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Technical Notes

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Condensed-Phase Chemical Interaction Between Ammonium Perchlorate and Hydroxy-Terminated Polybutadiene

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Introduction

COMPOSITE propellants containing hydroxy-terminated polybutadiene (HTPB) and wide distributions of ammonium perchlorate (AP) particle size (very fine and coarse) have demonstrated unusual combustion characteristics including a suppressed burning rate over a wide pressure range and intermediate pressure extinction. The role of fine AP is generally thought to be significant; however, the exact mechanisms responsible have not been universally agreed upon. Binder melt effects and the possible interaction of binder melt material with fine AP have been gaining attention.[1,2] Still there is need for additional research on and better understanding of the fundamental combustion mechanisms of mixtures of fine AP and HTPB.

Previous work on the thermal decomposition of AP with fuel additives has been done at relatively slow heating rates (10 deg/min). That work has shown that there can be a significant interactive effect between AP and fuel additives, particularly with smaller AP particles.[3,4] Fuels tested included polymer binders [polybutadiene acrylic acid (PBAA), polysulfide (PS), and polyurethane (PU)] and powders [carbon black, polymethylmethocrylate (PMMA) and PS]. At low heating rates all fuels tested showed a tendency to lower the temperature of the major exothermic event over that for pure AP and increase the heat of reaction. Also, there was some evidence that over the limited range of heating rates available the kinetics of the high-temperature AP/binder decomposition were independent of heating rate. Still it is well established that chemical decomposition kinetics in general can vary with heating rate, particularly over large heating rate ranges. Thus there is a need for similar studies at combustion condition-like heating rates.

Experimental Method

In this study the condensed phase decomposition of mixtures of fine AP and HTPB was investigated at higher heating rates than have been reported in the past. This was accomplished by using thin films (30–60 μm) of HTPB polymer cured either with dimeryl diiocyanate (DDI) or isophorone diiocyanate (IPDI) rapidly thermally pyrolyzed by CO_2 laser irradiation. Using a nominal laser flux of 100 W/cm^2, heating rates of 10^2–10^3 K/s were achieved. This energy was absorbed relatively uniformly over a thin layer of polymer. The distribution of volumetric energy absorption is related to the absorption coefficient of the target material. The intrinsic absorption coefficient of HTPB binder and AP at room temperature has been reported as 315 and 240 μm, respectively,[5] giving mean free photon paths (absorption depths) of about 30 and 40 μm. Because the absorption coefficients are so similar in magnitude between AP and HTPB at this wavelength, selective absorption effects should be negligible between AP and binder. Sample thickness varied between 30 and 60 μm. The fraction of laser energy absorbed by the sample film would correspondingly range between 60 and 90%. Most of the laser energy not absorbed on the first pass through the film was absorbed by the glass slide substrate. Temperature was measured with a 5-μm foil thermocouple embedded in the sample that had an estimated response time of the order of microseconds. Usually in rapid heating experiments where the sample is conductively heated, thermal conduction in the sample (in this case binder) would limit the response. However, in this study because the sample was radiatively heated with relatively uniform, in-depth absorbed energy, response-time limitation was effectively removed. As a result the actual response time was estimated to be of the order of the thermal conduction time constant in the thermocouple (microseconds), which effectively eliminated thermal lag as a concern in the interpretation of the results. The experiments were performed at slight positive pressure and under inert gas (nitrogen) atmosphere to eliminate any gaseous flame and its associated conductive heat feedback.

Sample Formulations

Sample formulations that were used are (mass fraction) AP (2 μm) = 0 and 73.1% and binder (DDI or IPDI) = 100 and 26.9%. The binder formulations used are (mass fraction) HTPB = 77.4 and 69.4%, IPDI = 5.9%, DDI = 13.9%, and dioctyl adipate = 16.7%. Two combinations were used for each curative (DDI or IPDI): pure binder (no AP) and 73% AP.

Sample Preparation and Setup

Sample slides were prepared by the following process. The ingredients were weighed to within 0.0001 g and placed in a plastic bag. The mixture was thereafter kneaded for 90 min to ensure homogeneous dispersion. The sample was created in the form of a thin film by using a spacer (60-μm-thick tape) with a square hole cut out. The spacer tape was adhered to a glass microscope slide and the thermocouple was placed so that the junction was in the center of the square cutout. The thermocouple was held in place against the glass slide by a magnet placed below the slide. A small drop of the binder mixture was then put on the thermocouple tip. A plastic cover (polypropylene or Teflon®) was placed on top of the slide and secured by a spring clip. The samples were cured at 60°C and atmospheric pressure for 5 days, resulting in film thicknesses of 30–60 μm. Thickness was measured after curing with a profilometer. The sample setup was placed inside a Plexiglas® chamber that was purged with nitrogen gas at slightly positive pressure to exclude oxygen. The sample was positioned on a stand at the focal point of a laser-beam integrator. Laser cali-

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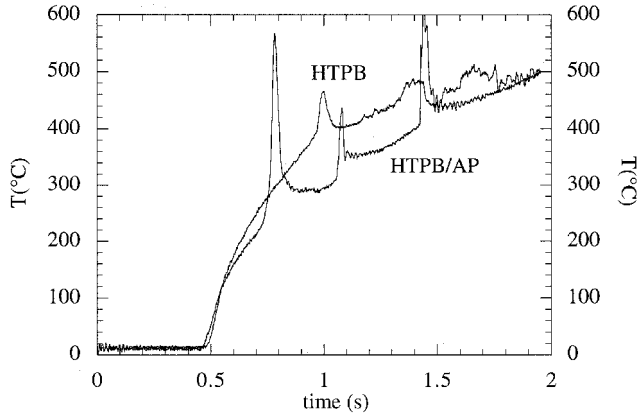

Fig. 1 Effect of fine AP on DDI-cured HTPB decomposition temperature history.

bration measurements showed that the mean laser flux at the position of the sample was 100 W/cm^2. Laser-power output was detected by photoelectromagnetic (PEM) detector monitoring a fraction of the laser beam and recorded.

