Published by :
http://www.ijert.org

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 6 Issue 03, March-2017

Effects of Bonding Agents, Curative Ratio and Burning Rate Modifiers on the Composite Polyurethane Studied by an Aging Program

Enew A. M.[*1], El-Marsafy S.[1], and Abadeer E.[*1].
[1] Cairo University,
Chemical Department,
Faculty of Engineering, Cairo University Rd,
Giza, Giza Governorate,12613, Egypt.

Rutkevičius M.[2]
[2]NC State University,
Department of Chemical and Biomolecular Engineering,
911 Partners Way, 27606, Raleigh, NC, USA.

***Abstract*— We developed and characterized a composite polyurethane polymer for use as a rocket motor. The effect of bonding agents, curative ratio, and burning rate modifiers to the composite mechanical, ballistic, and thermal characteristics were analyzed by applying an accelerated aging program for 26 weeks at a temperature of 65°C.The aging program allowed to estimate the motor service life time. Within the hydroxy terminated polybutadiene (HTPB) propellant matrix we varied the bonding agents (MAPO, HX-752, and MAT4), curative isocyanide and hydroxyl (NCO/OH) group ratio, and the copper chromite (burning rate modifier) content. A novel composite engineered for improved propellant of solid rocket motors using the new percentage for the first time, which can be applied in the future.**

***Keywords*—Composite polyurethane polymer; bonding agents; Curative ratio; burning rate modifiers; Solid propellant; Aging program.**

I. INTRODUCTION

Solid rocket motors are subjected to various loading during storage, shipment and firing. Due to these several loading conditions, cracks can increase in solid propellant grains because of immoderate loads. In order to determine the reliability and the definitive shelf life of solid rocket motors various studies evaluated the extent and distribution of stress and strain. As the mechanical properties of solid propellants are dependent on the rate of strain, temperature and ageing time, it is important to evaluate the effects of these different parameters on tensile properties for the required class of solid propellants[1-3].The viscoelastic nature of the propellant causes high loading rate and temperature dependence for the mechanical properties [4].The variations of temperature along storage time are found to be the main reason for the propellant strain and stress leading to decrease in quality that brings significant change in the tensile strength, percentage elongation and elastic modulus, so the mechanical properties should remain stable enough to resist the shocks and vibration during transportation and rough handling in order to avoid accidental cook off [5-6].

A good review of the solid propellant fracture field was written by G. H. Lindsey and et-al [7]. Golotina and et-al, discussed a structural model for elastomers filled with particles of two fractions. In each fraction the particle diameter varied randomly, but between the fractions, the average particle diameter differed by several orders of magnitude[8].Using this model, the mechanical behavior of composite polymers, filled with various volume contents of solid particles can be investigated. It was found that the small particles inside the matrix behave as a homogeneous medium more than the large ones. Xu F and et-al concluded that severe stressing and high temperatures caused damage which can be noticed in particle cracking and dewetting along particle polymer interfaces, void nucleation and growth, and used a model to investigate the effect of crack damage on the mechanical behavior for composite polymers by predicting the material response under high loading paths [9]. Vratsanos and et-al, realized a predictive model for the mechanical behavior of composite polymer; he found that the results indicate both real microstructure and simulated microstructure based models are efficient methods to investigate elastic and plastic constants of particle reinforced composites [10]. An illustration of the combustion of AP monopropellant, HTPB and AP/HTPB in detail was shown in research carried by B. Plihal and et-al [11], they showed that the bond strength between the propellant and inhibitor material controls mechanical strength and a poor bond leads to failure. Sergey A.R and et-al, characterized the effects of propellant composition on the acceleration. Enhancement in burning rate at low pressures was observed with increasing Butacene content in the propellant composition [12].

