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Laser Pyrolysis of Hydroxyl-Terminated Polybutadiene

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A method was developed for measuring the dynamic regression rate and plume transmission loss during laser pyrolysis of polymeric binder materials. This method was applied to an investigation of the thermal decomposition of hydroxyl-terminated polybutadiene. Measurements of steady regression rate and surface temperature during constant flux laser pyrolysis were correlated using a zeroth-order, single-step model to obtain global decomposition kinetic constants and the heat of decomposition. At these heating rates (10^2–10^4 K/s) the activation energy was $E_c = 11$ kcal/mole ($E_s = 5.5$ kcal/mole). This is substantially lower than the values that have been obtained by lower heating rate (0.1–1 K/s) methods such as thermogravimetric analysis, differential thermal analysis, and differential scanning calorimeter, indicating that the rate-controlling decomposition step is a strong function of heating rate. It was also found that the addition of carbon black as an opacifier lowers the regression rate significantly, probably due to carbon accumulation on the surface. Pulsed laser pyrolysis tests gave a two-peaked, nonlinear response with one peak near 1 Hz corresponding to condensed phase processes and another peak near 300 Hz corresponding to gas phase processes.

Nomenclature

A_s = pre-exponential factor in simple Arrhenius surface pyrolysis expression
A_0 = pre-exponential factor in zeroth-order pyrolysis expression
A_1 = pre-exponential factor in first-order pyrolysis expression
C = specific heat of condensed phase, 2.5 J/g-K (0.6 cal/g-K)
E_c = activation energy of condensed phase global decomposition reaction
E_s = effective surface activation energy, $E_c/2$
f_r = fraction of radiant energy transmitted through surface reaction layer
K_a = absorption coefficient of condensed phase material
m = mean or steady mass flux, $\rho_c r_b$
Q_c = condensed phase heat of decomposition, <0 endothermic
q_c = mean conductive heat flux from gas to condensed phase
q_r = mean absorbed radiant heat flux
R = universal gas constant
r_b = mean or steady regression rate
T_s = surface temperature
T_0 = initial temperature
$Y_{p,s}$ = mass fraction of unreacted polymer at surface, 0.01
α_c = thermal diffusivity of condensed phase, 1*e*-3 cm^2/s
ρ_c = density of condensed phase, 0.92 g/cm^3

Introduction

HYDROXYL-TERMINATED polybutadiene (HTPB) has been the preferred binder in composite propellants in the recent past. Renewed interest in hybrid propulsion has also focused attention on HTPB since it is the primary solid fuel candidate for such systems. It is therefore desirable to obtain improved understanding of the pyrolysis characteristics of HTPB under high heating rate rocket conditions (10^2–10^6 K/s).

The laser is a convenient tool for studying polymer pyrolysis at high heating rates. When the target is mounted on a sensitive force transducer its steady regression rate can be found from the instantaneous mass loss as measured by the force transducer. One advantage of the laser technique is that the radiation is monochromatic and a variety of wavelengths are available. Substantial powers can be concentrated in the monochromatic beam of the laser and wavelength can be selected for highest possible opacity for any given material. For example, the 10.6-μm CO$_2$ laser is well suited for HTPB processing since the absorption coefficient at 10.6 μm is on the order of several hundred cm^{-1}. Also, the temporal profile of the laser flux can be easily modified, allowing for the characterization of the material response in both steady and unsteady regimes. One area of concern with laser processing is obstruction of the laser energy by the plume formed during the process. The plume obscures the incoming radiation and in many cases significantly reduces the flux that reaches the surface of the target. Therefore, an important aspect of laser pyrolysis is a method for measuring the transmissivity of the laser-generated plume.

The pyrolysis of HTPB and various other solid propellant binders was investigated by Cohen et al.,[1] using a focused xenon arc image radiant source. Carbon black powder (3%) was added to the HTPB to increase its absorption coefficient. Use of a cross-linking agent was not mentioned. Samples of 3-mm (1/8-in.) diameter were confined in glass rings at the focus of the arc image. The steady-state regression rate r_b was measured by weighing the sample before and after the test and the surface temperature was measured using an optical pyrometer. These data were used to construct Arrhenius plots from which kinetic constants were extracted ($E_s = E_c/2 = 16.9$ kcal/mole). An energy balance was used at the lower flux conditions to determine the heat of decomposition ($Q_c = -430$ cal/g). The maximum radiant flux was 1200 W/cm^2 (290 cal/cm^2-s) and the regression rate in inert gas atmosphere ranged from 0.04 to 0.4 cm/s. Over this range it was concluded that the kinetics were independent of pressure and heating rate. It was found that the kinetic constants could not be correlated with polymer structure and a weak-link degradation mechanism (boiling) was proposed as the process by which HTPB degrades at high heating rates. Areas of concern mentioned in the study were plume transmission losses at fluxes above 146 W/cm^2 (35 cal/cm^2-s), the sample burning out of the focal

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plane of the arc image, and starting and ending transients. To avoid errors from these factors, mass loss was plotted vs exposure time, the beginning and ending nonlinear regions were ignored, and only the central linear portions of the data were used to determine regression rate.

