Relaxation of crosslinked networks: theoretical models and apparent power law behaviour

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The viscoelastic behaviour of crosslinked polymer networks is discussed. Models of the long time relaxation based on the retracing of dangling chains are described. It is pointed out that the theories all predict a power law time relation for the relaxation behaviour but differ in their predictions of the crosslink density dependence of the power law exponent. The experimental data of Chasset and Thirion are examined. It is shown that the power law relation works only over a limited time span, with deviations occurring at long times and more markedly for more highly crosslinked systems. Furthermore, the validity of time–crosslink density superposition for networks is confirmed, thereby precluding an exponent dependent on crosslink density in any power law representation of the data.

(Keywords: crosslinking; networks; viscoelasticity)

INTRODUCTION

In recent years there has been renewed interest in the relaxation behaviour of crosslinked polymer networks in the terminal region. In particular, several models[1–6] have been proposed based on the assumption that the long time relaxation is due to 'dangling' chains that are attached to the network at only one end. The theories all predict that the long time relaxation follows a power law in time but differ in their predictions of the crosslink density dependence of the power law exponent. These models are described in the next section.

The experimental data generally cited in support of a power law relaxation are taken from studies by Chasset and Thirion[7–11] on dicumyl peroxide crosslinked natural rubber, which has been analysed by Dickie and Ferry[12] using a power law with an exponent dependent on crosslink density. However, Chasset and Thirion, who also suggest power law behaviour, note that a power law representation of their data is valid over only a limited time scale. Moreover, they use a time–crosslink density correspondence principle to reduce their data, which is supported by Plazek[13] and Arenz[14], and such a time–crosslink density reduction is incompatible with a power law having an exponent dependent on crosslink density. In view of this apparent conflict, it is desirable to re-examine in some detail both the ability of the power law to describe the relaxation data and the validity of a time–crosslink density superposition of the data. This is done below.

THEORIES

deGennes[1] has proposed that the viscoelastic relaxation of an entangled dangling chain in a crosslinked polymer network occurs by a 'retracing' mechanism in which the unattached chain end diffuses towards the chain end which is attached to the network. This process, which is illustrated in *Figure 1*, is accompanied by the creation of an unentangled loop. By calculating the form of the probability of an unentangled loop of N segments to be $P_L(N) \sim \exp\{-\alpha N\}$ and assuming that the time needed to form this loop T_L is inversely proportional to $P_L(N)$, deGennes obtained the result that $N \sim \alpha^{-1} \ln T_L$. He then estimated $l(t)$, the number of segments in the unentangled loop that has formed at time t during retracing, by replacing N and T_L with l and t respectively, so that $l(t) \sim \alpha^{-1} \ln t$. Finally, deGennes assumed that the stress contribution of a dangling chain of N segments is proportional to the number of segments that have *not*

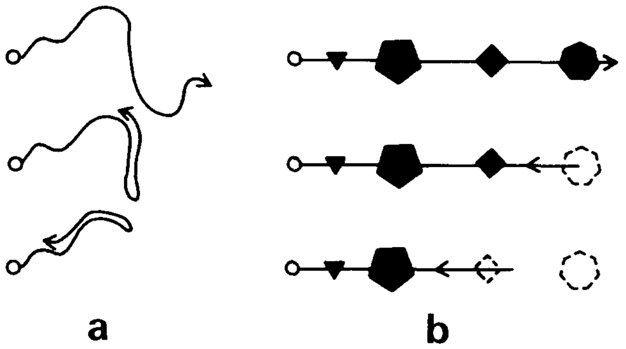

Figure 1 The retracing mechanism of dangling chain relaxation: (a) the unentangled loop formation which accompanies retracing and is the focus of some theoretical treatments[1–4]; (b) the various discrete entanglements occurring along the chain contour, which become successively disentangled during retracing and are the focus of one of the theoretical models[6]

