Influence of static strain on the dynamic mechanical properties of poly(diethyleneglycol isophthalate) networks

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Time-dependent mechanical properties of small amplitude were superimposed on strained poly(diethyleneglycol isophthalate) networks. The tan δ loss peak associated with the glass–rubber relaxation shifts to lower temperatures as the static strain increases for values of the elongation ratio λ lower than 4, suggesting that volume effects overcome entropic effects in this region. However, for values $\lambda > 4$, the opposite occurs. The activation enthalpy is a linear function of the activation entropy, but the compensation law does not hold in the present system. Information on network topology is obtained by analysing the experimental results using theories that predict the value of the loss modulus as a function of the generalized momenta of the elastic chains.

(Keywords: static strain; dynamic mechanical properties; networks)

INTRODUCTION

The study of the influence of static strain on the dynamic mechanical properties of polymer networks is an interesting subject with important basic implications[1]. Thus the location of the glass–rubber transition in the loss tan δ *versus* temperature plot for elongated networks is the result of the increase and decrease in free volume and conformational entropy, respectively, caused by static strain[1–5]. If the former effect is dominant, the location of the maximum of the glass–rubber absorption will be shifted to lower temperature, whereas the opposite will occur if it is the latter.

Other important issues in the analysis of the glass–rubber transition of elongated networks are to investigate whether the free-volume interpretation of the dynamic mechanical response is valid and whether the compensation law holds[6–8]. Although some of these issues were addressed in a previous paper[2], the results obtained were not conclusive because they were limited by the fact that the elongation ratio λ was less than 2. Therefore, the present work is focused on the analysis of the glass–rubber transition of polymer networks under moderate and large static strains, with the aim of gaining a deeper insight into the effect of orientation of the chains on the mechanical properties of networks in general.

EXPERIMENTAL

Hydroxyl-terminated poly(diethyleneglycol isophthalate) (PDEI) chains were obtained by the standard melt-phase procedure from dimethyl isophthalate and diethylene glycol, in the presence of isopropyl titanate, following the procedure described elsewhere[9]. The polymer was dissolved in chloroform and precipitated several times with methanol in order to remove low-molecular-weight species and cyclic oligomers. The polymer was fractionated at 30°C using chloroform/methanol and the fraction of molecular weight 5900 was used in the preparation of the networks. The networks were obtained at 80°C by end-linking the hydroxyl-terminated chains with an aromatic triisocyanate using the method described elsewhere[9]. The sol fraction of the networks was about 5%.

Dynamic mechanical measurements were performed on unstrained and strained strips, cut from the PDEI networks, with a d.m.t.a. apparatus at four frequencies (0.33, 1, 3 and 10 Hz) by multiplexing. In order to get good reproducibility of the experimental results, the thermal history was similar in all the experiments. Thus the strip was stretched at 60–65°C in the measuring frame, previously removed from the head driver, until the desired elongation ratio λ was reached. The strip was permitted to relax and was then kept overnight in a vacuum oven at room temperature to remove all traces of humidity. The temperature range of measurements was -50 to -60°C; the heating rate on both the high- and low-temperature sides of the glass–rubber transition was 1°C min^{-1}, whereas it was only 0.5°C min^{-1} at temperatures close to that of the peak maximum.

The value of the glass transition temperature of the networks, measured with a DuPont TMA apparatus, amounted to 17°C.

