

# Dynamic Mechanical Study on the Thermal Aging of a Hydroxyl-Terminated Polybutadiene-Based Energetic Composite

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**ABSTRACT:** In an attempt to determine the aging behavior of hydroxyl-terminated polybutadiene-based composite solid propellants, viscoelastic measurements were used to study the effect of thermal aging on this kind of energetic material. Accelerated-aging tests at 40, 60, and 80°C were performed for 5000 h. The changes in the dynamic mechanical properties, including the storage modulus ( $E'$ ) and loss factor or damping efficiency ( $\tan \delta$ ), with time and temperature were measured to determine the aging rate and likely mechanisms occurring during this process. An Arrhenius analysis based on the determination of relative rate constants showed a linear tendency from  $\tan \delta$  values, whereas

a significant curvature was found from  $E'$  values. In addition, the effects of external (surface) and internal (core) sampling in the intensification of the aging process were analyzed. The results confirmed dynamic mechanical analysis as a powerful tool for determining the aging characteristics of composite propellants. This technique allows the evaluation of the actual state of a propellant grain with a small sample and a straightforward measurement. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2397–2405, 2003

**Key words:** aging; composites; polybutadiene

## INTRODUCTION

Composite propellants are highly particle-filled elastomers used in solid rocket motors. These propellants are made by the insertion of a finely divided solid oxidizing agent into a plastic, resinous, or elastomeric matrix. The matrix material usually provides the fuel for the combustion reaction, although solid reducing agents are frequently included in the compositions. Composite solid propellants based on hydroxyl-terminated polybutadiene (HTPB) have become the workhorse propellants in present-day solid rocket motors worldwide.<sup>1,2</sup> The urethane network obtained by the curing of HTPB with a suitable diisocyanate provides a matrix for the inorganic oxidizer and metallic fuel, which are dispersed in the propellant grain.

Because solid propellants are composed of a large percentage of energetic ingredients, it is expected that prolonged storage might result in deterioration. Chemical aging may be the result of thermal, oxidative, or hydrolytic reactions. The changes observed may include softening, hardening, swelling, discoloration, and gas evolution. Various ingredients may interact with one another or with the atmosphere to produce irreversible changes, which can seriously affect both ballistic and mechanical properties.<sup>3</sup>

Although many chemical and physical analysis techniques have been used in aging studies of solid propellants, the most applied method has been the measurement of changes in some prominent mechanical properties such as Young's modulus or the tensile strength. Although a moderate environment may have little effect on the service life of a propellant over a short period of time, extremes of temperature and temperature cycling may have a significant effect in a much shorter period of time. The most common method of evaluating a propellant's aging characteristic is accelerated-aging testing. Propellant grains are aged at a range of temperatures, and mechanical properties are measured during the aging period through tensile tests on samples cut from propellant blocks or grains. In these traditional aging programs, propellant samples are tested to failure. The change rate of a mechanical property is then determined for each temperature. Under the assumption that identical aging mechanisms are activated at the storage temperatures, the aging rate constant can be fit through an Arrhenius equation (where  $k$  is the aging rate constant, factor  $A$  is the pre-exponential constant,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature):

$$k = Ae^{(-E_a/RT)} \quad (1)$$

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nisms that are not present under normal operating conditions. The aging processes have been well analyzed by the Layton model.<sup>4,5</sup> Mechanical properties, such as hardness, maximum stress, strain, and Young's modulus, change with the aging time according to the Layton equation:

$$P = P_0 + k \ln(t/t_0) \quad (2)$$

where  $P$  is the property at any time of aging,  $P_0$  is the property at the end of curing (unaged),  $k$  is the rate of change of the property,  $t$  is the aging time, and  $t_0$  is the time at the end of curing. Therefore, the aging behavior has been well described by the Layton model in combination with the Arrhenius description for the acceleration factor. In general, the mathematical description of the degradation of energetic materials by kinetic models can be highly complex because of the competition of various reactions with different kinetic orders and autocatalysis.<sup>6</sup> The traditional aging programs present a series of drawbacks because a large amount of material is required for a complete characterization, and this results in high material, storage, and handling costs.

The advantages of dynamic testing for the characterization of these energetic materials have been recognized, and so this technique has been applied in the field of composite solid propellants.<sup>7-18</sup> However, despite the importance of HTPB-based propellants for rocket motor engines and the obvious concern about property changes due to aging, very few comprehensive investigations appear to be available in the open literature about the use of dynamic testing for determining the aging behavior of these specific materials.<sup>12-18</sup> In addition, to our knowledge there is only one article in which aging kinetic data obtained from this technique are reported.<sup>12</sup> By the testing of samples at low strains with this procedure, the samples can be repeatedly tested throughout the entire aging program. Although the failure properties of the material are not attained with this approach, it appears that the small strain response properties are sufficient to provide an adequate aging characterization and service life assessment. Another very important aspect is that with this technique, small specimens obtained directly from rocket motors or other specimens of unusual geometry can be tested that cannot normally be tested by traditional methods.

