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Mechanical Properties of HTPB Composite Propellants in the Initial Period of Service Life

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Uniaxial tensile tests of different composite solid rocket propellant compositions, based on hydroxyl-terminated polybutadiene (HTPB), have shown that mechanical properties extensively change after curing, up to 100% of their initial values, during the first few months. After that period, they stabilize and start to return slowly in the opposite direction. Careful measurements of these features are necessary in order to control the production quality of the propellant and for a comparison of different propellant compositions or batches. Furthermore, time distributions of the mechanical properties in the initial period after production and short-time aging should not be neglected, because they strongly affect the propellant grain structural analysis and a correct estimation of rocket motor reliability

Key words: **composite rocket propellant, mechanical properties, aging, tensile strength, deformation, modulus of elasticity.**

Nomenclature

a_T	– Time-temperature shift factor
D	– Cumulative damage
E	– Modulus, initial, tangent, elasticity
R	– Strain rate,
t	– Time
ε , ε_0	– Strain, Initial strain,
ε_m , ε_{m0}	– Ultimate (Allowable) strain, Initial strain
ξ	– Reduced time
$\eta(t)$	– Propellant aging factor
η_E , η_σ , η_ε	– Aging factor for modulus, stress, strain
σ_m	– Tensile strength (Ultimate stress)
σ_{m0} , $\sigma_m(t)$	– Initial strength, Time-dependent strength

Introduction

COMPOSITE solid rocket propellants are continuously exposed to chemical (natural) aging, starting immediately after casting. This is reflected in the change of their physical properties. In the initial period after production, especially the changes in mechanical properties are visible [1-3]. The first effects, hardening and softening due to migration of plasticizer [4, 5], occur even during the curing process.

The changes of propellant physical properties do not finish completely over the curing process and continue afterwards with reduced intensity, regardless of the expectation that they should be minimized at the end of the process.

The parameters of the curing are chosen to finish the process as quickly as possible, but to improve efficiently stabilization of the physical properties.

These two conflicting requirements must be adapted to each other. Therefore, due to the lack of completion of the curing process, the physical properties of the propellant continue to change afterwards. These changes depend on a degree of completion of the polymerization process.

After production, the mechanical properties of viscoelastic propellants depend not only on strain rate and temperature [6-10] but also on real time [1-3, 11, 12]. This dependence on real time in the initial period after propellant production is the main topic of this paper.

Monitoring and analysing different HTPB composite propellant compositions in the Military Technical Institute (MTI) have shown that in a short period after production, the changes in propellant mechanical properties are extensive. These changes strongly affect the calculation results of the propellant grain margin of safety and the structural reliability analysis, and they must not be neglected.

According to the results of uniaxial tension tests carried out in the Solid Rocket Propellant Department of the MTI, the changes of the propellant mechanical properties due to chemical aging take place in two phases. During the first phase, which is 2 or 3 months long, sometimes slightly longer, up to 6 months [12], there is an intensive change of the mechanical properties of HTPB based composite propellants. If it is not expected for a rocket motor to be in use in the very beginning after the propellant grain production, the first phase may be neglected. For instance, for service life predictions [11], the initial values of the mechanical properties are considered using specimens at the propellant age of two months.

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This approach may be valid if it is possible to store and keep propellant after production, until it is stabilized. However, that is not always the case. Sometimes, especially for small rockets, the first phase should not be neglected, because it is needed for a rocket to be immediately delivered to a customer or to be ready soon after production, as in the case of an anti-hail rocket [12], designed in the MTI for civilian use. In addition, mechanical tension tests in the initial phase are required due to monitoring of various propellant compositions and their comparison. In the second phase of the propellant aging, mechanical properties change slowly, in the direction opposite to the first phase [12], similarly as concluded in [13].

The data obtained by measuring the changes of mechanical properties in the initial period may be used for a correction of the results of a complete uniaxial mechanical characterization of virgin propellants, in order to make master curves for the ultimate stress, strain and relaxation modulus.

Parameters of propellant production

Curing parameters

In the production process of composite propellants, producers themselves define their own optimal production parameters and terms of casting and curing. For example, the following curing parameters are used in different situations: (50°C and 120 hours) are used in [13], while 65°C and 7 days are used in [14]. These conditions are usually defined on the basis of own production experience [15] and the analysis of diisocyanate to total hydroxyl ratio (NCO/OH) [14]. During the cure, propellant properties are unstable due to the migration of a plasticizer [4, 5, 14, 16] until it reaches the equilibrium [4]. Variations from these parameters, as well as propellant properties, depend on a number of influencing factors [17], like percentage and composition of polymer binder, type, granulation and amount of oxidizer powder, different additives, etc.

In the MTI, for a class of HTPB-based composite propellants with ammonium perchlorate (AP) as oxidizer, it was found that the optimal curing parameters (temperature and time duration) are about 70°C and 120 hours. Sometimes, small deviations from these parameters are allowed because it is believed that they should not change the optimal curing conditions significantly and, therefore, these parameters are usually adopted as standard values for a whole class of similar propellant compositions.

Propellant compositions

Seven similar solid propellant compositions were tested, composed of 23.4 % HTPB-based binder, 75% ammonium-perchlorate (AP) as crystalline oxidizer, 1% aluminum (Al) metal fuel powder, 0.5% lithium-fluoride (LiF) as burning rate depressant and 0.1% carbon black powder (C) as burning stabilizer. Within the HTPB-based binder, isophorone-diisocyanate (IPDI) as curing agent (crosslinker) was used, as well as dioctyl-adipate (DOA) as plasticizer, 2,2-methylene-bis-(4-methyl-6-tertiary-butyl phenol) (AO22) as antioxidant and triethylene-tetramine (TET), as bonding agent. The differences between the compositions are related to oxidizer granulations and mass fractions of plasticizers and curing agents.

