VOL. 18, NO. 3, MAY-JUNE 1981

AIAA 80-1273R

HTPB Propellant Aging

A.G. Christiansen,* L.H. Layton,†, and R.L. Carpenter‡
Thiokol Corporation, Brigham City, Utah

Three HTPB propellants, varying in solids loading from 88% to 91%, were selected and developed for evaluation studies including aging. The 88%-solids propellant was verified to fit a previously developed aging model. The aging model has been further successfully applied to the measured mechanical-property aging data for the higher-solids propellants with excellent definition of behavior as well as HTPB propellants from other programs. The model has been used to predict long-time mechanical-property behavior from thermally accelerated tests and the results agree with 6 yr of measured aging data. The predicted failure properties can be used with motor requirements to determine service life for the grain of the motor system for a preselected margin of safety. Data are shown comparing the aging rate for the various composite propellants. Analysis of the aging results has provided a mathematical expression for the broad-spectrum aging behavior.

Introduction

A PROGRAM was initiated in 1972[1] to develop HTPB propellants for ballistic missile use. Five formulations were developed with solids loading ranging from 88 to 91% and burning rate ranging from 0.364 to 0.464 in./s. Each of the formulations was made in sufficient quantity to perform an aging study for a 5-yr period although only 8 months of aging were planned under the program. Three of the formulations were selected for continued-aging evaluation. A program was designed to utilize the available propellant in a 10-yr aging study.[2] A total of 6-yr aging has been completed, and the data reported and discussed in this paper are from this study.

In a separate 1-yr aging study[3] one of the three HTPB propellants—TP-H1139—was used to develop or confirm an existing aging model characteristic of the HTPB propellants. The aging model confirmed in this program has been used to predict long equivalent room-temperature aging times from thermally accelerated aging data. As real-time aging data became available, they were compared with the predicted results.

The aging model has also been successfully used to evaluate the results of the Longer Life SRAM propellant and to determine the equivalent room-temperature long-time behavior. Because this HTPB propellant is used in a major missile system, some of the results are included in this aging report.

Technical Discussion

Aging-Model Evaluation

It was shown for PBAN and CTPB propellants[4,5] that an understanding of the chemistry of aging is necessary to interpret the observed aging behavior. The techniques developed for these propellants were applied to the chemical-aging study for TP-H1139, an HTPB propellant. The study was directed toward evaluation of thermally accelerated aging without the added complications of humidity and mechanical load during aging. The propellant was cast in 0.5-gal cartons and cured at 135°F for 10 days. The cured propellant was aged at four temperatures: 75, 110, 135, and 150°F.

Presented as Paper 80-1273 at the AIAA/SAE/ASME 16th Joint Propulsion Conference, Hartford, Conn., June 30-July 2, 1980; submitted Aug. 25, 1980; revision received Feb. 9, 1981.

*Chemist, Wasatch Division.
†Supervision, Mechanical Properties Section.
‡Senior Mathematician, Mechanical Properties Section, Wasatch Division.

During the propellant cure and continuing into the aging period, chemical analyses were performed to determine the concentration of hydroxyl and isocyanate as a measure of the completion of the cure reaction. The concentration of isocyanate decreased and became less than a measurable amount during the cure time (as shown in Fig. 1) for three different cure temperatures. The propellant was formulated with a greater equivalent amount of hydroxyl than isocyanate, and the concentration of hydroxyl remaining at the end of cure and throughout the aging period was approximately 23 milliequivalents per 100 g of propellant for all curing and aging temperatures. These data strongly indicate that the hydroxyl-isocyanate reaction that takes place during cure is completed at the end of cure and does not contribute to the aging changes.

As crosslinks are formed in an otherwise linear polymer, the material becomes insoluble in solvents although it swells to the limit of the crosslinking network. Additional crosslinks produce more insoluble (gel) and less soluble (sol) polymer. Therefore, the measure of the amount of gel has been used as an indirect measure of the amount of crosslinking. Gel data show that crosslinking is directly related to the temperature of aging as depicted in Fig. 2. Since the curing reaction has ceased, it is assumed that the observed aging effect is due to reactions at sites of unsaturation in the polymer chain as found in the PBAN and CTPB propellants.

