Research paper

Assessment of the Shelf Life of Composite Solid Propellants in Air and Nitrogen Atmospheres through Thermal Ageing

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Abstract: This work introduces dynamic mechanical thermal analysis (DMTA) as an efficient method for the assessment of the shelf life of solid composite solid propellants in air and nitrogen atmospheres. The samples were aged at three temperatures 323.15, 333.15, and 343.15 K for 60, 120, and 180 days. The two different methods of Arrhenius and Berthelot were used to compare the effects of air and nitrogen atmospheres on the ageing of composite solid propellants. Damping (*Tan δ*) of composite solid propellants was used to determine the shelf life of the samples based on the loss of half of the physical property *Tan δ* (50% drop in damping). For the air atmosphere, the calculated activation energy for the degradation reactions of the samples was 86.26 kJ·mol⁻¹. Both models, Arrhenius and Berthelot, confirmed that the shelf lives of the samples under the nitrogen atmosphere are more than four times those in an air atmosphere.

Keywords: composite solid propellant, inert atmosphere, dynamic mechanical thermal analysis, DMTA, damping, ageing

Symbols and abbreviations

A	Pre-exponential factor
E'	The storage modulus

E'' The loss modulus
E_a Activation energy [kJ·mol^{-1}]
k Reaction rate constant
k_1 The reaction rate constant at temperature T_1
k_2 The reaction rate constant at temperature T_2
R Universal gas constant [J·mol^{-1}·K^{-1}]
T Absolute temperature [K]
t_1 Shelf life at temperature T_1
t_2 Shelf life at temperature T_2
$Tan\ \delta$ Damping
$Tan\ \delta_r$ Initial damping or the value of damping before ageing
T_g Glass transition temperature
t_T Reaction time to reach a certain extent of reaction

1   Introduction

High energy materials contain energetic groups and have wide applications in civil and military applications [1-4]. They can release heat, energy, and light when subjected to impact [5], friction [6], electric spark [7], heat [8], and shock [9]. Propellants, explosives, and pyrotechnics are the three categories of energetic materials. Among different categories of propellants, composite solid propellants can provide high combustion performance where their specific impulse values are up to about 300 s [10, 11]. Composite solid propellants have three main components, binder, oxidizer, and metal fuel. Hydroxyl-terminated polybutadiene (HTPB), ammonium perchlorate (AP), and aluminum (Al) are usually used as the binder, oxidizer, and metal fuel, respectively. The binder that constitutes the matrix that retains the solid oxidizer can act as a fuel [4]. This is the most commonly used polymer in composite solid propellants because it allows loading of solids up to about 91% while maintaining acceptable mechanical properties. HTPB contains a 1,3-butadiene homopolymer terminated at each end with a hydroxyl functional group and has been used widely as the binder for composite solid propellants.

Since many years can elapse before a composite solid propellant is used after the formulation and curing process, it can undergo ageing, which is an inevitable process. The physical and mechanical properties of solid propellants can become changed with time and environmental conditions in a short period after production [12, 13]. Ageing can degrade the physical properties of composite solid propellants over time, and may include two types of ageing, mechanical

and chemical [14]. Mechanical ageing can occur by destruction done to the grain during storage, handling, or transport. Chemical ageing is one of the most important problems for the assessment of the shelf life of chemical propellants, and can arise from different sources, such as oxidation, and thermal or hydrolytic reactions [10, 15]. This often decreases the efficiency and performance of composite solid propellants, because ageing can exhibit different behaviour, such as hardening, softening, swelling, discoloration, and gas production [16, 17]. Thus, chemical ageing can be identified in the maintenance of composite solid propellants and plastic bonded explosives (PBXs) [10] by different methods, such as sol-gel, Fourier transform infrared (FTIR) spectroscopy, thermal analysis, and mechanical property tests [18-20]. These methods, as well as the new approaches of laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy [21-26], are used for the analysis and investigation of ageing effects.

Some effort has been made in recent years to estimate the shelf life of some classes of propellants. Judge [27] monitored unstressed propellant samples during prolonged storage at elevated temperatures in order to investigate the ageing kinetics and mechanisms of a composite solid propellant. Judge *et al.* [28] characterized a solid rocket propellant based on glycidyl azide polymer (GAP) binder concerning its thermal and chemical stability and storage life by a variety of test methods. Shekhar [29] used elongation as a degradation parameter for the prediction of the shelf life of composite solid propellants. Gorgi and Mohammadi [30] compared the shelf life of an amine-based liquid propellant using the Berthelot and Arrhenius approaches. Bihari *et al.* [14] used dynamic mechanical thermal analysis (DMTA) to determine the activation energy of related events in composite solid propellants. Xie *et al.* [31] focused on the transformation of the relaxation modulus and complex modulus of HTPB composite solid propellants through DMTA. Pakdehi *et al.* [32] applied the accelerated ageing test method to predict the shelf life of dimethylaminoethyl azide (DMAZ). The effective parameters were temperature, the type of gaseous atmosphere and its pressure over the liquid fuel, and moisture. Elbasuney *et al.* [33] assessed the shelf life of modified double-base propellants using Van't Hoff's formula and artificial ageing at 343.15 K for up to 120 days. They quantified the total heat released and the heat flow with ageing time by differential scanning calorimetry (DSC) and thermal activity monitor III (TAM III), respectively. Adel *et al.* [34] investigated the ageing softening behaviour of a composite solid propellant by measuring its mechanical and ballistic properties during prolonged storage at both elevated and room temperatures.

