

Nonlinear Viscoelastic Constitutive Equation of Solid Polymers: Irreversible Thermodynamic Theory

조광수, 김상용

서울대학교 섬유고분자공학과

1. Introduction

There has been a lot of efforts to develop a constitutive equation for solid polymers which can show yield, strain softening, rate sensitivity, temperature effect and a curved unloading path [1-6]. Before these efforts, there were attempts to understand the mechanism of the yield of solid polymers [7-14].

We have developed a new nonlinear viscoelastic constitutive equation of solid polymers, which can predict the yield behavior, describe rate- and temperature-sensitivity of stress-strain curves and suggest new mechanism of the yield. Since our theory is based on the irreversible thermodynamics, we have not assumed artificially simplified molecular motions or structures such as disclination [10] and dislocation [11]. Our theory also includes the previous theories [2, 3] as a special case.

2. Introduction to Irreversible Thermodynamics

We use a summation convention over repeating index. It is assumed that the rate of

specific entropy, s is

$$T \frac{ds}{dt} = T \frac{ds_{flow}}{dt} + T \frac{ds_{in}}{dt} \quad (1)$$

where T is the temperature, $T ds_{flow}/dt$ is the rate of entropy due to entropy flux from the surrounding volume elements and $T ds_{in}/dt$ is the rate of entropy production due to irreversibility of the system.

From the second law of thermodynamics the rate of entropy production must be non-negative.

$$T \frac{ds_{in}}{dt} \geq 0 \quad (2)$$

We assume Fickian approximation (Fourier heat conduction law) for heat flux:

$$h_i = -k_{ij} \frac{\partial T}{\partial x_j} \quad (3)$$

From the definition of specific free energy

$$f(T, e_{ij}, q_{ij}^n) = u - Ts \quad (4)$$

where e_{ij} is the strain and q_{ij}^n are the internal variables, which stands for the measure of deviations from equilibrium. Combining the above equations in suitable ways, we have

$$s = -\frac{\partial f}{\partial T}, \quad \sigma_{ij} = \frac{\partial f}{\partial e_{ij}} \quad (5)$$

and

$$\frac{\partial f}{\partial q_{ij}^n} \frac{dq_{ij}^n}{dt} \leq 0 \quad (6)$$

3. Evolution Equations of Internal Variables

We assume isothermal conditions. We propose following evolution equations for internal variables:

$$\frac{dq_{ij}^n}{dt} = \gamma_n \left(\tilde{L}_{ijkl}^n e_{kl} - \tilde{M}_{ijkl}^n q_{kl}^n \right) \quad (7)$$

(no summation over n)

where

$$\gamma_n \equiv \exp\left(-\frac{\Delta E_n}{RT + W_n}\right) \quad (8)$$

$$\tilde{L}_{ijkl}^n = \tilde{L}_1^n \delta_{ij} \delta_{kl} + \tilde{L}_2^n \delta_{ik} \delta_{jl}$$

$$\tilde{M}_{ijkl}^n = \tilde{M}_1^n \delta_{ij} \delta_{kl} + \tilde{M}_2^n \delta_{ik} \delta_{jl}$$

Equation (8) states that material is assumed to be isotropic and internal variable, microstate strain tensors are symmetric. ΔE_n stands for activation energy, R is gas constant, and W_n is function of the deformation which can be expressed as the invariants of strain. We call them deformation work:

$$W_n \equiv \Omega_{ijkl}^n e_{ij} e_{kl} \quad (9)$$

where Ω_{ijkl}^n is positive definite 4th order tensor.

Following Valanis [15], we assume that the inequality of 2nd law of thermodynamics is

$$\frac{\partial f}{\partial q_{ij}^n} \frac{dq_{ij}^n}{dt} = -\sum_{n=1}^N b_{ijkl}^n \frac{dq_{ij}^n}{dt} \frac{dq_{kl}^n}{dt} \leq 0 \quad (11)$$

where $b_{ijkl}^n \equiv \tilde{b}_1^n \delta_{ij} \delta_{kl} + \tilde{b}_2^n \delta_{ik} \delta_{jl}$ is the viscosity tensor of 4th order. The interpretation of the tensor b_{ijkl}^n as a viscosity proposes the following formula:

$$b_{ijkl}^n \equiv \frac{b_1^n}{\bar{\epsilon}_0^n + (\bar{\epsilon})^{m_n}} \delta_{ij} \delta_{kl} + \frac{b_2^n}{\bar{\epsilon}_0^n + (\bar{\epsilon})^{m_n}} \delta_{ik} \delta_{jl} \quad (10)$$

where b_1^n and b_2^n are functions of the temperature and the strain, $\bar{\epsilon}_0^n$ is a material constant which guarantee the existence of zero-rate viscosity and

$$\bar{\epsilon} \equiv \sqrt{\frac{2}{3} \frac{de_{ij}}{dt} \frac{de_{ij}}{dt}} \quad (11)$$

is the effective strain rate and m_n is a material constant that stands for rate-sensitivity of the viscosity.