With the information that the HTPB polymer changes through the same chemical reaction during aging as the binders of other composite solid propellants, the same aging model is expected to define the aging trend. The maximum uniaxial tensile stress shown in Fig. 3 indicates that an ex-

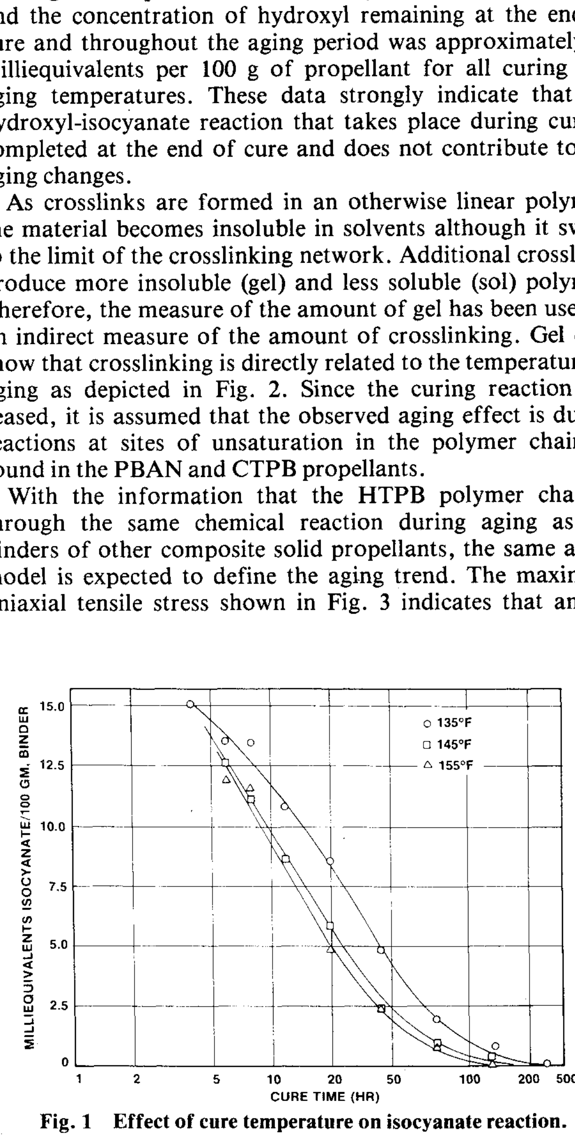

Fig. 1 Effect of cure temperature on isocyanate reaction.

cellent fit of the data is obtained when compared with the aging model:

$$P = P_0 + k \log t / t_0$$

where P is the mechanical property at any arbitrary age time, P_0 is the mechanical property at the end of cure, k is the rate of change of the property, t is the aging time, and t_0 is the time at end of cure. Other properties were equally as well described in similar data plots, and the temperature dependence is in agreement with the Arrhenius equation for the rate constant.

A direct correlation was achieved between the property and the change in percent gel at common age periods as shown in Fig. 4. The results for all aging temperatures fall on the same line, indicating that the aging temperature caused a different rate of chemical reaction but did not change the chemical-reaction mechanism.

A prediction was made using the model equation for TP-H1139 propellant. With time expressed in weeks, the value of k was found to be 9 psi per logarithmic decade of time at the 77°F aging condition for the maximum stress parameter. The 10-yr extrapolation is shown in Fig. 5. As the aging data became available, they were plotted on the extrapolated curve as shown by the solid points. The results to 6 yr agree extremely well with the predicted maximum stress. If a new value of k is determined after 6 yr, it is found to be 10 psi instead of the 9 psi per logarithmic decade of time, or an error of less than 3 psi in the 10-yr prediction.

