Effect of plasticiser diffusion on the mechanical properties of double base propellants

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Abstract

To understand the life limitations of bi-propellant solid rocket motors, a typical motor was explored outside its design envelope. Plasticiser concentration has a big influence upon mechanical properties of solid propellant. The aim of this work was to measure the effect of plasticiser diffusion on the mechanical properties of boost and sustain propellants held in intimate contact with each other and to use data to model the change in stress capability of a motor at different temperatures. It is hoped that this methodology will lead to a greater understanding of the whole life assessment of weapon systems.

INTRODUCTION

Due to the unstable nature of energetic materials, weapon systems have finite life spans. All energetic materials undergo ageing processes, which affect their performance, reliability and operational safety. Hence, there is a need to monitor the chemical components in a weapon system to maximise its service life. The benefits to be gained by accurate prediction of service life include reduced whole life-cycle costs, improved safety, improved effectiveness and operational and procurement flexibility. Often, the life of a system is dominated by chemical degradation processes. However, in the case the system studied in this work, the lifetime was found to be dominated by plasticiser migration.

The motor in this work consists of rubber modified cast double base propellants - boost and sustain. The boost propellant is a very soft elastic material typical of this family of materials. The sustain propellant is much harder and has mechanical properties more typical of cast double base propellant, being less extensible. The composition is summarised in Table 1. Although nitro-glycerine (NG) and triacetin (TA) is present in both materials, they are at a higher concentration within the boost. As the plasticisers move from the boost to the sustain, the shear modulus of the boost increases and that of the sustain decreases. There is a concomitant increase in the volume of the sustain propellant and decrease in the volume of the boost propellant. The changes in volume, the application of temperature cycling and other ageing processes are thought to cause the motor to crack which increases the likelihood of catastrophic failure upon firing.

Component	Sustain	Boost
NC	25	19
NG	37	45
Stabilisers	1	1
Nitramine	21	21
Triacetin	4	8
Rubber	3	3
Other	9	3

Table 1. Nominal propellant composition.

There are two main ways to conduct accelerated ageing. The first is to raise the temperature of the store to a constant high temperature for a period of time, the second is to cycle the motor through range of high temperatures. The latter is preferred by many agencies as it more accurately represents the environment seen during a motor's lifetime. Certain stresses can be induced in the rocket motor due to differential expansion of the components. Such stressing is more likely to reveal failure of components such as seals etc. In case bonded rocket motor charges there can be a significant stress built up in the propellant which can damage the propellant or propellant interfaces. However, it is thought that in the case of the motor under consideration, expansion due to temperature changes is a smaller effect relative to expansion/ contraction caused by volume changes during diffusion processes approaching equilibrium.

Diffusion is a stochastic process driven by concentration gradients of a mobile species. Fick’s law of diffusion is commonly used to model transport properties in polymers and is based on the hypothesis that the rate of change of the concentration is proportional to the gradient of the concentration gradient. Assuming isotopic material behaviour,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Equation 1 Fick’s second law of diffusion

Where C is the concentration and D is the Diffusion Coefficient (units length^2 time^{-1}).

This second order partial differential equation can be solved analytically for materials with simple geometries and boundary conditions. For the experimental configuration in this work, it can be shown that the mass uptake is

$$\frac{M - M_o}{M_\infty - M_o} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2}\left\{1 \quad + \quad \sqrt{\pi}\sum_{n=1}^{\infty}(-1)^n \, ierfc\frac{nl}{\sqrt{Dt}}\right\}$$

Equation 2 Fractional mass change versus time

Where M_∞ is the final equilibrium mass, M_o is the initial mass, M is the instantaneous mass at time t and l is the sheet thickness. This shows that the fractional mass change (compared to the mass change to reach equilibrium) is initially proportional to the square root of time. This can be used to deduce the diffusion constant, D, from experimental data of mass uptake versus time.

This paper quantifies the plasticiser diffusion process as a function of temperature and the effect on the propellant shear modulus and volume. This enables the estimation of the risk of failure due to reduced shear modulus within the propellant, from the age of the propellant and the temperature conditions over the motor's service lifetime.

