Effects of thermal ageing on the properties and lifetime prediction of hydroxyl-terminated polybutadiene

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Thermal ageing of hydroxyl-terminated polybutadiene propellant binders was carried out at various temperatures between 50 and 100°C. The changes caused by this treatment in properties such as melt viscosity, functional end-groups, molecular weight, tensile strength, elastic modulus and ultimate elongation were examined. The viscosity and average molecular weight increased with the ageing temperature and ageing period. A decrease in ultimate elongation and an increase in elastic modulus were observed. Tensile strength of the matrices prepared by curing hydroxyl-terminated polybutadiene with isophorone diisocyanate did not change. Lifetime for usability was predicted from the application of the Arrhenius equation to be 7 years.

(Keywords: polybutadiene; hydroxyl termination; thermal ageing)

INTRODUCTION

Composite propellants generally consist of a solid-phase oxidizer and a polymer which serves the dual purpose of a binder and a fuel. For fuel/binders, polymeric materials, usually with rubbery consistency, are used. They are frequently prepared as prepolymers so as to assist mixing and also reduce the time of the subsequent curing process. Among the rubber-like propellants are polyurethanes, polysulfides and pastisol propellants. Polyurethanes are prepared by the reaction of diisocyanate materials with polyglycols containing functional hydroxyl groups. The most commonly used polyglycols are the hydroxyl-terminated polybutadiene (HTPB) prepolymers. HTPB has some advantages over other binders, such as permitting a solid loading of up to 92% while retaining the desired mechanical properties and the ability to cure at low temperatures.

The ballistic and mechanical properties of the propellants depend on the properties of their components. Therefore, the chemical structure, functionality, viscosity and variations in these properties become important in the function of the propellant. The necessity to obtain large quantities and their long-term storage may cause alterations in their properties. The mechanisms of these changes are not well understood and for that reason ageing of binders and propellants is being investigated by many researchers.

Among the changes due to ageing are hardening caused by crosslinkage through the double bonds present in the main chain of polyurethane and carboxyl-terminated polybutadiene (CTPB)-based propellants[1]. A relationship between the changes in the chemical structure and the mechanical properties during ageing was established[2]. Depending on the ageing temperature and duration, complete curing and increase in crosslink density and at higher temperatures gel formation as a result of further reactions of urethanes with allophanate formations, were observed[3,4]. The ratio of the components such as HTPB and the isocyanate curing agent[5], or the molecular weight of HTPB[6] were found to affect the properties of the matrix. For example, higher amounts of diisocyanate component or lower molecular weight of HTPB led to stiffer matrices affecting all the mechanical properties.

Thermogravimetric analysis revealed that heating rate, sample mass or the nature of the terminal groups did not affect the kinetic parameters. The activation energy for the thermal decomposition was found to be around $110\,\mathrm{kJ\,mol^{-1}}$ (ref. 7).

From accelerated ageing studies in the temperature range 40–75°C of five cast composite propellants, it was shown that the primary component altered at the exposed surface is the binder whereas in the interior it is the oxidizer[8]. It has also been suggested that oxidative attack by perchlorate causes crosslinking, leading to hardening[9].

Although various diisocyanates are used as curing agents for HTPB, isophorone diisocyanate (IPDI) is one of the most commonly used. The details of the cure reaction were examined and found to obey the second-order rate equation[10].

Since the mechanical and ballistic properties of propellants are affected by the properties of the components used, their ageing and lifetime gain importance. In this study, thermal ageing of HTPB was examined at various temperatures and the alterations in chemical, physical and mechanical properties were measured. From these changes and an Arrhenius-type temperature–time relation, the lifetime of HTPB was predicted.

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EXPERIMENTAL

Materials

Hydroxyl-terminated polybutadiene (HTPB, R45-M), isophorone diisocyanate (IPDI), tetrahydrofuran (THF) and Irganox 1010 were obtained from Atlantic-Richfield Chemical Corporation, Fluka A.G., Merck A.G., and Chemische Fabrik Freising Corporation, respectively, and all the chemicals were used as obtained without further purification.

Thermal ageing and characterization of HTPB

The thermal ageing of HTPB was achieved by placing the liquid polymer samples into beakers and incubating in an oven maintained at a constant temperature. Samples were examined at certain time intervals as described below.