Since the mechanical properties of solid rocket propellants depend on temperature, temperature changes cause significant effects on the tensile

strength, percentage elongation, and elastic modulus of a propellant [35]. The oxygen in air can influence the binder and the metal fuel, which contributes to chemical ageing [36, 37]. Due to the importance of increasing the shelf life of composite solid propellants, the purpose of the present work was to investigate the effects of an inert atmosphere in their ageing process. Thus, the results of DMTA in two atmospheres, air and nitrogen, were used to estimate the shelf life of aged samples of AP/Al/HTPB-based composite solid propellants with the same composition. The two different methods of Arrhenius [38] and Berthelot [29] were used to compare the effects of air and nitrogen atmospheres on the ageing of these composite solid propellants.

2 Material and Methods

2.1 Preparation of the composite solid propellants
The weight percentages of the composite solid propellant samples were:
– 16% HTPB R 45 binder,
– 73% AP,
– 10% Al powder, and
– 1% additives,
which were supplied from Iran's Defense Industries, of industrial grade. Toluene di-isocyanate (TDI) at an [NCO]/[OH] equivalent ratio of 1.00 was used to cure the polymer samples, where the [NCO]/[OH] equivalent ratio is defined as the equivalent ratio between the materials containing NCO groups (TDI) and those containing OH groups (HTPB). The mechanical properties of the cured composite solid propellants depend on this ratio.

The samples were prepared as rectangular cubic-shaped samples with dimensions 30×10×3 mm. To achieve reliable results, it was important to prepare the samples with uniform surfaces and thickness in different areas. Nineteen samples were prepared, where one sample was considered as a reference sample and the remaining samples were used in the accelerated ageing program. The accelerated ageing method was used to prepare the aged propellant samples because this approach reduces the time scale by keeping the sample at higher temperatures [27, 39]. This approach simulates the material behaviour under different time-temperature conditions, focusing especially on the in-service conditions. Ageing of 18 samples was conducted at three temperatures 323.15, 333.15, and 343.15 K during 60, 120, 180 days in air and nitrogen atmospheres.

2.2 The use of DMTA

DMTA measures the viscoelastic properties of materials by applying an oscillating force to the sample and analyzing the response of the material to this force. It provides a measure of the stiffness and damping as the modulus and tangent delta (*Tan δ*) values, respectively. The modulus may be given as the storage modulus (*E′*) in-phase component and the loss modulus (*E″*) out of phase component. The value of *E′* shows the elastic response of a material, and measures the stored energy. The value of *E″* also provides the viscous response of a material and estimates the energy dissipated as heat. *Tan*(*delta*), damping or *Tan δ*, is the ratio of loss to storage, and assesses the energy dissipation of the material.

DMTA was used to measure the visco-elastic properties and glass transition temperature (T_g) of the polymer samples. Its measurements were conducted on a Tritec 2000 DMTA instrument (Triton Technology Ltd, UK). A liquid nitrogen cooling component and a heating system were used to operate below and above ambient temperature. DMTA is a quite suitable method for evaluating the visco-elastic behaviour of polymeric materials. Since DMTA provides T_g and the mechanical properties of the material, such as elastic modulus and loss modulus, its results can be used to estimate the ageing rate of energetic materials.

Three ovens (Heraeus oven T5028, Heraeus Instruments GmbH & Co. KG, Hanau, Germany) with fluctuations of ±0.75 ºC were used for the accelerated ageing process. Two sets of three steel chambers containing air or nitrogen atmospheres were designed where each chamber contained three samples. The three chambers were equipped with inlet and outlet valves for introducing air or nitrogen (99.99%) atmospheres in a sealed manner. They were located in three separate ovens at temperatures of 323.15, 333.15, and 343.15 K. DMTA tests were performed on samples of the first, second, and third series after subjection to the stated temperatures for 60, 120, and 180 days, respectively. The DMTA test was performed on all samples at a frequency of 1 Hz and a temperature range of 173.15 to 373.15 K, at a heating rate of 5 K·min⁻¹, and the three-point bending deformation method. In addition, the ASTM D5023-07 method was used to test the samples [40].

