

# **Development of a Theoretical Framework for Understanding the Effect of Ageing on the Mechanical Response of PBX based Systems**

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## **Abstract**

This report presents models for the degradation of properties and mechanical response due to ageing of PBX materials such as propellants. The models show how the chemical crosslinks formed in the binder during the ageing process of a composite propellant cause deterioration in its ability to tolerate mechanical deformation; firstly as a reduction in the test criterion of strain to maximum stress, and secondly in its ability to withstand the shrinkage strain on cooling to temperatures of -60°C, which reflect conditions that might be experienced in service. Suggestions are presented in terms of linking these models into continuum based hydrocodes.

## **Introduction**

There is general recognition within MoD that many weapons are currently being disposed of with residual life available and that significant cost savings will be made if full life realisation is achieved. It has been demonstrated that where improved understanding of ageing processes and acquisition of true environmental data has been achieved, significant extension to the useful life of weapon systems has resulted. It has also become apparent that a significant knowledge gap exists in the understanding of life-dependent failure in munitions. A deep and comprehensive understanding of the system and its failure modes is required if whole life cost savings are to be achieved via life extension.

Solid propellant rocket motors generally deteriorate with age. The ageing arises from a combination of their inherent chemical and physical instability, and the effects of the environments which they experience, including temperature, humidity, atmospheric oxygen and complex mechanical stimuli. There is considerable knowledge of some aspects of these effects for individual systems, and much experimental data has been accumulated, involving a large amount of effort and expense. However, there is a growing requirement for a theoretical understanding of the effect of ageing on mechanical properties for polymer based systems to be able to assess new materials and compositions, where there is little empirical data.

This paper attempts to develop a model for the mechanical properties of and criteria for failure in a propellant with increased binder degradation due to thermooxidative crosslinking with age. The approach is highly novel and builds on existing approaches based on Quantitative Structural Property Modelling (QSPM) [1,2]. The model gives a first estimate of properties that might be considered 'typical' of

composite propellants and other energetic materials such as PBX. The model is a semi-empirical approach, based upon the energy of molecular interactions, but all the model parameters can be derived from 'first principles' methods such as quantum mechanics if required. The approach is tested against existing data for a HTPB/AP composite propellant system used in rocket motors. The technique is readily applicable to the development of pragmatic physically-based algorithms for use in hydrocode analysis of real systems.

### Propellant as a Particulate Composite

We aim to predict the degradation in mechanical properties with time of a model propellant system with an approximate composition (weight %):

|  |     |
|--|-----|
| Energetic particles<br>(e.g. ammonium perchlorate) | 88% |
| HTPB Binder  | 9%  |
| Di-octyl Sebacate (plasticizer)                    | 3%  |

To a first approximation, we take this to be a particulate composite with about  $f_b \approx 21\%$  by volume of 'soft' binder and 79% volume of filler particles that are much 'harder'. Taking the main body of rigid particles to have the particle size fractions of the ammonium perchlorate, we estimate a typical binder thickness between particles of  $d \approx 5 \mu\text{m}$ ; here we used the volume fractions and the surface area per unit mass of the particles in the given particle sizes, but have not yet included any particle size distributions around the average values for a distribution in  $d$ .

Since the volume fraction of binder is  $f_b \approx 21\%$ , the linear fraction of binder in any deformation axis is  $f_b/3 \approx 7\%$ . Using additivity rules for compliance, and taking the particles to have a much higher modulus than the binder,  $E_b$ , the composite tensile modulus is  $E_c \approx E_b / 0.07 = 14 E_b$ .

### Damage Model

The key hypothesis of this work is that properties of a particulate composite such as this propellant deteriorate as the connectivity between the binder and the harder particles is lost by damage such as 'debonding' at interfaces. This damage is quantified very simply in terms of the elastic modulus of the propellant by reducing the modulus in direct proportion to the probability of debonding events. These events are taken to have an Arrhenius-like exponential probability due to a mechanical energy input to the material relative to an activation energy characteristic of the debonding process. If energy is taken to be proportional to strain squared, the input and activation energy terms can be quantified by the strains  $\varepsilon$  and  $\varepsilon_a$  respectively in the relation for  $E_c$  relative to its undamaged value  $E_{co}$

$$E_c = E_{co} \left( 1 - \exp \left( - \left( \frac{\varepsilon_a}{\varepsilon} \right)^2 \right) \right) \quad (1)$$