Viscosity measurements were performed with a Brookfield Synchro Lectric RVP Model viscometer using spindle no. 2 at 25°C and at 2.5 rev min^{-1}. Molecular weights were determined viscometrically in tetrahydrofuran at 25°C. The viscosity-average molecular weight, M_v, was calculated from the relation given below[11]:

$$[\eta] = 1.515 \times 10^{-3}(M_v)^{0.525}$$

where $[\eta]$ is the intrinsic viscosity. The hydroxyl values of HTPB samples were measured by the phthalation method and calculated as follows[12]:

$$HV = \{(B - A) \times 1.701N\}/W$$

where HV denotes hydroxyl value (as wt%). A and B are the volumes (ml) of NaOH solution of normality N required for the sample and for the blank, respectively, and W is the weight of sample (g).

In the spectroscopic analysis of the samples, the liquid polymer is smeared on KBr crystalline pellets and *FT*i.r. spectra were taken with a Nicolet-20SXB spectrophotometer. These samples were later aged at 100°C by incubating the KBr crystals in an oven. *FT*i.r. spectra were taken at certain time intervals.

Thermal analyses were carried out under a nitrogen atmosphere and at a heating rate of 5°C min^{-1} with a Du Pont 910 model DSC connected to Du Pont 1090 recorder and Du Pont 951 TGA.

Preparation of polymeric matrices

Polymeric matrices were prepared by using the untreated or the aged HTPB samples (91%) and mixing them with IPDI (8%) and antioxidant Irganox 1010 (1%). In the first step of the preparation, HTPB and Irganox 1010 were mixed in a horizontal mixer (IKA-Duplex Kneter ZFO Model) at 65°C for 30 min under vacuum. IPDI was then added and the solution was mixed for a further 15 min, poured into Teflon moulds and cured for 7 days at 65°C.

Mechanical testing of polymeric matrices

The mechanical properties of the polymeric matrices were measured at 25°C, using an Instron Tensile Tester (Model 1185) (with a crosshead speed of 5 cm min^{-1}) connected to a Hewlett-Packard 85 computer.

RESULTS AND DISCUSSION

The optimum mixing temperature which leads to minimum viscosity was determined prior to the examination of the physical and mechanical properties of thermally aged materials. As shown in the equation below, there is an inverse relation between the temperature and viscosity of liquids:

$$\eta = \exp(E_v/RT)$$

where η is the viscosity, E_v is the activation energy for viscous flow, T is temperature and R is the gas constant.

The viscosity of the original HTPB sample was found to be 50 P at 22°C and as expected a decrease was observed with increase in temperature. The minimum viscosity was found to be approximately 5 P in the temperature range 60–80°C (*Figure 1*), and 65°C was chosen as the optimum mixing temperature for the preparation of the polymeric matrices.

Activation energy for viscous flow was calculated to be 34.75 kJ mol^{-1} for HTPB from the plot of ln η *versus* $1/T$ (*Figure 2*).

Effects of thermal ageing on properties

Viscosity. The effect of ageing on the viscosities of the samples is shown in *Figure 3*. It can be seen that an

