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Applicability of Dynamic Mechanical and Thermal Methods in Investigation of Ageing Processes of Double Based Rocket Propellants*)

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Abstract: Ageing of double based rocket (DBR) propellants, as a consequence of chemical decomposition reaction, as well as physical processes (migration of low molecular constituents: plasticizers, etc.) has significant influence on their relevant properties (e.g. decrease of molar mass of nitrocellulose, decrease of stabiliser content, decrease of specimen mass, change of mechanical and thermal properties, etc.).
The change of relevant properties of DBR propellants limits their safe and reliable service life. Even more, under certain conditions decomposition of a DBR propellant may become autocatalytic, which can lead to self-ignition of the DBR propellant. Because of that, it is very important to find out reliable methods for determination of propellant stability at a given moment of time, as well as to predict self-ignition probability under given conditions.
In this work we studied dynamic mechanical and thermal properties of DBR propellants artificially aged for different period of time at 90 °C, in order to detect and quantify changes in dynamic mechanical and thermal properties that can be used in the propellants stability assessment. Dynamic mechanical properties were studied by dynamic mechanical analysis (DMA), while thermal properties were studied using differential scanning calorimetry (DSC) and thermogravimetry (TGA).
The obtained results showed that the ageing caused significant changes of DMA, DSC and TGA curves' shape. The changes are quantified by some of characteristic points on DMA, DSC and TGA curves. It was found out that the most sensitive

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parameters/characteristic points to the ageing process at DMA curves are: storage modulus at 25 °C, storage modulus at softening region, peak width and height on loss modulus curve, glass transition temperature, loss modulus at viscoelastic region, tanδ maximum at viscoelastic region, while the most sensitive parameters at DSC and TGA curves are: peak height and width, heat of reaction, max. heat flow rate, mass loss at a given time, and rate of mass loss at a given time.

Keywords: ageing, DBR propellant, dynamic mechanical analysis, differential scanning calorimetry, mechanical properties, thermal properties, termogravimetry

Introduction

Double based rocket propellants, as well as other materials and living organisms, are subject to the ageing processes. There are a number of parameters that can influence degradation of relevant material properties, such as temperature, time, moisture, light, atmospheric conditions, stresses produced during production and use of materials, etc.

Nitrocellulose and other nitrate esters (nitro-glycerine, etc.), which are the main ingredients of the DBR propellants, because of relatively low bound energies (155-163 kJ/mol), and a low value of activation energy (120-190 kJ/mol) are subject to a slow chemical decomposition even at the room temperatures [2, 4-9].

The thermal decomposition of nitrocellulose and nitro-glycerine starts with the homolytic breakdown of the O-NO_2 bond of the aliphatic nitrate esters, thus forming nitrogen dioxide and corresponding alkoxyl radical. The released NO_2 radical immediately undergoes consecutive reactions with other decomposition products or with other propellant ingredients. During this process NO_2 is reduced to NO, N_2O, N, HNO_2 and HNO_3.

Another main decomposition pathway is the neutral to acid hydrolysis of the nitrate esters. The reaction is catalysed by moisture and residual acids, or by water and acids formed during decomposition process [10].

The summary reaction of the thermal decomposition is autocatalytic, and accompanied by the heat generation. The heat released, due to very low propellant conductivity, can accumulate in the propellant grain, and under certain conditions can lead to the propellant self-ignition [3, 11].

Apart from chemical ageing, DBR propellants are subjected to ageing due to physical processes such as migration of low molecular constituents (e.g. nitro-glycerine), or crack formation/propagation that can be initiated by residual stress at rocket grain [4,12]. Ageing due to chemical reactions, as well as due to physical processes, changes their relevant properties (e.g. nitrocellulose mean molar mass, stabiliser content, specimen mass, mechanical and thermal properties, ballistic properties, etc.). During use, these changes can result in dangerous failures, such as explosion of rocket motors. Therefore, it is necessary to find out reliable methods for determination of propellant stability at a given moment of time, as well as to predict self-ignition probability under given conditions.

By now, a number of methods have been used for determination of propellant stability at a given moment of time. In order to predict propellant stability during some period of time (service life time), it is necessary to find out the processes which have the greatest influence on the ageing of the investigated propellant, to determine their rates and to quantify them as accurately as possible [1].

Some quantitative methods based on the measurements of propellants relevant parameters (such as stabiliser content, decrease of mean molar mass of nitrocellulose, specimen mass loss, gas formation, heat generation, etc.) can be used to predict the safe service life time [10, 13-15].

In this work we studied dynamic mechanical and thermal behaviour of artificially aged DBR propellants by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermogravimetry (TGA) in order to check applicability of these methods in propellants stability studies. The results of our previous investigation of these topics are reported in papers [1-2, 16-18].

Experimental

The study was carried out on the double based rocket propellant containing ~54% of nitrocellulose, ~35% of nitro-glycerine, ~3% of dietilftalate, ~3% centralite, and ~5% of other additives. In order to quantify changes of mechanical and thermal properties of the propellant, caused by the ageing processes, the samples of artificially aged propellant were performed by DMA, DSC, and TGA analysis.

The propellant was cut up into rectangular shape of the following dimensions: 50 x 10 x 2.5 mm, and then subjected to artificial ageing in glass tubes at 90 °C (single-temperature aging). The samples for DMA, DSC and TGA measurements were taken periodically (Table 2-4, 6-7), while the total ageing time was 82 days.

