

A constitutive model of polymer materials including chemical ageing and mechanical damage and its experimental verification

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The influence of chemical ageing and microcrack damage on the mechanical behaviour of polymer materials is studied. The theoretical model is derived from irreversible thermodynamics, chemical reaction kinetics and a crack extending model. Ageing tests, swelling tests, acoustic emission tests and relaxation tests have been done to determine the material constants of the constitutive equations. The consistency between the theory and the experiments is quite good when the model is applied to HTPB composite solid propellant materials.

(Keywords: chemical ageing; damage; constitutive law; viscoelasticity)

INTRODUCTION

Chemical ageing and mechanical damage of polymer materials is an important problem that affects the service lifetime of polymer materials and their components. Chemical ageing changes the macromolecular structures of polymer materials and mechanical damage changes the mesostructures of polymer materials. All these changes have interactive effects and will lead to the degradation of mechanical behaviour of polymer materials. Therefore, the constitutive relations of these kinds of materials should include some parameters related to the chemical structures and mechanical damage of the materials.

An early and successful model that links the shear modulus with the crosslink density of rubbery materials belongs to the physics of rubber elasticity¹. A linear relation has been found from statistical analysis of an idealized crosslink network. Some modifications have also been given by Flory². Valanis and Peng³ and Peng⁴ have tried to introduce crosslink density as a chemical parameter into constitutive equations to study the ageing problem, but they only gave some qualitative analysis and did not use any experimental results to verify their model. Aifantis⁵ and Christensen⁶ have also emphasized the importance of the interactive mechanical and chemical degradation.

Damage mechanics developed since the late 1950s provides us with an effective way to study the influence of microdefects on the mechanical behaviour of engineering materials. But little work has been done on the interaction between chemical ageing and mechanical damage. Chemical ageing changes the damage threshold and damage evolution rate. On the other hand, mechanical damage can accelerate the chemical reaction rate. Hence, the interactive effects of chemical ageing and mechanical damage cannot be ignored.

In this paper, we give a constitutive model to govern the influence of chemical ageing and mechanical damage.

The thermosenscence of polymer materials is taken into consideration. The evolution equation of the ageing variable is derived from the chemical reaction kinetics. Assuming that the damage consists of penny-shaped microcracks, an explicit evolution equation of the damage variable is derived. HTPB composite solid propellant material, which is a highly particle-filled composite material with polymer material as matrix, is used in experiments. In our experiments, swelling tests have been done to determine material constants of the chemical reaction kinetics equation. Acoustic emission (AE) tests have been done to determine the damage threshold. Stress relaxation tests have been done to determine relaxation modulus and simple tension tests of specimens aged for different times are used to verify our model.

THEORETICAL MODEL

Irreversible thermodynamics equations

We study the case of network polymer materials and assume that the main characteristics of ageing reaction can be represented by the variation of crosslink density v .

When chemical ageing and mechanical damage coexist, the specific Helmholtz free energy per unit volume of viscoelastic materials, ψ , can be written as:

$$\psi = \psi(\varepsilon_{ij}, T, D, v, q_i) \quad (1)$$

where ε_{ij} is the strain tensor, T is the absolute temperature, D is the damage variable, v is the crosslink density and q_i ($i = 1, 2, 3, \dots, n$) are internal variables, which represent the average displacement of molecules moving across a potential barrier⁷. The state equations are derived from irreversible thermodynamics^{8,9}:

$$\sigma_{ij} = \rho \frac{\partial \psi}{\partial \varepsilon_{ij}} \quad (2a)$$

$$s = - \frac{\partial \psi}{\partial T} \quad (2b)$$

$$\mu = \rho \frac{\partial \psi}{\partial v} \quad (2c)$$

$$Y_D = -\rho \frac{\partial \psi}{\partial D} \quad (2d)$$

$$Y_i^q = -\rho \frac{\partial \psi}{\partial q_i} \quad (2e)$$

where ρ is the density of the material, s is the entropy per unit volume, μ is the chemical potential of crosslinking reaction, Y_i^q is known as the driving force of viscous deformations and Y_D is known as the driving force of damage.