The approximate properties of the binder composition are as follows: molecular weight: 2800 g/mol, hydroxyl functionality: 2.4-2.6 OH value: 44.2 mg.

The NCO/OH ratio between the isocyanate groups of IPDI to the hydroxy groups was 0.86.

The propellant formulations were mixed in a Baker-Perkins planetary 1-gallon mixer at 60°C. The curing agent was added to the mixture at the end of the mixing process. The curing was performed for 5 days at 70 ºC.

Virgin propellant and the initial mechanical testing

During the implementation of a complete program of mechanical characterization in order to prepare stress, strain and relaxation modulus master curves [6-10] for a fresh propellant, a need appeared to better define the propellant from the standpoint of its age. The master curves are required for a propellant grain structural analysis. The term „virgin propellant“ [18, 19] refers to the moment right after production. In practice, it is not possible to conduct such a program in the short term. A complete propellant mechanical characterization has to be carried out in a wide range of various test conditions, with statistically acceptable number of replicates in each test regime [7, 9, 10]. These tests are more extensive and include a number of different test temperatures (in the range between -60°C and +50°C) and different strain rates, using constant crosshead speeds in the range between 0.5 and 1000 mm/s, with statistically acceptable number of replicates in each test regime [7, 9, 10, 19].

This procedure sometimes could take up to 2 or 3 months [12]. However, during those 2-3 months, propellant mechanical properties are extensively changed and it is necessary to determine the intensity of these changes and an acceptable way to take them into account.

The propellant tested in the moment right after production should be called "new" or "virgin" because it is important to distinguish it in relation to the term "unaged", that some authors [5, 20, 21] use for a propellant that has not been subjected to accelerated aging. It is usually expected for a propellant to be in use for many years. It means that the term "aging" involves a long process, and the term "unaged" could wrongly imply a wide period in the beginning of the service life. In that way, a significant error could be made due to the strong change of the propellant mechanical properties in the initial period after production.

Time dependence of the propellant ultimate mechanical properties

There is not much information in literature about the changing of the propellant mechanical properties in the initial period after propellant grain production. Most of the information deals with the effects of plasticizer's content and its migrations in order to analyze the propellant hardening or softening, especially in the area between the propellant and the layer, as well as the impact of this phenomenon on the propellant adhesion with the bond. There is a lack of information in literature about the effects of natural aging in the initial period on the propellant itself.

Since this issue is not sufficiently considered in literature, it could be wrongly concluded that the aging effect on mechanical properties could be neglected in the beginning of the rocket motor service life.

Some information about the initial tests has been found in [13], where it has been concluded that the maximum stress (σ_m) and the modulus (E) increase first sharply, then slightly, while the strain values (ε_m) decrease in the same manner.

On the other hand, Sutton [22], for instance, suggests that changes occur only due to the effects of load, and he does not consider the effects of natural aging. It was found that the decrease in mechanical properties is primarily due to cumulative damage [2, 12, 18, 23, 24, 25].

Sometimes, propellant aging is considered as a unique result of a simultaneous action of chemical and physical effects as well as the effects of mechanical loads [5].

Usually, the effect of environmental loads, primarily temperature, is often treated in literature separately, as cumulative damage [6, 9, 10], and mainly after a long period of storage, using the methods of accelerated aging [3, 11, 26].

For the structural analysis of the propellant grain, it is necessary, first of all, to determine the ultimate mechanical properties of the propellant [6, 8-10]. They are needed for a failure analysis and a comparison with the values of real stresses or strains, which may be significantly variable, depending on the environmental influence or the variable pressure or the thrust of the rocket motor [27]. The allowable stress and strain are time dependent features, $\sigma_m(t), \varepsilon_m(t)$. These values of tensile strength and allowable strain, in accordance with Heller's model [2, 12, 18] are the products of the initial values that represent a new propellant ($\sigma_{m0}, \varepsilon_{m0}$), aging factors ($\eta_\sigma, \eta_\varepsilon$) and cumulative damage $(1-D)$, Eqs.1-2:

$$\sigma_m(t) = \sigma_{m0} \cdot \eta_\sigma(t) \cdot \left[1 - D(t)\right] \tag{1}$$

$$\varepsilon_m(t) = \varepsilon_{m0} \cdot \eta_\varepsilon(t) \cdot \left[1 - D(t)\right] \tag{2}$$

The HTPB composite propellant is a viscoelastic material and the ultimate values of its mechanical properties are highly dependent on temperature and strain rate [7, 9, 10].

In Eqs. (1) and (2), these ultimate values of a new propellant ($\sigma_{m0}, \varepsilon_{m0}$) are formally represented as constants due to real time, because they are related exactly to the initial moment of time after the end of curing. These features are variables, usually presented in the form of master curves [6-10, 12] that depend on temperature and strain rate.

Ideally, the master curves should be performed immediately after curing, before the natural aging process begins. However, the procedure of the master curves determination could take a long time, sometimes up to several months [12]. At the end of this period, the propellant is no longer "new" or "virgin" because its mechanical properties are changed, and it is necessary to determine the intensity of these changes in order to find an acceptable way to take them into account.

The aging factor is a ratio between a current value of a mechanical property and its initial value. This value is variable and may be represented by its time dependence.

For different mechanical properties: tensile strength, allowable strain and initial modulus, the aging factors (η_σ, η_ε, η_E) are also different.