The dynamic mechanical measurements (DMA) were carried out using *TA Instruments* DMA, Model 983. The DMA measurements were carried out using samples of the rectangular bar shape (50 x 10 x 2.5 mm), while the measuring conditions were:

heating rate:	2 °C/min
frequency of an oscillatory load:	1 Hz
amplitude of deformation:	± 0.2 mm
length to thickness ratio (*L*/*T*):	~10
temperature range:	-120 °C to +80 °C

The differential scanning calorimetry (DSC) measurements were carried out using *TA Instruments* DSC, Model 2910. The DSC measurements were carried out using samples weighing 1.0 ±0.2 mg. The samples were tested in aluminum sample pans covered by perforated cap, with a heating rate of 5 °C/min, and under nitrogen atmosphere with flow rate of 50 mL/min.

Isothermal thermogravimetry (TGA) measurements were carried out using *TA Instruments* SDT, Model 2960. The TGA measurements were carried out using samples weighing 1.0 ±0.2 mg. The samples were tested in aluminum sample pans, at 100 °C, and under nitrogen atmosphere with a flow rate of 50 mL/min.

The degree of change of some parameter was calculated using the following equation:

$$y_P = \frac{(P_0 - P_t)}{P_0} \cdot 100 \tag{1}$$

where: y_P – degree of change of some parameter, P_0 – parameter value at the beginning of the ageing, and P_t – parameter value after some time of ageing.

The ageing times at 90 °C ($t_{90°C}$) were, with assumption that ageing mechanism at 90 and 30 °C are the same, transformed into corresponding ageing times at 30 °C ($t_{30°C}$), in accordance with the following equation [1]:

$$t_{30°C} = t_{90°C}\, \alpha_{10}^{[(90-30)/10]} \tag{2}$$

where reaction rate accelerating factor (α_{10}) is taken to be equal 3.

Results and Discussion

Samples of non-aged and aged double based rocket propellants were subjected to DMA, non-isothermal DSC and isothermal TGA tests. For this preliminary investigation, because of the limitation of the experiment duration time, the selected ageing temperature was 90 °C, which is much higher than the normal storage temperature.

Dynamic mechanical properties

Change of storage modulus with ageing

Storage modulus vs temperature curves of a non-aged DBR propellant and the DBR propellants aged for different period of time at 90 °C are given in Figure 1.

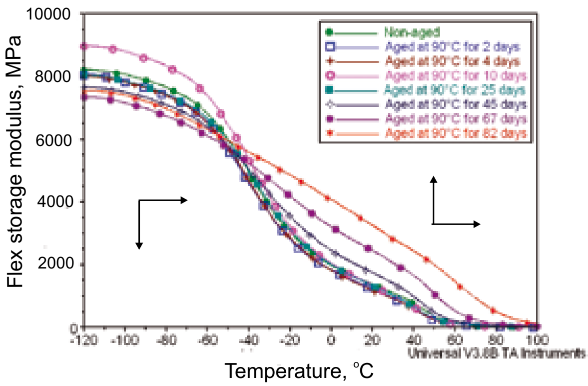

Figure 1. Storage modulus curves of a non-aged propellant and the propellants aged for different period of time at 90 °C as a function of temperature (arrows asign a trend of changes).

From Figure 1 it is evident that *E´-T* curve was shifted with the ageing time to higher temperatures, as well as to higher values of modulus. An increase of the storage modulus is indicator of reduced flexibility of nitrocellulose macromolecules. Reduced flexibility of the macromolecular chain, in this case is a result of reducing amount of the energetic plasticizer (nitro-glycerine). The plasticizer migration from the propellant grain interior to the surface, and their vaporization, cause shortening of distances between macromolecules, and an increase of intermolecular forces. These processes have significant effect on flexibility of the nitrocellulose macromolecule units.

In order to quantify changes in the storage modulus, caused by artificial ageing of the DBR propellant, several characteristic points on *E´-T* curves are analyzed, Figure 2, Tables 1, 2.

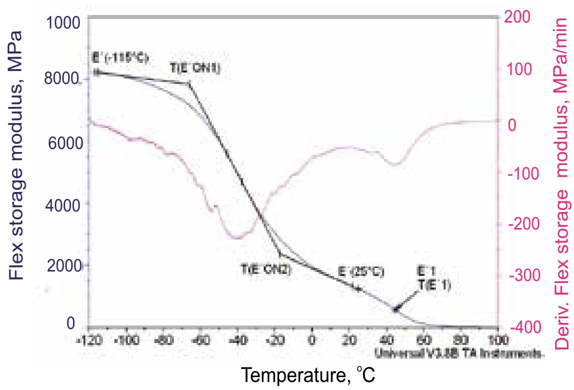

Figure 2. Typical E'-T curve of DBR propellant, along with derivative E'–T curve.

Table 1. Some characteristic points/parameters on DMA curves

No.	**Characteristic points on *E´-T* curves**	Denotation	Unit
1.	storage modulus at -115 °C,	$E'_{(-115°C)}$	MPa
2.	storage modulus at 25 °C	$E'_{(25°C)}$	MPa
3.	extrapolated onset temperature at the beginning of transition from glassy to viscoelated stage	$T_{(E'ON1)}$	°C
4.	extrapolated onset temperature at the end of transition from glassy to viscous stage	$T_{(E'ON2)}$	°C
5.	storage modulus at max. decreasing rate of storage modulus in softening region	E'_1	MPa
6.	temperature at maximum decreasing rate of storage modulus in softening region	$T_{(E'1)}$	°C
No.	**Characteristic points on *E˝-T* curves**	Denotation	Unit
1.	loss modulus at -115 °C	$E''_{(-115°C)}$	MPa
2.	loss modulus at 25 °C	$E''_{(25°C)}$	MPa
3.	peak width at half height	W_{peak}	°C
4.	peak height	h_{peak}	MPa
5.	glass transition temperature (peak maximum temperature)	T_g	°C
6.	loss modulus at viscoelastic region (close to softening point)	E''_1	MPa
7.	extrapolated onset temperature at beginning of transition from viscoelastic to viscous stage	$T(E''_{ON1})$	°C
8.	extrapolated onset temperature at the end of transition from viscoelastic to viscous stage	$T_{(E''ON2)}$	°C
No.	**Characteristic points on tan*δ* -*T* curves**	Denotation	Unit
1.	tan*δ* at -115 °C	$\tan\delta_{(-115°C)}$	
2.	extrapolated onset temperature at begining of glass transition	$T(\tan\delta_{ON1})$	°C
3.	tan*δ* maximum in viscoelastic region	$\tan\delta_{max}$	
4.	extrapolated onset temperature at end of glass transition	$T(\tan\delta_{ON2})$	°C