The second law of irreversible thermodynamics (Clausius–Duhem inequality) takes the following form:

$$-\frac{J_q}{T} \text{grad } T + Y_D \dot{D} + Y_i^q \dot{q}_i - \mu \dot{v} \geq 0 \quad (3)$$

where J_q is heat flux and $\text{grad } T$ is the gradient of temperature T .

The deformation kinetics equations

The evolution equations of the internal variables q_i have been derived by Valanis⁷ and modified by us^{8,9}. For small deformations, the deformation kinetics equation takes the form:

$$\dot{q}_k + H_k^2 \frac{\partial \psi}{\partial q_k} = 0 \quad (4)$$

where H_k are functions of v and $H_k \geq 0$. For simplicity, the specific Helmholtz free-energy function is taken to be a quadratic function of state variables:

$$\psi = \frac{1}{2} E_{ijkl}^0 \varepsilon_{ij} \varepsilon_{kl} + D_{ijk} \varepsilon_{ij} q_k + \frac{1}{2} C_{ij} q_i q_j + B_{ij} \varepsilon_{ij} \theta + A_i q_i \theta + \frac{1}{2} F \theta^2 + \psi_0(T, D, v) \quad (5)$$

where E_{ijkl}^0 , D_{ijk} , C_{ij} , B_{ij} , A_i and F are functions of D , v and T . Here $\theta = T - T_0$, and T_0 is a reference temperature. Einstein summation rule is used in (5) and following formulae of this paper.

Substituting (5) into (4) and (2), we found q_i and the viscoelastic stress–strain law by Laplace transformation:

$$q_i(t) = -Q_{mnp}^i \int_{-\infty}^t \{1 - \exp[-\lambda_p(t-\tau)]\} \frac{\partial \varepsilon_{mn}(\tau)}{\partial \tau} d\tau - R_p^i \int_{-\infty}^t \{1 - \exp[-\lambda_p(t-\tau)]\} \frac{\partial \theta(\tau)}{\partial \tau} d\tau \quad (6a)$$

$$\sigma_{ij} = \int_{-\infty}^t E_{ijkl}(t-\tau) \frac{\partial \varepsilon_{kl}(\tau)}{\partial \tau} d\tau + \int_{-\infty}^t F_{ij}(t-\tau) \frac{\partial \theta(\tau)}{\partial \tau} d\tau \quad (6b)$$

$$E_{ijkl}(t) = E_{ijkl}^e H(t) + E_{ijkl}^v \exp(-\lambda_p t) \quad (6c)$$

$$F_{ij}(t) = F_{ij}^e H(t) + F_{ij}^v \exp(-\lambda_p t) \quad (6d)$$

where Q_{mnp}^i , R_p^i , E_{ijkl}^e , E_{ijkl}^v , F_{ij}^e , F_{ij}^v and λ_p are functions of D and v . $H(t)$ is the Heaviside function.

For one-dimensional loading conditions, it is easy to show that the relaxation modulus $E_{ijkl}(t)$ can be expressed as a Prony series:

$$E(v, t) = E_0(v) + \sum_{i=1}^n E_i(v) \exp(-\lambda_i t) \quad (7)$$

The equation of chemical reaction kinetics

The evolution equation of the crosslink density v is derived from chemical reaction kinetics^{8,11}:

$$\frac{dv}{dt} = \frac{k_B T}{h} f(v) \exp\left(-\frac{E_c}{k_B T}\right) \quad (8)$$

where k_B is the Boltzmann constant, h is the Planck constant, E_c is the activation energy of the ageing reaction and $f(v)$ is the partition function. We take $f(v)$ to be a quadratic function of v as follows^{8,11}:

$$f(v) = A(v_m - v)(1 + Cv) \quad (9)$$

where A and C are material constants, and v_m is the maximum crosslink density that the material can reach. Substituting (9) into (8) and integrating over time from 0 to t gives:

$$v = \frac{v_m - B \exp[-\beta_1(t, T)]}{1 + CB \exp[-\beta_1(t, T)]} \quad (10)$$

in which

$$B = \frac{v_m - v_0}{1 + Cv_0} \quad v_0 = v|_{t=0}$$

$$\beta_1 = \frac{Ak_B(1 + Cv_m)}{h} \int_0^t T \exp\left(-\frac{E_c}{k_B T}\right) dt$$

