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Investigation of the role of aziridine bonding agents on the aging of the composite solid rocket propellant (CSRP)

Amged A Ali, ZHANG Jiarwei, CAI Guobiao

School of Astronautics,

Beijing University of Aeronautics and Astronautics, Beijing 100191, China

Abstract: The role of bonding agents on the aging characteristics is one of the important research topics. Aging program of the prepared propellant samples was conducting as follows:

Five samples, two free of bonding agents, and three containing an aziridine based bonding agents (MAPO, HX 752, MAT4), four samples based on different bonding and curing agents all were aged at 70 °C.

The prepared bonding agent "MAT4" gave remarkable improvements and resulted in highly stable mechanical properties comparing with HX 752 or MAPO. The selected bonding agents family inhibited the rate of decomposition of the propellants during the aging periods and supported the propellant matrix against decomposition at the elevated temperatures.

Key words: propellant matrix; accelerated aging; bonding agents; analysis techniques; mechanical properties; curing agents

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Aging behavior of CSRP is affected by many factors, such as temperature, mechanical stresses, and humidity. Temperature accelerates the possible aging reactions depending on their activation energy. When the mechanical stresses exceed a certain threshold, degradation of the binder-solid adhesion occur^[1].

Aging of composite propellants can be followed up via a number of experimental tests and then it will not be difficult to estimate and predict the propellant useful shelf or storage life from the recorded changes in physical and chemical properties during thermal and mechanical cycles^[2].

Aging studies can be helpful for estimating

and predicting the shelf life of a given propellant grain. Tests are often performed at elevated temperatures to obtain advance information concerning the chemical reactions, which may occur during aging. It is therefore necessary to study these reactions individually to understand their mechanisms and to develop the aging model^[3].

Separation of the CSRP ingredients and their chemical analysis via the sol-gel technique were employed in the aging studying^[3]. Recently other techniques such as the dynamic mechanical analysis (DMA)^[4], tensile mechanical analysis (TMA)^[5], thermal and penetrometer^[6], become useful.

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Amged A Ali, Born in 1966 at Cairo, Egypt. In 1989, he received B.Sc. Chemical Engineering from The Military Technical College in Cairo. Presently he is a PhD candidate at Beijing University of Aeronautics and Astronautics, China, in the specialty of Propulsion Engineering of Aeronautics & Astronautics. His research interests include Aging of Solid Rocket Motor. E-mail: naghmaged@hotmail.com

1 Model evolutions between accelerated and natural aging in HTPB (CSRP)

Exposing the propellant samples to elevated temperature chemical change rates will be accelerated according to the Arrhenius equation. For this reason the HTPB propellants could never be exposed to temperatures above 70 °C. Assuming that only one type of reactions occurs at the sites of instauration in the polymer chain, one can write:

$$\frac{dP}{dt} = \frac{C}{t} \tag{1}$$

Where *C* is the rate of change of the property *P*

The integration of this equation produces the aging model:

$$\int_{P_0}^P dP = C \int_{t_0}^t 1/t \, dt, \quad P - P_0 = C \ln t/t_0$$

$$P = P_0 + C \ln t/t_0. \tag{2}$$

For *t* = *t*₀ = 1 week, it is *P* = *P*₀ (property after curing time). In fact, if it is hypothesized that a certain propellant characteristics *P* = assumes the value after a time *t*₀, by accelerated aging, and after a different time *t_n*, by natural aging.

$$P_{t_a} = P_0 + C_a \ln \frac{t_a}{t_0}$$

$$P_{t_n} = P_0 + C_n \ln \frac{t_n}{t_0} \tag{3}$$

Since *P_{t_a}* = *P_{t_n}* at the end of curing i. e. at *t*₀ = 1 week, therefore

$$P_0 + C_a \ln t_a = P_0 + C_n \ln t_n$$

$$\ln t_n = \frac{C_a}{C_n} \ln t_a \tag{4}$$

For accelerated aging temperature $\frac{C_a}{C_n} = K$, putting time *t* in week (w):

$$\ln W_n = K \ln W_a \quad \text{or} \quad W_n = W_a^K \tag{5}$$

This relationship correlates the time of accelerated aging to the natural aging and allows predicting the propellant shelf life from the two constant *C_n* (at 25 °C) and *C_a* (at different temperatures)^[7].