5.	tanδ at -115 °C	tan$\delta_{(25°C)}$	
6.	extrapo. onset temp. at beginning of transition from viscoelastic to viscous stage	$T(\tan\delta_{ON3})$	°C
7.	extrapo. onset temp. at the end of transition from viscoelastic to viscous stage	$T(\tan\delta_{ON4})$	°C

In Tables 2-4 and 6-7, the values of the characteristic points at the DMA, DSC and TGA curves according to time of ageing at 90 °C are shown. Also, it is specified degree of change, and measurement uncertainty (mean value ± 2σ) for every characteristic point.

Table 2. Values of some characteristic points on E´-T curves of DBR propellants aged for different period of time at 90 °C

Ageing time at 90 °C, days	Corresponding ageing time at 30 °C, years**	$E'_{(-115°C)}$ MPa	$T_{(E'ON1)}$ °C	$T_{(E'ON2)}$ °C	$E'_{(25\ °C)}$ MPa	E'_1 MPa	$T_{(E'1)}$ °C
Non-aged	Non-aged	8248	-67.18	-16.43	1213	572,04	42.42
2	4	8063	-69.48	-15.67	1097	582,6	39.90
4	8	7997	-67.99	-16.46	1048	493,5	42.50
10	20	8961	-68.13	-16.40	1194	513,5	43.70
25	50	8043	-67,65	-14.84	1181	621,1	41.80
45	90	7655	-71.27	-6.60	1580	790,1	43.70
67	134	7327	-77.07	-	2260	1248,0	47.20
82	164	7540	-91.37	-	3044	1438,0	60.70
Degree of change (after 82 days of ageing at 90 °C) / % *		8.59	36.00	105.48	132.28	151.22	34.89
Mean value ± experimental standard deviation		8249 ± 369	-67 ± 1.51	-16.43 ± 0.60	1218 ± 97.8	572,4 ± 26.8	42.42 ± 1.79

*- Calculated according to Eq. 1, **- Calculated according to Eq. 2.

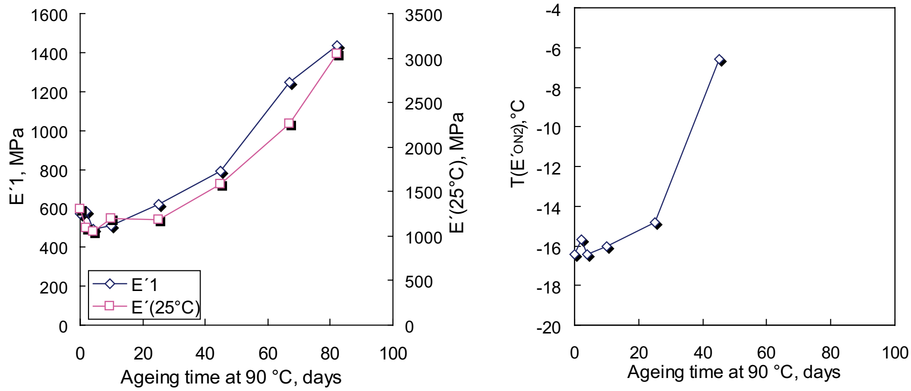

Figure 3. Changes of some characteristic points on *E´-T* curves of DBR propellants aged for different period of time at 90 °C.

From Table 2 and Figure 3 it is evident that some of characteristic points at *E´-T* curve (*E´*(25 °C), T(E'_{ON2}, *E´1*) are change significantly with the time of ageing. For example, degree of change of storage modulus at the maximum decreasing rate in the softening region, *E´1*, after 82 days of ageing at 90 °C is more than 150%.

The changes of storage modulus at the maximum decreasing rate in the softening region, *E´1*, becomes higher than measurement uncertainty limits (Table 2) after 10 days of ageing at 90 °C (i.e. after ~20 years of ageing at 30 °C), while the changes of other parameters become higher than measuring uncertainty limits after 25 days of ageing at 90 °C (i.e. after ~50 years of ageing at 30 °C). This means that, on the basis of the *E´-T* curve measurements, a reliable conclusion on DBR propellant stability, i.e. its age, may be set out only after this period of ageing.

The accelerated change of all characteristic points at the *E´-T* curves begins after 45 days of ageing at 90 °C. This is related to the intensive degradation of nitrocellulose chain.

Change of loss modulus with ageing

From the *E˝-T* curves of DBR propellants aged for different period of time at 90 °C (Figure 4) is evident that ageing causes significant quantitative and qualitative changes on the *E˝-T* curves. For example, peak height at the glass transition region decrease (from ~ 420 MPa for non-aged propellant to ~180 MPa for propellant aged 82 days at 90 °C), peak width increases, and the complete *E˝-T* curve is shifted to higher temperatures.

Very intensive changes on the *E˝-T* curve begin after 45 days of ageing at 90 °C. After that time of ageing, begins intensive decrease of peak height, and very intensive increase of the peak width, that after 67 days of ageing even resulted with the splits of the main peak into two separate peaks.