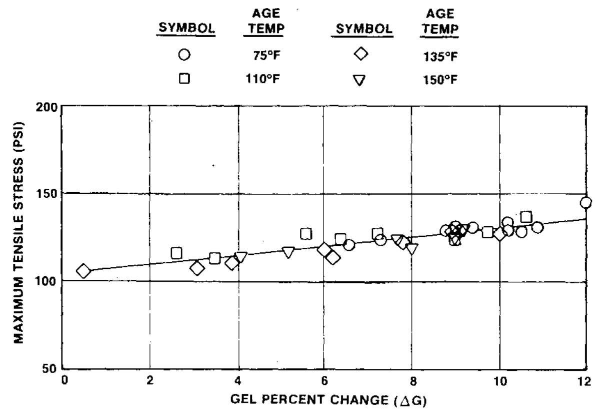

Fig. 4 Maximum tensile stress as a function of age-induced change in gel, 75°F test temperature.

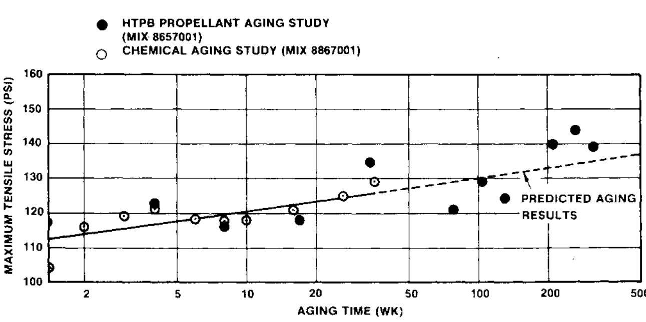

Fig. 5 Effect of aging at 77°F on maximum uniaxial tensile stress: a comparison of predicted with measured data for TP-H1139 propellant.

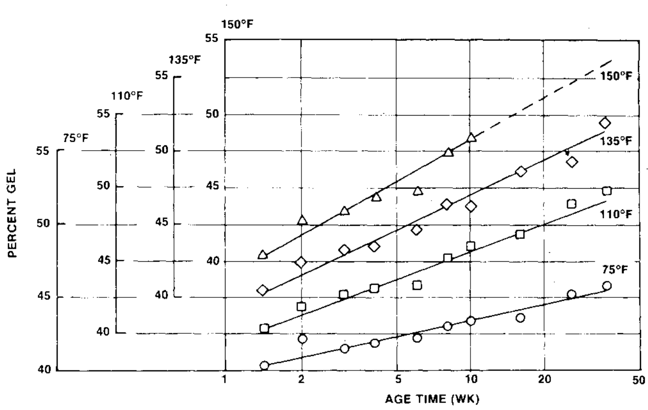

Fig. 2 Aging effect on percent gel in the binder, TP-H1139 propellant.

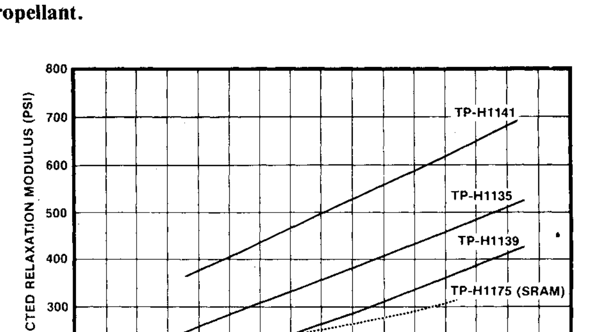

Fig. 6 Comparison of relaxation modulus aging effects. Propellants were aged at 77°F and ambient pressure (modulus taken at 1000-s test time from 3% strain data).