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been retraced, so

$$\sigma(t)_{\mathrm{dG}} \sim N - l(t) \tag{1}$$

Curro and Pincus[2] append to the deGennes model the distribution of dangling chain lengths in a *randomly crosslinked* network, so that

$$\begin{aligned}\sigma(t)_{\mathrm{CP}} &\sim \sum_{N=l}^{\infty} [N - l(t)]\,W(N) \\ &\sim \int_{l}^{\infty} (N-l)W(N)\mathrm{d}N \\ &\sim \exp[-ql(t)]\end{aligned} \tag{2}$$

where $W(N) \sim q(1-q)^{N-1} \approx qe^{-qN}$ is the probability of having an N-segment dangling chain and q is the probability of a segment being crosslinked, which is obviously given by the ratio of crosslink density to segment density, ν/ρ. Using the deGennes $l(t)$ relation, they get

$$\begin{aligned}\sigma(t)_{\mathrm{CP}} &\sim \exp[-q(\ln t)/\alpha] \\ &\sim \exp[\ln(t^{-q/\alpha})] \\ &\sim t^{-a\nu}\end{aligned} \tag{3}$$

where $a = (\alpha\rho)^{-1}$. An alternative definition of a in the CP model has also been given by Curro *et al.*[3] as $a = N_e(\alpha\rho)^{-1}$, where N_e is the average number of monomer units between entanglements and is taken to be independent of crosslink density.

Thirion and Monnerie[4] have recently modified the deGennes–Curro–Pincus analysis. Using the unentangled loop probability function calculated by Helfand and Pearson[5], Thirion and Monnerie follow the deGennes analysis[1] and obtain $t \sim (l/N_e)^{3/2}\exp\{\beta l/N_e\}$, where $\beta = \frac{1}{2}\ln[z^2/4(z-1)]$ and z is the lattice coordination number. Then, carrying out the Curro–Pincus polydispersity calculation[2], they obtain equation (3), with $a = N_e/\beta$. They also assume that $N_e \sim d^2$ and $d \sim \nu^{-1/3}$, where d is the spatial distance between crosslinks so that $N_e \sim \nu^{-2/3}$ and equation (3) becomes

$$\sigma(t)_{\mathrm{TM}} \sim t^{-b\nu^{1/3}} \tag{4}$$

where $b = \beta^{-1}$.

Rather than using the equilibrium configurational statistics of an unentangled loop to estimate the kinetics of retracing, a more direct treatment of the movement of the free chain end towards the fixed chain end during retracing would be preferable. This has been done in terms of a diffusion process by Curro *et al.*[3] and in terms of a random walk process by Gaylord *et al.*[6]

Curro *et al.*[3] have calculated

$$\sigma(t)_{\mathrm{CPH}} \sim \int_{0}^{\infty} Nf(t)W(N)\mathrm{d}N \tag{5}$$

where $f(t)$ is the average fraction of a dangling chain that contributes to stress by virtue of having *never* been visited by the free chain end and is given by

$$f(t) \sim \int_{x_e}^{L_{eq}} \left(1 - \frac{y}{L_{eq}}\right) g(y,t)\mathrm{d}y \tag{6}$$

where $g(y,t)$ is the probability density for the penetration to y (and no further) of a one-dimensional diffusion process in a quadratic potential field, L_{eq} is the equilibrium contour length of the dangling chain and x_e is the root-mean-square tube fluctuation about L_{eq}. In their model, the free end moves along the primitive path of the chain (or along the axis of the tube surrounding the chain), pushing out unentangled loops and resulting in a decrease in entropy, which is viewed as creating the potential in which the free end is diffusing. The resulting $f(t)$ expression is complex, requiring a numerical evaluation of equation (5), but by using approximate forms of $f(t)$ in equation (5), they obtain

$$\sigma(t)_{\mathrm{CPH}} \sim t^{-\gamma\nu} \tag{7}$$

where $\gamma = N_e/(\rho\beta)$ and N_e is taken to be independent of crosslink density.