2 Experimental techniques

2.1 Preparation of the MAT 4 and melting of the HX-752

MAT4 is prepared according to the following sequence: Mixing 74.4793 g of MAPO with 17.7193g of adipic acid (C₆H₁₀O₄) and 7.8009g of tartaric acid (C₄H₆O₆) in a clean flask, heating up to 40 °C using a water bath for 40min. until a viscous solution is formed, then put the product in the refrigerator.

Note This condensation reaction is hazard (exerted higher energy) and needs high precision during preparation.

The HX-752 bonding agent is always delivered on the iced form since it must be kept at - 18 °C to save its effectiveness, so before using HX-752 it must be left in the ambient temperature for about 7 h. and then put in an electrical oven at 40 °C for 4h.

Note it is recommended to use it within 5 h at most after melting unless loses its effectiveness.

2.2 Group (A) propellant formulation

The five prepared samples mentioned in Table 1, Three of them were based on (MAPO, HX-752, and MAT4) and other two were free of bonding agent with varying curing ratio.

Table 1 Propellant formulation of the group (A)

Ingredients	composition based on				
	MAPO S1	HX752 S2	MAT4 S3	NBA1 S4	NBA2 S5
HTPB/ %	9.60	9.60	9.60	9.82	9.58
IPDI/ %	0.69	0.69	0.69	0.71	1.02
DOZ/ %	2.40	2.40	2.40	2.45	2.39
MAPO/ %	0.3				
HX-752/ %		0.3			
MAT4/ %			0.3		
AI/ %	16.0	16.0	16.0	16.0	16.0
APC/ %	71.0	71.0	71.0	71.0	71.0
(NCO/OH)	0.78	0.78	0.78	0.78	1.15

2. 3 Group (B) propellant formulation

As mentioned in Table 2, two different bonding agents HX-752, MAT4 were employed. Besides pay attention to the major applied curing agents IPDI, and HMDI to examine if there is remarkable effect of the curing agent on the samples aging, hence we prepare four samples have the same curing ratio ($NCO/OH = 0.82$).

Table 2 Propellant formulation of the group (B)

Ingredients	composition based			
	MAT4 (IPDI)	MAT4 HMDI	HX- 752 (IPDI)	HX- 752 HMDI
HTPB/ %	9.80	9.94	9.80	9.94
IPDI/ %	0.74		0.74	
HMDI/ %		0.57		0.57
DOZ/ %	2.45	2.48	2.45	2.48
MAT4/ %	0.3	0.3		
HX- 752/ %			0.3	0.3
AI/ %	16.0	16.0	16.0	16.0
APC/ %	71.0	71.0	71.0	71.0
(NCO/OH)	0.82	0.82	0.82	0.82

2. 4 Preparation of propellant specimen

The cured sample boxes tested via an X-ray unit to assess the inner homogeneity of the grain, air bubbles, porosity and foreign matter in propellant grain. then cut the grain to standard dumbbell shape (JANNAF), the propellant specimens numbered and put in aluminum bags purged with nitrogen and put in the ovens to start the aging program.

2. 5 Mechanical properties of the propellant specimen

Every change occurring in the propellant during the aging time causes the change of the mechanical properties which measured using a LRX-5K material testing machine. This system has the opportunity to measure manually and automatically using DAPMAT software. Tested samples fitted in the two jaws and adjusting the required measuring parameters, the machine

works until the cutting of the specimen. Test is repeated at least three times for each testing temperature.

3 Results and discussions

3. 1 Mechanical properties of group (A) aged samples

From Fig. 1 maximum stress results can be divided into three sections:

- 1) Sample (NOBA-I) prepared without B. A. and curing ratio 0.78 exhibit low value of (σ_m) and during the aging period (σ_m) value start to increase which may indicate that the aging temperature and time of aging affect on the propellant matrix and lead to increase (σ_m).
- 2) Sample without B. A. and curing ratio 1.15 (NOBA-2) illustrates the role of curing ratio which leads to increase the (σ_m), since $NCO/OH >$ stoichiometric value shows a complete reaction of all OH of HTPB, hence a hard matrix established.
- 3) Sample based on HX-752 shows a relatively high value of (σ_m) from the beginning and increased with aging time. The same occurs on using MAPO but in case of MAT4 (σ_m) is approximately stable during aging period^[8].

