Viscoelastic Behavior in a Hydroxyl-Terminated Polybutadiene Gum and Its Highly Filled Composites: Effect of the Type of Filler on the Relaxation Processes

José L. de la Fuente,[1] Marta Fernández-García,[2] María L. Cerrada[2]

[1]Instituto Nacional de Técnica Aeroespacial, I.N.T.A., Carretera de Ajalvir, p.k. 4, 28850 Torrejón de Ardoz, Madrid, Spain
[2]Instituto de Ciencia y Tecnología de Polímeros (C.S.I.C.), Juan de la Cierva 3, 28006 Madrid, Spain

ABSTRACT: Investigations have been ongoing to learn the rheological and/or mechanical behavior of composite solid propellants based on hydroxyl-terminated polybutadiene (HTPB). The mechanical properties of these materials are related to the macromolecular structure of the binder as well as to the content and nature of the fillers. The viscoelastic behavior of an HTPB binder and its composites with different types of fillers was surveyed by dynamic mechanical analysis over a wide range of temperatures. This technique has clearly demonstrated a two-phase morphology developed in these systems. The temperature location, intensity, and apparent activation energy of the distinct relax-ations are discussed. The dependency of the relaxation processes on filler content in a series of composites has elucidated the interactions between the filler particles and the existing hard- and soft-segment domains within the polyurethane matrix. It was observed that the nature of the filler significantly affects the relaxation process associated with the hard-segment domains of the polymeric structure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1705–1712, 2003

Key words: viscoelastic properties; hydroxyl-terminated polybutadiene (HTPB); polyurethanes; fillers; hard and soft segments

INTRODUCTION

Composite solid propellants based on hydroxyl-terminated polybutadiene (HTPB) have at present become the worldwide workhorse propellants in solid-fuel rocket engines.[1,2] The polyurethane network obtained by curing HTPB with a suitable diisocyanate provides an adequate matrix for inorganic oxidizer and metallic fuel that are dispersed in the propellant grain.

The essential structural and processing requirements accomplished by solid propellants have become increasingly more extreme because of the increase in both the variety of designs and the complexity of rocket engines. Therefore, there has been a constant endeavor to more fully understand the mechanical behavior of HTPB-based composite solid propellants. The tremendous importance of the mechanical aspects mainly arises from the highly technological engineering applications of these materials. Accordingly, a detailed analysis of each propellant is required. The mechanical behavior of composites strongly depends on time, temperature, loading procedure, and loading history.[3,4] Such behavior is significantly determined by the viscoelastic nature of the polymeric matrix.

Consequently, the mechanical properties in these composite solid propellants primarily depend on the inherent properties of the matrix, particle size, shape, distribution, the concentration of the solid ingredients [generally ammonium perchlorate (AP) and aluminum], and the binder–filler interface and their interactions. Therefore, the mechanical and failure responses of solid propellants and propellant-like materials might be semiquantitatively predicted from the molecular structure/physical property relationships.[5–8]

An essential requirement in the selection of a particular polymeric component as matrix is that it must exhibit good mechanical properties. Therefore, the use of different types of polyurethanes is typical for the above-mentioned applications because of the alternating hard and soft segments within their structure.[9] The segments usually segregate to form two aggregated pseudophases as a result of thermodynamic differences. Hence, the hard domains act as multifunctional crosslinking and reinforcing fillers within the flexible soft segments. Materials that combine high modulus and elastomeric properties[9] are thus attained. In addition to their use in the manufacture of propellants, polyurethanes based on polybutadiene are used in a wide range of applications,[10,12] such as sealants, adhesives, waterproof and anticorrosion coatings, foams, electrical insulation, and elastomers. These polyurethanes also serve as interesting model systems in which there is no possibility of hydrogen

bonding between the hard and soft segments, in contrast to the more familiar polyester or polyether polyurethanes. A number of investigations have been carried out to examine their morphological features and transition behavior as a function of chemical structure, composition, and processing conditions.[13–19]

On the other hand, the viscoelastic properties in an elastomeric network are strongly affected by the inclusion of particulate fillers.[20] The effects of such filler inclusion have been analyzed by either typical studies related to filler volume fraction/equilibrium modulus ratios or the more scarce examination of filler impact on promoting nonlinear viscoelastic response and thermorheological complexity in composite materials.[20–23] However, the role of filler particles within composites arising from the complex interaction between filler/polymer and the broad variety of possible binder/filler combinations remains far from being completely understood. Particulate fillers used in elastomers are generally classified as either reinforcing or nonreinforcing. On the one hand, the term *reinforcing* is used for systems in which the filler strongly interacts with the binder and, consequently, enhances rupture strength.[24] On the other hand, *nonreinforcing* fillers interact only weakly with the binder and provide little or no augmentation of rupture properties. This classification is, however, empirical at best, with most examples falling between the extremes of an idealized behavior.

