Research Article

Investigation on Aging Model of Solid Propellant Using the Degree of Crosslinking

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Solid propellant is the main part of solid rocket motor (SRM). To further investigate the service life of SRM, aging of solid propellant should be concerned. The aim of this study is to propose a new aging constitutive model of solid propellant using the degree of crosslinking. The aging development equation of viscoelastic Poisson’s ratio (VPR) and relaxation modulus are considered in establishing the model. A series accelerated aging experiments accompanied with some tensile tests are designed to verify the new model. Aging experiments show that degree of crosslinking (DCL) can be used to act as a link to facilitate the communication between chemical aging and aged mechanical parameters well.

1. Introduction

Aging of the solid propellant will seriously affect the mechanical property of the solid propellant, especially the VPR and relaxation modulus [1–6]. It has been proved that a microchange of Poisson’s ratio strongly affects structural integrity of the solid rocket motor (SRM) [7–9]. A solid propellant grain is the power origin and main structural part of SRM. The life of the solid propellant grain plays a decisive role in the service length of SRM. It is very essential to establish a new aging model of the solid propellant.

The start point of life prediction research of solid propellant grains is the study on the aging of the solid propellant. There are some methods, like mechanical property method [10–12], activation energy method [13–15], dynamic mechanical property method [15, 16], and DCL method [17, 18], used in the aging research. The mechanical property method always based on the aging phenomenon during natural aging or accelerated aging. The mechanical property is watched and fitted by some mathematical method. Unlike mechanical property method, dynamic mechanical property method does not research based on the aging mechanism; the results always come from apparent measurement. The aging development equation of mechanical property is obtained based on the aging kinetic equation of polymer in the activation energy method. However, much more research results were funded by the DCL method. Chemical property and the relationship with mechanical property are studied in the DCL method. Zhou [19] proposed an aging development equation of relaxation modulus based on this method and a constitutive model of solid propellant considering aging effect. Furthermore, experimental data shows that the increase of the DCL will company with the decrease of Poisson’s ratio during aging process [20]. Therefore, it is feasible to use the DCL in establishing the aging development equation of VPR.

The paper proposed a new aging constitutive model of solid propellant based on the aging development equation of VPR and relaxation modulus. To determine and verify the parameters of the constitutive model, accelerate aging tests and uniaxial tensile tests are designed. Figure 1 shows the research idea of the whole paper.
2. Aging Model

During the age process of propellant, the crosslinking network will change for the unstable of polymer binder matrix. The DCL is always used to represent the degree of aging. Furthermore, the DCL can be expressed as chain members of branching point, numbers of branching point, and average mean molecular weight. In this paper, the molarity of crosslinking chain segment is used to represent the DCL. Zhou [19] had given the development equation of the DCL.

\[ \mu(t_a) = \frac{\mu_m - B e^{-\beta^c (t_a, T)}}{1 + \alpha^c B e^{-\beta^c (t_a, T)}}, \]  

(1)

where \( t_a \) is the aging time, \( E_0^c \) represents the activation energy in aging reaction, \( \alpha^c \) is the undetermined parameter, \( \mu_m \) is the maximum DCL, and \( \mu_0 \) is the initial DCL. Coefficients \( B \) and \( \beta^c \) have the form

\[ B = \frac{\mu_m - \mu_0}{1 + \alpha^c \mu_0}, \]

\[ \beta^c = \beta_0^c \int_0^{t_a} T \exp \left( -\frac{E_0^c}{k_B T} \right) d\tau, \]

(2)

where

\[ \beta_0^c = \frac{A k_B (1 + \alpha^c \mu_m)}{R}, \]

(3)

where \( k_B \) is the Boltzmann constant and \( A \) is the speed constant of aging reaction.

For the aging test in constant temperature, \( T_0 \), \( \beta^c \) can be degraded into the next form

\[ \beta^c = \beta_0^c T_0 \exp \left( -\frac{E_0^c}{k_B T_0} \right) t_a. \]

(4)

For the homogeneous isotropic material, the aging slack variable can be expressed fully by relaxation modulus \( E(t, t_a) \), and shear modulus \( G(t, t_a) \) with aging parameters [19].

\[ E(t, t_a) = E^0(t) + [\mu(t_a) - \mu(0)] E^1(t), \]

(5)

\[ G(t, t_a) = G^0(t) + [\mu(t_a) - \mu(0)] G^1(t), \]