More recently, Chen and Brill[2] studied the decomposition kinetics of HTPB using simultaneous mass and temperature change SMATCH/Fourier transform infrared (FTIR) spectroscopy. The thin-film samples were heated by conduction from an rf induction-heated metal substrate mounted on a cantilevered quartz tube. The change in natural vibration frequency of the quartz tube allowed the dynamic mass loss to be measured. The method has the advantage of maintaining a nearly isothermal sample, but at the same time achieving relatively high heating rates (250–350 K/s). A second-order reaction was found to fit the mass loss data best. Various cross-linking agents were investigated and a noticeable effect on the kinetics was reported.

The data obtained by bulk heating techniques (such as SMATCH/FTIR) can be applied to linear regression of nonuniformly heated samples (at comparable heating rates) by solving the one-dimensional species and energy equations. For high activation energy, analytic solutions are available showing that when $E/RT >> 1$, the bulk, isothermal activation energy E_c is effectively halved in the resulting linear pyrolysis expressions, $E_s = E_c/2$. The activation energy obtained by SMATCH/FTIR was $E_c = 11.3$ kcal/mole for isophorone diisocyanate (IPDI) cross-linked HTPB. This corresponds to a substantially lower value of effective linear pyrolysis activation energy ($E_s = 5.7$ kcal/mole) than that reported by Cohen et al. ($E_s = 16.9$ kcal/mole).

Another approach that has been suggested is extrapolating low heating rate kinetic data to high heating rates. This approach was used by Lengelle et al.[3] for various hybrid rocket fuel candidates, including HTPB. Differential scanning calorimetry (DSC), which has a typical heating rate of 0.2 K/s, was used to obtain $E_c = 48.6$ kcal/mole and a global reaction order of one for HTPB. This E_c value is substantially higher than the SMATCH/FTIR value reported by Chen and Brill (11.3) and somewhat higher than the effective value of Cohen et al. (33.8). Measured data of Ref. 1 were compared with predictions based on a first-order reaction and the DSC kinetic data. A comparison of surface temperatures revealed differences of 100 K, an amount that was judged reasonable in view of the uncertainty created by the use of an IR pyrometer to measure temperature in a polymer with sharp temperature gradients.

There has been a considerable amount of controversy over the validity of extrapolating kinetic and thermochemical properties for polymers obtained under low heating rate, relatively isothermal conditions to high heating rate, nonisothermal linear pyrolysis conditions.[4] Such extrapolation assumes that the high heating rate linear pyrolysis decomposition mechanism is the same as that of the low heating rate bulk degradation.[5] Beck[6] reviewed the pyrolysis data of propellant binders, including HTPB, and argued that kinetic data extracted from bulk heating were dependent on both the heating rate and sample mass, and that extrapolating the relevant parameters to a linear pyrolysis situation was unwarranted. He further suggested that the activation energies obtained at high heating rates are too low to correspond to the breaking of any specific bond and instead correspond to the physical transport of mass through the solid or gas desorption. This view is supported by Akita[7] who stated that polymer combustion was controlled more by physical factors (heat transfer and mass flow) than by chemical factors. With regard to HTPB in particular, Chen and Brill's results support this view. In addition to the higher heating rate SMATCH/FTIR studies, Chen and Brill also performed low heating rate thermogravimetric analysis (TGA) tests (0.2 K/s) and found for HTPB, $E_c = 46$ kcal/mole, which agrees well with the DSC results of Lengelle et al., but is much higher than their SMATCH/FTIR results. They conclude that at high heating rates surface desorption of polymer fragments is the rate-controlling process, not some chemical bond breaking. These findings seem to have been confirmed by Radhakrishnan and Rama Rao[8] who obtained an activation energy of $E_c = 12$ kcal/mole using pyrolysis gas chromatography.

