Effects of Crosslink Density on Relaxation Modulus of Aged Polymer

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Abstract. In order to study the effects of crosslink density on relaxation modulus of aged polymer materials, an analytic expression was obtained based on the deformation kinetics model of polymer and the assumption that the Helmholtz free energy of materials can be represented as a quadratic form of internal variables on isothermal condition. This expression shows that crosslink density has effects on equilibrium modulus, transient modulus and relaxation rate in different ways. In a special case, a crosslink density-time corresponded principle exists when the polymer is lightly cross-linked and the crosslink density has a common influence on equilibrium and transient parts of relaxation modulus.

1. Introduction
Most of the polymers can take place chemo-thermomechanical ageing during their service life due to different environment influences such as oxygen, radiation, ozone and mechanical stresses [1]. As it is well known, ageing due to environmental influences plays a major role in polymers properties. So it gets more and more important to understand and predict there properties change during their whole lifetime. It is widely that the network of polymer undergoing crosslink and scission process is the main mechanism of oxidation-aged polymer. The result of crosslink and scission reaction is the change of mechanical properties of polymer [2], such as relaxation modulus, elongate ratio and fracture strength, and the change of chemical or structure properties such as the crosslink density, gel fraction, fourier transform infrared spectroscopy. A large amount of experiments have shown that there is a good coherence between mechanical and chemical properties. So it is quite convenient to represent the ageing level of polymer by using the change of chemical properties, such as crosslink density and gel fraction [3]. However, most of relationships were established by fitting a pre-given formula which lacking of objectivity. This paper presents a relationship between crosslink density and relaxation modulus based on the viscoelastic deformation kinetics [4] and irreversible thermodynamics of internal variables.

2. Viscoelastic deformation kinetic
Under the assumption of small deformation, the Helmholtz free energy of polymer can be represented as

\[ \varphi = \varphi(\varepsilon, T, q^r) \quad (r = 1, 2, ..., n) \]

(1)
Where \( \varepsilon \) is the strain tensor, \( T \) is absolute temperature, and \( q \) is the internal variables used to describe the motion of macromolecular.

It is well known that, the motion of macromolecular is usually impeded by surrounding macromolecules. In view of energy, the constraints provided by surrounding molecules can be considered as an energy trap, and a molecular have to possess amount of energy to get rid of this tap. According to Boltzmann principle, the probability of a molecular in the energy state \( e_i \) is equal to \( g_i \exp(-e_i/kT) \), here \( g_i \) is the weighting coefficients and \( k \) is the Boltzmann constants.

If the height of energy trap is \( e_i' \), and the total number of molecular is \( N \), the total number of activated state is

\[
N' = N\alpha e^{-\varepsilon^2/kT} \sum_{i,\varepsilon > 0} \alpha e^{-\varepsilon/kT}
\]

(2)

Where \( e_i' = e_i - e_0 \), \( \alpha = \sum_{i} g_i e^{-e_i/kT} \).

Without external loadings, the energy trap is symmetric in all directions, thus there is no flow of molecules in macro-scale. In the case of external loading, the energy trap will tilt in the direction of loading. It is reasonable to assume that the tilt degree is linearly proportional to the thermodynamics flow, namely

\[
e' = e'_{\phi} \pm \phi_{\gamma} = e_0 \pm \phi_{\gamma} \frac{\partial \varphi}{\partial q}
\]

(3)

Where \( e' \) is the height of energy trap after tilting, and \( \phi_{\gamma} \) is a material constant.

The net number of molecules that partake in the forward motion is

\[
\Delta N_{\phi} = 2\Delta N \sinh \left( \frac{\varphi_{\gamma}}{kT} \frac{\partial \varphi}{\partial q} \right) e^{-\varepsilon/kT} \sum_{i,\varepsilon > 0} g_i e^{-e_i/kT}
\]

(4)

If \( \lambda_{\gamma} \) is the average time taken by a molecule to transverse a distance \( \lambda_{\gamma} \) across a trap, then the net average velocity of molecules in the conventional forward direction is

\[
v_{\phi} = \frac{\Delta N_{\phi} \lambda_{\gamma}}{N \tau_{\gamma}}
\]

(5)

Substituting Eq.(5) into (6) arrives at the so-called viscoelastic deformation kinetic equation

\[
\frac{\varepsilon}{\varepsilon'_{\phi}} + K_{\phi} \sinh \left( \frac{K_{\phi} \varepsilon}{K_{\phi} \varepsilon'} \right) = 0
\]

(6)

where

\[
K_{\phi} = \frac{2\alpha \lambda_{\gamma}}{\tau_{\gamma}} \sum_{i,\varepsilon > 0} g_i e^{-e_i/kT}, \quad K_{\phi} = \frac{\gamma_{\gamma}}{kT}
\]

When \( K_{\phi} \) is smaller enough, the above Eq.(6) can be linearized as
3. Relaxation behavior of cross-linked polymer

In terms of cross-linked polymer, the molecule can be classified into two parts, one is chemical crosslink chains, and the other is physical entanglement chains. The entanglement chains have much more motion freedom than cross-linked one. If $\nu_c$ and $\nu_e$ are used to represent the crosslink density and entanglement density, and $M_c$ and $M_e$ are average molecular weight, respectively. Then we have

$$\nu_c M_c + \nu_e M_e = \rho$$  \hspace{1cm} (8)

Where $\rho$ is the density of polymer.