The damage variable and its evolution equation

We consider the case in which the microdefects are penny-shaped cracks and assume that the distribution function of microcracks is only dependent on the initial radius a_0 of microcracks. For elastic materials, the tension modulus \bar{E} of the damaged material has the following relation with the elastic modulus E of undamaged material^{8,10}:

$$\bar{E} = (1 - \kappa D_0)E \quad (11a)$$

$$\kappa = \frac{4(10 - 3\nu_1)(1 - \nu_1^2)}{15\pi(2 - \nu_1)} \quad (11b)$$

where ν_1 is Poisson's ratio and D_0 is the damage variable, which is defined as:

$$D_0 = \frac{4}{3} \pi n_1 \int_0^\infty a_0^3 p(a_0) da_0 \quad (12)$$

and n_1 is the microcrack density per unit volume, a_0 is the initial radius of a penny-shaped crack, and $p(a_0)$ is the distribution function of microcracks and satisfies the following condition:

$$\int_0^\infty p(a_0) da_0 = 1$$

To derive the evolution equation of D , we assume that:

(i) A microcrack will begin to extend if the stress intensity factor K_I satisfies the condition $K_I = K_I^c$ with K_I^c the threshold of stress intensity factor K_I .

(ii) If the extending condition is satisfied, a microcrack will extend to radius d suddenly. Here d is determined by the size of filled particles.

Thus, the microcrack radius a is written as:

$$a = a_0 + (d - a_0)H(a_0 - a_{th}) \quad (13)$$

where a_{th} is the critical value of radius a and is a function of stress. $H(x)$ is the Heaviside function. The damage

variable D takes the following form:

$$D = D_0 + D_{\Delta v} \quad (14a)$$

$$D_{\Delta v} = \frac{4}{3} \pi n_1 \int_0^\infty (a^3 - a_0^3) p(a_0) da_0 \quad (14b)$$

The physical meaning of D_0 is the damage related to the initial defects induced by manufacturing factors, and $D_{\Delta v}$ is the damage related to microcrack extending process. Generally, D_0 is small and there is no effective way to measure it. Therefore, we ignore it and take $D = D_{\Delta v}$ approximately.

If the maximum radius of initial defects is Kd ($K \leq 1$), the stress threshold to extend damage is obtained by setting $a = Kd$ and $\sigma_n = (\sigma_n)_{\max}$. Here σ_n is the normal stress acting on the microcrack surface. For simple tension, we have:

$$\sigma_{th} = \frac{K_1^c}{2} \left(\frac{\pi}{Kd} \right)^{1/2} \quad (15a)$$

$$\frac{a_{th}}{Kd} = \left(\frac{\sigma_{th}}{\sigma_n} \right)^2 \quad (15b)$$

Because σ_n depends on microcrack orientation, a_{th} also depends on microcrack orientation.

We take the distribution function $p(a_0)$ of microcracks to be an exponential function of a_0 as follows:

$$p(a_0) = \frac{\beta}{Kd(1 - e^{-\beta})} \exp\left(-\frac{\beta a_0}{Kd}\right) H(Kd - a_0) \quad (16)$$

In the condition of simple loading, $\sigma_n = \sigma \cos^2 \theta$, where σ is the tension stress. Substituting (15) and (16) into (14) and integrating, we have:

$$D_{\Delta v} = \frac{4}{3} \pi n_1 d^3 g(\sigma_{th}/\sigma) \quad (17a)$$

$$g(x) = \left[e^{-\beta x^2} - \varepsilon^{-\beta} + K^3 e^{-\beta} \left(1 + \frac{3}{\beta} + \frac{6}{\beta^2} \right) + \frac{6K^3}{\beta} (e^{-\beta} - e^{-\beta x^2}) - K^3 e^{-\beta x^2} \left(x^6 + \frac{3}{\beta} x^4 + \frac{6}{\beta^2} x^2 \right) \right] / (1 - e^{-\beta}) \quad (17b)$$

Hence, an explicit form of damage variable D as the function of stress is obtained. If unloading exists, σ should be replaced by the maximum stress $(\sigma)_{\max}$ in the loading history.

