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The Localization Model of Rubber Elasticity

Jack F. Douglas

Summary: While the unusual elastic properties of rubbery polymer materials have been studied for literally centuries, a quantitative theoretical description of these properties in terms of molecular structural parameters remains a challenging task. Classical network elasticity theories are based on the concept of flexible volumeless network chains fixed into a network in which there are no excluded volume, or even topological, interactions between the chains and where the chains explore accessible configurations by Brownian motion. In this type of model, the elasticity of the deformed network derives from the entropic changes in this idealized network arising from a deformation of the network junction positions. The shortcoming of this approach is clear from the observation that unswollen rubbery materials are nearly incompressible, reflecting the existence of strong intermolecular interactions that restrict the polymer chains to an exploration of their local molecular environments. The imposition of a deformation of these solid rubbery materials then necessitates a consideration of how local molecular packing constraints become modified under deformation and the impact of these changes on the macroscopic elasticity of the material as a whole. Many researchers have struggled with this difficult problem, but we focus on the simple 'localization model' of rubber elasticity introduced by Gaylord and Douglas (GD), which provides an attractive and mathematically simple minimal model for the network elasticity of rubbers having strong intermolecular interactions in the dense polymer state. GD assume that the network chain segments are localized at the network junctions, as in classical elasticity theory, but they also consider the chains to be localized along their contours by a local harmonic potential arising from inter-particle packing interactions, as in atoms in a simple harmonic crystal. This is the familiar Edwards-De Gennes 'tube' model of polymers in the condensed state. The existence of the tube means that the entropy of the network chains is reduced relative to chains without this constraint, but the crucial problem is how this entropy change becomes *modified* as the material becomes deformed. GD approach this problem by first observing that both the volume of the material and the network chains are essentially invariant under deformation so they require that the dimensions of the confining tube to also be a deformation invariant where this constraint is applied at a segmental level. The properties of the resulting 'localization model' of elasticity of dry and swollen rubbers are summarized and some extensions of the model to describe chain finite extensibility and stiff polymer networks are briefly summarized.

Keywords: crosslinking, modulus, rubber, stress, swelling

Model Formulation

Models of network elasticity have concentrated on minimal aspects of rubber networks. In particular, the classical rubber elasticity models of Wall and Flory,[1]

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James and Guth,[2] Edwards[3] and many others have focused on the consequences of network connectivity. Classical theories idealize rubbery materials as idealized networks of random walk chains whose junctions deform approximately affinely in response to a macroscopic deformation, thereby changing the entropy of the system. More recent work has emphasized inter-chain interactions or 'entanglement' interactions defined in terms of the topological constraint of chain un-crossability and correlations arising from molecular packing.

A minimal statistical mechanical model of rubber elasticity must incorporate three main features of the network chains:

1) A connected network of flexible chains[1–3]
2) 'Entanglement' constraints[4–7]
3) Finite volume of chains[8]

The localization model (LM) of rubber elasticity directly addresses these effects.[9,10]

As a first approximation, the localization model takes the free energy $\Delta F_{\mathrm{network}}$ of the network per unit volume to be proportional to the number of chains per unit volume ν_{d} where $\Delta F_{\mathrm{chain}}$ is the chain free-energy of deformation,

$$\Delta F_{\mathrm{network}} \sim \nu_{\mathrm{d}}\, \Delta F_{\mathrm{chain}}$$

This result, which derives explicitly from classical elasticity network model calculations, assumes that each chain sees an *equivalent* molecular environment arising from its interaction with surrounding chains and this approximation thus amounts to a mean field approximation[11] when applied more generally. For a cross-linked network, the number of chains per unit volume is taken to be proportional to the number of cross-links per unit volume, the cross-link density.

The second basic approximation is to assume that the network chains are Gaussian chains in our estimation of the chain connectivity contribution to $\Delta F_{\mathrm{network}}$. This approximation has its limitations, especially for large network extensions and for cases where the network chains are stiff or semi-flexible. (The treatment of finite extensibility effects and chain semi-flexibility are relatively well-understood and we return to incorporating these effects below.) For the present, we are concerned with understanding the basic nature of non-classical 'entanglement' contributions to network elasticity arising from inter-chain interactions that exist at high polymer concentrations.