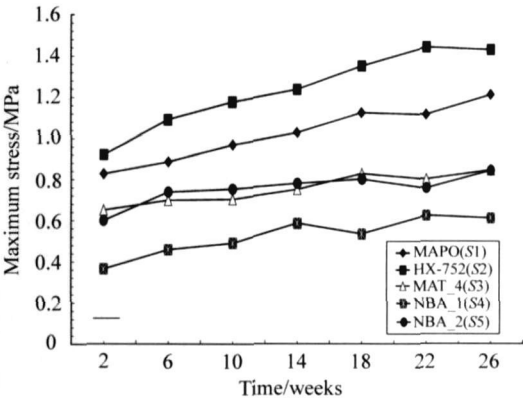


Fig.1 Maximum stress of group a aged propellant samples

Fig. 2 presents the strain at the maximum stress (ϵ_m) as follows:

- 1) The samples free of bonding agents were not offer the required values of (ϵ_m) and also decreased during aging period.
- 2) Sample based on HX-752and MAPO

shows a good result of (ϵ_m), and begin to decrease through the aging time

3) Samples based on MAT4 show a good result at zero time aging and during the aging time.

Hence one can say that the bonding agents are therefore essential for improving the (ϵ_m) of the propellant samples.

The (ϵ_m) of all samples were decreased due to the effect of the temperature on the propellant matrix which leads to the migration of plasticiser and the deterioration of the bonding agents, rupture of the adhesion force between the oxidizer and the binders matrix.

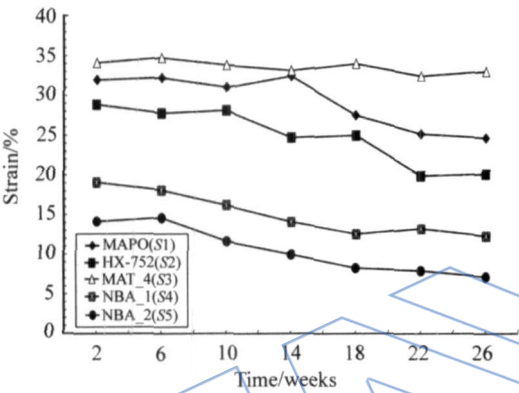


Fig. 2 Strain at maximum stress of group A propellant samples

Fig. 3 represents the results of young's modulus as follows:

1) Samples (HX-752 and NOBA-2) shows high rate of increase of E_0 , the same occurs in case of samples based on (MAPO and NOBA-I).

2) Samples based on MAT4 shows stable results of E_0 during the aging period.

From the above results of the mechanical properties of the different propellant samples aged at 70 °C we can conclude that:

1) Samples free from bonding agents havent performed the desired mechanical properties.

2) Low percentage (0.3%) of bonding agents of the aziridine family improves the mechanical properties.

3) Aging at elevated temperature such as 70 °C during aging period leads to decrease of the mechanical properties of the propellant samples.

4) Migration of the plasticizer and deterioration of bonding agents were the essential reason of cleavage of the AP-binder matrix which leads to cracks and rapture of the propellant grain.

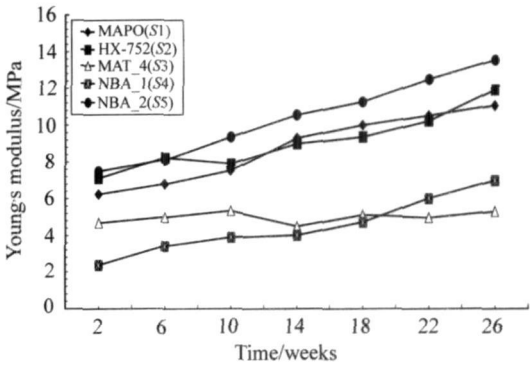


Fig. 3 Young's modulus of group A aged propellant samples

3. 2 Mechanical properties of group(B) aged sample

From Fig. 4 maximum stress (σ_m) can be illustrated as follows:

1) Maximum stress (σ_m) of samples based on MAT4 were approximately the same during the aging period, the role of the curing agent type appeared as the sample cured by HMDI the rate of increase (σ_m) was slightly higher than the sample based on IPDI.

2) Maximum stress (σ_m) of samples based on HX-752 was increased with the aging time besides the stress of HMDI sample was slightly higher than IPDI sample.