4. Specific Free Energy

We expand the specific free energy as a Taylor series about the reference temperature as follows

$$f = \frac{1}{2} A_{ijkl} e_{ij} e_{kl} + \frac{1}{2} \sum_{n=1}^N B_{ijkl}^n q_{ij}^n q_{kl}^n - C_{ijkl}^n q_{ij}^n e_{kl} \quad (12)$$

where

$$\mathfrak{R}_{ijkl} \equiv \mathfrak{R}_1 \delta_{ij} \delta_{kl} + \mathfrak{R}_2 \delta_{ik} \delta_{jl} \quad (13)$$

$$\mathfrak{R} = A, B^n, C^n$$

Since we expand the series about a reference temperature, the moduli A_{ijkl} , B_{ijkl}^n and C_{ijkl}^n are not dependent on the strain and the microstate strain. They may be decreasing functions of the temperature such as

If a material is stable, the moduli A_{ijkl} and B_{ijkl}^n are positive definite:

$$\mathfrak{R}_0 \equiv \mathfrak{R}_1 + \frac{1}{3}\mathfrak{R}_2 \geq 0, \quad \mathfrak{R}_2 \geq 0 \quad (\mathfrak{R} = A, B^n) \quad (14)$$

The second law of irreversible thermodynamics gives following formulas:

$$\frac{B_2^n}{\gamma_n \tilde{M}_2^n} = \frac{b_2^n(T, e_{mn})}{\tilde{e}_0^n + \tilde{e}^{m_n}} \quad (15)$$

$$\frac{B_1^n \tilde{M}_2^n - B_2^n \tilde{M}_1^n}{3\gamma_n \tilde{M}_0^n \tilde{M}_2^n} = \frac{b_1^n(T, e_{mn})}{\tilde{e}_0^n + \tilde{e}^{m_n}}$$

$$C_2^n = \frac{B_2^n \tilde{L}_2^n}{\tilde{M}_2^n} \geq 0 \quad (16)$$

$$C_0^n \equiv C_1^n + \frac{1}{3}C_2^n = \frac{B_0^n L_0^n}{M_0^n} \geq 0$$

$$\tilde{L}_2^n = \tilde{L}_2^n (\tilde{e}_0^n + \tilde{e}^{m_n}) \geq 0$$

$$\tilde{L}_0^n \equiv \tilde{L}_1^n + \frac{1}{3}\tilde{L}_2^n = \tilde{L}_0^n (\tilde{e}_0^n + \tilde{e}^{m_n}) \geq 0 \quad (17)$$

$$\tilde{M}_2^n = M_2^n (\tilde{e}_0^n + \tilde{e}^{m_n}) \geq 0$$

$$\tilde{M}_0^n \equiv \tilde{M}_1^n + \frac{1}{3}\tilde{M}_2^n = M_0^n (\tilde{e}_0^n + \tilde{e}^{m_n}) \geq 0$$

$$b_2^n = \frac{B_2^n}{\gamma_n \tilde{M}_2^n} \geq 0 \quad (18)$$

$$b_0^n = b_1^n + \frac{1}{3}b_2^n = \frac{B_0^n}{\gamma_n \tilde{M}_0^n} \geq 0$$

5. Constitutive Equation

Now we can calculate the stress tensor by the integration of the evolution equation:

$$\frac{dq_V^n}{dt} = 3\gamma_n (\tilde{e}_0^n + \tilde{e}^{m_n}) (L_0^n e_V - M_0^n q_V^n) \quad (19)$$

$$\frac{dp_{ij}^n}{dt} = \gamma_n (\tilde{e}_0^n + \tilde{e}^{m_n}) (L_2^n e'_{ij} - M_2^n p_{ij}^n)$$

(no summation over n)

where

$$p_{ij}^n \equiv q_{ij}^n - \frac{1}{3}q_V^n \delta_{ij}, \quad q_V^n \equiv q_{kk}^n \quad (20)$$

$$e'_{ij} \equiv e_{ij} - \frac{1}{3}e_V \delta_{ij}, \quad e_V \equiv e_{kk}$$

If we contrive a new variable which called internal time z_n ,

$$z_n(t) \equiv \int_0^t (\tilde{e}_0^n + \tilde{e}^{m_n}) \exp\left(\frac{-\Delta E_n}{RT + W_n}\right) ds \quad (21)$$

