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Effects of Plasticizers, Antioxidants and Burning Rate Modifiers on Aging Performance of the HTPB/ HMDI Composite Solid Propellant

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Abstract: The effects of plasticizers, antioxidants and burning rate modifiers on the aging performance of the composite solid propellant based on hydroxyl-terminated polybutadiene(HTPB)/hexamethylene diisocyanate (HMDI) were explored by applying an accelerated aging program for 90 day at 70 ℃. The HTPB propellant matrix with the diisooctyl sebacate (DOS) as plasticizers and diisooctyl azelate (DOZ), antioxidants as *N*, *N'*-Diphenyl-p-phenylenediamine (AO) and 2, 2'-methylenebis (4-methyl-6-tert-butylphenol) (cyanox 2246) and burning rate modifiers as barium ferrite (BF), copper chromites (CC) and ferric oxide (FO) were varied. Results show that sample (S1) which based on DOS decreases the stress value and increases the strain value which considered to be an excellent start for aging program. Sample (S3) containing AO presents the higher resistance to oxidation showing the better performance that reflects on increasing the shelf life of the composite solid propellant motor. Sample (S5) which based on BF enhances the ballistic performance among over the other tested two samples. The accelerated aging program allowed us to estimate the motor in-service lifetime.

Key words: polybutadiene(HTPB)/hexamethylene diisocyanate (HMDI) composite solid propellant; plasticizers; antioxidants; burning rate modifiers; aging program

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1 Introduction

Composite solid propellant (CSP) is generally composed of a polymeric matrix based on prepolymer HTPB loaded with an oxidizer as ammonium perchlorate (AP), plasticizers such as DOS or DOZ, metallic fuel as an aluminum powder (Al) and a cross-linking agent as hexamethylene diisocyanate (HMDI) [1]. Since 1965 the use of home-polymers with functional end called telechelics led excessively better performing electrometric binders since they offered a higher solid loading and a wide operating temperature range [2]. The final formulation should have good mechanical and ballistic properties, and it should not deteriorate with aging effects or exposure to different environmental influences [3].

The mechanical properties of the composite solid propellant are dependent on the type and the quantity of the binder and solid fillers particles. Moreover, the composite solid propellant ballistic performance is mostly dependent on the particles size and shape of the oxidizer and metallic fuel [4].

Plasticizers reducing the viscosity of the slurry and affecting the mechanical properties by lowering the glass transition temperature (T_g) of the binder and increasing its strain, which has a remarkable effect on the shelf life of the composite propellant [5].

The antioxidants materials is essential to delay aging of the propellant in various ambient conditions. The antioxidants functions in HTPB composite

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solid propellants are to intercept the oxygen-based radical species that, otherwise, lead to undesired additional cross-linking reaction [6].

The research on optimizing the concentration of different antioxidants being used in the formulations of composite solid propellant indicates that, a small mass fraction per percent up to 1% antioxidants are sufficient to retard the auto-oxidation occurred along aging time [7].

The burning rate modifiers are divided into burning rate accelerators, burning rate moderators and burning rate stabilizing agents.

First, the burning rate accelerators are used to accelerate the decomposition of the oxidizer. It is essential to control the utilization of accelerators for their migration tendency by grafting the accelerators into the polymer chain.

Second, the burning rate moderators classified into two types, the first type like alkaline salts modifying the decomposition kinetics of the oxidizer, the second one such as ammonium nitrate which lowering the propellant burning temperature .

Finally, the burning rate stabilizing agents like carbon black is used to block the radiation of the burning front, which tends to heat the propellant below the burning surface, accelerating its combustion and creating low-pressure fluctuations [8].

Composite solid rocket propellant motors are often designed to specific applications such as a tactical missile propellant or a space booster propellant; each of them has different performance, different burning rate and specific chemical ingredients [9].

The viscosity of the mixture also is an essential factor in the casting process and processability. There are other factors besides the binder which affect it as shape, size, content and surface properties of the solid fillers in propellant formulation [10-12].

Temperature variation along the storage time is the main reason that affects the stress and strain values of the solid grains, thus the mechanical properties should be stable enough to resist the vibrations and shocks occurred during handling and transportations to prevent the occurrence of an accidental cook-off [13].