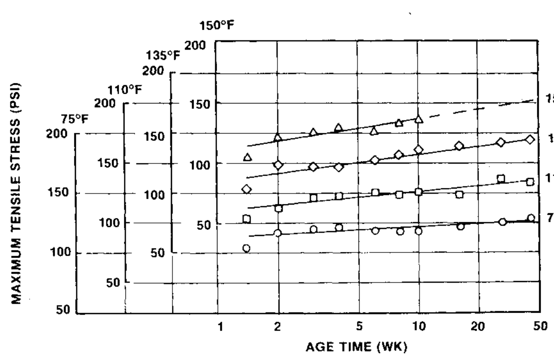

Fig. 3 Aging effect on maximum tensile stress, 75°F test temperature.

Table 1 Comparison of aging rates for composite propellants

	Aging rates[a] at 77°F					
Propellant	TP-H1011	ANB-3066	TP-H1135	TP-H1139	TP-H1141	TP-H1175
Binder type	PBAN	CTPB	HTPB	HTPB	HTPB	HTPB
Bonding agent	None	None	HX-752	HX-752	HX-752	HX-752 HEMAP
Maximum tensile stress (psi)	15	20	17	9	14	17
Strain at maximum stress, %	−5.0	−4.0	−3.5	−2.5	−1.0	+1.0
Relaxation modulus (psi)	110	115	85	80	95	55

[a] The tabulated values are a change in the indicated property per logarithmic decade of time in weeks.

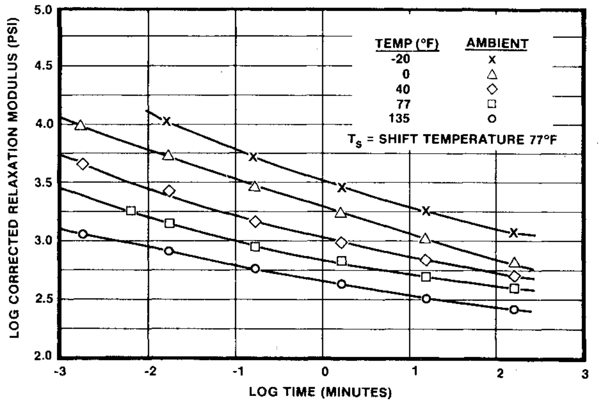

Fig. 7 Relaxation modulus curves for TP-H1135 propellant, aged 72 months at 77°F and tested at 3% strain; temperatures indicated.

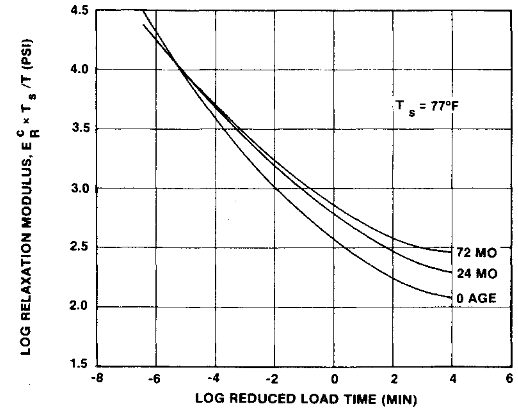

Fig. 10 Master relaxation modulus vs reduced time showing effect of age: TP-H1135 propellant, aged at 77°F.

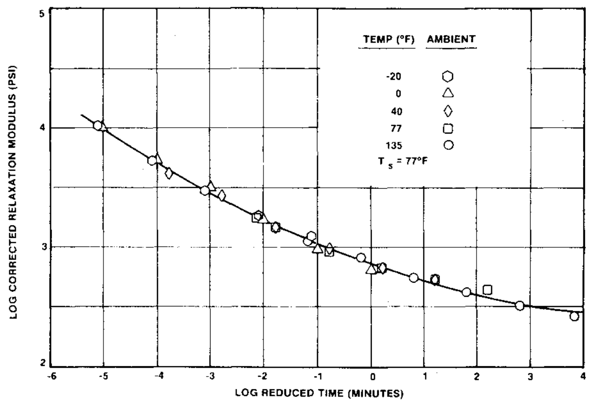

Fig. 8 Relaxation modulus master curve for TP-H1135 propellant, mix 8577001, aged 72 months at 77°FF; tested at 3% strain and ambient.

