

Mechanics of a rate-dependent polymer network

Q. YU[†] and A. P. S. SELVADURAI*[‡]

[†]Department of Aeronautics and Astronautics, Stanford University, Durand Building,
496 Lomita Mall, Stanford, CA 94305-4035, USA

[‡]Department of Civil Engineering and Applied Mechanics, McGill University,
817 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

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Pure rubber-like materials usually have little or no rate-dependency during finite straining. In contrast, polymeric materials can exhibit rate-dependent rubber-like responses in the large-strain range. A thermodynamic analysis points to the existence of rate-effects for an elastic network. The presence of reversible crystallization with a rate-dependent feature changes the conformation mobility of the network structure and, subsequently, contributes to the alterations in its elasticity. The internal energy of an elastic polymer network, however, exhibits a step-wise dependence on the applied strain-rates; it alters only at discrete values of strain-rates, every pair of which differs with a unique value that can be described as a *sensitivity parameter*. At loading rates lower than this parameter, the rate-effects of the polymeric network are absent.

1. Introduction

A characteristic feature of a rubber-like material at ambient temperatures is the ability to undergo large strains that are typically void of strain-rate effects and energy dissipation during cycles of loading at ambient temperatures (figure 1) [1–3]. In contrast, elastomers and other polymeric materials can experience significant hysteresis and energy dissipation during cycles of loading that are conducted at temperatures below their glass-transition temperature [4, 5]. The hysteresis in these materials can be attributed to small amounts of crystallite that can be present in the material and which can also be formed during the exothermic processes, particularly stretching [6, 7]. Interestingly, *in situ* monitoring of the microstructure of a rubber-like material during deformation indicates that crystallites can form during the loading stage and disappear upon release of the applied strain [7]. This infers the existence of certain reversible crystallites that can transform between the crystallite and amorphous phases depending on the local strain field of the network.

Semi-crystallite polymers, which contain more crystallites, can exhibit a rubber-like response at extremely low loading rates above the glass-transition temperature [8]. These networks, however, can exhibit rate-effects at higher

*Corresponding author. Email: patrick.selvadurai@mcgill.ca

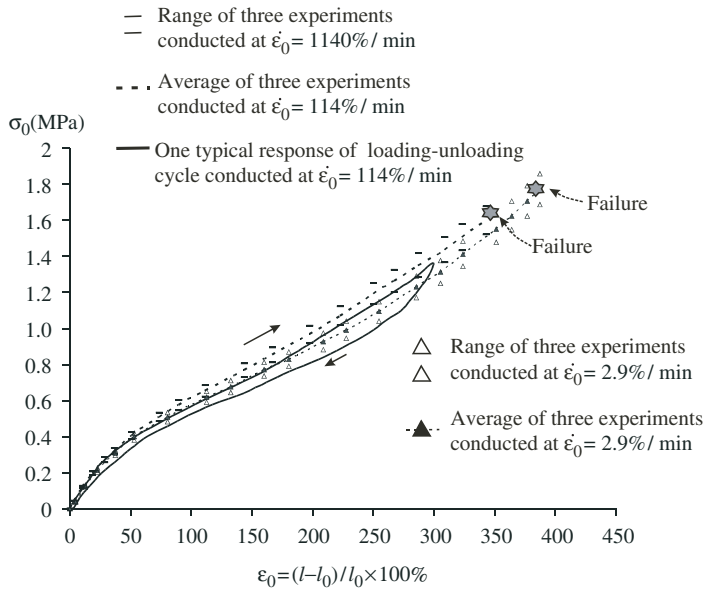


Figure 1. A rubber-like network showing negligible rate-effects [3].

loading rates [9]. Figure 2 illustrates the mechanical behaviour of plasticized poly(vinyl)chloride subjected to stretch loads at various rates [10, 11].