II. MATERIALS AND METHODS

Hydroxyl terminated polybutadiene (HTPB), hexamethylene diisocyanate (HMDI),a cross-linking agentdioctylazelate (DOZ), a plasticizerMAT4(as bonding agent, from a condensation reaction product of 2 mole of MAPO,0.7mole of adipic acid and 0.3 mole of tartaric acid), 1,l'(1.3 phenylene dicarbonyl), Bis -2-methylaziridine (HX-752), Bonding agent, and Reactive amine percent: >96%.Tris [1-2(Methyl) aziridinyl] phosphine oxide (MAPO), a Bonding agent, Reactive amine percent: > 96%. Ammonium perchlorate (AP), an oxidizer, Purity: 99.26 %. Aluminum powder (Al), Metallic Fuel, Purity: ≥ 98%. Copper chromites (CC), a Burning rate accelerator.2,2methylbis(4-methyl6-tertibutyl)phenol(cyanox2246),as anti oxidant. All chemicals except cyanox were purchased from Abu Zaabal Company for Specialized Chemicals, Cairo, Egypt, cyanox were purchased from Sigma Aldrich.Different formulations of the selected.

Propellant samples with different bonding agents, curative ratio, and copper chromites were prepared to investigate the effect of these materials on the mechanical properties for the composite propellant. Four samples were prepared, one without any bonding agent and the other three samples based on HX-752, MAPO, and MAT4 respectively as shown in Table 1.

TABLE1. PROPELLANT FORMULATIONS BASED ON BONDING AGENTS

Ingredient	NBA(S1)	HX-752(S2)	MAPO(S3)	MAT4(S4)
HTPB + A.O (%)	10.7552	10.5247	10.5247	10.5247
HMDI (%)	0.5560	0.5441	0.5441	0.5441
DOZ (%)	2.6888	2.6312	2.6312	2.6312
MAPO (%)	--	--	0.3	--
HX-752 (%)	--	0.3	--	--
MAT4 (%)	--	--	--	0.3
Al (%)	17.0	17.0	17.0	17.0
APC 400 µ	40.0	40.0	40.0	40.0
APC 200 (%)	19.0	19.0	19.0	19.0
APC 7-11 µ	10.0	10.0	10.0	10.0
(NCO/OH)	0.72	0.72	0.72	0.72

Five samples of the same composition with different curative ratios as shown in Table 2, where MAT4 was used.

TABLE2. PROPELLANT FORMULATIONS WITH DIFFERENT CURATIVE RATIOS

Ingredients	S5	S6	S7	S8	S9
HTPB + A.O (%)	10.4548	10.4780	10.5013	10.5247	10.5474
HMDI (%)	0.6315	0.6025	0.5733	0.5441	0.5158
DOZ (%)	2.6137	2.6195	2.6254	2.6312	2.6368
MAT4 (%)	0.3	0.3	0.3	0.3	0.3
Al (%)	17.0	17.0	17.0	17.0	17.0
APC 400 µ (%)	40.0	40.0	40.0	40.0	40.0
APC 200 µ (%)	19.0	19.0	19.0	19.0	19.0
APC 7-11 µ (%)	10.0	10.0	10.0	10.0	10.0
(NCO/OH)	0.84	0.80	0.76	0.72	0.68

Four samples with the same composition, one without any copper chromites (CC) and three with different percent of copper chromites as shown in Table 3.

TABLE3. PROPELLANT FORMULATIONS BASED ON COPPER CHROMITES

Ingredients	S10	S11	S12	S13
HTPB + A.O (%)	10.5247	10.5247	10.5247	10.5247
HMDI (%)	0.5441	0.5441	0.5441	0.5441
DOZ (%)	2.6312	2.6312	2.6312	2.6312
MAT4 (%)	0.3	0.3	0.3	0.3
CC (%)	--	0. 5	0.7	1.0
Al (%)	17.0	16.5	16.3	16.0
APC 400 µ (%)	40	40	40	40
APC 200 µ (%)	19	19	19	19
APC 7-11 µ (%)	10.0	10.0	10.0	10.0
(NCO/OH)	0.72	0.72	0.72	0.72

Sample (S13) according to the selected ratios for bonding agents, curative ratio, and copper chromites were prepared as in Table 4. Finally an aging program was applied (samples aged at 65°C, for 26 weeks). Mechanical properties were analyzed every two weeks throughout the 26 weeks program while ballistic performance was analyzed every four weeks. Thermal analysis and scanning electron microscopy for the aged propellant sample were measured.