Gaylord *et al.* calculate

$$f(t) \sim \int_{0}^{N} \left(1 - \frac{y}{N}\right) q(y,t)\mathrm{d}y \tag{8}$$

where $q(y,t)$ is the probability density for the maximum displacement of a one-dimensional continuous-time random walk with a pausing-time distribution of the form $\psi(t) \sim t^{-1-\delta}$. The physics of this model is depicted in *Figure 1*. The retracing is viewed as a fractal time process which occurs by the movement of the free chain end along the chain contour, accompanied by the successive dissolution of *discrete* entanglements at various locations along the chain. Each disentanglement is an irreversible barrier passage event and $\psi(t)$ represents the distribution of barrier heights due to the differing natures of the various entanglements. The quantity δ lies between 0 and 1 (δ is expected to be independent of crosslink density, swelling and, perhaps, temperature). The resulting expression is

$$f(t) \sim \frac{N^2 t^{-\delta}}{\Gamma(1-\delta)} \tag{9}$$

Calculating

$$\sigma(t)_{\mathrm{GWD}} \sim \int_{0}^{\infty} f(t)W(N)\mathrm{d}N \tag{10}$$

they obtain

$$\sigma(t)_{\mathrm{GWD}} \sim t^{-\delta} \tag{11}$$

Equations (3), (4), (7) and (11) all have the same power law form, t^{-m}. However, they differ in several ways. Equations (3), (4) and (7) are a result of assuming a

Table 1 Crosslink density and estimate of equilibrium modulus, $E_\infty = 1/J_\infty$, for the relaxation data of Chasset and Thirion[9] and the creep data of Dickie and Ferry[12] on samples of natural rubber crosslinked using dicumyl peroxide (as reported by Dickie and Ferry[12])

Sample	Crosslink density, ν (mol cm^{-3})	$E_\infty/3$ (dyn cm^{-2}) Dickie and Ferry[12]	Chasset and Thirion[9]	Ratio D–F:C–T
F	4.6×10^{-5}	1.91×10^{6}	1.95×10^{6}	0.98
G	6.2×10^{-5}	2.24×10^{6}	2.57×10^{6}	0.87
H	8.0×10^{-5}	2.63×10^{6}	3.24×10^{6}	0.81
I	1.20×10^{-4}	3.72×10^{6}	4.47×10^{6}	0.83
J	1.69×10^{-4}	4.79×10^{6}	5.62×10^{6}	0.85

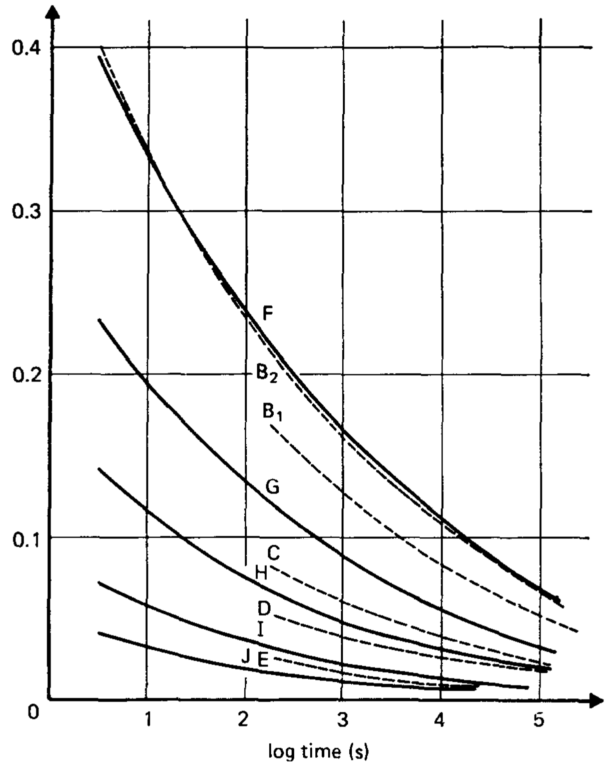

Figure 2 Transient response $r(t) = E(t)/E_\infty - 1$ *versus* log time as reported by Thirion and Chasset[9] for natural rubber and SBR crosslinked with dicumyl peroxide; $T = 30°C$

polydispersity of dangling chain lengths due to randomly crosslinking the network; different types of polydispersity will result in other forms. Equation (11) always has a power law form, irrespective of the distribution of dangling chain lengths. Additionally, the power law exponents in equations (3), (4) and (7) are functions of the crosslink density, while the exponent in equation (11) is not explicitly related to crosslink density.