In order to define the time-dependence of the aging factors in the beginning of the service life, in the MTI's Department for composite propellants, uniaxial tension tests were carried out for several different HTPB propellant compositions, over the period of 45 days after production.

Experiment

Two groups of uniaxial tension tests have been carried out. The first group of was performed on seven different HTPB compositions. They were tested on a universal Instron-1122 tester under standard conditions (+20°C and 50 mm/min).

For the uniaxial tension tests, standard propellant specimens of „JANNAF-C" type [9] were used. In all cases, a statistical sample of 7-9 specimen replicates was included. The initial tests for each propellant composition were performed exactly two days after curing and this moment was treated as the beginning of the propellant service life ($t = 0$). This is the moment when the propellant can be treated as "new" or "virgin". Starting from the next day, in every moment, the propellant is considered not as "new", but as a material which has been subjected to aging.

Including the initial tests, all seven propellant compositions were tested two or three times in the same, standard conditions, at irregular intervals, over a period of 45 days. After that, over the next 10 months, two propellant compositions from the group of seven were additionally tested, also in standard conditions.

In parallel, in the second group of tests, one propellant composition was tested in different strain rate regimes at standard temperature (20°C). Nine different tester cross-head speeds in the range between 0,2 and 1000 mm/min were used. The tests were performed in two different periods, approximately 15 days and 105 days after curing. The objective of this group of tests was to better explain the aging influence on the mechanical properties of the propellant.

Test results

The results for the first set of uniaxial tension tests (seven different compositions) in standard conditions (+20°C, 50 mm/min) are presented in Table 1.

The propellant tensile strength (σ_m), the allowable strain (ε_m) and the initial modulus (E) were measured. Since the absolute values of the measured propellant properties are not suitable for comparison, the aging factor distributions are made, as the ratios of their current and initial values. The aging factors for the initial modulus and the allowable strain distributions are shown in Figures 1 and 2.

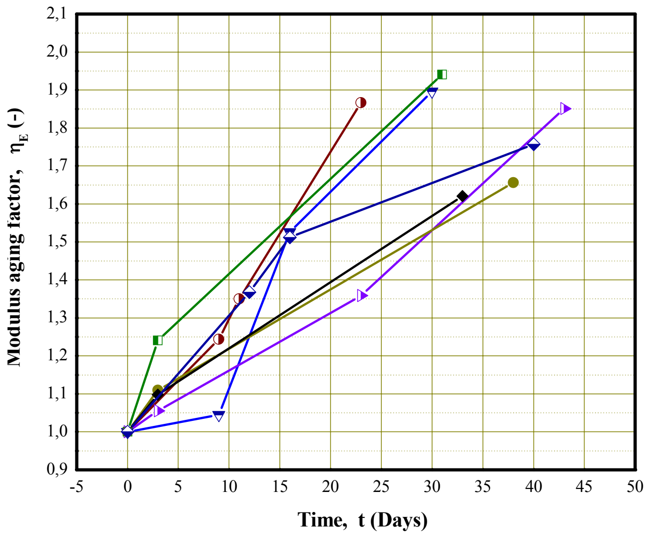

Figure 1. Modulus aging factor for seven different HTPB compositions over 45 days

Different symbols correspond to different propellant compositions. The uniaxial aging factor for tensile strength is shown in Fig.3.

Table 1. Mechanical properties for different short-aged HTPB propellants (+20ºC)

	Propellant code	Time, t	Time, t-2	Strain, ε_m	SD(ε_m)	$\varepsilon/\varepsilon_0$	Modulus, E	SD(E)	E/E_0	Strength, σ_m	SD(σ_m)	σ/σ_0
		Days	Days	%		-	MPa	MPa	-	MPa	MPa	-
1.	VM 115	2	0	37.56	0.62	1.00	3.204	0.080	1.00	0.632	0.010	1.00
		5	3	30.88	0.31	0.82	3.558	0.060	1.11	0.626	0.006	0.99
		40	38	17.01	1.24	0.45	5.308	0.156	1.66	0.575	0.006	0.91
2.	VM 116	2	0	44.01	5.61	1.00	2.405	0.060	1.00	0.592	0.008	1.00
		5	3	36.71	2.36	0.83	2.986	0.052	1.24	0.588	0.004	0.99
		33	31	20.24	1.54	0.46	4.668	0.163	1.94	0.563	0.010	0.95
3.	VM 117	2	0	62.52	1.13	1.00	2.022	0.144	1.00	0.490	0.088	1.00
		11	9	53.87	1.62	0.86	2.113	0.033	1.04	0.518	0.003	1.06
		18	16	36.88	1.67	0.59	3.086	0.230	1.53	0.548	0.004	1.12
		32	30	29.90	0.32	0.48	3.833	0.109	1.90	0.572	0.006	1.17
4.	VM 118	2	0	66.24	1.97	1.00	1.494	0.127	1.00	0.416	0.008	1.00
		11	9	55.00	0.63	0.83	1.859	0.022	1.24	0.452	0.006	1.09
		13	11	54.81	1.74	0.83	2.017	0.064	1.35	0.483	0.051	1.16
		25	23	36.46	4.02	0.55	2.790	0.194	1.87	0.537	0.006	1.29
5.	2183 N	2	0	31.78	0.55	1.00	4.206	0.151	1.00	0.701	0.004	1.00
		5	3	28.43	0.31	0.89	4.620	0.495	1.10	0.717	0.009	1.02
		35	33	17.48	0.34	0.55	6.819	0.173	1.62	0.775	0.003	1.10
6.	2224 N	2	0	41.74	0.62	1.00	3.351	0.015	1.00	0.720	0.012	1.00
		5	3	34.40	0.39	0.82	3.535	0.083	1.06	0.701	0.002	0.97
		25	23	26.17	0.31	0.63	4.554	0.265	1.36	0.658	0.013	0.92
		45	43	22.17	0.25	0.53	6.202	0.044	1.85	0.585	0.009	0.81
		82	80	17.66	1.01	0.42	6.846	0.212	2.04	0.562	0.033	0.78
		144	142	16.49	0.06	0.40	6.973	0.219	2.08	0.550	0.007	0.76
		274	272	20.46	0.84	0.49	6.725	0.111	2.01	0.583	0.012	0.81
7.	VM 133	2	0	27.43	0.15	1.00	4.495	0.230	1.00	0.784	0.008	1.00
		14	12	22.00	0.34	0.80	6.150	0.418	1.37	0.650	0.006	0.83
		18	16	19.34	0.59	0.70	6.797	0.502	1.51	0.608	0.012	0.78
		42	40	14.73	0.40	0.54	7.898	0.597	1.76	0.571	0.044	0.73
		106	104	12.51	0.22	0.46	8.330	0.197	1.85	0.582	0.010	0.74
		185	183	12.89	0.15	0.47	9.036	0.396	2.01	0.629	0.005	0.80
		300	298	14.15	0.36	0.52	8.829	0.208	1.96	0.663	0.007	0.85