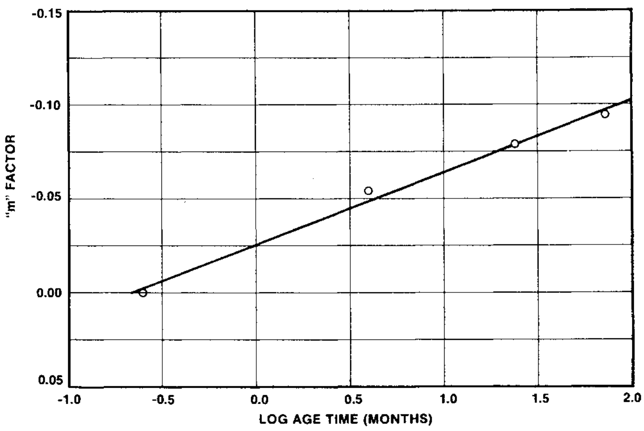

Fig. 11 *m* factor vs log age time for TP-H1135 propellant.

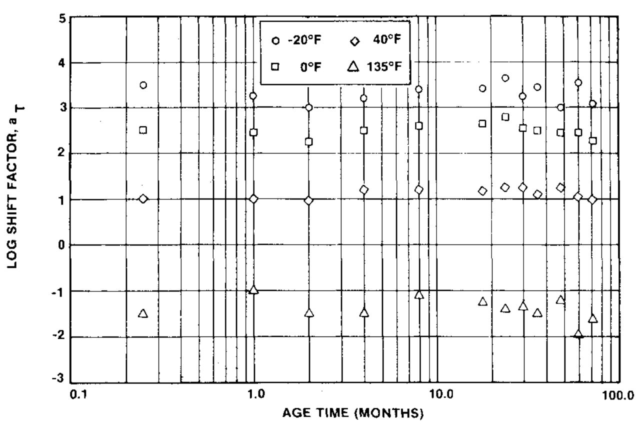

Fig. 9 Relaxation modulus shift factors as a function of age time for TP-H1135 propellant, aged at 77°F.

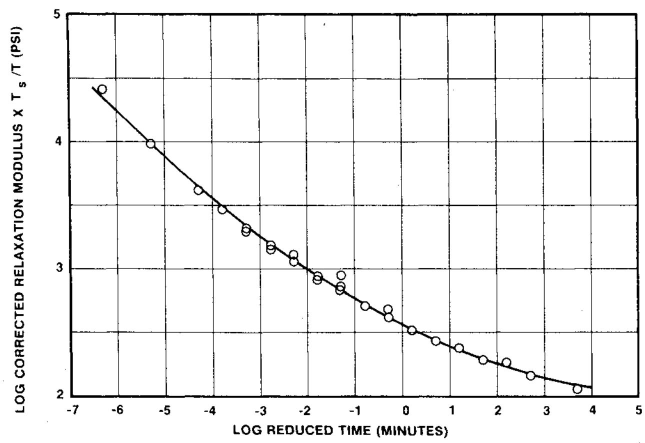

Fig. 12 Quadratic fit of relaxation modulus master curve for TP-H1135 propellant at zero-age time.

Comparison of HTPB Propellants

The three HTPB propellants that were aged in the 6-yr study were TP-H1135 (90% solids), TP-H1139 (88% solids), and TP-H1141 (91% solids). These propellants represent some of the important HTPB propellants being used and considered for use in current missile systems. An important observation of HTPB propellants is that the change in mechanical properties with age is less than that for the PBAN and CTPB propellants (Table 1). Since the chemical reaction for aging appears to be the same for all of these composite propellants, it causes one to wonder why a difference in aging rate exists. All HTPB propellants have been formulated with a chemical bonding agent that is designed to coat the ammonium perchlorate oxidizer. Since the AP is responsible for the aging reaction[4] and the AP surface is coated in HTPB propellants, it is reasonable to expect that the coating has reduced the aging rate.