EXPERIMENTAL

Unaged boost and sustain propellant were milled to dimensions 6mm x 10mm x 50mm.

Samples of boost and sustain propellant were pressed together, and tightly wrapped in aluminium foil to limit nitro-glycerine loss. Boost and sustain propellant control samples were also separately wrapped in aluminium foil and all materials were aged isothermally at 70, 60 and 50°C. After ageing, the duplex boost/sustain sample was separated and the propellants were individually wrapped in aluminium foil and allowed to equilibrate for one week at 60°C. Changes in masses were recorded at each stage. After ageing, the samples were mechanically tested using dynamic mechanical analysis (DMA) and chemically analysed by nuclear magnetic resonance (NMR) spectroscopy.

Dynamic mechanical analysis was performed using an RDA2 rheometer in control strain mode according to test parameters outlined in Table 2. A sinusoidal deformation is applied to one end of the rectangular bar and the resultant torque measured. By comparing the input signal to the output signal three parameters characteristic of the material, the shear modulus G' , the loss modulus G" and the loss angle (delta) are generated. These parameters are measured as a function of temperature and sometimes frequency to produce a complete mechanical fingerprint of the material.

Parameter	**Value**
Geometry Type	Torsion Rectangular
Length	~30 mm (measured)
Width	~10 mm (measured)
Thickness	~6 mm (measured)
Frequency	1.0 rad/s
Initial Temperature.	-110.0 °C
Final Temperature	70 °C
Temperature Increment	3.0 °C
Strain	0.1%

Table 2. DMA test parameters.

NMR measurements were performed on a Bruker Avance 400 spectrometer (proton frequency 400MHz) fitted with a 5mm QNP probe. The cross-section of the propellant was sliced using a microtome and then extracted overnight, at room temperature, in deuterated chloroform with a known mass of tetrakis(trimethylsilyl)silane internal standard. Stabiliser and plasticiser mass percents were calculated by ratioing the areas of the relevant NMR peaks to the area of the internal standard.

The motor structure analysis was determined using Finite Element Modelling via the Abaqus suite.

RESULTS AND DISCUSSION

Ageing of Propellants

As diffusion is thought to dominate life limiting process of the motor grain initial work was performed measuring changes in mass transport of plasticisers and density in the two propellants. The diffusion constant was calculated by measuring the mass transport of plasticisers between the boost and sustain propellants held in intimate contact with each other. It is assumed that the plasticisers partition in equal quantities in both propellants.

Figure 1 illustrates the square root of time versus fraction completed plasticiser migration. Up to fractions of 0.5 to 0.75, the diffusion plot is linear – the gradient of this part of the data yields the diffusion constant. The high temperatures were chosen to reduce the experimental time, but are not representative of the storage temperature of the motor (typically 20°C storage for 20 years and up to 60°C for 3 months operational use). The values of D at the lower temperatures were extrapolated from the Arrhenius plot of the diffusion constants (Figure 2). Even at 70°C, the diffusion process is too slow to reach equilibrium after 50 days. Extrapolation of the data suggests that 99% completeness in 6mm thick plaques would be achieved in 120 days at 70°C (Table 3). In a real motor, mass transfer is dependent on the geometry of the motor. An analytical solution is not practical and hence diffusion phenomena in the motor grain were investigated using a finite element model as described in a later section.

Temperature / °C	**Diffusion coefficient / mm^2 day^{-1}**	**Time to 99% equilibrium / years**
70.00	0.136	0.32
60.00	0.105	0.42
50.00	0.081	0.55
40.00	*0.06*	*0.74*
30.00	*0.044*	*1.02*
20.00	*0.032*	*1.43*
10.00	*0.023*	*2.05*

Table 3. Time to 99% equilibration in 6mm thick sheets – data in italics extrapolated.

During the ageing process, nitrate degradation caused stabiliser consumption. For example at 70°C, all the pNMA had converted to nitroso-pNMA within 50 days (Figure 3). It is assumed that there is sufficient stabiliser to prevent excessive gas evolution due to nitrate decomposition – hence the cracking due to gassing is discounted.