The laser pyrolysis method of studying HTPB decomposition has been adopted in this study because of the experimental convenience of the method. However, the technique of radiation-induced polymer pyrolysis still involves a number of difficulties, most of which are related to the one-dimensional equations used to analyze the data. One major difficulty is accurately quantifying the heat transfer to the target. This problem involves considerations such as correct calibration of the radiant flux (including plume transmission losses) and sample size. Sample size is somewhat restricted by the type of radiation source and power available. In general, larger samples have less lateral heat loss, but dilute the laser flux. Uniformity of the incident flux is important, requiring some type of spatial smoothing of the incident beam. Better uniformity can sometimes be achieved by reducing the sample size and wasting part of the beam, but lateral heat transfer concerns limit the acceptable size of the sample. Beam divergence can also be a problem. High-power diffuse sources (such as arc-image lamps) require collection by large mirrors and refocusing, resulting in relatively small F-numbers (large divergence or solid angle). Such systems suffer from very small depths-of-focus and accompanying short test times. Short test times are undesirable because of the need to avoid starting and ending transients. In this regard lasers are advantageous because of their high degree of collimation. However, high-power lasers have nonuniform multimode beam profiles that require spatial smoothing. Some beam integrators (such as the Spawr used in this study) introduce a degree of divergence into the beam that is small, but nevertheless undesirable.

Another problem is the possible formation of a liquid layer on the surface (as was observed in this study for HTPB). If the sample is left unconfined on the sides (to reduce lateral heat transfer) the liquid layer runs down the sides, resulting in nonplanar regression. Confinement of the sample must be done carefully so as not to introduce unacceptable (or unquantifiable) lateral heat transfer. Note that lateral heat transfer problems may not always be heat loss to the surroundings, but can possibly be heat gain from the confining material if that material were being heated by absorption of the radiation streaming past the sides of the target. Glass, for example, absorbs broadband IR energy very efficiently.

The opacity of the target material is also an important concern. For similarity to conductive heating at the surface it is preferable that the intrinsic absorption index of the target material be high enough that most of the radiation is absorbed in the thin reaction zone at the surface (but not so high that reflection losses become significant). Addition of opacifiers such as carbon black can increase the absorption coefficient, but may introduce other unwanted effects and may even alter the degradation process and the apparent regression rate.

The measurement of regression rate is also an area of concern. Real-time monitering of the regression rate is preferred, but usually requires a transducer in the vicinity of the target. Unwanted heating and thermal drift of the transducer can be a significant problem when concentrated laser irradiation is involved. Although laser pyrolysis is a very useful method, the task of maintaining nearly ideal physical conditions without introducing additional uncertainties is a complicated one.

Experimental Procedure

The HTPB samples used in this study were cross-linked with IPDI. While a cross-linking agent may not be desirable in hybrid rocket applications it is an important additive in composite propellants. A 90/10 HTPB/IPDI mass ratio was used. Although HTPB is sufficiently opaque at 10.6 μm, an opacifier is not necessary for CO_2 laser processing and carbon black is still being considered as an additive in hybrid rockets.[9,10]

Therefore, samples were prepared both with and without carbon black to measure its effect on regression rate. In the carbon samples, 1% mass fraction of submicron Cabot Regal (300R GP-3020) carbon black powder was added. The samples were mixed for 90 min, placed under a vacuum of approximately 0.03 atm for 30 min to release bubbles that formed during mixing and cured at 60°C for 2–3 days. Two sample sizes were tested, 10 by 10 mm squares (confined by thin aluminum walls) and 3.35-mm-diam cylinders confined in glass tubes. The smaller samples gave lower plume transmission loss (higher plume transmissivity). The two configurations were used to test the effect of lateral heat transfer. Since the regression rates were found to be similar between the two sample types at the same absorbed heat flux (after correction for plume transmission), it was concluded that lateral heat transfer between the confining walls (either aluminum or glass) and the HTPB was negligible.

The laser pyrolysis technique developed in this study involves three kinds of tests: 1) regression rate tests, 2) plume transmission tests, and 3) microthermocouple measurements. In the regression rate tests, a small sample of HTPB is placed on a vertically oriented force transducer. The transducer is calibrated so that its voltage output can be converted into mass loss. Before the laser is fired, the transducer signal is constant, reflecting the fact that no mass is being lost from the sample. After the laser shutter is opened and the sample begins to pyrolyze, the signal decreases, because of the mass loss of the sample (recoil force because of the momentum flux of the pyrolyzing gases was negligible for instantaneous fluxes below 2000 W/cm^2). For a constant laser flux the slope of the signal (time derivative) quickly reaches a maximum steady value. This value corresponds to the steady-state regression rate of the sample. Two types of force transducer were used, a Hottinger Baldwin Messtechnik (HBM) Q11 transducer and a Kistler 504E4 piezoelectric force transducer. The latter has better frequency response (for unsteady tests), but is more thermally sensitive and lacks true dc capability; the Q11 was used primarily for the steady regression rate tests. Aluminum and Space Shuttle thermal tile were used to thermally insulate the force transducers. With these measures, transducer thermal drift was eliminated. Regression rate tests were conducted in a partially sealed chamber that was flushed with argon and helium before each test and maintained at a slight positive pressure during the test to reduce oxygen infiltration. A weak flame was still observed in the gas phase, but for most conditions (all steady regression tests) the standoff distance of the flame (>2 cm) was such that conductive heat feedback from the flame to the sample was negligible. This was verified with thermocouple measurements. A KCl window was used to transmit the laser beam into the test chamber.

