Dynamic Mechanical Properties of Artificially Aged Double Base Rocket Propellant and the Possibilities for the Prediction of Their Service Lifetime

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Abstract: The ageing of double base (DB) rocket propellants, as a consequence of the chemical reactions and physical processes that take place over time, has a significant effect on their relevant properties, such as chemical composition and mechanical and ballistic properties. The changes to relevant properties limit the safe and reliable service life of DB rocket propellants. Accordingly, numerous research efforts have been undertaken to find reliable methods to measure the changes caused by ageing in order to assess the quality of DB rocket propellants at a given moment of their lifetime, and to predict their remaining service lifetime. In this work we studied the dynamic mechanical properties of DB rocket propellant artificially aged at temperatures of 80, 85 and 90 °C, in order to detect and quantify changes in the dynamic mechanical properties caused by ageing, and to investigate the possibilities for the prediction of service lifetime. Dynamic mechanical properties were studied using a dynamic mechanical analyser (DMA). The results obtained have shown that ageing causes significant changes in the storage modulus (E´), the loss modulus (E″) and the tan δ curves' shape and position. These changes are quantified by following some characteristic points on the E´-T, E″-T, and tan δ-T curves (*e.g.* glass transition temperatures; storage modulus, loss modulus and tan δ at characteristic temperatures, *etc*.).

It has been found that the monitored parameters are temperature and time dependent, and that they can be shown to be functions of the so called 'reduced time of artificial ageing'. In addition, it has been found that, on the basis of known changes in viscoelastic properties as a function of time and ageing temperature, and the known kinetic parameters of the ageing process, it is possible to calculate (determine) the change in the properties at any ageing temperature provided that the mechanism of the ageing process does not change. Unfortunately, the use of

kinetic parameters obtained by artificial ageing at high temperatures (above 60 °C) for the prediction of the propellant lifetime will not give reliable results, because the mechanisms of ageing at 85 °C and 25 °C are not the same.

Keywords: ageing, double base rocket propellants, dynamic mechanical analysis, glass transition temperature, life-time prediction, loss modulus, softening temperature, storage modulus, tan δ

Introduction

For safety reasons, research and understanding of the ageing processes is particularly important in the field of energetic materials such as double base (DB) rocket propellants. The ageing of DB rocket propellants (as a consequence of chemical reactions and physical processes), has a significant effect on their relevant properties, such as chemical composition, mechanical and ballistic properties. The changes in their relevant properties limit their safe and reliable service life.

Nitrocellulose (NC), which is the main ingredient of DB rocket propellants, because of its relatively low activation energy (120-190 kJ mol^{-1}) is subject to a slow chemical decomposition even at room temperature [1-5]. The thermal decomposition of NC and nitroglycerine (NG) starts with the homolytic breakdown of the O-NO$_2$ bond of the aliphatic nitrate ester group, thus forming nitrogen dioxide and the corresponding alkoxyl radicals [1, 2, 6-8]. The released NO$_2$ radicals immediately undergo consecutive reactions with either other decomposition products, or with other propellant ingredients. The resultant reaction of thermal decomposition is autocatalytic, and is accompanied by heat generation [6]. Due to the low heat conductivity of propellants, the heat released can accumulate in the propellant grain, and under certain conditions (high storage temperature, large diameter of propellant grain *etc*.), can lead to propellant explosion [6, 9].

Apart from ageing due to chemical reactions, DB rocket propellants are subject to ageing due to physical processes such as diffusion and migration of low molecular constituents (*e.g.* NG, phlegmatisers, plasticizers), crack formation and propagation that can be initiated by residual stresses in the rocket grain, *etc*. [10-12].

The chemical and physical processes of ageing of DB rocket propellants affect their viscoelastic properties, such as tensile strength, modulus of elasticity, glass transition temperature, *etc*. These changes can induce crack formation

and propagation that can finally result in potentially dangerous failures, *e.g*. rocket motor failure during launching. Therefore, knowledge of the viscoelastic properties of DB rocket propellants at a given moment of their lifetime, as well as prediction of the behaviour of DB rocket propellants during their remaining storage time under certain storage conditions, is of great importance.

Many researchers have studied the ageing of propellants caused by chemical reactions [1-3, 5-8, 13-16], but there is less information in publicly accessible literature on ageing due to physical processes [12, 17-19]. However, it is obvious that chemical, physical, mechanical and structural stabilities are mutually connected. For example, plasticiser migration and evaporation and/or cleavage of NC macromolecule will cause a decrease in the propellant structural integrity and the propellant's mechanical stability that will have a great influence on the propellant's dynamic mechanic properties [9, 17-20]. Unfortunately, experience has shown that there is no simple correlation between different kinds of stabilities: *e.g*., a propellant can be perfectly stable physically but unstable chemically, and vice versa [21].

In order to predict propellant stability during a given period, it is necessary to discover the processes which have the greatest influence on ageing (at a given ageing temperature), to determine the rates of these processes, and to quantify them as accurately as possible. Some quantitative methods are based on the determination of changes in stabiliser content, decreases in the mean molar mass of NC, specimen mass loss, heat generation, mechanical properties, *etc*. [1, 7, 8, 22].

In this work we have studied changes in the dynamic mechanical properties of DB rocket propellants artificially aged at temperatures of 80, 85 and 90 °C, in order to detect and quantify changes in their dynamic mechanical properties caused by ageing, and to investigate the possibilities for predicting their remaining service lifetime. Some of the results obtained by other authors and during our previous investigations of this topic, are reported in papers [20, 23-27, 31, 32, 34].