Rate-dependent phenomena were also observed in other research on poly(ethylene terephthalate) or PET material at temperatures slightly above its glass-transition temperature [12, 13] (see also figure 3a). Sweeney and Ward [9] and Matthews *et al.* [12] attributed this phenomenon to the rate-dependency of the chain entanglement density of the molecular structure. In the research conducted by Salem [14, 15], no volume fraction of the crystallite for the PET material was observed during deformation, until a certain critical strain was observed. It is of interest to note that the relationship between this critical strain and the shear rate correlates with that between the chain entanglement density and the shear rate at temperatures slightly above the glass-transition temperature, both of which follow a logarithmic variation (figure 3b).

It is well known that conformational mobility of the various polymeric networks can be affected by their slight crystallinity [16, 17]. From this observation, we can conclude that there can be some form of rate-sensitive transition between an amorphous phase and a crystallite phase within the polymeric network, acting as an additional contribution to its elasticity similar to the effects of chain entanglement. The transient phase (here referred to as *crystallite transient*) forms during a deformation and can readily transform into a crystallite when the conditions are favourable (accompanied by an *irreversible* heat generation resulting from the phase transformation). The crystallite can then transform back to the amorphous phase upon release of the local strain (where irreversible heat has not yet been generated). Evidence of the existence of such transient phases in a polymer during deformation has been confirmed experimentally [13, 18, 19] where the transient phase can either

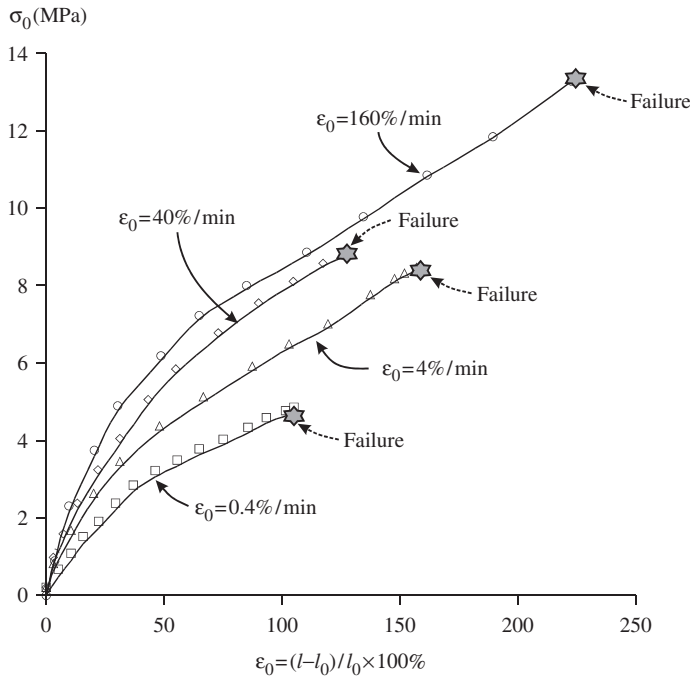


Figure 2. A plasticized PVC showing rate-dependencies [10].