On the condition of constant stain loading, there are relaxation motions of crosslink chains and entanglement chains. If $e^{c''}$ and $e^{e''}$ are used to represented the energy needed to get rid of the hiders provided by surrounding crosslink chains and entanglement chains. As a first approximation,

$$e^{c''} = e_0^{c''} + \gamma_c \Delta\nu_c, \quad e^{e''} = e_0^{e''} + \gamma_e \Delta\nu_e$$  \hspace{1cm} (9)

where and are material constants. $e_0^{c''}$ and $e_0^{e''}$ are the heights of energy trap at initial state. $\Delta\nu_c$ and $\Delta\nu_e$ are the changes of crosslink density and entanglement density relative initial state.

In general, ageing almost has no influence on the density of material. Thus the right hand of Eq.(8) can be regarded as a constant. Substituting Eq.(8) into (9) gets

$$e^{c''} = e_0^{c''} - \bar{\gamma}_c \Delta\nu_c, \quad \bar{\gamma}_c = \gamma_c \frac{M_c}{M_e}$$  \hspace{1cm} (10)

If $q^{c,i}$ and $q^{e,i}$ are used as internal variables to represent the motions of crosslink chains overcome the hinders provided by surrounding crosslink chains and entanglement chains, then the evolution Eq.(6) can be rewritten as [5]

$$\phi_{x} + K_{x}^{c'} K^{c''} \frac{\partial \phi}{\partial q^{c,i}} = 0$$  \hspace{1cm} (11)

$$\phi_{e} + K_{e}^{c'} K^{e''} \frac{\partial \phi}{\partial q^{e,i}} = 0$$  \hspace{1cm} (12)

where $K_{x}^{c'}$, $K_{x}^{e'}$, $K_{x}^{c''}$ and $K_{x}^{e''}$ are the material constants which are independent of change of crosslink density. Are material parameters which are related to the change of crosslink density, given as follows:

$$K_{x}^{c'} = \frac{2a x^{c'}}{\tau_x^{c'}} \exp \left( - \frac{\delta^{c''}}{kT} \right) \sum_{\lambda d' ; g'} g' \exp \left( - \frac{\delta^{c''}}{kT} \right)$$

$$K_{x}^{e'} = \frac{2a x^{e'}}{\tau_x^{e'}} \exp \left( - \frac{\delta^{e''}}{kT} \right) \sum_{\lambda d' ; g'} g' \exp \left( - \frac{\delta^{e''}}{kT} \right)$$

$$K_{x}^{c''} = \frac{\gamma^{c''}}{kT}, \quad K_{x}^{e''} = \frac{\gamma^{e''}}{kT}$$
\[ K^{c\epsilon} = \frac{v_c M_c}{\rho} \exp(-\gamma_c \Delta v_c) \]
\[ K^{e\epsilon} = \left(1 - \frac{v_e M_e}{\rho}\right) \exp\left(\frac{\gamma_e \Delta v_e}{1}\right) \]

Where \( r^{c\epsilon} \) is average time for a crosslink chain to overcome the hinders provided by surrounding crosslink chains with a motion distance of \( \lambda^{c\epsilon} \), and \( r^{e\epsilon} \) is the average time a crosslink chain to overcome the hinders provided by surrounding entanglement chains with a motion distance of \( \lambda^{e\epsilon} \).

In the same way, if \( q^{c\epsilon}_i \) and \( q^{e\epsilon}_i \) are used as internal variables to represent the motions of entanglement chains overcome the hinders provided by surrounding crosslink chains and entanglement chains, then we have

\[ q^{c\epsilon}_i + K^{c\epsilon}_{c\epsilon} K^{c\epsilon} \sinh \left(K^{c\epsilon}_{c\epsilon} \frac{\partial \phi}{\partial q^{c\epsilon}_i}\right) = 0 \]  
\[ q^{e\epsilon}_i + K^{e\epsilon}_{e\epsilon} K^{e\epsilon} \sinh \left(K^{e\epsilon}_{e\epsilon} \frac{\partial \phi}{\partial q^{e\epsilon}_i}\right) = 0 \]

where the coefficients are same with one in Eq.(11) and (12), except the replacement of \( c \) with \( e \) in subscript.