The main objective of this study is to broaden our knowledge of applying dynamic mechanical analysis to the aging study of HTPB propellants. The kinetic data obtained, from the variation of both the storage modulus ( $E'$ ) and loss factor or damping efficiency ( $\tan \delta$ ), through different accelerated thermal aging programs have been analyzed according to Arrhenius methodology. In addition, the superficial effect in the aging processes has been examined. The new results

presented here demonstrate the considerable reproducibility (based on the excellent agreement with literature data) and versatility of this technique for providing better predictions of the service life.

## EXPERIMENTAL

### Materials

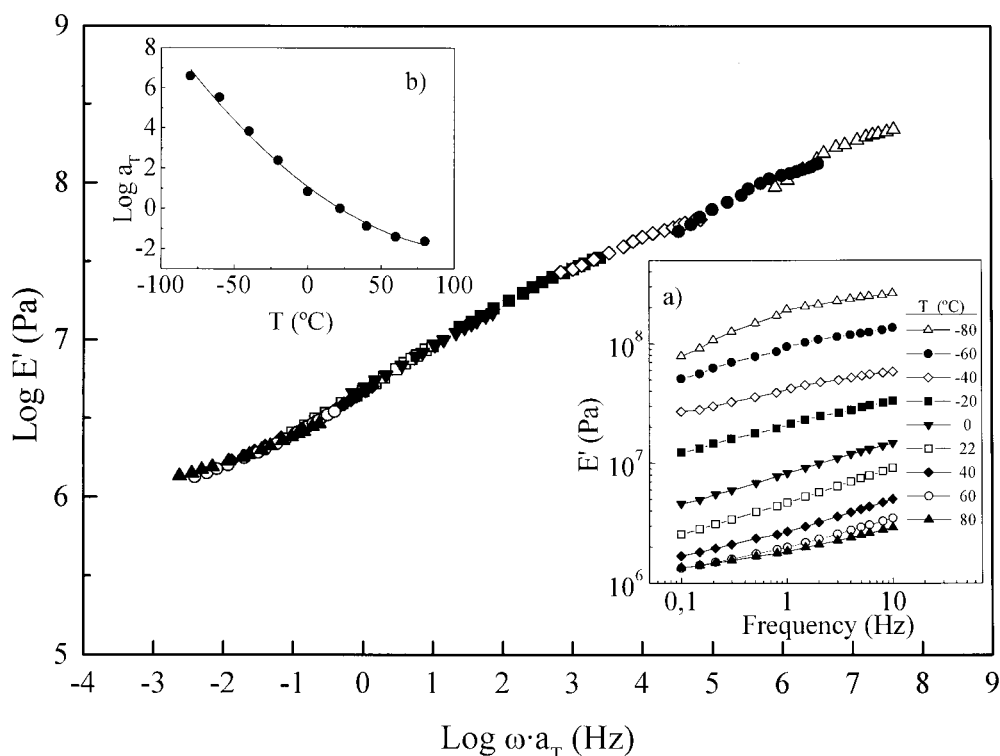
The HTPB-based propellant selected for this study contained 88% solid loading, 68% ammonium perchlorate (an oxidizer, with two particle sizes, 200 and 6  $\mu\text{m}$ ; SNPE, Saint Medard En Jalles, France), 20% 7  $\mu\text{m}$  aluminum (ECKA, Fürth, Germany), and 12% of a binder. The binder composition involved 9.2% HTPB (R-45M, Elf Atochem, Paris, France), 2% of a plasticizer (dioctyl adipate; BASF, Ludwigshafen am Rhein, Germany), a small percentage of a bifunctional aziridine, which was used as a bond (adhesion) promoter (0.2%; Dynamar HX-752, 3M, St. Paul, MN), and 0.05% of an antioxidant (Irganox 565, Ciba-Geigy, Barcelona, Spain). The cure reaction was between the hydroxyl groups of the prepolymer and the isocyanate groups of the curing agent, isophorone diisocyanate (0.55%; Hüls Española S.A., Barcelona, Spain). The formulation was prepared in a vertical mixer (IKA-HKV5 Planetron, Staufen, Germany) and cured 10 days at 60°C. More detailed information about the composition and the preparation process is given elsewhere.<sup>19</sup>

### Accelerated-aging experiments

Thermal aging programs on propellant blocks were carried out in temperature-controlled ( $\pm 1^\circ\text{C}$ ) commercial air-circulating aging ovens (A.S.L., Derby, UK, and Heraeus, Hanau, Germany) under ambient atmospheric conditions. The propellant samples were aged for over 5000 h at 40, 60, and 80°C. Dynamic mechanical properties were periodically measured during the aging period. For the observation of possible changes in the mechanical properties between different areas from the propellant blocks, both surface (external) and core (internal) propellant samples were extracted and tested.

### Dynamic mechanical measurements

All dynamic mechanical measurements were carried out in a Perkin Elmer DMA-7 analyzer (Norwalk, CT). A liquid-nitrogen cooling accessory was used for sub-ambient operations. The measuring system was a parallel plate 5 mm in diameter. Propellant samples used in this study were prepared in the form of rectangular bars (6 mm  $\times$  8 mm  $\times$  2 mm) and were tested in a compression mode. Therefore, the measurements were performed at room temperature by the subject-



**Figure 1** Log  $E'$  of an unaged HTPB propellant displayed as a function of  $\log \omega a_T$ . For the master curve, the reference temperature  $T_0$  is 22°C. Inset a shows isothermal  $E'$  values as a function of frequency; inset b shows the temperature-dependent shift factors  $a_T$  used for superposing the data.

tion of the samples to oscillatory frequencies of 0.01–50 Hz and low strains. Dynamic mechanical properties were also determined by the measurement of the viscoelastic dissipation as a function of temperature. The temperature range studied was  $-100$  to  $100^\circ\text{C}$ , the heating rate was  $2^\circ\text{C}/\text{min}$ , and the single frequency point of 1 Hz was chosen. The variation in the obtained results by the repetition of an experiment under identical conditions was less than 10%. In all cases, three specimens were tested for each condition of time and temperature, and average values are reported.