Before initiating our modeling of the entanglement contribution to $\Delta F_{\mathrm{network}}$, we make some general physical observations that constrain our theoretical development: 1) Dry rubbery materials are normally nearly incompressible because of strong repulsive inter-segment interactions, despite the random coil nature of the polymers. 2) Confinement of network chains to a volume on the order of the hard core volume of the chains alters the average chain entropy relative to an unconfined chain. The question is then how you calculate this entropy change under deformation conditions?

The Feynman-Kac functional limit theorem (FKLT) implies that confining a chain by *any* means leads to a *universal* change in the chain free energy of the flexible polymer chains, $F_{\mathrm{confinement}} \sim \langle R^2 \rangle / \xi^2$, where $\langle R^2 \rangle$ is the mean squared dimensions of the unconfined chain and ξ is the *localization length* describing the scale over which the chain is localized.[12] $\langle R^2 \rangle$ is proportional to the chain length, N, so that $F_{\mathrm{confinement}}$ is extensive in the chain length. This limiting scaling relation is also known as 'ground state dominance'[13] based on a quantum analogy with the Brownian chain model. More generally, we have the more general scaling relation, $F_{\mathrm{confinement}} \sim \langle R \rangle^{\mathrm{df}} / \xi^{\mathrm{df}}$ for generalized random walks (having independent steps, but whose variance in step length is not finite) where $\langle R \rangle$ is the mean chain size and d_f is the fractal dimension of the chain, i.e., $\langle R \rangle \sim N^{1/\mathrm{df}}$. Evidently, we again obtain a confinement contribution $F_{\mathrm{confinement}}$ that is again extensive in N. In the presence instance, this localization effect derives from the hard core repulsive interactions between a given chain and its surrounding chains so that $F_{\mathrm{confinement}}$ is entropic in nature. In other words, hard core excluded volume interactions confine the chains to 'tube-like' regions localized around some average chain conformation and this chain confinement gives rise to a change of the entropy per link of the polymer chain. The FKFLT provides the fundamental mathematical underpinning of the tube model of polymer melts and rubber elasticity.

So far we have based our model on two fundamental limit theorems of broad mathematical and physical significance- the central limit theorem describing the statistical properties of random walk chains and the FKLT describing how the free energy of these chains changes with confinement (or the mathematical equivalent of this effect). This provides a sound foundation for a general theory of flexible polymer networks with strong localizing inter-chain interactions in the melt state. The problem of calculating how $F_{confinement}$ becomes modified by macroscopic deformation of the rubbery material is more difficult. It seems reasonable to assume that under quasi-equilibrium conditions of deformation that the FKLT relation still applies and the crux of the LM modeling then reduces to estimating how ξ varies with deformation. There is certainly no reason to believe that ξ should vary affinely with the extent of macroscopic deformation λ_i along the laboratory-fixed axes, as might reasonably be argued for the coordinates defining the chain junctions in the network.

Gaylord and Douglas[9] approached this basic problem by assuming, as Edwards[14] had done before, that the network chains are contained within a random tube with local harmonic confining potential that is composed of segments that are oriented along three directions (x, y, z) in the lab-fixed frame. The harmonic tube model for the inter-chain interaction potential is chosen simply for mathematical convenience. The FKLT theorem ensures that essentially any reasonable confining potential will lead to the same limiting results. We note that Heinrich et al. have also developed a popular tube model of rubber elasticity,[15] based on the same chain localization concept, but these authors do not invoke the packing arguments to specify the molecular parameters in their model and change in elasticity with network swelling.

The random tube model can now be constructed by viewing the random tube as consisting of straight tube sections lying along the macroscopic deformation axes. The distribution function describing the distribution of the chain monomers within a random tube segment then factorizes into a product of Gaussian functions defined in terms of coordinates along the tube axis and a coordinate normal to the tube axis. Because of the separability property of random chains the random tube segments can be imagined to be aligned along the three macroscopic deformation axes with equal probability, a construction first introduced by James and Guth in their approximate treatment of finite- extensibility effects on network elasticity.

To calculate the free energy change with deformation, the junction positions are taken to deform affinely, $R_i = \lambda_i \cdot R_{io}$, where R_{io} is the initial distance between a given network chain end along the i^{th} macroscopic deformation coordinate direction. This argument leads to the classical affine network model of rubber elasticity. Of course, the affine deformation assumption is an approximation and other models of rubber elasticity take this as a starting point of their development.[16] It is this author's opinion that non-affine contributions do not really address the inter-chain interaction effects responsible for 'entanglement' contributions to the elasticity of dry rubbers.