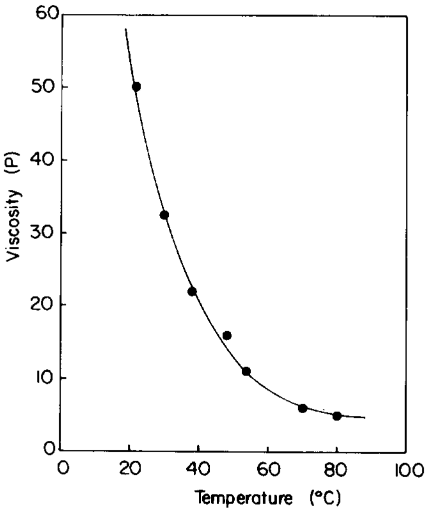

Figure 1 The effect of temperature on the viscosity of HTPB

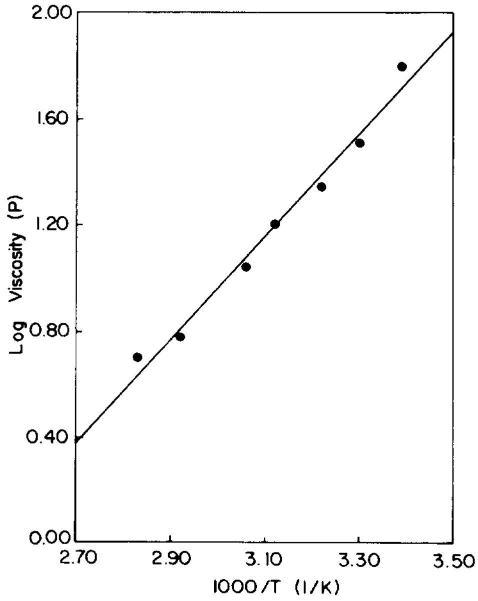

Figure 2 The relation between viscosity and temperature for HTPB

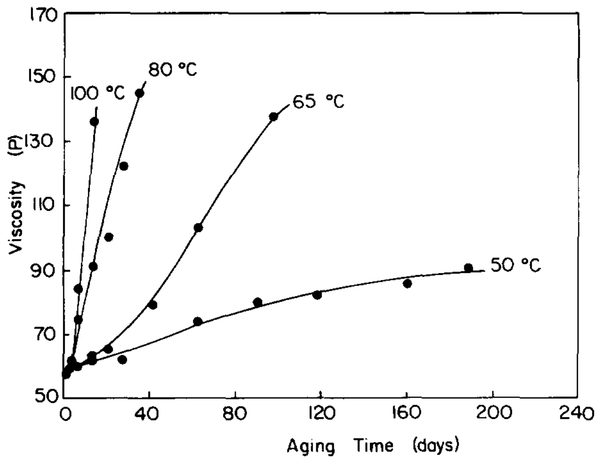

Figure 3 Effect of thermal ageing on the viscosity of HTPB

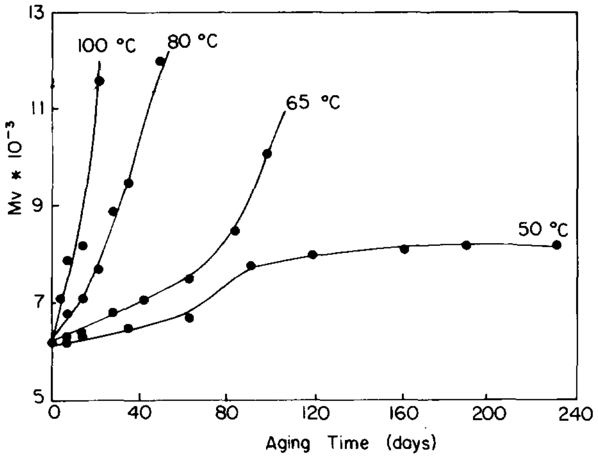

Figure 4 Effects of thermal ageing on M_v of HTPB

increase in viscosity takes place during ageing at all temperatures tested although the rate of increase is higher at higher temperatures. While about 30% increase takes place in a 3-month period at 50°C, almost 400% increase was observed in just 3 weeks at 100°C. The increase in viscosity with ageing can be explained by the formation of crosslinks between the double bonds of HTPB. Higher temperatures accelerate opening of the double bonds and the formation of crosslinks. Similar observations are reported for CTPB[13-15]. The decrease in the amount of double bonds expected from the above explanation is also supported by the *FT*i.r. spectra.

Molecular weight. The ageing temperature and ageing duration affect the molecular weight of HTPB as shown in *Figure 4*. An increase in the parameters used in ageing cause an increase in M_v. Higher temperatures and longer periods cause greater increases in M_v. For example, while the samples aged at 50°C for 3 months showed about 25% increase in M_v, the samples aged at 100°C for 3 weeks demonstrated an 87% increase. These also indicate that the rate of formation of crosslinks is higher than the rate of chain scission reactions[16].

Functional groups. With the HTPB sample aged at 100°C (*Table 1*), the *HV* increased by 53% after 35 days. This increase can be explained by the formation of radicals which are then converted to peroxides in the presence of oxygen. These peroxides may eventually lead to hydroxides or carboxyl compounds[17].

*Chemical structure. FT*i.r. spectra of the aged samples revealed an increase in the OH peaks at 3300 cm^{-1} (*Figures 5* and *6*). The reason for this increase in the hydroxide groups was explained previously. Also, carboxyl absorption peaks, which were almost absent in the original samples, were observed after ageing. This can be due to further reactions of peroxide bonds, the incipient oxidation of the unsaturated bonds (observed as a decrease in the peak at 1080 cm^{-1}) or as a combination of all these. A decrease in the vinyl absorption peaks (910 and 966 cm^{-1}) was observed, possibly as a result of thermal breakage of double bonds and their further reactions such as crosslinkings.