2.3 The Arrhenius and Berthelot models

The Arrhenius model [38] is very important for the assessment of the shelf life of different types of energetic compounds. It can be written as follows:

$$k = A \cdot e^{-\frac{E_a}{RT}} \tag{1a}$$

or

$$ln\,k = \ln A - \frac{E_a}{RT} \tag{1b}$$

where k is the reaction rate constant, A is the pre-exponential factor, E_a is the activation energy (kJ·mol^{-1}), R is the universal gas constant (J·mol^{-1}·K^{-1}), and T is the absolute temperature (K). The value of E_a is an important parameter in the Arrhenius equation and is generally taken as a constant for the given temperature range. The penetration and k depend on the speed of the molecules and the frictional resistance to this motion. A convenient rate equation for the degradation reaction should be chosen for predicting the shelf life of a composite solid propellant using the Arrhenius approach. It can be expected that there is a linear relationship between the logarithm of the failure time and the inverse of T because the changes in matter are due to chemical reactions, volatility, or diffusion [38, 41]. The correlation of the shelf life at two temperatures is given as follows:

$$\ln\left(\frac{t_2}{t_1}\right) = \ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{2}$$

where t_2 is the shelf life at temperature T_2 and t_1 is the shelf life at temperature T_1. The ratio of t_2/t_1 is inversely proportional to the ratio of k_1/k_2 where k_1 and k_2 are the reaction rate constants at T_1 and T_2, respectively.

The Berthelot equation [29] is another way to assess the shelf life of energetic materials. It is expressed as follows:

$$\log t_T = a + b \cdot T \tag{3}$$

where t_T is the reaction time to reach a certain extent of reaction; a and b denote the undetermined coefficients. The Berthelot equation shows that the log of time to base 10 is directly proportional to temperature. It assumes that the reaction rate changes by the same amount for the same difference in temperature, which can be given as follows [29]:

$$\frac{t_2}{t_1} = \frac{k_1}{k_2} = 10^{(B\times(T_1 - T_2))} \tag{4}$$

where B is the undetermined coefficient.
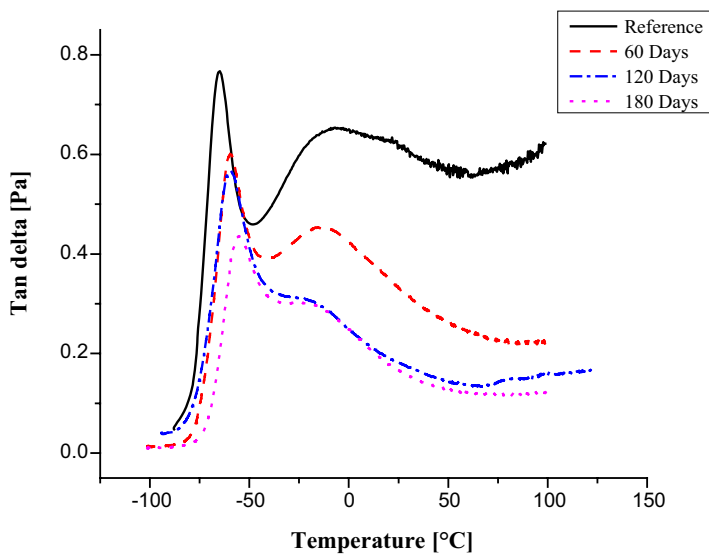
3   Results and Discussion

3.1 Comparison of damping and the modulus of composite solid propellant samples

One unique value for the degradation cannot be assigned for composite solid propellants with different compositions and purity of constituents because different mechanisms of degradation have diverse activation energies. The actual activation energy for the degradation of damping of a given propellant formulation has to be specified. Lower and higher values of activation energies are obtained as compared to the normal value if the degradation mechanisms are diffusion-controlled and kinetics controlled, respectively.
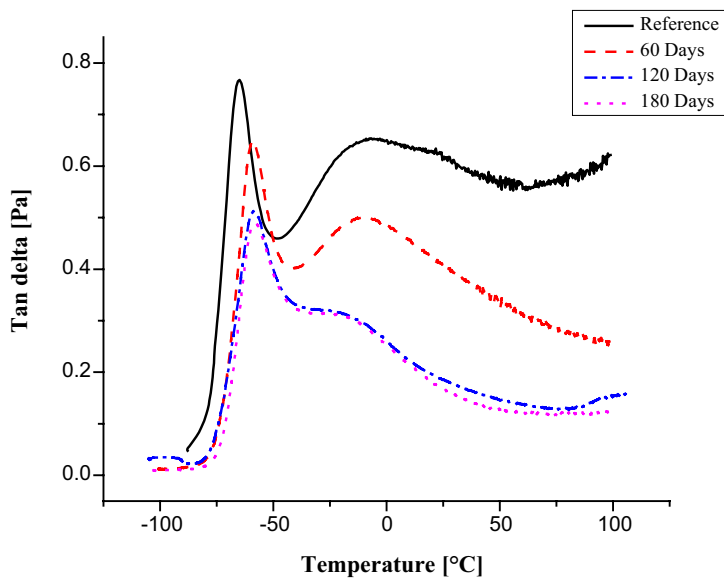
Degradation of composite solid propellants can occur by different mechanisms, including oxidation of the polybutadiene matrix, loss of plasticizer by migration and evaporation, and dewetting from the oxidizer or binder cohesive failure. Of the mentioned mechanisms, increasing the propellant temperature can enhance oxidation and plasticizer migration. Thus, molecular reactions or diffusion will be accelerated according to kinetic relationships. To simulate long-term ageing within a reasonable period, rocket motors or propellant samples are often aged at temperatures higher than ambient to accelerate ageing.