## RESULTS AND DISCUSSION

### Viscoelastic spectrum

Before an aging study, a precise knowledge of the dynamic mechanical behavior of the composite material is extremely important. However, the mechanical properties of these propellants (like polymeric solids) depend strongly on the time, temperature, loading procedure, and loading history.<sup>1</sup> To fully describe the mechanical properties of a propellant in a particular mode, we must perform a set of experiments covering all the time–temperature space experimentally accessible. These data can then be numerically and graphically collated and used as a description of the material.

An example of the small deformation response properties of the HTPB propellant is presented in Figure 1(a); a strain amplitude of 0.2% was used. This plot shows the effect of temperature and frequency on  $E'$ . Data were collected over 2 decades of logarithmic frequency and at temperatures ranging from  $-80$  to  $80^\circ\text{C}$ . Through isothermal variations of  $E'$  versus the frequency, the typical behavior of the composite materials has been observed.<sup>11</sup> The curves at the highest temperature indicate an equilibrium modulus of 1.8 MPa, and the curves at the lowest temperatures indicate a maximum or glassy modulus of 200 MPa.  $E'$  increases in a regular fashion with increasing frequency or decreasing temperature, suggesting that the time–temperature superposition of these data may be possible. In this figure is shown the master frequency curve obtained from the different isotherms by a shift operation in the horizontal axis toward the reference curve, which is that at  $22^\circ\text{C}$  ( $T_0$ ). The horizontal shift factors ( $a_T$ ) used to superpose the  $E'$  data are represented in inset b and are described with the Williams–Landel–Ferry equation.<sup>20</sup> In our case, this curve does not show any better fit with the introduction of  $T_0/T$ , and so this factor is omitted. In a strict sense, the frequency–temperature reduction performed can be questionable because of the thermorheological complexity of the material under study.<sup>9,10</sup> In fact, the

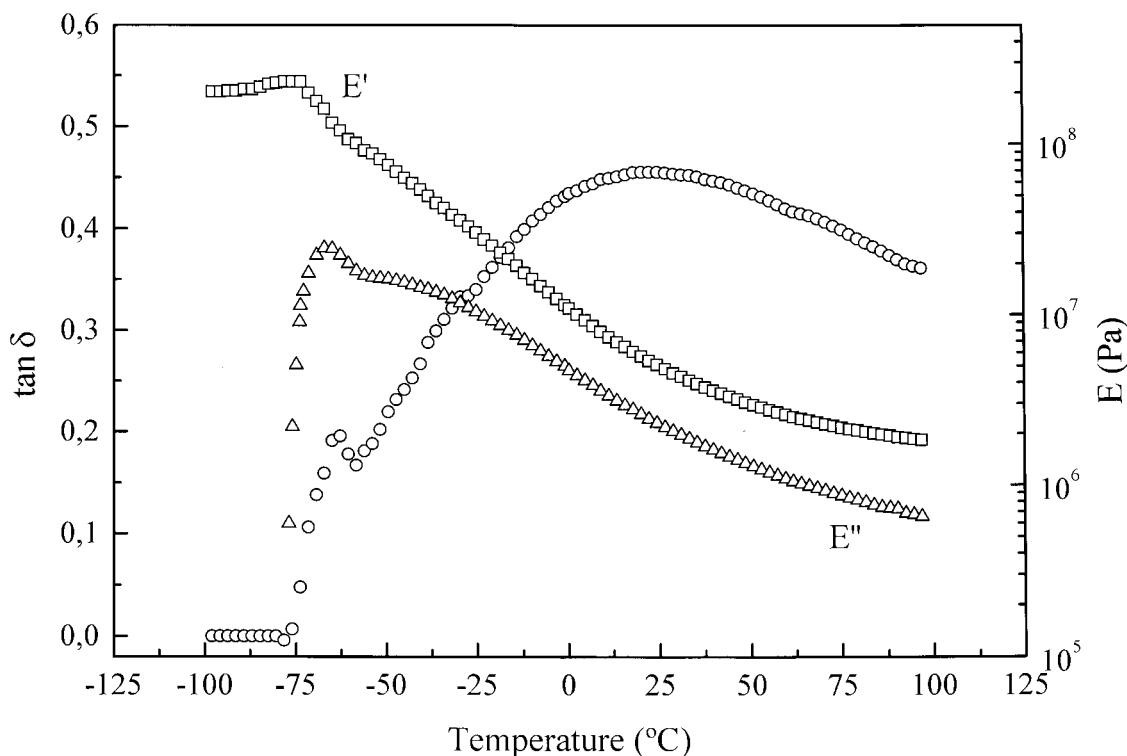


Figure 2  $E'$ ,  $E''$ , and  $\tan \delta$  of an unaged HTPB propellant as a function of temperature at a frequency of 1 Hz.