The aging trends of the relaxation modulus for the three HTPB propellants are shown in Fig. 6. The slope of the three lines is surprisingly similar although they are displaced by an amount equal to the difference in initial relaxation modulus. Note that the increasing order of the modulus curves corresponds to the increasing order of the solids loading of the three propellants. Also plotted on this figure is the aging result of the SRAM propellant TP-H1175 (86% solids, HTPB). It is apparent that this propellant exhibits a reduced aging effect from that of the other three propellants. An improved bonding agent was used with this propellant, and it has apparently caused the reduced aging rate.

The relaxation modulus was measured at several test temperatures at each aging period during the 6 yr for each of the three propellants. The data for TP-H1135 were plotted and are shown in Fig. 7. The results shown in this plot have been empirically shifted to produce the master relaxation curve shown in Fig. 8. The shift factors to accomplish the reduced-time master curves are very similar, and for any one propellant the shift factor remains the same for other properties such as maximum stress, strain at maximum stress, and modulus.

The shift factors have been plotted as a function of aging time, and the results for TP-H1135 propellant are shown in Fig. 9. There is a small variation in value from one test period to the next, but the net effect is no change during the aging period. This indicates that the change in modulus due to increased crosslinking during aging has no effect on the shift factor required to provide the master curves and that the time-temperature superposition principle reasonably defines the relationship between results obtained at different loading rates and temperatures.

One last comparison is made by observing the master relaxation modulus curves at various aging times. It can be seen in Fig. 10 that the relaxation curves are rotated counterclockwise with increased aging time, producing the effect of no aging change at the short-time end of the curves and increased modulus at the long-time end of the curves. Indeed it is possible for a crossover to occur such that opposite aging effects are produced. This has been observed before with other composite solid propellants, and it is comforting that all three propellants exhibit the same behavior.

Predicting Relaxation Modulus

It was noted that any point on an age-time relaxation-modulus master curve (E_t) can be made to correspond to a point with the same relaxation modulus on the zero time curve (E_0) by a time shift. In an attempt to predict relaxation moduli, an operator M_t was sought such that M_t would operate on the zero-time curve and transform it into the age-time curve corresponding to age-time t; i.e., $M_tE_0=E_t$. Physically, the operator M_t was thought of as corresponding to the aging process of the propellant: At any age time, the propellant relaxes slower (due to increased crosslinking during aging) than it would at zero-age time. This suggests that M_t should have the effect of a "time contractor": $E_t(\xi)=M_tE_0(\xi)=E_0(\mu(t,\xi))$, where μ is the time contractor function, ξ is reduced time, and t is the age time. In essence, the function μ_t slows down the zero-age-time relaxation clock, transforming the zero-time curve into the age-time curve.

The function μ_t (which defines the operator M_t) must possess three characteristics (besides fitting the empirical data): 1) It must reduce to the zero-age-time expression at zero-age time $[\mu_t(0,\xi)=\xi]$. 2) Since relaxation modulus curves at various age times (for a propellant) tend to converge at some reduced time (ξ_0), the age-time expression μ_t must also show convergence for all age times; i.e., $\mu_t(t,\xi_0)=\xi_0$. 3) The age-time curves must be dependent upon one variable—age time. Although a number of expressions will meet these three criteria, the one chosen—because of simplicity—is $\mu_t(t,\xi)=m_t(\xi-\xi_0)^P+\xi$, where m_t is the aging factor corresponding to age-time t, ξ_0 is the convergence point, and P is a constant determined by the shape of the relaxation curve. It should be noted that at zero-age time, m_0 must be equal to zero since $\mu_t(0,\xi)=\xi$. Note also that as ξ approaches ξ_0, $\xi-\xi_0$ approaches zero and $m_t(\xi-\xi_0)^P+\xi$