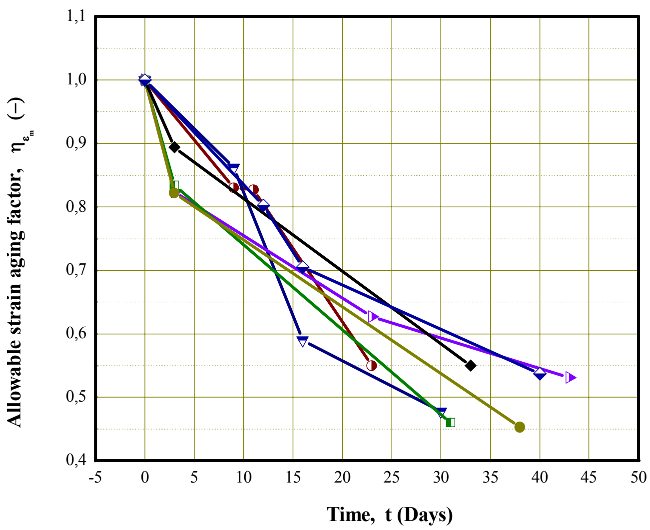

Figure 2. Allowable strain aging factor for seven different HTPB propellants over 45 days

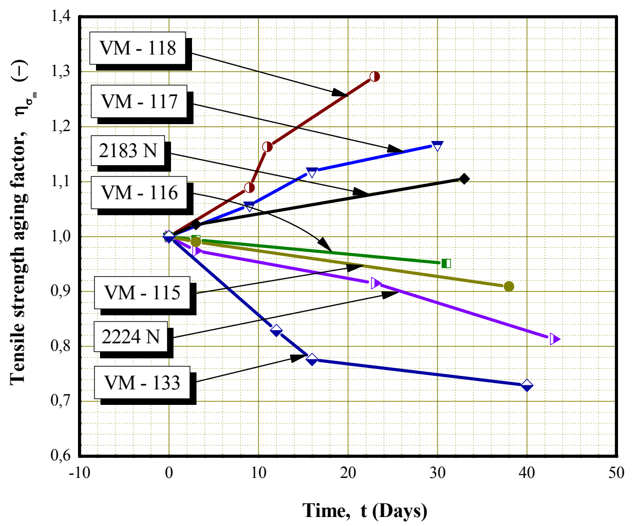

Figure 3. Tensile strength aging factor for seven different HTPB propellant compositions over 45 days

The test results in Figures 1-3 show significant relative changes in the mechanical properties, for each composition in the tested group of composite propellants based on HTPB, over the 45-day period after production.

The aging factor distributions for the tensile strength, the allowable strain and the initial modulus, over the period of ten months for two selected compositions (N°6, N°7), are shown in Figures 4-6.

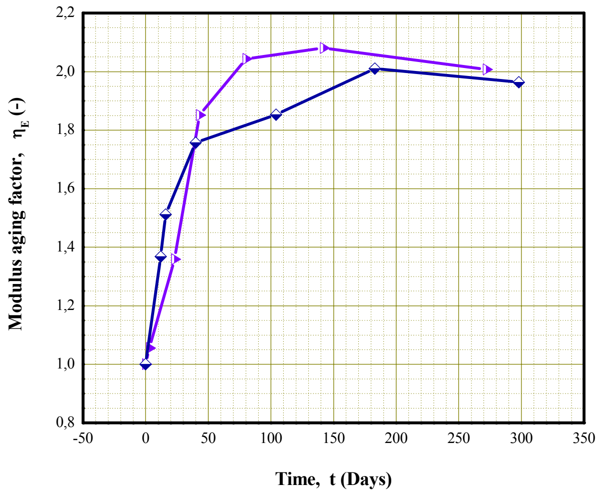

Figure 4. Modulus aging factor for two different HTPB propellant compositions over 10 months

