Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201300020

Life Prediction of NEPE Propellants

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Abstract: NEPE propellants were prematurely aged at 65, 70, 75, and 80 °C, respectively. The strength limit of NEPE propellants was tested by the uniaxial tension test. Based on the aging mechanism of the micro-phase structure and the macro-mechanical properties of NEPE propellants, the aging process was divided into three stages: post curing stage, microstructure gradual degradation stage and accelerated chemical aging stage. Because nitrate ester is hardly to decompose at ambient temperatures, the post cure of NEPE propellants only occurs at higher temperatures. Thus, the life prediction of NEPE propellants should ignore the time of post cure. The service life of NEPE propellants at ambient temperatures should be determined by the second stage of high temperature accelerated aging. By analyzing the tensile strength of NEPE propellants aged at 65, 70, 75, and 80 °C, the service life prediction equation of NEPE propellants was established and the service life was predicted.

Keywords: NEPE propellants · Aging · Microstructures · Tensile strength · Life prediction

1 Introduction

Nitrate Ester Plasticized Polyether (NEPE) propellants are cross-linking propellants. They are polymer-bonded high explosives. Previous studies show that the failure of NEPE propellants is mostly caused by the micro-phase structure aging [1–3]. Aging will result in degradation of the mechanical properties and failure of the structural integrity [4].

At present, the most common method of evaluating a propellant's aging characteristics is accelerated aging testing [5]. Based on chemical reaction kinetics and time-temperature superposition principle, this method can be used to establish the time-temperature superposition model of propellants by increasing the ambient temperature impact factor. The service life of propellants in the storage environment can be estimated by the model.

In early studies, the most used model for service life prediction of propellants was the Berthelot equation. The properties were tested after the propellants have been aged at high temperature and data were used for life prediction at first hand, whereas for NEPE propellants the aging process does not obey the Berthelot equation. So, the equation must be improved for life prediction of NEPE propellants.

In this paper, the aging process was divided into three stages based on the trend of cross-linked network concentration and the aging mechanism of micro-phase structure of NEPE propellants. A statistical model between the micro-phase structure and macro-mechanical properties of NEPE propellants was established. Combined with the tensile strength tested by the uniaxial tension test, a service life prediction equation based on the Berthelot equation was established. Finally, the service life was assessed by the improved Berthelot equation.

2 Experimental

2.1 Accelerated Aging Test

NEPE is a high polymer. A typical composition is given in Table 1.

The NEPE propellant samples were of cuboid shape. The samples were sealed and aged at high temperature for different times. The test matrix is shown in Table 2.

2.2 Determination of Strength at Break Data

The strength limit of the NEPE propellant was tested by the uniaxial tension test. Figure 1 shows a sample for the uniaxial tension test. Figure 2 shows the strength limit data of NEPE propellant samples. σ_b is the stress at break of the NEPE propellant.

Figure 2 figures out that the strength limit data of the NEPE propellant varies in the aging process. In the initial period of aging, the strength limit data rises. Then it decreases and increases again after a period of time. In the last period of aging, the strength limit data declines fast. From that, the aging process of NEPE propellant could be divided into three stages. The first stage with strength limit data increasing is post curing stage. The second stage, in which the strength limit data decline wavelike, is known as micro-phase structure gradual degradation stage. And the

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Table 1. Composition of NEPE.

	AP	Al	HMX	BTTN and NG	PEG	Binder	C2
Content	8%	17%	48%	17%	3.5%	3.5%	3%

Table 2. Samples test matrix.

Aging temperature [°C]	Aging time [day]										
80	4	6	8	10	12	14	16	18	20	22	24
75	10	20	25	30	34	38	41	44	47		
70	15	30	45	55	65	75	80	85	90	95	
65	20	40	60	80	100	120	130	140	150		

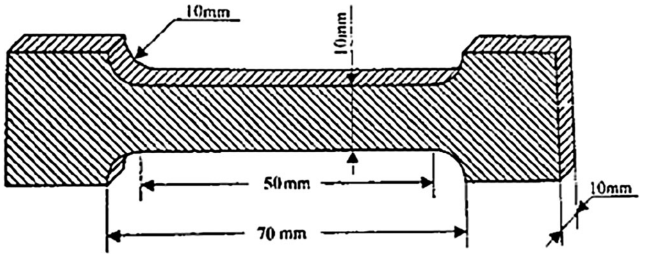

Figure 1. Tensile specimens.

