An Investigation of Composite Propellant Accelerated Ageing Mechanisms and Kinetics

Michael D. Judge*

Bristol Aerospace Limited, Rockwood Propellant Plant, P.O. Box 874, 660 Berry Street, Winnipeg, Manitoba, R3C 2S4 (Canada)

This paper is dedicated to the memory of France Beaupré

Abstract

The ageing kinetics and mechanisms of a composite solid rocket propellant were investigated by monitoring unstressed propellant samples during prolonged storage at elevated temperatures. For samples confined under air during ageing, it was determined that oxidative cross-linking of the propellant binder was the main degradation mechanism over time. Plasticizer loss was a significant ageing mechanism only for those samples aged unconfined. In addition, there was an indication that ambient humidity had a significant but reversible effect on propellant mechanical properties. Arrhenius mathematical relationships were derived in order to ascertain the extent to which ageing was accelerated by increased propellant temperature. An activation energy for binder oxidation of between 71 and 74 kJ/mol was determined.

Keywords: Rocket, Propellant, Ageing.

1 Introduction

All solid propellant-fuelled rocket motors are assigned a storage life at the end of which their safe operation cannot be guaranteed. In most cases, the integrity of the solid propellant is the deciding factor in determining the motor storage life. In order to ascertain a motor's service lifetime, therefore, it is necessary to predict the extent to which the propellant will degrade over time. This involves determining both the type of ageing mechanisms exhibited by the propellant and also the relative rates of these mechanisms at various temperatures.

The ageing mechanisms of solid propellants vary based on their constituents; double base propellants composed of nitrocellulose and nitroglycerin will degrade very differently than composite propellants based on ammonium perchlorate-loaded polybutadiene binders. The research reported here is concerned solely with composite propellants. In the literature, it has been variously reported that composite propellants may degrade by oxidation of the polybutadiene matrix, loss of plasticizer by migration and evaporation, and dewetting from the oxidizer or binder cohesive failure [1 – 3]. Of these mechanisms, oxidation and plasticizer migration are phenomena related to molecular reactions or diffusion which will therefore be governed by kinetic relationships and will be accelerated by increasing the propellant temperature. For this reason, motors or propellant samples are often aged at temperatures higher than ambient in order to simulate long-term ageing within a reasonable time period – a process referred to as accelerated ageing.

However, there appears to be no consensus within the literature as to which mechanism of propellant degradation is dominant or the degree to which these mechanisms are accelerated by increased temperature. It is of particular importance to understand the degree to which propellant degradation is accelerated by increased temperature since this relationship is necessary to design accelerated ageing test protocols for the determination of motor lifespan. The purpose of this research project was to provide further data with the aim of helping to resolve these issues. The scope of this research was limited to the analysis of unstressed propellant samples and therefore does not directly address the ageing mechanisms of binder dewetting or cohesive failure.

2 Experimental

Sample blocks of a non-metallized ammonium perchlorate/hydroxy-terminated polybutadiene (AP/HTPB) composite propellant were obtained from a full-scale production batch manufactured at Bristol Aerospace's Rockwood Propellant Plant. The propellant formulation included an inert plasticizer and an iron-based burn rate catalyst. Following cure, propellant blocks were cut into individual sample specimens of approximately 3 cm × 1 cm × 12 cm.

Much consideration went into determining the manner in which samples should be contained while ageing. Since propellant inside a weather-sealed rocket motor is confined and essentially deprived of air, except for the small amount of air initially present in the bore and a very small additional amount which may diffuse through the weatherseal over time, one could argue that test samples should be aged while sealed in airtight containers. However, the intent of this

* E-mail: mjudge@bristol.ca

 0721-3113/03/2803-0114 $ 17.50+.50/0

research was not necessarily to duplicate the ageing rates in a motor, but to determine which ageing mechanisms predominate and also their relative rates at varying temperatures. For this reason, it was decided that samples would be aged in semi-confined conditions which would approximate the confinement of a motor case but would still allow a constant ingress of oxygen to the container so as not to disallow the potentially crucial ageing mechanism of binder oxidation. Samples were therefore placed into glass containers under ambient atmospheric air. The containers were not sealed airtight, but rather had loose-fitting lids placed overtop to provide some degree of confinement while allowing ambient air exchange. Only a token attempt to control ambient humidity was made, by placing the sample jars inside metal boxes containing desiccant packs. Samples were aged under these conditions at three temperatures; 38 °C, 43 °C and 60 °C. The ageing temperatures were purposely kept relatively low since literature references suggest that more extreme temperatures can lead to degradation reactions and kinetics not normally present at lower temperatures. At monthly intervals, a sample from each temperature was withdrawn from ageing and tested. Samples were tested at monthly intervals for a period of 21 months.