The nonlinear behavior and thermorheological complexity of these important materials have been considered in the literature.[25–27]. Despite the importance of HTPB-based propellants for rocket engines and the obvious concern about structure and properties relationships, very few comprehensive investigations appear to be available in the open literature. There are only a few studies in which the viscoelastic response has been examined in an HTPB gum and propellants under small deformation by using dynamic mechanical analysis.[25,26] Stacer and Husband[26] estimated the apparent activation energies of secondary relaxations induced by the presence of fillers from decomposition of the time–temperature shift factor for filled versus unfilled materials. Moreover, a thermorheologically complex behavior has been observed in these filled elastomers. This complexity has been related to this secondary relaxation process, which seems to be caused by the interphase of the polymer weakly adsorbed onto the surfaces of the filler particles.

The main goal of this study was to analyze the viscoelastic behavior of an unfilled elastomeric binder and several HTPB solid composites by dynamic mechanical measurements under small deformation. The temperature localization and intensity of the distinct relaxations are discussed. The effect of the different types of fillers on these processes was also analyzed in these systems, showing that the relaxation exhibited at higher temperatures is considerably affected by the nature of the fillers. To our knowledge, there is no publication in the extant literature that has surveyed the effect of the nature of fillers on the two relaxation processes exhibited in these composites; our aim in this current investigation was to make an original contribution to this important research.

EXPERIMENTAL

Materials

The hydroxyl-terminated polybutadiene–based propellant (HTPB1) selected for this study contained 88% solids loading, 68% ammonium perchlorate (oxidizer, with two particle sizes, 200 and 6 μm, from SNPE, Saint Medard En Jalles, France), 20% 7 μm aluminum (ECKA, Fürth, Germany), and 12% of binder. The binder composition consisted of 9.2% of HTPB (R-45M; Elf Atochem, Paris, France); 2% of plasticizer (dioctyl adipate; BASF-AG, Ludwigshafen, Germany); a small percentage of a bifunctional aziridine, which was used as bond promoter (0.2%, Dynamar HX-752, 3M Corp., St. Paul, MN); and 0.05% of antioxidant (Irganox 565; Ciba-Geigy, Switzerland). The curing reaction took place between the hydroxyl groups of the prepolymer and the isocyanate groups of the curing agent isophorone diisocyanate (IPDI, 0.55%; Hüls Española S.A., Barcelona, Spain). Another highly filled elastomer analyzed in this study was based on the same binder formulation (HTPB2), but changing AP by sodium chloride (with approximately the same particle size distribution, from Panreac, Barcelona, Spain), solid percentages of which were 66% NaCl and 15% Al. In addition, two elastomeric liner formulations based on the same binder were examined, composed of different fillers: one with carbon black (25%, 25 nm, 98% carbon content, 0.7% sulfur content, 110 m^2/g surface area, pH 4; Printex-U, Degussa A.G., Frankfurt am Main, Germany) (HTPB3) and the other with hydrated aluminum silicate, kaolin (25% sp. gr., 2.2 particle size retained on 200 BSS, purity 99%; Ricardo Molina S.A., Barcelona, Spain) (HTPB4). (Liners are composites with an approximately 25–40 wt % filler content that are used as structural interfaces between the device wall and the propellant within the engine to facilitate damping and to enhance adhesion by stabilizing the propellant grain during environmental storage and engine operation.) All the formulations were prepared in a vertical mixer (IKA-HKV5 Planetron, Staufen, Germany) and cured for 10 days at 60°C. More detailed information about the preparation processes is given elsewhere.[28] Unfilled and filled composite specimens under study were prepared in the form of rectangular bars (6 × 8 mm cross section; 2 mm thickness).

Measurements

Dynamic mechanical measurements were carried out in a Perkin–Elmer DMA7/TA7/DX analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) in the compression mode. A liquid nitrogen–cooling accessory was used for subambient operation. The measuring system consisted of a 5-mm-diameter parallel plate. Two different types of experiments were performed: (1) isothermal measurements at room temperature, by applying oscillatory frequencies ranging from 0.01 to 50 Hz under low strains; and (2) isochronal experiments, by measuring viscoelastic dissipation as a function of temperature. In the isochronal experiments, the temperature ranged from -100 to $100°C$ at a heating rate of $2°C$ min^{-1}. The frequencies chosen were 0.1, 1, 5, and 10 Hz.

The dependency of frequency on temperature was considered in the isochronal experiments to follow an Arrhenius behavior in the relaxation mechanism associated with the glass transition, although it was attributed to cooperative motions.[29] This approximation can be made without a significant error, given that the analyzed frequencies are low enough to be fitted to such a linear behavior just mentioned. The experimental precision in the obtained data, based on standard deviation from multiple measurements, on different samples was less than 10% of the reported value.