Ageing of the propellant may cause oxidative, cross-linking of the polymeric binder, migration of the additives, and recrystallization of the oxidizer [42]. Cross-linking through double bonds of the main chain can produce hardening of propellants during ageing. The decomposition of AP in trace amounts can generate perchloric acid ($HClO_4$), which catalyzes the cross-linking of the polymeric chains through the double bonds [43]. The generated $HClO_4$ enhances the cross-linking of the polymeric chains with increases in time and temperature [42, 44].
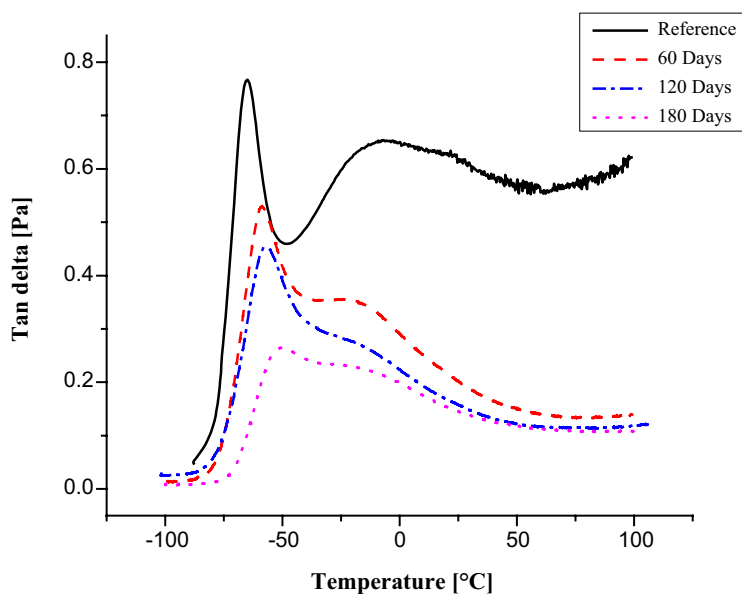
Figures 1 and 2 show the *Tan δ* and the modulus curves of the samples at different time intervals. Figure 1 allows a comparison of T_g and *Tan δ* for three time periods, 60, 120, and 180 days, and shows the temperature dependencies of T_g and *Tan δ* for all aged and unaged samples. Since damping is a characteristic of sample flexibility, T_g provides the temperature region where an amorphous material changes from a glassy phase to a rubbery phase upon heating. The value of *Tan δ* has a maximum value of T_g when it is plotted against temperature. As shown in Figure 1, the DMTA curves have two peaks. The first and second peaks show the polymer's soft and hard segments, respectively, where the second peak is broader [33].
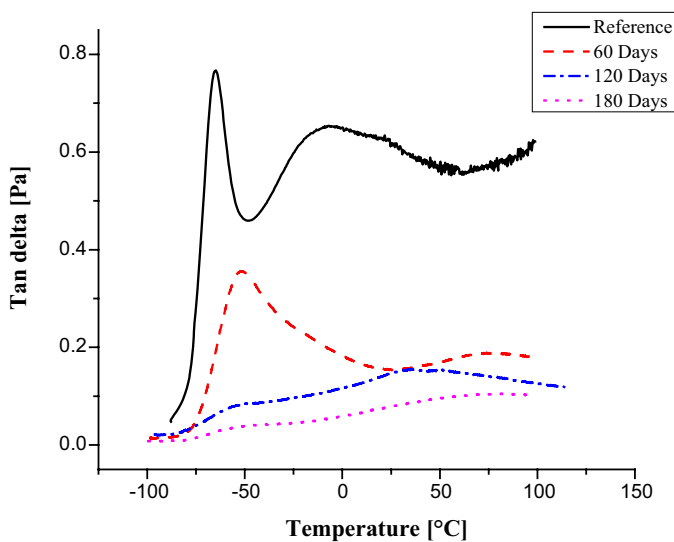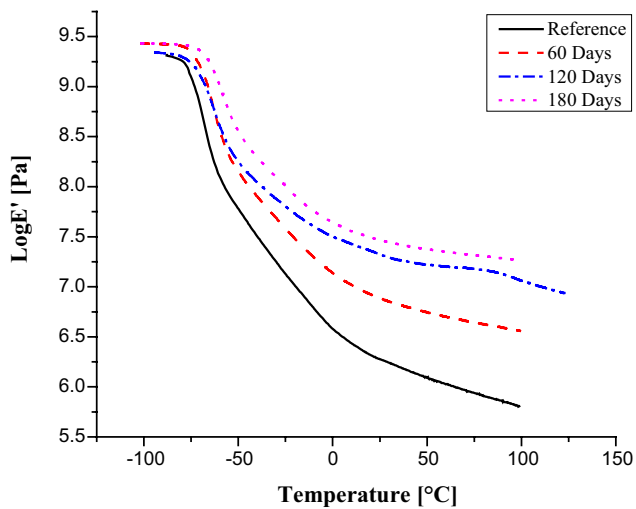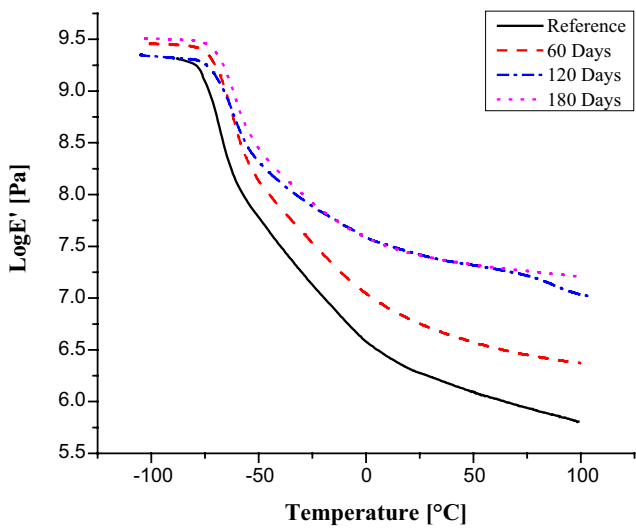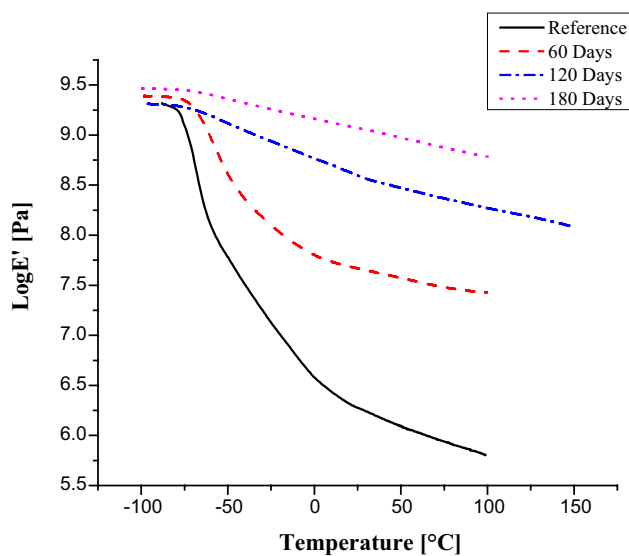
(a)