To illustrate the general form of a stress-strain relation for a propellant, let the initial modulus and activation strains take arbitrary values of unity,  $E_{co} = 1$  and  $\varepsilon_a = 1$ , and plot stress,  $\sigma$ , as a function of applied strain,  $\varepsilon$ , in Figure 1, which has a peak stress at a strain around  $\varepsilon_a$ .

$$\sigma = \left( 1 - \exp\left(-\left(\frac{1}{\varepsilon}\right)^2\right) \right) \varepsilon \quad (2)$$

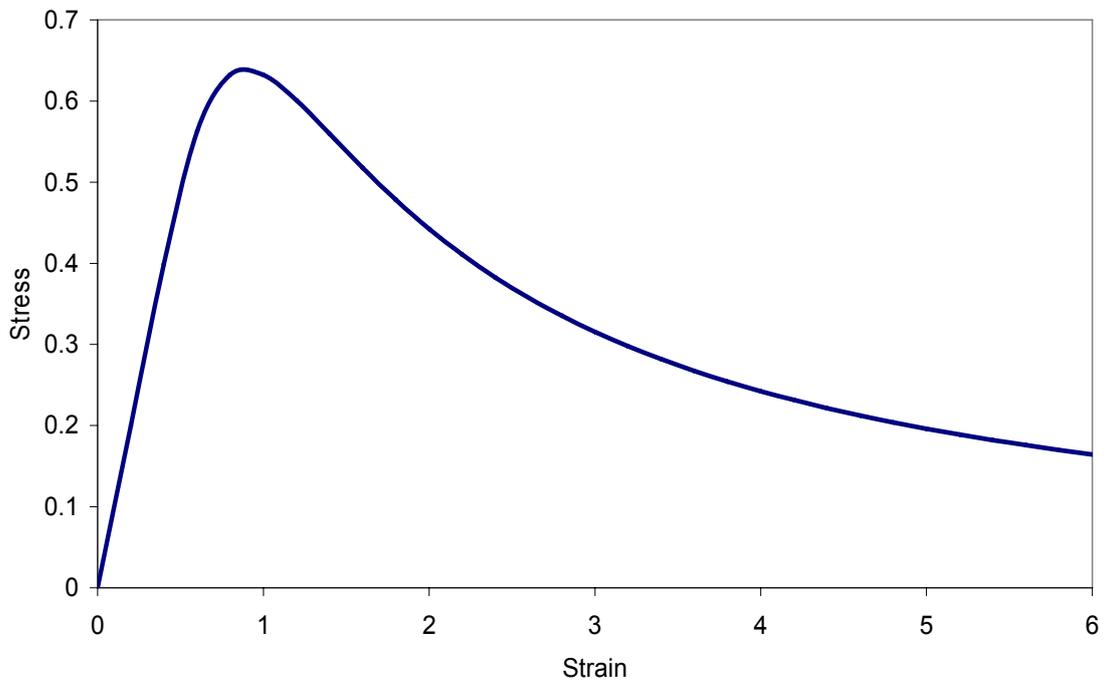
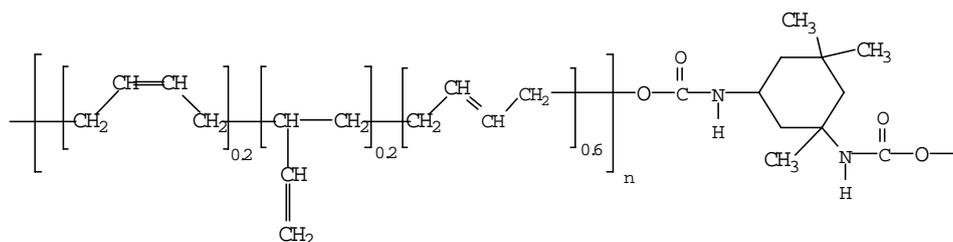


Figure 1. Model illustration of stress-strain plot for a propellant material.

The next problem is to quantify the parameters in the damage model and examine how these parameters change with ageing of the material. For simplicity, we assume that the main changes occur in the polymeric binder, and that most of the energy of deformation is absorbed also in the more compliant binder.