In this work, the effects of plasticizers, antioxidants and burning rate modifiers on aging performance of the composite solid propellant were studied by applying an accelerated aging program for 90 d at 70 ℃, leading to figure out their effect on the shelf life of the solid motor.

2 Materials and Experimental Method

All the chemicals used in this work were of high purity; HTPB as a prepolymer, DOS and DOZ as a plasticizer, HMDI as a cross-linking agent , MAT4 (from a condensation reaction product of 2 mol of MAPO, 0.7 mol of adipic acid and 0.3 mol of tartaric acid) as a bonding agent, AO and cyanox 2246 as an antioxidant, barium ferrite (BF), copper chromites (CC) and ferric oxide (FO), as burning rate modifiers, Al as a metallic fuel, AP as an oxidizer . All the chemicals used during this research except AO and cyanox 2246 were obtained from Abu Zaabal Company for specialized Chemicals, Cairo, Egypt, AO and cyanox 2246 were purchased from Sigma Aldrich.

Different formulations according to the weight percentage of the selected propellant samples with various plasticizers, antioxidants and, burning rate modifiers were prepared to investigate the effect of these materials on the aging performance of the composite propellant. As a first step to investigate the effect of plasticizers, two samples were prepared, sample S1 with DOS and the other sample S2 with DOZ as shown in Table 1.

For the effect of different antioxidants being used, two samples were prepared; one based on AO as S3 and the other one S4 based on cyanox 2246. Applying an accelerated aging program for 90 days at elevated temperature fixed at 70 ℃ in order to investigate which sample will be higher resistance to oxidation reactions and showing the better performance along the aging program which consequently will reflect on the rocket motor lifetime. The formulations were shown in Table 2, where DOS was used.

Table 1 Propellant formulations with different plasticizers

ingredient	mass fraction/%	
	S1	S2
HTPB	10.5247	10.5247
HMDI	0.5441	0.5441
MAT4	0.3	0.3
DOS	2.6312	-
DOZ	-	2.6312
Al (22 μm)	17.0	17.0
AP (400 μm)	40	40
AP (200 μm)	19	19
AP (7-11 μm)	10.0	10.0
(NCO/OH)	0.72	0.72

Table 2 Propellant formulations with different antioxidants

ingredient	mass fraction/%	
	S3	S4
HTPB	10.5247	10.5247
AO	0.5247	-
Cyanox 2246	-	0.5247
HMDI	0.5441	0.5441
MAT4	0.3	0.3
DOS	2.6312	2.6312
Al (22 μm)	17.0	17.0
AP (400 μm)	40	40
AP (200 μm)	19	19
AP (7-11 μm)	10.0	10.0
(NCO/OH)	0.72	0.72

Three composite propellant formulations being prepared based on different burning rate modifiers with the same weight percentage, sample S5 with BF, and sample S6 with CC and the last one S7 containing FO. These formulations were tested under the same aging program conditions using the 2-inch motor technique. Different formulation represented in Table 3, containing DOS and AO.

These composite solid rocket propellants formulations were prepared by using the casting technique under vacuum. The casting process technique was done in a stainless steel bowl of 10 kg capacity provided with double wall jacket, where a circulating liquid could be either cooled or heated. The stainless steel bowl was equipped with a vertical mixer with three blades which are rotating in an orbital motion.

Table 3 Propellant formulations with different burning rate modifiers

ingredient	mass fraction/%		
	S5	S6	S7
HTPB	10.00	10.00	10.00
AO	0.5247	0.5247	0.5247
HMDI	0.5441	0.5441	0.5441
MAT4	0.3	0.3	0.3
DOS	2.6312	2.6312	2.6312
BF	0.5	-	-
CC	-	0.5	-
FO	-	-	0.5
AP (22 μm)	16.5	16.5	16.5
AP (400 μm)	40	40	40
AP (200 μm)	19	19	19
AP (7-11 μm)	10.0	10.0	10.0
(NCO/OH)	0.72	0.72	0.72

The first step was precisely weight for the HTPB, Al, bonding agent and the burning rate modifier then applying well-mixed process at 500 $r \cdot min^{-1}$ for 5 min at 40 ℃ without applying vacuum, then continue the mixing process, but under vacuum for 2 min at 1500 $r \cdot min^{-1}$. At these conditions, the mixing process was continued with rising temperature until reaching 70 ℃. Then dividing the oxidizer into four equal portions after drying it and added, then stirring without vacuum for 8 min for every portion. After adding the last portion of the AP the mixing was kept under vacuum for 18 min.