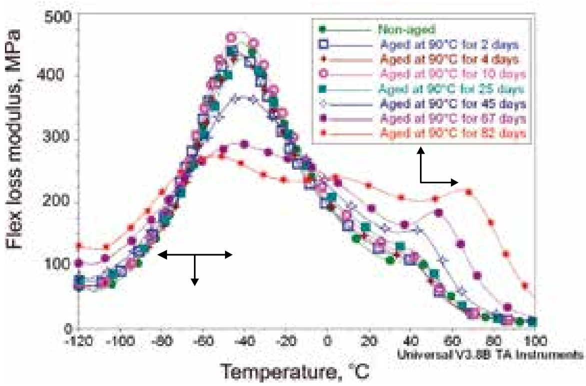

Figure 4. Loss modulus curves of non-aged propellant and the propellants aged for different period of time at 90 °C as a function of temperature (arrows asign a trend of changes).

From Figure 4 and Table 3 is visible that the temperature of the peak maximum at the glass transition region, Tg, shifts to the lower temperatures, while at the same time, the temperature of the peak maximum at the viscoelastic region increases.

Increase of the peak width and presence of two peaks at the *E*″-*T* curves, after 67 days of ageing at 90 °C, indicates an increase in the heterogeneity of system. This is probably a consequence of the very intensive decomposition reaction of low-molecular components of the DBR propellant (nitro-glycerine, stabiliser, etc.), as well as the splits of the nitrocellulose macromolecules.

In order to quantify these changes in the loss modulus, caused by artificial ageing of DBR propellant at 90 °C, several characteristic points on the *E*″-*T* curves were analysed, Figure 5, Tables 1, 3.

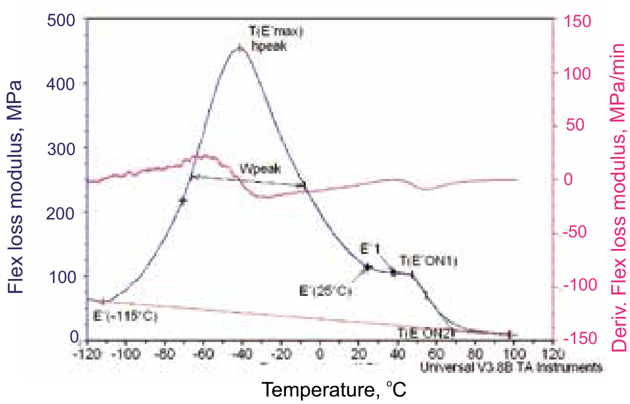

Figure 5. Typical *E″-T* curve of DBR propellant, along with derivative *E″-T* curve.

Table 3. Values of some characteristic points on *E″-T* curves of DBR propellant aged for different period of time at 90 °C.

Ageing time at 90 °C, days	Correspon-ding ageing time at 30 °C, years**	$E''_{(-115°C)}$ MPa	W_{peak} °C	T_g °C	h_{peak} MPa	$E''_{(25°C)}$ MPa	E''_1 MPa	$T_{(E''ON1)}$ °C	$T_{(E''ON2)}$ °C
Non-aged	Non-aged	64.0	59.28	-41.98	421.68	123.4	111.7	44.76	62.90
2	4	63.4	57.45	-43.12	401.30	126.1	112.1	43.68	63.49
4	8	63.7	57.16	-41.62	399.40	130.2	112.1	44.56	62.68
10	20	70.6	57.84	-42.00	431.00	136.0	120.2	45.08	63.61
25	50	78.3	61.09	-39.90	378.20	147.1	127.5	44.91	64.84
45	90	76.5	78.52	-41.79	329.10	162.7	155.2	46.51	68.83
67	134	102.8	140.68	-45.59	229.0	180.9	180.7	54.26	78.92
82	164	126.2	166.8	-51.89	179.9	223.0	213.7	69.53	91.54
Degree of change (after 82 days of ageing at 90 °C) / % *		97.13	181.38	30.59	72.68	58.39	91.35	45.64	36.02
Mean value ± experimental standard deviation		64.02 ± 6.7	59.28 ± 1.12	-41.98 ± 0.72	421.68 ± 18.47	123.4 ± 6,7	111.7 ± 5.1	44.76 ± 1.80	62.90 ± 2.05

*- Calculated according to Eq. 1, **- Calculated according to Eq. 2.

It is evident from Table 3 and Figure 6 that characteristic values at the *E″-T* curves (loss modulus at -115 °C, peak width at half-height, peak height, loss modulus at viscoelastic region, etc.) are sensitive to ageing processes. The changes of majority of parameters become higher than measuring uncertainty limits after 10 days of ageing at 90 °C (i.e. after ~20 years of ageing at 30 °C).

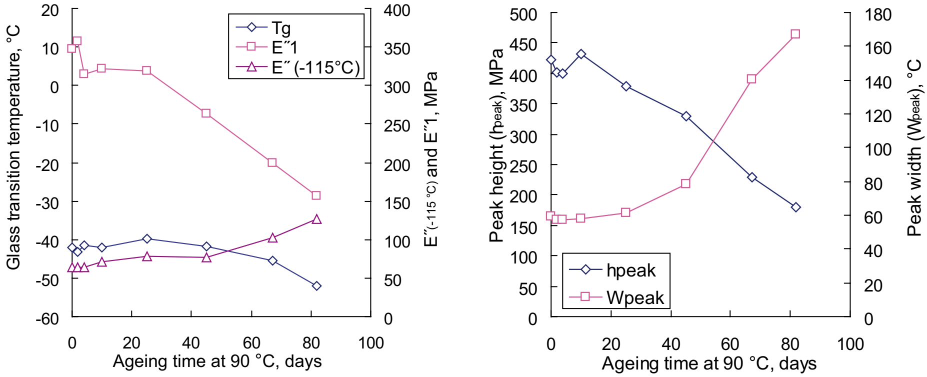

Figure 6. Changes of some characteristic points on *E″-T* curves of DBR propellant aged different period of time at 90 °C.