Experimental

Materials
DB rocket propellant samples with the following chemical composition: 57.9 wt% of NC, 26.7 wt% of NG, 8.5 wt% of dinitrotoluene, 2.9 wt% of ethyl centralite, and 4.0 wt% of other additives, were studied. The samples of DB rocket propellant tested for dynamic mechanical analysis (DMA) were cut off from a propellant grain (prepared by the extrusion process) and prepared as

rectangular bars of size: 40 ±0.05 × 10 ±0.05 × 2.5 ±0.05 mm; the direction of sample cutting was axial. The distance between the clamps of the DMA analyser, or the active length of the sample measured, was ~25 mm, in order to achieve a length (L) to thickness (T) ratio of 10 (L/T = 10).

Methods

Accelerated ageing experiments

Prepared samples of DB rocket propellant, having dimensions 40 ±0.05 × 10 ±0.05 × 2.5 ±0.05 mm, were artificially aged in closed glass tubes at temperatures of 80, 85 and 90 °C. The volume of the glass tubes was 100 cm^3, whilst the mass of the sample in the tubes was approximately 10 g. The aged propellant samples were periodically taken out from the tubes and their viscoelastic properties were tested using a dynamic mechanical analyser.

Dynamic mechanical measurements

Dynamic mechanical analysis was carried out using TA Instruments, DMA 983 analyser, operating at dual bending mode loading. A liquid nitrogen cooling accessory was used for sub-ambient temperature operations. The experiments were performed under the following experimental conditions: temperature range -120 to 100 °C; heating rate 2 °C·min^{-1}; fixed frequency of 1 Hz, and amplitude of deformation ±0.2 mm. The samples were subjected to uncontrolled cooling to -120 °C, and were then temperature equilibrated at -120 °C for 5 minutes. Temperature equilibration at -120 °C was followed by controlled heating at 2 °C·min^{-1} up to 100 °C.

Such a slow heating rate was chosen in order to reduce the thermal lag between the heater and the sample, as well as to reduce thermal gradients within the sample, whilst other parameters were chosen following the general guidelines for DMA analysis, as well as our own experience [20, 28, 32, 33].

Results and Discussion

DMA curves (storage modulus, loss modulus and tan δ) gave information about the viscoelastic properties of the materials. As they are very sensitive to molecular motion, transitions, relaxation phenomena, structural heterogeneity, and morphology, the study of the changes in the DMA properties of DB rocket propellant also gave useful information about the structural changes that occur during propellant ageing [20, 32].
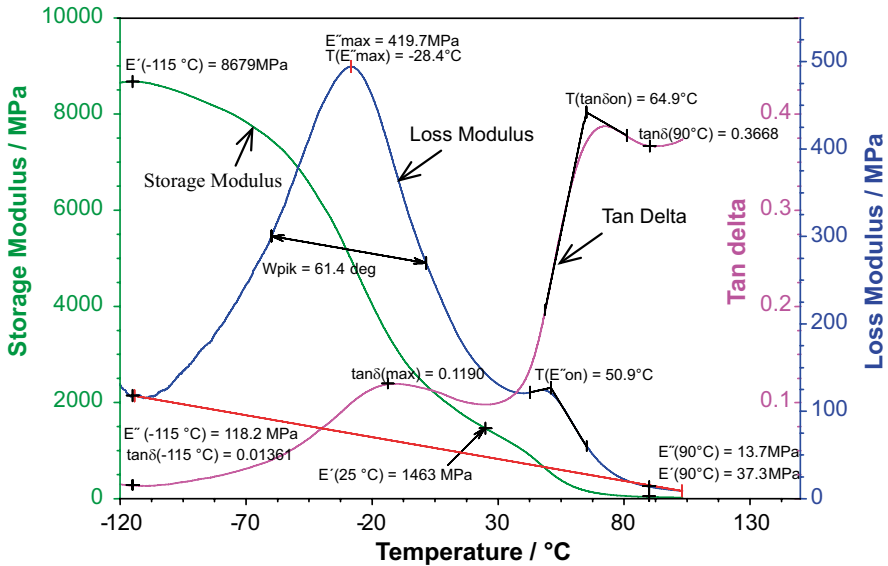
Figure 1. DMA thermogram of unaged a DB rocket propellant (storage modulus, loss modulus and tan δ *vs.* temperature.

It is obvious from the DMA thermogram of a non-aged DB rocket propellant (Figure 1) that the storage modulus ($E´$) in the glassy state has a maximum value ($E´_{(-115°C)}$ = 8.679 GPa). As the temperature increases, the storage modulus decreases, showing a maximum rate of decrease in the glass transition region ($-60 °C < T_g < -5 °C$). In the glass transition region the storage modulus decreases about 6 fold (from 8.679 GPa at -115 °C to 1.463 GPa at 25 °C). On further heating, the value of the storage modulus decreases slightly until it reaches the softening point, *i.e.* the transition from the viscoelastic to the viscous state (at ~50 °C).

It is known that the transition from the glassy to the viscoelastic region does not occur at a rigidly defined point – it occurs within a range whose width depends on the material properties of the sample tested. It is established in the standardisation agreement [28] and also in the NATO Standardisation Agreement – STANAG 4540 [29] that the temperature of the glass transition (T_g) corresponds to the maximum of the loss modulus curve in the glass transition region. Thus, it was found that the glass transition temperature of non-aged propellant was -28.4 °C. Another local maximum of the loss modulus value at ~50 °C corresponds to the softening temperature of the propellant sample.