(6)

where \( E^0(t) \) is the unaged relaxation modulus, \([\mu(t_a) - \mu(0)] E^1(t) \) represents the aged relaxation modulus, and \( G^0(t) \) and \([\mu(t_a) - \mu(0)] G^1(t) \) represent the unaged and aged shear modulus, respectively. However, the change of DCL, \( \mu(t_a) - \mu(0) \), is used rather than relative change of DCL, \( \tilde{\mu} = [\mu(t_a) - \mu(0)]/\mu(0) \). In order to keep the uniform dimension, the paper selects the relative change of DCL in the modified aging development equation.

\[ E(t, t_a) = E^0(t) + \tilde{\mu}(t_a) E^1(t), \]

\[ G(t, t_a) = G^0(t) + \tilde{\mu}(t_a) G^1(t). \]

(7)

In Equations (5) and (6), the VPR never changes during the aging process which did not correspond to the phenomenon above. Zhou [19] had proved the validity of Equation (5). But Equation (6) had not been verified. It seems hard
to find a suitable model for aged VPR from the two equations. Based on the elastic physics of rubbery, for the ideal crosslinking network, the shear modulus can be expressed as

\[ G = \mu RT, \]  

(8)

where \( \mu \) represents DCL, \( R \) is the Planck constant, and \( T \) represents the temperature.

But, for the real crosslinking polymer film, the crosslinking network is always incomplete. Flory [21] gives the modified form of Equation (8):

\[ G = RT\left(\mu - \frac{2\rho}{M}\right), \]  

(9)

where \( \rho \) is the density and \( M \) is the unaged initial molecular weight.

To express simply, Equation (9) can be rewritten as

\[ G = RT(\mu - k). \]  

(10)

For the homogeneous isotropic elastomers, shear modulus, tensile modulus, and Poisson's ratio have the relationship

\[ G(t) = \frac{E(t)}{2(1 + \nu)}, \]  

(11)

Considering two time status as shown in Figure 2, \( T_0 \) and \( T_1 \), where \( T_0 \) is the initial time and \( E_0 \) represents initial tensile modulus. The DCL at \( T_0 \) and \( T_1 \) are \( \mu_0 \) and \( \mu \) separately.

The corresponding shear modulus at \( T_0 \) and \( T_1 \) can be expressed based on Equation (11):

\[ (\mu_0 - k)RT = \frac{E_0^0}{2(1 + \nu_0)}, \]  

(12)

\[ (\mu - k)RT = \frac{E^0 + \mu E_1^1}{2(1 + \nu_1)}, \]

where \( E_0^0 \) represents the unaged tensile modulus, \( E_1^1 \) represents the aged tensile modulus, and \( \nu_0 \) and \( \nu_1 \) represent unaged and aged Poisson’s ratio.

### Table 1: Tests for determination of aging development equations of relaxation modulus and VPR.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Aging time (days)</th>
<th>Number of tests</th>
<th>Stretching velocity (mm-min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75°C</td>
<td>0, 3, 5, 7, 9, 11, 16, 21, 26, 31, and 41</td>
<td>3</td>
<td>---</td>
</tr>
<tr>
<td>20°C</td>
<td>0, 3, 5, and 7</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>20°C</td>
<td>5, 11, 26, and 31</td>
<td>---</td>
<td>1.68, 3.36, and 5.04</td>
</tr>
</tbody>
</table>

Figure 3: Test specimen and image of testing scenarios.

Figure 4: Measurement of DCL during the aging period.
the basic shape of curve.

\[ \nu(t, t_a) = v_0(t) + \delta_1 \frac{\Delta \mu(t_a)}{[\mu(t_a) - k][\mu_0 - k E^1(t) - 1]} \left[ 1 + v_0(t) \right] + \delta_2, \]

where \( \delta_1 \) and \( \delta_2 \) are undermined coefficients.

Using the correspondence principle and considering the aging development equation of VPR and relaxation modulus, for isotropic materials, the aging constitutive model of the solid propellant using the degree of crosslinking can be written as

\[ \sigma_{ij}(t) = S_{ij}(t) + \frac{1}{3} \delta_{ij} \sigma_{kk}(t), \]

with

\[ S_{ij}(t) = \int_{-\infty}^0 \nu(\xi - \xi', t_a) \frac{\partial \delta_{ij}(\tau)}{\partial \tau} d\tau = \int_{-\infty}^0 E(\xi - \xi', t_a) \frac{\partial \delta_{ij}(\tau)}{\partial \tau} d\tau, \]

\[ \sigma_{kk}(t) = 2 \int_{-\infty}^0 \nu(\xi - \xi', t_a) \frac{\partial \delta_{kk}(\tau)}{\partial \tau} d\tau = \int_{-\infty}^0 E(\xi - \xi', t_a) \frac{\partial \delta_{kk}(\tau)}{\partial \tau} d\tau, \]

where

\[ \bar{\varepsilon}_{kk} = \varepsilon_{kk} - 3a_{ij}^T \Omega. \]

In which, \( \theta \) and \( \xi \) are reduced time, \( a_{ij}^T \) is the expansion coefficient, and \( \Omega \) is the change of temperature.

