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Dynamic Mechanical Properties of NEPE Propellant with Minimum Signature and its Binder Film

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Abstract: The dynamic mechanical properties of NEPE propellant with minimum signature and its binder film were measured by dynamic mechanical analyzer. The results show that the mechanical loss (loss tangent and loss module) curves of the propellant and its binder film consist of α and β relaxations, which are caused by motion of the binder molecules and motion of plasticizer molecules associated with binder sidegroups, respectively. It is found that the magnitudes of $\tan \delta$ (loss tangent) and loss modules of two relaxation processes of the propellant are obviously higher than those of the binder film because of the addition of nitramine in propellant. It is also found that viscoelastic coefficients from WLF equation and activation energy from relaxation processes of the propellant are lower than those of the binder film, which gives proofs that nitramine increases the free volume of the binder system and weakens the interactions of the molecular chains, further explains why the mechanical loss, $\tan \delta$, of the propellant is higher than that of the binder film.

Key words: polymer materials; solid propellant; dynamic mechanical characteristic; elastic-viscosity property

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1 Introduction

Nitrate ester plasticized polyether (NEPE) propellant with minimum signature were widely applied in various types of missiles, including Tow-2 antitank and AGM air-field missiles^[1-3], for its excellent energy, mechanical and low signature properties. We have researched this type of propellant with σ_m (maximum stress) approaching 0.72 MPa at +50 °C and ε_m (maximum strain) higher than 40% at -40 °C. However, it is an exploring issue to identify this type of propellant could be applied in rocket motor, because the rocket motor loaded with the propellant will get continuous and periodic force effects during transportation (air-, land- or ship-carrier) and long-term storage process, the propellant might undergo separation with the inhibiting layer and the integrality of the rocket motor will be destroyed. Therefore, whether the propellant with the mechanical properties mentioned above could endure the effects of dynamic mechanical process is essential for its safe application, transportation and storage in associating weapon systems. Research-

ers^[4,5] had studied the effects of various parameters on the dynamic mechanical characteristics of the propellant. In this paper, the dynamic mechanical and viscoelastic properties of NEPE propellant with minimum signature and its binder film were measured and compared.

2 Experimental

2.1 Sample preparation

The compositions of NEPE propellant with minimum signature (NP) are polyether binder system (8wt% - 10wt%), nitrate ester plasticizers (23wt% - 30wt%), NC (0.4wt% - 1.0wt%), RDX (55wt% - 60wt%) and other additives (3wt% - 5wt%).

The compositions of its binder film (BF) were same as those of NP but without solid ingredients (such as RDX, ballistic modifier, carbon and ballistic stabilizer, etc.).

NEPE propellant with minimum signature and its binder film were prepared in a 5-liter planetary vertical mixer, and the polymer/plasticizer, nitramine (RDX) and ballistic modifiers (not included in BF), etc. were added and stirred until well wetted, then the mixer was vacuumized. The curing agent and catalysts (TPB) were added and mixed for another 20 min under vacuum. The slurry were casted under vacuum and cured at 50 °C.

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2.2 Instrument and experimental methods

The dynamic mechanical properties of the samples were measured by the dynamic mechanical analyzer (model DMA2980, TA Corp.) with frequencies in 1, 5, 10, 20 and 40 Hz, a clamp of single cantilever model over a span of 4 mm, temperature range from $-120\text{ }^{\circ}\text{C}$ to $+40\text{ }^{\circ}\text{C}$ (temperature interval $4\text{ }^{\circ}\text{C}$) and a $5\text{ }\mu\text{m}$ amplitude. The samples were cut into rectangle slats with a length of 20 mm, a width of 10 mm and a thickness of 2 mm.

3 Results and discussion

3.1 Dynamic mechanical analysis curves of NEPE propellant with minimum signature (NP) and its binder film (BF)

The dynamic mechanical analysis (DMA) curves, including E' (storage modulus), E'' (loss modulus) and $\tan\delta$ (loss tangent) of NP and BF at 1, 5, 10, 20 and 40 Hz were shown in Fig. 1 and Fig. 2.

It was found that α and β transition relaxation peaks can be observed on the $\tan\delta$ curves of NP and BF. It is considered that α transition is caused by motion of chain segment of binder, while β transition by motion of plasticiz-

er molecules associated with binder sidegroups. Since β transition is more significant than α transition (in Fig. 1 and 2), which is difficult to determine the specific temperature range of α transition. T_g (glass transition temperature) is the peak temperature of E'' curve on 1 Hz corresponding to its β transition process. Thus, T_g of NP and BF were $-60\text{ }^{\circ}\text{C}$ and $-56\text{ }^{\circ}\text{C}$, respectively. Considering the temperature interval for the test was $4\text{ }^{\circ}\text{C}$, T_g of NP and BF were approximately equal.