RESULTS AND DISCUSSION

Poly(diethyleneglycol isophthalate) chains, like poly(diethyleneglycol terephthalate) chains, do not

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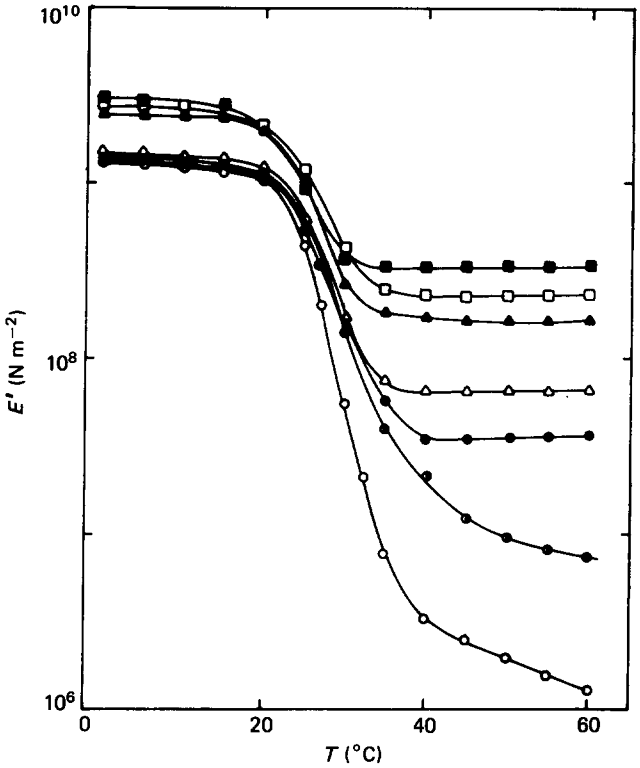

Figure 1 Temperature dependence of the storage modulus E' for poly(diethyleneglycol isophthalate) networks under different elongation ratios λ. Values of $\lambda = 5.18$ (■), 4.34 (□), 3.69 (▲), 2.72 (△), 1.85 (●), 1.30 (◑), 1.00 (○)

crystallize from the bulk even after a long time, presumably because the closeness of the glass transition to the melting temperature hinders the crystallization process; these polymers only crystallize from very dilute solutions. Nor is crystallinity developed in strained networks, as was shown elsewhere[9]. Therefore the changes in shape and position of the glass–rubber peak of strained networks made up of PDEI molecules must be caused only by the orientation of the chains in the amorphous state.

Time-dependent mechanical deformations of small amplitude were superimposed on large static deformations. The temperature dependences of both the storage modulus and the loss tangent for strained networks in which the elongation ratio ranges from $\lambda = 1$ to $\lambda = 5.2$ are shown in *Figures 1* and *2*, respectively. In *Figure 2* we observe a well defined peak associated with the glass–rubber transition, whose position shifts to slightly lower temperatures with increasing static strain for values of λ up to 4. Then it shifts to higher temperature until a value of $\lambda = 5.2$ is reached, and finally the position of the maximum of the peak seems to be displaced to lower temperatures for larger values of λ. These results suggest that, for $1 < \lambda < 4$, volume effects overcome entropic effects; whereas, in the interval $4 < \lambda < 5.2$, the latter effects are dominant, presumably as a consequence of the sharp reduction in conformational space of the phase, which drastically decreases the conformational entropy. For values of $\lambda > 5.2$, mechanical degradation, which increases the molecular weight between crosslinking points as well as the number of dangling chains, may be responsible for the decrease in the apparent glass transition temperature observed for the networks under the highest static strain used in this work.

Normalized tan δ *versus* frequency plots were used to investigate whether the glass–rubber transition of strained networks can be interpreted in terms of the free-volume theory[10,11]. Taking the isotherm corresponding to 31°C as reference, the master curves shown in *Figure 3* were obtained for the networks under different static strains. For the sake of clarity we have only represented the master curves corresponding to $\lambda = 1$ and 2.72 and, for comparison purposes, the curve corresponding to a single relaxation time is also shown. It can be seen that the width of the master curves narrows as the static strain increases, as a result of the fact that the growing number of viscoelastic mechanisms involved in the relaxation phenomena in the unstrained state are not permitted as the static strain increases.