### 3. Experimental Procedures

To determine the parameters in the development equation of the DCL, the next tests are designed. Some results related to the DCL and relaxation modulus can be found in the previous work [22]. According to their research, DCL can be used to describe the aged relaxation modulus well.

The DCL of the propellant is determined at the designed aging time in Table 1 at the constant temperature of 75°C. The determined data is used in fitting the curve overusing aging time. The fitted curve will establish the foundation of the next tests.

The designed tests below are to determine the parameters in the aging development equations of the relaxation modulus and VPR. Furthermore, the fitting results are used to directly verify the reasonability of the two equations.

The relaxation modulus and VPR are determined at the designed aging time by using the test specimen as shown in Figure 3(a). The determination of VPR will use the digital image correction method (DICM) which is proposed by Cui et al. [1] as shown in Figure 3(b). The fitted parameters will be used in the calculation of theory value in the next tests.

The determined aging development equations of the relaxation modulus and VPR should be verified by some tests. The stretch tests are very effective tests.
The longitudinal stress measured by the force sensor is used to verify the aging development equations of relaxation modulus while the transverse strain measured by DICM is used to verify the aging development equations of VPR.

The longitudinal stress has the next form during stretch tests

\[ \sigma_x(t) = \int_0^t E(t) \frac{\partial \varepsilon_x}{\partial t} dt. \]  

(20)

Introducing the aged relaxation modulus in Prony series (see Equation (40)), the longitudinal stress has the form

\[ \sigma_x(t) = E_0 \varepsilon_x + \mu \left( t' \right) E_1 \varepsilon_x + \sum_{n=1}^{N_2} \left[ E_n \mu \left( t' \right) E_n \right] e^{-\tau_n t} \frac{\partial \varepsilon_x}{\partial t} dt. \]  

(21)

Simplifying the above equation

\[ \sigma_x(t) = E_0 \varepsilon_x + \mu \left( t' \right) E_1 \varepsilon_x + \sum_{n=1}^{N_2} \left[ E_n \mu \left( t' \right) E_n \right] \left[ 1 - e^{-\tau_n t} \right] \frac{\partial \varepsilon_x}{\partial t} dt. \]  

(22)

where \( R_V \) is stretching velocity, \( \varepsilon_x = R_V t \).

For the linear elastic materials, the volume strain tensor \( \varepsilon_{kk} \) in stretch tests has the form

\[ \varepsilon_{kk} = \varepsilon_x + \varepsilon_y + \varepsilon_z = \left( 1 - 2\nu \right) \varepsilon_x, \]  

(23)

where \( \nu \) is Poisson’s ratio, \( \varepsilon_x \) and \( \varepsilon_z \) represent two transverse strains, and \( \varepsilon_x \) represents the longitudinal strain.

The corresponding expression in complex domain based on the elastic-viscoelastic corresponding principles can be expressed as

\[ \tilde{\varepsilon}_{kk}(s) = \tilde{\varepsilon}_x(s) - 2s\tilde{\varepsilon}_y(s)\tilde{\nu}(s), \]  

(24)

where \( s \) is the Laplace transform variable.

Considering the Laplace inversion of the above equation, the volume strain tensor \( \varepsilon_{kk} \) has the form

\[ \varepsilon_{kk}(t) = \varepsilon_x(t) - 2 \int_0^t \varepsilon_x(t') \frac{\partial \tilde{\varepsilon}_x(t')}{\partial t} dt. \]  

(25)

The stretching velocity in the stretch tests is a constant. The above equation can be simplified as

\[ \varepsilon_{kk}(t) = R_V t - 2R_V \int_0^t \nu(t) dt. \]  

(26)

Considering the symmetry of the problem and combining Equations (28) and (35), transverse strain can be expressed as

\[ \varepsilon_y(t) = -R_V \int_0^t \nu(t) dt. \]  

(27)