The glass-transition temperature (T_g) was also measured by differential scanning calorimetry (Perkin–Elmer DSC7/TA7/DX with liquid nitrogen for low temperatures). The temperature scale was calibrated using the melting point of high-purity chemicals (lauric and stearic acids and indium). Samples ($\sim$ 40 and $\sim$ 10 mg for filled and unfilled composites, respectively) were scanned at $10°C$ min^{-1} under dry nitrogen (20 cm^3 min^{-1}). The T_g value was estimated from the midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The T_g value provided is the average for several measurements performed for each sample.

RESULTS AND DISCUSSION

Figure 1 shows the characteristics found in the binder and HTPB1 propellant responses under a strain amplitude of 0.2%. This figure displays the effect of frequency on the storage modulus E', at different indicated temperatures. E' increases in a regular fashion with increasing frequency or decreasing temperature, suggesting that time–temperature superposition of these data might be held in both materials. However, the different isothermal curves do not collapse into a master curve for the propellant in the whole frequency

range analyzed by shifting them along the horizontal axis, considering the curve at $22°C$ as reference (T_0), as depicted in Figure 2. There is not a superposition of E' data at the lowest temperatures and highest frequencies for the HTPB1 propellant. This feature indicates a thermorheological complexity of the material under study, as previously observed in similar highly filled composite solid propellants.[25,26] Such thermorheological complex behavior is probably caused by the variation of the strength of filler–filler and filler–matrix interactions with temperature. Accordingly, a decrease of temperature is not equivalent to a frequency increase. However, the unfilled gum exhibits thermorheological simplicity in the same range of frequencies and temperatures, likely because of the absence of the aforementioned interactions. In addition, the analysis performed concerning the effect of the strain amplitude on the viscoelastic parameters confirmed the nonlinear response throughout the entire range of strains examined for the filled elastomeric material under study. These results were similar to those previously reported.[25]

Figure 2 also displays several additional features concerning the viscoelastic response of the HTPB1 propellant and gumstock. At low temperatures or high frequencies, slopes in E' curves are maximized for both, although the propellant does not exhibit as good linearity as that of the unfilled gum. This temperature/frequency region of the viscoelastic spectrum is commonly termed the *transition region,* referring to the material transition from a soft elastomer to, at first instance, a leathery and then a hard glassy solid. At higher temperatures or lower frequencies, the value of E' is observed to approach the equilibrium value. This portion of the curve is termed the *rubbery plateau.* The frequency boundary between transition and equilibrium or plateau zone is designated $\omega_{tr,}$ as indicated in Figure 2. Its value is estimated by the intersection of the tangents corresponding to the equilibrium zone and transition region of the curve, as shown in Figure 2 for the unfilled gum. In the HTPB1 propellant, however, this frequency boundary is only intuitively observed in the range of temperatures and frequencies analyzed here. The presence of fillers often masks and/or broadens this transition. Accordingly, the obtained quasi-master curve seems to indicate that it appears at higher temperatures or lower frequencies.

The time dependency of the mechanical behavior of a linear viscoelastic material at constant temperature can be well represented by a dynamic mechanical spectrum, and the dependency on temperature is given by a shift factor a_T. The horizontal shift factors used to superpose the E' data were described using the Williams–Landel–Ferry (WLF) equation.[30] The values of C_1 and C_2 were estimated for the binder at 7.86 and $221°K$, respectively, and 8.09 and $196°$ K, respec-
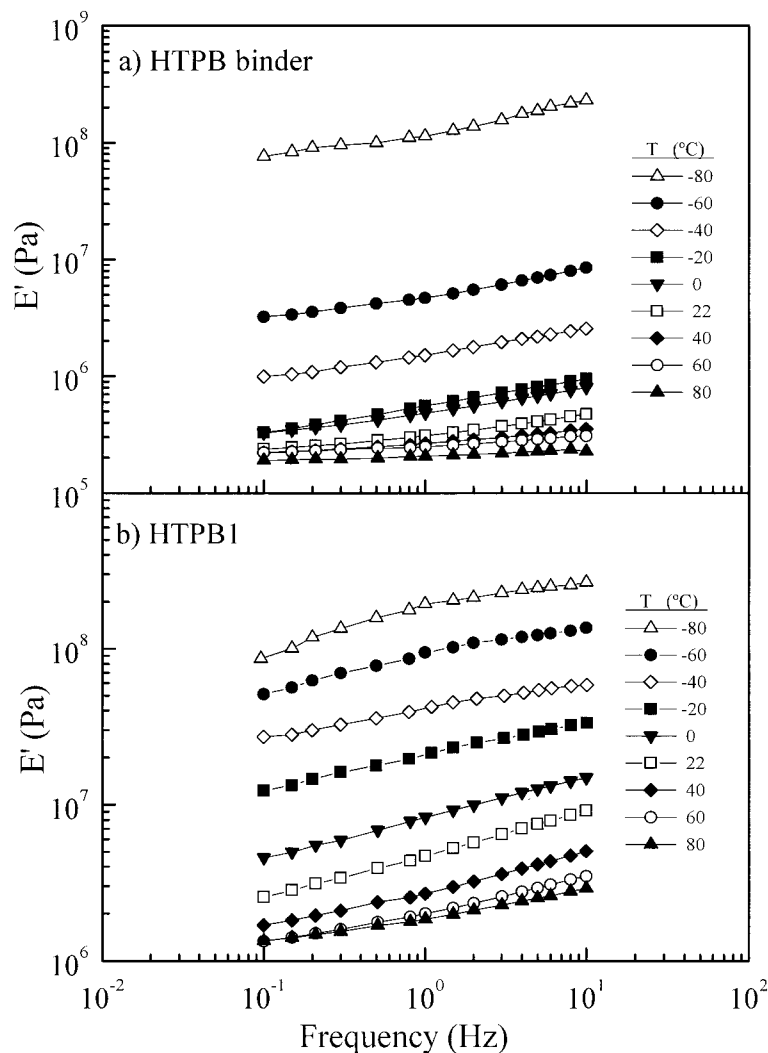
Figure 1 Isothermal storage modulus as a function of frequency for the binder (upper plot) and HTPB1 propellant (lower plot).