A technique for measuring the laser energy transmitted through the plume formed by the pyrolysis gases and particulates was also developed. Copper capillary tubing was used to pass transmitted laser energy reaching the HTPB sample surface through the sample to a photoelectromagnetic (PEM) detector. The transmissivity was obtained from the ratio of the plume-attenuated signal and the initial signal, before laser irradiation. The laser output was continually measured on-line using a second PEM detector monitoring a fraction of the laser power. This signal was calibrated and used to obtain the incident (before plume transmission loss) power. Reflection loss of the laser energy at the sample surface was estimated from the Fresnel relations to be 5%. Spatial variations in the laser beam profile were smoothed using a multiple mirror Spawr beam integrator. The beam was expanded onto the integrator that focused the beam into a 1 by 1 cm square at the sample.

Temperature through the pyrolysis zone was measured by embedding microthermocouples in the sample. Type S (platinum/platinum-10% rhodium) 5-μm thermocouple wire was used. These measurements were used to obtain the surface temperature T_s and an estimate of the conductive heat flux at the gas interface q_c. Details of these measurements are available in Ref. 11.

Data Analysis

The one-dimensional steady-state energy equation for the HTPB sample at T_0 is

$$T_s = T_0 + \frac{Q_c}{C} + \frac{q_r + q_c}{\rho_c r_b C} \tag{1}$$

For all steady-state runs (constant laser flux) the conductive heat flux was negligible compared with the radiative flux $q_c << q_r$. The condensed phase decomposition can be modeled by a single-step E_c and Q_c (<0 endothermic). Assuming a zeroth-order reaction [rate of consumption of unreacted polymer $= A_0 \rho_c \exp(-E_c/RT)$] and high activation energy ($E_c/RT >> 1$) gives the following result:

$$r_b^2 = \frac{A_0 \alpha_c R C T_s^2}{E_c[C(T_s - T_0) - (Q_c/2) - (f_r q_r/\rho_c r_b)]} \exp\left(\frac{-E_c}{RT_s}\right)$$
$$\text{where} \quad f_r = \exp\left(\frac{-K_a \alpha_c R T_s}{r_b E_c/2}\right) \tag{2}$$

This expression was first obtained by Merzhanov[12] (neglecting radiation). Lengelle[13] derived a similar result using activation energy asymptotics for arbitrary reaction order between zero and one (still neglecting radiation). Ibiricu and Williams[14] later extended the expression to include a radiant flux, assuming the radiation was all absorbed beneath the reaction layer. The expression was further extended to account for partial absorption of radiation in the reaction layer by introducing the transmissivity of the reaction layer f_r.[15] The validity of Eq. (2) has been confirmed for the adiabatic gas condition and high activation energies through numerical solution of the governing equations.[15] For purposes of comparison, the simple Arrhenius and first-order reaction rate expressions used by Cohen et al.[1] and Lengelle et al.,[3] respectively, were also evaluated:

$$r_b = A_s \exp[(-E_s)/RT_s] \tag{3}$$

$$r_b^2 = \frac{A_1 \alpha_c R T_s}{E_c\{(-\ell n\, Y_{p,s})[1 - (T_0/T_s) - (Q_c/CT_s)] + (Q_c/CT_s)\}}$$
$$\times \exp\left(\frac{-E_c}{RT_s}\right), \quad \text{for} \quad q_r = 0 \tag{4}$$

The pre-exponential factors (A_0 and A_1) in Eqs. (2) and (4) have units of inverse seconds, whereas A_s in Eq. (3) has units of centimeters per second. The properties of HTPB were assumed to be $\rho_c = 0.92$ g/cm^3, $C = 0.6$ cal/g-K, $\alpha_c = 1e\text{-}3$ cm^2/s, $T_0 = 300$ K, and $K_a = 500$ 1/cm.