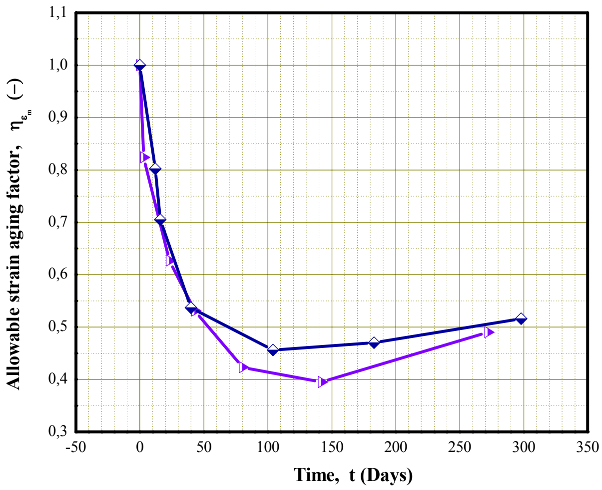

Figure 5. Allowable strain aging factor for two different HTPB propellant compositions over 10 months

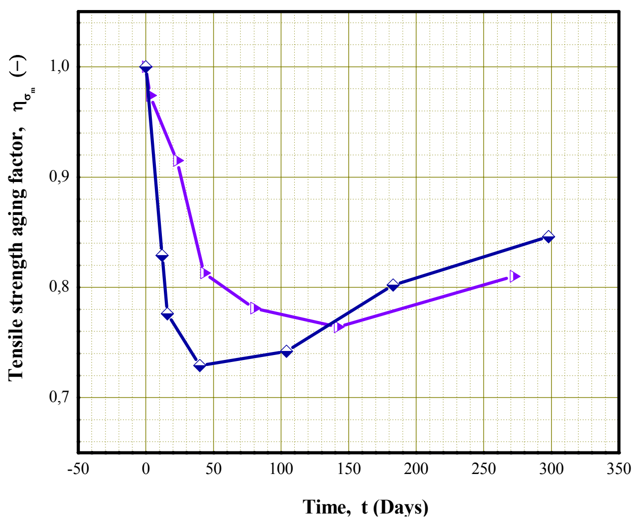

Figure 6. Tensile strength aging factor for two different HTPB propellant compositions over 10 months

In the second group of tests, uniaxial tension tests in two different periods for the HTPB composition labeled in Tab. 1 as N^o 7 were done at constant temperature (+20^{o}C).

The tests were carried out at nine different cross-head speeds: 0.5, 1, 2, 5, 10, 20, 50, 100 and 200 mm/min.

At first, the tests were carried out approximately 15 days after curing. The second set was done 105 days after curing. The measured values for three characteristic mechanical properties (σ_m , ε_m , E) are shown in Table 2.

In the uniaxial tension tests at constant temperature for an arbitrary composite propellant as a linear viscoelastic material, a linear dependence of tensile strength vs. strain rate at constant temperature is expected[7, 8, 10, 28].

Table 2. Mechanical properties of the HTPB propellant in two different periods

Propellant age	Cr.-head speed	Strain rate	Time, log t	Strength	SD(σ_m)	Modul	SD(E)	Strain	SD(ε_m)
Days	mm/min	R (s^{-1})	log (1/R)	MPa	MPa	MPa	MPa	%	
17	0.5	0.000121	3.9155	0.286	0.002	4.265	0.099	12.74	0.07
16	1	0.000243	3.6145	0.363	0.003	4.538	0.089	15.33	0.34
15	2	0.000486	3.3134	0.421	0.003	4.925	0.134	16.76	0.28
12	5	0.001215	2.9155	0.468	0.018	4.860	0.112	18.61	0.77
15	10	0.002430	2.6145	0.499	0.010	6.078	0.322	17.61	0.22
12	20	0.004859	2.3134	0.546	0.015	5.859	0.289	19.84	0.64
16	50	0.012148	1.9155	0.608	0.012	6.797	0.502	19.34	0.59
18	100	0.024295	1.6145	0.714	0.009	6.826	0.312	21.50	1.12
18	200	0.048591	1.3134	0.736	0.021	8.044	0.281	21.65	1.41
106	0.5	0.000121	3.9155	0.266	0.004	5.889	0.112	8.39	0.12
105	1	0.000243	3.6145	0.235	0.005	5.689	0.147	7.88	0.29
106	2	0.000486	3.3134	0.267	0.001	6.232	0.212	10.62	0.50
106	5	0.001215	2.9155	0.403	0.017	7.100	0.218	10.14	0.53
105	10	0.002430	2.6145	0.476	0.012	7.239	0.412	11.39	0.45
106	20	0.004859	2.3134	0.499	0.022	8.042	0.179	11.10	0.17
104	50	0.012148	1.9155	0.582	0.010	8.330	0.197	12.51	0.22
105	100	0.024295	1.6145	0.667	0.005	9.150	0.200	14.04	0.89
105	200	0.048591	1.3134	0.719	0.022	9.518	0.338	14.07	1.08

The dependences of all the three characteristic mechanical properties for propellant N°7 are also linear. These dependences on strain rate in two different periods are shown for the initial modulus, the allowable strain and the tensile strength, in Figures 8-10, respectively.