Results and Discussion

The most significant effect observed in this study was that of including fine AP in the binder. Figure 1 shows the effect of fine AP on decomposition temperature history for DDI curing (similar results were obtained for IPDI). The DDI curve (without AP) shows the typical nonenergetic binder response (similar for IPDI and DDI). For the first 0.5 s of heating, up to 400°C, the temperature follows a profile typical of inert heating, as verified by heat transfer computational simulations. This profile has a steep initial slope that decreases gradually with time. Decomposition begins at 400°C, usually with a rapid, weakly exothermic event, as indicated by a small temperature spike. A significant decrease in the mean slope of the curve also occurs at this point, indicating the onset of a slower, endothermic decomposition process. Further discussion of HTPB decomposition chemistry, including DDI/IPDI, temperature, and pressure effects has been given by Chen and Brill[6] and Arisawa and Brill.[7] In contrast to the pure HTPB behavior, the samples that included AP began decomposing at a lower temperature, between 250 and 300°C, with a rapid, strong exothermic event (first spike in Fig. 1). This was followed by a slower endothermic process as indicated by the slow recovery of the mean profile, whose process was punctuated by additional rapid exothermic events (second and third spikes in Fig. 1). The main significance of these observations is that because AP (lightly pressed powder with no binder) samples did not show the 250–300°C spike, that event must correspond to an exothermic condensed-phase interaction between fine AP and binder. At low heating rates AP exhibits an orthorhomic to cubic phase transition at 240°C associated with free rotation of the perchlorate anions.[8] Perhaps the 250–300°C exothermic event seen in Fig. 1 for HTPB/AP is also associated with the onset of perchlorate ion-free rotation facilitating reaction with the surrounding binder.

Summary

Rapid thermal pyrolysis (10^2–10^3 K/s) was performed on thin film (30–60 μm) mixtures of fine AP and HTPB binder with CO_2 laser energy and simultaneous temperature measurement with foil microthermocouples. A strong condensed-phase chemical interaction was found to occur between fine AP and HTPB as had been previously reported for similar polymers under slow heating conditions.[4] Without AP, endothermic binder decomposition begins at about 400°C, often with a weakly exothermic initiatory event. A significant difference in decomposition was observed with the addition of fine (2 μm) AP: a relatively strong exothermic event occurs at 250–300°C, which is attributed to chemical interaction between fine AP and HTPB (pure AP so rapidly heated does not exhibit this event). This suggests that in the combustion of HTPB propellants containing fine AP, such as wide AP particle size distribution propellants, the condensed phase chemistry between fine AP and HTPB may play a significant role.

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References

[1]Chakravarthy, S. R., Price, E. W., and Sigman, R. K., "Binder Melt Flow Effects in the Combustion of AP-HC Composite Solid Propellants," AIAA Paper 95-2710, July 1995.

[2]Price, E. W., Shakravarthy, S. R., Sigman, R. K., and Freeman, J. M., "Pressure Dependence of Burning Rate of Ammonium Perchlorate-Hydrocarbon Binder Solid Propellants," AIAA Paper 97-3106, July 1997.

[3]Waesche, R. H. W., and Wenograd, J., "The Effects of Pressure and Additives on the Kinetics of Decomposition of Ammonium Perchlorate," Western States Section, Combustion Inst., WSCI-67-8, East Hartford, CT, April 1967.

[4]Waesche, R. H. W., "Calculation of Solid Propellant Burning Rates from Condensed-Phase Decomposition Kinetics," AIAA Paper 69-145, Jan. 1969.

[5]Isbell, R. A., and Brewster, M. Q., "Optical Properties of Energetic Materials from Infrared Spectroscopy," *Journal of Thermophysics and Heat Transfer*, Vol. 11, No. 1, 1997, pp. 65–71.

[6]Chen, J. K., and Brill, T. B., "Chemistry and Kinetics of Hydroxyl-Terminated Polybutadiene (HTPB) and Diisocyanate-HTPB Polymers During Slow Decomposition and Combustion-Like Conditions," *Combustion and Flame*, Vol. 87, 1991, pp. 217–232.

[7]Arisawa, H., and Brill, T. B., "Flash Pyrolysis of Hydroxyl-Terminated Polybutadiene (HTPB): Implications of the Kinetics and Mechanism to Combustion of Organic Polymers," *Combustion and Flame*, Vol. 106, 1996, pp. 131–154.

[8]Jacobs, P. W. M., and Whitehead, H. M., "Decomposition and Combustion of Ammonium Perchlorate," *Chemical Reviews*, Vol. 89, 1969, pp. 551–590.

Modeling the Effect of Unsteady Chamber Conditions on Atomization Processes

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Introduction

THE dynamic behavior of fluid flow through an orifice (injector) brought about by unsteady chamber conditions has been theorized to be a possible explanation for high-frequency combustion instabilities in liquid rocket engines.[1,2] Reba and Brosilow[3] studied the effects of large-amplitude axial acoustic disturbances in the injection chamber on jet breakup length and periodicity of droplet formation for liquids injected into

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