Mechanical properties. Thermogravimetric analysis (t.g.a.) thermograms of the original and the samples aged for 14 days were almost the same. For both, degradation started at about 360°C and 90% of the original weight was lost in the 360 to 500°C range.

From differential scanning calorimetry (d.s.c.) thermograms, glass transition temperature (T_g) values of the original and the aged samples were found to be -81 and -77°C, respectively. The increase in the T_g values can be explained by the decrease in the free volume resulting from the crosslink formation or entangled chains during the ageing process.

Examination of polymeric matrices. Mechanical properties of the HTPB–IPDI matrices prepared with aged HTPB were examined and the results are shown in *Figures 7* and *8*. As can be seen from the figures, the changes and the rate of these changes are lower at low temperatures. While the matrix aged at 50°C demonstrated almost no change in 1 week in elastic modulus and percentage elongation, the matrix aged at 100°C had a change from 0.21 to 0.48 MPa and from 170% to 115% in elastic modulus and percentage elongation, respectively. For all samples a decrease in elongation at break values and an increase in elastic modulus values were observed with the duration of ageing. These changes in mechanical properties can be explained by the formation of crosslinks (as implied by the increase in viscosity and molecular weight of HTPB) and the increase in the functional hydroxide groups caused by ageing because during matrix preparation, additional crosslinks are formed as a result of the reactions between the hydroxide groups of HTPB and isocyanate groups of IPDI.

Lifetime prediction. Absorption of thermal energy and thermal ageing trigger various reactions leading to

Table 1 Effects of thermal ageing at 100°C on hydroxyl functional groups of HTPB

Ageing time (days)	Functional end groups (% OH)
0	1.64
3	1.70
7	1.79
14	1.90
21	2.04
35	2.51