To estimate $\xi(\lambda_i)$, we argue that the hard core volume of the chain and localizing tube are comparable and *invariant* to deformation.

The assumption of affine displacement is taken to mean that that length of the tube segments along the deformation axis deform affinely,

$$L = \lambda_x L_o,$$

where L_o is the length of the undeformed tube. The invariance of the tube volume with this deformation implies that the length of the tube times its cross-sectional area is the same before and after deformation, $L\ \xi_x^2 = L_o\ \xi_{xo}^2$. This impies that $\xi_x = \lambda_x^\beta\ \xi_o$, where $\beta = -1/2$ and $\xi_{xo} = \xi_{yo} = \xi_{zo} \equiv \xi_o$. This scaling relation is obviously quite different from an affine variation, $\xi_x = \lambda_x\ \xi_o$. Rubinstein-Panyukov[17] have made arguments that β is positive ($\beta = ½$), as in the affine assumption model. Their calculation is based on a model of *topological invariance* of the network under macroscopic deformation in a model that does not consider chain packing effects.

These considerations lead to the LM model[9] expression for the free-energy density of a dry rubber,

$$\Delta F_{LM} = (G_c/2)\,\Sigma_{x,y,z}\,(\lambda_i^2 - 1) + G_e\,\Sigma_{x,y,z}\,(\lambda_i - 1) \tag{1a}$$

where the classical network theory shear modulus G_c is proportional to the cross-link density (ν_x) and thermal energy ($k_B T$),

$$G_c = C_o\,\nu_x k_B T, \tag{1b}$$

In the affine network model of Wall and Flory the prefactor is $C_o = 1$ and in the classical non-affine ‘phantom model’ of James and Guth,[2] Deam and Edwards,[3] where the network junctions can fluctuate with the constraint of excluded volume interactions, $C_o = ½$. More generally, C_o depends on the details on network structure (dangling ends, network functionality, etc.),[18] and C_o is considered to be a measurable parameter characterizing a given network.[19] In the absence of other information, we take the ‘phantom’ elasticity model estimate, $C_o \approx ½$, as an estimate of the ‘front factor’. The entanglement contribution G_e to the free energy density of the network,

$$G_e = \gamma\,G_c + G_N^*, \tag{1c}$$

includes a cross-term proportional to G_c [and thus ν_x; see Eq. (1b)] and a cross-link independent term that is identified with the plateau modulus of the polymer melt, G_N^*.[9] Much is known about the dependence of G_N^* on molecular parameters.[20] We note that Eq. (1a) is consistent with the Valanis-Landel separable form of the strain energy density of rubbery materials, a property of the strain energy density that has been established to be a good approximation for many rubbery materials.[21] The Valanis-Landel property greatly simplifies calculation of the deformation properties of rubbers.

This expression implies the remarkable result that for polymers with a low cross-link density (so that the rubber is barely a solid) elastic modulus reduces to that of a polymer melt and that the cross-links have rather little contribution to the elasticity. At high cross-link densities, the shear modulus of the rubber scales in linear proportion to ν_x as in classical elasticity theory.

The Elasticity of Dry Rubbers

Calculations of the stress - strain relations for dry rubber are then remarkably simple for the LM model.[9] Under uniaxial deformation($\lambda_x = \lambda$; $\lambda_y = \lambda^{-1/2}$; $\lambda_z = \lambda^{-1/2}$) of an incompressible material in three dimensions, we have the stress τ,

$$\tau = d\,[\Delta F_{network}/V_o]/d\,\lambda, \tag{2}$$

where V_o is the dry rubber volume. Eq. (2) then implies the simple relation,

$$\tau = G_c\,(\lambda - \lambda^{-2}) + G_e\,(1 - \lambda^{-3/2}). \tag{3}$$

The stress relative to its classical variation ($\lambda - \lambda^{-2}$) defines a reduced stress:

$$I(\lambda) \equiv \tau/(\lambda - \lambda^{-2}) = G_c + G_e(1 - \lambda^{-3/2})/[\lambda(1 - \lambda^{-3})]. \tag{4}$$

For large deformations ($\lambda \rightarrow \infty$) this expression reduces to an asymptotic *Mooney-Rivlin* relation,[22]

$$I(\lambda) \sim G_c + G_e\,(1/\lambda). \tag{5}$$

so that G_c and G_e can be identified approximately with the Mooney parameters $2C_1$ and $2C_2$ that are normally considered in characterizing dry rubbers under extension. Blokland[23] has provided an extensive tabulation of C_2 for a variety of rubbers at relatively high cross-link densities and we tentatively suggest the approximation $\gamma \approx 1/3$ as a useful approximation in the absence of direct measurement.