ANALYSIS OF THE RELAXATION DATA

The data of Chasset and Thirion

Chasset and Thirion[7–11] carried out stress relaxation experiments in uniaxial extension on natural rubber crosslinked with dicumyl peroxide. The crosslink density was changed by varying the time of cure of networks containing 3.5% dicumyl peroxide. The tests were performed at 30°C and an elongation of $\lambda = 1.5$. They report relaxation data from approximately 3 to 1.6×10^5 s. Crosslink densities were determined by swelling in benzene. Their sample designations and crosslink densities are shown in *Table 1*.

Chasset and Thirion treated their data as follows: they first assumed that the relaxation response can be expressed as the product of a time dependent term and a strain dependent term. Also, because the system is a network they assumed that there exists an equilibrium response E_∞. The relaxation modulus $E(t)$ can be expressed as:

$$E(t) = E_\infty[1 + r(t)] \qquad (12)$$

where $r(t)$ is the transient term. Chasset and Thirion reported values for $r(t) = \{[E(t)/E_\infty] - 1\}$ *versus* $\log t$. Their results for natural rubber and styrene-butadiene rubber (SBR) are reproduced in *Figure 2*. They observed that a possible representation for $r(t)$ was a power law in time. Then equation (12) can be rewritten as

$$E(t) = E_\infty[1 + (t/t_0)^{-m}] \qquad (13)$$

However, Chasset and Thirion[7–11] specifically note[8,9] that 'deviations [from the power law behaviour] are often observed at long times'. This is clearly seen in the Chasset and Thirion[8,9] curves of the first derivative approximations to the spectrum $h_1(\tau)$ associated with the transient term $r(t)$, which are shown in *Figure 3*. If the behaviour of $r(t)$ were truly a power law in time, then $\log(h_1) \simeq \log[\mathrm{d}r(t)/d \log t]$ *versus* $\log t$ would follow a straight line of slope $-m$ for each set of data. While this is approximately true over several decades of time, the deviations from linearity at long times are quite apparent and are more pronounced for the more highly crosslinked networks. On the other hand, Dickie and Ferry[12] report values of m for a power law behaviour of the data of Chasset and Thirion for samples F, G and H as well as for several systems of their own. Because of these two apparently contradictory conclusions, we will examine the data treatments used by Chasset and Thirion and by Dickie and Ferry. We will also reanalyse the data for the natural rubber networks ourselves.

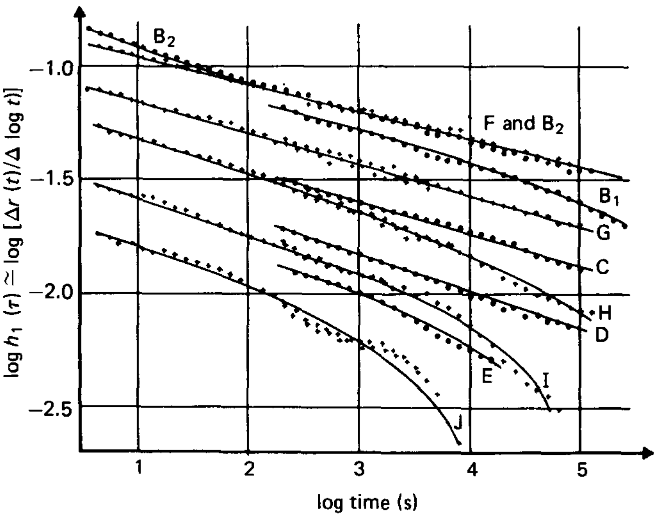

Figure 3 Double logarithmic representation of the first derivative approximation to the relaxation spectrum *versus* time for natural rubber and SBR crosslinked with dicumyl peroxide (after Thirion and Chasset[9]); $T = 30°C$

Table 2 Results from nonlinear least squares regression analysis[15] on stress relaxation data of Thirion and Chasset[9] for dicumyl peroxide crosslinked natural rubber