It is noted that the shear modulus of the material of the control propellants (the shear modulus, G') does not vary much other than that due to loss of volatile plasticisers (Figure 4). Despite ageing, there is little evidence to suggest that the propellants' moduli are grossly altered due to chain scission processes of either the polyurethane or the nitrocellulose.

However, as expected, the mechanical properties of the propellant held in intimate contact with each other do change substantially due to plasticiser migration – the modulus of the boost propellant doubles while the sustain decreases by a half. The plots of shear modulus of both boost and sustain propellants versus plasticiser fraction (Figure 5) demonstrate that the moduli (within the error of measurement) appear to be independent of the temperature of the migration experiment.

Helium pycnometry measurements indicated that the density of both propellants did not vary by greater than 1% during plasticiser migration (up to 10% changes in the plasticiser concentration). That is to say, upon migration and at equilibrium, the boost propellant should shrink and the sustain propellant swell. The consequence of this would be to cause strains and stresses in the motor grain and thereby potentially cause cracking.

Finite Element Modelling

The lifecycle of the motor under test comprises; a storage phase where the storage temperature is relatively stable (25°C) - most of the ageing/diffusion occurs during this long time period. Upon deployment, there are typically 9 months in temporary storage, then up to 90 days where temperature conditions can be at extremes (60°C) and more varied. Launch occurs at temperatures down to -33°C.

The geometry of the motor is complex – it basically consists of concentric cylinders of an inner boost propellant and outer sustain propellant. The thickness of both propellants varies along the conduit. At the nozzle end, the propellant is slotted through both propellants. Figure 6 illustrates the mid section. The motor was modelled with a mesh element (quadratic) every 10mm other than at interfaces and edges where the mesh density was doubled. Only one quarter of the propellant charge was modelled due to the symmetry.

The plasticiser migration was modelled directly using a mass diffusion analysis. This only provided information on the plasticiser concentrations – it did not include the displacement degrees of freedom necessary to model the swelling behaviour. It was assumed that the solubility of the plasticiser was the same for both boost and sustain propellant.

The swelling behaviour was modelled by using an analogy between Fick's law of mass diffusion (equation 1) and Fourier's law of heat transfer (equation 3)

[1, 2] by substituting appropriate material parameters. With temperature replaced by the concentration variable, it was not possible to simultaneously model diffusion processes and temperature changes. However the event time for the thermal transfer is thought to be significantly shorter than that of the mass diffusion, and hence the two events were assumed to take place sequentially, and the body was in a thermal steady state condition throughout the mass diffusion. It was also assumed that the swelling coefficient was only weakly dependent on temperature (above the glass transition temperature) hence the same value as measured at 25°C temperature was used during the modelling.

$$Q = -k \frac{dT}{dx} \qquad \text{equation 3}$$

where: Q = Heat flux, heat flow per unit area and per unit time. [J/m^2s]
k = Thermal conductivity [J/mKs], dT/dx= Temperature gradient [K/m].

The pseudo-thermal conductivity was derived from the diffusion constant, specific heat and material density (in metric units). The swelling coefficient was derived using the same mass uptake versus time data as the diffusion and was the slope of the strain versus mass concentration fraction. The strain value was calculated from the cube root of the fractional change in volume, assuming isotropic material behaviour. The density of both aged boost and sustain was approximately constant so that the fractional volume change was equated with the fractional mass change.

An example of stress evolution over 20 years at 25°C due to mass transport of plasticisers from the boost to the sustain is illustrated in Figure 7. Over a period of 20 years stresses become greater at the interface, sharp edges near the slots and in the conduit. A side view cross-section (Figure 8) confirms stress build up at the interface, and at the base of the slots. It is thought that additional stresses induced by thermal cycling could potentially crack the motor. This is currently being investigated.