The constitutive law in simple tension

Based on above discussions, the constitutive law of particle-filled polymer materials including chemical ageing and mechanical damage is written as:

$$\sigma = \int_0^t E(v, t - \tau) \frac{\partial \varepsilon(\tau)}{\partial \tau} d\tau \quad (18)$$

where

$$\bar{E}(v, t) = (1 - \kappa D) E(v, t) = [1 - \gamma g(\sigma_{th}/\sigma)] E(v, t) \quad (19a)$$

$$\gamma = \frac{16(10 - 3v_1)(1 - v_1^2)d^3 n_1}{45(2 - v_1)} \quad (19b)$$

and v is the crosslink density given by (10) and $E(v, t)$ is the relaxation modulus of undamaged materials given by (7). To take into account the influence of crosslink density

v and not to make analysis and experimental data processing too difficult, we take the relaxation modulus $E(v, t)$ as a linear function of v :

$$E(v, t) = (E_0^0 + E_0^1 \Delta v) + \sum_{i=1}^n (E_i^0 + E_i^1 \Delta v) \exp(-\lambda_i t) \quad (20)$$

where $\Delta v = v - v_0$, E_i^0 , E_i^1 and λ_i ($i = 0, 1, 2, \dots, n$) are material constants.

EXPERIMENTAL DETERMINATION OF MATERIAL CONSTANTS

In the above-derived constitutive model, there are so many factors that affect the stress-strain law that we have to look for an effective way to determine the material constants independently as much as possible so that we can distinguish the influence of different factors such as ageing, damage and viscoelasticity. In this paper, relaxation tests, accelerated ageing tests, swelling tests and AE tests were used to determine material constants of the derived constitutive model.

The material used in our experiment is HTPB composite solid propellant material. This material is a particle-filled composite material in which the weight percentage of fillers is as high as 85%. Ageing reaction is accelerated at elevated temperature of $T = 65^\circ\text{C}$.

Swelling tests

The swelling test was used to measure the crosslink density v . The size of the specimens is $10 \times 10 \times 15 \text{ mm}^3$. The specimens were first put into the thermostat to age and then swelled in toluene for 8 days. The swelled specimens were compressed in special equipment to measure the slope S of the load-displacement curve and v was calculated by the following formula²:

$$v = \frac{h_0 S}{3A_0 R T} \quad (21)$$

where h_0 and A_0 are the height and cross-sectional area of the specimen before swelling respectively, R is the gas constant and T is the absolute temperature. Experimental results of v are shown in *Figure 1*. Since ageing temperature is kept constant, it can be found that $\beta_1 = \beta_2 t$, where:

$$\beta_2 = \frac{A k_B (1 + C v_m)}{h} T \exp\left(-\frac{E_c}{k_B T}\right)$$

is a constant. To determine the material constant in (10), we construct a positive-definite function as follows:

$$y(v_m, \beta_2, B, C) = \sum_{i=1}^n \left(v_i - \frac{v_m - B \exp(-\beta t_i)}{1 + C B \exp(-\beta t_i)} \right)^2 \quad (22)$$

where t_i is ageing time, v_i is measured crosslink density at time t_i , and the summation is taken over all experimental data shown in *Figure 1*. v_m , β , B and C are determined by minimizing y . Let

$$\frac{\partial y}{\partial v_m} = 0, \quad \frac{\partial y}{\partial \beta_2} = 0, \quad \frac{\partial y}{\partial B} = 0, \quad \frac{\partial y}{\partial C} = 0 \quad (23)$$

and solve these equations by iteration. We found that:

$$v = \frac{0.1012 - 0.0961 \exp(-0.0595 t_a)}{1 - 0.837 \exp(-0.0595 t_a)} (10^{-6} \text{ mol mm}^{-3}) \quad (24)$$