(b)

(c)

(d)

Figure 1. Comparison of damping of the composite solid propellant samples as a function of temperature for different times in air and nitrogen atmospheres, where reference is unaged sample: (a) 323.15 K (air), (b) 343.15 K (air), (c) 323.15 K (N₂), and (d) 343.15 K (N₂)

(a)

(b)

(c)

(d)

Figure 2. Comparison of the modulus of the composite solid propellant samples as a function of temperature for different times in air and nitrogen atmospheres, where reference is unaged sample: (a) 323.15 K (air), (b) 343.15 K (air), (c) 323.15 K (N_2), and (d) 343.15 K (N_2)
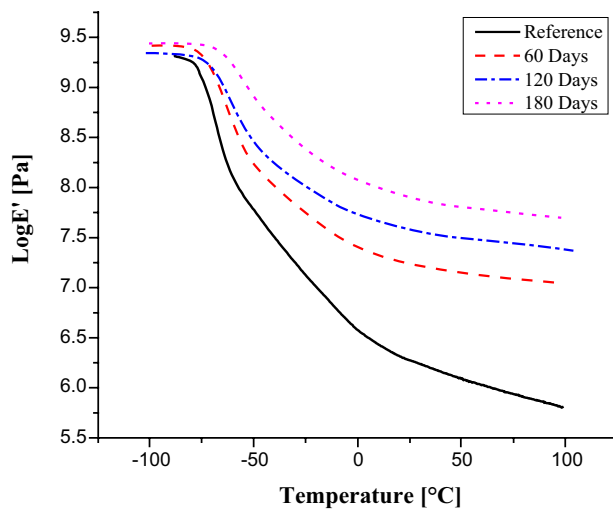
3.2 Calculation of the shelf life of the samples in air and nitrogen atmospheres

The DMTA results were used to investigate the effects of temperature as well as atmosphere, air or nitrogen, on the samples. Damping is used as a parameter for the efficiency of polymeric materials. The basis of ageing in the samples was taken as the loss of half of the physical property *Tan δ* (50% drop in damping). The results showed that the *Tan δ* decreased more at higher temperatures than at lower temperatures. The results of the changes in the values of *Tan δ vs.* ageing temperatures are listed in Table 1. For a nitrogen atmosphere, only the measured values of *Tan δ* at the high temperature 343.15 K are given because there was no appreciable change at lower temperatures.