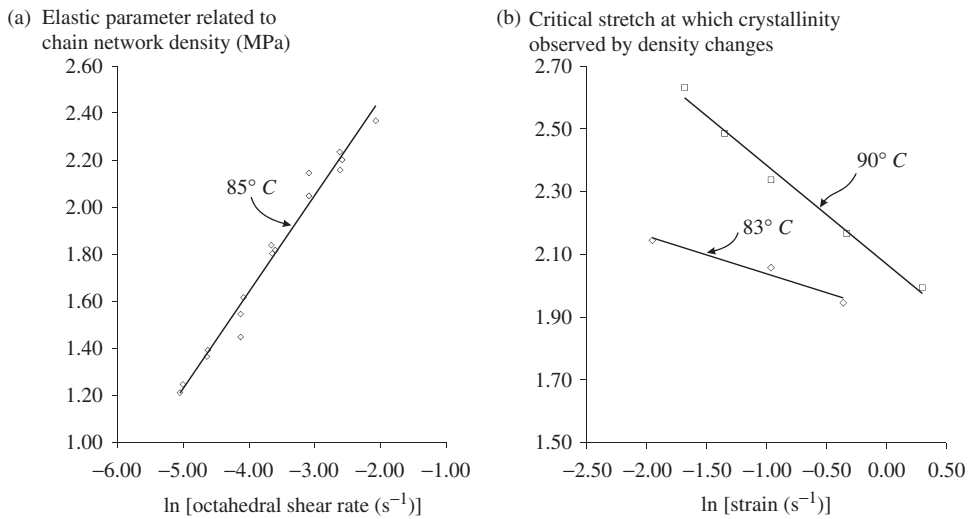


Figure 3. Rate-dependency of a PET network above glass-transition temperature. (a) Rate-dependency of parameter [12]. (b) Rate-dependency of critical stretch for the initiation of crystallinity [14].

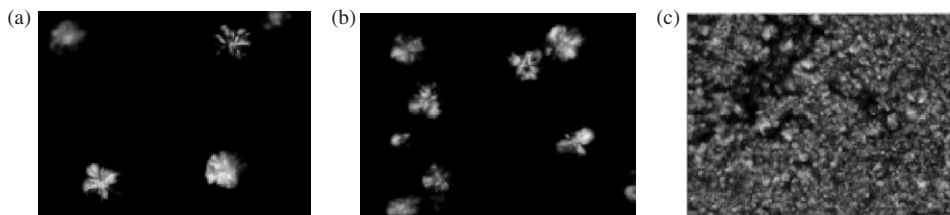


Figure 4. Effect of shear rate on the crystallization of a polypropylene melt [27]. (a) Without shear treatment (time = 60 min). (b) Shear treatment of 10 s at shear rate 0.5/s (time = 60 min). (c) Shear treatment of 10 s at shear rate 0.5/s (time = 60 min).

form or disappear based on the localized strain condition, similar to the phenomenon observed in rubber-like materials [7]. Owing to the presence of these transient phases, the conformation mobility can alter forming either a *rigid-amorphous phase* [20] or a *meso-amorphous phase* [21, 22], which contributes to the network elasticity [23]. In fact, the formation of the transient phase or *nucleus* is quite common during polymer melt crystallization [20, 24–26]. The effect of shear rate is mainly to increase the growth rate and density of the population of nuclei [27–29] (figure 4).

This paper attempts to formulate more rigorously the possibility of the existence of such rate-dependent networks by considering the activities of the *crystallite transient* inside the material. The appreciable differences in the rate-dependent behaviour between a pure rubber-like material and certain polymeric materials, such as PET, at temperatures above the glass-transition temperature, under an arbitrary deformation will be examined along with the thermodynamic constraints. It will be shown that crystallite transient exists naturally inside a rate-dependent elastic network that satisfies the first thermodynamic law.

2. Thermodynamic considerations for a rate-dependent elastic network

Consider a network structure with a certain crystallinity. The free energy of its amorphous phase is characterized by a function of $A(\Xi, D_{ij}, \vartheta)$ [30], where D_{ij} is a tensor of strain measurement; ϑ denotes absolute temperature of a thermodynamic state; $\Xi(t)$ is a state variable of the network structure [31]. In cases where breakage of the main chain molecules is involved, $\Xi(t)$ can be interpreted as a state of damage to the network [32]. In cases where the network behaviour is a function of the strain-rate, we can interpret $\Xi(t)$ as either the value or the absolute value of the strain-rate experienced by the material [10]. As such, the free-energy function A can then be written as [31–33]:

$$A = A(\Xi, D_{ij}, \vartheta). \quad (1)$$

The main factors influencing the free energy of this amorphous structure are the external work applied, the heat supplied and the behaviour of the crystallinity

contained in the network. We first assume that the contribution of crystallinity can be a function of the local strain field D_{ij} , the absolute temperature ϑ and a state variable Ξ such as strain-rate, i.e.