Results

Measurements of plume transmissivity are shown in Fig. 1. The larger 10-mm-square samples produced a much more opaque plume (lower transmissivity) than the smaller 3 mm samples. Thus, for a given laser power, the flux reaching the surface of the 10 mm samples was less than that for the 3-mm samples. Furthermore, the transmissivity decreased noticeably with increasing incident laser flux for the 10-mm samples while remaining relatively constant (aside from data scatter) for the 3-mm samples. Nevertheless, the regression rates were the same for the two sample types at the same absorbed flux q_r (after correction for plume transmission). From this it was concluded that lateral heat transfer was not affecting regression rate in the small samples. As a result it was possible to achieve higher regression rate measurements with the 3-mm samples.

Figure 2 shows the effect of carbon black on regression rate. These results show that adding this opacifier reduces the re-

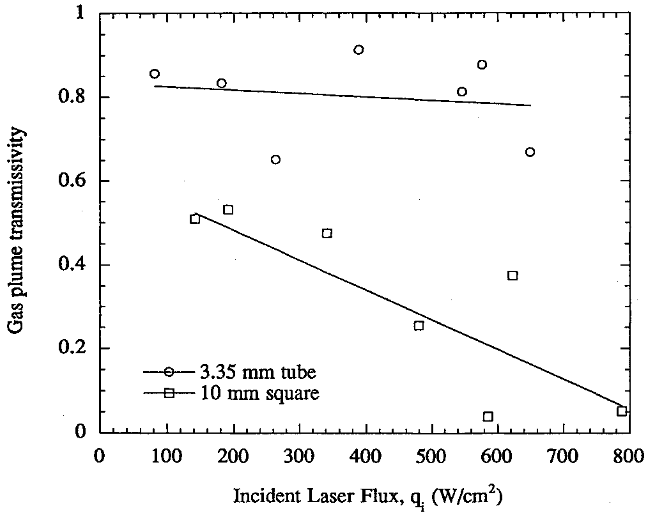

Fig. 1 Laser plume transmissivity.

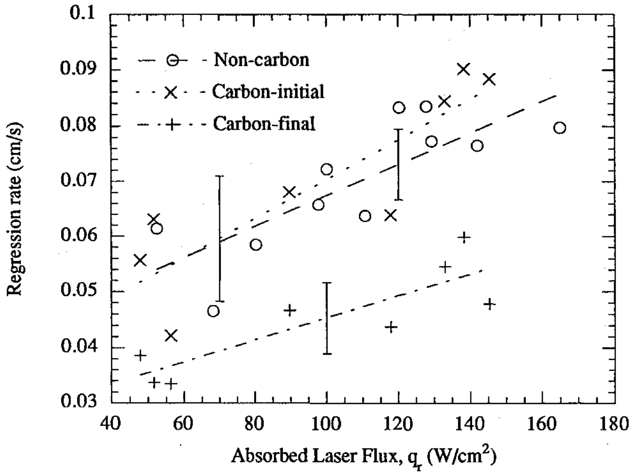

Fig. 2 Regression rates for 1%-carbon and noncarbon samples.

gression rate. For tests with carbon the mass loss vs time signal mean slope at the beginning of the test would be the same as that for the noncarbon samples (for the same absorbed flux), indicating that the initial regression rate was the same as that for nonopacified HTPB. But unlike the noncarbon samples the mean slope would not stay constant over the course of the test, but slowly decreased, indicating that the regression rate was decreasing. These results are shown in Fig. 2, where the initial carbon regression rates are similar to the noncarbon rates, but the final carbon rates (taken from the slope at the end of the test) are reduced by 30–40%. It was also observed that if the laser pyrolysis was interrupted and the sample surface examined microscopically, there was a very noticeable difference between the surface of the noncarbon and carbon samples. The noncarbon samples would remain smooth and planar, like the original surface. The carbon samples would develop a rough, carbonaceous layer with molten binder rivulets between protruding carbon agglomerates. Formation of this carbonaceous layer on the surface is thought to be responsible for the observed reduction in regression rate in the carbon black samples. Tests were not extended to long enough times to determine how close the measured final regression rates for the carbon samples were to the limiting (long time) value. Based on the observed trend the steady regression rate of a carbon sample would not be any greater than 70% of the corresponding noncarbon value (for the same absorbed flux).