The glass transition temperature, as well as the width and height of the loss modulus peak in the glass transition region, are dependent on the characteristics

of the system investigated, *i.e*. its homogeneity, crystallinity, mobility of NC macromolecules, its structure, mean molecular mass, chemical compatibility, *etc*. The relatively large width of the loss modulus peak (peak width at half height was 61.4 deg) of the tested propellant may be related to its variability, taking into consideration the relatively wide range in NC molecular weight variability, whilst the glass transition temperature and the loss modulus peak height, are connected with the NC mean molecular mass and the mobility of NC macromolecules [10, 11].

Generally, the tan δ can be related to the mobility of the NC macromolecules [10]. In the glassy state tan *δ* is low (tan $\delta_{(-115°C)}$ = 0.0136) due to the low flexibility of the NC macromolecules in the glassy state. Tan *δ* has a local maximum in the glass transition region (tan δ_{max} = 0.1190), and dramatically increases in the softening region due to the greatly increased flexibility of the NC macromolecules.

In order to detect and quantify changes in the viscoelastic properties of DB rocket propellant due to ageing, several characteristic points on the *E´-T, E˝-T*, and *tan δ -T* curves were selected. These points are illustrated in Figure 2 and explained in Table 1.
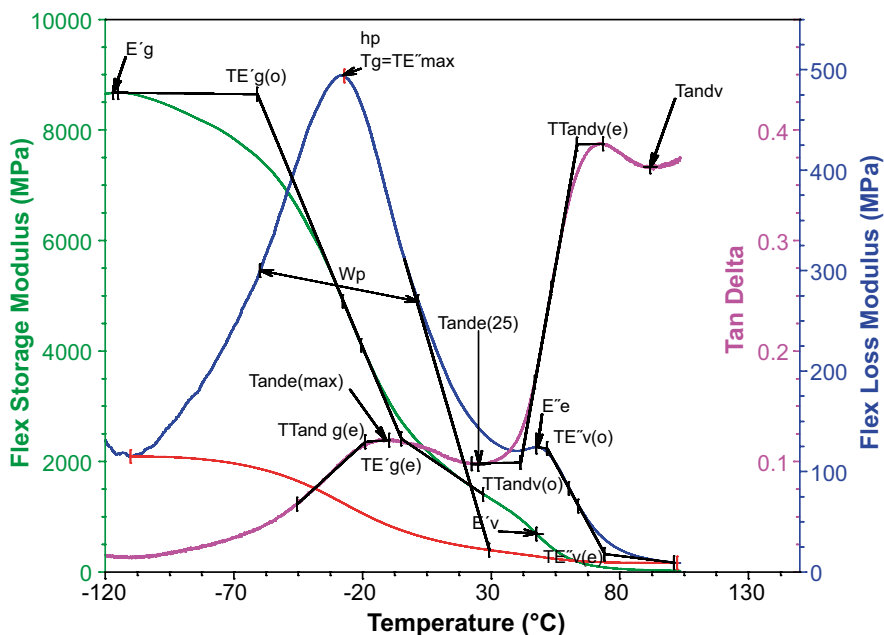

Figure 2. Characteristic points/parameters on the DMA curves obtained during the ageing of DB rocket propellant samples.

Table 1. Characteristic points/parameters on the DMA curves followed during ageing

Characteristic points on E'-T curves	Denotation	Unit
Storage modulus in glassy state (at -115°C)	E'_g	MPa
Extrapolated onset temperature at the beginning of transition from glassy to viscoelastic state	$T_{E'g(o)}$	°C
Extrapolated endset temperature at the end of transition from glassy to viscoelastic state	$T_{E'g(e)}$	°C
Storage modulus at maximum velocity of decreasing of storage modulus during transition from viscoelastic to viscous state (at the inflection point on E'-T curve)	E'_v	MPa
Characteristic points on E''-T curves	Denotation	Unit
Peak width at half height, at the glass transition temperature range	w_g	°C
Peak height in the glass transition area	h_g	MPa
Glass transition temperature (peak maximum temperature)	T_g	°C
Loss modulus in viscoelastic area (before softening point)	E''_e	MPa
Extrapolated onset temperature at the beginning of transition from viscolelastic to viscous state (softening point)	$T_{E''v(o)}$	°C
Extrapolated endset temperature at the end of transition from viscoelastic to viscous state (softening point)	$T_{E''v(e)}$	°C
Characteristic points on tan δ-T curves	Denotation	Unit
Extrapolated endset temperature at the end of transition from glassy to viscoelastic state	$T_{\tan\delta\,g(e)}$	
Tan δ maximum in viscoelastic region	$\tan\delta_{e(max)}$	°C
Tan δ at 25 °C	$\tan\delta_{e(25)}$	
Extrapolated onset temperature at the beginning of transition from viscoelastic to viscous state	$T_{\tan\delta v(o)}$	°C
Extrapolated endset temperature at the end of transition from viscoelastic to viscous state;	$T_{\tan\delta v(e)}$	°C
Tan δ in viscous state (immediately after transition to viscous state)	tan δ_v	

To quantify the sensitivity to ageing of the individual parameters on the DMA curves, the so-called 'degree of a given property change' was calculated by the equation:

$$Y_p = \frac{|P_t| - |P_0|}{|P_0|} \cdot 100 \qquad (1)$$

where: Y_p is the degree of a given property change, P_0 is a given property at the beginning of DB propellant ageing, and P_t denotes the values of a given property after a certain ageing time.