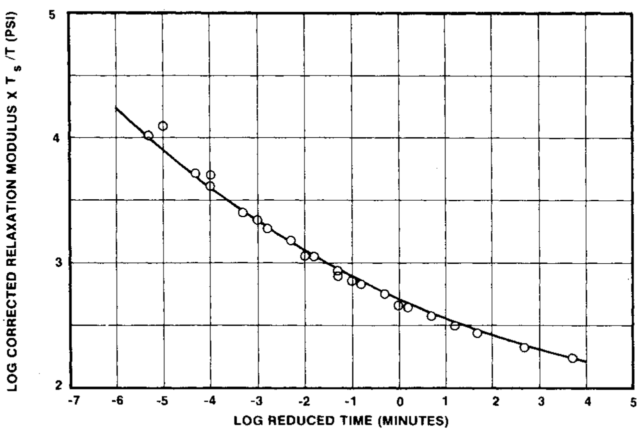

Fig. 13 Predicted relaxation modulus master curve for TP-H1135 at 4-months age time.

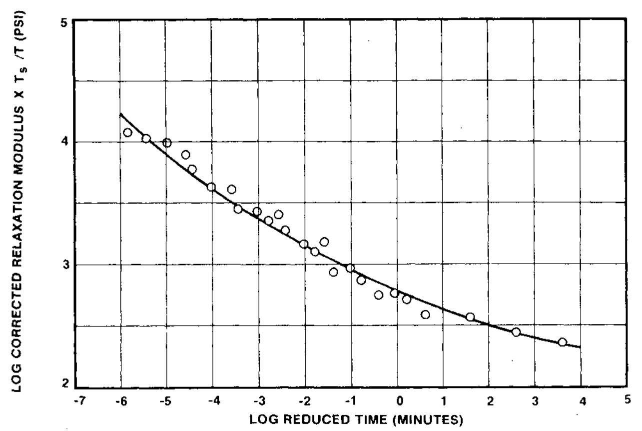

Fig. 14 Predicted relaxation modulus master curve for TP-H1135 propellant at 24-months age time.

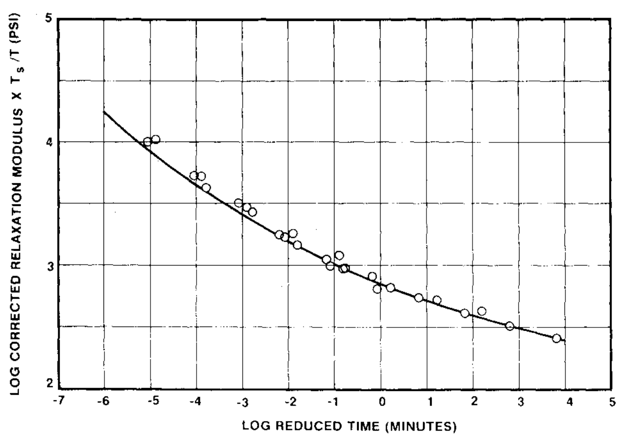

Fig. 15 Predicted relaxation modulus master curve for TP-H1135 propellant at 72-months age time.

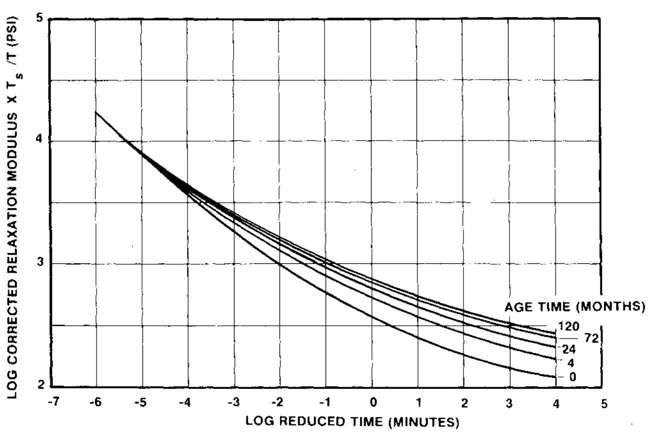

Fig. 16 Predicted relaxation modulus master curve.

approaches ξ_0, which results in convergence of all age-time master curves at time ξ_0.