CONCLUSIONS

In the case of the motor studied in this work, the life limiting factor was found to be due to plasticiser migration rather than chemical degradation. Mass transport of the plasticisers from boost to sustain propellant was found to alter propellant volume and mechanical properties. The modulus of the boost propellant doubled while the sustain decreases by a half near the equilibrium of diffusion. Density measurements also suggested that plasticiser diffusion caused swelling and shrinkage of the sustain and boost propellant respectively.

Finite element modelling indicated that mass transport of plasticisers caused stress to increase in three regions – the conduit, the propellant interface and sharp edge regions such as the slots.

ACKNOWLEDGEMENTS

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REFERENCES

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FIGURES

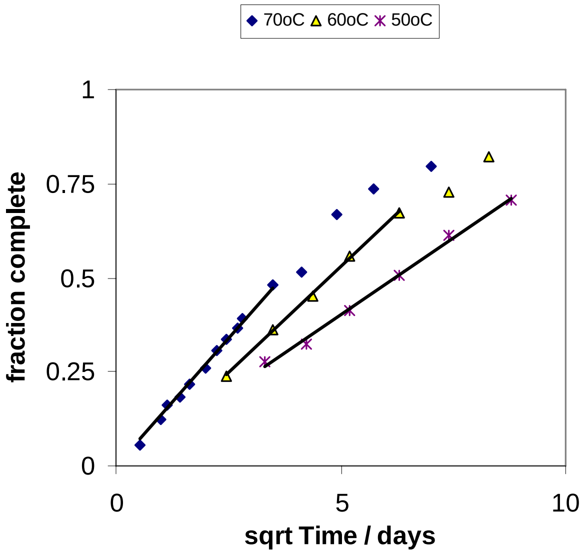

Figure 1. Fractional mass changes versus square root of time.

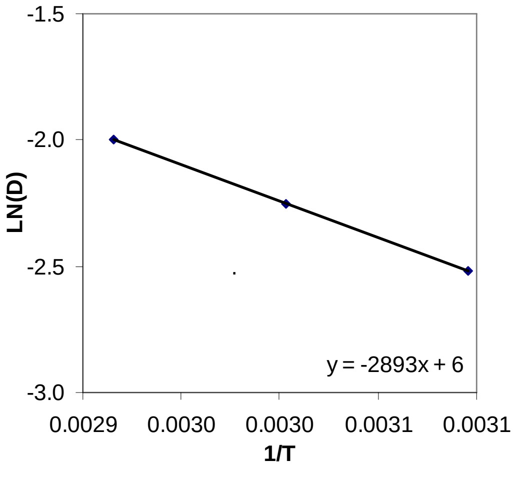

Figure 2. Arrhenius plot of the diffusion.

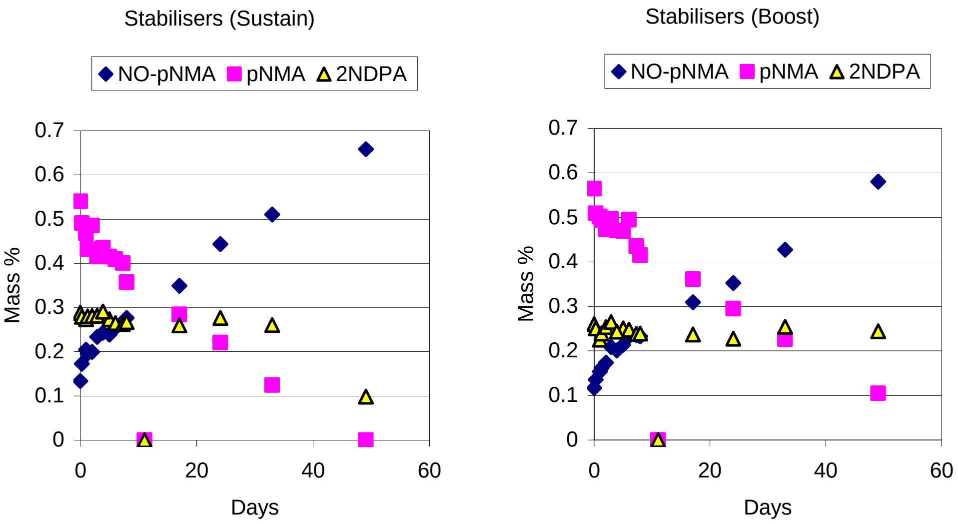

Figure 3. Stabiliser consumption in the control propellants.