TABLE4. COMPOSTION OF THE FORMULATED SAMPLE

Ingredients	S13
HTPB + A.O (%)	10.5247
HMDI (%)	0.5441
DOZ (%)	2.6312
MAT4 (%)	0.3
CC (%)	1.0
Al (%)	16.0
APC 400 µ (%)	40
APC 200 µ (%)	19
APC 7-11 µ (%)	10.0
(NCO/OH)	0.72

The thermal analytical measurements (TAM) can describe the materials phase changes with the enthalpy changes accompanying them. Therefore, their thermal behavior can be investigated under these phases by the accurate analysis of the thermo-grams belonging to each ingredient. Thermal analysis performed by TA instrument (model SDT Q600 V20.5 Build 15) simultaneous TGA-DSC thermo gravimetric analyzer. The analyses were conducted for a total sample mass of 16.0 ± 0.4 mg.

A known amount of sample was loaded and evenly spread on the alumina micro crucible. The samples were heated under nitrogen flow (100 ml/min) from 50 to 550°C, at 10°C /min.TGA, DSC and/or DTA techniques is hoped to be deeply help in the combustion properties evaluations through the direct application of their results at the propellant combustion zone. That will be applied by the direct handling of their digital data results to calculate their decomposition characteristic (kinetic) parameters. Thermal analysis techniques such as DSC and TGA we reemployed successfully to evaluate the thermal characteristics of CSRP and to examine the performance of these formulations [13-15]. The thermal analysis was done for two samples, fresh sample and at the end of the accelerated aging program.

The pre-polymer (HTPB), metallic fuel powder, copper chromites and bonding agent were precisely weighed and well mixed at 40 °C for 5 minutes without vacuum at 500 rpm, then for 2 minutes with vacuum at 1500 rpm. The mixing was continued at these conditions with rising temperature until it reaches 70°C. The dried oxidizer was divided into four equal portions and added, then stirring without vacuum for 8 minutes for every portion. After adding the forth portion the mixing was kept under vacuum for 18 minutes. The mixture then cooled to reach 40°C. The mixing then stopped, the accurately calculated weight of the curing agent (HMDI) was added, and the stirring was continued for 5 minutes at this temperature without vacuum then for 20 minutes under vacuum. The vacuum was released with nitrogen and stirring continued for 5 minutes. Finally, sample of the mixture was taken for a quality control, and then the mixture was left to be cured and hardened for one week at 58°C.

MTS machine was used for the determination of the tensile strength and elongation of vulcanized rubber according to ASTM D 412-92. Shore (A) hardness of the aged specimens was measured according to the ASTM –D2240 specification using Zwick hardness tester 3102 and for constant time of measuring 30 second. To measure the ballistic performance at 25°C, samples were assembled with a nozzle offering a pressure range of 40-70 bar on firing, the conditioned motor was mounted on the test stand in the testing area and fired.

SEM micrographs were taken with 55 VPSupra, ZEISS, Germany. The thermal decomposition was analyzed using SDT Q600 V20.5 Build 15 at certain heating rates (10°C/min) and up to 500°C in dynamic nitrogen atmosphere. Samples characteristics were recorded before and after the tests.

III. RESULTS AND DISCUSSION

The required value of mechanical properties for the composite propellant based on HTPB at temperature 25°C as shown in table 5.

TABLE5. REQUIRED MECHANICAL PROPERTIES OF THE PROPELLANT SAMPLE AT 25°C

Mechanical properties	25°C
Maximum stress (σ_m) > Kg/cm^2	> 6.62
Strain at maximum stress (ε_m)%	33-50
Young's modulus (E) Kg/cm^2	30-62
Hardness (shore A)	50 – 75

To study the effect of bonding agent type on the propellant samples we prepared four samples, one without any bonding agent and the other three samples containing an aziridine based bonding agent (MAPO, HX-752, or MAT4) as shown in Table 1. The mechanical properties of the propellant were affected by adding the bonding agents, as the bonding agents increased the cohesion between the binder and the filling solids. *Fig. 1* reveals the stress, strain, Young’s modulus and hardness of the prepared propellant samples. The sample without bonding agent does not satisfy the required value of the tensile stress, strain, Young’s modulus, and hardness, but the other three samples offered a good value of the tensile stress, strain, Young’s modulus and hardness especially the sample based on MAT4. Sample without bonding agent also had the lowest value for the hardness and addition of bonding agent increased the hardness for the propellant formulation.