tively, for the propellant. These values are in agreement with those reported in the literature.[31] The temperature dependency of the horizontal shift factors with temperature seems to point out two different regions: one for the lowest temperatures and the other for the highest temperature zone. It seems that two different processes could overlap in this temperature range (Fig. 3).

Figure 4 shows the viscoelastic response in terms of E', loss modulus E'', and loss tangent tan δ, for the binder and HTPB1 propellant at 1 Hz as a function of temperature. Both materials exhibit two main relaxation processes over the temperature range studied. However, the incorporation of fillers significantly modifies the molecular mobility, as observed by comparing the gum and propellant curves. The relaxation at lower temperature, in the range from −75 to −50°C, is attributed to the glass-transition temperature T_g^{soft}, in the soft-segment regions of the plain polyurethane and the propellant. The location of T_g^{soft} agrees with

that found by DSC measurements. The other one, a broad mechanism appearing at higher temperature, corresponds to motions within short hard-segment units. This second process is usually referred to as the glass transition of the hard linking segments T_g^{hard}, although it actually seems to be a secondary relaxation attributed to the short length of the hard segments in the composites under study. There are two main common features for these two processes when the gum and propellant are compared, the variation in either the intensity or the relaxation time distribution. On the one hand, the glass-transition process shows a much higher intensity in the soft-segment regions within the gum than the same mechanism in the propellant. This diminished intensity is partially caused by the movement restrictions imposed by the introduction of fillers in those initially mobile regions. However, the intensity reduction observed is quite important. Consequently, in addition to the high filler content another factor seems to be responsible for the decrease in
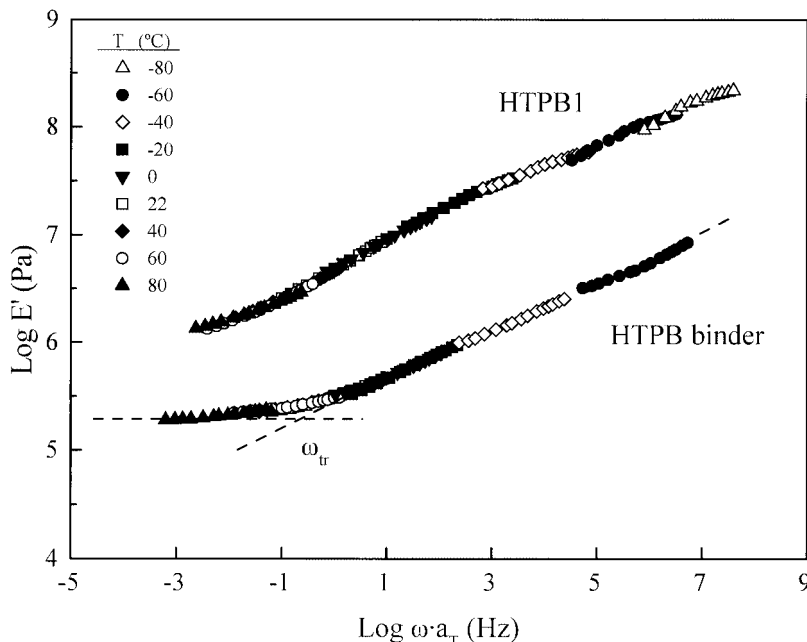
Figure 2 Manual time–temperature reduction for the binder and HTPB1 propellant. Reference temperature $T_0 = 22°C$.

mobility. In HTPB1 the main filler used is AP and, accordingly, hydrogen bonds can be established between fillers and binder (**Scheme 1**).