Measurements of regression rate as a function of absorbed laser flux for carbon-free HTPB are shown in Fig. 3. These

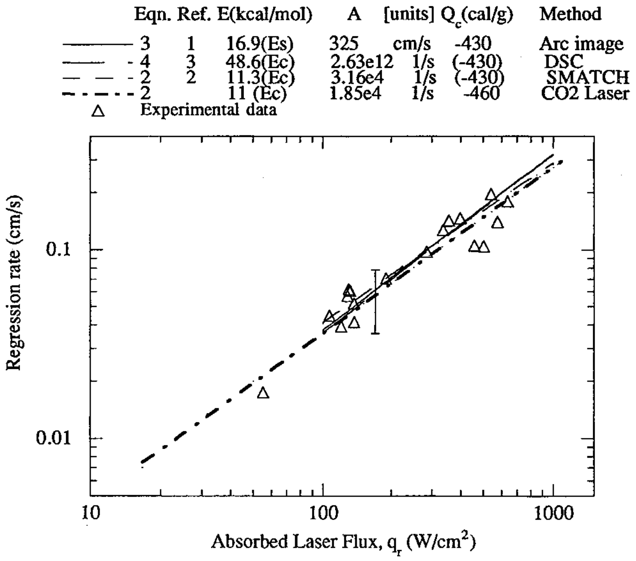

Fig. 3 Regression rate vs absorbed flux (no carbon).

results agree well with the arc-image results of Cohen et al., as indicated by the fact that the Arrhenius curve fit obtained from their data (solid line in Fig. 3) passes through the laser pyrolysis experimental data points. This agreement may be fortuitous, however, since the arc-image samples had 3% carbon and the laser pyrolysis samples had none. As discussed earlier it was found that small amounts of carbon reduce regression rate. Another difference between the two cases is that the glass confinement rings (which were used in both studies), might have allowed a substantial lateral transmission of the low *f*-number, broadband arc-image radiation to the sample but not the collimated 10.6-μm laser radiation. (Recall that comparison of regression rates from 10-mm aluminum-confined samples and 3.3-mm glass-confined samples indicated that lateral heat transfer effects were negligible for the laser pyrolysis tests.) These two differences (carbon and lateral heat transfer) would have off-setting effects on the regression rate and may explain the similarity in measured r_b results between the arc-image and laser pyrolysis studies.

Figure 3 shows that several correlations fit the measured regression rate data. In addition to the arc-image-based simple Arrhenius correlation of Cohen et al.,[1] the DSC-based first-order reaction of Lengelle et al.,[3] fits well as does the zeroth-order decomposition relation using the SMATCH/FTIR data of Chen and Brill.[2] What this suggests is that regression rate vs absorbed heat flux alone is not enough information. Nearly any activation energy and any reaction order could be made to fit. Additional information such as surface temperature is needed. The fourth theoretical curve shown in Fig. 3 is that obtained in this study and is based on fitting both regression rate and surface temperature data.

Surface temperature results are plotted in Fig. 4 as $1/T_s$ vs absorbed flux. The dashed curve was obtained from the zeroth-order decomposition model using E_c = 11 kcal/mole, Q_c = −460 cal/g, and $A_0 = 1.85e4$ s^{-1}. The solid curve is based on the Arrhenius pyrolysis expression and the data of Cohen et al. The primary difference between the laser pyrolysis results of this study and the arc-image results of Cohen et al. is lower surface temperatures in this study. This difference may be related to the different methods used, microthermocouples vs an optical pyrometer, or it may be related to the difference in samples. As discussed, carbon was found to accumulate on the surface when included in the sample. It is possible that surface temperatures measured pyrometrically from a carbon-coated surface irradiated by broadband radiation would be systematically higher than those measured with thermocouples in a car-

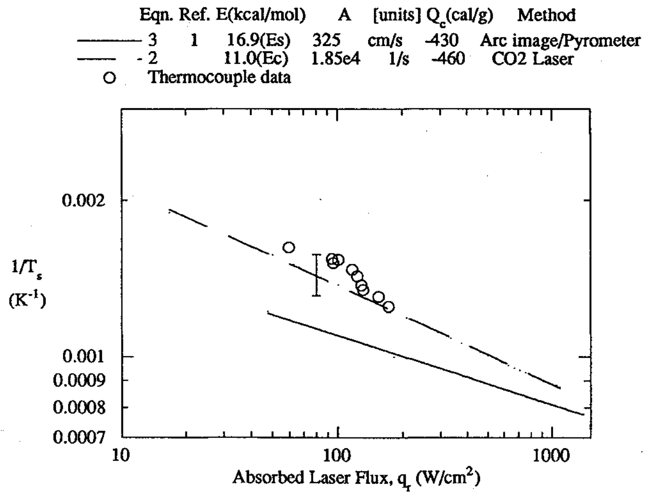

Fig. 4 Surface temperature vs absorbed flux (no carbon).