Testing of the samples consisted of the following: mechanical properties analysis, sol-gel fraction analysis and plasticizer depletion. The specifics of each test are detailed below. While it would have been beneficial to also determine the extent of anti-oxidant depletion on ageing, it has been demonstrated in the past that the two anti-oxidants employed in this propellant formulation are chemically bound into the cross-linked polybutadiene binder matrix and cannot be extracted for meaningful quantitative analysis [4].

Mechanical properties analysis was carried out by die-cutting miniature JANNAF-type "dogbone" specimens from the sample slabs. Three specimens were cut from each sample slab. Samples were clamped into an Instron apparatus using a grip distance of 5.1 cm, a specimen gage length of 3.6 cm and a crosshead speed of 5.1 cm/minute. Samples were tested at room temperature and ambient humidity. The samples were pulled to failure and the Instron software computed maximum stress, strain at maximum load and modulus.

Sol-gel analysis was carried out via solvent extraction of the soluble portion of the propellant. A 15 g portion of propellant was taken from each sample and cut into small pieces. This portion was then extracted overnight in methylene chloride in a standard Sohxlet extraction apparatus. The solvent was then removed by evaporation and the extracted portion was weighed. The ratio of the solvent-extracted portion weight to the initial sample weight was reported as the sol-gel fraction value.

Plasticizer content was determined by taking the dried Sohxlet extract and adding 50 mL acetonitrile to re-dissolve the plasticizer. The plasticizer content was then analysed via HPLC under the following conditions: isocratic mobile phase of 90% acetonitrile/10% THF (v/v) at 1.2 mL/minute, Waters Nova-Pak C-18 column (60 A, 4 μm, 3.9 mm x 150 mm), refractive index detector, 50 μL sample injections. Under these conditions, IDP eluted as a broad peak at approximately 5.2 minutes, as confirmed by the analysis of standard IDP solutions.

Finally, in order to ascertain the extent to which sample confinement affected plasticizer loss, a simple additional test was carried out. At each of the three ageing temperatures, propellant sample slabs of known weight were aged unconfined for six weeks. After ageing, these samples were first weighed to determine weight loss and then tested as described above for mechanical properties and plasticizer depletion.

3 Results and Discussions

3.1 Plasticizer Migration

Table 1 below summarizes the plasticizer levels in the propellant samples as determined by HPLC analysis at each ageing temperature during the first ten months of ageing.

Within the experimental error inherent in the test method, none of the samples showed significant loss of plasticizer, even after ten months of ageing. It is of interest to note that, as will be described below, the 60 °C samples had degraded substantially in their mechanical properties after ten months of ageing. This indicates that the observed changes in mechanical properties are not the result of plasticizer loss.

Given the fact that the plasticizer is not physically bound into the binder matrix, the lack of any loss after prolonged ageing was somewhat unexpected. However, it is evident that the degree of confinement of the propellant during ageing has a pronounced effect on the degree of plasticizer loss. This was demonstrated during analysis of the unconfined aged samples, the data from which are summarized in Tables 2 and 3.

It can be seen that all samples showed significant weight loss, which can only be attributed to plasticizer evaporation from the samples. From the other data presented in these tables, it can be seen that these samples showed very high levels of IDP loss after the relatively short six week period of ageing; losses which were not observed in the confined samples even over much longer time periods. In addition,

Table 1. Propellant plasticizer levels after monthly ageing periods – confined samples.

Months	38 °C	43 °C	60 °C
0	2.2%	2.2 %	2.2%
3	2.1	2.2	2.4
4	2.4	2.3	2.3
6	1.9	2.0	2.1
7	1.9	2.0	2.1
8	1.8	2.0	2.0
9	2.0	2.1	2.1
10	2.1	2.2	2.1

Table 2. Weight loss, soluble fraction and plasticizer content of samples aged unconfined.