	Parameters				
	Regression 1[a]		Regression 2[b]		
Sample	m	t_0 (s)	m	t_0 (s)	$\hat{E}_\infty$
F	$0.157 \pm 1.3 \times 10^{-2}$	$9.44 \times 10^{-3} \pm 6.6 \times 10^{-4}$	$0.119 \pm 6.3 \times 10^{-4}$	$7.13 \times 10^{-3} \pm 6.7 \times 10^{-5}$	$0.937 \pm 1.3 \times 10^{-3}$
G	$0.173 \pm 1.6 \times 10^{-3}$	$7.41 \times 10^{-4} \pm 7.2 \times 10^{-5}$	$0.132 \pm 1.0 \times 10^{-3}$	$1.89 \times 10^{-2} \pm 8.0 \times 10^{-6}$	$0.964 \pm 1.2 \times 10^{-3}$
H	$0.189 \pm 4.3 \times 10^{-4}$	$1.05 \times 10^{-4} \pm 2.9 \times 10^{-6}$	$0.185 \pm 1.4 \times 10^{-3}$	$8.91 \times 10^{-5} \pm 5.9 \times 10^{-6}$	$0.999 \pm 4.8 \times 10^{-4}$
I	$0.205 \pm 1.19 \times 10^{-3}$	$8.70 \times 10^{-6} \pm 7.4 \times 10^{-7}$	$0.179 \pm 1.5 \times 10^{-3}$	$1.92 \times 10^{-6} \pm 2.0 \times 10^{-7}$	$0.995 \pm 2.9 \times 10^{-4}$
J	$0.220 \pm 9.7 \times 10^{-4}$	$1.69 \times 10^{-6} \pm 1.2 \times 10^{-7}$	$0.230 \pm 3.3 \times 10^{-3}$	$1.02 \times 10^{-5} \pm 5.4 \times 10^{-7}$	$1.001 \pm 2.5 \times 10^{-3}$

[a] $1+r(t)=1+(t/t_0)^{-m}$

[b] $1+r(t)=E_\infty[1+(t/t_0)^{-m}]$

The power law interpretation

The major difficulty involved in determining the actual transient response of a crosslinked system is the estimation of the value of E_∞. From equation (12) we can see that as $r(t)$ approaches zero (or $E(t)/E_\infty$ approaches unity) a small error in E_∞ can lead to a large error in $r(t)$. Dickie and Ferry[12] actually treat E_∞ as a floating parameter to force the data to fit a power law of the form of equation (1). And, in fact, their estimates of E_∞ for the Chasset–Thirion data differ significantly from those reported by Chasset and Thirion. The differences can be seen in *Table 1* by comparing the values of modulus (as $E_\infty = 3/J_\infty$) reported by Dickie and Ferry[12] from creep with those of Chasset and Thirion from stress relaxation.

We now turn to the question of the magnitude of the power law exponent m as a function of crosslink density. If we assume that $r(t)=(t/t_0)^{-m}$, we can carry out nonlinear least squares fits to the Chasset and Thirion data to obtain m. We have done the analysis on data obtained by digitizing the curves for the natural rubber samples F to J on a photographic enlargement of the Thirion–Chasset published version of *Figure 2*. We examine two approaches: first, the Chasset and Thirion estimate of E_∞ is used. Second, the value of E_∞ is allowed to 'float' in the regression analysis. The values of m obtained by both methods are shown in *Table 2*. Also shown are the values of the normalized equilibrium modulus $\hat{E}_\infty$ obtained for fits of the second type. The trend of m with crosslink density is shown in *Figure 4*. There are three important things to note in *Table 2* and *Figure 4*. First, the value of m obtained from the curve fitting procedure is very sensitive to the value of E_∞, e.g. for a 4% change in E_∞ ($\hat{E}_\infty = 0.964$) for sample G, m changes by 30%. Second, the accuracy of the determination of crosslink density, $v=\rho/M_c$, based on swelling measurements by Thirion and Chasset is itself uncertain. Third, unlike the representation of m *versus* v given by Curro and Pincus (who only consider data for the three lowest crosslink density samples F, G and H), m is either not a linear function of v and/or has an extrapolated non-zero value at zero crosslink density (see *Figure 4*). Finally, we note that the values of m obtained from this analysis of the Chasset and Thirion data are greater than those obtained by Dickie and Ferry. We can obtain values similar to theirs by using specific values of $\hat{E}_\infty$ corresponding to the differences between the E_∞ values of Dickie and Ferry and those of Chasset and Thirion shown in *Table 2*.