Various functions of the measured variation of *Tan δ*, such as exponential, logarithmic, second-order polynomial, and power-law variations were fitted to time. It was found that the best-fit curve, with the highest correlation coefficient (R^2), was obtained for the natural logarithmic plot of *Tan δ*. A plot of ln(*Tan δ*) as a function of time should therefore give a straight line passing through the point *Tan $δ_r$*, the initial damping or the value of damping before ageing, with a slope of the reaction rate constant. Figure 3 shows a graph of ln(*Tan δ/Tan $δ_r$*) *versus* time at three temperatures of 323.15, 333.15 and 343.15 K, where *Tan $δ_r$* is used here to have a dimensionless ratio of *Tan δ/Tan $δ_r$*.

Table 1.　The measured *Tan δ* values at different times for three ageing temperatures

Air atmosphere			
Temperature [K]	Time [days]	*Tan δ*	ln(*Tan δ/Tan $δ_r$*)
323.15	0	0.76	0
	60	0.65	−0.1563
	120	0.51	−0.3989
	180	0.49	−0.4389
333.15	0	0.76	0
	60	0.45	−0.5241
	120	0.26	−1.073
	180	0.15	−1.623
343.15	0	0.76	0
	60	0.35	−0.7754
	120	0.1	−2.028
	180	0.04	−2.944

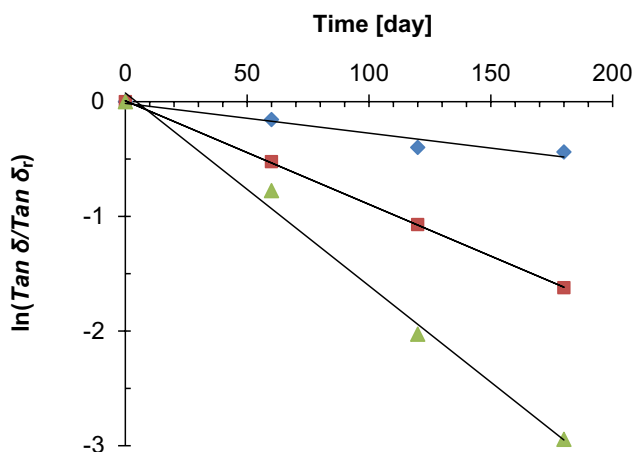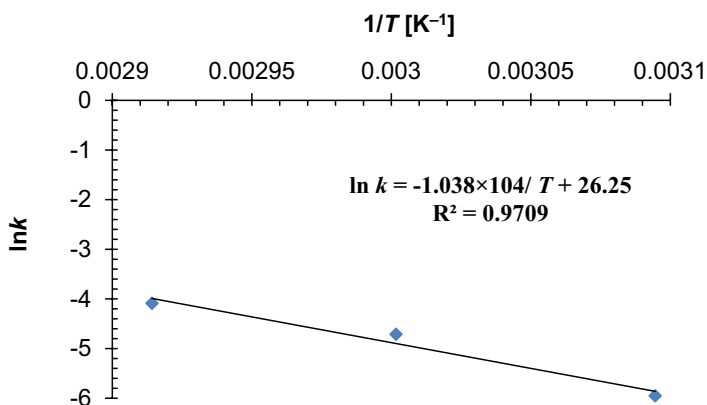| Nitrogen atmosphere			
Temperature [K]	Time [days]	*Tan δ*	ln(*Tan δ/Tan δ*$_r$)
343.15	0	0.76	0
	60	0.53	–0.3604
	120	0.45	–0.5241
	180	0.26	–1.073

Figure 3. The measured values of ln(*Tan δ/Tan δ*$_r$) *vs.* time (days) for temperatures: (♦) 323.15, (■) 333.15 and (▲) 343.15 K in an air atmosphere

Table 2 gives the three different values of *k* that were obtained from the slopes of the resulting lines at the three stated temperatures. According to the Arrhenius plot for the assessment of shelf life, Figure 4 shows the variation of ln*k* as a function of $1/T$, where *T* is given in K (0.003095, 0.003002, and 0.002257 K^{-1}). The values of ln*k* for different accelerated ageing temperatures can be used to define the effect of temperature on the degradation rate or to predict the shelf life of the samples. The reaction rate constants were determined at 323.15, 333.15, and 343.15 K using the slopes from Figure 3. The calculated activation energy for the degradation of the samples was 86.26 kJ·mol^{-1}. This value corresponds to the calculated reaction rate constant values at the stated temperatures in an air atmosphere. Thus, the shelf life at ambient temperatures, such as room temperature, can be obtained by extrapolation.