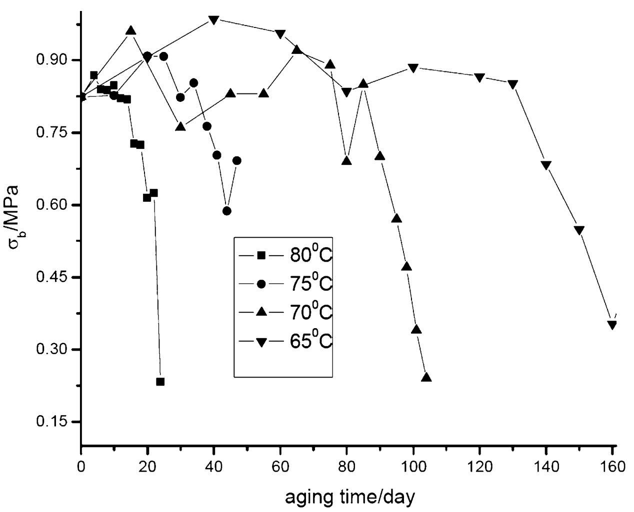

Figure 2. Data of σ_b as function of aging time.

third stage for the strength limit data decline linearly, is named accelerated chemical aging stage.

3 Theoretical Analysis

There are many internal factors that affect aging of the NEPE propellant and the following two are keys: (1) phase separation between binder and plasticizer, and (2) aging of microstructure in the binder [6–8]. The two factors both can lead to decline of the mechanical properties. NEPE propellants have a micro-crystalline region with isocyanate hard molecular chains. The micro-crystalline region dispersed in the oligomeric polyol (matrix phase) due to the thermodynamics incompatible. This is called micro-phase separation. Appropriate micro-phase separation can improve the mechanical properties of propellants, while excessive micro-phase separation will destroy the adhesive network system and result in separation of the nitrate ester plasticizer. Then the two-phase separation will reduce the propellants' low-temperature mechanical properties. Therefore, the macro-mechanical properties can reflect the change of micro-phase structure. So the relationship between the micro-phase structure aging process and macro-mechanical properties is the key for NEPE propellants life assessment.

Early research figured out that the cross-linked network concentration of NEPE propellants can affect the tensile strength. So the cross-linked network concentration represents a vital link between macro-mechanical properties and micro-phase structure aging process. Based on the trend of cross-linked network concentration and the aging mechanism of micro-phase structure, combined with the tensile strength, the high temperature accelerated aging of NEPE propellants can be divided into three stages.

Finally, from the view of chemical reaction kinetics and statistics, on the foundation of Berthelot equation, the equation for the life prediction of NEPE propellants was established.

3.1 Three Aging Stages of NEPE Propellants

3.1.1 Post Curing Stage

The products of nitric esters (NG and BTTN) decomposition and isocyanate generate cross-linked hard molecular chain. Reaction can be simplified as follows:

$$R{-}NCO + R'{-}OH \rightarrow RNHCOOR'$$

Due to the increasing of the hard molecular chains concentration, the tensile strength increases accordingly. At the same time, the carbamate and carboxyl restrict the rotating of main chain. This leads to the elongation decreases on the macro-mechanical properties. In fact, the nitric esters decomposition generally occurs at high temperature, while the actual storage temperature is below 30 °C. Thus, the life prediction should eliminate the post-curing effect brought by nitric esters decomposition and life prediction at ambient temperatures should ignore the initial stage in high temperature aging.

3.1.2 The Microstructure Gradual Degradation Stage

When approaching the end of isocyanate reaction in NEPE propellants, the tensile strength limit achieves a maximum. The degradation reaction of propellants at high temperature becomes major. The hard molecular chains in propellants are easy to degrade and fracture than the soft molecular chains. This is irreversible chemical aging. In this stage, decomposition temperature of nitric esters is higher than the actual service temperature of propellants. NO_x generated by nitrate ester decomposition accelerates the degradation of polyether. But stabilizers can neutralize NO_x so that the propellant is confirmed in thermal aging environment.