This hypothetical interaction mechanism between AP and polymer matrix has been demonstrated in the literature.[32] The linear polyurethane here analyzed can lead to the same proposed structure, although this interaction was investigated by means of FTIR spectroscopy between AP and bonding agents, such as aziridine compounds. This hindrance in motion, arising from the high content in fillers and the additional bonding, also provokes a slight broadening in the relaxation time distribution within the solid filled composite. The temperature location of this relaxation is shifted to higher temperatures in the composite as a result of the mobility reduction caused by filler incor-

poration. Temperature shifts ranging from 3 to 8°C are common in similar systems.[26]

On the other hand, the relaxation related to short hard-segment units (T_g^{hard}) exhibits a small difference
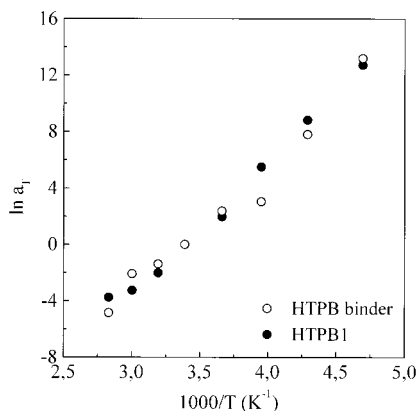

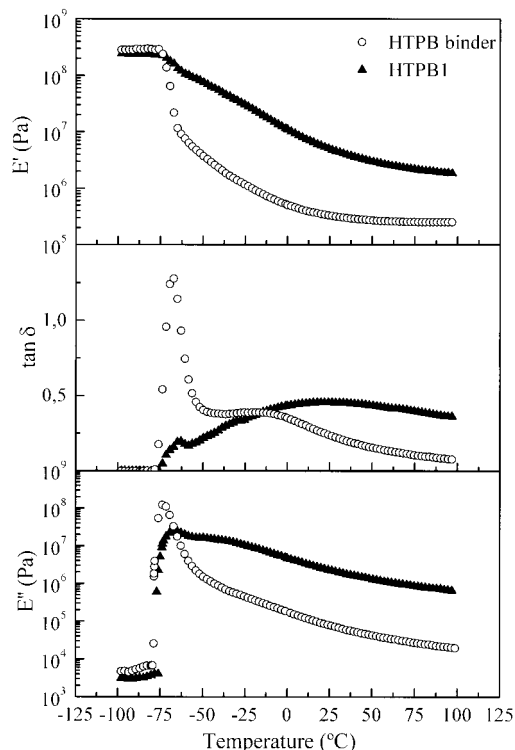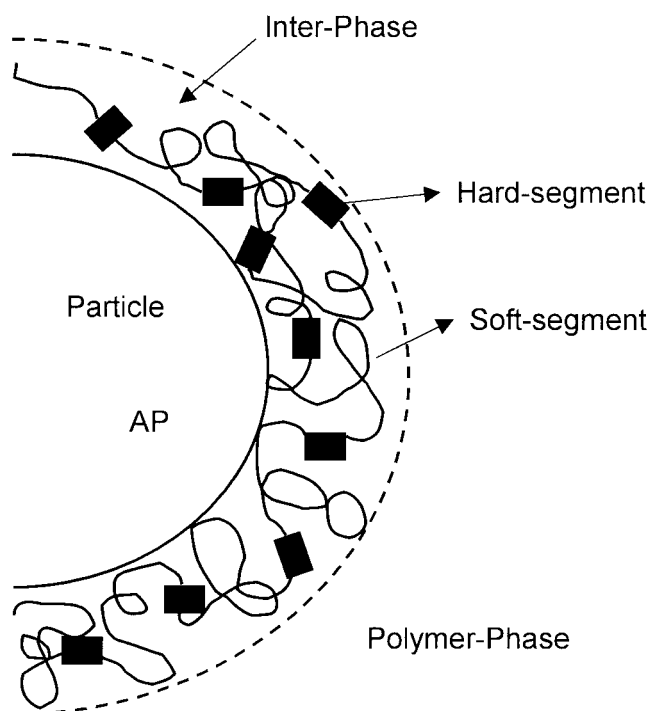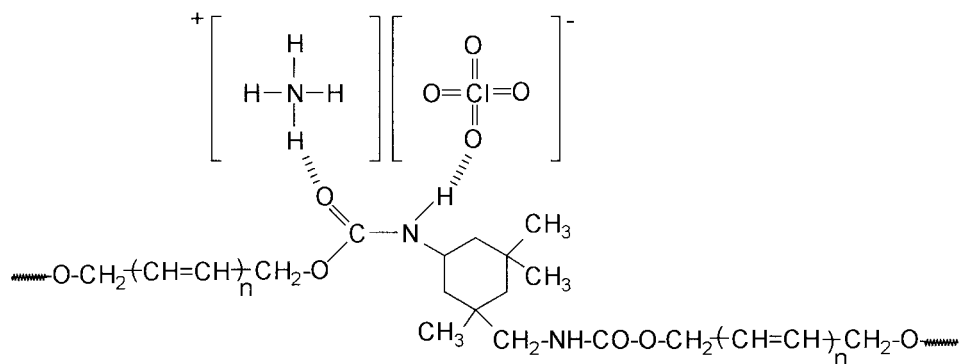**Figure 3** Shift factor dependency on temperature for binder and HTPB1 propellant.