4. Aged relaxation modulus

For convenience, let \( m_1 = m_2 = 1 \) and \( q_1 = q^{c\epsilon}_1 \), \( q_2 = q^{c\epsilon}_2 \), \( q_3 = q^{e\epsilon}_3 \) and \( q_4 = q^{e\epsilon}_4 \). As usual, the Maxwell model in Fig.1 is used to represent the viscoelastic behavior of polymer.

![Figure 1. Maxwell model.](image)

The Helmholtz free energy is given as

\[ \phi = \frac{1}{2} a_i \varepsilon^2 + \frac{1}{2} \sum_{i=1}^4 a_i (\varepsilon - q_i)^2 \]  

Where \( a_i (i = 0,1,2,3,4) \) are the stiffness of springs in Fig.1.

Substituting Eq.(15) into (13), we have
\[ q_i = \varepsilon \left[ 1 - \exp(-\beta_i t) \right] \quad (i = 1, 2, 3, 4) \]  \hspace{1cm} (16)

where

\[ \beta_i = \frac{2 \lambda_i v_i M_i}{\varepsilon_i^r} \exp \left( -\frac{e_i^c r}{kT} - \gamma_i \Delta \epsilon_i \right) \]
\[ \beta_2 = \frac{2 \lambda_2 v_2 M_2}{\varepsilon_2^r} \left( 1 - \frac{v_2 M_2}{\rho} \right) \exp \left( -\frac{e_2^c r}{kT} + \gamma_2 \Delta \epsilon_2 \right) \]
\[ \beta_3 = \frac{2 \lambda_3 v_3 M_3}{\varepsilon_3^r} \exp \left( -\frac{e_3^c r}{kT} - \gamma_3 \Delta \epsilon_3 \right) \]
\[ \beta_4 = \frac{2 \lambda_4 v_4 M_4}{\varepsilon_4^r} \left( 1 - \frac{v_4 M_4}{\rho} \right) \exp \left( -\frac{e_4^c r}{kT} + \gamma_4 \Delta \epsilon_4 \right) \]

According to the dissipative inequality of thermodynamics, the stress-strain relation can be written as

\[ \sigma = \frac{\partial \phi}{\partial \varepsilon} = a_0 + \sum_{i=1}^{4} a_i \exp(-\beta_i t) \varepsilon \]  \hspace{1cm} (17)

Then the relaxation modulus is given as

\[ E(t) = a_0 + \sum_{i=1}^{4} a_i \exp(-\beta_i t) \]  \hspace{1cm} (18)

For lightly cross-linked polymer, \( \beta_1 \) and \( \beta_3 \) approach to zero and the main obstacles for a molecular motion come from the entanglement chains.

On the other hand, according to the theory of rubber elasticity, there is a relationship between shear modulus and crosslink density, namely

\[ G = \nu RT \]  \hspace{1cm} (19)

Where \( R \) is the gas constant. For comparison, the above equation can be rewritten as

\[ G(\nu) = \nu_0 RT \left( 1 + \frac{\nu - \nu_0}{\nu_0} \right) = G_0 (1 + \Delta \nu') \]  \hspace{1cm} (20)

Where \( G_0 \) and \( \nu_0 \) are the shear modulus and crosslink density at the initial state, and \( \Delta \nu' \) is the relative change of crosslink density.

On the basis stated above, we assume that the stiffness of springs in Fig.1 fulfill those relationship

\[ a_0(\nu) = a_0^0 (1 + \Delta \nu') \]  \hspace{1cm} (21)
\[ a_i(\nu) = a_i^0 (1 + \chi_i \Delta \nu') \quad (i = 1, 2, 3, 4) \]  \hspace{1cm} (22)

Where \( a_0^0 \) and \( a_i^0 \) are the stiffness of springs when crosslink density is \( \nu_0 \), and \( \chi_i \) is a weight coefficient taking value in \([-1, 1]\). If \( \chi_i > 0 \), it means that the obstacle come from crosslink chains is dominant. While \( \chi_i < 0 \), it means the most obstacles come from entanglement chains.
Substituting Eq.(21) and (22) into (18), and consider the lightly cross-linked circumstance, then we have

\[
E(t, v) = a'^0 (1 + \Delta v') + \sum_{i=1}^{2} a'^i (1 + \chi_i \Delta v') \exp(-a'_{\Delta i} \tau_i)
\]

where

\[
\tau_i = \frac{2 \lambda \epsilon_{\nu} a_{\nu}}{\tau_{\epsilon_{\nu}}} \left[1 - \frac{v M}{\rho}\right] \exp\left(-\frac{\epsilon_{\nu}}{kT}\right)
\]

\[
\tau_{\Delta i} = \frac{2 \lambda \epsilon_{\nu} a_{\nu}}{\tau_{\epsilon_{\nu}}} \left[1 - \frac{v M}{\rho}\right] \exp\left(-\frac{\epsilon_{\nu}}{kT}\right)
\]

\[
a'_{\Delta i} = \exp\left(\frac{\chi_i \Delta v_{\nu}}{kT}\right)
\]