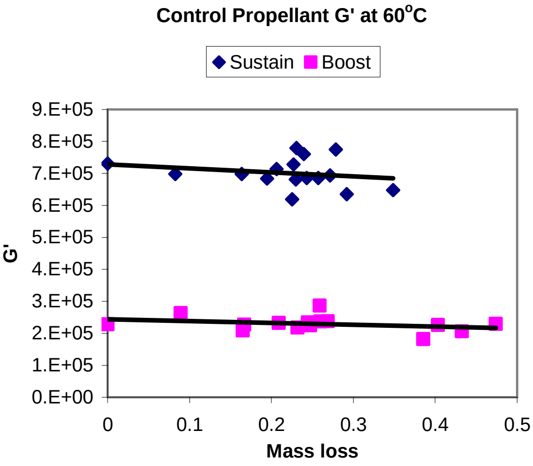

Figure 4. Elastic modulus G' (at 60°C) of control propellant aged at 70°C versus mass % loss of volatiles.

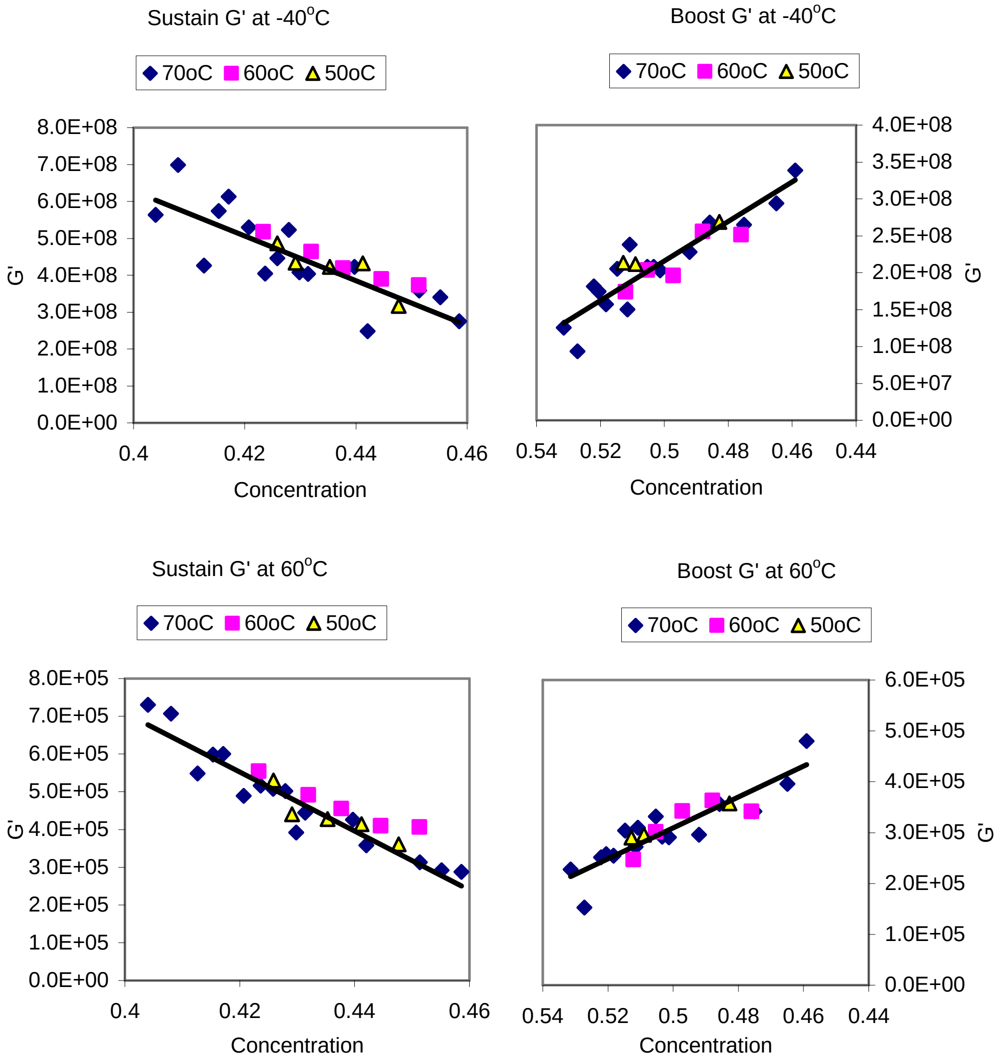

Figure 5. Shear modulus of propellant versus fraction concentration of plasticisers. Top – G' measured at -40°C, bottom – G' measured at 60°C.

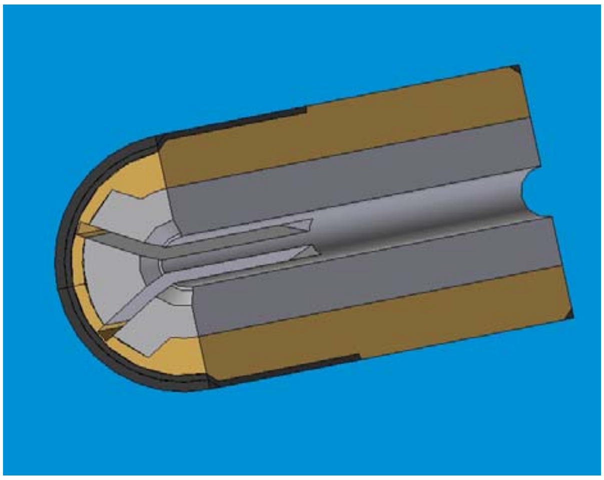

Figure 6. Section showing the geometry of the motor charge. Brown and grey areas are the sustain and boost propellants respectively.