Changes in DB rocket propellant parameters in the course of ageing, as measured by the DMA technique

Changes of individual parameters of DB rocket propellant samples during ageing at 80, 85 and 90 °C, as measured by means of DMA, are shown in Figures 3-5.
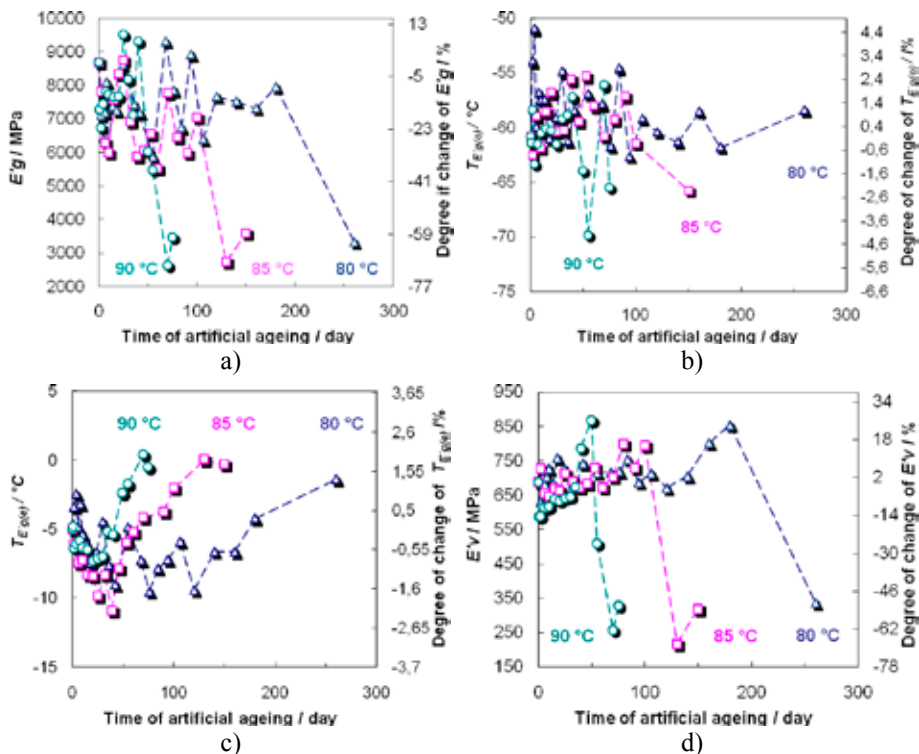
Storage Modulus

a)

b)

c)

d)

Figure 3. Change of characteristic points/parameters on the E'-T curves (a − storage modulus in glassy state (at -115 °C); b − extrapolated onset temperature at the beginning of the transition from glassy to viscoelastic state; c − extrapolated endset temperature at the end of the transition from glassy to viscoelastic state; d − storage modulus at maximum velocity of decreasing of storage modulus during transition from viscoelastic to viscous state (at the inflection point on the E'-T curve)) *vs*. ageing time at 80, 85, and 90 °C.
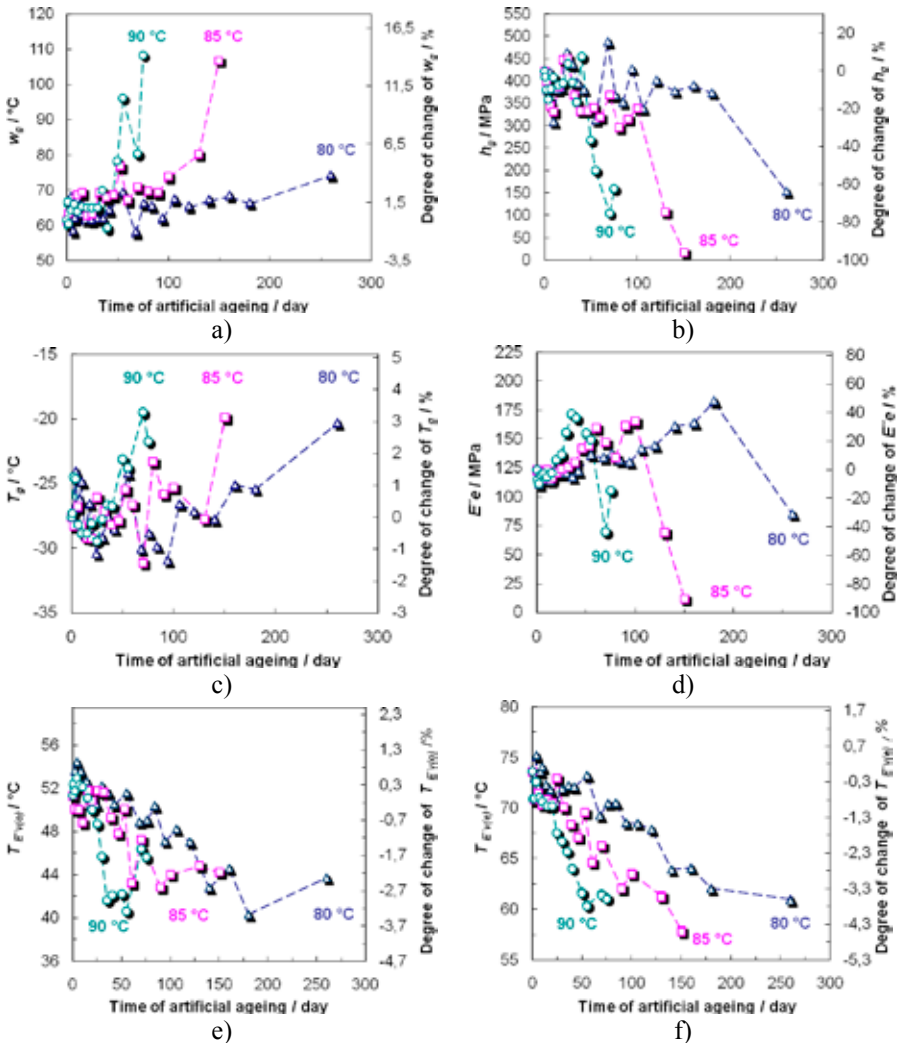
Loss Modulus

