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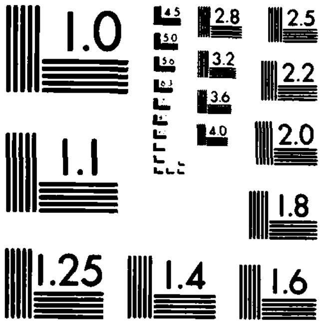
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A1

On Shrinkage and Molecular Extension

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Many authors have been concerned with the shrinkage of oriented specimens which occurs when they are heated.[1-17] The earlier work dealt largely with crosslinked and other reversible systems, applying thermoelasticity and stress optical measurements to the study of networks and oriented crystallization under stress.[1-4] Later studies have concentrated on measuring shrinkage to help characterize the structure of the oriented sample.[5-17] In particular, shrinkage should be directly related to the extension of molecules in the sample.

In recent papers Porter and coworkers[13,14] defined a "molecular draw ratio", MDR, essentially by using the original undrawn state as reference. The purpose of this paper is to show that use of the final shrunk isotropic state as a reference state for the shrinkage gives a more logical and correct formula for molecular extension. It also allows comparison with systems where the "undrawn" state is inaccessible.

When an isotropic ideal rubber elastic material is deformed, the measured extension ratio λ in a given direction is identical to the extension ratio of the molecular network M. If the network is allowed to return to isotropy by removal of external stress or increase of temperature, the sample will recover completely, that is, it will return to its original dimensions. A cross-linked material which is glassy or partially crystallized may remain extended under zero stress, but will recover completely when the temperature is raised. Consider now a polymeric material that is not crosslinked, where the molecular network is made up of impermanent entanglements. When this material is deformed, the measured extension ratio is made up of two parts, reversible elastic extension of the molecular network and irreversible slippage and disentanglement. If the network is allowed to return to isotropy only part of the deformation is recovered. Under these conditions, can the molecular network extension be determined, and how is it related to the measured lengths?

If the material is amorphous, measurement of x-ray orientation function and birefringence will give the degree of molecular orientation. However this does not allow the extension ratio of the molecular network to be determined unless the entanglement density is known. As disentanglement occurs during deformation[9,18,19] the entanglement density is not known in general. If the material is semi-crystalline, the results of such experiments are even more difficult to interpret. X-ray results give the crystal orientation, and when the draw ratio is high, the orientation is almost perfect and differences between samples are difficult to distinguish. For these reasons, a relation between molecular extension and the measured lengths would be very desirable.

To be specific, consider a sample shown in Fig. 1, of original undeformed length L_o which is extended by uniaxial tension to an extended length L_T. On heating to a temperature above the melting point of any crystals in the sample, it shrinks to an intermediate length, L_S, at which it is again isotropic. If both deformations are elastic, then we expect $L_S = L_o$, and molecular extension $M = L_T/L_o = L_T/L_S$. If both deformations are elasto-plastic, then we cannot define M exactly, instead there are two inequalities: $L_T/L_o > M > L_T/L_S$. If the initial drawing is elasto-plastic but the recovery is pure rubber elastic, a completely unconstrained relaxation, then $L_T/L_o > M = L_T/L_S$. To be even more specific, let us take $L_o = 1$, $L_T = 10$, $L_S = 3$ as a numerical example, and put the numerical result in parenthesis after the formula $M = L_T/L_S$ (=10/3). This seems very reasonable, but it requires detailed justification since the formulae used by Porter and coworkers[13,14,17] are quite different.

Image the shrunken sample, length L_S, to be redrawn with no molecular slippage to L_T. Then an isotropic sample is being extended by extension ratio

L_T/L_S and recovering completely. The molecular extension ratio M will be identical to the observed extension ratio. This notional redrawing emphasizes that $M = L_T/L_S$ is equivalent to using the shrunk isotropic state as reference state to measure deformations. It also suggests that if M is associated with some physical reality of the extended sample, it must have the same value after each redrawing cycle, since there is no slippage. The more cycles of (isotropic $L_S \leftrightarrow$ extended L_T) the more difficult it is to see that some original (isotropic L_0) state from which the sample was irreversibly deformed can be relevant.