The mixture was then cooled until reaching the temperature 40 ℃. The mixing then stopped and the accurately calculated weight of the HMDI was added, the stirring was continued without vacuum for 5 min at 40 ℃ then for 20 min under vacuum. The vacuum was released with nitrogen, and the mixing was continued for 5 min. Finally, the sample of the mixture was taken for a quality control via an X-ray unit to assess the inner homogeneity of the grain, air bubbles, porosity, cracks and foreign matter in the propellant grain, and then the mixture was left to be cured and hardened and cured at 55−60 ℃ for 10 d.

Stress-strain relation and modulus of elasticity were measured experimentally for the prepared samples, using an efficient Zwick material testing according to ASTM D412-92. JANNAF dog bone samples as shown in Fig. 1 was tested in a uni-axial tensile test at room temperature (25 ℃) and atmospheric pressure.

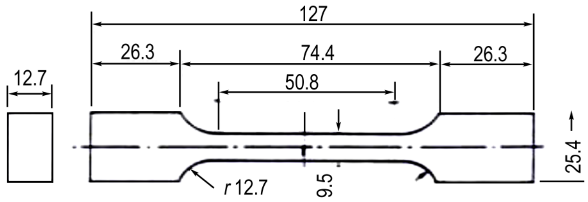


Fig.1 Uniaxial tensile JANNAF testing specimen (unit in mm)

Hardness (SHORE A) of the aged composite propellant samples was measured according to the ASTM D2240 specification using Zwick hardness tester 3102, applying constant time rate of measuring 30 s.

The ballistic performance for the composite solid propellant samples was measured at 25 ℃ by using the 2-inch motor, samples as solid grains were assembled with a nozzle offering a pressure range of (40-80) bar on firing as shown in Fig. 2, the conditioned propellant motors were fixed on the test stand in the testing field and fired.

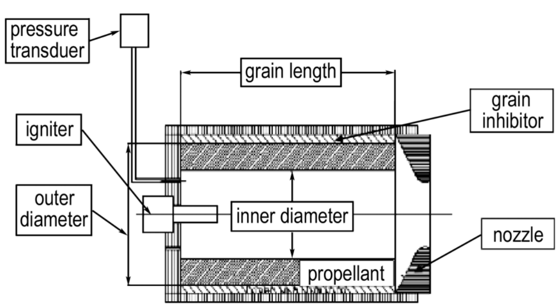


Fig.2 Test stand for the 2-inch motor technique

The thermal decomposition for propellant samples was analyzed at specific heating rates (10 ℃·min^{-1}) and up to 500 ℃ in a dynamic nitrogen atmosphere using SDT Q600 V20.5 Build 15 (temperature accuracy 0.001 ℃).

The scanning electron microscopy SEM Technique was performed using the scanning electron microscope Supra 55 VP manufactured by ZEISS, Germany.

3 Design of Aging Program

Physical and chemical processes are related to diffusion phenomena or molecular reactions that governed by the kinetic relationships which can be accelerated by applying high temperature.

Despite using the antioxidant, oxidative loads takes place during the manufacturing process, at the kneading and at the curing of the final composition leading to the presence of some oxidative pre-damaging immediately after the production. These pre-damaged areas can be easily affected by aging processes leading to enlarge during the aging time to give micro and/or macro-fractures before and during the operation of the service life of the propellant.

Therefore, due to the presence and the growth of these micro-fractures along the service life of the solid rocket propellants can cause cohesive critical cracks take place during the ignition phase, these cracks increased the area of the burning surface lead to an out-of-design state. To study these phenomena, the aging program developed in was applied to evaluate the aging mechanisms involved in the accelerated aging program at 70 ℃ for 90 d. The relation between the normal and accelerated aging program is represented in Table 4 and given in detail in the paper of Bohn [14].