3.2 Effects of solid ingredients on dynamic mechanical properties

It is known that high content of nitramine (55wt% - 60wt%) has obvious effect on the dynamic mechanical properties of NEPE propellant with minimum signature. The differences of E' , E'' and $\tan\delta$ curves of NP and BF at 1 and 40 Hz were shown in Fig. 3 and the detail data of $\tan\delta$ and E'' are listed in Table 1.

It was found from Fig. 3 that E' ($T_{E'} < -70\text{ }^{\circ}\text{C}$) and E'' ($T_{E''} < -40\text{ }^{\circ}\text{C}$) of NP were higher than those of BF in low temperature stage (or the glass state), while less than those of BF in the viscoelastic state ($T_{E'} > -50\text{ }^{\circ}\text{C}$ and $T_{E''} > -40\text{ }^{\circ}\text{C}$). These indicate that high content of solid components (especially nitramines) can enhance the viscoelastic properties of the binder matrix in low temperature (with $T < -50\text{ }^{\circ}\text{C}$) and decrease them as temperature increases.

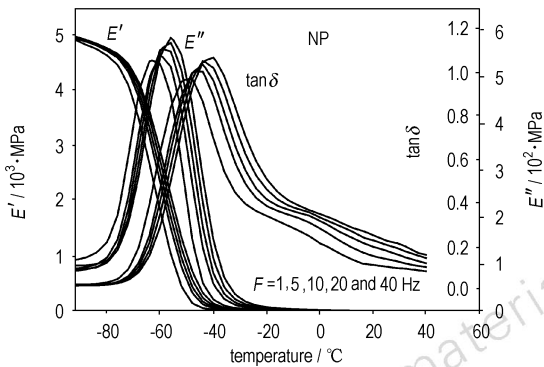


Fig. 1 DMA curves of NP

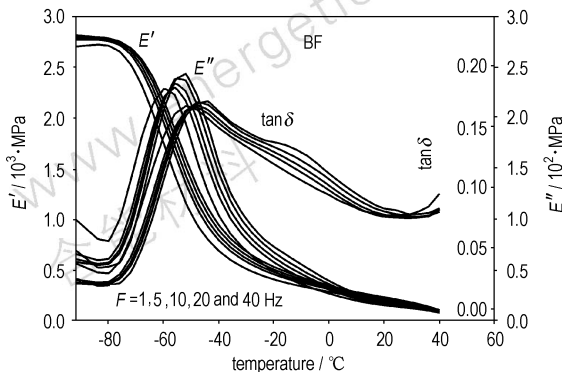


Fig. 2 DMA curves of BF

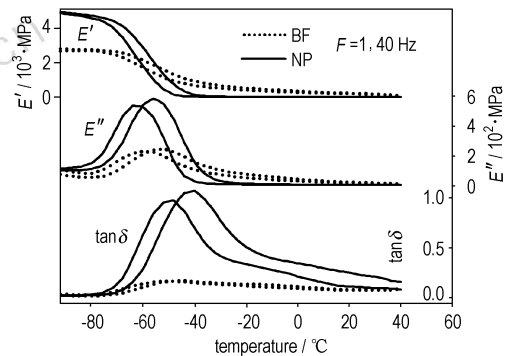


Fig. 3 Comparison of E' , E'' and $\tan\delta$ of NP and BF at 1 and 40 Hz

Table 1 Peak maximums of $\tan\delta$ of NP and BF at 1 and 40 Hz

sample	f/Hz	$\tan\delta$ maximums		E'' maximums/ $10^2 \cdot \text{MPa}$
		α	β	β
BF	1	-	0.167	2.22
BF	40	0.136	0.171	2.43
NP	1	0.356	0.973	5.42
NP	40	0.392	1.070	5.83

It was also found from Fig. 3 and Tab. 1 that the peak magnitudes of $\tan \delta$ and E'' on β relaxation of NP were obviously higher than those of BF by addition of solid ingredients (RDX). The reason might be that huge amount of loosen interphase^[6,7] is formed between RDX particles and the binder matrix by addition of RDX for its inert surface properties. Therefore, the cross-link degree of the binder matrix approaching the interphase is weakened, which increases the loss of α transition and peak maximum. On the other hand, high content of RDX particles with loosen interphase between the binder matrix (in NP) also increase the amount of free-volume of the system, thus, the motion of plasticizer molecules associated with binder sidegroups in NP is more active than that in the binder film BF, which can significantly increase the loss of β transition peak magnitude, correspondingly.

3.3 Master curves of NP and BF

The effects of solid components on NP and BF were further analyzed by their master curves. The master curves of E' to f (frequency) and horizontal shift factor α_T to T (temperature) of NP and BF corresponding to 1, 5, 10, 20 and 40 Hz were obtained on the basis of "time-temperature superposition" principle (WLF equation), with T_g as T_s (reference temperature). The results are shown in Fig. 4 and Fig. 5.

According to WLF equation:

$$\log \alpha_T = \frac{C_1 (T - T_s)}{C_2 + T - T_s} \quad (1)$$

Where α_T , horizontal shift factor; T_s , reference temperature; C_1, C_2 , experiment constant.