Surveying previous literature, most papers contain shrinkage data[3-8,11,13,15,16] and shrinkage, S, is often thought to be self-evident and not defined. When it is defined, it is $(L_T - L_S)/L_T$ in the terms of Fig. 1. (0.7 in the numerical example) In Sattler's paper[3] an extension, D, is defined as $1/(1-S) = L_T/L_S$ and in refs. 3 and 4 $1/(1-S)$ is used in place of λ in stress birefringence calculations. L_T/L_S is also sometimes called the contraction.[2,7,8] The literature can be confusing, for in many cases, when the material is found as fibers from solution[5,6,10-12] or supplied in an oriented form[2-4,15] the "original unstretched length L_0" is not applicable or available and the length of the fully oriented material is described as "original length". Thus in refs. 10 and 12 the function used is described as "length/original length" but this is equivalent to L_S/L_T. Some authors[13,16] use "Recovery", R, which is defined as $(L_T - L_S)/(L_T - L_0) = S/(1 - 1/\lambda)$ (=7/9). This is the fraction of the original deformation which is recovered. Kahar et al.[9] use different functions, as follows:

$\lambda = L_T/L_0$ $\qquad \varepsilon = (L_T - L_0)L_0$ (=9)

$\lambda' = L_S/L_0$ $\qquad \varepsilon' = (L_S - L_0)L_0$ (=2) (inferred from text ref. 9)

Shrinkage strain $\varepsilon - \varepsilon' = (L_T - L_S)/L_0$ (=7)

residual strain $\varepsilon'/\varepsilon = (L_S - L_0)/(L_T - L_0) = 1 - R$ (=2/9)

The use of nominal strains rather than extension ratios is due to the small deformations in this study of PMMA. The deformations could be fully recovered at high temperature and finite residual strains ($L_S > L_o$) were measured at lower temperatures.

This leaves the "molecular draw ratio" or MDR of Porter and co-workers previously mentioned as a reason for this paper. Three formulae are given for MDR; L_S/L_o (=3) and $R.L_T/L_o$ (=7.77) in reference 13 which is corrected in a corrigendum and in reference 14 to $\{(L_T - L_S)/L_o + 1\}$ (=8). The first formula was presumably a typographical error of some sort. The second two are quite similar at high λ as they can be expressed as λR and $\lambda R + (1 - R)$. Neither was explained by the authors, but it is easy to create reasons for their use: λ is the extension ratio. R is the fraction of the deformation that is recoverable. Recoverable deformation comes from the molecular extension, so MDR = λR. However, this is faulty since the extension ratio λ is mixed with deformation, or strains, since $R = (L_T - L_S)/(L_T - L_o) = (\frac{L_T - L_S}{L_o})/(\frac{L_T - L_o}{L_o})$ is a ratio of strains.

Modifying R to $R' = (\frac{L_T - L_S}{L_o} + 1)/(\frac{L_T - L_o}{L_o} + 1)$ which is a ratio of extension ratios, gives $R' = (L_T - L_S + L_o)/L_T$ (= 0.8) and so $\lambda R' = (L_T - L_S + L_o)/L_o$ (=8) which is the definition of MDR used in ref. 14. The critical feature in this derivation, easily passed over, is the choice of L_o as the divisor for strain when the initial and final states are L_T and L_S. If L_S is chosen as the divisor, the reference length, then the modified R becomes

$$R'' = (\frac{L_T - L_S}{L_S} + 1)/(\frac{L_T - L_o}{L_o} + 1) = \frac{L_T}{L_S}/\frac{L_T}{L_o} = L_o/L_S \ (= 0.33)$$

and $\lambda R'' = L_T/L_o \cdot L_o/L_S = L_T/L_S = M$ (=3.33).

As can be seen from the numerical example, the difference between these formulae for molecular extension can be very significant. Taking data from ref. 13, where $\lambda = 36$, $R = 0.51$, the calculated MDR was 18.4 and the correction of ref. 14 would bring that to 18.8. However, $M = L_T/L_S$ is 2.0. Such low values do not seem to be realistic for a material that has undergone a 36x deformation and has a modulus of 40 GPa.[13] It seems much more likely that the shrinkage is not completely slippage free, that the contraction was hindered, and so $M = 2.0$ is only a lower limit. The correction in ref. 14 stated that by a change of procedure, R could be increased to 0.7 and several other authors have noted changes in shrinkage due to specimen thickness[6,10] and heating conditions.[6,7,13] Other sample types of high deformation ratios shrink almost completely back to their original length[7,8,16,17] with $R \cong 0.98$.