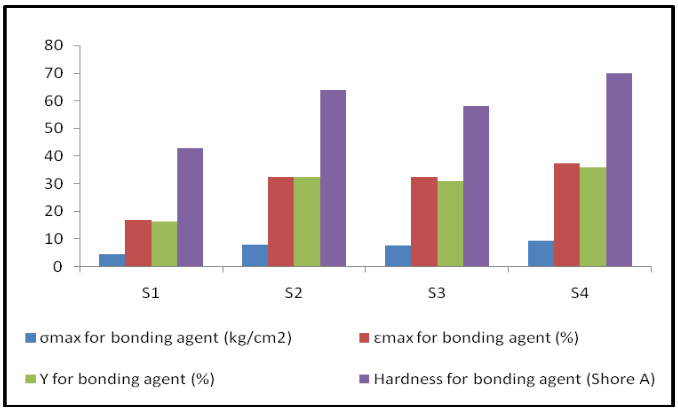

Fig. 1. Effect of bonding agents on the prepared propellant samples

In another set of samples the propellant curative ratio (NCO/OH) was varied from 0.84 to 0.68 and the mechanical properties of the propellant were analyzed. All the samples were based on MAT4 as the main bonding agent (as shown in table 2). The curative ratio controls the propellant mechanical properties. *Fig. 2* shows that, as the curative ratio was increased, the maximum stress at break increased. All samples had more than 33% strain values except sample S5.

The samples had similar value of Young’s modulus varying according to curative ratio percentage and logically increased from sample (S9) to sample (S5). Knowing that aging the samples will influence their physical properties, particularly due to increased drying and induced toughness, the samples with lower Young’s modulus (i.e. S8 and S9) would perform better.

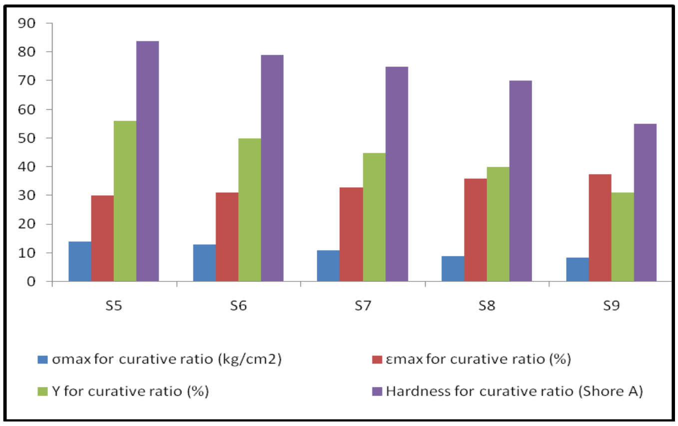

Fig. 2. Effect of Curative Ratios on the prepared propellant samples

Burning rate accelerators were used to modify the propellant burning rate [16, 17]. These products accelerate the decomposition of the oxidizer by lowering its decomposition temperature, it is very important to control the use of accelerators for their migration tendency, this can overcome by the grafting the accelerators into the polymer chain [18, 19].

We prepared four samples, one without copper chromites and three with different copper chromites content as shown in table 3 to determine its effect to the burning rate. We noticed that sample (S13) showed higher burning rate as shown in *Fig. 3*, and this percentage of copper chromites (1%) considered a good start for aging program.