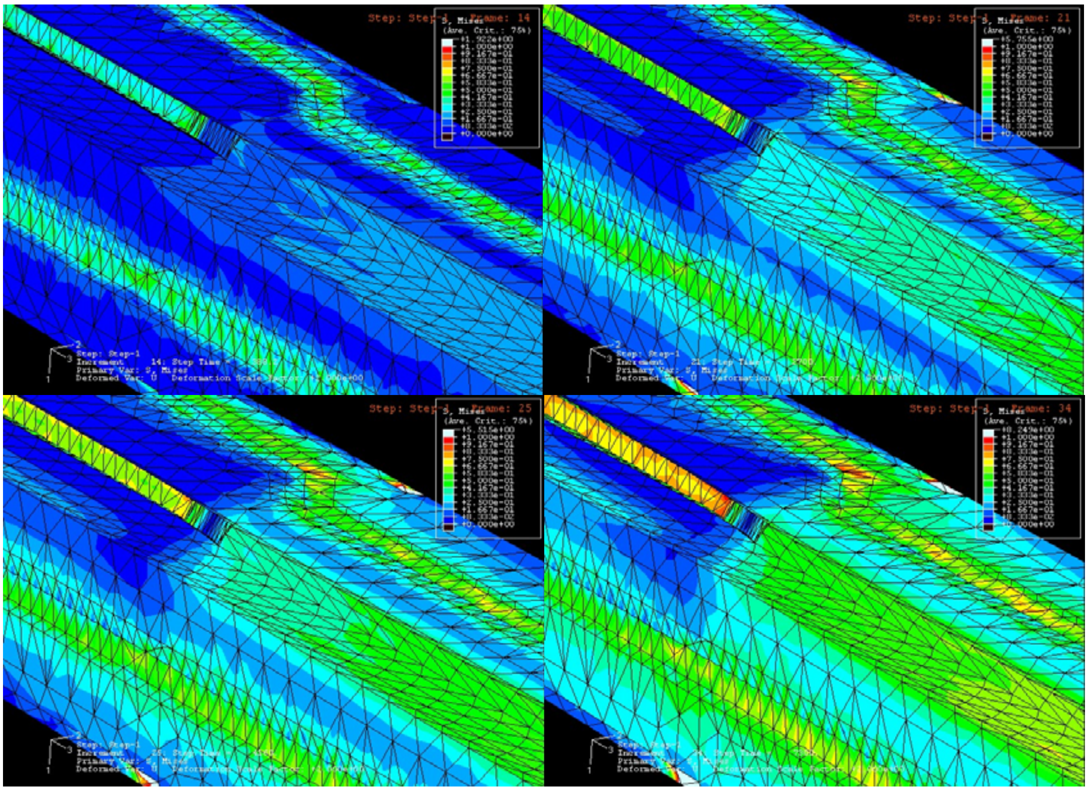

Figure 7. Evolution of stress over 20 years (from top left 1.1 years, top right 7.4 years, bottom left 12.5 years, bottom right 20 years).