Figure 4 Storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) curves for the binder and HTPB1 propellant as a function of temperature at a frequency of 1 Hz.

Scheme 1 Hydrogen bonding structure between AP and polyurethane binder.

in intensity but its broadness is considerably enlarged in the propellant. The incorporation of fillers increases the rigidity of the whole material and, consequently, the stiffness in the composite is higher than that in the gum, thus provoking a slightly higher intensity in this relaxation. As occurred in the other process, the significant broadening of the relaxation time distribution arises because of the fillers and the hydrogen bonds introduced by them. In the HTPB1 composite solid propellant there is an interface of polymeric matrix weakly adsorbed onto the surfaces of the AP filler particles, which makes mobility more difficult. Moreover, the increase of intensity and broadness of the relaxation related to hard segments might be caused by the introduction of new damping mechanisms that do not exist in the polymeric material without rein-

forcements. Those additional mechanisms could consist of frictions, either particle–particle (where particles are touching one another in weak agglomerates) or particle–polymer (where there is essentially no adhesion at the interface), as well as a damping excess in the polymer attributed to induced thermal stresses or changes in polymer conformation or morphology near the interface.

A shift of the temperature in the relaxation maxima is observed in Figure 5 for HTPB binder with frequency. This dependency allows estimation of the apparent activation energy of the distinct relaxation processes. Similar results were found for the HTPB1 composite propellant. The different natures of both of the observed mechanisms is reflected in the apparent activation energy values obtained. Therefore, the activa-
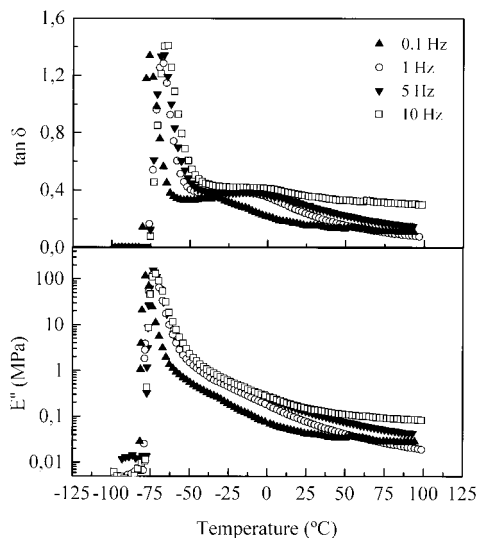
Figure 5 Temperature dependency of the loss modulus and loss tangent of HTPB binder at the four different frequencies analyzed.

tion energy associated with the T_g^{soft} process, which is attributed to the cooperative motions of long soft segments, is much higher (>400 kJ mol^{-1}) than that associated with the labeled T_g^{hard} relaxation, which implies the motion of the short linking rigid segments (about 80 kJ mol^{-1}).

Moreover, different types of fillers have been used for preparing other composites based on the same polymeric binder HTPB, to survey the effects that both the filler nature and the filler amount added could provide. Therefore, another highly filled composite, HTPB2 (with NaCl as filler), has been explored as well as two other composites used as liners, HTPB3 and HTPB4 (with carbon black and kaolin as fillers, respectively, as discussed in the Experimental section). The viscoelastic parameter explored was tan δ. Damping is extremely sensitive to all kinds of relaxation processes, structural heterogeneity, and the morphology of multiphase systems such as crystalline polymers, polyblends, and filled or composite materials. Moreover, recent articles have demonstrated that damping might also be used as a powerful analytical tool for measuring network parameters in a polyurethane matrix[33] and to examine the changes in the aging process of this extremely active composite.[34] Accordingly, Figure 6 shows the variation of tan δ with temperature for the several composites compared to the unfilled HTPB binder to obtain deeper insight into the viscoelastic behavior exhibited by these materials.