From the view of the polymer chain statistic, when the propellant is in the rubbery state, the internal energy in polymer chain of NEPE propellants is changeless during the uniaxial tensile test. In the thermodynamics, tensile strength in ideal state is as follows:

$$\sigma_b = 3\alpha kT\varepsilon \quad (1)$$

Where, σ_b is the tensile strength, α is the number of standard cross-linked network chain in propellants per unit volume, namely cross-linked network concentration, k is the Boltzmann constant, T is the absolute temperature, and ε is the elongation, respectively.

Equation 1 figures out that the tensile strength can reflect the change of cross-linked network concentration. When the number of hard molecular chains or the degree of micro-phase separation increase, the cross-linked network system will be enhanced and the hard molecular chain concentration and thus the tensile strength increase. In this stage, the tensile strength can objectively reflect the concentrations of hard molecular chains. Thus, the tensile strength was selected as criteria to measure aging process of NEPE propellants.

Later in this stage, the aging mechanism is more complex. On the one hand, by the high temperature aging, the soft molecular chain begins to degradate and the micro-phase separation is enhanced. The hard molecular chain concentration and the tensile strength increase. On the other hand, with a decreasing stabilizer content, the nitrate ester decomposition is accelerated. The hard molecular chain is easier to be oxidatively degraded and its concentration may be reduced. Thus, at the end of the second stage, the tensile strength has a second peak.

3.1.3 Accelerated Chemical Aging Stage

In the third stage, the decrease of stabilizer content induces that NO_x is neutralized insufficiently. Thus, the NO_x concentration in propellants increases. This will accelerate the molecular chain degradation, not only thermal degradation but also oxidative degradation. The degradation leads the entire mechanical system to collapse and thus the tensile strength falls fast on the macroscopic scale. Because the mechanical properties failed, this stage will not be included in the life of NEPE propellants.

In the whole aging process, the hard molecular chain in NEPE propellants increases and then decreases and thus its concentration may have one or more peaks.

3.2 Equation Derivation

The three stages of NEPE propellants aged at high temperatures show that the post curing reaction of NEPE propellants is insufficient according to the uneven distribution of isocyanate. The post curing reaction at room temperature is not obvious. Therefore, the data can be used for the service life prediction of NEPE propellants at ambient temperature from the end of post curing reaction to the mechanical failure.

From the view of dynamics and statistics, this paper established a relationship between aging degree and temperature. The rate equation of chemical reaction kinetics is follow:

$$r = \frac{d\alpha}{dt} = kf(\alpha)$$

Among them, r is the reaction rate, α is the reactant concentration, $f(\alpha)$ is the function of concentration, k is the reaction rate constant. Separating the variables from Equation 2:

The integral form of Equation 3 is as follows:

$$\frac{d\alpha}{f(\alpha)} = kd\tau$$

Equation 4 established a correspondence relationship between concentration and aging time.

$$\int \frac{1}{f(\alpha)} d\alpha = \int kd\tau = k\tau$$

In the three aging stages of NEPE propellants, the cross-linked network concentration α can be described as follows: in the first stage, α increased from the initial value α_u to the maximum value α_{max} during post-curing, the time is defined as post curing stage τ_1. In the second stage α varied from the maximum value α_{max} to the second peak α_β. This stage is named as micro-phase aging stages τ_2. In the third stage where the chemical aging is dominant, α declined from α_β to α_{min}. The time is called chemical aging stage τ_3.

Due to the post curing reaction is not obvious at room temperature, τ_2 is the time for NEPE propellants service life prediction.

$$\int_{\alpha_{\max}}^{\beta} \frac{1}{f(\alpha)} d\alpha = \int_{\tau_{\max}}^{\tau_\beta} k d\tau = k(\tau_\beta - \tau_{\max}) = k\tau_2$$

$$G(\alpha) = k\tau_2 \tag{6}$$

In the micro-phase aging stage, at different aging temperature, the aging processes of NEPE propellants are similar because the aging law is not changing with temperature. Only the size of peak and the time reaching the peak varied.