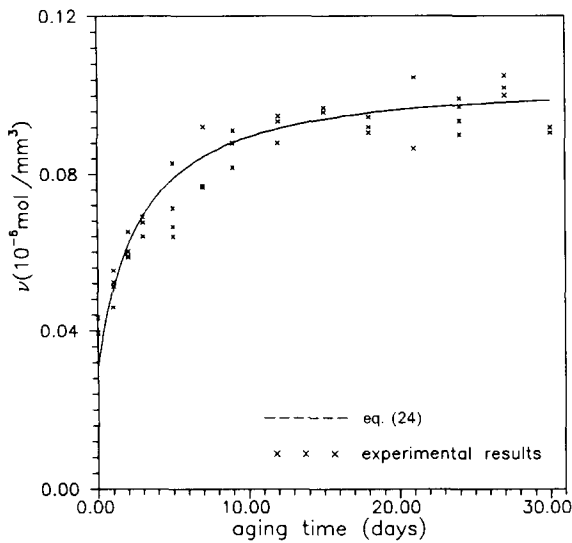


Figure 1 Comparison between equation (24) and experimental results for crosslink density ν of HTPB propellants

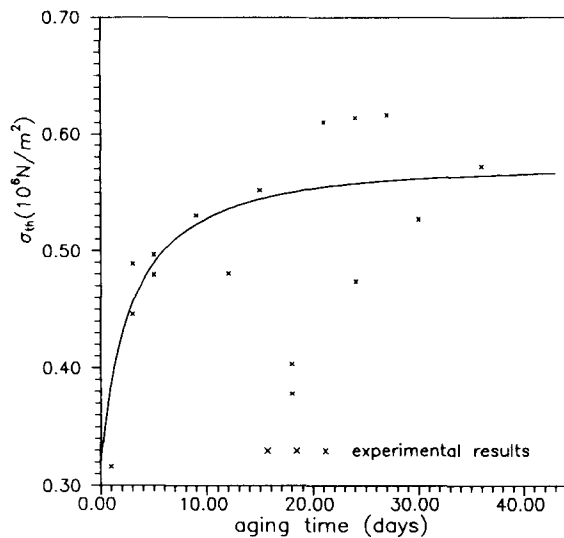


Figure 2 Damage threshold measured by AE test

where the unit of time t_a is 1 day. To avoid confusion, t_a is used to denote ageing time in all figures of this paper. The full curve in Figure 1 corresponds to equation (24).

Acoustic emission tests

Acoustic emission tests were used to determine stress threshold σ_{th} of damage. A four-channel AE equipment made by the Physics Acoustic Emission Co. of USA (type 3004) was used. From our experimental results, it is found that ageing has no obvious influence on σ_{th} , which is the strain threshold of damage. The experimental results of σ_{th} are shown in Figure 2, where the full curve corresponds to threshold σ_{th} calculated from $\epsilon_{th} = \text{const} = 0.0318$.

Relaxation tests

From the results of AE tests, it is known that there is an obvious threshold σ_{th} for microcracks to begin to extend. If the relaxation tests are done in the condition $\sigma < \sigma_{th}$, there will not be any new damage. Therefore, the relaxation modulus $E(\nu, t)$ in (20) can be obtained directly from the tests. Part of the experimental results are shown in Figure 3. To reduce the difficulty in determining too