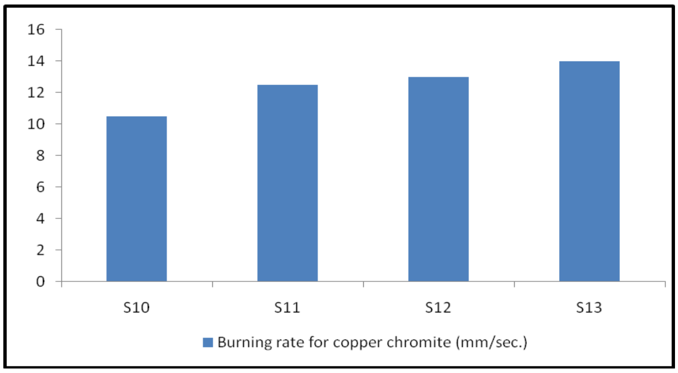

Fig. 3. Effect of copper chromites on the propellant samples.

The aged formulated propellant sample behavior in term of stress value during aging program at temperature (65°C) decreased by (34%), whereas strain increased by (81%), also the Hardness (Shore A) decreased by (24%) compared to the unaged sample, see Figure 4.

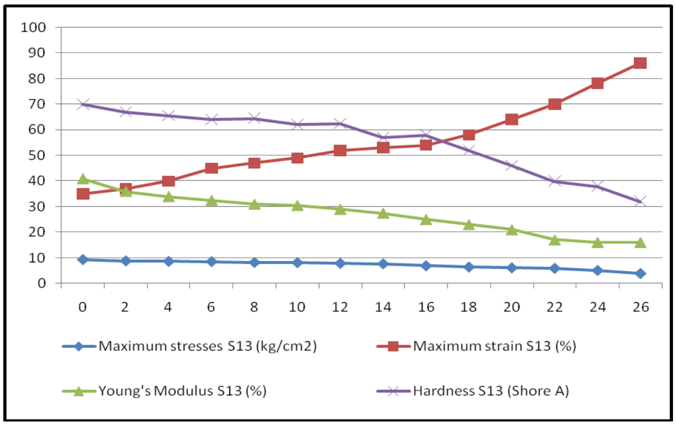

Fig. 4. The Mechanical properties of the aged formulated propellant sample

The effects of the aging time on the propellant sample ballistic characteristics were shown in table 6 which explain a very slight increase which can be neglected in both the working pressure by (0.06%) and the delivered burning rate by (0.025%). This increase were considered due to the aging time and the long time heat exposure of the grain in the oven, but finally this increase is within the norms and we can say that the aging mainly affecting the mechanical properties and have tiny effect on the ballistic characteristics as shown in Table 6.

TABLE6. THE BALLISTIC CHARACTERISTICS OF THE FORMULATED PROPELLANT SAMPLE

Week	Propellant(Kg)	Tb(Sec.)	Pav(Bar)	R(mm/sec)
0	0.373	1.986	66.32	14.35
4	0.372	1.946	66.62	14.58
8	0.377	1.932	70.00	14.68
12	0.374	1.943	70.20	14.7
16	0.374	1.940	70.18	14.7

The thermal analysis was done for two samples, the following two steps observed respectively, are in the ranges 270 – 350 and 350 –370 ºC, these steps are related to the partial HTPB/HMDI binder and total AP thermal decomposition and represent a total of 71.2% mass loss (28.1% first step and 43.62 second step).

The last mass loss step located at 370 – 675 ºC is related to the residual HTPB/HMDI binder and corresponds to 5.4% of the initial sample mass of the urethane crosslinked HTPB 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 DSC curves show that the first stage is endothermic and the second stage is exothermic. The endothermic event is quite similar for both samples, this event occurs around 250°C and it was not considered because it represents a phase transition of AP from the orthorhombic to the cubic form. Also the exothermic event is quite similar for both samples as this phenomena take place around 362°C, as shown in both *Figs. 5 and 6*.