By assuming that all the relaxation times involved in the glass–rubber transition of each strained network have the same temperature dependence, the ratio $a_T = \tau_i/\tau_{i,0}$ between the relaxation times τ_i and $\tau_{i,0}$ associated with the viscoelastic mechanism i at temperatures T and T_0, respectively, can be expressed by the Vogel–Tamman equation[12]:

$$\ln a_T = A' + m/(T - T_\infty) \qquad (1)$$

where

$$A' = -m/(T_0 - T_\infty) \qquad (2)$$

T_∞ being the temperature at which the free volume would be zero were it not for the formation of the glassy state.

The slope m in the $\ln a_T$ *versus* $1/(T - T_\infty)$ plot is related to the free-volume expansion coefficient α_f and to the specific volume by the expression:

$$m = Bv/\alpha_f \qquad (3)$$

where B is a constant whose value is believed to be close to unity.

By comparing the Vogel and the Doolittle[13] equations,

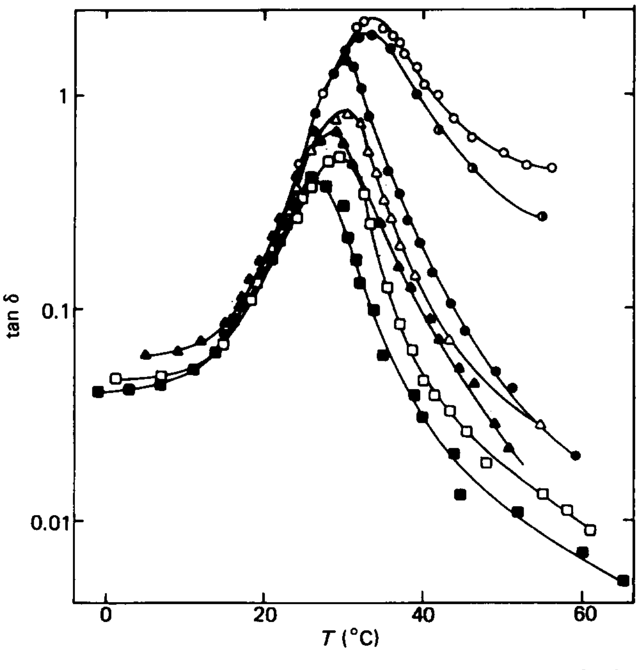

Figure 2 Temperature dependence of the loss tan δ for poly(diethyleneglycol isophthalate) networks under different elongation ratios (as in *Figure 1*)