Table 2. Three different values of *k* for samples at three ageing temperatures

Temperature [K]	Linear equations	R^2	k
323.15	$\ln(Tan\ \delta/Tan\ \delta_r) = -2.599 \cdot 10^{-3}t - 0.01465$	0.9415	$2.599 \cdot 10^{-3}$
333.15	$\ln(Tan\ \delta/Tan\ \delta_r) = -9.028 \cdot 10^{-3}t + 0.007645$	0.9999	$9.028 \cdot 10^{-3}$
343.15	$\ln(Tan\ \delta/Tan\ \delta_r) = -1.681 \cdot 10^{-2}t + 0.07592$	0.9926	$1.681 \cdot 10^{-2}$

Figure 4.   The plot of ln*k* *vs.* 1/T (Arrhenius plot) for the air environment

The Berthelot plot for 50% damping of the samples is shown in Figure 5. The shelf lives of the samples at several temperatures were calculated by using the Arrhenius and Berthelot plots. Table 3 compares the calculated shelf life using the two approaches for 293.15, 323.15, 333.15, and 343.15 K for the air and the nitrogen atmospheres. Several points can be deduced from the calculated results:

(a) Since there are no appreciable changes of damping in the nitrogen atmosphere for 323.15 and 333.15 K, it can be expected that the activation energy of the degradation reactions of the propellant is higher in the nitrogen atmosphere.

(b) The results of the changes of damping at 343.15 K and the calculated activation energy were used to estimate the shelf life of the propellant in a nitrogen atmosphere.

(c) The shelf life of the samples decreases with increasing temperature.

(d) Both models, Arrhenius and Berthelot, confirmed that the shelf lives of the samples under a nitrogen atmosphere are more than four times longer than for an air atmosphere.

(e) The predicted shelf lives by the two models are close to each other for the two different atmospheres.

Figure 6 compares the predicted shelf life of the samples using the Arrhenius and Berthelot plots in the temperature range 293.15-343.15 K for the air environment. As shown, at a low temperature of 293.15 K (normal storage conditions), the Berthelot approach gives a lower value of the shelf life for the samples than the Arrhenius model.

Table 3. Comparison of the fuel shelf life predicted using the Arrhenius and Berthelot approaches

Temperature [K]	Shelf life obtained with the Arrhenius approach [year]		Shelf life obtained with the Berthelot approach [year]	
	Air	Nitrogen	Air	Nitrogen
293.15	8.257	31.69	7.277	31.69
323.15	0.5592	–	0.6940	–
333.15	0.2133	–	0.2711	–
343.15	0.08607	0.3304	0.1059	0.3304

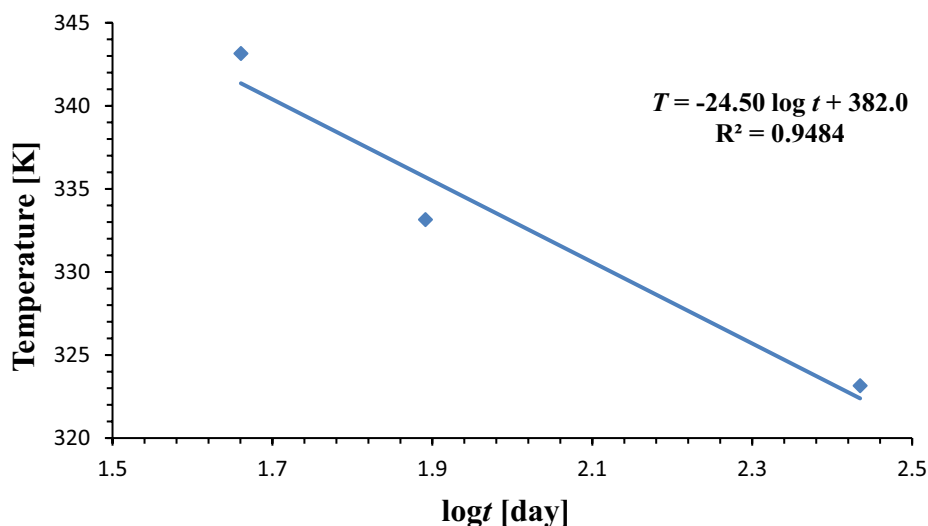
$T = -24.50 \log t + 382.0$
$R^2 = 0.9484$