From Table 3 and Figure 6 can be seen that a significant change of characteristic parameters begins after 45 days of ageing at 90 °C. The change of the DBR propellants properties after 45 days of ageing was especially influenced at characteristic parameters related with softening point ($T(E''_{ON1})$, $T(E''_{ON2})$), which before that time of ageing were almost constant. Intensive increase of softening point after 45 days of ageing is probably the result of increased intermolecular forces, as a consequence of decreased amount of plasticizer (nitro-glycerine) and increased heterogenity of the system (nitrocellulose chain breakdown).

Change of tanδ with ageing

Tanδ vs. temperature curves of a non-aged the DBR propellant and DBR propellants aged for different period of time at 90 °C are given in Figure 7.

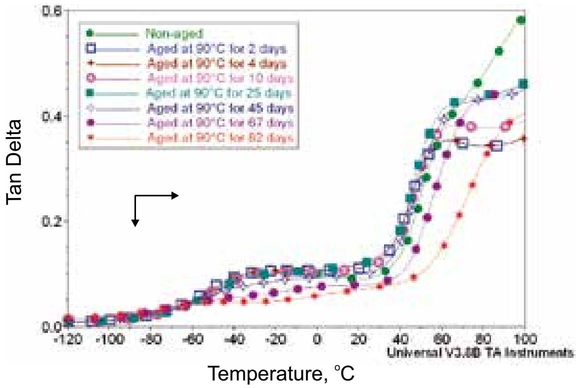

Figure 7. Tanδ -T curves of non-aged DBR propellant aged for different period of time at 90 °C (arrows asign a trend of changes).

From the tanδ−T curves of DBR propellants aged for different period of time at 90 °C, shown in Figure 7, is obvious that the shape of tanδ-T curves changes considerably with the ageing. At temperatures below the glass transition region, the value of tanδ remains almost unchanged, while in the glass transition region, viscoelastic region, and in the softening temperature region the value of tanδ decreases significantly. From Figure 7, it can be seen that with the ageing time the tanδ□□-T curve shifts to higher temperatures. All these changes, especially increased softening point, are the indication that by the ageing the amount of plasticizer in the propellant decreases.

In order to quantify these changes in the tanδ, several characteristic points on tanδ-T curves were analysed, Figure 8, Tables 1, 4.

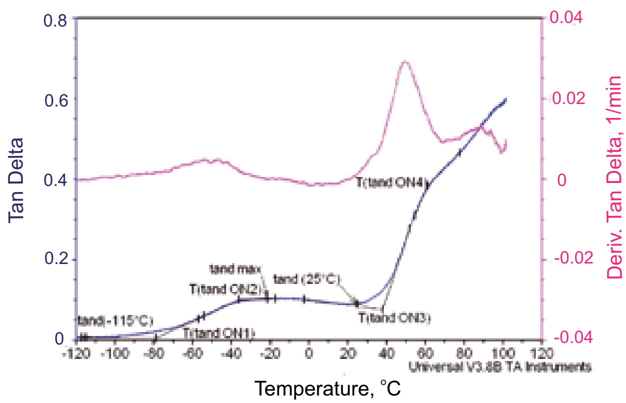

Figure 8. Typical tanδ-T curve of DBR propellant, along with derivative tanδ-T curve.

Table 4. Values of some characteristic points on tanδ-T curves of DBR propellant aged for different period of time at 90 °C

Ageing time at 90 °C, days	Correspon-ding ageing time at 30 °C, years**	tan$\delta_{(-115°C)}$ MPa	T(tanδ_{ON1}) °C	T(tanδ_{ON2}) °C	tanδ_{max} MPa	tan$\delta_{(25\ °C)}$ MPa	T(tanδ_{ON3}) °C	T(tanδ_{ON4}) °C
Non-aged	Non-aged	0.0078	-76.90	-36.38	0.1074	0.1164	35.50	57.32
2	4	0.0079	-75.09	-36.87	0.1059	0.1150	32.99	55.22
4	8	0.0080	-76.37	-36.89	0.1074	0.1242	34.22	54.71
10	20	0.0079	-76.38	-36.12	0.1035	0.1139	35.28	55.29
25	50	0.0097	-75.34	-35.29	0.1024	0.1246	35.45	56.41
45	90	0.0103	-78.43	-35.10	0.0909	0.1030	36.61	59.19
67	134	0.0139	-94.46	-45.47	0.0604	0.0800	43.18	70.16
82	164	0.0167	-98.21	-56.67	0.0481	0.0733	55.15	89.16
Degree of change (after 82 days of ageing at 90 °C) / % *		113.74	27.72	104.7	55.21	24.71	43.25	59.19
Mean value ± experimental standard deviation		0.0078 ± 0.001	-76.90 ± 3.04	-36.38 ± 1.09	0.1074 ± 0.0025	0.1164 ± 0.0145	35.50 ± 1.98	57.32 ± 2.52

*- Calculated according to Eq. 1, **- calculated according to Eq. 2.

Although, changes of the characteristic parameters at the tanδ–T curves are evident (Figures 8 and 9, Table 4), for the majority of the parameters, they still remain within measurement uncertainty up to 45 days of ageing at 90 °C (i.e. ~ 90 years of ageing at 30 °C). An exceptions is the tanδ maximum in the viscoelastic region (tanδ_{max}), which seems to be very sensitive to ageing. The values of the tanδ maximum in viscoelastic region, reaches the measurement uncertainty limits after 10 days of ageing at 90 °C (i.e. after ~20 years of ageing at 30 °C), so that parameters should be considered to one of the parameters that can be used for prediction of the DBR propellant life time.