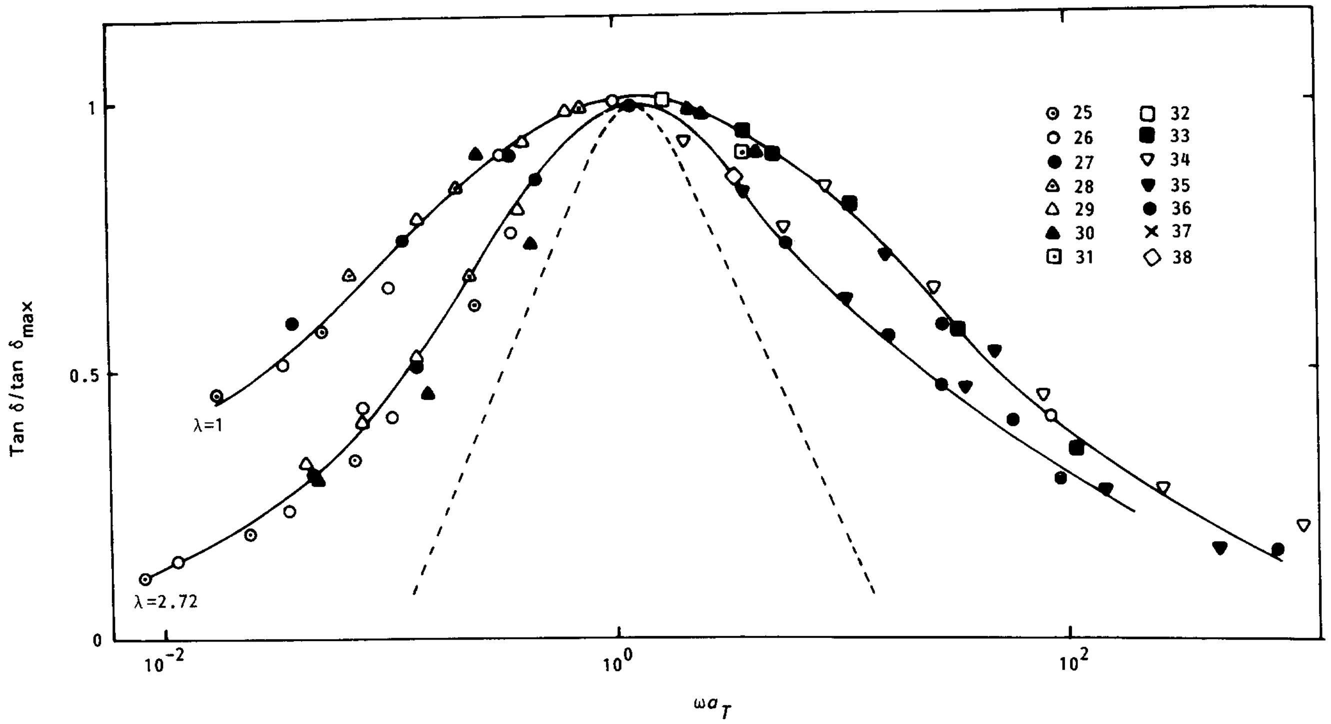

Figure 3 Master curves at 31°C for the normalized loss tangent of poly(diethyleneglycol isophthalate) networks at $\lambda = 1$ and $\lambda = 2.72$. The broken curve represents the loss tangent for a single relaxation time

Table 1 Values of the relative free volume, expressed in terms of ϕ/B, and the expansion coefficient α_f as a function of the elongation ratio for poly(diethyleneglycol isophthalate) networks at T_g

λ	$10^2\phi/B$	$10^4\alpha_f$
1.00	1.98	3.96
1.30	1.92	3.84
1.85	1.94	4.04
2.72	1.91	3.98
3.69	1.84	4.00
4.34	1.75	3.72
5.18	1.56	3.55

one obtains:

$$m = (B/\phi)/(T - T_\infty) = (B/\phi_g)/(T_g - T_\infty) \quad (4)$$

$$\alpha = (\phi/B)/(T - T_\infty) \quad (5)$$

where ϕ and ϕ_g represent the relative free volume at T and T_g, respectively.

Values of T_∞ for each static strain were obtained by fitting the experimental results to straight lines in the ln a_T *versus* $1/(T - T_\infty)$ plot, as suggested by equation (1). The value obtained for T_∞ was −33°C in all the cases. Values of both ϕ_g/B and α, shown in *Table 1*, were obtained in turn from equations (4) and (5), respectively, by correcting the glass transition temperatures of the strained networks according to the displacements of the temperatures associated with the maximum of the peaks of the glass–rubber absorption. The results obtained for both ϕ_g/B and α seem to support the free-volume interpretation of the glass–rubber relaxation of unstrained and strained networks, as both quantities lie within the range of values reported for these parameters in most amorphous systems.

Since the glass–rubber relaxation is an activated process, the dynamic mechanical results could also be interpreted in terms of the Eyring equation[14]:

$$\omega = (kT/h)\exp(\Delta S^\ddagger/k)\exp(-\Delta H^\ddagger/kT) \quad (6)$$

where ω is the frequency associated with the relaxation, $\Delta S^\ddagger$ and $\Delta H^\ddagger$ represent the activation entropy and enthalpy, respectively, and k and h are the Boltzmann and Planck constants. According to the theory, the activation parameters are given by[6–8]:

$$\Delta H^\ddagger = \Delta V^\ddagger/K \quad (7)$$

$$\Delta S^\ddagger = \Delta V^\ddagger\alpha'/\beta \quad (8)$$

where $V^\ddagger$ is the activation volume, α and β represent the thermal expansion and compressibility coefficients, respectively, and K is a constant whose value is believed to be 4.