The reduced stress in the LM model can be generalized to d-dimensions:

$$\tau = G_c\,[\lambda - \lambda^{-(d+1)/(d-1)}] + [2\,G_e/(d-1)]\,[\lambda^{2/(d-1)-1} - \lambda^{-2/(d-1)(d-1)-1}], \quad (6)$$

which reduces to the classical–like expression $\tau = G_c\,[\lambda - \lambda^{-1}]$ in high dimensions[24] and an expression applicable to the elasticity of membranes (e.g., polymerized Langmuir films) for $d = 2$.[25]

Previous comparisons of the LM model to experiment show that this simple model compares very well with uniaxial compression and extension measurements as well as biaxial extension,[9] and torsional deformation measurements on dry rubbers.[26] Moreover, the LM performs rather well on the complex problem of network elasticity of rubbers cross-linked in a deformed state.[27] The LM is critically compared to other models by Han et al.[28] The torsional deformation measurements of McKenna et al.[26] are particularly notable because these measurements were performed over an appreciable range of cross-linking densities. These measurements (where C_o was fixed to ½) yielded a G_e having exactly the form predicted by Eq. (1), i.e., G_e is linear in and extrapolates to G_N^* in the limit of vanishing cross-linking density. This is very reassuring regarding the physical soundness of the LM model. We next consider the extension of the LM model to describe the change in elasticity of rubber subjected to swelling.

The Elasticity of Swollen Rubbers

The theoretical prediction of the elasticity of swollen networks from information about the dry rubber is a challenging problem. Before addressing this problem, we note some insightful comments and observations made by Gumbrell et al.[8] on this topic:

> "The change in C_2 [non-classical contribution to rubber elasticity; see Eq. (5)]] with volume swelling can be associated with the finite volume of the rubber molecules. This leads to a reduction in the number of possible configurations as two molecules cannot occupy the same space at the same time nor can they pass through one another. The reduction of configurations from this cause would naturally be less in the swollen than in the dry state and in highly swollen rubbers deviations from ideal behavior due to this cause will be small."

> "The value of C_2 is found to be large in dry rubbers and decreases to zero at high degrees of swelling."

The first issue that we must address, in a way consistent with the formulation of the LM model, is the concentration dependence of the plateau modulus of a polymer melt. In a melt of high molecular mass polymers, the chains are only *transiently localized* into their local tube environments on the time scale of the stress relaxation time, the terminal time. The system thus responds elastically when perturbed at relatively high frequency measurements, while the system flows over long time scales. Cross-linking locks chains into a *permanently localized state*- an amorphous solidification transition.[29]

In the limit $\nu_d \rightarrow 0$ (high molecular mass polymer melt), the entanglement contribution G_e is simply due to chain localization due to inter-chain interactions:

$$G_e(\nu_d \rightarrow 0) \approx G_N^{*[9,12]} \text{ where } \Delta F_{\text{localization}} \sim G_N^* \sim \nu_d \langle R^2 \rangle / \xi^2.$$

If we imagine the network as being comprised of one single molecule (tube) of length N that fills space, then the change in system volume upon swelling $V_o \rightarrow V$ implies the change in the correlation length

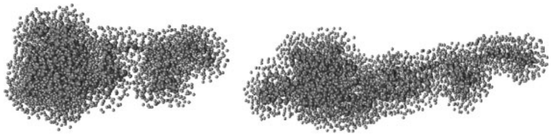

Figure 1.
Molecular dynamics simulation of chain deformation under macroscopic extension (the macroscopic deformation direction (x) is along the horizontal direction; left chain is before deformation and the right is after deformation. dark grey spheres indicate chain segments and the gray segments are those of surrounding chains in the proximity of the illustrated test chain. The number of chain segments in the test chain environment is nearly invariant- consistent with an invariance of the tube volume with deformation. Figure is for schematic purposes only.