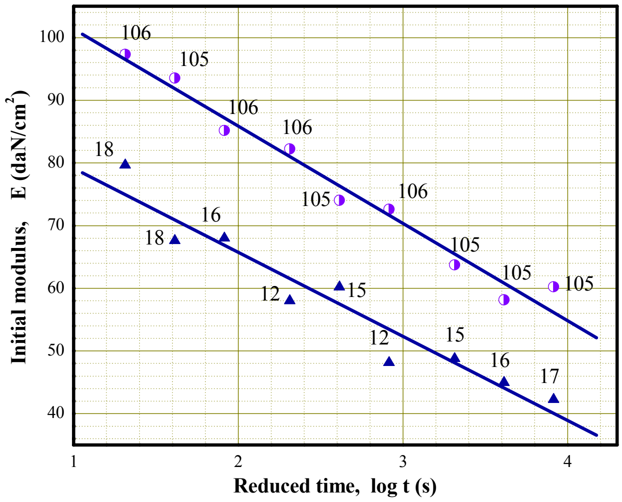

Figure 7. Modulus vs. strain rate and aging time

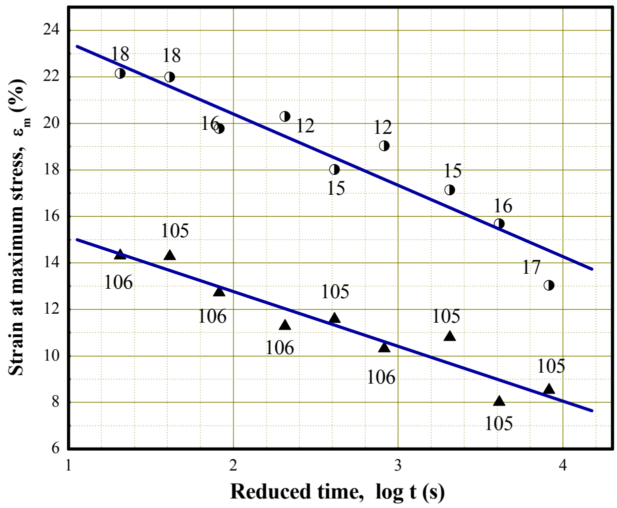

Figure 8. Allowable strain vs. strain rate and aging time

The tester cross-head speed (V) is constant in each tension test and allows the direct determination of the specimen strain (ε) and the strain rate ($\dot{\varepsilon}$):

$$\varepsilon = \frac{V}{l_0} \cdot t = \dot{\varepsilon} \cdot t \tag{3}$$

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon}(s^{-1}) = R = \frac{V(\text{mm/min})}{60 \cdot l_0(\text{mm})} \tag{4}$$

l_0 - Effective gage length; 68,6 mm.

ε - Strain

All three plots have the same abscissa (19) which represents the reciprocal of the propellant specimen strain rate ($\dot{\varepsilon}^{-1} = R^{-1}$). The abscissa of each of these diagrams has the dimension of time. The logarithmic scale of the abscissa is suitable for further analyses. Since all the measurements were done at standard temperature (+20°C), the time-temperature shift factor (a_T) [7, 9, 10, 28] does not affect the results.

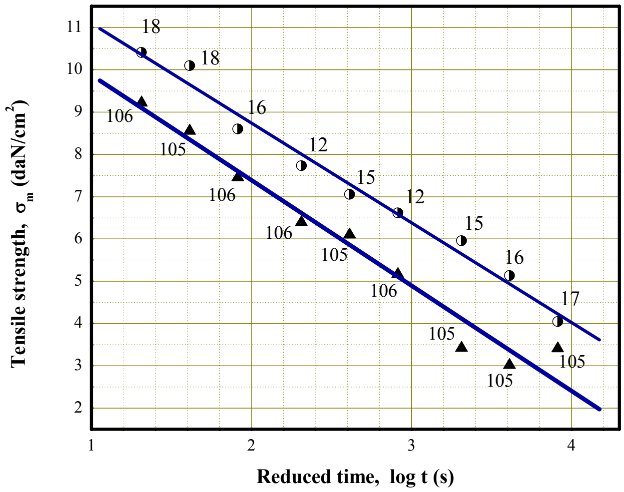

Figure 9. Tensile strength vs. strain rate and aging time

Discussion

During the first 45 days after production, in the initial period after curing, for the whole considered group of seven different HTPB-based propellant compositions (Table 1), intensive changes in their mechanical properties appear. The basic tensile tests for analysing the influence of short-term aging on the propellant mechanical properties, were carried out only at standard temperature (+20°C). The initial modulus (E) increases in 45 days (Fig.1) and approximately doubles its value. In contrast, the allowable strain (ε_m) decreases, in all cases, and falls bellow 50% of its initial value (Fig.2). The initial values of the tensile strength (σ_m) (Fig.3) may change in both directions. They may increase or decrease, depending on the propellant composition, but the maximum change in 45 days does not exceed 30%.

The propellant compositions labeled in Table 1 as No6 and No7 were selected for testing during the next several months. The results (Figs 4-6) have shown that after a certain period, all the mechanical properties become stabilized. Then, they even begin to change in opposite directions, returning slowly to the initial state, as it was concluded in [12, 13].

Sometimes, structural analysts ignore the initial changes of the mechanical properties. This neglecting is probably compensated for, because the tension tests are performed using the specimens that have been stored for some time after production and whose mechanical properties became stabilized. However, that is not always possible, because storage of propellant itself or propellant grain series in manufacturers stock is too expensive. Moreover, it is not easy to recognize exactly the moment of the mechanical properties stabilization. This period is very likely to exceed 2 months, which was adopted as a time limit in the case [11]. There are also other reasons not to ignore the changes in the mechanical properties of the propellant in the initial period.

One of the most important reasons for testing and monitoring the composite propellant mechanical properties in the initial period is a need to compare different propellant compositions. To make this comparison have its full meaning, it is necessary to define the exact terms of comparing the mechanical properties of different propellants.

The moment of initial testing after curing is especially important because mechanical properties rapidly change in this period.