In accordance with the Berthelot equation:

$$\ln k = b + aT \tag{7}$$

Here a and b are constants. From Equation 5 and Equation 6, the next equation can be get.

$$\ln\tau_2 = \ln G(\alpha) - b - aT$$

$$\ln\tau_2 = C_1 + C_2 T \tag{8}$$

In Equation 8,

$$C_1 = \ln G(\alpha) - b$$

$$C_2 = -a \tag{9}$$

Equation 8 is the Berthelot equation for NEPE propellants life prediction [9].

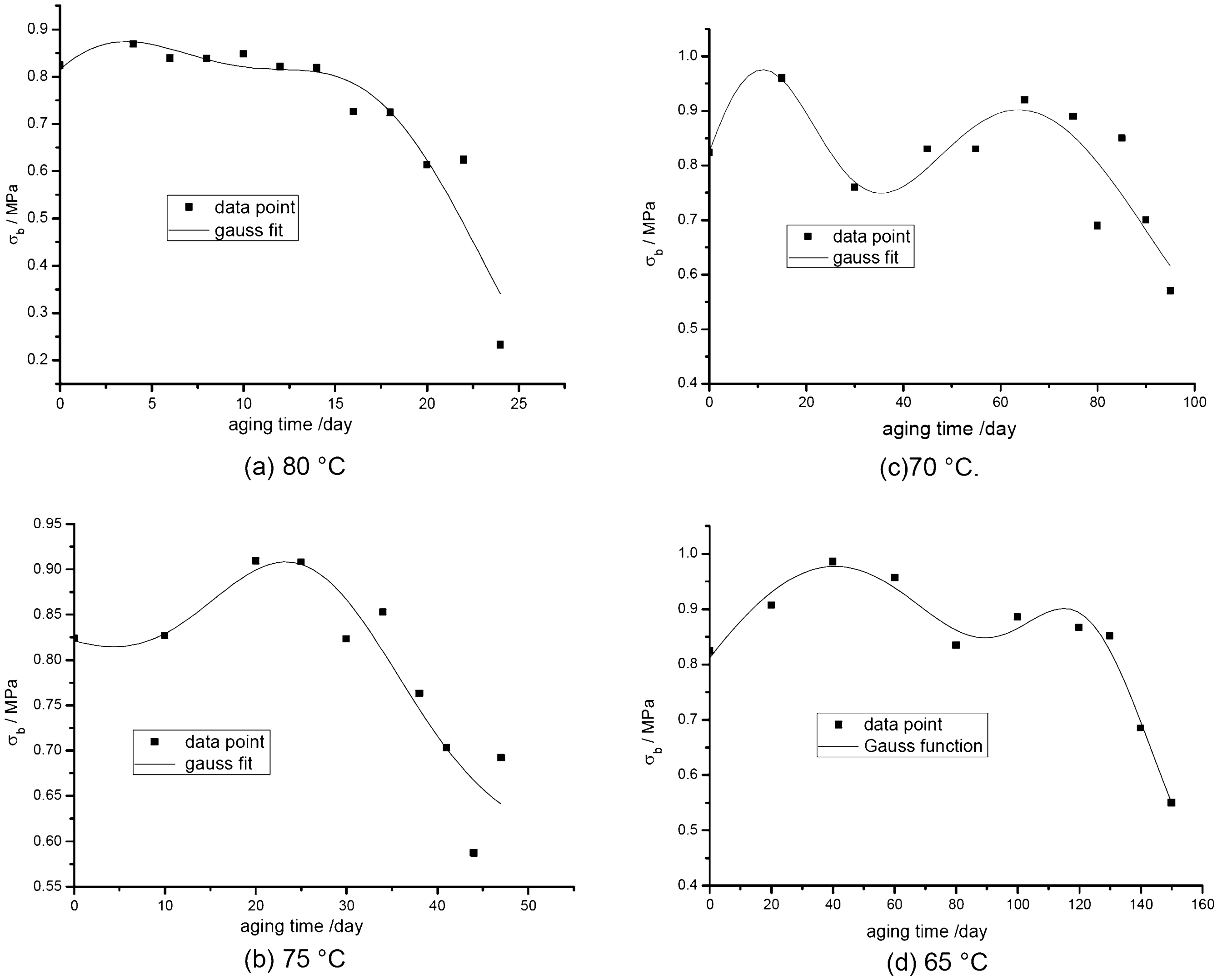

Figure 3. Data of σ_b as function of aging time.