Both the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ increase as the elongation ratio increases and, as shown in *Figure 4*, the activation enthalpy is a linear function of the activation entropy. The fact that the straight line corresponding to the $\Delta H^\ddagger$ *versus* $\Delta S^\ddagger$ plot does not pass through the origin suggests that in the present system the compensation law does not hold. For example, the compensation temperature defined as:

$$T_c = \Delta H^\ddagger/\Delta S^\ddagger \quad (9)$$

changed from 364 K for $\lambda = 1$ to 340 K for $\lambda = 5.2$.

The changes in activation enthalpy caused by the static strain can be interpreted as the result of an increase in the barriers opposing Brownian motion involved in the glass–rubber relaxation. On the other hand, the activation entropy is associated with complex relaxations in which cooperative intramolecular motions and intermolecular interactions are involved[15]. The increase in activation entropy with increasing static strain is

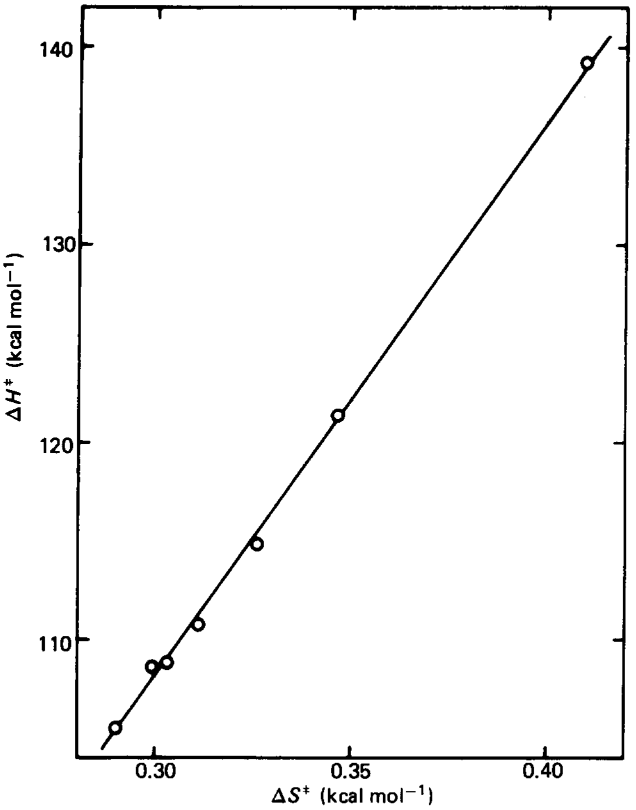

Figure 4 Dependence of the activation enthalpy on the activation entropy for strained poly(diethyleneglycol isophthalate) networks

consistent with the decrease in conformational entropy caused by the orientation of the chains. Finally, the average value obtained for the expansion coefficient, i.e. $(7.06 \pm 0.17) \times 10^{-4}\ \mathrm{K}^{-1}$, from equations (7) and (8) is in fair agreement with the value obtained for this parameter by picnometry, i.e. $5.5 \times 10^{-4}\ \mathrm{K}^{-1}$ (ref. 9).

The experimental results indicate that the loss modulus of strained networks increases with the static strain. This experimental fact is explained by Borodin and Khazanovich[16] as a consequence of the finite extensibility of the chains. The theory is based upon a general relationship between the stress tensor and correlation functions of the dissipative momentum flux, and provides information on the structure of the networks, more specifically on the second ζ^2 and successive momenta ζ^{2n}, and on the properties of the extended polymer chains.