### Unaged Binder Properties

The binder is taken to be HTPB-isocyanate with a nominal structure:



However, the actual composition of the binder is adjusted to change the crosslink density and distribution to optimise the mechanical properties. Analysis of binders suggests that the average molecular weight between crosslinks is about 15.5 kD in

a typical practical system. The Group Interaction Modelling (GIM) method allows the viscoelastic properties of a polymer to be predicted in detail if we know the composition and macromolecular morphology of the material [2]. We have made such predictions for a plasticized HTPB binder system, but the current model does not require this level of detail to demonstrate the principles of ageing effects.

Figure 2 shows DMTA plots for an HTPB-DOS binder (not the precise propellant binder), with elastic modulus as a function of temperature. We see a sharp transition at about  $-60^{\circ}\text{C}$  for the poly(butadiene) domains, where the first large drop in modulus occurs. A higher temperature and more gradual transition is seen at about  $-20^{\circ}\text{C}$ , which is associated with the interaction between butadiene and higher energy segments such as the isocyanate; here the modulus falls more gradually to a typical high temperature value of about 0.26 MPa.

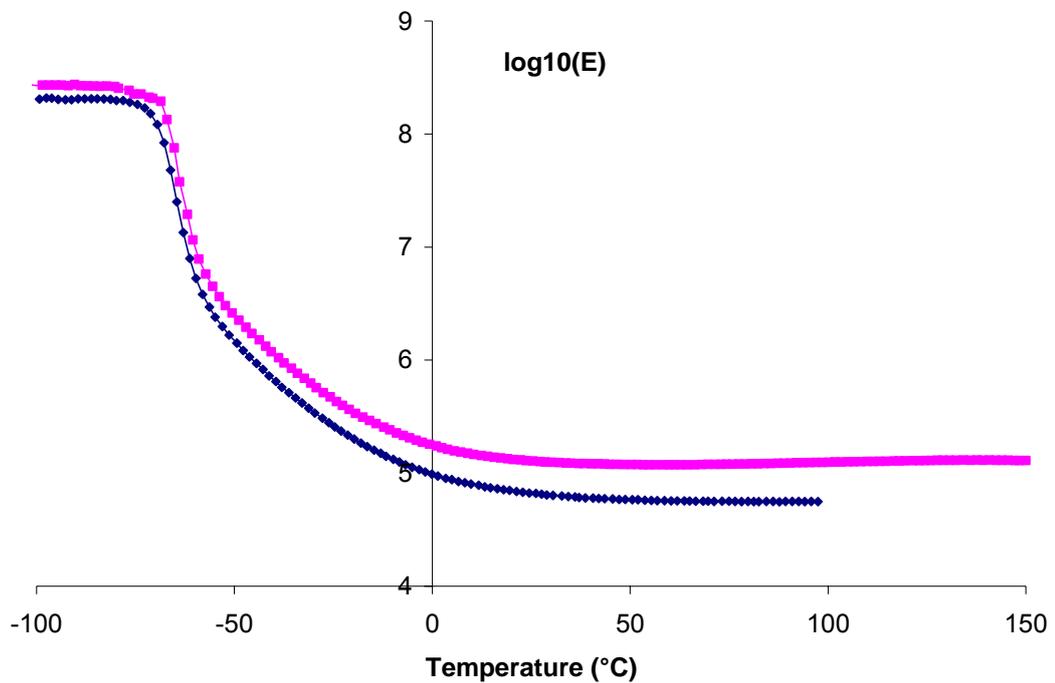


Figure 1. DMTA plots of elastic modulus for an HTPB-DOS binder system.