Both HTPB2 and HTPB1 composites contain high levels of fillers, although sodium chloride was used to replace ammonium perchlorate in HTPB2 (with the same multimodal particulate systems to obtain similar dense packing); the incorporation of NaCl considerably increased the mobility in HTPB2 propellant. Con-

sequently, the intensity of T_g^{soft} is significantly higher, although its temperature location is quite similar to that in the HTPB1 composite. This variation in T_g^{soft} intensity (much lower in HTPB1) is attributed to the existence of hydrogen bonding in HTPB1, which promoted the packing of denser chains within the composite and thus hindering the motion. However, NaCl fillers do not allow establishing this type of intermolecular bonding and thus the mobility of the chains in the glass-transition region is increased. The absence of additional bonding is also obvious in the relaxation appearing at higher temperatures associated with the short, rigid crosslinking segments. Therefore, its location and magnitude are rather similar in HTPB2 to those found for the T_g^{hard} in the binder.

Common characteristics to those just detailed for HTPB1 and HTPB2 are encountered in HTPB3 and HTPB4, depending on the possibility of forming such intermolecular hydrogen bonds, although the amount of filler in these latter two composites is much lower. The incorporation of carbon black makes the cooperative motions more difficult in HTPB3 than those in HTPB4 and, thus, the intensity of T_g^{soft} is diminished in the former liner. Carbon black allows the additional bonding, similar to that in HTPB1, although the content of carbon black is more than half that of ammonium perchlorate. Because of this difference in filler amount, T_g^{soft} intensity is higher in HTPB3 than in HTPB1, although lesser than in HTPB4 with similar filler content. Additional common features are again observed between HTPB3 and HTPB1 in the relaxation related to the hard segments, that is, the behavior observed qualitatively, independent of the filler content. The intermolecular hydrogen interactions within chains cause a broadening of the relaxation time distribution, although the intensity of this relaxation is considerably reduced because of the smaller content of fillers in HTPB3. On the other hand, the
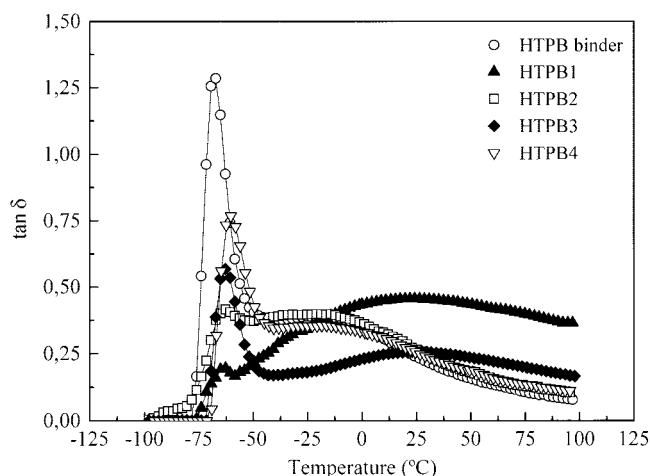

Figure 6 Tan δ as a function of temperature for binder and different composites based on HTPB.

impossibility of forming additional bonding increases the intensity of T_g^{soft} in HTPB4, with respect to HTPB3, because of the facility of motions in that temperature range. Moreover, the relaxation associated with the hard crosslinking segments remains practically unaltered compared to that for the binder, which also occurred in HTPB2. The differences in filler content between HTPB2 and HTPB4 composites are exclusively shown in the cooperative motion of segments (i.e., the T_g^{soft}), as depicted in Figure 6.

CONCLUSIONS

A thermorheological complexity was found in HTPB1 in contrast to the thermorheologically simple behavior shown by the corresponding elastomeric binder over the temperature and frequency range analyzed. Such a complexity seems to be caused by the variation of the strength of filler–filler and filler–matrix interactions with temperature. In addition, the analysis performed with respect to the effect of the strain amplitude on the viscoelastic parameters confirmed the nonlinear response in HTPB1 throughout the entire range of strains.

Analyses of the various types of fillers shows the importance of the nature of fillers on the two main relaxation processes, thus allowing classification of fillers for this particular binder: reinforcing for the AP and carbon black; nonreinforcing for NaCl and kaolin. The relaxation that appears at lower temperatures and is attributed to the glass-transition temperature of the soft segment of the polyurethane (polybutadiene chain) is almost constant in its location with the type and content of fillers. On the other hand, its intensity is significantly affected by either the reinforcing (AP or carbon black) or the nonreinforcing (NaCl and kaolin) nature of the filler and its content. The location and intensity of the relaxation appearing at higher temperatures, T_g^{hard}, associated with motions within the hard segments, practically did not change with the incorporation of nonreinforcing fillers independently of content. However, the introduction of reinforcing fillers provokes an important shift toward higher temperatures and a broadening of the distribution of relaxation times. The results presented here have demonstrated that the rheological and mechanical behaviors are strongly influenced in these elastomeric composites by the existence of soft and hard microdomains in the architecture of the polyurethane and by the content and nature of the fillers and their potential of establishing additional hydrogen bonds.