$$\Psi = \Psi(\Xi, D_{ij}, \vartheta). \quad (2)$$

The first law of thermodynamics prescribes local energy balance, which can be written in the incremental form:

$$\dot{A}(\Xi, D_{ij}, \vartheta) = T_{ij}\dot{D}_{ij} - \nabla \cdot \mathbf{h} + \dot{\Psi}(\Xi, D_{ij}, \vartheta) - \dot{\vartheta}S - \dot{S}\vartheta \quad (3)$$

where T_{ij} is a stress tensor; \mathbf{h} is a vector representing heat flux and S denotes entropy of a thermodynamic state. We now define a new energy function $W = A - \Psi$. Equation (3) can then be rewritten as

$$\dot{W}(\Xi, D_{ij}, \vartheta) = T_{ij}\dot{D}_{ij} - \nabla \cdot \mathbf{h} - \dot{\vartheta}S - \dot{S}\vartheta. \quad (4)$$

The second law of thermodynamics can be expressed by the local expression for the Clausius–Duhem inequality:

$$\dot{S} + \nabla \cdot \left(\frac{\mathbf{h}}{\vartheta} \right) \geq 0. \quad (5)$$

Combining equations (4) and (5), we have [30, 34]:

$$\left(S - \frac{\partial W}{\partial \vartheta} \right) \dot{\vartheta} + \left(T_{ij} - \frac{\partial A}{\partial D_{ij}} + \frac{\partial \Psi}{\partial D_{ij}} \right) \dot{D}_{ij} - \frac{\partial W}{\partial \Xi} \dot{\Xi} - \frac{1}{\vartheta} \mathbf{h} \cdot \nabla \vartheta \geq 0. \quad (6)$$

Since $\dot{\vartheta}$, \dot{D}_{ij} , $\dot{\Xi}$ are arbitrarily specified, equation (6) then requires that

$$\begin{aligned} S &= \frac{\partial W}{\partial \vartheta} \\ T_{ij} &= \frac{\partial A}{\partial D_{ij}} - \frac{\partial \Psi}{\partial D_{ij}} = \frac{\partial W}{\partial D_{ij}} \end{aligned} \quad (7)$$

and

$$-\frac{\partial W}{\partial \Xi} \dot{\Xi} - \frac{1}{\vartheta} \mathbf{h} \cdot \nabla \vartheta \geq 0. \quad (8)$$

Since $\dot{\Xi}$ and $\nabla \vartheta$ are independent, equation (6) requires [30, 32–36] that

$$\frac{\partial W}{\partial \Xi} \dot{\Xi} \leq 0. \quad (9)$$

This process, when equations (8) or (6) are trivially satisfied, is reversible [33]. In cases, however, where heat generation is involved, equation (8) will be strongly satisfied and the process is irreversible. The phase transformation from an amorphous phase to a crystallite phase, however, usually involves heat generation [37] and, therefore, is irreversible. It can be shown that, for a certain local temperature ϑ , the constraint (9) imposed by the second law of thermodynamics can be trivially satisfied if the crystallite transient, which does not transform into a crystallite, is present.

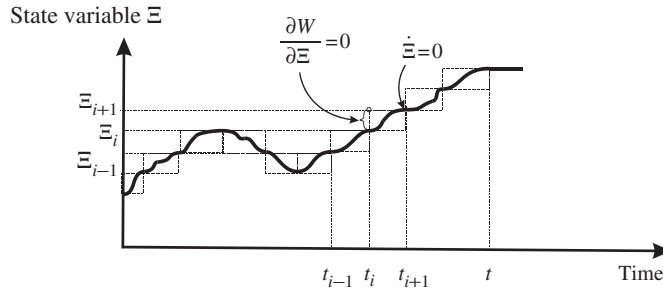


Figure 5. A discretized evolution of a state variable.