Figure 4.   Change of characteristic points/parameters on the E''-T curves (a – peak width at half height, in the glass transition area; b – peak height in the glass transition area; c – glass transition temperature (peak maximum temperature); d – loss modulus in viscoelastic area (before softening point); e – extrapolated onset temperature at the beginning of the transition from viscoelastic to viscous state (softening point); f – extrapolated endset temperature at the end of the transition from viscoelastic to viscous state (softening point)) *vs.* ageing time at 80, 85, and 90 °C.
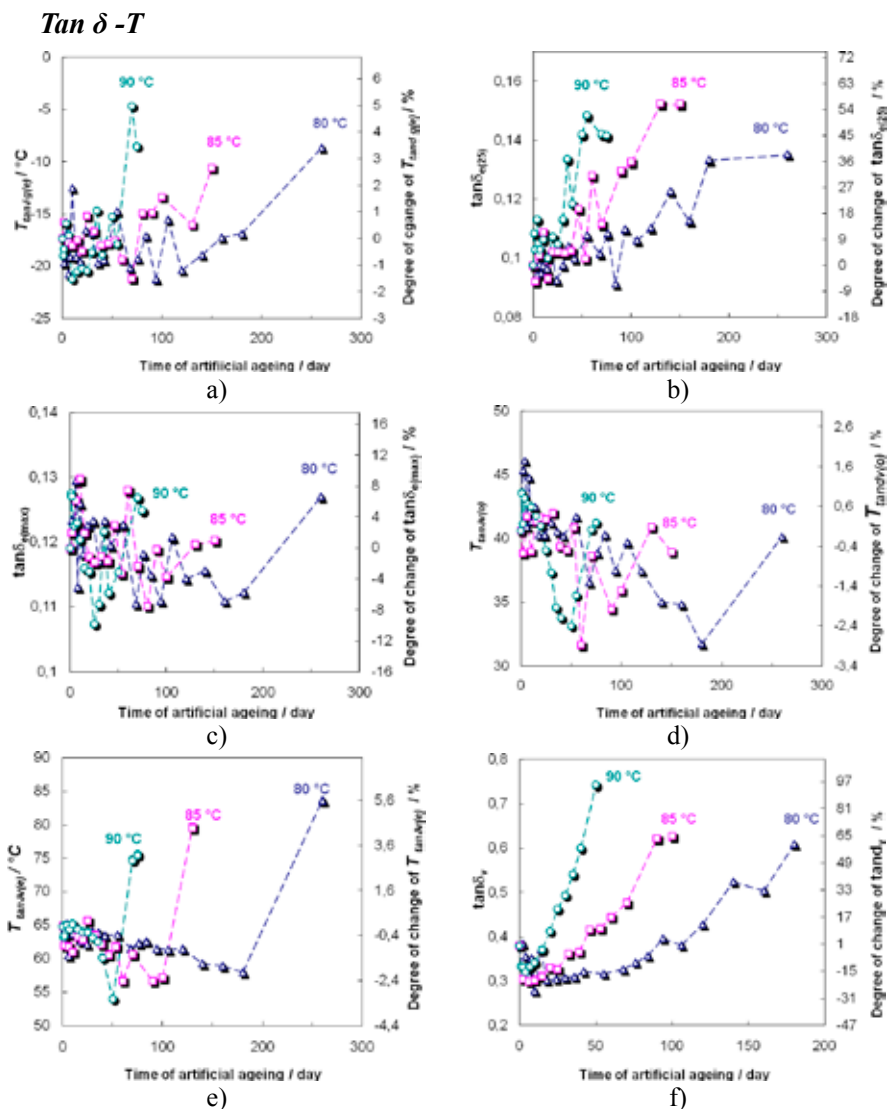
Tan δ -T

Figure 5.   Change of characteristic points/parameters on the *tan δ -T* curves
(a − extrapolated endset temperature at the end of the transition from
glassy to viscoelastic state; b- tan *δ* at 25°C, c – tan *δ* maximum
in viscoelastic region; d − extrapolated onset temperature at the
beginning of the transition from viscoelastic to viscous state;
e − extrapolated endset temperature at the end of the transition from
viscoelastic to viscous state; f – tan *δ* in viscous state (immediately
after transition to viscous state)) *vs*. ageing time at 80, 85, and 90 °C.