4 Results and Analysis

4.1 Life in High Temperature Aging

The tensile strength data was fit with bimodal Gaussian function. The first peak (post curing peak) is the first central point of the fitting function. The second peak (micro-phase aging peak) is the second central point of the fitting function. Fitting curves are shown in Figure 3.

As obvious from Figure 3(a), the first peak is on the 1.96 day and the second peak is on the 17.49 day. Thus, the life of NEPE propellants aged at 80 °C is as follows:

$$\tau_2 = 17.49 - 1.96 = 15.53 \text{ days}$$

The life of NEPE propellants aged at other temperature also can be calculated as above. They are shown in Table 3. R is the relevance between the fitting function and data.

4.2 Service Life Prediction

Based on the data in Table 3, the relationship between life and aging temperature is established (Figure 4). Where *X* axis is the aging temperature and *Y* axis is $\ln\tau_2$. Figure 4 figures out that the aging temperature and $\ln\tau_2$ have a linear relationship.

From Figure 4, C_1 and C_2 in Equation 8 can be calculated:

Table 3. Life at higher temperatures.

Aging temperature [°C]	Characteristic time [day]			
	τ_{max}	τ_β	τ_2	R^2
80	1.96	17.49	15.53	0.90139
75	0	25.21	25.21	0.86081
70	8.83	63.87	55.04	0.75834
65	40.50	123.96	83.46	0.97507

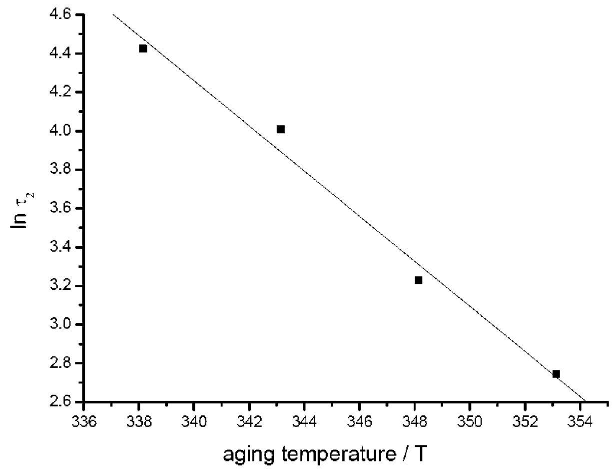

Figure 4. $\ln\tau_2$ as function of aging temperature.

$$C_1 = 43.87396$$

$$C_2 = -0.11651$$

Thus, the service life prediction equation for NEPE propellants is:

$$\ln\tau_2 = 43.87396 - 0.11651 * T \tag{10}$$

The service life of NEPE propellants at 25 °C is:

$$\tau_{25\circ} = 9449 \text{ days} = 25.9 \text{ years} \tag{11}$$

Thus, the service life of NEPE propellants at 25 °C is 25.9 years.

5 Conclusion

(1) The cross-linked network concentration represents a vital link between macro-mechanical properties and micro-phase structure aging process. Based on the trend of cross-linked network concentration and the characteristic of uniaxial tension strength, the high temperature aging of NEPE propellants can be divided into three stages: post curing stage, microstructure gradual degradation stage, and accelerated chemical aging stage.

(2) Nitrate ester is hardly to decompose at ambient temperatures, so the post curing reaction should be ignored at normal temperature. According to this reason, the service life prediction at normal temperature of NEPE propellants should be based on the second stage of high temperature aging.

(3) A new service life prediction equation for NEPE propellants was established and the service life at 25 °C was assessed.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 11072032).

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Received: February 13, 2013
Revised: May 31, 2013
Published online: September 19, 2013