The first fundamental assumption we make is that, for any fixed strain state D_{ij} , W is a *continuous function* of the state variable Ξ . As such, the dependency can be either positive or negative. For a continuous evolution of the state variable $\Xi(t)$ with time t , there will be a corresponding evolution of the internal energy W .

Let us first consider those intervals of Ξ (say $\Xi \in [\beta_0, \beta_1]$) where $\partial W/\partial \Xi \geq 0$. For time intervals where $\dot{\Xi} < 0$, the constraint (9) imposed by the second law of thermodynamics can be automatically satisfied. We can now focus on the time intervals where $\dot{\Xi} \geq 0$; following Septanika and Ernst [31] we can discretize the history (where $\dot{\Xi} \geq 0$) into a series of step-intervals $t \in (t_i, t_{i+1})$, where $i=0, 1, 2, \dots$ are integers. It should be noted that at the transition between each interval (at $t = t_i$), the slope of $\Xi = \Xi(t)$ with respect to time t vanishes (figure 5), i.e.

$$\dot{\Xi} = 0 \quad \text{at } t = t_0, t_1, \dots, t_i. \quad (10)$$

At time $t \in (t_i, t_{i+1})$, however, $\dot{\Xi} \geq 0$. It is an unusual finding that the rate of change of Ξ vanishes at certain points for an arbitrary history of $\Xi = \Xi(t)$; this phenomenon is associated with the reduced deformability of the local network associated with the formation of the crystallite transient and will be discussed later. We can now proceed to establish the results when such a discretization is permitted.

At time $t \in (t_i, t_{i+1})$, the second thermodynamic requirement (9) prescribes that:

$$\frac{\partial W}{\partial \Xi} = 0 \quad \text{at } t \in (t_i, t_{i+1}); \quad (i = 0, 1, 2, \dots) \quad \text{for fixed } D_{ij}, \vartheta \quad (11)$$

or correspondingly,

$$W(\Xi, D_{ij}, \vartheta) = \text{constant}; \quad \Xi \in (\Xi_i, \Xi_{i+1}) \quad \text{for fixed } D_{ij}, \vartheta. \quad (12)$$

Combining (10) and (11), the second law of thermodynamics from time t_{i-1} to t_{i+1} can be trivially satisfied provided:

$$\frac{\partial W}{\partial \Xi} \dot{\Xi} = 0 \quad \text{for fixed } D_{ij}, \vartheta \quad (13)$$

which implies that the process is reversible [33].

Now let us consider that the dependence of the internal energy function W on the internal variable Ξ is significant from time t_{i-1} to t_{i+1} . (If the dependence of the energy function W on the internal variable Ξ is insignificant, the second law

of thermodynamics, implied by (13), is automatically satisfied with $\partial W/\partial \Xi = 0$.) Therefore, energy W differs at levels of Ξ_i ($i=0, 1, 2, \dots$), i.e.:

$$W(\Xi_i) < W(\Xi_{i+1}); \quad (i = 0, 1, 2, \dots) \quad \text{for certain } D_{ij}, \vartheta. \quad (14)$$

We note, however, that a discrepancy with (12), arises when $(\Xi_{i+1} - \Xi_i) \rightarrow \infty$, which infers that the energy function W has no dependency on Ξ . In order to resolve this discrepancy, we introduce the concept of a *sensitivity parameter* Ξ_c into the description of the crystallized network such that the energy W differs at two material states that have a difference larger than Ξ_c , i.e.:

$$W(\Xi_i) < W(\Xi_i + \Xi_c) \quad \text{for certain } D_{ij}, \vartheta \quad (15)$$

or

$$W(\Xi_i + \delta, D_{ij}, \vartheta) = \begin{cases} W(\Xi_i, D_{ij}, \vartheta); & 0 \leq \delta < \Xi_c \\ W(\Xi_i + \Xi_c, D_{ij}, \vartheta); & \delta \geq \Xi_c \end{cases} \quad (16)$$

The existence of the critical *sensitivity parameter* Ξ_c for the material becomes our second fundamental assumption.