Sample Description	% Weight Loss	Sol-Gel Fraction	IDP % after Ageing
38 °C Sample 1	0.301 %	0.0624	1.07 %
43 °C Sample 1	0.342	0.0619	1.10
60 °C Sample 1	1.988	0.0456	0.65

Table 3. Mechanical properties of samples aged unconfined.

Sample	Stress	Strain	Modulus
38 °C Sample 1	0.958 MPa	34 %	5.47 MPa
43 °C Sample 1	0.965 MPa	34%	5.47 MPa
60 °C Sample 1	1.32 MPa	19%	20.6 MPa

these unconfined samples – especially the 60 °C sample – showed a very pronounced loss of mechanical properties. This loss of mechanical properties was much greater than that shown by the confined samples after far longer periods of ageing.

The phenomenon of plasticizer loss on ageing has been noted in the literature but there appears to be no consensus as to how important this aspect of ageing is. Keizers et al. tested aged AP/HTPB propellants over time and concluded that plasticizer loss was the main cause of age-related degradation [5]. However, this study used samples aged in air with no confinement. Samples, which were confined by plastic bags or sealed in glass, showed substantially less plasticizer loss, which mirrors our own observations. Other authors, such as Bunyan, do not consider plasticizer loss as a necessarily major effect of ageing [1]. Torry and Cunliffe found that propellant samples aged in sealed glass jars exhibited measurable loss of the plasticizer [6]. However, a careful reading of their data indicates that the plasticizer levels (in dry environments) did not decline until after a very long period at a high temperature; at least 300 days of ageing at 70 °C. Furthermore, plasticizer loss under humid ageing conditions was attributed not to migration but to hydrolysis of the dioctyl sebacate plasticizer.

The effects of confinement on IDP loss can be understood in terms of the evaporation rates of this compound. In order to escape from the propellant, the IDP must first migrate to the propellant exposed surface and then evaporate into the ambient air. If the IDP does not evaporate, it will presumably remain on the propellant surface and can be reabsorbed. Any confined liquid will only evaporate up to the point where its vapour pressure in the confined space is reached. A literature value for IDP vapour pressure was not available, but the vapour pressure of this compound can be estimated using the Riedel equation and the molecular structure of IDP. In this case, the vapour pressure of IDP is estimated at 2.09 Pa at 333 K. Since the propellant samples were placed in two-liter jars, the ideal gas equation can be used to calculate the grams of IDP, which must evaporate before this vapour pressure can be reached. This value is 4.83×10^{-4} grams. It is obvious therefore that after a minute amount of IDP evaporates from the confined propellant, its vapour pressure is reached and equilibrium between evaporation and condensation occurs. Therefore, we can see that any confinement of propellant samples will completely preclude the loss of IDP from the propellant. This explains why no IDP loss was seen in the propellant samples aged in semi-sealed glass jars. By extrapolation, we can conclude that IDP loss will not occur in propellant inside a sealed rocket motor and that this is not a significant ageing mechanism for composite propellant. In the opinion of the author, the manner in which the sample is confined during ageing tests will determine whether or not plasticizer loss is found to be the primary mode of ageing although other factors, such as the cross-link density of the propellant tested, and the particular plasticizer used, will also play a role.

3.2 Mechanical Properties

The mechanical properties of the confined propellant samples degraded over the time period studied, with the greatest changes seen in those samples aged at the highest temperature. Figures 1, 2 and 3, below, show graphically the changes in modulus, stress and strain over time.

One aspect of mechanical properties change over time, which was unexpected, but of particular interest was the apparent cyclical and partially reversible nature of these changes. This phenomenon is most noticeable in the stress data but the effect can also be seen in the modulus and percent strain graphs. From these data, it appears that the propellant stress value increases and decreases rhythmically over the ageing period, although the overall average trend is an increase. A possible explanation may be found by considering the climactic conditions in this geographic region. Since the propellant was not fully sealed from the ambient atmosphere during heating, it would also be