The static strain dependence of the loss modulus in strained elastomers is given by the following expansions[16]:

$$E''(\omega) = E''_g(\omega)[1 + (4/15)\zeta^2(2\lambda^2 + \lambda^{-1}) + (1/875)\zeta^4 \times (864\lambda^4 - 24\lambda + 564\lambda^{-2}) + \ldots] \quad (10)$$

$$E''(\omega) = E''_g(\omega)[1 + (3/10)\zeta^2\lambda^2 + (3/700)\zeta^4(1275\lambda^4 - 370\lambda + 712\lambda^{-2}) + \ldots] \quad (11)$$

These two limiting cases refer, respectively, to a freely jointed chain with constant relaxation times and to a chain with constant diffusion coefficient whose relaxation times strongly decrease with extension. In these equations $E''_g(\omega)$ is the loss modulus in the model of Gaussian subchains and ζ^{2n} represents the generalized momenta defined as[16]:

$$\zeta^{2n} = (1/N_c) \sum_{\nu=1}^{N_c} (h_\nu/L_\nu)^{2n}(N_\nu/\bar{N}) \quad (12)$$

$$\bar{N} = \sum_{\nu=1}^{N_c} (N/N_c) \quad (13)$$

where h_ν is the end-to-end distance of the νth chain in the network and L_ν its contour length; N_c and N_ν represent the number of chains in the network and the number of linkages in the νth chain.

Curves showing the static strain dependence of the loss modulus at different temperatures and frequencies are presented in *Figure 5*. Since the second and fourth momenta are frequency-independent and only slightly dependent on temperature, equations (10) and (11) are useful to determine the values of these quantities. Thus the best values obtained for ζ^2 and ζ^4 using equation (12) are shown in *Table 2*, the average values of the second and fourth momenta being 0.296 and 0.0079, respectively. It should be stressed that theory gives a good account of the experimental results for values $\lambda < 4$. However, for $\lambda > 4$, the experimental values of $E''(\omega)$ decrease with increasing static strain, in sharp contrast with the theoretical values, which increase continuously. Finally, slightly larger

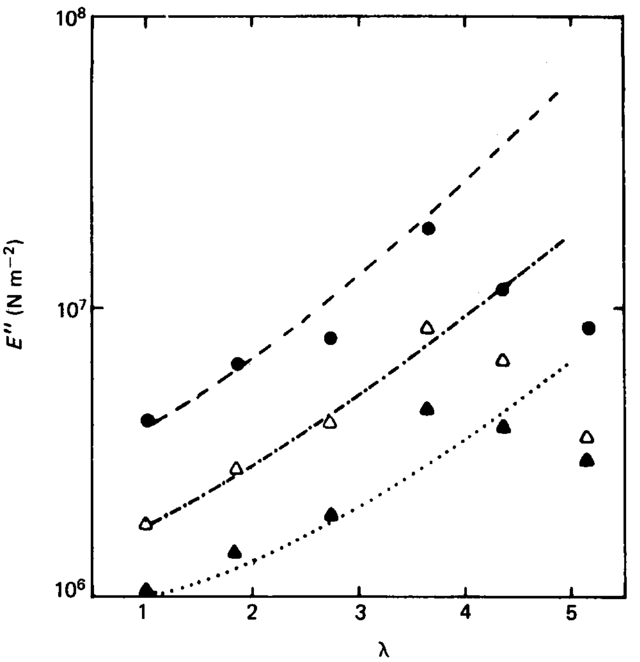

Figure 5 Variation of the loss modulus E'' at 1 Hz with the static strain in poly(diethyleneglycol isophthalate) networks: (●), (△) and (▲) indicate the experimental values of E'' at 40, 45 and 50°C, respectively. The curves represent the values of E'' obtained by means of equation (10)

Table 2 Values of E''_g and the second and fourth momenta defined in equation (12) as a function of the frequency and temperature