Table 4 Aging program condition

aging condition	temperature /℃	aging time		
normal	25	5 years	10 years	15 years
accelerated	90	5 d	10 d	15 d
	80	12 d	25 d	40 d
	70	30 d	60 d	90 d
	60	75 d	150 d	220 d

4 Results and Discussion

Figure 3 reveals the stress, strain, Young's modulus and hardness (SHORE A) of the two prepared propellant samples based on DOS(S1) and DOZ(S2). From Fig. 3, it was noticed from the maximum stress and strain at maximum stress values that the sample S1 based on DOS lowering the maximum stress value and increase the elasticity (strain values) which considered as an advantage to start the aging program with such values that led to increasing the composite propellant service life. Due to the previous results, Young's modulus and hardness values are expected as they really depend on stress/strain values.

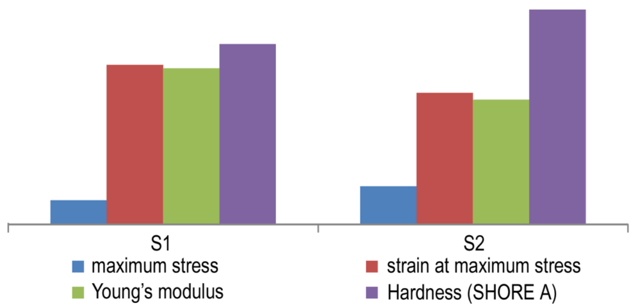


Fig.3 Effect of plasticizers on the prepared propellant samples

In another set of samples, two samples were prepared with different antioxidants. Sample S3 based on AO and sample S4 based on cyanox 2246, investigate the effect of both antioxidants on the mechanical properties of composite propellant by applying an accelerated aging program for 90 d at temperature 70 ℃.

Figure 4 explain that a general increasing trend for maximum stress, Young's modulus, and hardness could be observed for both formulations along aging time against a correspondent decrease in elongation at break was observed, thus revealing a marked tendency of propellant hardening. A severe embrittlement was observed for the sample S4 aged for times longer than 60 d which approximately about 10 years, whereas sample S3 showed a greater resistance and higher effectiveness on stabilization the HTPB/HMDI binder by withstanding a period of 80 d before embrittlement was observed which is approximately about 14 years for the motor in-service lifetime.

In order to determine the effect of burning rate modifier on the ballistic performance along aging program, three samples S5 S6, S7 shown in Table 3 were prepared. It was noticed that sample S5

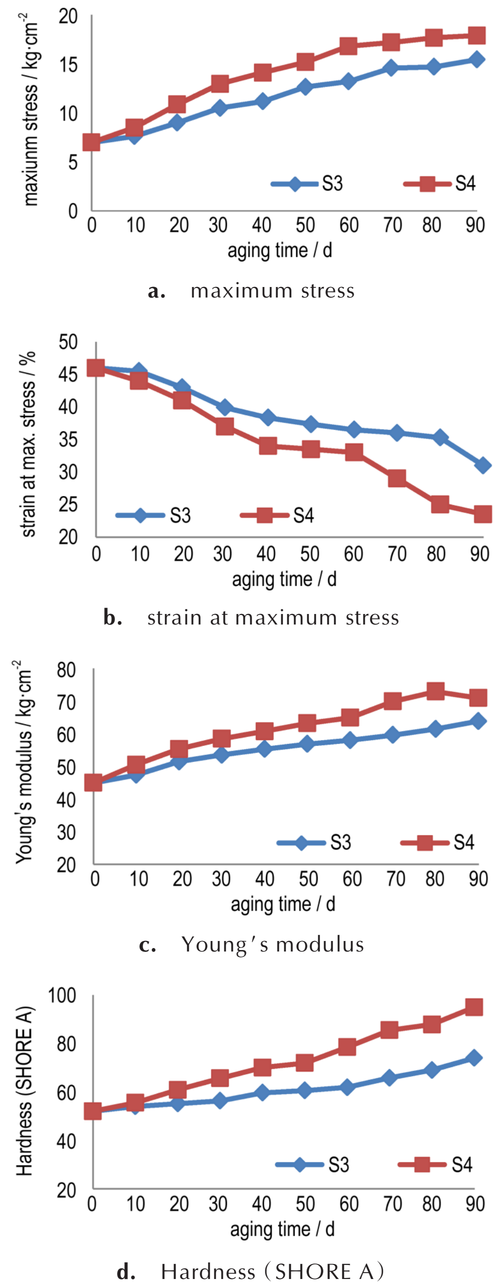
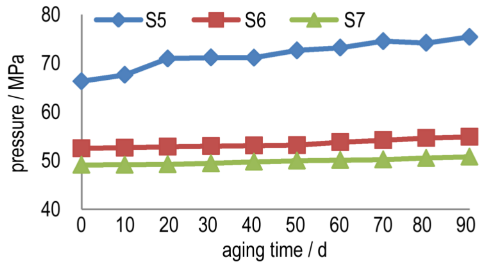