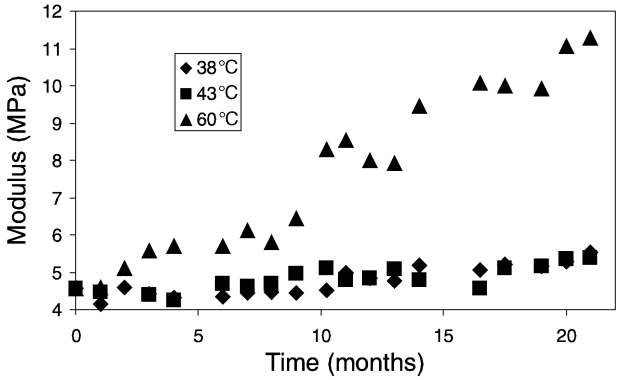

Figure 1. Propellant modulus values over the ageing period.

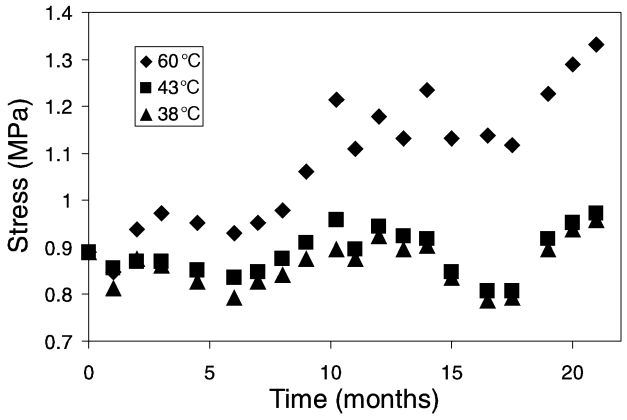

Figure 2. Propellant stress values over the ageing period.

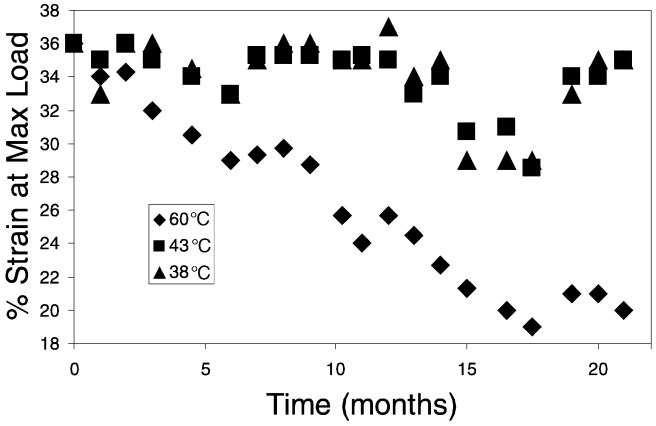

Figure 3. Propellant strain values over the ageing period.

exposed to the ambient humidity. In this region of Canada, temperature extremes between the seasons lead to wide fluctuations in relative humidity. The period of the cyclic trend observed in mechanical properties roughly corresponds to one year, with the lowest stress values occurring during the more humid summer months. It therefore appears that an increase in relative humidity decreases the propellant stress value. Furthermore, this decrease is at least partly reversible. One reason for this phenomenon may be that absorption of water by the binder matrix acts to further plasticize the propellant. The effects of humid ageing of propellant have been noted in the literature by Torry and Cunliffe [6] cited earlier where it was observed that polybutadiene rubber samples aged under high humidity exhibited lower modulus values than dry samples despite having higher cross-link densities. It was postulated that this effect could have been due to water occluded in the humid-aged samples.

The property least affected by annual variations appears to be the propellant modulus and so this data was used to obtain inputs for the Arrhenius relationship between temperature and degradation rate. The Arrhenius equation defining the relationship between reaction rate and temperature may be written as follows.

$$\mathrm{Log}_{10}[K] = A - \frac{E_a}{2.3 \cdot R \cdot T} \tag{1}$$

Where:

K is the reaction rate constant at a given temperature
A is an empirically derived constant
Ea is the activation energy for the reaction
R is the Ideal Gas constant
T is the temperature of the reactants in Kelvin.

The above equation may also be re-arranged to give

$$\mathrm{Log}_{10}\left[\frac{K_2}{K_1}\right] = \frac{E_a}{2.30 \cdot 1.99} \cdot \frac{T_2 - T_1}{T_2 \cdot T_1} \tag{2}$$

Where:

K_2 and K_1 are reaction rate constants at temperatures T_2 and T_1 respectively.