It can be seen from above equation that crosslink density has influences on equivalent modulus, transient modulus and relaxation rate. Especially, when \( \chi_i \to 1 \), Eq.(23) can be rewritten as

\[
E(t, v) = a'^0 \left[a'^0 + \sum_{i=1}^{2} a'^i \exp(-a'_{\Delta i} \tau_i)\right]
\]

\[
= a'^0 E(a'^0 t, v_0)
\]

where \( a'_{\Delta i} = 1 + \Delta v' \). The above equation shows that, in a double logarithm coordinate, by a vertical and a horizontal translation, the relaxation modulus curves of different crosslink density will coincide together. In other words, a crosslink density-time superposition principle exists in lightly cross-linked polymer.

5. Validation

For validation the model proposed above, two kinds of materials were used. One is the natural rubbers, and the other is solid composite propellant. The latter is lightly cross-linked, while the former have a higher level of crosslink density.

5.1. Relaxation behavior of natural rubbers

Relaxation modulus of natural rubbers with different crosslink density [6], given in Table 1, was shown in Fig.2, and the parameters in Eq.(18) is shown in Table 2. It can be seen that the equivalent modulus \( E_{\infty} \) and transient modulus \( E_i \) and the relaxation time \( \tau_i \) are all dependent on crosslink density. This phenomenon is consistent with Eq.(23).

| \( v/(10^{-3} \text{molcm}^{-1}) \) | F | G | H | I | J |
|----------------------------------|---|---|---|---|---|
| \( E_{\infty}/\text{MPa} \)       | 0.585 | 0.771 | 0.972 | 1.341 | 1.686 |
Figure 2. Transient response $\frac{E(t)}{E_\infty} - 1$ versus log time.

Table 2. Transient modulus and relaxation time.

| $E_i$ / MPa | $\tau_j$ / $10^2$ s |
|-------------|---------------------|
| $E_1$       | $E_2$               | $E_3$       | $E_4$       | $\tau_1$ | $\tau_2$ | $\tau_3$ | $\tau_4$ |
| F           | 11.3                | 193.1       | 4348.3      | 223327    | 8        | 6.1      | 4.5       | 6        |
| G           | 9                   | 138.8       | 2776.6      | 163923    | 6.4      | 5.15     | 3.9       | 4.2      |
| H           | 10.6                | 146.2       | 2569        | 170112    | 5.6      | 3.9      | 2.5       | 3.1      |
| I           | 9.5                 | 142.1       | 2241.9      | 87220     | 4.2      | 2.9      | 1.6       | 2        |
| J           | 7.9                 | 64.6        | 926.1       | 41170     | 2.8      | 2.2      | 1.4       | 1.5      |

5.2. Relaxation behavior of solid composite propellant

The material used is hydroxyl-terminated polybutadiene based (HTPB) composite propellant with different ageing time under temperature of 50℃, 60℃ and 70℃. The crosslink density was tested on a nuclear magnetic resonance (NMR) spectroscopy.

The dynamic modulus of aged propellants with different crosslink densities was given in Fig.3. It can be seen that, by only a vertical transform, relaxation curves of different crosslink densities can be overlapped. It seems that crosslink density has almost no influence on the relaxation rate of material. This may be due to the high fraction of filled particles. It is well known that the filled particles can absorb the chain nearby the particles, and the obstacle for a chain to take place motion is mainly the particles rather than cross-linked chains or entanglement chains.

Figure 3. Storage modulus versus frequency with different crosslink densities.
6. Conclusion
Based on the viscoelastic deformation kinetic, an explicit and analytical formula which describe the relation between relaxation modulus and crosslink density is proposed. It shows that the crosslink density has influences on long-term and transient parts of relaxation modulus and relaxation rate. For lightly crosslinked polymer, a crosslink density-time superposed principle exists only crosslink density has a common influence on long-term and transient parts of relaxation modulus. As for particle filled lightly cross-linked polymer, for example, the HTPB solid composite propellants, a vertical transform is enough to overlap the relaxation cures with different crosslink densities. Because of the absorb interaction between filled particles with matrix, the main obstacle for the motion of a chain is the particles’ absorb interaction, rather than the impediments provided by crosslinked chains and entanglement chains.

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