ω (Hz)	T (°C)	$10^{-6}E''_g$ (N m^{-2})	ζ^2	ζ^4
0.33	40	1.99	0.316	0.0020
0.33	45	1.00	0.285	0.0013
1	40	3.14	0.300	0.0210
1	45	1.46	0.313	0.0105
1	50	0.83	0.245	0.0056
3	40	6.68	0.310	0.0060
3	45	2.96	0.273	0.0095
3	50	1.37	0.278	0.0117
3	55	0.83	0.310	0.0108
10	50	2.99	0.291	0.0114
10	55	1.84	0.307	0.0028
10	60	1.15	0.321	0.0026

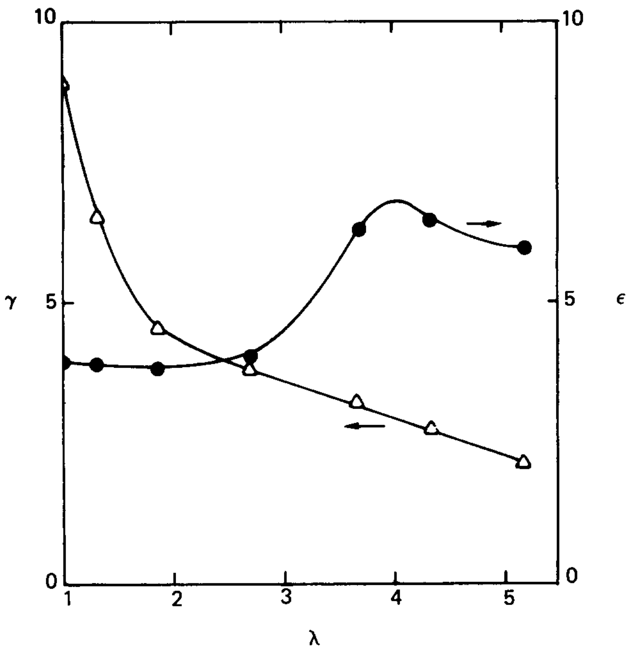

Figure 6 Variation of ε (●) and γ (△) with the static strain. The units of ε and γ are, respectively, $\mathrm{N\,m^{-2}\,K^{-1}}$ and $\mathrm{K^{-1}}$ (see the text for the definitions of ε and γ)

values are obtained for ζ^2 and ζ^4 if equation (11) instead of equation (10) is used in the calculations.

It is informative to relate the loss area in the isochronal plots with the static strain. From classical thermodynamics it can be shown that:

$$(\partial E'/\partial T)_\omega = -(\partial E'/\partial \ln \omega)_T(\partial \ln \omega/\partial T)_{E'} \qquad (14)$$

$$(\partial \ln E'/\partial T)_\omega = -(\partial \ln E'/\partial \ln \omega)_T(\partial \ln \omega/\partial T)_{E'} \qquad (15)$$

where E' represents the storage modulus. These relationships lead to[17]:

$$E'_{T_2} - E'_{T_1} \simeq (2E_a/\pi R)\int_{T_1}^{T_2} E''\,\mathrm{d}(1/T) \qquad (16)$$

$$\ln(E'_{T_2}/E'_{T_1}) \simeq (2E_a/\pi R)\int_{T_1}^{T_2} \tan\delta\,\mathrm{d}\ln(1/T) \qquad (17)$$

from which the areas under both E'' and $\tan\delta$ *versus* $1/T$ can be estimated. Values of

$$\varepsilon = \int_{T_1}^{T_2} E''\,\mathrm{d}(1/T) \quad \text{and} \quad \gamma = \int_{T_1}^{T_2} \tan\delta\,\mathrm{d}\ln(1/T)$$

at 1 Hz are shown in *Figure 6*. It can be seen that ε increases as the static strain increases, reaching a maximum at $\lambda = 4$. On the contrary, a sharp decrease in the values of γ can be detected in the interval $1 < \lambda < 2$, and the decrease is only moderate for $\lambda > 4$. It is worth noting that the mechanical loss, expressed by the loss modulus, presents a maximum at the elongation ratio at which the stress *versus* the reciprocal of the elongation ratio plot exhibits an anomalous increase in the modulus[9].

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