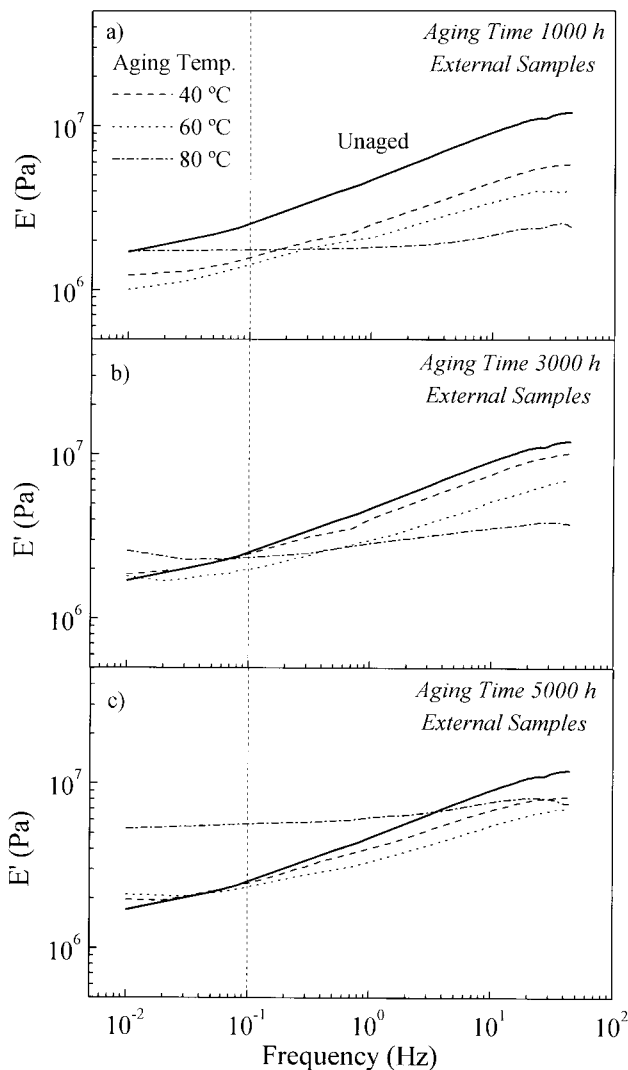
temperature might change the strength of filler–filler and filler–matrix interactions, and so decreasing the temperature could not be equivalent to increasing the frequency. Note the worse superposition of  $E'$  data at lower temperatures and frequencies.

In Figure 2, the  $E'$ , loss modulus ( $E''$ ), and  $\tan \delta$  values for an unaged sample of the HTPB propellant are shown as a function of temperature at a frequency of 1 Hz. Two maxima in the values of  $\tan \delta$  can be observed. At this point, it is necessary to make certain considerations. On the one hand, the segregation of hard and soft segments and the expected formation of domain structures for this kind of polymer have to be taken into account. The morphology and properties of the HTPB containing polyurethane elastomers have been the subjects of a number of publications.<sup>21–25</sup> Their morphological features and transition behavior have been examined as a function of the chemical structure, composition, and processing conditions. It has been found that the glass-transition temperature ( $T_g$ ) of soft-segment regions is independent of the hard-segment content and is very close to that of the original HTPB.<sup>25</sup> The unusual transition observed at higher temperatures is related to the hard-segment regions. On the other hand, in composite materials there are numerous cases in which fillers increase the damping, probably because of the introduction of new damping mechanisms<sup>26</sup> that are not present in the pure polymer (particle–particle friction, in which particles touch one another as in weak agglomerates;

particle–polymer friction, in which there is essentially no adhesion at the interface; and excess damping in the polymer near the interface due to induced thermal stresses or changes in the polymer conformation or morphology). Therefore, the first peak at  $-65^\circ\text{C}$  is determined to be  $T_g$  of the propellant (soft-segment region). At temperatures below  $T_g$ , the damping can be small, and nearly all the energy stored in deforming the material is quickly recovered when the stress is removed because molecular slipping and other motions are frozen in. The widespread transition around  $22^\circ\text{C}$  can possibly be attributed to short hard-segment units, although others damping mechanisms, which have been related to an interface of the polymer weakly adsorbed on the surfaces of the filler particles<sup>9</sup> (ammonium perchlorate), may also be present. Its origin is still not clear, and it is the object of further investigations.

### Propellant aging

Accelerated-aging tests are performed to obtain information about aging characteristics in a relatively short period. Chemical and physical aging processes can be accelerated by the storage temperature of the propellant being increased. By the performance of accelerated-aging tests at a number of temperatures, predictions can be made about the long-term behavior under nominal operating conditions.