$\xi \sim \xi_o \phi^{-1/(d-1)}$ and where cross-link density becomes, $\nu_d = \phi\, \nu_{do,}$ where ϕ is the polymer volume fraction. These relations then imply that the plateau modulus of the diluted melt $G_N(\phi)$ scales as,

$$G_N(\phi) = G_N^* \phi^{(d+1)/(d-1)} \text{ or } G_N(\phi; d = 3) \sim G_N^* \phi^2. \qquad (7)$$

Notably this scaling has nothing to do with the fractal character of the chains. This scaling relation is simply a consequence of chain packing. The same packing argument implies that G_N^* scales in inverse proportionality to the chain cross-sectional area A since $\xi^2 \sim A$.[12] The entanglement contribution to the elasticity of polymer networks, and even polymer melts, should then be reduced in chains with bulky sidegroups.

To calculate the tension of a swollen rubber subjected to deformation,[30] we define a swelling factor to describe the first swelling part of the deformation ($V_o \lambda_s^3 = V$), where λ_s is swelling factor. This deformation is followed, for example, by a *uniaxial* deformation ($\lambda_x = \alpha$; $\lambda_y = \alpha^{-1/2}$; $\lambda_z = \alpha^{-1/2}$) so that the tension $\tau(\alpha)$ is equal, $\tau = d\,[\Delta F_{network}/V]/d\alpha$ or explicitly the LM predicts,

$$\tau = G_c \phi^{1/3} (\alpha - 1/\alpha^2) + (\gamma G_c + G_N^* \phi) \phi^{2/3} (1 - \alpha^{-3/2}) \qquad (8)$$

The concentration dependent reduced stress $I(\alpha,\phi) \equiv \tau/(\alpha - 1/\alpha^2)\ \phi^{1/3}$ is then equals,

$$I(\alpha,\phi) = G_c + (\gamma G_c + G_N^* \phi) \phi^{1/3} (1 - \alpha^{-3/2})/\alpha(1 - \alpha^{-3}) \qquad (9)$$

And in the large extension limit this reduces as before to Mooney-Rivlin form,

$$I(\alpha,\phi) = G_c + 2C_2(\phi)/\alpha,\ \alpha \to \infty \qquad (10)$$

at large extensions (i.e., $\alpha \to \infty$) where $G_c \equiv 2C_1$ and $G_e(\phi) \approx 2C_2(\phi)$ and the 'Mooney parameter' C_2 exhibits a non-trivial concentration scaling,

$$2C_2(\phi) \approx (\gamma G_c + G_N^* \phi) \phi^{1/3}. \qquad (11)$$

Although C_2 generally vanishes upon swelling, as noted by Gumbrell et al., there is a *qualitative* difference in the concentration dependence of the entanglement contribution to the elasticity of rubbery materials having relatively high and low cross-linking densities. For lightly cross-linked materials where the chain localization term related to the plateau modulus dominates, we predict that the Mooney parameter should drop off rapidly with concentration,

$$C_2(\phi) \sim G_N^* \phi^{4/3},\ \nu_x \to 0, \qquad (12)$$

while for highly cross-linked rubbers the scaling becomes like that of classical rubber elasticity theory,

$$C_2(\phi) \sim G_c \phi^{1/3},\ \nu_x \to \infty \qquad (13)$$

Numerous observations on lightly (specifically $C_2(\phi)$ exhibits a concentration power law near 1 and power law 4/3 has sometimes been noted[31–33]) cross-linked rubbers are consistent with Eq. (11). Douglas and McKenna[30] have shown that the scaling relation Eq. (13) holds rather well for relatively highly cross-linked natural rubber. The accord of the LM with these *qualitative* changes in the elasticity of rubbers, depending on the cross-linking density, is again quite encouraging.

Conclusion

The non-ideal contribution to rubber elasticity can be large in unswollen rubbers, even larger than the contribution arising from chain cross-links. The localization model attributes this non-ideal contribution to strong inter-chain interactions that influence the chain entropy.

- Comparison of localization model to dry rubber deformation data provides a reasonable description of the elasticity of rubbers in all modes of deformation considered so far.
- Localization model predicts that elasticity of lightly and highly cross-linked rubbers changes in a *qualitatively different* fashion with network dilution.

In view of the simplicity of the analytic form of the model, the physically sensible nature of the parameters derived from it, and its success in capturing qualitative aspects of rubber elasticity in both dry and swollen rubbers, we conclude that the model is a useful working tool in modeling rubbery materials.