It is obvious from Figures 3-5 that the characteristic points on the E'- T, E''- T, and *tan δ* -T curves change with ageing. The changes are relatively small in the case of storage modulus (*e.g.* Figure 3, the changes are almost within the measuring error range), but in the cases of loss modulus and tan δ, the changes are significant (Figures 4 and 5).

The most distinctive change visible in the loss modulus curve, is an increase of the peak width (*e.g.* after 75 days of ageing at 90 °C the peak width changes by about 14%, Figure 4a), whilst the most distinctive change visible in the *tan δ* -T curve, is the continuous increase of tan δ in the viscous state (Figure 5f).

The discontinuous changes, visible at the end of the ageing period (*e.g.* Figures 3a, 3d, 4a, 4b, 4d, and 5e), are due to mechanical degradation of the sample after a long period of ageing (appearance of gas bubbles, crack formation, sample bending, *etc*.). These points are excluded from the analytical treatment of data.

The effect of ageing of DB rocket propellant samples on the characteristic points/parameters of the DMA curves shown in Figure 3 (a-d), 4 (a-f), and 5 (a-f), may be summarised as follows:
a) Storage modulus
   ▪ decrease in the storage modulus in the glassy state (at -115 °C);
   ▪ negligible increase in the extrapolated onset temperature at the beginning of the glass transition;
   ▪ increase in the extrapolated endset temperature at the end of the glass transition, and
   ▪ increase in the storage modulus in the softening range until the point of intensive mechanical degradation of the sample, where it suddenly 'decreases'.
b) Loss modulus
   ▪ increase in the peak width and decrease in the peak height in the glass transition area;
   ▪ increase in the glass transition temperature, and
   ▪ decrease in the softening temperature.
c) Tan δ - T
   ▪ decrease in tan δ maximum in the viscoelastic region;
   ▪ increase in tan δ at 25 °C;
   ▪ decrease in the temperature of transition from the viscoelastic to the viscous state (softening);
   ▪ continuous increase in tan δ in the viscous state.

Changes in DB rocket propellant parameters as measured by DMA *vs.* structural changes in the DB rocket propellant caused by artificial ageing

It is known that the properties of DB rocket propellants obtained by DMA, are affected by the structural parameters of the DB propellant system investigated [10]. On the other hand, results have shown [1, 2, 6, 12, 20] that the changes in DMA parameters of DB propellants, are most significantly affected by a decrease in NG content in the tested propellant, as a consequence of NG migration to the surface of the propellant grain and further NG evaporation, cleavage of NC macromolecules, and decomposition of NG and NC. The effects of a reduction in NG content and the cleavage of NC macromolecules are in opposition.

Whilst reduction in the NG content causes a decrease in the mobility of the DB propellant system, cleavage of NC macromolecules causes an increase in the mobility of the system. Thus, the changes in the DMA properties of DB rocket propellants are a consequence of the simultaneous effects of various structural changes in the propellant caused by its ageing. These changes, and their effect on the DMA parameters, may be summarised as follows:

a)   Increase in the glass transition temperature (T_g) of the DB rocket propellant, which indicates a reduction in the mobility of the NC macromolecules, is a consequence of plasticizer/NG loss in the propellant samples [10, 20];

b)   Increase in the softening temperature in the last stage of ageing ($T_{E''v(o)}$), is a consequence of the combined effects, *i.e.* decrease in NG content (dominant) and decrease in NC macromolecular mobility [10, 20];

c)   Increases in the storage modulus and the loss modulus in the softening range (E'_v, E''_e), is a consequence of an increase in the degree of crystallinity of the system due to a reduction in the NG content [20, 30];

d)   Decrease in tan δ in the viscoelastic region (tan $\delta_{e(max)}$), is a consequence of the inhibiting effect of the crystalline phase on the flexibility of macromolecules in the amorphous phase due to a reduction in the NG content [20, 30];

e)   Decrease in peak height (h_g) and increase in peak width (w_g) in the glass transition temperature range, is a consequence of an increase in the degree of crystallinity due to a reduction in the NG content [30], and an increase in the system heterogeneity due to the cleavage of NC chains [11, 30, 34];

f)   Increase in tan δ at room temperature and in the viscous region (tan $\delta_{e(25)}$, tan δ_v), is the result of a decrease in the mean molecular mass of NC [10, 34]; and

g)   Decrease in the softening temperature ($T_{E''v(o)}$, $T_{E''v(e)}$, $T_{\tan\delta v(o)}$, $T_{\tan\delta v(e)}$) is caused by a significant decrease in the mean molecular mass of NC at a later stage of the propellant degradation process, or by cleavage of NC chains [10, 34].

Degree of change in DB rocket propellant parameters as measured by DMA

As is visible from the results, the DMA parameters studied for DB rocket propellants (glass transition temperature, peak height and peak width obtained from the loss modulus curve, softening point, *etc.*) are dependent on the time and temperature of the propellant ageing. From a practical point of view, we were interested in establishing a correlation which would allow the degree of change of a given property of the propellant, both as a function of time and temperature, to be predicted *i.e.* to predict the time necessary to achieve a certain degree of change of a given property of the propellant.

If the time (t_2) which is necessary to achieve a certain degree of change of a given property of the tested propellant at the reference temperature (T_2) is known, then one can use the following empirical equation to calculate the time (t_1) to achieve the same degree of change of the same property at temperature (T_1) [35]:

$$t_1 = t_2 \cdot a_{10}^{\left(\frac{T_2 - T_1}{10}\right)} \tag{2}$$

where a_{10} is the acceleration factor of the propellant's given property change.