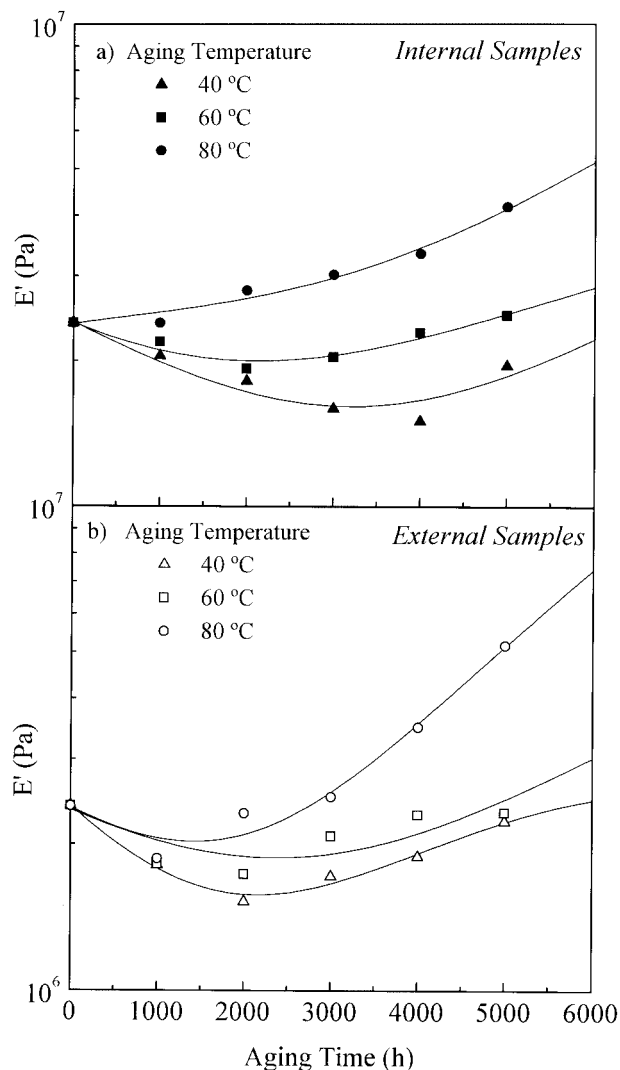


**Figure 3**  $E'$  as a function of frequency for propellant samples (external) aged at 40, 60, and 80°C after (a) 1000, (b) 3000, and (c) 5000 h of aging.

Accelerated-aging tests at moderate temperatures of 40, 60, and 80°C have been performed for a total time period of 5000 h. A very important factor to consider in any aging study is the effect of external (surface) and internal (core) sampling in the intensification of this process. This work has intensively attended this effect by a sampling of different zones of the propellant blocks. Figure 3 shows the evolution of  $E'$ , measured at different frequencies and at room temperature, with the aging temperature and time for external samples of propellant. Several important features of the aging spectrum of this material can be seen. After 1000 h [Fig. 3(a)], there is very little difference in the shapes of the curves of the samples aged at 40 and 60°C and the unaged samples, and a vertical shift to lower moduli can be observed. However, the sample aged at 80°C shows practically a constant value of the modulus over the wide frequency range. This decrease

in  $E'$  is proportional to the aging temperature. Therefore, the lowest modulus value is found for 80°C, and this indicates that during this time the propellant samples have undergone a softening. After 3000 h of aging [Fig. 3(b)], at the highest temperature, an increase in the modulus is only observed in the zone of low frequencies. The samples aged at 40 and 60°C present the same behavior mentioned previously. After 5000 h [Fig. 3(c)], the dynamic moduli of the propellant samples increase with time and with rising temperature, as expected. This is clearly seen for the sample aged at 80°C and is at least observed in the region of low frequencies for the samples aged at lower temperatures. An increase in  $E'$  indicates that the material has become more brittle or glasslike.

Figure 4(a,b) shows for internal and external samples, respectively, the evolution of  $E'$  (at a fixed frequency of 0.1 Hz) with time for the different aging



**Figure 4**  $E'$  (measured at a frequency of 0.1 Hz) as a function of the aging time for (a) internal and (b) external propellant samples aged at 40, 60, and 80°C.

temperatures. At 40 and 60°C, the  $E'$  values of the propellant samples undergo a moderate increase after a softening period, which depends on the temperature. There is a significant increase in  $E'$  when the temperature is 80°C. The aging reaction constants ( $k$ ) are estimated from the slopes of these lines. Upon an examination these figures, the curvature over the complete range of time in all the samples can be observed. This curvature places us in the dilemma of choosing a region for the determination of the slope. Therefore, in the internal samples, for example, the slopes were determined between 3000 and 5000 h of aging for temperatures of 60 and 80°C and between 4000 and 5000 h for 40°C (fit by a straight line with a good regression coefficient). Also, it is important to note that, under our experimental conditions, the modulus variation is not a function of the logarithm of time, but instead increases at a much faster rate according to the results found by Husband.<sup>12</sup>

These observations may be rationalized as follows. Softening is usually the result of binder chain scission or crosslink degradation and may be produced by hydrolytic reactions or thermal decomposition. Moisture effects are particularly pronounced because they do not only relate to hydrolysis but also may interrupt the binder–filler interface. We believe that at the beginning of the aging and at temperatures of 40 and 60°C, for which a significant softening period is observed, the aging is mainly due to physical processes such as ingredient migration and particle dewetting. However, it is reasonable to think that continued cure reactions or further reactions of urethanes with allophanate formations take place simultaneously. These produce a large crosslink density because an increase in the modulus is observed later, although other effects can also lead to a higher modulus, such as a loss of volatile plasticizers. These mechanisms are often chemical reactions, which may be the dominant cause of aging effects at higher temperatures. Different authors<sup>27,28</sup> have demonstrated this fact, analyzing the thermal degradation on the HTPB binder. Moreover, they have concluded that the fillers have a relatively small influence on the thermal aging of these highly filled elastomers.<sup>28</sup>