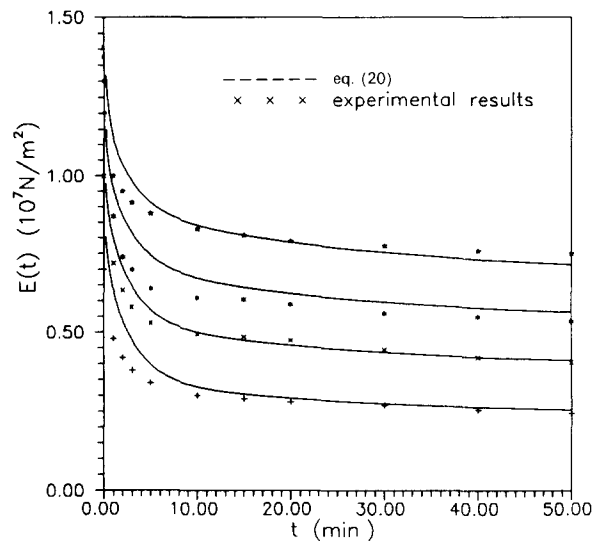


Figure 3 Comparison between equation (20) and experimental results for relaxation modulus of ageing HTPB propellants

many material constants, we take $\lambda_i = 10^{i-1} \lambda$ and $n = 4$. The material constants in (20) are determined from these experimental results in the same way as in determining material constants of (10) and are given in the following:

$$\begin{aligned} E_0^0 &= 2.3677 & E_0^1 &= 7.8135 \times 10^7 & E_0^2 &= 1.1548 & E_0^3 &= 1.8493 \times 10^7 \\ E_0^4 &= 4.0586 & E_1^1 &= -1.5526 \times 10^7 & E_1^2 &= 1.5320 & E_1^3 &= 1.7767 \times 10^7 \\ E_1^4 &= 6.4697 & E_1^4 &= 12.452 \times 10^7 & \lambda &= 0.0366 \end{aligned}$$

where the unit of E_i^j ($j = 0, 1; i = 0, 1, 2, 3, 4$) is MN m^{-2} .

Determination of material constants in damage equation

Because of the difficulties in measuring microcracks directly, the coefficients in the distribution microfunction of microcracks cannot be found directly from their definitions. We had to use some indirect methods to determine K and β defined in (16).

The experimental results of simple tension tests for specimens that have been aged for 1, 3, 5, 7, 9 days respectively were used in determining K and β . Numerical results showed that K did not affect the numerical precision seriously, so we take $K = 0.1$. Taking γ as a function of β , we found that $\beta = 0.5$ and $\gamma = 1.046$ can fit the experimental results best.

COMPARISON BETWEEN THEORY AND EXPERIMENTS

Having determined the material constants, in the condition of constant tension strain rate $\dot{\epsilon}$, we can find the stress-strain law of ageing HTPB materials by integrating (18). The result is:

$$\sigma = [1 - \gamma g(\sigma_{th}/\sigma)] \left(E_0^0 + E_0^1(\nu - \nu_0) + \sum_{i=1}^n \frac{\dot{\epsilon}}{\lambda_i} [E_i^0 + E_i^1(\nu - \nu_0)] [1 - \exp(-\lambda_i \epsilon / \dot{\epsilon})] \right) \quad (25)$$

where ν is given by (24), and $g(x)$ is given by (17b).

The comparison between (25) and tension test results is given in Figures 4 to 7. It can be seen that the consistency between the theory and the experiments is pretty good. The derived constitutive model is successful in predicting the mechanical behaviour of HTPB materials aged as long as 43 days at elevated temperature.

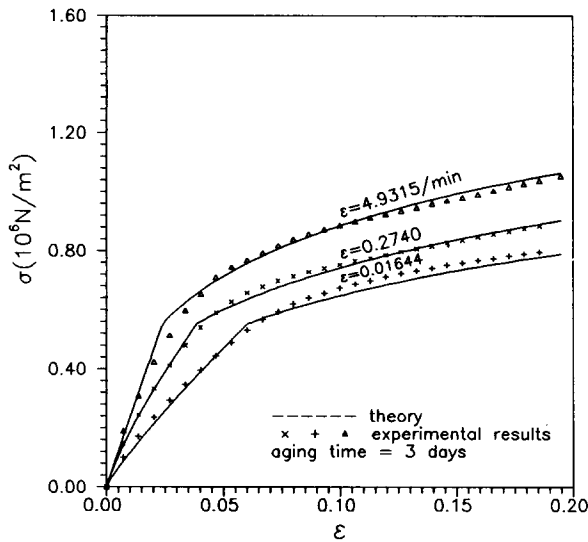


Figure 4 Comparison between theory and experiment of stress-strain law when ageing time = 3 days