The acceleration factor (a_{10}) of the reaction/change is defined as the ratio of the reaction constants at two temperatures that differ by 10 K ($a_{10}=k(T_2)/k(T_1)$). The results of the (a_{10}) calculation presented in [20] have shown that it is significantly influenced by the ageing temperature. However, for the temperature range used for artificial ageing (80-90 °C), the values of a_{10} can be taken as constant, and approximately equal to 3.6 [20].

We reduced the experimental data for DB rocket propellant property changes obtained by DMA for the propellant samples aged at 80 and 85 °C to temperature 90 °C ($T_2 = 90$ °C) by applying modified Eq. 2:

$$t_{red} = t \cdot 3.6^{\left[-\left(\frac{90-T}{10}\right)\right]} \tag{3}$$

where: t is the time to reach a certain degree of property change at temperature T, t_{red} is the so-called reduced time, *i.e.* the time to reach the same degree of property change at $T = 90$ °C.
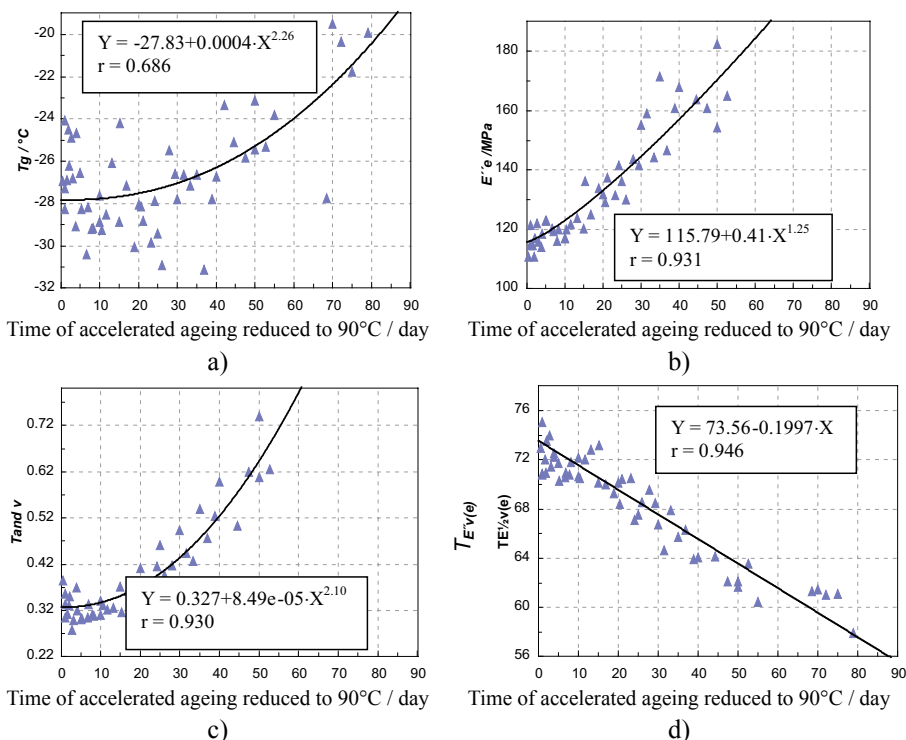
Figure 6. DMA parameters of DB rocket propellant samples as a function of the so called reduced time of accelerated ageing − all data reduced to a temperature of 90 °C (a − temperature of glass transition; b − loss modulus in viscoelastic region (before softening point); c − tan delta in viscoelastic range (before softening point); d − extrapolated endset temperature at the end of the transition from viscoelastic to viscous state (softening point)).

In this way we obtained one master curve (Figure 6) showing the DMA parameters of the DB rocket propellant as a function of reduced time (t_{red}). Such a presentation of the results indicates more clearly the trend of the propellant's given property change and enables further mathematical treatment/processing of the results. For example, the change of the propellant's given property (P_T), measured by DMA using the reduced time (t_{red}), can be described by the following expressions:

$$P_T = P_0 + a \cdot t_{red}^n \qquad\qquad (4)$$

or

$$P_T = P_0 + a \cdot t_{red} , \tag{5}$$

where: P_0 is a given property value before ageing, P_T is the given property value after ageing for t_{red} time, a and n are constants.

Applying Eq. 4 or Eq. 5, and Eq. 2, it is possible to calculate the time required to reach a certain degree of change of the given property at any temperature (Table 2). However, we also used some literature data, on the kinetics of NC decomposition in DB propellant and on the kinetics of NG evaporation, to predict the time required to reach a certain degree of change of the established property. These kinetic data were used because NC decomposition has a dominant effect on the change in DMA properties at higher temperatures, while NG evaporation has a dominant effect at room temperature [20].