### Unaged Composite Stress-Strain Profiles

The composite propellant is expected to lose its strength when the binder detaches from the particles. A relation between distance between failure sites and the applied stress or strain can be derived using a criterion for elastic energy density to create free surface area in the material [2, p.180]; in this case the most likely site is cohesive cavitation in the binder very close to the particle surface. If  $\epsilon_{ab}$  is the activation strain in the binder for failure initiation, and  $\Gamma$  is the energy per unit area of free surface with a distance  $d$  between surfaces.

$$\epsilon_{ab} = \sqrt{\frac{12\Gamma}{dE_b}} \quad (3)$$

Without specific bonding complications, the surface energy takes an approximate generic value for polymers  $\Gamma \approx 0.15 \text{ J/m}^2$ . Taking a typical binder thickness between particles of  $d \approx 5 \text{ }\mu\text{m}$  as the distance between cavitation sites in the binder, we can estimate the activation strain as

$$\epsilon_{ab} \approx \frac{600}{\sqrt{E_b}} \quad (4)$$

If we take the strain in the composite to scale with strain in the binder and the volume fraction of binder,  $\epsilon_c \approx f_b \epsilon_b$ , we can suggest a first estimate of the strain in the composite to cavitate in the binder, using the model value of  $E_b \approx 0.26 \text{ MPa}$  around particles, to be  $\epsilon_{ac} \approx 0.26$

$$\epsilon_{ac} \approx 0.21 \epsilon_{ab} \approx \frac{126}{\sqrt{E_b}} \approx 0.26 \quad (5)$$

We can now predict a stress-strain response for the unaged composite using this value of  $\epsilon_{ac} = 0.26$  and an initial modulus  $E_{co} \approx 14 E_b \approx 4 \text{ MPa}$  in the relation

$$\sigma = 4 \left( 1 - \exp\left(-\left(\frac{0.26}{\epsilon}\right)^2\right) \right) \epsilon \text{ MPa} \quad (6)$$

Figure 2 shows predicted stress-strain plots for the unaged propellant composite using the very simple model given above with a peak stress at  $\epsilon_p = 0.24$ . Clearly, we need to understand the distribution of failure events in the binder to develop a better model relation for stress-strain in a propellant, but the general physical principles will be along the same lines as the above argument. Figure 2 also shows an experimental stress-strain plot for propellant at  $20^\circ$ , which is in good general agreement with the predicted relations. The model predictions look reasonable as a starting point for more detailed validation and model parameterisation in future work.

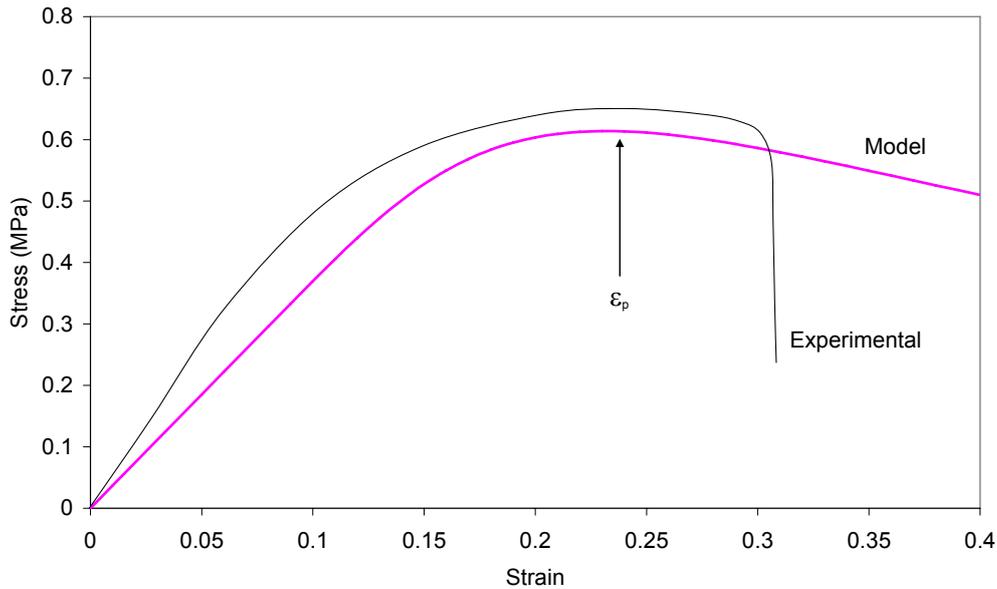


Figure 2. Predicted and experimental stress-strain plots for unaged propellant.