Future Work

There is an obvious need for extensions of the Localization Model to describe important aspects of really rubbery materials. Obvious problems include:

- The incorporation of finite extensibility effects
- The incorporation of chain semi-flexibility effects and the treatment of stiff networks
- Treatment of cross-linking history effects. In particular, can we take account of cross-linking history effects by fixing G_N in G_e by its value under cross-linking conditions, G_N (effective) $= G_N(\phi = \phi_x)$?

Finite extensibility effects in flexible polymer networks clearly represent an issue in deformed swollen rubbers[34] and in highly deformed networks.[35] The Langevin model has served very well in capturing the main effect of finite extensibility and an obvious extension of the LM model is simply to replace the Gaussian network contribution by the usual Langevin function expression in the localization model. By construction, this accords with the LM model in the small deformation limit. Meissner[36] has shown that a combination of Langevin model and the Mooney-Rivlin expression performs very well in desribing finite extensibility in networks and in view of the relation between this model and the LM model we expect this generalization of the LM model to perform well under general deformations for which the Mooney-Rivlin relation fails. There are economical approximations to the Langevin free energy density that allow the 'economical' analytic form of the LM model to be largely preserved.[37]

Correspondingly, there are available expressions for the free-energy of deformation of semiflexible polymers[38] that can be directly incorporated in the localization model, provided that the fractal dimension d_f of the chain contribution to the localization term in the network free-energy density is suitably modified.

Networks of stiff rod-like polymers are very common in biological systems (tubulin, actin and other structural fiber forming proteins) and more recently these networks have become of interest in connection with carbon nanotube materials.[39] We can obtain a simple extension of the localization model by appealing to some analytic results of Vilgis et al.[40] Vilgis et al. formulated an integral Equation approach to semi-flexible chain network theory, extending the JG-Edwards theory of flexible chains and found that $\Delta F_{\mathrm{network}}$ was the *same* as flexible chains for small deformations, but an exponential scaling was obtained at high extensions λ,

$$\Delta F(\lambda) \sim \exp[\beta \lambda^2],\ \lambda \to \infty,\ \beta = \text{constant} \tag{14}$$

If we analytically continue the localization model so that it is recovered in the small deformation limit, we obtain a model for the elasticity of rod networks with entanglement interactions,

$$\Delta F_{\mathrm{network}} = (G_c/2\delta)\{\exp[\delta(\Sigma_{x,y,z}\lambda_i^2 - 1)] - 1\} + G_e \Sigma_{x,y,z}(\lambda_i^{(1/2\nu)} - 1) \tag{15}$$

where δ is a parameter that characterizes the strain hardening in the stiff chain network, and where ν is the reciprocal fractal dimension d_f of the network chains, i.e., $\langle R_g^2 \rangle \sim N^{2\nu}$. The leading term in Eq. (15) corresponds to the phenomenological Fung model of the free energy density of biological tissues,[41] which has enjoyed wide success in modeling biological materials. Note that the connectivity term in Eq. (15) exhibits strain hardening for large extensions and that the localization term gives rise to strain softening. The interplay between these terms could make the stress-strain behavior quite rich in this class of networks. In would be interesting to see how well Eq. (15) performs in comparison with real networks of stiff fibers and polymers.

There is evidence indicating that networks cross-linked in a highly swollen state exhibit classical rubber elasticity to a good approximation when the rubber is dried.[42] Since swelling virtually eliminates the entanglement contribution in the localization model, this phenomenology is consistent with the suggestion above that cross-linking history effects might be generally modeled by the simple identification G_N^* (effective) $= G_N(\phi = \phi_x)$ in the localization model. This would mean that effective entanglement contribution to the network elasticity would equal G_N^* (effective) $= G_N^*$ $(\phi_x/\phi)^2$, where G_N^* is the plateau modulus of the equilibrated polymer melt. Subjecting the polymer material to vigorous deformation before cross-linking should also have the effect of delocalizing the chains from the clusters that define the entangled polymer state[12] and this should also lead to a reduction in the entanglement trapping factor *Te* [5,19] between G_N^* (effective) and G_N^*. These possibilities for modifying the entanglement contribution to the network history through changes of the deformation and swelling history of the polymer melt before cross-linking require further investigation.

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