In order for both equations (12) and (16) to be satisfied, it must be true that

$$\Xi_{i+1} - \Xi_i \geq \Xi_c. \quad (17)$$

Let us first assume that $\Xi_{i+1} - \Xi_i > \Xi_c$, in this case there is a positive value $\tilde{\beta} > 0$ such that $\Xi (= \Xi_i + \Xi_c + \tilde{\beta}) < \Xi_{i+1}$. From (16), we then have

$$W(\Xi, D_{ij}, \vartheta) = W(\Xi_i + \Xi_c, D_{ij}, \vartheta). \quad (18)$$

Since $\Xi \in (\Xi_i, \Xi_{i+1})$, from (12), we have

$$W(\Xi, D_{ij}, \vartheta) = W(\Xi_i, D_{ij}, \vartheta). \quad (19)$$

The discrepancy between equations (15), (18) and (19) for certain D_{ij} and ϑ then allows us to state that

$$\Xi_{i+1} - \Xi_i = \Xi_c \quad (20)$$

or

$$\Xi_i = \Xi_0 + i\Xi_c \quad (21)$$

where Ξ_0 is the original state of the network. At intervals of Ξ (say $\Xi \in [\beta_1, \beta_2]$) where $\partial W/\partial \Xi \leq 0$, similar comments to (21) can be addressed. A more general form of (21) then becomes

$$\Xi_i = \Xi_0 + m\Xi_c \quad \text{where } m = \dots -2, -1, 0, 1, 2, \dots \text{ is an integer.} \quad (22)$$

The result (equation (22)), therefore, states that the internal energy function W actually shows a *continuous step-wise* dependency on the state variable Ξ . While the internal energy function in the form of $W(\Xi, D_{ij}, \vartheta)$ is *continuous*, it can only alter at certain discrete state variables of $\Xi_0, \Xi_1 \dots \Xi_m$ where $\partial W/\partial \Xi \neq 0$ and $\Xi = 0$. The difference between any two discrete states is then characterized by a *sensitivity parameter* Ξ_c (figure 6). This is similar to the concepts of *natural units* or *quanta*

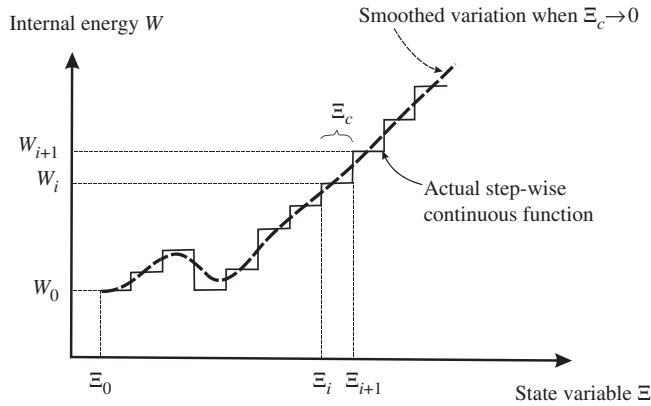


Figure 6. A step-wise internal energy function.

discovered by Planck [38] in the study of black-body radiation, the discrete energy levels around the hydrogen atom interpreted by Bohr [39], and the discrete molecular states introduced by Einstein [40]. More recent work conducted by Pugno and Puoff [41] showed both experimentally and theoretically that certain materials and structures at a nanoscale could exhibit quantized strength.

The question that still remains is, however, what physical mechanism drives such a step-wise evolution pattern? To answer this, we need to interpret the state variable as the strain-rate $\dot{\gamma}_0$, where γ_0 is a generalized strain defined in terms of the local strain field D_{ij} , i.e.:

$$\gamma_0 = g(D_{ij}). \quad (23)$$

Sweeney and Ward [9] and Matthews *et al.* [12] defined the strain-rate $\dot{\gamma}_0$ as the octahedral shear rate. Their definition of strain-rate can be reduced to the infinitesimal shear rate multiplied by a constant when the infinitesimal strain measurement is used. Selvadurai and Yu [10] defined the strain-rate $\dot{\gamma}_0$ in terms of three principal stretch rates by considering an equal contribution from each direction while neglecting the contribution of those directions where principal stretches are less than unity. The strain-rate in such a definition reduces to the normal strain-rate ϵ_0 for uniaxial states. Such a definition of strain-rates tends to agree with the observation that the crystallite actually orients along the principal directions during a biaxial test and the intensity of crystallite population in a specimen is highest in regions subjected to equi-biaxial stretching [42].