### Crosslinking Effect on Properties

Before discussing the kinetics of the ageing process, we can consider the effect of crosslinking upon the mechanical and other physical properties of the binder and the resultant composite properties. We assume here that a crosslink site is the result of two of the poly(butadiene) double bond sites reacting. The main change in the polymer is to reduce the number of degrees of freedom at each crosslink site. In the case of each four-arm site, the polymer loses 6 degrees of freedom in the GIM model.

The main effects upon physical properties of losing degrees of freedom through crosslinking are to increase the glass transition temperature and to increase the elastic modulus. With high crosslinking, the polymer eventually becomes a brittle glass with a modulus of the order GPa. However, for most practical ageing problems, the extent of crosslinking to cause operational hazards is relatively small, such that we can use the physics of rubberlike elasticity to model the effect of ageing.

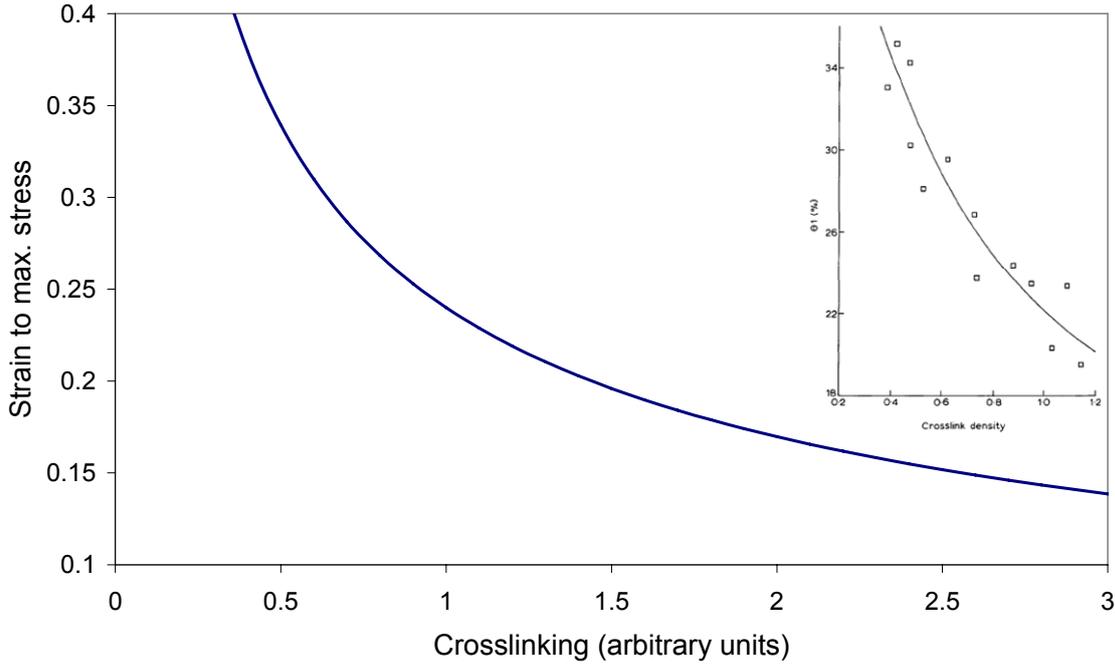


Figure 3. Predicted strain to maximum stress from crosslink density. Inset shows experimental observations [3].

Equation (3) suggests that the strain to failure or the maximum in the stress-strain response is inversely proportional to elastic modulus, so we need to calculate the effect of increased crosslinking on elastic modulus in the binder. For the sake of simplicity for these crosslinked polymers, let the modulus be inversely proportional to the molecular weight between crosslinks,  $M_x$ , as per the standard statistical theory of rubber elasticity. Before ageing, we estimated  $M_x \approx 15,500$ , which we will take here as a reference crosslink density,  $X$ , of unity, such that increased crosslinking is expected to reduce strain to maximum stress,  $\epsilon_p$ , in the form

$$\epsilon_p \approx \frac{0.24}{\sqrt{X}} \quad (7)$$

which is plotted in Figure 3. Experimental values of crosslink density suggest a typical increase in its value over extended ageing by a factor of about 3, which corresponds to a reduction in strain by a factor of about 1.7, from 0.24 to 0.14. The form of this relation agrees very well with the experimental plots published previously and shown for reference as an inset in Figure 3 [3]. Note that these results are all relative, and starting from a lower degree of crosslinking gives a commensurately higher strain capability.