The procedure of a complete propellant mechanical characterization is very long and the period of its duration is sufficient to significantly alter all characteristic mechanical properties. It is not possible to complete the whole procedure quickly, immediately after curing. For example, for a statistical sample of 7÷9 JANNAF-C specimen replicates, at single regime with a constant temperature and cross-head speed of 0,2 mm/min, an average elongation at the break point of a specimen is approximately 10 mm.

The full test procedure can last even longer than three months. During these three months, the mechanical properties of the propellant change significantly. The tests in this study have shown that these changes are of the order of 100%. In order to get true values of the initial properties, it is necessary to make corrections due to the aging in the initial period after propellant production.

For an illustration, there are significant differences between the absolute modulus values for different HTPB-based propellant compositions (Table 1). The ratio between the maximum value and the minimum value is in the range between one and three. However, the values of the modulus aging factors are similar for all tested compositions (Fig.1), as well as their time-distributions during the initial period.

For example, it is possible to define an approximate average function of a mechanical property distribution in the beginning of the service life, for a whole group of different propellants of the same type, as in the case of seven tested HTPB compositions. This function can be used for a preliminary structural analysis, with a very small error.

In Fig.10 the field contains initial values of the modulus aging factor for all the seven tested compositions (Table 1).

For the period after 45 days, up to 10 months, only the tests for the two propellant compositions (N^o 6 and N^o 7) were made, but it seems that it is enough to see the possibility of defining an approximate mathematical distribution function that could be used in the absence of more complete results.

In addition, according to the results in Table 1 and Fig.2, such a relationship may also be determined for the allowable strain aging factoras well as for all tested compositions. This regression curve is decreasing exponentially.

For the tested group of HTPB compositions (Table 1), it is not possible to define an equation that describes a general aging factor dependence for tensile strength, because there is scattering in both directions (Fig.3).

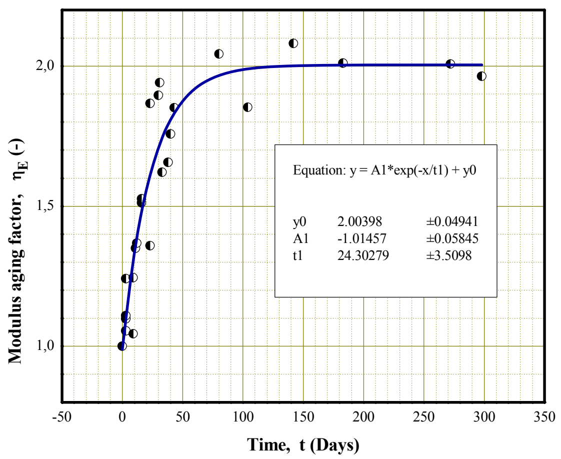

Figure 10. General modulus aging factor

However, the values of the first two aging factors, for the modulus and the allowable strain (η_E, η_ε), could be sufficient for a preliminary structural analysis of propellant grains with complex star-shaped channels [6, 22, 29]. According to [2, 9, 10], for the inner-bore surface as the most critical zone of a propellant grain, a failure analysis should be performed by comparing bore strains with strain failure data, rather than by using the stress criterion. In this case, it is possible to perform the analysis, even if there is no data on the tensile strength.

The second set of tests was carried out for two reasons:

1. To explain the effects of the initial aging on the mechanical properties and the connectivity between real time, strain rate and temperature, as a basis for the time-temperature dependence which is characteristic for viscoelastic materials;
2. To show that the master curves of the propellant mechanical properties may be translated along the time axis, only on the basis of periodical tests in standard conditions (+20^{o}C, 50 mm/min). It means that, when the master curves are determined for a “new” propellant, the uniaxial tension tests are sufficiently representative for monitoring the propellant mechanical properties over time in all operating regimes.

In the second set, only one propellant composition has been tested, in different time- and strain rate conditions. The visual effect of these tests can be seen in Figures 8-10. There are proper distinctions between the values measured after 15 days and the values measured 105 days after production.

Three pairs of regression lines that correspond to different time points, for all the three characteristic propellant mechanical properties ($E, \varepsilon_m, \sigma_m$), in each diagram, are linear and it seems that they are approximately mutually equidistant. It means that the aging effect on the propellant mechanical properties is approximately the same for all different strain rates.

The values of the propellant initial modulus are shown in Fig.8. On the abscissa, the reciprocal values of the strain rate (time) are shown in the logarithmic time scale. For the time ($\log t = 1.9155 \approx 2$) which corresponds to the standard cross-head speed, ($50\ \mathrm{mm/min}$), there are two different values of the modulus: for the propellant tested after 15 days, $E_{15} \approx 6,6\ \ \mathrm{MPa}$, and for the propellant tested after 105 days, $E_{105} \approx 8,4\ \ \mathrm{MPa}$. Over the period 15-105th day, the modulus is changed more than 25%.

This difference is less than the modulus change from its initial value, because there is also a change that occurred during the first 15 days after production. This result shows that the changes in mechanical properties during this period are important.

Besides the basic results that show a large impact of the initial aging on the propellant mechanical properties, one can get some additional conclusions. All the tests in this study were carried out only at standard temperature (+20^{o}C). It is always questionable how the ambient temperature affects the process of properties change due to aging. When it is assumed, for small strains, that a composite rocket propellant is a linear-viscoelastic material, there exists a strong time-temperature dependence [6-10].

The second set of tests has shown that the different strain rates do not affect a relative change of propellant mechanical properties due to aging, because the regression lines for two different time points are approximately equidistant, with the same slope. The aging in this period affects only the spacing along the abscissa between the regression lines. This is expected, because the abscissa corresponds to the time line.