4. Results and Discussion

As illustrated in Figure 4, the initial DCL of propellant is nonzero for the crosslinking reaction during the natural storage before accelerate aging test. The DCL increases sharply during the initial phase (1-10 days) and fluctuates wildly for the sudden change of storage temperature. As
aging time goes by, the propellant begins to adapt to the high temperature. The increase of the DCL becomes slow. But the DCL still increases with time. At the end of aging period, the DCL increases slowly and even comes to a standstill, but the data still appears fluctuation. Equation (28) is the fitted results of DCL. The fitted curve is obtained by the least square method.

\[
\mu(t_a) = \frac{4.519 - 3.0390e^{-0.0657t_a}}{1 - 0.4284e^{-0.0657t_a}}.
\]  

(28)

The parameters of the aging development equations of relaxation modulus are fitted by the DCL curve and relaxation modulus measured. The parameters of Prony series of the aging development equations of relaxation modulus (see Equation (29)) are illustrated in Table 2, while the number of the terms in the Prony series is 5. Figure 5 gives the relaxation modulus under different aging times and its fitting curve. As illustrated, the relaxation modulus increases with the aging time which means the propellant hardens during the aging process.

\[
E(t, t_a) = E_{\infty}^0 + \mu(t_a)E_{\infty}^1 + \sum_{n=1}^{N_\varepsilon} [E_n^0 + \mu(t_a)E_n^1]e^{-t/t_\varepsilon^n},
\]  

(29)

where \(E_{\infty}^0\) and \(E_{\infty}^1\) are the equilibrium relaxation modulus, \(N_\varepsilon\) is the number of terms in the Prony series, \(t\) represents time, and \(E_n^0\), \(E_n^1\), and \(t_\varepsilon^n\) are undetermined coefficients.

Based on the results of DCL, aging development equations of the relaxation modulus, and VPR measured at different aging times, the parameters in the aging development equations of VPR are fitted. Figure 6(a) illustrates the original fitted curve of the aging development equations of VPR. The original curve seems cannot fit the experimental data well, but the experimental data reflects some regulations of the aging development of VPR. VPR decreases with aging time. The curves of VPR at different aging times have the similar shape. Figure 6(b) illustrates the modified curve of the aging development equations of VPR measured at different aging times (stretching velocity = 5.04 mm·min⁻¹).
VPR. The modified curve fits the experimental data pretty good. Furthermore, the data witnessed that the VPR decreases while the increase of DCL in literature [20]. Equation (30) gives the modified aging development equation of VPR. The fitting curve shows that the aging development equations of VPR can predict the VPR of the propellant during the aging process directly.

\[
\nu(t, t') = \nu_0(t) + 0.0803 \left(\frac{\Delta \mu(t')}{\mu(t') - 0.4427} - \frac{\mu_0 - 0.4427 E(t)}{E(t)} - 1\right) [1 + \nu_0(t)] + 0.0002.
\]

Figure 7 gives the curves of longitudinal stress vary with time under different stretching velocity. The longitudinal strain is 5% at the end of stretch tests to avoid introducing damage effect. The experimental data fits the longitudinal stress predicted very well. Furthermore, longitudinal stress increases with stretching velocity which is in accord with theory.

Figure 8 illustrates the curves of longitudinal stress vary with longitudinal strain under different aging times. The fitting results prove that the modified aging development equation of relaxation modulus is reasonable during the aging process indirectly.

Figure 9 illustrates the curves of transverse strain vary with time under different stretching velocity. The measured data fits the predicted well, while the data is small. Furthermore, the stretching velocity has no directly effect on transverse strain. Figure 10 gives the curves of transverse strain vary with longitudinal strain under different aging times (stretching velocity = 5.04 mm·min\(^{-1}\)).

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\]
5. Conclusion

To accurately describe the aging properties of the solid propellant, chemically related changes DCL is used to act as a link to facilitate the communication between chemical aging and aged mechanical parameters. With the aged mechanical parameters, a new aging constitutive model of solid propellant is proposed from the aging phenomenon of propellant. The DCL curve is generated first through accelerate aging tests. In addition, the parameters of the aging development equations of relaxation modulus are fitted by the DCL curve and relaxation modulus measured. Stretch tests reveals that the modified aging development equation of VPR and aging development equation of the relaxation modulus are reasonable in different aging periods. Compared with the traditional statistical methods, the DCL method as well as the validation examples is more convincing. The method in this research provides a new method to further investigate the aging properties of the solid propellant.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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