### Ageing Criteria

The strain at maximum stress,  $\epsilon_p$ , in a propellant has been shown to be a useful measure of propellant ageing, with a value of 20% being taken as a lower limiting criterion for the lifetime of propellant [3]. Typical values of  $\epsilon_p$  for unaged samples are usually about 25%, such that a change from 25 to 20% represents the tolerable

effect of ageing on mechanical properties. The above discussion on the effect of crosslinking suggests this to be equivalent to an increase in crosslinking from 1 to 1.5 of our arbitrary units, or a reduction in molecular weight between crosslinks from about 15.5kD to 10kD. This represents one extra crosslink every 500 butadiene segments or an approximate fraction of 0.002 new crosslinks in the available butadiene segments.

The link between the  $\epsilon_p$  strain criterion and in-service performance has been made by temperature cycling tests, where propellant is exposed to cycles of temperature from  $-50^\circ\text{C}$  (223K) to  $+63^\circ\text{C}$  (336K). Samples that fail the strain criterion are found to crack at low numbers of cycles. Although a complete model to link thermal cycling and the strain criterion is not possible here, due to an incomplete knowledge of the effect of geometry of the propellant in its housing upon the stress-strain distribution, it is appropriate to make a first attempt for discussion. The starting hypothesis is that thermal contraction at low temperatures generates a tensile stress that induces 'debonding' between binder and particles that is the basis of the strain criterion.

Starting with thermal expansion, the values of thermal expansion coefficient for the binder and AP particles have been predicted as 0.0016 and 0.00044  $\text{K}^{-1}$  respectively [2]. Using a volumetric fraction of 0.21 for the binder suggests a composite thermal expansion coefficient of 0.00069  $\text{K}^{-1}$ . Given the constrained geometry of the composite at a curved surface, we assume here that volumetric shrinkage is effectively identical with the linear hoop shrinkage at the surface; this can be evaluated later by detailed simulations if the model proves interesting. Thus, shrinkage strain,  $\epsilon_T$ , in the composite at a surface after a temperature change from equilibrium of  $\Delta T$  is suggested to be

$$\epsilon_T \cong 0.00069 \Delta T \quad (8)$$

The next step is to estimate the change in the strain criterion due to reductions in temperature. The change in tensile modulus with temperature is shown in Figure 2, and modulus is seen to increase by a factor of about 20 from ambient to  $-50^\circ\text{C}$ , for example. This suggests a reduction in the strain criterion by a factor of about 4.5 due to the proportionality in equation (3). For cracks to develop, the thermal shrinkage strain must be greater than the new criterion at low temperatures.

$$0.00069 \Delta T > \frac{\epsilon_p}{4.5} \quad (9)$$

Taking an ambient temperature of 293K as equilibrium,  $\Delta T = 70$  degrees at the lower cycle temperature of 223 K. The criterion in equation (9) for cracks to develop is satisfied when  $\epsilon_p < 0.22$  in this first model suggestion. Thus, we see a quantitative link between cracking at low temperature and the  $\epsilon_p$  strain criterion.

Figure 4 compares a model stress-strain plot with experimental results at  $-40^\circ\text{C}$ , to show that the model predictions are again in general agreement with trends observed in practice up to the onset of failure events; the strain to maximum stress reduces and the maximum stress value increases over the initial predictions shown in Figure 2. The stress reduction after the maximum point reduces more steeply

than observed, which is probably due to neglecting stress- and energy relaxation in the binder after 'debonding' events.