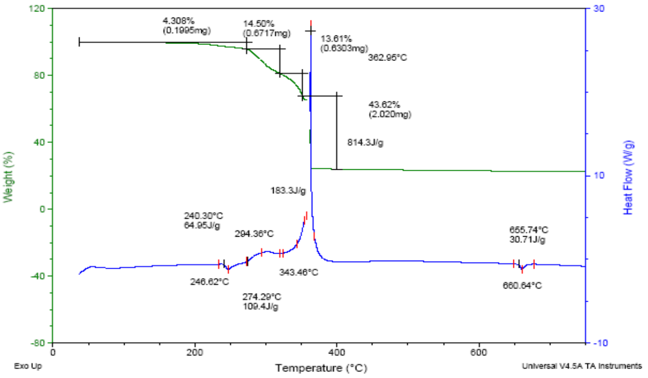

Fig. 5. TGA and DSC for the fresh formulated sample

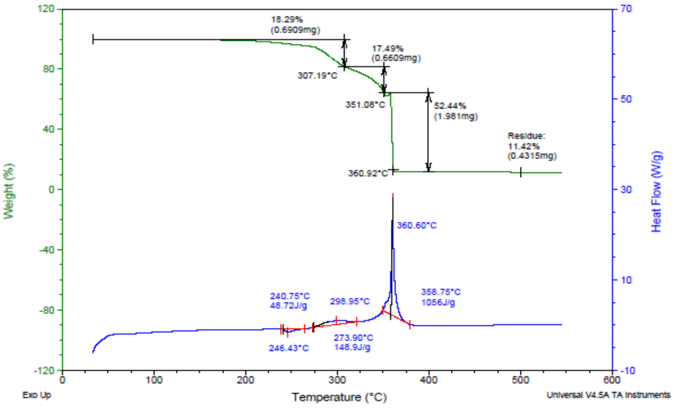

Fig. 6. TGA and DSC for the aged formulated sample

SEM analyses were done for the aged propellant sample tested at the same strain rates. *Fig. 7* showed us a significant difference compared to the unaged composite.

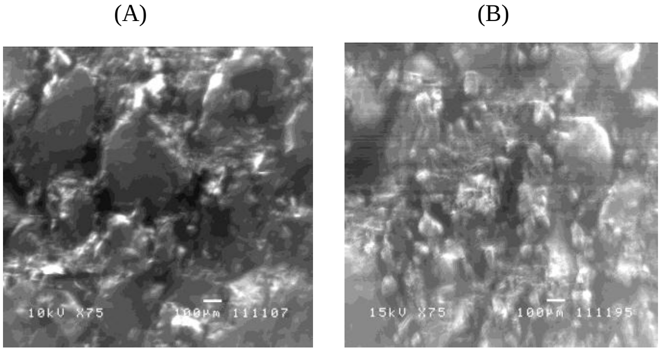

Fig. 7. SEM analysis for (A) Fresh sample; (B) Aged sample

The appearance of fractured particles in the surface of AP particles had decomposed and this leads to crack growth along the aging program.

IV. CONCLUSION

We designed an approach for methodology to explain the behavior of a novel propellant composite formulation, we noticed that a significant increased by about (81%) for the strain value at the end aging program, this behavior lead to settlement of the solid fillers along the propellant grain and this will affect the cigarette burning for composite propellant cause an explosion to the motor case. The formulated sample gives the required result and never goes away from limits till the 16 weeks.

Comparing composite solid propellant within corporation MAT4 as bonding agent and a higher value of curative ratio, the value (0.84) in order to achieve longer service life for the propellant. Using of the bonding agent (MAT4) improves the propellant mechanical properties more than the other used bonding agent such as HX-752 and MAPO. Strain corresponding to maximum stress depended on the used bonding agents; MAT4 had highest strains preserved the value of the strain. MAPO and HX-752 had poorest performance.

Selection of the curative ratio (NCO/OH) was also important to the mechanical properties of the produced propellant sample, particularly to enhance its properties during aging time.

Small percentage of copper chromites (1.0%) increased the burning rate about (30%) without influencing sample production properties or mechanical properties upon aging.

The aging program helped to developing a new composite propellant formulation with the required mechanical behavior, also using advanced analysis techniques such as TGA and SEM enables us to get a full account on the behavior of formulated propellant sample during aging program.