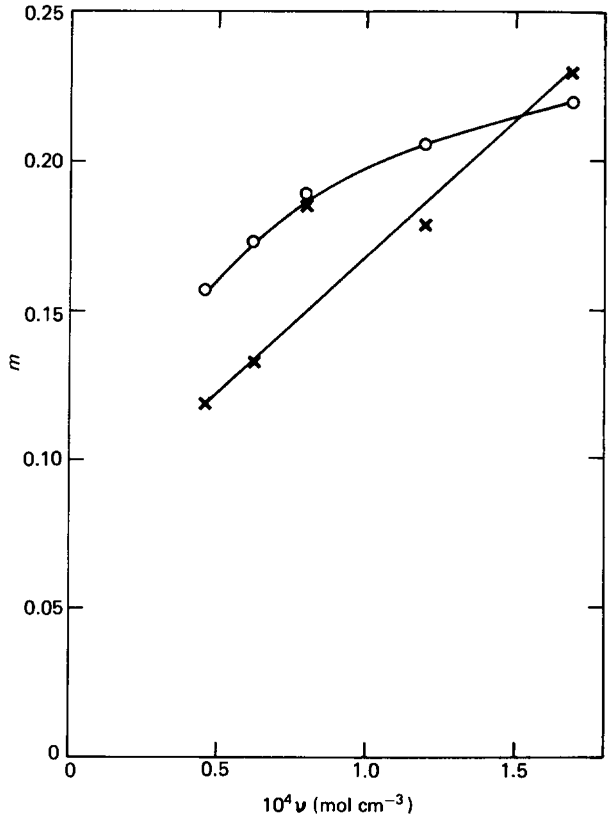

Figure 4 Power law exponent m *versus* crosslink density for data of Chasset and Thirion[9] reanalysed as described in text: ○, assuming $1+r(t)=1+(t/t_0)^{-m}$; ×, assuming $1+r(t)=\hat{E}_\infty[1+(t/t_0)^{-m}]$

Time–crosslink density superposition

Thirion and Chasset[8,9,11] remarked that the curves for $r(t)$ at different crosslink densities could be superimposed onto a single reduced curve by a simple shift along the time axis. Such a time–crosslink density correspondence principle was also found by Arenz[14] and by Plazek[13] for crosslinked rubbers. If a time–crosslink density superposition principle is valid for networks, there are two important observations to be made. First, the shape of the relaxation spectrum (function) will be independent of crosslink density, only shifting along the time axis when crosslink density changes. Thus equation (12) can be rewritten as:

$$E(t/a_v)=E_\infty(v)[1+r(t/a_v)] \tag{14}$$

Table 3 Parameters used to perform time–crosslink density superposition of Thirion and Chasset[9] relaxation data for dicumyl peroxide crosslinked natural rubber

Sample	Δr_v	$\log a_v$
F	0	0
G	-0.0073	-1.672
H	-0.0105	-3.116
I	-0.0064	-4.580
J	-0.0068	-5.800

where v is the crosslink density and a_v is the crosslink density shift factor. Second, if the relaxation function is a power law in time, then time–crosslink density correspondence requires that m be independent of crosslink density (which agrees with the more or less parallel nature of the linear portions of the curves in *Figure 3*). A power law representation of data from isothermal experiments on differently crosslinked networks may, however, give an apparent dependence of m on v, which, moreover, would then depend on temperature.

We can now demonstrate the time–crosslink density superposition of the Chasset–Thirion[8,9] data and show how the results vary from a power law. Before presenting the reduced data, we note that the data shown in *Figure 2* and the spectra shown in *Figure 3* are only approximately superimposable by simple shifts along the time axis. However, as we show below, the data for $r(t)$ (*Figure 2*) can be superimposed very well using corrections of less than 1.1% in the value of E_∞ assumed by Chasset and Thirion. The superposition was applied by making very small vertical shifts of an amount Δr_v on the plots of $r(t)$ *versus* $\log t$ and then performing the shift along the time axis. This amounts to an error in E_∞, which is reasonable since E_∞ is an estimated parameter. Furthermore, as seen in *Figure 2*, the values of $r(t)$ for samples I and J approach a finite non-zero constant value. This value should be very close to the equilibrium value, i.e. when $r(t)=0$. In *Table 3* we show the vertical shift in $r(t)$ as Δr_v and the horizontal shifts in $\log (t)$ as $\log a_v$, using sample F as the reference. Note that the largest correction to E_∞, i.e. the vertical shift, is for sample H and is less than 1.1% ($\Delta r_v = -0.0105$). We also note that these small corrections to E_∞ result in a much larger relative correction to $r(t)$ as it approaches zero. *Figure 5* depicts a double logarithmic representation of the reduced or master curve obtained from these shifts. We now see that the possibility of a power law, which would be a straight line with slope $-m$ in *Figure 5*, exists only over a limited time range*.

