best fitted the data. In addition to this data fitting procedure two other schemes were tried: (1) The curves were forced to pass through the experimental small-strain modulus value ($[f^*]_{\lambda=1}$), by proper selection of one parameter, thereby leaving only one adjustable parameter to be fitted by the data. (2) Both parameters were determined by 'best-fitting' the model in extension only. The relative agreement of the models with the data were not altered by the different schemes used and the qualitative results discussed below are independent of the way the data are handled.

RESULTS AND DISCUSSION

The best-fit model parameters obtained for the two sets of

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Table 1 Functional forms used to fit data

Model	Ref.	Reduced stress $[f^*]$	Fitted parameters	Max $[f^*]$
Edwards[a]	4	$\mu RT\left[\frac{2}{3}+\frac{\beta}{3J}+\frac{(1-\alpha)}{3(1-\alpha J)}+\frac{\alpha J(1-\alpha)}{6(1-\alpha J)^2}-\frac{\alpha}{6J(1-\alpha J)}\right]$	α, β	$\lambda = 1$
Marrucci	6	$a + b/J$	a, b	$\lambda = 1$
Gaylord	7	$a + b\left(\frac{1-\lambda^{-3/2}}{\lambda-\lambda^{-2}}\right)$	a, b	$\lambda^{-1} = 1.587$
Doi–Edwards–Marrucci–Graessley	8,9	$a + b\left\{\langle\lvert \underline{E}\cdot\underline{u}\rvert\rangle\left[\frac{\partial}{\partial\lambda}(\langle\lvert\underline{E}\cdot\underline{u}\rvert\rangle)\right](\lambda-\lambda^{-2})^{-1}\right\}$ where $\langle\lvert\underline{E}\cdot\underline{u}\rvert\rangle = \frac{1}{2}\int_0^{\pi}[\lambda^2\cos^2\theta+\lambda^{-1}\sin^2\theta]^{1/2}\sin\theta\, d\theta$	a, b	—
Flory[b]	11	$[f^*_{ph}]\ \{1 + [\lambda K(\lambda) - \lambda^{-2}K(\lambda^{-1/2})]\ (\lambda-\lambda^{-2})^{-1}\}$ where $K(\lambda_t) = \frac{B}{(1+B)}\frac{\partial B}{\partial(\lambda_t^2)} + \frac{Bg}{(1+Bg)}\frac{\partial(Bg)}{\partial(\lambda_t^2)}$; $g = \lambda_t^2[\kappa^{-1}+\zeta(\lambda_t-1)]$; $B = (\lambda_t-1)[1+\lambda_t-\zeta\lambda_t^2]\ (1+g)^{-2}$	κ, ζ	$\lambda^{-1} > 1$

[a] $J = \left(\frac{\lambda^2+2\lambda^{-1}}{3}\right)^{1/2}$; μRT was estimated from network data

[b] $[f^*_{ph}]$ was estimated from network data; network assumed to be perfect and tetrafunctional

Table 2 Regression results for tested models

		PDMS		Natural rubber	
		parameter value	correlation coefficient	parameter value	correlation coefficient
Edwards	α	0.05	0.67	0.1	0.49
	β	2.96		2.0	
	μRT†	0.55		1.05	
Marrucci	a†	0.604	0.67	1.175	0.51
	b†	0.473		0.573	
Gaylord	a†	0.356	0.97	0.681	0.90
	b†	1.430		2.165	
Doi–Edwards–	a†	0.094	0.57	−0.251	0.69
Marrucci–Graessley	b†	3.084		6.848	
Flory	κ	10	*	12	*
	ζ	0.0		0.0	
	$[f^*_{ph}]$†	0.65		1.05	

† Value given in Pa x 10^{-5}

*No correlation coefficient was calculated because regression routine was used to fit the data

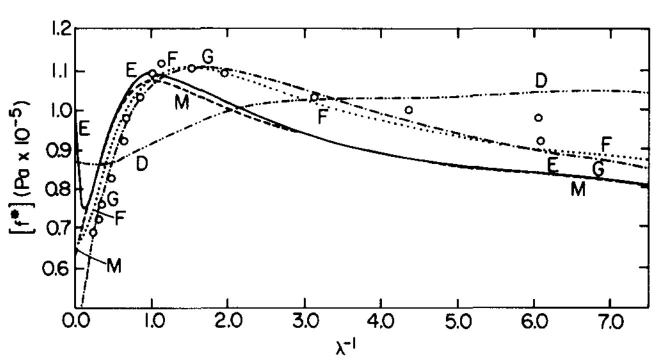

Figure 1 Reduced force dependence on strain in uniaxial extention–compression for PDMS chemically cross-linked with 3% dicumyl peroxide (Pak and Flory[13]). The theoretical curves are indicated by: (———) Edwards[4], (– – –) Marrucci[6], (–·–·–) Gaylord[7], (–··–··–) Doi–Edwards–Marrucci–Graessley[8,9], (.....) Flory[11]