References

1. Boyars, C.; Klager, K., Eds. Propellants: Manufacture, Hazards, and Testing; American Chemical Society: Washington, DC, 1969.
2. Ross, D. L.; Levins, D. A.; Hill, M. E.; Bedford, C. D.; Woolfolk, R. W. High Energy Propellant Material Research: A Technical Assessment, Report PYU-3494. SRI International: Menlo Park, CA, 1982.
3. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymer and Composites, 2nd ed.; Marcel Dekker: New York, 1994.
4. Ferry, J. D. Viscoelastic Properties of Polymers; Wiley: New York, 1980.
5. Kelley F. N. In: Propellants: Manufacture, Hazards, and Testing; Boyars, C.; Klager, K., Eds.; American Chemical Society: Washington, DC, 1969.
6. Kelley, F. N.; Williams, M. L. Rubber Chem Technol 1969, 42, 1175.
7. Williams, M. L.; Kelley, F. N. In: Polymer Networks: Structure and Mechanical Properties; Chompff, A. J.; Newmann, S., Eds.; Plenum Press: New York, 1971.
8. Landel, R. F.; Fedors, R. F. Mechanical Behavior of Materials, Vol. III; Society of Materials Science: Tokyo, 1972.
9. Schneider, N. S.; Brunette, C. M.; MacKnight, W. J. Adv Urethane Sci Technol 1981, 8, 49.
10. John, W. C.; Bogart, V.; Gibson, P. E.; Cooper, S. L. J Polym Sci Part B: Polym Phys 1983, 21, 65.
11. Hsein, K. H.; Tsai, C. C.; Tseng, S. M. J Membr Sci 1990, 49, 341.
12. Frontini, P. M.; Rink, M.; Pavan, A. J Appl Polym Sci 1993, 48, 2023.
13. Chamberlin, Y.; Chakar, A.; Pascault, J. P. Rev Caoutch Plast 1982, 621, 153.
14. Xu, M.; MacKnight, W. J.; Chen, C. H. Y.; Thomas, E. L. Polymer 1983, 24, 1327.
15. Bengtson, B.; Feger, C.; MacKnight, W. J.; Schneider, N. S. Polymer 1985, 26, 895.
16. Chen, C. H. Y.; Briber, R. M.; Thomas, E. L.; Xu, M.; MacKnight, W. J. Polymer 1983, 24, 1333.
17. Vilar, W.; Akcelrud, L. Polym Bull 1995, 35, 635.
18. Zawadzki, S. F.; Akcelrud, L. Polym Int 1997, 42, 422.
19. Desai, S.; Thakore, I. M.; Sarawade, B. D.; Devi, S. Eur Polym J 2000, 36, 711.
20. Kraus, G. Angew Makromol Chem 1977, 60/61, 215.
21. Payne, A. R. J Appl Polym Sci 1962, 6, 57.
22. Payne, A. R. J Appl Polym Sci 1964, 8, 266.
23. Payne, A. R.; Whittaker, R. E. Rubber Chem Technol 1971, 44, 340.
24. Barbin, W. W.; Rodgers, M. B. In: Science and Technology of Rubber; Erman, J. E.; Eirich, F. R., Eds.; Academic Press: San Diego, 1994; Chapter 9.
25. Stacer, R. G.; Hübner, C.; Husband, D. M. Rubber Chem Technol 1990, 63, 488.
26. Stacer, R. G.; Husband, D. M. Rheol Acta 1990, 29, 152.
27. Stacer, R. G.; Husband, D. M.; Stacer, H. L. Rubber Chem Technol 1987, 60, 227.
28. Rodríguez, O. Tesina de Licenciatura, Universidad Complutense de Madrid, Spain, 1997.
29. McCrum, N. G.; Read, B. E.; Williams, G. Anelastic and Dielectric Effects in Solid Polymer; Dover: New York, 1991.
30. Williams, M. L.; Landel, M. L.; Ferry, J. D. J Am Chem Soc 1955, 77, 3701.
31. Stacer, R. G.; Husband, D. M. Propellants Explosives Pyrotechnics 1991, 16, 167.
32. Hori, K.; Iwama, A. Propellants Explosives Pyrotechnics 1990, 15, 99.
33. Sekkar, V.; Bhagawan, S. S.; Phabhakaran, N.; Rama Rao, M.; Ninan, K. N. Polymer 2000, 41, 6773.
34. de la Fuente, J. L.; Rodríguez, O. J Appl Polym Sci 2003, 87, 2397.