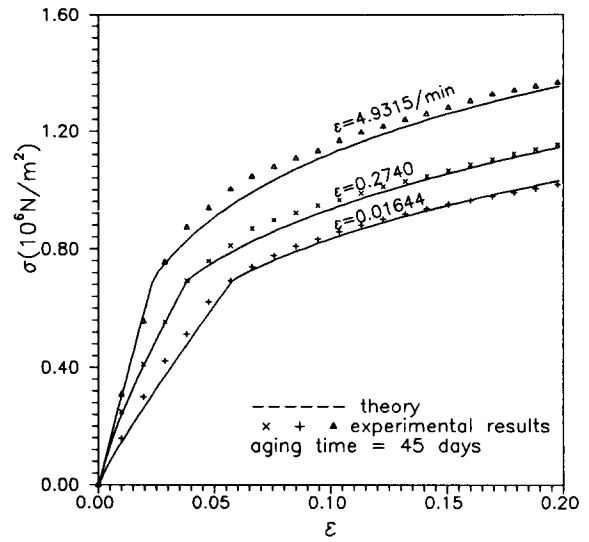


Figure 7 Comparison between theory and experiment of stress-strain law when ageing time = 45 days

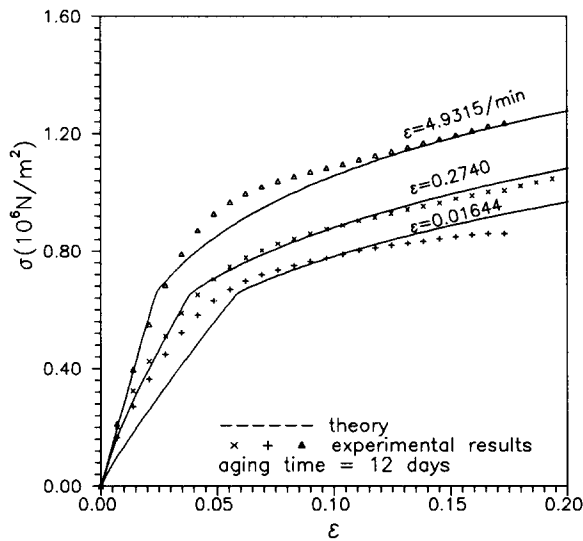


Figure 5 Comparison between theory and experiment of stress-strain law when ageing time = 12 days

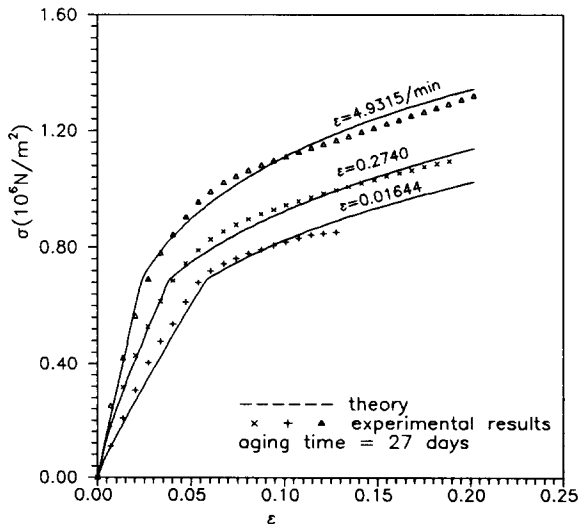


Figure 6 Comparison between theory and experiment of stress-strain law when ageing time = 27 days

CONCLUSIONS

A constitutive model of viscoelastic materials including chemical ageing and mechanical damage has been derived from irreversible thermodynamics, chemical reaction kinetics, deformation kinetics and the microcrack extending model. Experimental results show that our model is rational and can be used to predict the behaviour of ageing polymer materials over quite a long period. Introducing chemical ageing and mechanical damage internal variables into the constitutive model offers us a new way to study the constitutive law of polymer materials including chemical ageing, mechanical damage and viscoelasticity.

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