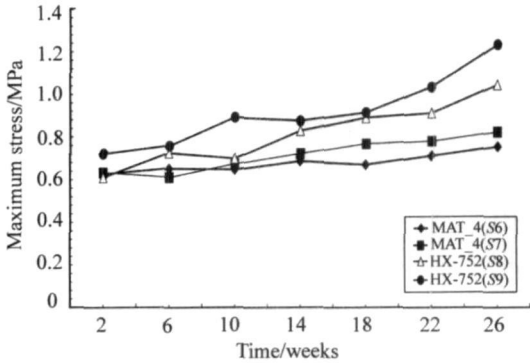


Fig. 4 Maximum stress of aged propellant samples of group (B)

3) Curing agent HMDI improve the maximum stress of the prepared samples, as in sam

ples based on MAT4 control the (σ_m) and samples based on HX-752 increase the rate of (σ_m).

Both results of (σ_m) of the propellant samples with different bonding agent were nearly the same as results of the samples of (A) group. The aging results are comparable with those found in the literature^[6].

From Fig.5 the results of (ϵ_m) are illustrated as follows:

- 1) The zero time properties of the four samples are within the specification.
- 2) The aging period produce two different behaviors, one for the samples based on MAT4 which has stable values of (ϵ_m), and the other behavior shows the decreasing rate of (ϵ_m) for the samples based on HX-752 was slightly rapid. Both behaviors confirm the different changes in the (ϵ_m) of the four samples.

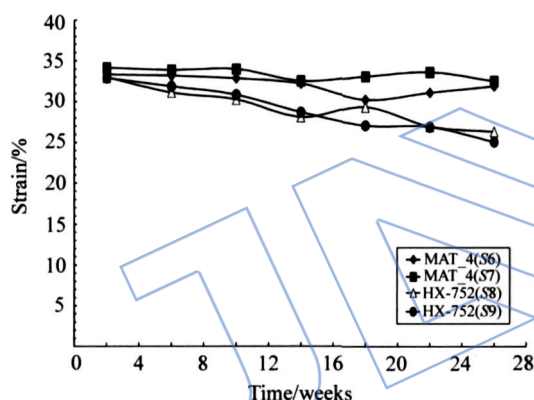


Fig.5 Strain at maximum stress of propellant samples of group (B)

From Fig.6 the young's modulus illustrates as follows:

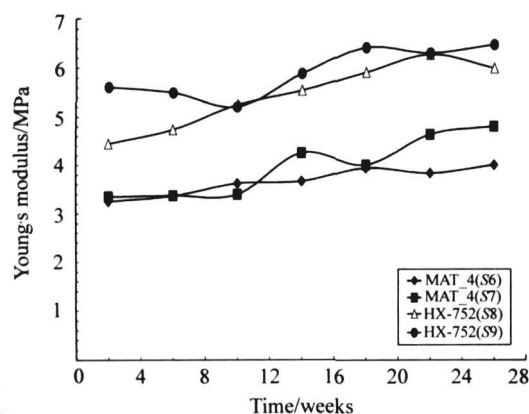


Fig.6 Young's modulus of propellant samples of group (B)

Samples based on MAT4 the young's modulus keep to certain limit due to the stability in both the maximum stress and the strain at (σ_m), Samples based on HX-752 the young's modulus slightly increased to a higher limits due to the increase of the (σ_m).

4 Conclusions

The following conclusions could be drawn from the present study which represents an approach for explain the role of the bonding agents affecting on the aging of the CSRP.

- 1) The used bonding agents in a very small percentage were essential for achieving the desired mechanical properties, and also for inhibiting the self-decomposition of the prepared propellant samples.
- 2) Use of the laboratory prepared bonding agent (MAT4) improves the propellants mechanical properties, more than the other used bonding agent such as HX-752 and MAPO.
- 3) Aging the propellant samples based on HX-752 illustrates an increase in the both maximum stress and young's modulus.
- 4) Strain corresponding to maximum stress depends on the used bonding agents, MAT4 comes first since it saves the value of the strain. MAPO and HX-752 come after MAT4, in the second and third rank respectively.

5) The curing aging type also affecting the propellant mechanical properties during aging. Since the samples cured by HMDI give a better maximum stress comparing with the samples cured by IPDI.

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