If it is taken that the rate of propellant degradation reactions is proportional to the rate of change of the propellant modulus, the slopes of the lines described in Figure 1 may be used as K_2 and K_1 inputs to the above equation to determine the reaction activation energy. The 38 °C and 43 °C data, when plotted, show no significant differences and so the slopes of the 38 °C line (the series which had the best R^2 value) and that of the 60 °C line were used with the Arrhenius equation to determine the activation energy for propellant degradation. The R^2 values for these lines are 0.79 and 0.95 respectively and their slope values are 7.6268 and 47.706. Using the equation above, these values give an activation energy value of 71.0 kJ/mol.

3.3 Sol-Gel Analysis

Figure 4 graphically summarizes the data obtained from sol-gel analysis of aged samples at all three temperatures. As can be seen from this graph, there is a significant decrease in sol fraction at all ageing temperatures, although the effect is most pronounced at 60 °C. There is some scatter in the data due to variations inherent in the extraction process, but the three lines are reasonably well described by linear equations. The R^2 values for the 43 °C and 38 °C data series are 0.84 and 0.76 respectively. Within the 60 °C data series, there is some indication that the line flattens out at around 16 months, which suggests that the samples are fully oxidized at this point, or at least that they have reached their maximum extent of oxidative cross-linking. If we discount the data points after 17 months, the R^2 value for this line is 0.98.

It is generally understood that a decrease in the solvent-extractable portion of the binder over time is due to increased cross-linking of the polyurethane. Since the plasticizer is also soluble in the extraction solvent and therefore contributes to the weight of the extracted fraction, one would expect that plasticizer loss would also lead to a decrease in sol fraction. However, since we have already

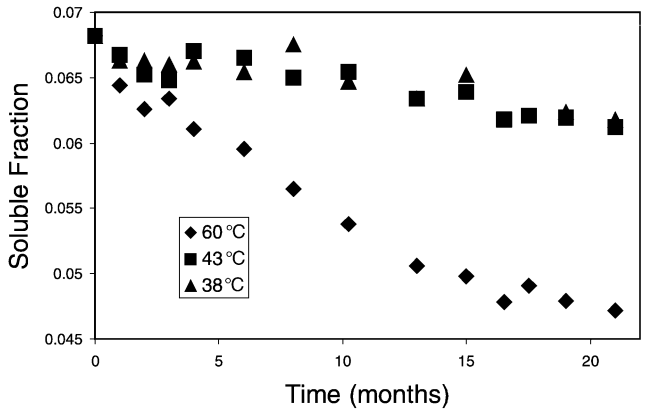

Figure 4. Propellant sol-gel values over the ageing period.

established that plasticizer depletion is not significant for these samples, the observed changes in the extractable fraction must be a consequence of oxidative cross-linking. The slopes of these lines can therefore be taken as proportional to the rates of oxidation of the propellant samples. The difference between the 43 °C and the 38 °C lines is very little compared to the data scatter, and therefore it is not of much benefit to evaluate the relative rates of all three ageing temperatures. If, however, we compare the relative slope rates of the 43 °C and the 60 °C lines, we can still use the Arrhenius equation to determine the activation energy for the propellant oxidation process. The respective slopes of these two lines are 2.7759×10^{-4} and 1.1467×10^{-3}. Inserting these values into the Arrhenius equation gives an activation energy for oxidative cross-linking of 74.3 kJ/mol.

This value for activation energy is very close to the value of 71.0 kJ/mol derived from mechanical properties measurements. In addition, both values are in general agreement with the range of propellant degradation energies found in the literature. Cunliffe et al. determined that the activation energy for the increase in AP/HTPB cross-link density during ageing was 88 kJ/mol [7]. Researchers at Sandia National Laboratories evaluated the ageing of HTPB/IPDI rubbers using oxygen consumption and changes in mechanical properties to follow degradation [8, 9]. This work determined that binder oxidation was the primary pathway for degradation on ageing and the activation energy for binder oxidation was found to be on the order of 70 kJ/mol at temperatures approaching ambient. This range of values for activation energy is likely at least partially the result of varying propellant and binder formulations and the effects of minor propellant constituents such as transition metal catalysts.