C_1 and C_2 could be presented as C_1^g and C_2^g (viscoelastic coefficient) from WLF equation when $T_s = T_g$, and activation energy E_a from relaxation processes for NP and BF were obtained, shown in Table 2.

Based on free-volume theory^[8]:

$$f_g^g = \frac{B}{2.303 C_1^g} \quad (2)$$

$$\alpha_f = f_g^g / C_2^g \quad (3)$$

Where f_g^g , free volume fraction, α_f , free volume expansion coefficient, B , constant.

It was found from Table 2 that C_1^g , C_2^g and E_a of NP were lower than those of BF. Thus, f_g^g and α_f of NP were higher than BF according Eqs. (2) and (3). The possible

reason might be that the free volume of the binder system in NP was increased by addition of solid ingredients in BF, which could weaken the interaction between the chains of binder matrix, thus the motion of chain segment becomes more flexible. In addition, E_a of NP less than that of BF also indicated that the mechanical relaxation process of NP is easier than that of BF, which is corresponding to the increasing of $\tan \delta$ magnitudes over test temperature range in NP comparing with BF mentioned above.

4 Conclusions

(1) The magnitudes of $\tan \delta$ and E'' over test temperature range of the propellant were obviously higher than those of the binder film by addition of nitramine in propellant.

(2) C_1^g , C_2^g from WLF equation and relaxation activation energy E_a of the propellant were lower than those of the binder film.

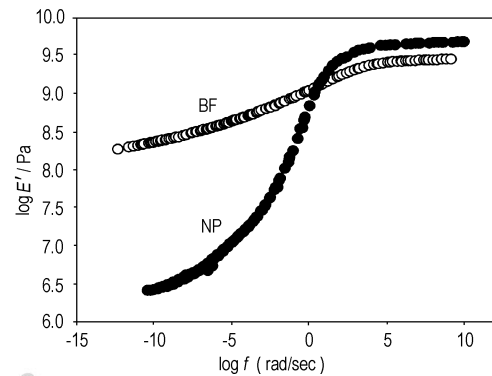


Fig. 4 The master curves of E' of NP and BF

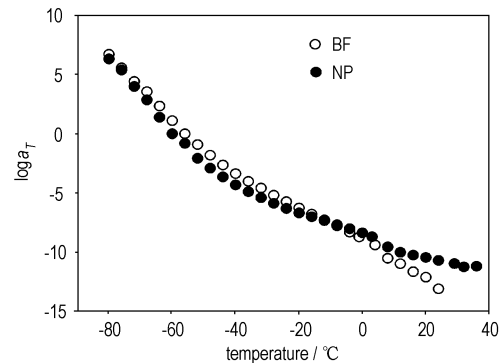


Fig. 5 The horizontal shift factor α_T curves of NP and BF

Table 2 The viscoelastic parameters and relaxation activation energy for NP and BF

sample	$T_s / ^\circ\text{C}$	C_1^g	C_2^g	$E_a / \text{kJ} \cdot \text{mol}^{-1}$
BF	-56	30.60	129.0	191.1
NP	-60	18.11	63.83	164.0

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微烟 NEPE 推进剂及其粘合剂胶片的动态力学性能研究

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摘要: 采用动态力学分析方法研究了微烟 NEPE 推进剂及其粘合剂胶片的动态力学性能。结果表明, 微烟 NEPE 推进剂及其粘合剂胶片的 $\tan \delta$ (损耗角正切) 曲线均存在 α 和 β 转变峰, 分别由增塑剂和粘合剂体系的玻璃化转变引起, 加入硝酸铵填料使两个转变过程的力学损耗 $\tan \delta$ 增大, 峰温向高温移动。微烟 NEPE 推进剂的试验常数和表观活化能均低于其粘合剂胶片对应的值, 表明加入硝酸铵填料会增大粘合剂分子运动的自由体积, 减弱分子链间的相互作用, 可以解释微烟 NEPE 推进剂的力学损耗 $\tan \delta$ 大于粘合剂胶片的原因。

关键词: 高分子材料; 固体推进剂; 动态力学性能; 粘弹特性

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Behavior of Non-isothermal Crystallization of DNTF(II) : Crystallization Kinetics in RDX

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Abstract: The non-isothermal crystallization of 3,4-dinitrofurazanfuroxan (DNTF) in RDX was studied by DSC. The results show that RDX reduces the super-cooling degree and eliminates heating-self. On the basis of Avrami and Avrami-Ozawa equations, the Avrami exponent n and Ozawa exponent m are obtained to be 3.12 and 2.48, respectively. The kinetic parameters E_a of DNTF non-isothermal crystallization is obtained by Kissinger equation to be $-378.19 \text{ kJ} \cdot \text{mol}^{-1}$. Moreover, the behaviors of non-isothermal crystallization of DNTF in RDX and HMX were compared.

Key words: physical chemistry; crystallization kinetics; non-isothermal crystallization; 3,4-dinitrofurazanfuroxan (DNTF); DSC