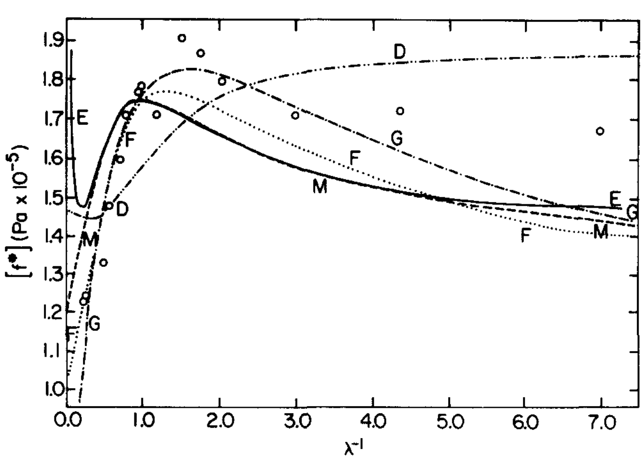

Figure 2 Uniaxial extension–compression for natural rubber vulcanized with sulphur (Rivlin and Saunders[12]). Curve legends are the same as in *Figure 1*

experimental data are listed in *Table 2* along with the regression correlation coefficients. No attempt was made to evaluate the physical soundness of these parameters. The results are also depicted in *Figures 1* (PDMS) and *2* (natural rubber).

The most striking features emerging from the Figures are the complete failure of the sliplink model (D) and the relatively little difference between the tube and junction fluctuation suppression models (E, M, G, F) over a very large portion of the strain range covered. The inability of the sliplink model to match the data here agrees with previous findings[8,9]. The close match between the Edwards and Marrucci tube models is expected since the reduced stress expression of the Marrucci model is the same as the reduced stress expression of the $\alpha = 0$ form of the Edwards model (cf. *Table 1*) and the regression analysis best fits the Edwards model for small α values (cf. *Table 2*). It is only at large extension ratios ($J > 1/\alpha$), representing the depletion of the surplus segment population in the Edwards model, that the difference between the E and M models is observable.

Three models (M, F, G) fit the extension data very well. However, this is not surprising since any two-parameter model is expected to fit the data in this range at least as well as the Mooney–Rivlin expression and therefore the use of extension data alone as a test for molecular theories is meaningless. Unfortunately the literature abounds with comparisons of this sort.

When the entire strain range is considered, the Gaylord tube model is somewhat better than the other two tube models in fitting the data.

The close agreement between the Gaylord and Flory models, well below experimental uncertainty, is quite surprising in view of the vast differences in the physical models used and the mathematical expressions obtained (cf. *Table 1*).

Finally, both sets of data indicate that $[f^*]$ reaches a maximum somewhere in the vicinity of $\lambda^{-1} = 1.4$ and definitely at $\lambda^{-1} > 1$. While there is no maximum in $[f^*]$ for the D model, a maximum does occur at $\lambda^{-1} = 1$ for the E and M models, at λ^{-1} between 1.3 and 1.5 for the F model and at $\lambda^{-1} = 1.587$ for the G model. Again, only the Flory and Gaylord models are in agreement with experiment.

To summarize, it has been shown that data covering a large range of strain, including both extension and compression, must be employed for the evaluation of network elasticity models. The Doi–Edwards–Marrucci–Graessley sliplink model does not accurately describe network elastic behaviour. Both the Gaylord tube model and the Flory constrained junction fluctuation model fit the stress–strain data well over the entire strain range as well as predict the correct position of the maximum in the reduced stress. The predictions of the two models are, in fact, practically indistinguishable. This may indicate that the stress–strain response of real networks is not sensitive to the exact mechanism by which topological constraints are imposed on networks, whether by restriction of junction motion (Flory) or by chain–chain interaction (Gaylord). Alternatively, it may indicate that uniaxial strain experiments are just not sensitive enough to distinguish between the models and that other modes of strain (e.g., biaxial, torsion), or solvent effects need to be studied in order to fully test the molecular models. This will be undertaken in a future publication.

REFERENCES

1 Edwards, S. F. *Proc. Phys. Soc.*, 1967, **92**, 9
2 DiMarzio, E. A., *ACS Polym. Prepr.*, 1968, **9(1)**, 256
3 deGennes, P. G., *J. Phys. Lett.*, 1974, **35**, L-133
4 (a) Edwards, S. F. *Br. Polym. J.*, 1977, **9**, 140;
(b) Edwards, S. F., personal communication
5 Gaylord, R. J. *Polym. Eng. Sci.* 1979, **19**, 263
6 Marrucci, G. *Macromolecules* 1981, **14**, 434
7 (a) Gaylord, R. J., *Polym. Bul.* 1982, **8**, 325;
(b) Gaylord, R. J., *Polym. Bull.* 1983, **9**, 181
8 Marrucci, G. *Rheol. Acta* 1979, **18**, 193
9 (a) Graessley, W. W. *ACS Polym. Prepr.* 1981, **22(2)**, 152;
(b) Graessley, W. W. *Adv. Polym. Sci.* 1982, **46**, 67
10 Ronca, G. and Allegra, G. *J. Chem. Phys.* 1975, **63**, 4990
11 (a) Flory, P. J. *J. Chem. Phys.* 1977, **66**, 5720;
(b) Erman, B and Flory, P. J. *J. Chem. Phys.* 1978, **68**, 5363;
(c) Flory, P. J. and Erman, B. *Macromolecules* 1982, **15**, 800
12 Rivlin, R. S. and Saunders, D. W. *Phil. Trans. Royal Soc. London, Ser. A*, 1951, **243**, 251
13 Pak, H. and Flory, P. J. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1845