REFERENCES

[1] George P. Sutton and Oscar Biblarz. Rocket Propulsion Elements [M], Jhon Wiley and Sons, seventh edition, pp. 447-454,1999.
[2] Marcel Barrere, et al. Rocket Propulsion [M]. Amesterdam: Elsevier Publishing Company, Chapter 4, 1960.
[3] Gligorijevic N., Rodic V. et-al. Structural Analysis Procedure for a Case Bonded Solid Rocket Propellant Grain [J]. Scientific Technical Review, vol. 61, no. 1, pp. 311, 2011.
[4] Probhas Bose and K M Pandey. Structural Failure Analysis of Rocket Motors [A].4th International Congress of Environmental Research [C], SVNIT, Surat, India, 1517,2011.
[5] K. M. Pandey et-al. Analysis of Manufacturing Process of Various Solid Propellants and Preferred Solid Propellant for Multi Barrel Rocket Launcher [A] National Conference on Advances in Manufacturing Technology [C], NITTTR, Chandigarh, India, pp. 15-16, 2012.
[6] P. Kevin et-al. Surface Science for Advanced Propulsion [R]. Storming Media Pentagon Report No A799613, Aug 1996.
[7] G. H. Lindsey et-al. Studies Pertaining to Solid Propellant Fracture [R]. Technical Report No AD 0739355, http://oai.dtic.mil.html.
[8] Golotina, L. A., Kozhevnikova, L. L., and Koshkina, T. B. Investigation of the mechanical behavior of two component granular composites in terms of structural models mechanics of composite materials [J]. Mechanics of Composite Materials,vol. 43, no. 2, pp. 127–132, 2007.
[9] Xu F., Aravas N., Sofronis P. R.M. Constitutive modeling of solid propellant materials with evolving micro-structural damage [J]. Journal of Mechanics and Physics of Solids, pp. 2052-2073, Vol 56, 2008.
[10] Vratsanos, V.A., Farris, R.J. A predictive model for the mechanical behavior of particulate composite. Part I: model derivation [J]. Polymer Engineering and Science. 33 (22), 1458–1465, 1993.
[11] B. Plihal et-al. Use of a Time-Dependent Brinell Hardness Test to Determine Some Mechanical Properties of Solid Propellants [J]. Journal of Battlefield Technology,vol. 3, no. 2, 2000.
[12]] Sergey A.R., Alexander V.F., Yuriy M.M., et al. Mechanical Properties of Composite Propellants and Effect of Propellant Stretch on its Burn Rate [J].International Journal of Energetic Materials and Chemical Propulsion, vol.9, no.3,pp.233-247, 2010.
[13] Mohmed A.Sadek,Saeed Hasanin and Hosam El Saed Mostafa “Investigation And Analysis Of The Role Of Energetic Reinforcements In Rocket Propellants” MTC,Cairo,1996.
[14] Alai Davenas. Solid Rocket Propulsion Technology [M].Oxford:Pergamon Press,1993, Chapter 4.
[15] Abdel-Wareth W. M. Study of the Combustion Behavior of the Low Oxygen Content Composite Solid Propellants [D].Cairo University, Faculty of Engineering, Cairo, Egypt, M. Sc. Thesis, 2006.
[16] Davenas A. Solid Rocket Propulsion Technology [M]. New York: Pergamon Press,1993: 415-437.
[17] Hori K, et al. On the Adhesion Between Hydroxy-Terminated Polybutadiene Fuel Binder and Ammonium Perchlorate Performance of Bonding Agents[J].Propellant, Explosives, Pyrotechnics, 1985, 176-180.
[18] Rocket propellant Hand Book. Boris Kit and Douglas S. EVERED, 1960.
[19] M. M. Telkar, C. V. Rode, R. V. Choudhary, S. S. Joshi, A. M. Nalawade, Shape Controlled Preparation and Catalytic Activity of Metal Nano-particles for Hydrogenation of 2-Butyne-1,4-diol and Styrene Oxide, Appl.Catal,A2004,273,11.