Table 2. Periods of ageing of DB rocket propellant samples at 90 °C, 25 °C and 55 °C required to reach their given property change in the range of 5% and 10%

Para-meter	Property change [%]	P_0/P_T	Time of ageing at 90 °C [day]	Time of ageing at 25 °C [year]			Time of ageing at 55 °C [year]		
				From NC kinetic	From NG kinetic	Eq.2	From NC kinetic	From NG kinetic	Eq.2
T_g	5	-27.83 / -26.44	36.90	3587.9	26.66	417.54	17.01	1.55	8.95
	10	-27.83 / -25.05	50.14	4875.3	36.23	567.36	23.12	2.10	12.16
$T_{E''v(e)}$	5	73.56 / 69.88	18.42	1791.0	13.30	208.43	8.49	0.77	4.47
	10	73.56 / 66.20	36.84	3582.1	26.62	416.86	16.99	1.54	8.93
E''_e	5	115.79/ 121.58	8.32	809.0	6.00	94.14	3.84	0.35	2.02
	10	115,79/ 127.37	14.48	1407.9	10.46	163.85	6.68	0.61	3.51
$tan\ \delta_v$	5	0.327 / 0.343	12.24	1190.1	8.84	138.50	5.64	0.51	2.97
	10	0.327 / 0.360	17.03	1655.9	12.30	192.70	7.85	0.71	4.13

The following kinetic models and kinetic data are used in the calculations [20]:

–   Kinetics of NC decomposition in DB propellant, determined on the basis of NC mean molecular mass degradation:
    Kinetic model, integral form:
    $-\ln(1-\alpha) = k \cdot t$
    $E = 145.096$ kJ/mol, $A = 3.6 \times 10^{14}$ s^{-1}
–   Kinetics of NG evaporation from DB propellant, determined on the basis of isothermal TGA analysis:
    Kinetic model, integral form:
    $(1/(1-n)) \cdot (1-\alpha)^{-(n-1)} - 1 = k \cdot t$
    $E = 77.21$ kJ·mol^{-1}, $A = 1.19 \times 10^{8}$ s^{-1}

The periods necessary to reach a certain (established/assumed) degree of change of the given property (5 or 10%) at different temperatures (25 and 55 °C), and calculated by different methods are shown in Table 2.

The results shown in Table 2 indicate that the glass transition temperature (T_g) has the least sensitivity to ageing (the longest time to reach a 10% property change), while the loss modulus in the viscoelastic area (E''_e) and tan δ_v are the most sensitive to ageing. If there is a criterion established for life-time prediction (for example a property change which must be below 10%), then the above calculations can be used to predict the life-time of a propellant at a given temperature, assuming that the ageing mechanism does not change with temperature.

Table 3.   Time of ageing to reach identical degrees of the given property change for naturally and artificially aged DB rocket propellant samples

Para-meter	Degree of property change after 17 years of natural ageing	Calculated time of ageing to reach the same degree of property change[*]				
		T = 90 °C [day]	T = 25 °C [year]	T = 35 °C [year]	T = 45 °C [year]	T = 55 °C [year]
T_g	20% (after 17 years)	70	50.58	18.41	7.14	2.93
E''_e	15% (after 17 years)	25	18.06	6.57	2.55	1.05

[*]Value calculated using data for the kinetics of NG evaporation

As expected, the results given in Table 2 show that the times necessary to reach the same degree of property change, calculated using the different kinetic data (kinetics of NC decomposition or kinetics of NG evaporation) are significantly different. In order to see which calculated result agrees best with the results obtained with a similar, naturally aged DB propellant, we used the literature data reported in [31]. According to these data a DB propellant having

similar composition was naturally aged for 17 years. The corresponding degree of property changes after 17 years was: 20% for Tg and 15% for E''_e. The analysis has thus shown that a much better agreement is obtained if the kinetic data for NG evaporation are used in the calculations (Table 3).

These results are in accord with the fact that at temperatures of natural ageing (T < 40°C) the process that has the dominant effect on DMA property changes of a DB propellant, is evaporation of NG [20]. It has also been noted by some authors that the ageing mechanism changes with temperature, and at lower temperatures one should use an activation energy value of 60 kJ·mol^{-1} to make a prediction of the lifetime or property change, whilst at temperatures above 45 °C, an activation energy of 140 kJ·mol^{-1} should be used [7].

It is obvious that an increase in reliability for the prediction of a DB propellant's given property, requires precise identification of all ageing processes at different temperatures, as well as reliable kinetic models and kinetic data. The reliability of a prediction of the above properties at room temperature, requires experimental data at temperatures as close as possible to room temperature to be obtained, because the ageing mechanism (or dominant ageing process) may be changed with a change of ageing temperature. Unfortunately, such experiments would be very long and sometimes inappropriate for practical use.

Conclusions

The results obtained by DMA have shown that accelerated ageing of DB rocket propellants, *i.e.* at elevated temperatures causes significant changes in their storage modulus (E'), loss modulus (E'') and tan δ curves. These changes may be quantified by the following specific characteristic points on the E'-T, E''-T and $tan\,\delta$-T curves, such as glass transition temperature/range, storage modulus, loss modulus, and tan δ, corresponding to characteristic DMA temperatures, *etc*. It has been found that the above parameters are temperature and time dependent, and can be described as a function of the so-called time of artificial ageing.

The least sensitive parameter to ageing is the glass transition temperature (T_g), whilst the most sensitive parameters are loss modulus and tan δ in the viscoelastic range (E''_e, $tan\,\delta_v$).

On the basis of the established/assumed degree of change of a given property (Eqs. 4 and 5) and Eq. 2, as well as on the basis of the kinetic parameters of the ageing process (kinetic model, activation energy, and pre-exponential factor), it is possible to predict the time necessary to reach a certain degree of change of the given property at a given temperature, assuming that the ageing mechanism

of DB rocket propellants does not change with temperature. The reliability of such predictions depends strongly on the reliability of the kinetic data used.

Acknowledgements

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