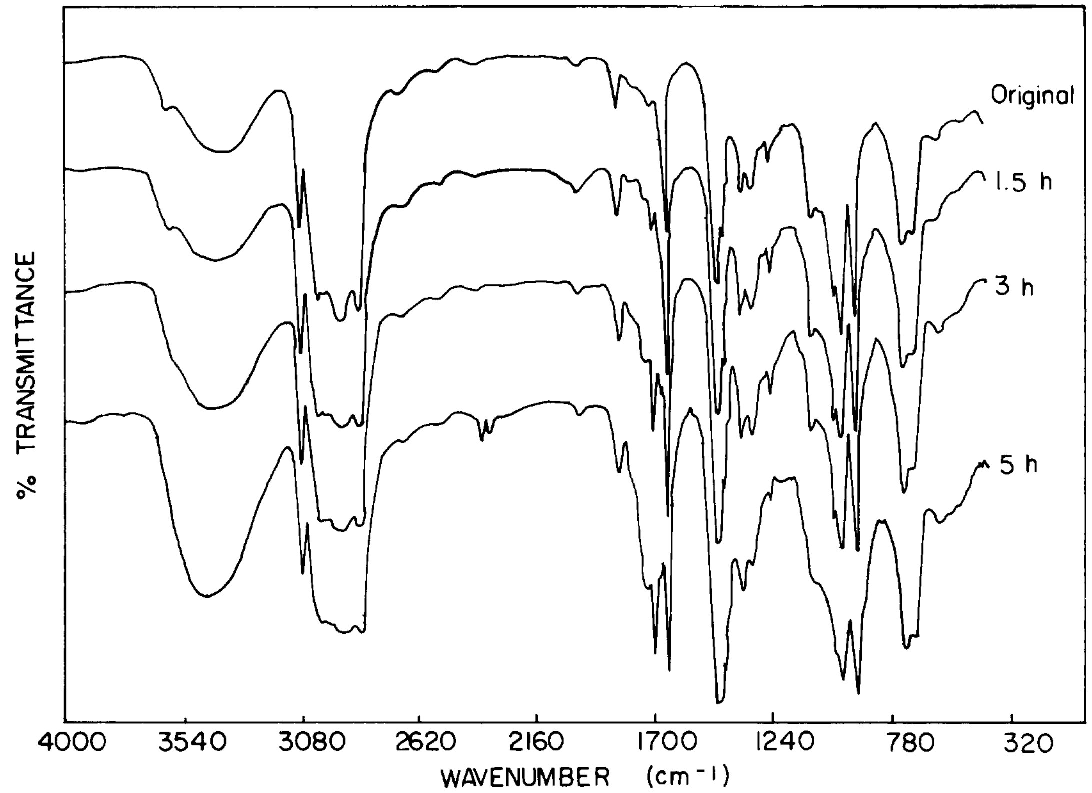

Figure 5 *FT*i.r. spectra of HTPB samples aged at 100°C

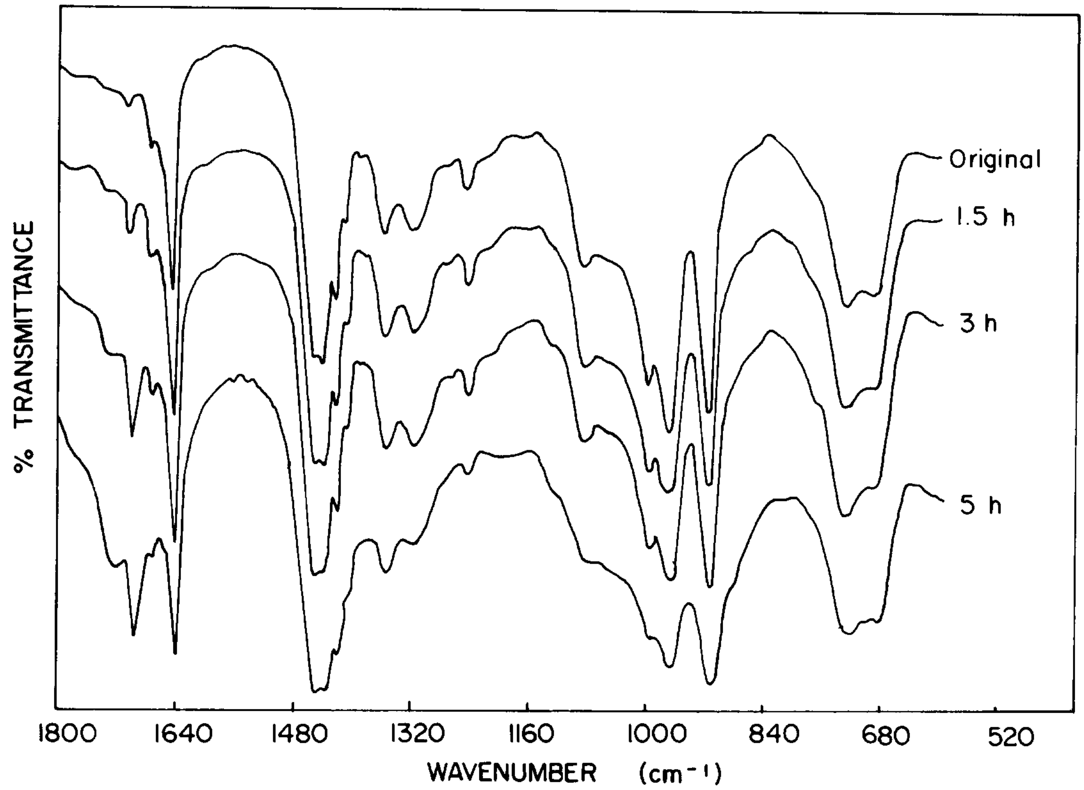

Figure 6 *FT*i.r. spectra of HTPB samples aged at 100°C (1800–520 cm^{-1} region)

molecular chain degradation causing physical ageing. On the other hand, an estimation of storage life is needed in order to define the duration in which the desired properties are retained. Generally a simplified form of an Arrhenius-type relation based on a time–temperature relation, is used for the prediction of lifetime. The time (t) required for a 50% deterioration in a physical property at various temperatures is used in this relation[18]:

$$t = t_0 \exp(E/RT)$$

where t is the lifetime, t_0 is the pre-exponential factor, E is the activation energy of the degradation process, T is the ageing temperature and R is the gas constant.