The age-time variable m_t can be determined empirically by equating an age-time-curve expression to the M_t-operated zero-time-curve expression at some ξ. By evaluating the m factor at various age times, a plot of the m factor vs age time can be produced. (As is the case with gel fraction, one should expect the m factor to be linearly related to the log age time since it should also be a function of crosslink density.)

The power P is simply the result of curve fitting through an iterative process.

An interesting feature (and an advantage) of this concept of time-change modeling is that the expression $E_t = E_0(m_t(\xi - \xi_0)^P + \xi)$ is independent of the function E_0 used to fit the master curves.

As an illustration of this predictive technique, the zero-time curve of TP-H1135 was fit using a quadratic for the function E_0. The value of P was determined to be 3/2, and the m factor was determined for the three age-time curves at log $\xi = 4$. (-6 was assigned to log ξ_0 since the master curves seem to cross or converge at that reduced time.) The m factors were plotted against log age time and are presented in Fig. 11. As was expected, the resulting plot is linear with log age time. Using these values for m_t and 3/2 for P, the resulting age-time curves were obtained and are presented in Figs. 12-15. The actual age-time data are superimposed on the resulting curves. A predicted master curve for 10-yr age time is presented in Fig. 16.

The inadequacy of the quadratic function (especially at the short-time end of the curve) to precisely fit the zero-time data is at least partially responsible for introducing error in the age-time curves in the same (short-time) region. If ξ_0 is not correctly determined, additional error (again, in the short-time region) will also be introduced.

Summary and Conclusions

An aging study has been performed to evaluate and characterize the aging behavior of HTPB propellants. It has been shown that HTPB propellants obey the Layton aging law as determined for the PBAN and CTPB composite propellants. The observed changes in mechanical properties are due to a chemical reaction occurring between the ammonium perchlorate and the polymeric binder. A direct correlation between the change in chemical crosslinks (determined from sol-gel measurements) and the mechanical properties supports the thesis that observed aging changes are caused by chemical reaction. Because the rate of chemical reaction is controlled by a diffusion process, normal chemical reaction kinetics do not apply.

The determination of mechanical properties at long aging times from short-time thermally accelerated aging data has been verified with 6-yr aging results. The rates of change of mechanical properties for the three HTPB propellants evaluated are very similar and are less than for the PBAN and CTPB propellants. The rate of change of mechanical properties of the SRAM propellant is less than the three HTPB propellants with which it is compared. Since the main difference is the bonding agent used, it is considered that a good bonding agent may also be an aging inhibitor.

The factor determined to provide the temperature shift of mechanical properties data, a_T, is not affected by aging. The master relaxation modulus curves, produced by shifting the results obtained at several test temperatures to a standard temperature, show that a rotation occurs during aging such that the aging rate becomes test-temperature and response-time dependent.

A method was devised for predicting relaxation moduli by operating on the zero-time relaxation master-curve equation and time shifting it to the desired age time. The method duplicates the age-related rotation (as seen empirically) of the master curves.

Acknowledgment

Work on this project was performed under AFRPL Contract F04611-75-C-004.

References

[1]Thompson, G. and Day, E.E., "Development of HTPB Propellant for Ballistic Missiles," Final Report, AFRPL-TR-75-23, May 1975.

[2]Christiansen, A.G., "Aging of HTPB Propellants," Final Technical Report, AFRPL-TR-79-88, Sept. 1979.

[3]Layton, L.H., "Chemical Structural Aging Studies on an HTPB Propellant," Final Technical Report, AFRPL-TR-75-13, April 1975.

[4]Layton, L.H., "Chemical Structural Aging," Final Technical Report, AFRPL-TR-74-77, Oct. 1974.

[5]Layton, L.H., "Chemical Aging Studies on ANB-3066 and TP-H1011 Propellants," Final Technical Report, AFRPL-TR-74-16, June 1974.