Now we consider a jump of strain-rate from a state of γ_0^i to γ_0^{i+1} at time $t \in (t_i, t_{i+1}]$; there will be corresponding alterations in the generalized stress τ_0 defined in terms of the local stress field T_{ij} such that

$$\tau_0 d\gamma_0 = T_{ij} dD_{ij} = \frac{\partial W}{\partial D_{ij}} dD_{ij} = dW \quad (24)$$

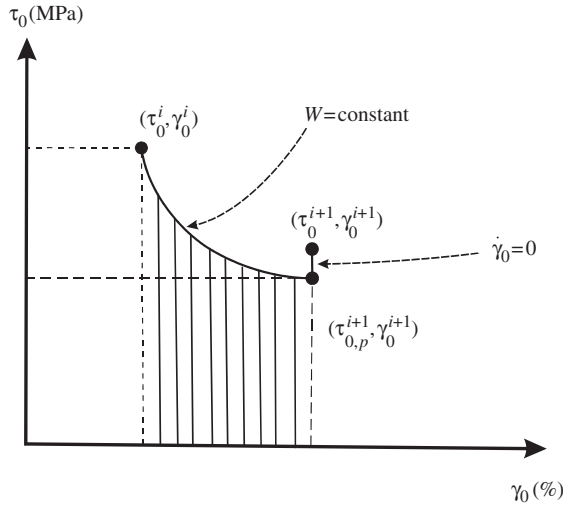


Figure 7. An allowable stress evolution between discrete states.

or

$$\tau_0 = \frac{\partial W}{\partial \gamma_0}. \quad (25)$$

According to equation (11), the energy W remains unaltered at $t \in (t_i, t_{i+1})$. Therefore, the evolution of stress at $t \in (t_i, t_{i+1})$ follows a path where $W = \text{constant}$, resulting in an intermediate stress state $(\tau_{0,p}^{i+1}, \gamma_0^{i+1})$ (figure 7). To illustrate this, we can interpret τ_0 as the shear stress and γ_0 as the shear strain in the infinitesimal elastic theory. The path of the constant level of energy W becomes $W = G\gamma_0^2/2 = \tau_0\gamma_0/2 = \text{constant}$, where G is the shear modulus. The effect of the evolution from (τ_0^i, γ_0^i) to $(\tau_{0,p}^{i+1}, \gamma_0^{i+1})$, however, results in external work $\int_{t=t_i}^{t=t_{i+1}} \tau_0 d\gamma_0$ being applied on the network (see the shaded area in figure 7). A certain amount of heat should, therefore, be generated to balance equation (4). The generation of heat, however, contradicts our former analysis for a reversible process as suggested by equation (13). We, therefore, require an alternative explanation; if we assume that one of the two terms A and Ψ that contribute to the definition of W actually has a negligible dependency on the local strain field D_{ij} during the evolution from (τ_0^i, γ_0^i) to $(\tau_{0,p}^{i+1}, \gamma_0^{i+1})$, it can consume a portion of external work $\int_{t=t_i}^{t=t_{i+1}} \tau_0 d\gamma_0$.