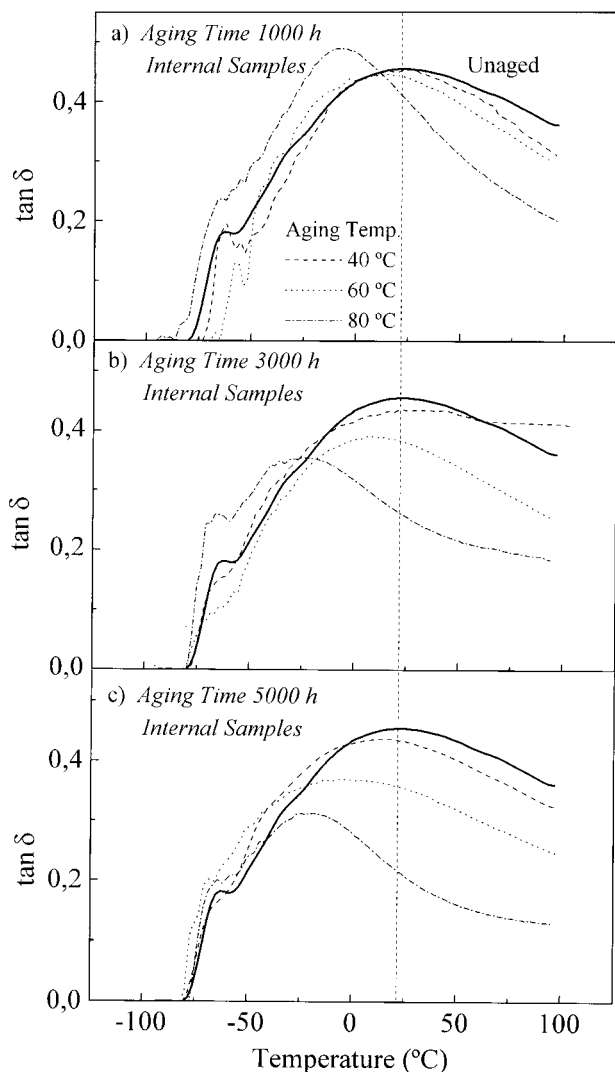
Figure 4 shows an important superficial effect, which can also be observed from the discoloration found in all the external samples aged at 80°C and for long aging times. Therefore, oxidation reactions (through the double bonds present in the main chain of polyurethane) play a relevant role in the aging reactions, which produce an increase in the crosslink density of copolyurethane networks. These results show that several mechanisms operate simultaneously in the thermal aging processes of this complex material. Some of them, thermally activated, may prevail at high temperatures but be relatively unimportant at lower temperatures. Besides, there is considerable ev-

idence that samples exposed directly to the atmosphere deteriorate much more rapidly (and possibly by different mechanisms) than those samples from the bulk of the propellant blocks.

However, it is well known that the damping parameter is extremely sensitive to all kinds of transitions, relaxation processes, structural heterogeneities, and morphologies of multiphase systems, such as crystalline polymers, polyblends, and filler or composite materials. The damping may also be used as a powerful analytical tool for measuring molecular weights, copolymer compositions, the degree and heterogeneity of crosslinking, the extent of curing reactions in thermoset resins, and so forth.<sup>29</sup> Moreover, in a very recent article, Sekkar et al.<sup>30</sup> showed the utility of this property by correlating it to the calculated network parameters of polyurethane based on HTPB. Therefore, this dynamic mechanical property is also considered very suitable for examining the changes in the aging process of this composite propellant.

Figure 5(a–c) shows the variation of  $\tan \delta$  as a function of temperature from –100 to 100°C at a fixed frequency of 1 Hz for internal samples aged for 1000, 3000, and 5000 h, respectively, at the three temperatures under study. As can be seen in Figure 5(a),  $\tan \delta$  undergoes a significant change even for a short aging period, such as 1000 h, especially when the temperature is 80°C. Moreover, these changes are more pronounced in the region corresponding to the secondary relaxation (ca. 22°C), the values of  $\tan \delta$  being reduced with the aging time and temperature. Throughout the different plots, it can be observed that the area under the curves decreases, and this indicates that the ability to absorb energy decreases, with consequent material embrittlement. Therefore, from the depletion in the  $\tan \delta$  values, in the zone of the secondary relaxation, additional data for the aging rates can be obtained. This suggests that the changes caused by the thermal aging are mainly related to the two-phase microstructure and more specifically to the hard domains. Furthermore, it also explains that the hard-segment region of the binder strongly interacts with the filler particles, such as ammonium perchlorate. Consequently, physical processes such as particle dewetting can be easily observed through the evolution of this relaxation, in addition to crosslinking reactions, which are the principal mechanism of thermal aging.