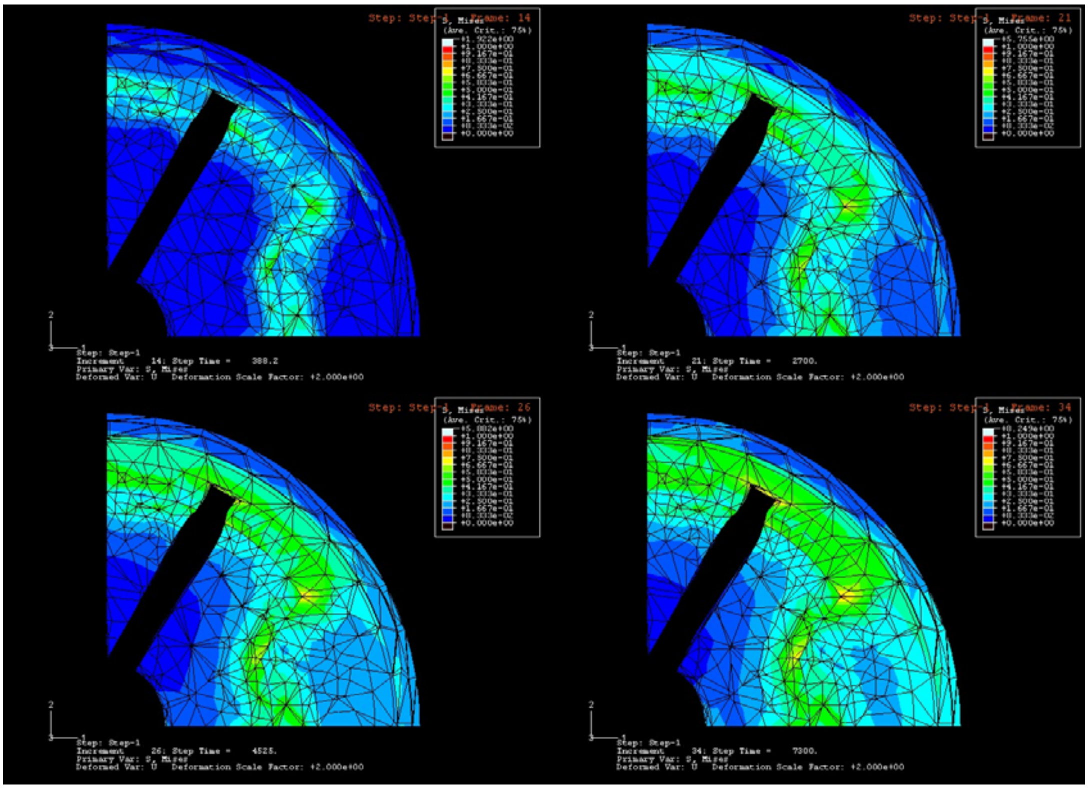

Figure 8. Evolution of stress over 20 years (from top left 1.1 years, top right 7.4 years, bottom left 12.5 years, bottom right 20 years).