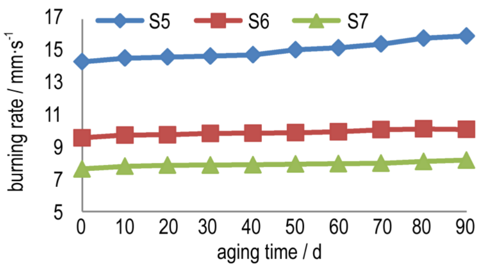
Fig.4 Effect of different antioxidants on the propellant mechanical properties along aging program

showed higher pressure and burning rate values at the beginning and during the aging program with remarkable increasing of ballistic values as shown in Fig.5, which consider more reliable to be used with such composite solid propellant formulation.

The DSC curves were shown in Fig.6 for fresh and aged samples S5 indicate that the first stage was endothermic and the second stage was exothermic. The TGA curves for the two samples show three

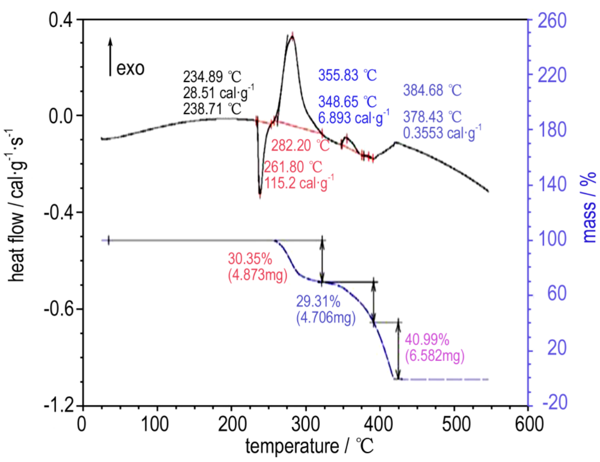


a. pressure values for samples S5, S6 and S7

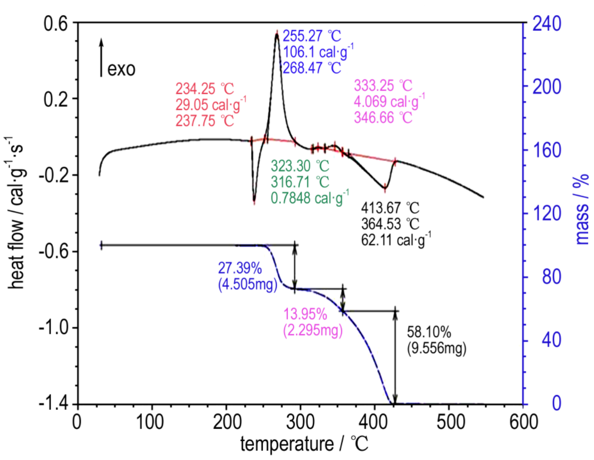


b. burning rate values for samples S5, S6 and S7

Fig. 5 Effect of different burning rate modifiers on the propellant ballistic performance along aging program



a. fresh sample

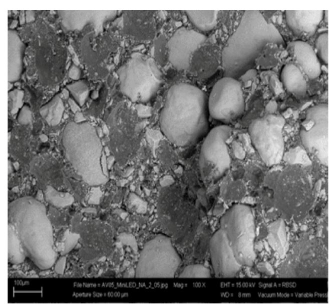


b. aged sample

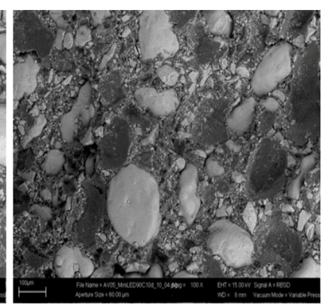
Fig. 6 TGA and DSC thermal analysis for fresh and aged propellant sample S5 (1 cal=4.18 J)

main steps in the thermal degradation process, the first step around 240−325 ℃ and it can be related to the DOS raw material degradation as pointed out, the following two steps observed respectively are in the ranges 325−390 ℃ and 390−430 ℃ as shown in Fig.6, these steps are related to the partial binder and total AP thermal decomposition where the last mass loss step is related to the residual binder showing that the urethane linkages are the first to cleave with the resultant loss of the crosslinking agent and the residual polymer decomposes as if it was an uncured binder. The differences in weight loss percentage and decompositions temperature between the fresh and aged samples explain the changes in burning rate along the aging time.