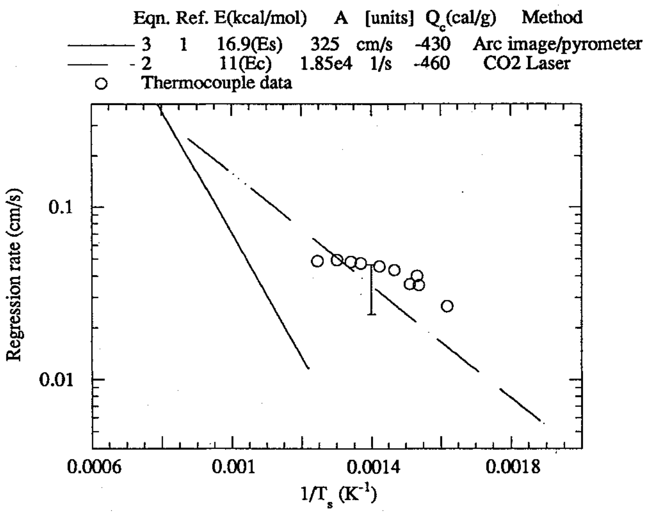

Fig. 5 Regression rate vs surface temperature (no carbon).

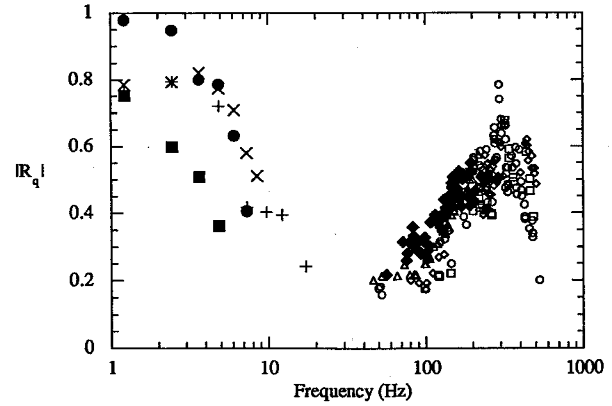

Fig. 6 Response function magnitude.

bon-free sample. Figure 5 shows the results rearranged as an Arrhenius plot, regression rate vs $1/T_s$.

Unsteady tests were also conducted using periodic pulsed laser input. In this case the instantaneous regression rate was obtained from the thrust recoil using a one-dimensional momentum balance rather than from mass loss. The time-domain thrust output and laser input signals were spectrally analyzed and the dimensionless response function R_q computed. Figures 6 and 7 show the magnitude and phase of the experimentally measured R_q for a variety of pulse train parameters (pulsewidth 1–100 ms, repetition rate 1–100 Hz, and mean flux 40–300 W/cm²). The response magnitude exhibits a local maximum at 1 Hz and another at 300 Hz. The low-frequency response is thought to be a combination of the thermal conduction relaxation response in the inert solid and the surface melt layer decomposition and desorption process. The characteristic frequencies of each of these processes can be estimated as follows:

$$f_c \approx r_b^2/\alpha_c = 0.6\ \text{Hz} \qquad f_s \approx (r_b^2/\alpha_c)(E_c/2RT_s) = 2\ \text{Hz} \tag{5}$$

The fact that E_c is relatively small results in only a slight frequency separation of the conduction and surface relaxation processes. The 300-Hz peak probably corresponds to the response of the gas phase flame. (As discussed later it was necessary in the unsteady tests for conditions to be such that gas phase flame conductive heat feedback was not negligible, unlike the steady tests.) The characteristic frequency for the gaseous thermal conduction relaxation response of a premixed, high-activation energy gas flame can be estimated similar to that previously for the condensed phase:

$$f_g \approx \frac{u_g^2}{\alpha_g} = \left(\frac{\lambda_c C_{p,g} \rho_c}{\lambda_g C \rho_g}\right) f_c, \quad \text{since} \quad \rho_c r_b = \rho_g u_g \tag{6}$$

Thermal conductivity λ and specific heat are similar between condensed and gas phases. The primary difference is in density, which is three orders of magnitude smaller for the gas phase at this pressure. This results in gas phase characteristic frequencies two to three orders of magnitude greater than in the condensed phase.

Two factors make the comparison of theoretical predictions with the unsteady measurements difficult at this time. The first

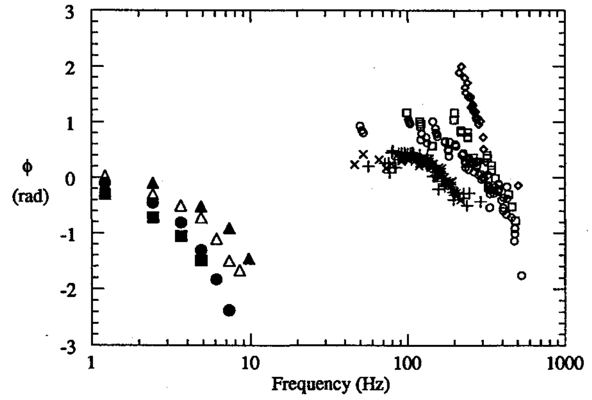

Fig. 7 Response function phase.