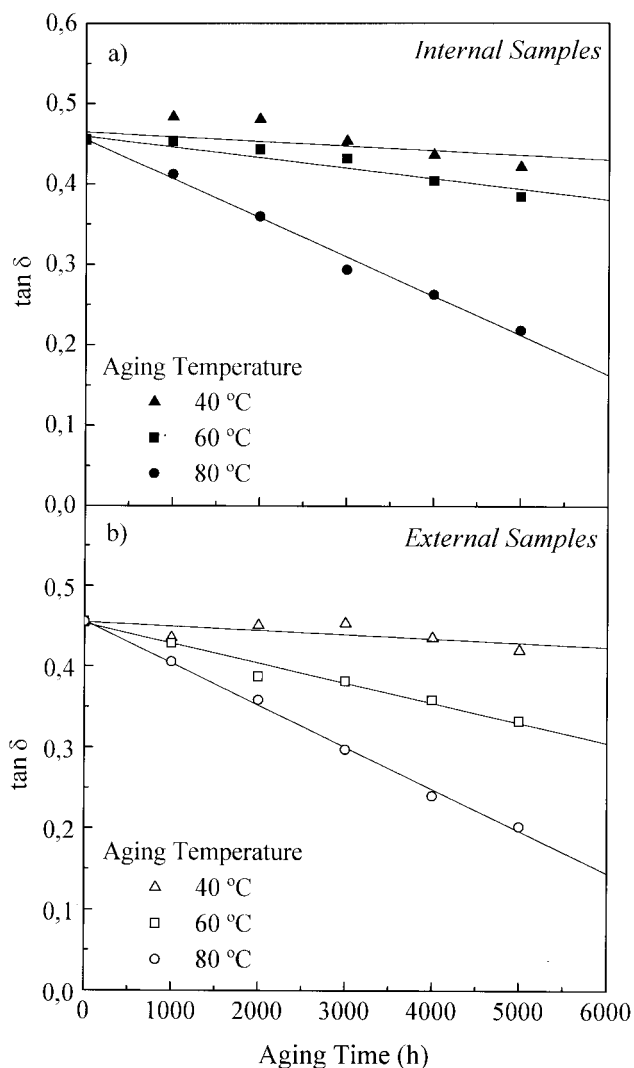
Figure 6(a,b) provides, for both internal and external samples, the variation of  $\tan \delta$  data (measured at 22°C) with the aging time for the different programs. In this case, the aging rate constants are equivalent to  $-\Delta(\tan \delta)/\Delta t$ . The variation of this viscoelastic parameter is again a function of time, not of the logarithm of time. In this case, the rate constant can be calculated for the total range of aging times, and practically all the resulting points can be fit with a straight line.



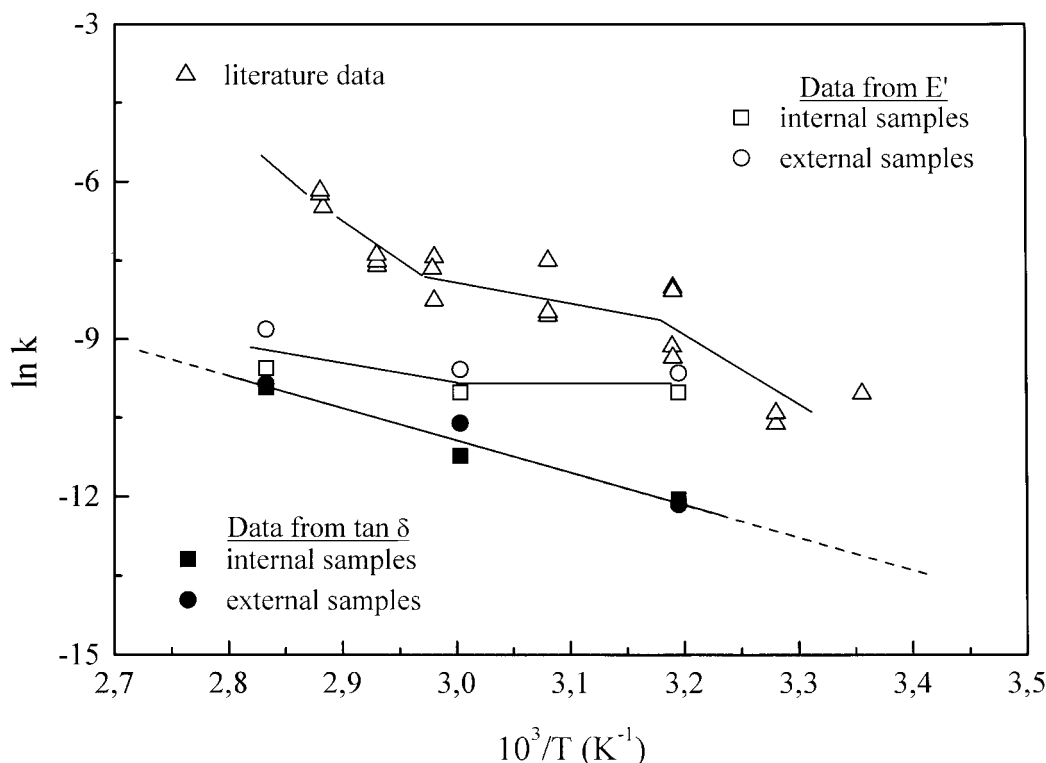
**Figure 5**  $\tan \delta$  as a function of temperature for propellant samples (internal) aged at 40, 60, and 80°C after (a) 1000, (b) 3000, and (c) 5000 h of aging.