It is known that not all physical or mechanical

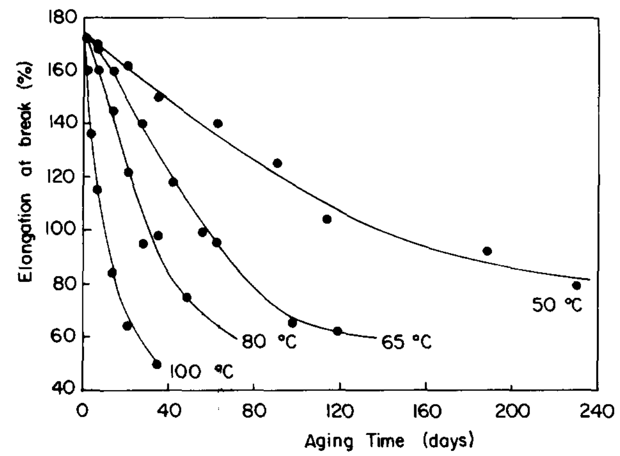

Figure 7 Effects of thermal ageing on elongation at break of HTPB–IPDI matrices

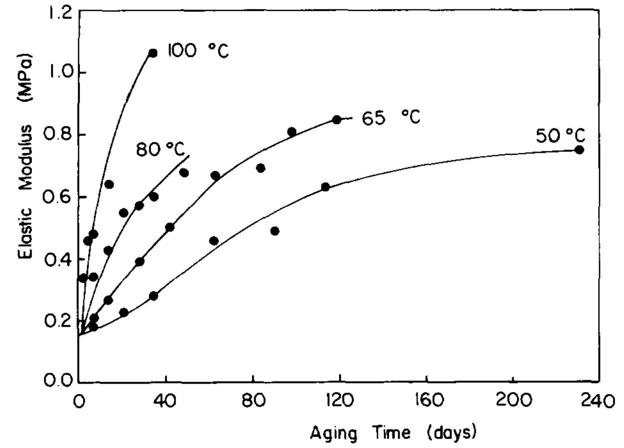

Figure 8 Effect of thermal ageing on elastic modulus of HTPB–IPDI matrices

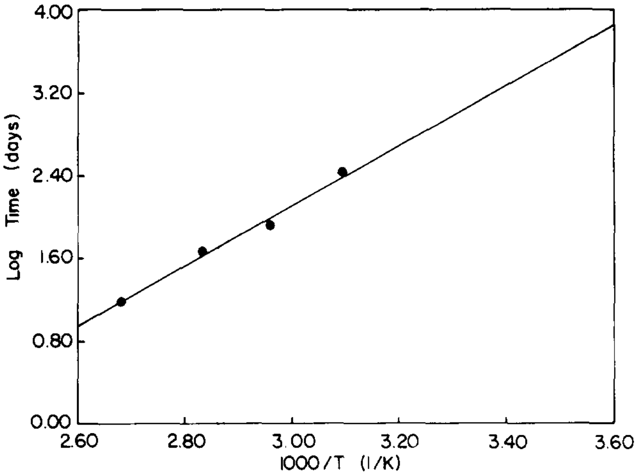

Figure 9 Lifetime prediction using elongation at break

Table 2 Ageing periods that correspond to reduction of elongation from 170 to 75%

	Ageing period (days)			
Property	50°C	65°C	80°C	100°C
Elastic modulus	195.0	87.0	56.0	12.3
Viscosity	205.0	52.7	14.6	9.1
Molecular weight	161.0	77.6	24.6	13.0

properties deteriorate with ageing or are sensitive to thermal degradation. Some properties may even improve with the effect of thermal energy. In this study, the value of percentage elongation at break, which is sensitive to ageing and shows a decrease, was chosen for the lifetime prediction. For the original sample, elongation at break was found to be 170%, and when this value decreased to 75% it was assumed to have reached the limit of usage. The time required to reach this value for each temperature was obtained from *Figure 8*, and the log time was plotted against the reciprocal of ageing temperature (*Figure 9*). The useful life of HTPB was predicted to be approximately 7 years from extrapolation to the normal storage temperature of 20°C.

The same approach was used in treating the other properties (e.g. elastic modulus, viscosity, molecular weight). The values for these properties which correspond to half of the ultimate elongation value (75% elongation), were obtained from the figures at four different ageing temperatures and the results are given in *Table 2*. The same type of Arrhenius plot was used and for all these given properties the lifetime was predicted to be about 7 years.

It can be thus concluded that the HTPB in this study, which is used as composite propellant binder, can be stored for 7 years at room temperature with its various properties maintained in the usable range.

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