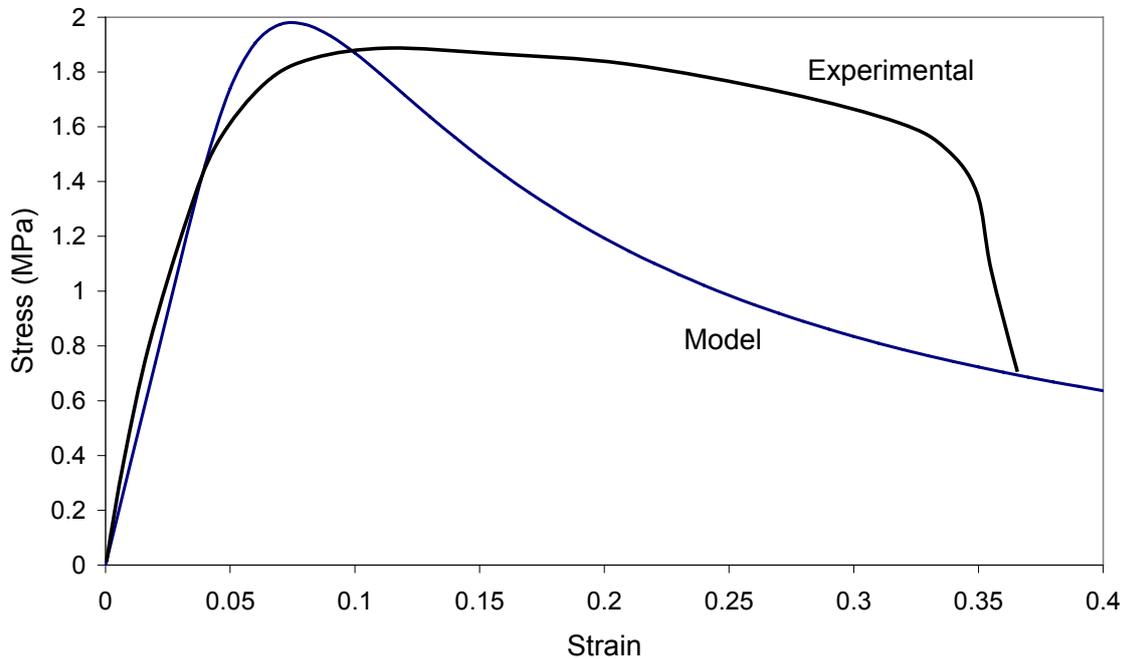


Figure 4. Comparison of model and observed stress-strain plots at  $-40^{\circ}\text{C}$ .

### Ageing Kinetics

The kinetics of crosslinking are too complex to model at a molecular level without significant effort and a better understanding of the reaction path for oxidation of the butadiene segments, which is not currently available. The number of composition variables is too great to evaluate an optimum reaction path for the oxidation process, even with extensive experimental data. Fortunately, a comprehensive experimental programme has been undertaken on thermooxidation in the binder, and the empirical relations from that work are more than adequate to estimate the effect of temperature and oxygen exposure upon the rate of crosslinking for degradation of mechanical properties [3]. This work has presented a model for the effect of fractional changes in the degree of crosslinking upon mechanical properties, and a combination of the empirical relations for crosslinking kinetics with this model for mechanical properties should provide a better understanding of the rate of deterioration of propellant performance under active service conditions.

### Future Model Development

A key aspect is that the approach described provides a valuable framework for future studies on new materials, where there is very little empirical data on the effect of ageing on the mechanical response. This is crucial given the current climate of munition procurement and the reliance of third party information concerning detailed propellant and explosive compositions and manufacturing processes. This framework will therefore facilitate a significant reduction of risk for new munitions in terms of predicting their life and hence should result in major cost benefits for MoD.

The model framework should be relatively straightforward to implement into continuum based hydrocodes, which can then be used for comparison with precise experiments over a wide range of input stimuli. Indeed the QSPM models for equations of state manifest themselves as a SESAME table look-up format of pressure, volume and temperature and thus are well suited for use in hydrocodes.

## Conclusions

The model hypothesis that the mechanical properties of a PBX composite are reduced by damage to the binder-particle connectivity has been used successfully to predict the mechanical properties of a composite propellant. Moreover, the model has been shown to reproduce the stress-strain profile of such materials quite well.

The models show how the chemical crosslinks formed in the binder during the ageing process of a composite propellant cause deterioration in its ability to tolerate mechanical deformation; firstly as a reduction in the test criterion of strain to maximum stress, and secondly in its ability to withstand the shrinkage strain on cooling to temperatures of  $-60^{\circ}\text{C}$ , which reflect conditions that might be experienced in service.

We propose that a combination of experimental ageing kinetics and the damage model can be used as an effective tool to understand and predict the operational life of propellant and other PBX materials under service conditions.

The model framework is amenable to implementation into continuum based hydrocodes, thus allowing validation over a wide range of input stimuli.

## References

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