The aging rate constant, obtained from  $E'$  and  $\tan \delta$  values, for each of the samples tested is given in Figure 7 along with the literature data<sup>12</sup> in an Arrhenius plot ( $\ln k$  vs  $1/T$ ). Despite the different experimental conditions for the dynamic mechanical measurements performed in this work, which do not correspond exactly to those of Husband,<sup>12</sup> the aging rate values obtained from  $E'$  can be favorably compared (within the experimental error) to values reported in a previous study (also obtained through modulus values). In addition, the same trend in the Arrhenius behavior is found. Between 40 and 60°C, an increase in the aging rate does not exist practically with the temperature rising. However, from 60 to 80°C, the aging rate dramatically increases with temperature, and this indicates that, in this interval of temperatures, it is likely that the relatively high activation energies of chemical degradation reactions are achieved. The ag-

ing rate values obtained from the evolution of  $\tan \delta$  with time are lower than those calculated with the variation of the modulus. These differences decrease when the temperature becomes higher. The Arrhenius behavior for these data can also be observed clearly in this figure. A good linearity is found in this case for the entire temperature range. However, to derive a value for the apparent activation energy from these data is very risky. It must be taken into account that aging is a complex phenomenon and that its mechanism is not known; therefore, an Arrhenius evaluation of the rate constant values is meaningless, yielding unreliable values that may not be reproducible. It is important to note the differences in the activation energy values described in the literature; for example, a value of approximately 21 kJ/mol was reported by Layton,<sup>5</sup> which was lower than that calculated by Husband<sup>12</sup> (~200 kJ/mol between 60 and 80°C) or



**Figure 6**  $\tan \delta$  (measured at 22°C) as a function of the aging time for (a) internal and (b) external propellant samples aged at 40, 60, and 80°C.



**Figure 7** Natural logarithm of  $k$  as a function of the inverse of the temperature for propellant samples (external and internal), as determined from  $E'$  and  $\tan \delta$  values, along with Husband's data.<sup>12</sup>

those values recently reported by Celina et al.<sup>28</sup> These authors found non-Arrhenius behavior over a wide and complete temperature range (25–125°C); the activation energy at the lower temperatures was approximately 70 kJ/mol, and that at the higher temperatures was 120 kJ/mol. However, under our experimental conditions, the aging rates measured for external samples are slightly higher than those determined through the analysis of internal samples.

Although the different tendencies of the Arrhenius behavior of the aging rate data obtained from  $E'$  and  $\tan \delta$ , along with the differences between them, can seem contradictory, the following considerations need to be considered. The crosslinking reactions seem to be the dominant process at high temperatures in this material, as mentioned before. It is known that crosslinking has a dramatic effect on the dynamic mechanical behavior above  $T_g$ . If the frequency of the test is too high, the modulus does not reach an equilibrium value, and the expected increase in the modulus with the degree of crosslinking becomes partly obscured by entanglements and imperfections, such as trapped entanglements or dangling crosslinked structures. However, the damping is a sensitive indicator of crosslinking. Therefore, at temperatures well above  $T_g$ , the modulus tends to increase whereas the damping decreases with a rising degree of crosslinking. It is important to note that the evolution of  $\tan \delta$  in a study of aging propellants may be a valuable tool for pre-

dicting the service life of these materials. However, thermally accelerated aging is different from the aging occurring during storage and transportation, during which, in addition to thermal stresses, other forces are also operative. Therefore, these data must be treated with caution, and further studies are necessary in this area.

## CONCLUSIONS

The thermal aging of HTPB-based propellants has been investigated at temperatures of 40, 60, and 80°C by means of dynamic mechanical analyses. These aging processes have easily been monitored with the changes in  $E'$  and  $\tan \delta$  with the temperature for a total time of 5000 h.  $E'$ , at low frequencies, increases as the aging and temperature increase. This increase in  $E'$  values takes place after a softening period that diminishes when the aging temperature becomes elevated. However,  $\tan \delta$  values present an opposite tendency, mainly in the temperatures range in which the secondary relaxation appears. Damping efficiency gradually diminishes with the aging temperature as the program progresses. The aging rate constants determined from both viscoelastic properties have been evaluated according to Arrhenius methodology. Kinetic data from  $E'$  have shown a significant curvature in the Arrhenius plot. However, a lineal regression has been found for kinetic data determined from  $\tan \delta$  values.  $\tan \delta$



seems to be more sensitive than  $E'$ , and so this property may be a new and efficient parameter for determining the service life of this composite material. These results demonstrate the importance of evaluating different viscoelastic parameters and the widest temperature range possible so that we can more confidently predict and extrapolate aging behavior. It is also important to note that a significant surface effect has been observed through the comparative analysis of both internal and external samples, mainly in the rate values obtained from the variation of the  $E'$  data at the highest temperature aging.

The dynamic mechanical measurements allow the evaluation of the actual state of a propellant grain with the help of small samples and a quick and easy procedure in comparison with traditional aging studies. In addition, the results of the comparison of the data presented with those reported previously in the literature<sup>12</sup> confirm the reproducibility of this technique in the aging studies of these energetic composites.

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