The abscissas in these diagrams represent the reciprocal values of the strain rate, with the time dimension. If a regression line that represents the strain rate dependence of a mechanical property is moved horizontally along the abscissa to meet and overlap another one, the movement along the timeline is equal to the aging impact in the observed period.

According to the time-temperature analogy, it can be concluded that ambient temperature also does not have influence on the effects of the aging process. This statement should not be confused with the real temperature influence on mechanical properties. It is known [6-10] that the absolute values of mechanical properties depend on temperature, but their relative change, compared to the initial values are the same, regardless of the environmental constant temperature value. It seems that relative changes due to natural aging are independent of different constant ambient temperatures. Thus, if the aging process does not affect the character of the strain rate dependence, it also will not affect the relative dependence on temperature.

Finally, it means that it is sufficient to test the aging effect on mechanical properties only at standard temperature.

When it is necessary to make an estimate of rocket motor reliability at an arbitrary time, the propellant mechanical properties have to be determined right for this time point.

This means that all points of each master curve for a virgin propellant, represented in Eqs 1 and 2 as formal constants ($\sigma_{m0},\varepsilon_{m0}$), have to be moved along the real-time axis, due to aging, in the same manner as the point that corresponds to the standard test regime.

Conclusion

In the production process of composite rocket propellant grains, in most cases it is necessary to carry out the quality control of ballistic and mechanical propellant properties immediately after curing. The quality control of the virgin propellant is important for production acceptance, monitoring and relative comparison of different compositions, and for a proper evaluation of the rocket motor reliability in the initial period of its service life.

During the short age period, the mechanical properties of the HTPB propellant extensively change. The stabilization of the propellant mechanical properties takes place up to 2-3 months after production, and sometimes even 6 months. Afterwards, the mechanical properties continue to change slowly, in a different way.

As it was said in the Introduction, this phenomenon is due to the lack of completion of the curing process. The physical properties of the propellant continue to change afterwards. These changes depend on a degree of completion of the polymerization process.

The time distribution of the aging factors can be used to correct the results of the uniaxial mechanical characterization which is planned to be done immediately after production, in different test regimes. Unfortunately, it is not possible to make this complete procedure in a very short time after production. It can last quite a long time and the measured values do not correspond to the real virgin values, due to the influence of initial aging. These results should be corrected.

Many authors neglect the changes of the propellant mechanical properties at the beginning of the rocket motor service life. However, the uniaxial tension tests during the short age period have shown that these changes are too large and they should not be neglected, because they significantly affect the quality of evaluation of rocket motor reliability and service life.

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Mehaničke osobine HTPB kompozitnog raketnog goriva u početnom periodu upotrebe

Jednoosni testovi istezanjem epruveta različitih sastava kompozitnih goriva na bazi hidroksi-terminiranog polibutadiena (HTPB) pokazali su da se mehaničke osobine goriva intenzivno menjaju posle umrežavanja, čak do 100% početnih vrednosti, tokom prvih nekoliko meseci. Mehaničke osobine se posle toga stabilizuju i počinju da se polako menjaju u suprotnom smeru. Pažljiva merenja ovih veličina su potrebna zbog kontrole kvaliteta pri izradi i poređenju različitih sastava i šarži goriva. Pored toga, vremenska promena mehaničkih osobina u početnom periodu posle izrade ne sme da se zanemari, jer značajno utiče na rezultate strukturne analize pogonskih punjenja i procenu pouzdanosti raketnog motora.

Ključne reči: **kompozitno raketno gorivo, mehaničke osobine, prirodno starenje, zatezna čvrstoća, deformacija, modul elstičnosti.**

Механические свойства ГТПБ композитного твёрдого ракетного топлива в начальном периоде использования

Одноосные испытания на растяжение пробирок различного состава композиционных топлив на основе гидрокси-планированого полибутадиена (ГТПБ) показали, что механические свойства топлива изменяются после интенсивной сети, даже и до 100% от начальных значений в течение первых нескольких месяцев. Механические свойства затем стабилизируют и начинают постепенно меняется в противоположном направлении. Тщательные измерения этих величин, необходимы для контроля качества в процессе разработки и ради сравнения различных составов и топливных партий. Кроме того, временные изменения механических свойств в начальном периоде после изготовления не следует пренебрегать, так как они существенно влияют на результаты структурного анализа ракетного топлива и на оценки надёжности ракетного двигателя.

Ключевые слова: **композитное ракетное топливо, механические свойства, естественное старение, прочность на растяжение, деформация, модуль упругости.**

Les propriétés mécaniques du HTPB propergol composite dans le période initial de l'utilisation

Les tests uniaxes par l'extension des éprouvettes de différents compositions des propergols composites à la base du polybutadiène hydroxyle terminé (HTPB) ont démontré que les propriétés mécaniques des propergols changeaient beaucoup après le durcissement jusqu'à 100 % des valeurs initiales au cours des premiers mois. Après cela les propriétés mécaniques se stabilisent et commencent de changer lentement en sens inverse. Les mesurages faits attentivement de ces valeurs sont nécessaires à cause du contrôle de qualité lors de la production et de la comparaison de différentes compositions et des charges de propergols. A part cela le changement temporel de propriétés mécaniques dans la phase initiale après la production ne doit pas être négligé car cela influence considérablement sur les résultats de l'analyse structurale des charges de propulsion et sur l'estimation de la fiabilité du moteur à fusée.

Mots clés: **propergol composite, propriété mécanique, vieillissement naturel, résistance à la tension, déformation, module d'élasticité.**