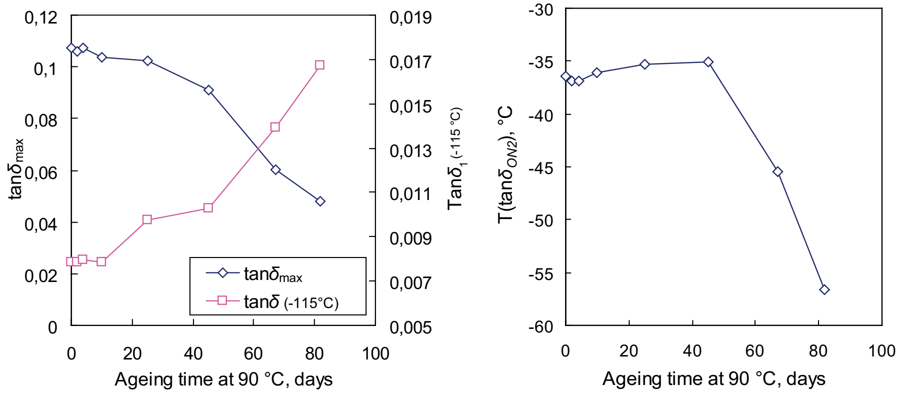

Figure 9. Changes of some characteristic points on tanδ-T curves of DBR propellant aged for different period of time at 90 °C.

Thermal properties

Change of non-isothermal DSC curves with ageing

Non-isothermal DSC curves of DBR propellants aged for different period of time at 90 °C are given in Figure 10.

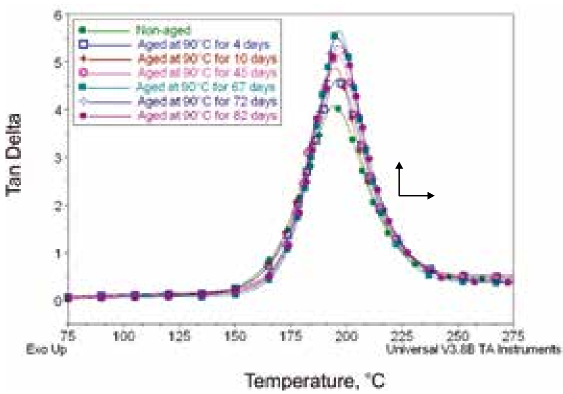

Figure 10. Non-isothermal DSC curves of DBR propellants aged for different period of time at 90 °C (arrows asign a trend of changes).

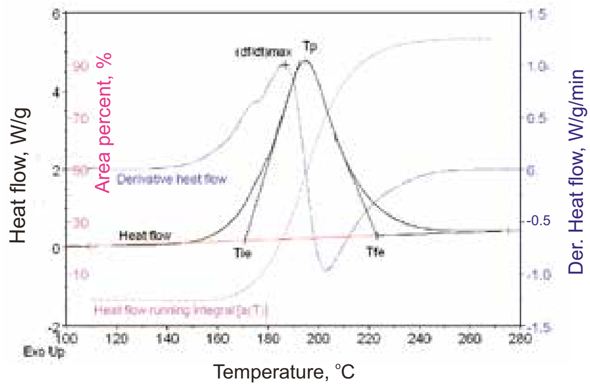

Figure 11. Typical non-isothermal DSC curve of DBR propellant, along with derivative heat flow curve and heat flow curve running integral (heating rate 5 °C/min).

Table 5. Some characteristic points/parameters on DSC and TGA curves

No.	**Characteristic points on DSC curves**	**Denotation**	**Unit**
1.	extrapolated peak onset temperature	T_{ie}	°C
2.	peak maximum temperature	T_p	°C
3.	extrapolated peak end-set temperature	T_{fe}	°C
4.	heat of reaction	H_r	J/g
5.	peak height	h_p	W/g
6.	peak width at half-height	w_p	°C
7.	conversion at maximum heat flow rate	$\alpha(d\Phi/dt)_{\max}$	%
8.	conversion at peak maximum	$\alpha(T_p)$	%
9.	maximum heat flow rate	$(d\Phi/dt)_{\max}$	W/(g min)
10.	maximum actual heating rate	$\beta_{\max}$	°C/min
No.	**Characteristic points on TGA curves**	**Denotation**	**Unit**
1.	maximum decomposition rate	$(dm/dt)_{max}$	%/min
2.	time to reach maximum decomposition rate	t [(dm/dt)$_{\max}$]	min
3.	degree of decomposition at maximal decomposition rate	m [(dm/dt)$_{\max}$]	%
4.	time to reach 10% sample mass loss	t (10 %)	min
5.	time to reach 15% sample mass loss	t (15 %)	min
6.	time to reach 20% sample mass loss	t (20 %)	min
7.	mass loss after 60 min	m (60 min)	%
8.	mass loss after 200 min	m (200 min)	%
9.	rate of decomposition after 10 min	(dm/dt)$_{10\ \mathrm{min}}$	%/min
10.	rate of decomposition after 20 min	(dm/dt)$_{20\ \mathrm{min}}$	%/min

From Figure 10, it is clear that ageing has caused significant changes of the DSC curves shape and position. For example, DSC peak height increases, peak width decreases, peak onset temperature increases, heat of reaction increases, maximum heat flow rate increases, etc. In order to quantify these changes in the DSC curves, several characteristic points on DSC curves were analysed, Figure 11, Tables 5, 6.