4 Conclusions

Based on the above data, oxidative cross-linking of the propellant binder is found to be the predominant degradation mechanism of unstressed, semi-confined composite propellant during accelerated ageing. The additional cross-linking of the binder resulting from oxidation manifests as significant changes in mechanical properties and soluble fraction over time. The oxidation reaction is accelerated with increasing temperature and has an activation energy on the order of 71 – 74 kJ/mol for this particular propellant formulation. Based on the lower value of 71.0 kJ/mol, one may calculate, using the Arrhenius equation that propellant degradation rates will increase by a factor of 33.1 between 20 °C and 60 °C. An appropriate accelerated ageing protocol to demonstrate a motor with a ten year lifespan at ambient could therefore consist of 16 weeks ageing at 60 °C.

Plasticizer loss proceeds rapidly in samples heated when unconfined and also leads to significant changes in propellant mechanical properties. However, plasticizer loss does not occur to an appreciable extent over a substantial time period when the propellant is aged in a sealed container since plasticizer evaporation will be inhibited by even partial confinement of the propellant. It appears that AP/HTPB propellant exposed to high ambient humidity will undergo a reversible loss of strain capability, possibly as a result of the plasticizing effect of absorbed water.

As a final note, the above results suggest that a weather-sealed rocket motor will not experience plasticizer loss during storage, meaning that the only probable temperature-accelerated ageing mechanism is oxidative cross-linking. However, the propellant grain is also protected from atmospheric oxygen during storage by the weatherseal, therefore one could argue that there are essentially no degradation reactions occurring in a sealed motor during accelerated ageing at elevated temperature. In addition, since holding the motor at an elevated temperature reproduces the state at which the grain was cured, this procedure may actually reduce grain stress and prevent cohesive failure of the binder. In light of this, it can be argued that the common practice of high temperature accelerated ageing of solid propellant motors is counterproductive.

5 References

[1] P. Bunyan, A. V. Cunliffe, A. Davis, and F. A. Kirby, The Degradation and Stabilisation of Solid Rocket Propellants, *Polym. Degrad. Stab.* **1993**, *40*, 239.

[2] K. K. Ninan, K. Krishnan, R. Rajeev, and G. Viswanathan, Thermoanalytical Investigations on the Effect of Atmospheric Oxygen on HTPB Resin, *Propellants, Explos., Pyrotech.* **1996**, *21*, 199.

[3] G. Jenaro, F. Rey, E. de la Cruz, and V. Perez, Ageing Behaviour of Composite Propellants, *AGARD-CP-586*, **1997**, p. 6/1.

[4] S. Désilets and S. Coté, Chemical Bond Between Stabilizers and HTPB Binders in Propellants, *Propellants, Explos., Pyrotech.* **2000**, *25*, 186.

[5] H. L. J. Keizers, Accelerated Aging of AP/HTPB Propellants and the Influence of Various Environmental Aging Conditions, *International Symp. Energetic Materials*, Phoenix, Arizona, September 24 – 27, **1995**, p. 200.

[6] S. Torry and A. Cunliffe, Humid Ageing of Polybutadiene Based Propellants, *31st Int. Annual Conference of ICT*, Karlsruhe, Germany, June 27 – 30, **2000**, p. 25/1.

[7] A. V. Cunliffe, A. Davis, and D. Tod, Ageing and Life Prediction of Composite Propellant Motors, *AGARD-CP-586*, **1997**, p. 8/1.
[8] M. Celina, A. C. Graham, K. T. Gillen, R. A. Assink, and L. M. Minier, Thermal Degradation Studies of a Polyurethane Propellant Binder, *Rubber Chem. Technol.* **2000**, *73 (4)*, 678.
[9] D. J. Harris, R. A. Assink, and M. Celina, NMR Analysis of Oxidatively Aged HTPB/IPDI Polyurethane Rubber: Degradation Products, Dynamics and Heterogeneity, *Macromolecules* **2001**, *34*, 6695.

Acknowledgements

The author wishes to gratefully acknowledge helpful discussions with the scientists at Defence R&D Canada – Valcartier.

(Received March 13, 2003; Ms 2003/006)