Figure 5. Temperature *versus* log*t* (Berthelot plot) for the air environment
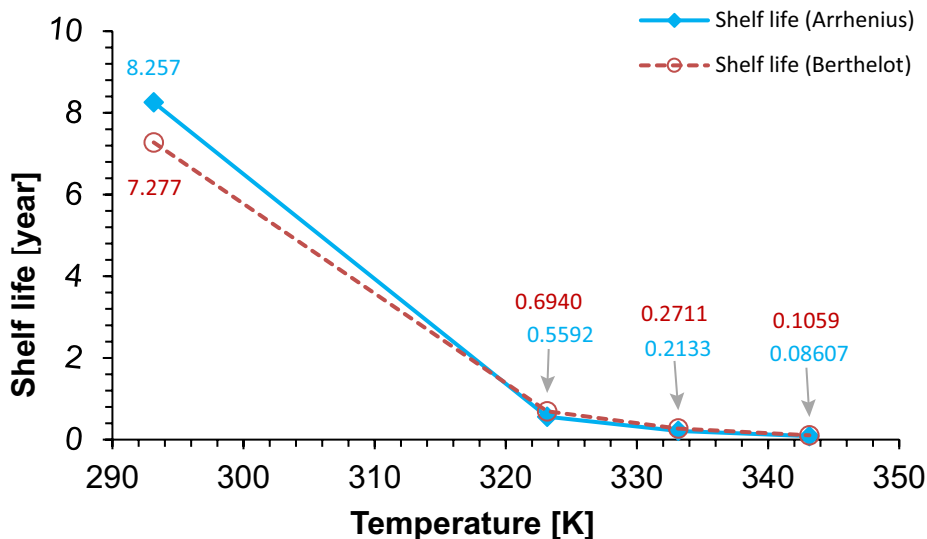
Figure 6.   Comparison of the predicted shelf life using the Arrhenius and Berthelot approaches

3.3 Assessment of the effects of oxygen molecules and temperature

The process of ageing indicates a decrease in the visco-elastic properties of the samples as a function of temperature and storage time. It reduces the elastic modulus through which the samples become stiffer and their flexibility decreases. The T_g values of the samples are also increased by an increase in temperature, in both hard and soft parts of the sample. The rates of the degradation reactions, such as crosslinking, increases for high storage times during accelerated ageing, which results in stiffening and destruction of the mechanical properties.

Cross-linking of the propellant binder is found to be the predominant degradation mechanism during ageing. Significant changes in the mechanical properties are apparent, caused by the additional crosslinking of the binder resulting from oxidation. Table 2 and Figure 1 show that T_g and the maximum loss of *Tan δ* for all samples are increased and decreased, respectively, with ageing. Since the motion of the chains in the polymer structure has a profound effect on the loss of *Tan δ*, it is a sensitive indicator of cross-linking. Decreasing the degree of cross-linking can increase the motion of the chain segments and thereby the increment of *Tan δ* [45]. Due to the cross-linking of the propellant binder, it was found that both C_2/CN in LIBS and maximum loss of *Tan δ* in DMTA were decreased with ageing [23].

For the particular propellant formulation used in this work, the oxidation reaction has an activation energy within about 86.26 kJ·mol^{-1}. This value is consistent with those predicted for composite propellants with different compositions in an air atmosphere, by Shekhar (72.8 kJ·mol^{-1} [29], and by Judge (71-74 kJ·mol^{-1} [27] for binder oxidation). The ratio of the degradation rates of composite solid propellants at temperatures 298.15 to 343.15 K will increase by a factor of 95.9 and 68.7 according to the Arrhenius and Berthelot approaches in an air atmosphere. Thus, appropriate accelerated ageing demonstrates that a rocket motor with lifespans of 8.2 and 7.3 years at a reference ambient temperature (293.15 K) are much higher than ageing at 343.15 K. The predicted shelf life of the composite propellant with the composition used in this study in an air atmosphere is lower than that estimated by Shekhar [29] only from 333.15 K, *i.e.* 20 years at 300.15 K, and Cerri *et al.* [46], *i.e.* 15-25 years at 298.15 K. Considering safety aspects, the lower values of the shelf life predictions are recommended for energetic materials.

For a nitrogen atmosphere, there is much less impact on the damping and the modulus of the samples than in an air environment at high temperatures after long times. Thus, the mechanical properties of composite solid samples are significantly preserved in an inert nitrogen atmosphere. Since oxygen availability is one of the contributing factors to ageing, its elimination has a positive effect on the relative prevention of ageing. For a nitrogen atmosphere, there is no appreciable oxidative crosslinking because temperature-accelerated ageing is the major probable mechanism.

4   Conclusions

♦   Assessment of the shelf life of a composite solid propellant is essential for the use of solid propellants.

♦   The method of DMTA at three temperatures 323.15, 333.15, and 343.15 K during 60, 120, and 180 days has been used in this work to predict the shelf life of the propellant samples in air and nitrogen atmospheres. Due to the lack of ageing of the sample in the nitrogen atmosphere at temperatures 323.15 and 333.15 K, experimental data at 343.15 K was used to assess an approximate shelf life of the samples.

♦   The Berthelot and Arrhenius approaches have been used for the prediction of the shelf life of the samples. For the air atmosphere, the oxidation reaction is accelerated with increasing temperature for a long time. This particular propellant formulation has an activation energy within about 86.26 kJ·mol^{-1}

in an air atmosphere. Both the Arrhenius and the Berthelot models confirm
that the shelf life of the samples decreases with increasing temperature.
♦   The use of a nitrogen atmosphere is a cheap method, with rapid usability
    for rocket motors, because the shelf lives of the composite solid propellants
    can be increased more than four times, compared to an air atmosphere.

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