In fact, the existence of a time–crosslink density correspondence emphatically argues against a power law relaxation function which is dependent on crosslink density. Rather, because the reduced function shown in *Figure 5* is sampled experimentally in different regions for different crosslink densities, the apparent crosslink density dependence of the power law exponent is simply a result of taking the data isothermally, rather than in an 'iso-corresponding state' manner. Thus one would expect the apparent dependence of m on crosslink density to vary with temperature.

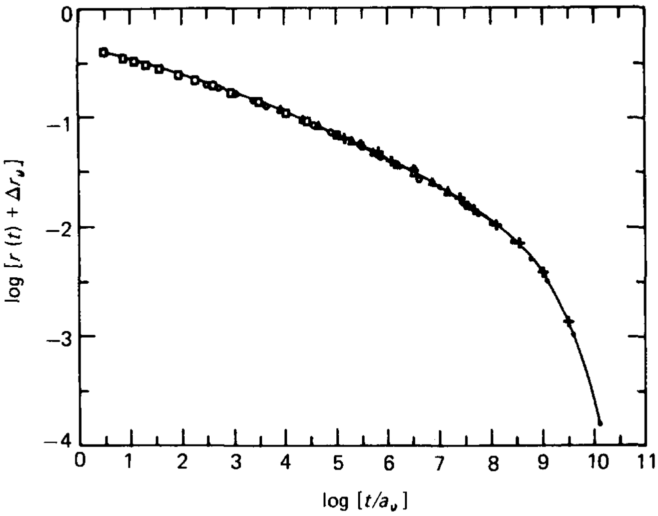

Figure 5 Double logarithmic representation of the reduced relaxation function $r(t/a_v)+\Delta r_v$ *versus* t/a_v for the Thirion–Chasset[9] stress relaxation data for dicumyl peroxide crosslinked natural rubber: □, sample F; ○, sample G; △, sample H; +, sample I; ●, sample J

CONCLUSION

The experimental data on the relaxation of crosslinked networks gives only limited support to power law time behaviour. Deviations from power law behaviour occur at long times and are more pronounced at higher crosslink densities. (It should be emphasized that small changes in the estimate of E_∞ have the largest effect on long time relaxation behaviour, which may explain, at least partially, the deviation from power law behaviour seen in *Figure 5*). Moreover, any power law representation of the relaxation behaviour must have an exponent that is independent of crosslink density in order to be compatible with a time–crosslink density correspondence.

A final point which needs to be raised is the following: In addition to the validity of a time–crosslink density correspondence principle for rubber networks, other investigators have observed that time–swelling[8,9] and time–temperature[8,9,13] correspondence principles are also valid for crosslinked networks. An important question then arises: why is the shape of the terminal region of the relaxation spectrum in crosslinked rubber independent of temperature, swelling and crosslink density, so that these parameters act only to change the position in time at which the relaxation occurs?

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* Our shifts are different from those obtained by Plazek[13] from creep measurements on the same materials. Both Plazek[13] and Dickie and Ferry[12] reported values of E_∞ (or $J_\infty = 1/G_\infty$). As noted in the text, this has a large effect on the value of $r(t)$ at long times. Although the Plazek results for $r(t)$ differ quantitatively from those reported here, they are qualitatively the same, i.e. power law behaviour is not observed. The shifts which we obtain are similar to those reported by Thirion and Chasset[8,9,11] while Plazek[13] and Arenz[14] obtain higher values in their experiments. This is simply indicative of the difficulty of obtaining a good estimate of E_∞ (or J_∞) and, therefore, an accurate portrayal of the transient response of rubber.

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