Table 6. Values of some characteristic points on DSC curves for DBR propellants aged for different period of time at 90 °C

Ageing time at 90 °C, days	Corresponding ageing time at 30 °C, year**	T_{ie}, °C	T_p, °C	T_{fe}, °C	H_r, J/g	h_p, W/g	w_p, °C	$\alpha(d\varphi/dt)_{max}$, %	$\alpha(T_p)$, %	$(d\varphi/dt)_{max}$, W/(g min)
Non-aged	Non-aged	168.38	193.71	224.76	1731	3.82	31.91	26.57	46.25	0.888
2	4	168.42	196.11	224.74	1795	4.09	30.51	26.59	46.08	0.884
4	8	167.98	196.80	225.08	1873	4.33	30.28	26.39	46.55	0.922
10	20	169.76	194.45	222.97	1910	4.57	27.53	27.27	45.92	1.087
45	90	172.71	195.97	221.45	1946	4.90	28.61	20.44	45.33	1.536
60	119	171.21	195.34	224.83	1901	4.88	28.46	28.25	45.67	1.296
67	134	173.81	191.43	222.57	1980	5.46	25.46	28.50	46.54	1.511
72	144	175.15	195.46	225.24	2178	5.32	28.16	29.82	42.96	1.489
82	164	175.55	195.51	225.21	2093	5.15	27.88	31.61	44.67	1.814
Degree of change (after 82 days of ageing at 90 °C) / % *		4.25	0.93	0.20	20.91	34.82	12.63	18.97	3.42	104.28
Mean value ± experimental standard deviation		172.16 ± 3.07	194.94 ± 2.00	220.71 ± 7.38	1810 ± 252	4.62 ±1.13	27.54 ±5.16	24.84 ± 5.04	45.86 ± 3.97	1.2 ± 0.38

*- Calculated according to Eq. 1, **- calculated according to Eq. 2.

From Table 6 and Figures 10, 12, it is visible that the changes are more intensive during the first 15 days of ageing at 90 °C (i.e. ~30 years of ageing at 30 °C), almost constant between 15 and 45 days of ageing, and then intensive again after that period. According to our findings intensive changes in the first 15 days of ageing at 90 °C are primarily due to nitro-glycerine evaporation and decomposition, while changes after 45 days of ageing are connected with intensive degradation of nitrocellulose (chain breakdown) [2].

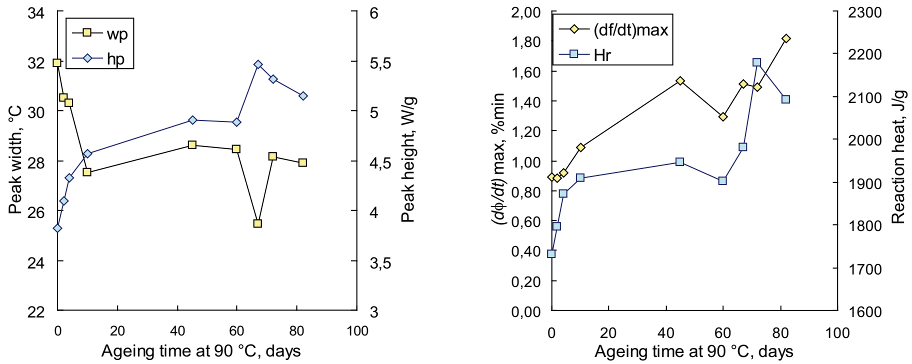

Figure 12. Changes of some characteristic points/parameters on DSC curve of DBR propellant with the ageing time at 90 °C.

Although changes of the DSC curves shape with the ageing, and consequently characteristic points on the DSC curves, are evident they still remain within the measuring uncertainty limits (± σ) up to 67 days of ageing at 90 °C (i.e. ~135 years of ageing at 30 °C). This means that, on the basis of non-isothermal DSC tests, a reliable conclusion on DBR propellant stability, i.e. its age, may be set out only after this period of ageing.

Change of isothermal TGA curves with ageing

Isothermal TGA curves of DBR propellants aged for different period of time at 90 °C are given in Figure 13.

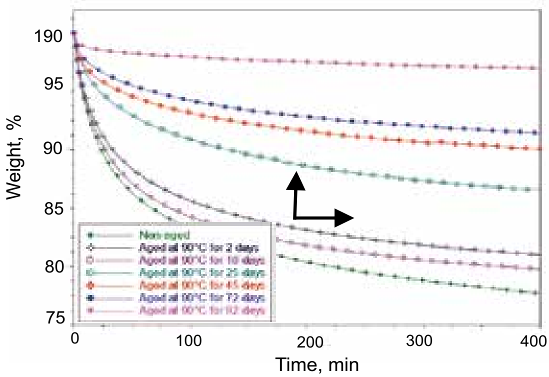

Figure 13. Isothermal TGA curves of DBR propellants aged for different period of time at 90 °C (arrows asign a trend of changes).

In order to quantify changes in the TGA curves caused by artificial ageing of the DBR propellant at 90 °C, several characteristic points on TGA curves were analysed (Figutre 14, Tables. 5, 7).

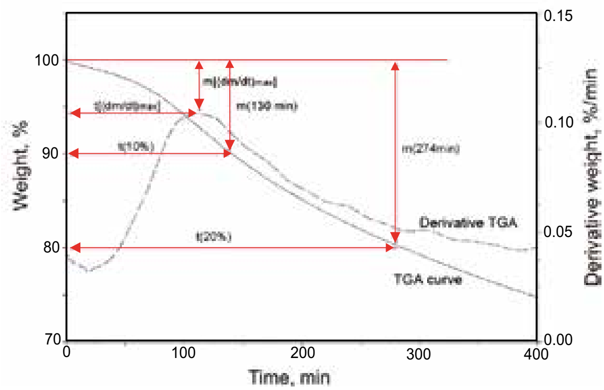

Figure 14. Typical isothermal TGA and derivative TGA curves of NC propellant.

Table 7. Values of some characteristic points on TGA curves for DBR propellants aged for different period of time at 90 °C.