For describing the state of a system, any functions of the state variables are equally valid. Thus when the calculated values of MDR are found to have a linear relationship to modulus in a particular set of samples[20], this is a valid correlation unaffected by the above arguments. But when a function is related to a particular physical property, here the extension of the molecular entanglement network, an independent measurement of the property determines the validity of the function.

Small angle neutron scattering of uniaxially oriented samples can give the molecular extension[21], since the radius of gyration parallel to the draw direction $R_g(1)$ is proportional to molecular extension and the radius of gyration perpendicular to the draw direction $R_g(2)$ is proportional to (molecular extension)$^{-1/2}$. For affine deformation when network elements deform in the same way as the whole molecules, the network extension should be $(R_g(1)/R_g(2))^{2/3}$. Unfortunately the only available data[21] refer to a case where the recovery was almost complete and then the differences between the MDR = $\{(L_T - L_S)/L_0 + 1\}$, and the molecular extension suggested here, $M = L_T/L_S$ become very small, Table 1. SANS from samples where the recovery is 80% or less would clearly distinguish between the two formulae (Table 2). The difference is greater at greater draw ratios, since as $\lambda \rightarrow \infty$, MDR $\rightarrow \infty$ but $M \rightarrow 1/(1-R)$. Comparison of such shrinkage results with SANS would only be worthwhile if one could be sure that the retraction from the oriented state was purely elastic with no further slippage or disentanglement. Such slippage would cause L_S to be too high and M to be too low.

It should also be pointed out that measurement of entanglement density and its decline on drawing at high temperatures by use of birefringence data[18] requires measurement of shrinkage.[15] The molecular orientation and thus the birefringence depends on the entanglement density and the network extension. Without shrinkage measurement the only extension available is λ. Only if the deformation is fully reversible will this be the same as network extension.

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TABLE 1

Comparison of M and MDR with SANS results[*]

λ[*]	MDR[*]	M[†]	SANS[*]
2.9	2.9	2.9	2.8
4.2	4.0	3.5	4.1
5.1	5.0	4.6	5.0
9.6	9.4	8.0	8.6

[*] Data from Table 1 of reference 21.

[†] $(MDR-1)/\lambda = 1-1/M$; $M = \lambda/(\lambda-MDR+1)$

Table 2

Comparison of M and MDR at lower recovery

λ	R	MDR[*]	M[*]
2	0.8	1.8	1.67
5	0.8	4.2	2.78
10	0.8	8.2	3.57
2	0.6	1.6	1.43
5	0.6	3.4	1.92
10	0.6	6.4	2.17

[*] $MDR = \lambda R+1=R$, $M = \lambda/(\lambda+R-\lambda R)$

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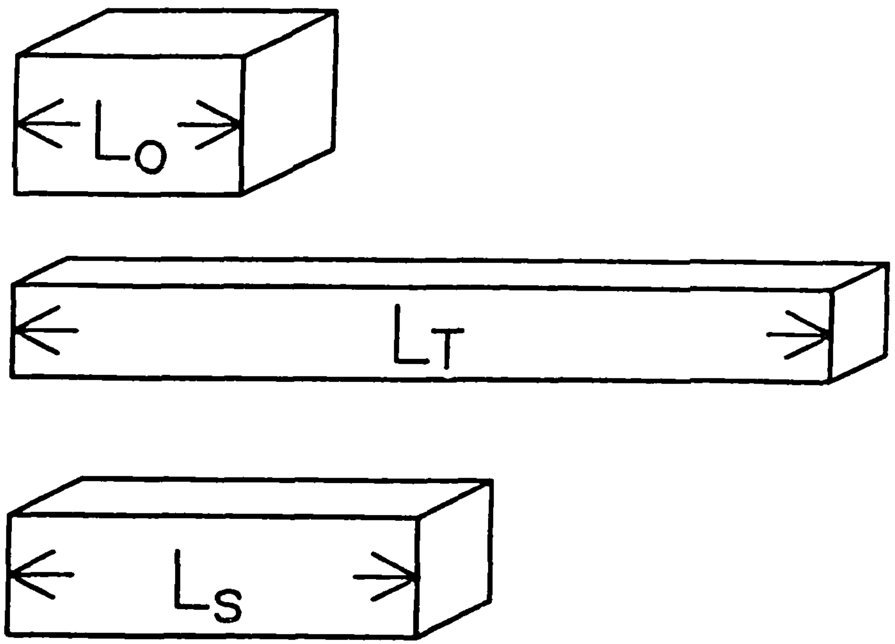
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