We take initial condition as $q_{ij}^n(0) = 0$ (for all n) and $e_{ij}(0) = 0$ for simplicity. Integrating the evolution equations of the internal time version, the stress is

$$\sigma_m(t) \equiv \frac{1}{3}\sigma_{kk} = K_E e_V(t) + \sum_{n=1}^N K_I^n \int_0^t e^{-3M_0^n [z_n(t) - z_n(\tau)]} \frac{de_V(\tau)}{d\tau} d\tau \quad (23)$$

$$\sigma'_{ij}(t) \equiv \sigma_{ij} - \sigma_m \delta_{ij} = G_E e'_{ij}(t) + \sum_{n=1}^N G_I^n \int_0^t e^{-M_2^n [z_n(t) - z_n(\tau)]} \frac{de'_{ij}(\tau)}{d\tau} d\tau$$

where

$$K_E \equiv A_0 - \sum_{n=1}^N K_I^n, \quad K_I^n \equiv \frac{L_0^n}{M_0^n} C_0^n \quad (24)$$

$$G_E \equiv A_2 - \sum_{n=1}^N G_I^n, \quad G_I^n \equiv \frac{L_2^n}{M_2^n} C_2^n$$

Equation (23) is identical to the formulas of Knauss and Emri [2] if we take $m_n = 0$ (for all n) and deformation work W_n as a function of stress invariant.

6. Yield Criteria and Mechanism

For mathematical simplicity, we consider only single mode, one-dimensional model and constant deformation rate such as $e = \dot{\epsilon} t$ where $\dot{\epsilon}$ is constant.

With the help of the theoretical results of Robertson[9], the experimental results of Theodorou and co-workers [16] and computer simulation of Jang and Jo [17], we propose the criterion of the yield as the maximum point of the rate of entropy production. This criterion gives following equation:

$$\tilde{\sigma} = G_E \tilde{e} + \frac{G_I \tilde{e}}{M\gamma\phi\tilde{e} - \tilde{\Omega}\tilde{e}^2} \quad (25)$$

where

$$\phi \equiv \frac{\tilde{e}_0 + |\dot{\tilde{e}}|^m}{\tilde{e}}, \quad G_E \equiv \left(A - \frac{L}{M} C \right) \quad (26)$$

$$G_I \equiv \frac{L}{M} C$$

and tilde means the point of the maximum rate of entropy production.

7. Conclusions

We have developed a nonlinear viscoelastic constitutive equation that includes the clock model of Knauss and Emri [2] as a special case. Our theory is based on the irreversible thermodynamics of the internal variables and is not an extension of the linear model by intuition.

We have started the theory from the viewpoint of irreversible thermodynamics and derived the yield equations only from the continuum theory.

8. Reference

- [1] Shay, Jr., R. M. and J. M. Caruthers, *J. Rheol.*, **30**, 781 (1986).
- [2] Knauss, W. G. and I. Emri, *Polym. Eng. Sci.*, **27**, 86 (1987).
- [3] Rendel, R. W., K. L. Ngai, G. R. Fong, A. F. Yee and R. J. Bankert, *Polym. Eng. Sci.*, **27**, 2 (1987).
- [4] Amoedo, J. and D. Lee, *Polym. Eng. Sci.*, **32**, 1055 (1992).
- [5] Spathis, G. and C. Maggana, *Polymer*, **38**, 2371(1997)
- [6] Drozdov, A. D., *Int. J. Solids Structures*, **35**, 2315 (1998)
- [7] Eyring, H., *J. Chem. Phys.*, **4**, 283 (1936)
- [8] Ree, T and H. Eyring, *J. Appl. Phys.*, **26**, 793 (1955)
- [9] Robertson, R. E., *J. Chem. Phys.*, **44**, 3950 (1966)
- [10] Argon, A. S., *Phil. Mag.*, **28**, 839 (1973)
- [11] Bowden, P. B. and S. Raha, *Phil. Mag.*, **29**, 149 (1974)
- [12] Brereton, M. G., R. A. Duckett, S. H. Joseph and P. J. Spence, *J. Mech., Phys. Solids*, **25**, 127 (1977)
- [13] Nanjai, Y., *Prog. Polym. Sci.*, **18**, 437 (1993)
- [14] Stachurski, Z. H., *J. Mater. Sci.*, **21**, 3231 and 3237 (1986)
- [15] Valanis, K. C., *Arch. Mech.*, **23**, 517-533 (1971)
- [16] Theodorou, M., B. Jasse and L. Monnerie, *J. Polym. Sci. Phys. Ed.*, **23**, 445 (1985)
- [17] Jang, S. S. and W. H. Jo, *Macromol. Theory Simul.*(1998) in press