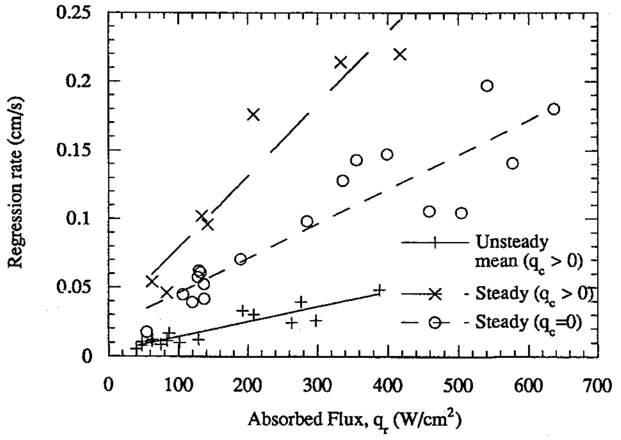

Fig. 8 Effect of gas flame conductive heat feedback and nonlinearity of response on mean regression rate.

is that the measured responses are nonlinear. The second is that the gas heat feedback was not negligible in these tests ($q_c > 0$). Both of these conditions are a result of the inherently low regression rate and low gas momentum flux of HTPB. To obtain a measurable thrust recoil response it was necessary to use the larger 10-mm samples and relatively large amplitude pulses and to operate the chamber with higher exhaust suction for lower transmission losses. The exhaust suction caused a slight negative pressure and greater air infiltration, which allowed the gas flame to move closer to the surface. Steady (constant laser flux) tests performed under these conditions confirmed that the regression rate was increased by the positive gas flame heat feedback as shown in Fig. 8 [compare steady ($q_c > 0$) and steady ($q_c = 0$) cases]. The effect of the nonlinearity of the response on the mean regression rates was to lower the mean rates below the steady (constant laser flux) values. This effect can be seen in the unsteady, mean ($q_c > 0$) regression rates of Fig. 8, which fall below not only the steady ($q_c > 0$) values, but also the steady ($q_c = 0$) values. (The effect of the extra gas flame heat feedback on mean regression rate was less than that of the nonlinearity of the response.) Nonlinearity of the response is not necessarily a fundamental obstacle. But a linear response is more desirable, both for reasons of experimental reproducibility and simplicity of modeling.

Conclusions

Thermal pyrolysis of HTPB/IPDI binder was studied using low divergence, uniform flux CO_2 laser radiation. Steady regression rate was measured during constant laser flux pyrolysis using a dynamic mass loss technique and surface temperature with microthermocouples. Plume transmission loss was also measured. Lateral heat transfer effects were eliminated as a source of error. Regression rate was measured on both 1% carbon- and noncarbon-containing samples. The presence of 1% carbon lowered the steady regression rate by at least 30%, probably due to accumulation of a carbon layer on the surface. Compared to the results of Ref. 1 for 3% carbon samples, the regression rates of the noncarbon samples in this study were similar while surface temperatures were approximately 200 K lower. The similarity in regression rates is unexpected, given the pronounced reduction in regression rate that was observed in this study with 1% carbon addition. Differences in spectral content and beam divergence between the CO_2 laser and arc-image systems may be important factors in this regard. The difference in surface temperature could also be due to differences in the two methods used, thermocouples in noncarbon samples vs pyrometric measurements of broadband arc-image irradiated carbon-containing sample surfaces.

Steady regression rates and surface temperatures were correlated using a zeroth-order, single-step, high activation energy model to obtain the global decomposition kinetic constants and the heat of decomposition. The effective sample heating rate ranged from 10^2 to 10^4 K/s. At these heating rates the global activation energy was $E_c = 11$ kcal/mole ($E_s = 5.5$ kcal/mole), in good agreement with Chen and Brill's[2] SMATCH/FTIR results measured at 250–350 K/s. This is substantially lower than the values that have been obtained by lower heating rate (0.1–1 K/s) methods such as TGA, DTA, and DSC, indicating that the rate-limiting process is a strong function of heating rate. At high heating rates typical of rockets some physical process (such as surface desorption of clipped polymer fragments[2]) appears to be the rate-limiting process.

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