Ageing time at 90 °C	Corres-ponding ageing time at 30 °C**	$(dm/dt)_{max}$, %/min	$t_{((dm/dt)max)}$, min	$m(dm/dt)_{max}$, %	$t_{(10\,\%)}$, min	$t_{(15\,\%)}$, min	$m_{(60\,min)}$, %	$m_{(200\,min)}$, %	$(dm/dt)_{10\,min}$, %/min	$(dm/dt)_{20\,min}$, %/min
Non-aged	0.0	0.997	2.47	1.55	23.47	66.81	14.51	34.13	0.4312	0.24
2	4.0	1.019	2.47	1.58	33.63	118.00	12.37	16.90	0.3396	0.19
10	20.0	0.986	2.47	1.73	27.15	82.60	13.66	18.22	0.3679	0.21
25	49.9	0.701	2.39	1.03	132.40		7.57	13.48	0.2228	0.16
45	89.9	0.644	1.84	0.84	399.20		5.78	8.41	0.1344	0.08
72	143.8	0.497	1.81	0.72			4.80	7.18	0.1078	0.08
82	163.8	0.270	2.55	0.60			1.77	2.49	0.0301	0.16
Degree of change (after 82 days of ageing at 90°C) / % *		72.92	3.24	61.29	1600.89	23.63	87.80	92.70	93.02	33.33
Mean value ± experimental standard deviation		1.248 ± 0.62	2.471 ± 0.42	2.052 ± 1.12	13.865 ± 9.11	30.117 ± 33.42	19.921 ± 5.81	23.636 ± 5.18	0.663 ± 0.27	0.358 ± 0.11

*- Calculated according to Eq. 1, **- calculated according to Eq. 2.

It is evident from Figure 13 and Table 7 that the ageing causes significant changes of TGA curves. For example, time to reach the same degree of mass loss increases with the ageing, mass loss after the same time period decreases, the rate of mass loss decreases (Figure 14), etc. The changes of majority of parameters become higher than measuring uncertainty limits (Table 7) after 10 days of ageing at 90 °C (i.e. after ~20 years of ageing at 30 °C).

TGA experiments were conducted using open aluminum sample pans and under 100 °C isothermal temperature. Under such conditions, the sample mass loss is predominantly a consequence of nitro-glycerin evaporation, and partly degradation of nitro-glycerine and nitrocellulose. Our previous experiments have shown that mass loss of NC propellant at 100 °C is less than 2% after 400 minutes [1], which is almost negligible comparing with mass loss due to nitro-glycerine evaporation and degradation.

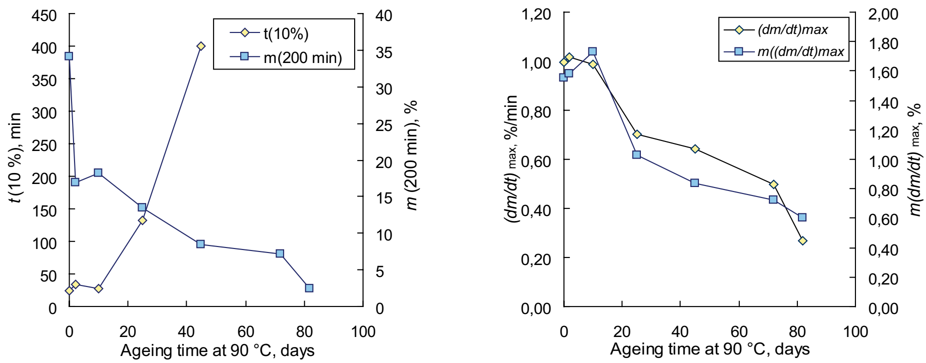

Figure 15. Changes of some characteristic points/parameters on TGA curve of DBR propellant with the ageing time at 90 °C.

The results of isothermal TGA measurements (Figure 15) clearly explain the conclusion that the dominant process during artificial ageing at 90 °C is nitro-glycerine evaporation and degradation (simultaneously). Because of that, the TGA curve of DBR propellant aged for 82 days at 90 °C becomes very close to TGA curve of NC propellant.

Taking into account all DSC and TGA experiments conducted on the DBR propellant, it is obvious that the ageing causes changes of their thermal properties. However, the changes of DSC parameters still remains within the measuring uncertainty limits during 67 days of ageing at 90 °C (i.e. ~135 years of ageing at 30 °C), while the changes of TGA parameters remain within the measuring uncertainty limits during the first 10 days of ageing at 90 °C (i.e. 20 years of ageing at 30 °C). This means that TGA is more sensitive than DSC to the ageing of DBR propellants.

Conclusion

The results presented in this paper have shown that artificial single-temperature ageing (at 90 °C) of DBR propellants causes significant changes of their mechanical and thermal properties. Obtained results have confirmed that dynamic mechanical analysis, differential scanning calorimetry and termogravimetry can be used to follow and to quantify these changes.

Obtained changes on DMA, DSC and TGA curves indicate that ageing processes have two stages. In the primary stage of ageing dominant processes are migration and evaporation of nitro-glycerine, while in the secondary stage of ageing a dominant process is intensive degradation of nitrocellulose polymer chain.

It was found out that the most sensitive parameters/characteristic points to the ageing process at DMA curves are: storage modulus at 25 °C, storage modulus at the softening region, peak width and height on loss modulus curve, glass transition temperature, loss modulus at the viscoelastic region, tanδ maximum in viscoelastic region, extrapolated onset temperature at the end of the glass transition, while the most sensitive parameters at the DSC and the TGA curves are: peak height and width, heat of reaction, maximum heat flow rate, mass loss at a given time, and rate of mass loss at a given time.

However, because of the relatively high measuring uncertainty and limited sensitivity (especially for DSC measurements) to the age of the propellants, it follows that DMA, DSC and TGA are not very too sensitive techniques to the propellants age, but they still may help in the propellants stability evaluation. In the future work we will try to find out optimal testing conditions which will give minimal measurement uncertainty.

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