SEM analysis was done for the sample S5 with a final composition based on DOS, AO, and BF. From the images shown in Fig. 7, It can be noticed that there was no aging effect on the fracture surface of the composite solid propellant, which means that there was no dewetting phenomena have been found.



a. fresh sample



b. aged sample

Fig. 7 SEM analysis for the final formulated propellant sample S5

5 Conclusions

From the uni-axial tensile tests for both composite solid propellant samples S1 and S2, sample S1 based on DOS improve the mechanical properties by increasing the strain rate, decrease the stress of the formulated samples which lead to reduce the chance of cracks formation along the aging time, these cracks will affect the cigarette burning of composite solid propellant as a result of irregular burning surface cause an explosion in the motor case.

Sample S3 which based on AO showed higher resistance to oxidation reaction along aging program that reflects on increasing the propellant motor shelf life-time for about 14 years.

Sample S5 based on BF showed higher pressure and burning rate values among over the other two samples leading to enhance the ballistic performance of the rocket motor.

References:

[1] Boyars C, Klager K, Propellants, Manufacturing, Hazards, and Testing [M]. Washington D.C: American Chemical Society, 1969: 67-187.

[2] Sutton G P. Solid rocket propulsion elements [M]. Sixth Edition, New York: Willy Interscience Publication, 2000: 424-437.

[3] Advisory Group. Structural assessment of solid propellant grains [R]. Advisory Group for Aerospace Research and Development, (AGARD). 7 Rue Ancelle, 92200 Neuilly-Sur-Seine, France, Report No. AGARD-AR-350, 1997.

[4] Mehilal, Shekhar J, Ramesh K, et al. Studies on high burning rate composite propellant formulations using TATB as pressure index suppressant [J]. *Central European Journal of Energetic Materials*, 2012, 9 (3): 237-249.

[5] Muthiah R, Somasundran U, Veghese T, et al. Energetics and compatibility of plasticizers in composite solid propellant [J]. *Defence Science Journal*, 1989, 39(2): 147-155.

[6] Désilets S, Cote S. Chemical bond between stabilizers and HTPB binders in propellants [J]. *Propellants, Explosives, Pyrotechnics*, 2000, 25: 186-190.

[7] Agrawal J, High energy materials [M]. WILEY-VCH Verlag GmbH & Co.KGaA, Weinheim, 2010: 277-280.

[8] Bozic V. Effects of burning rate modifiers on the modified polyvinyl chloride-based propellants [C]//2010 International Conference on High Energetic Materials and Dynamics of Ultrafast Reactive Systems, Varna, Bulgaria, 2010.

[9] Davenas A. Solid rocket propulsion technology [M]. New York, Pergamon Press, 1999: 415-437.

[10] Rhocaog L, Fikert P. Fine-tuning the mechanical properties of hydroxyl-terminated polybutadiene/ammonium perchlorate-based composite solid propellants by varying the NCO/OH and triol/diol ratios [J]. *Journal of Applied Polymer Science*, 2002, 84(11): 2072-2079.

[11] Kakavas P. Mechanical properties of propellant composite materials reinforced with ammonium perchlorate particles [J]. *International Journal of Solids and Structures*, 2014, 51(10): 2019-2026.

[12] Hany N, Elsyed S, Said A. Effect of composition on the mechanical properties and burning rate of metalized fuel-rich composite propellants [C]//34th International Annual Conference of ICT, Karlsruhe, Germany, 2003.

[13] Pandey K. Analysis of manufacturing process of various solid propellants and preferred solid propellant for multi barrel rocket launcher [C]//National Conference on Advances in Manufacturing Technology, NITTTR, Chandigarh, India, 2012.

[14] Bohn M. Prediction of equivalent time-temperature loads for accelerated ageing to simulate preset in-storage ageing and time-temperature profile loads [C]//40th International Annual Conference of ICT, Karlsruhe, Germany, 2009.