It then becomes possible that the activity of crystallite has a negligible dependency on the local strain condition, i.e.

$$\frac{\partial \Psi}{\partial D_{ij}} \rightarrow 0 \quad \left(\text{or } \frac{\partial \Psi}{\partial \gamma_0} \rightarrow 0 \text{ in figure 7} \right). \quad (26)$$

The stress determination in (7) then strictly becomes

$$T_{ij} = \frac{\partial A}{\partial D_{ij}}. \quad (27)$$

The best interpretation of the contribution of the portion of external work $\int_{t=t_i}^{t=t_{i+1}} \tau_0 d\gamma_0$ to Ψ on the crystallite activities is that it causes the formation and, particularly, the orientation of the *crystallite transient*. When such formation and orientation reach critical values, it becomes sufficient that conformation mobility of the proximate amorphous phase reduces [16, 17, 20]. The local network then forms a more rigid amorphous phase such that the local deformability of the network structure reduces [20]. As the local deformability of the network reduces to a minimum, the acceleration term of the local strain ($d\dot{\gamma}_0/dt$) vanishes. At this point, the energy level A alters, which contributes to the elasticity of the network. A series of strain-rates, when ($d\dot{\gamma}_0/dt$) vanishes, comprise a discrete pattern of strain-rates where the network elasticity shows a rate-dependency.

For a pure rubber-like material with no crystallite transient, however, there is no mechanism that allows the discretization of an arbitrary history $\Xi(t)$ into a series of step-intervals $t \in (t_i, t_{i+1})$, the transition between which Ξ vanishes. Therefore, a pure rubber-like material is strictly insensitive to the state variable Ξ , i.e.:

$$\frac{\partial W}{\partial \Xi} = 0. \quad (28)$$

This proves that in general, pure rubber-like materials are insensitive to strain rate effects.

3. Rate-independent processes

The level of free energy A alters at discrete strain-rates $\pm\dot{\gamma}_c, \pm 2\dot{\gamma}_c, \dots, \pm m\dot{\gamma}_c$, where m is an integer. When the local strain-rate is extremely low such that $|\dot{\gamma}_0| < \dot{\gamma}_c$, the network shows no rate-dependency (i.e. $\partial W/\partial \dot{\gamma}_0 \rightarrow 0$). When no phase transformation is involved, the polymeric network shows a pure rubber-like response [43]. Otherwise, the network crystallizes at a rate similar to the quiescent condition. The relation between the internal function and the strain-rate can then be written as follows:

$$W = \begin{cases} W(\dot{\gamma}_c, D_{ij}, \vartheta); & |\dot{\gamma}_0| \leq \dot{\gamma}_c \\ W(\dot{\gamma}_0, D_{ij}, \vartheta); & |\dot{\gamma}_0| > \dot{\gamma}_c \end{cases} \quad (29)$$

A similar condition holds when the strain-rate is extremely large (i.e. $\dot{\gamma}_0 \rightarrow \pm\infty$) such that from (9) we obtain $\partial W/\partial \dot{\gamma}_0 \rightarrow 0$. During high speed loading, the network, therefore, shows no signs of crystallization [18, 19]. On the other hand, the local distribution of the strain-rate inside the entire network might not necessarily be uniform. As such, the crystallite transient can either form or disappear when local conditions are favoured. This can result in diffused X-ray diffraction patterns of a deformed network at moderate strain-rates [19].

4. Conclusions

The existence of a rate-dependent elastic network is discussed in association with the activity of the crystallite transient within a polymer. The externally applied strain can cause the formation and, particularly, the orientation of crystallite transient. As such, the local deformability of a polymer network can reduce to an extreme value when the acceleration term of its local strain vanishes and the conformation mobility of the network alters, which subsequently affects its elasticity. Since the formation and orientation of the crystallite transient is rate-sensitive, the elasticity of the network can also exhibit rate-effects. The thermodynamic analysis further demonstrates that the elasticity of the network actually shows a step-wise dependence on the strain-rate. The internal energy of the network only alters at discrete values of strain-rates, every pair of which differs with the sensitivity parameter. At loading rates lower than this sensitivity parameter, the rate-effects of the polymer network are absent and the polymer exhibits a pure rubber-like response.

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