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Plateau Burning Behavior of Ammonium Perchlorate Sandwiches and Propellants at Elevated Pressures

Satyanarayanan R. Chakravarthy,* Edward W. Price,† Robert K. Sigman,‡ and Jerry M. Seitzman§
Georgia Institute of Technology, Atlanta, Georgia 30332-0150

Further results on combustion of sandwiches made of alternating layers of ammonium perchlorate (AP) and a matrix of AP particles in polymeric binder in an expanded pressure range of 0.345–13.78 MPa (50–2000 psig), over a wide range of matrix lamina thicknesses, are reported. Inclusion of a nanoparticle-size burning rate catalyst in the matrix is also considered. The sandwich burning rates indicate plateaus over the 6.89–13.78 MPa (1000–2000 psig) pressure range for select ranges of matrix lamina thickness. These are correlated with similar plateau trends in the burning rates of composite propellant formulations with bimodal particle size distribution of the oxidizer and appropriate choice of coarse AP size, wherein the fine AP/binder matrices are of identical composition to those tested in the sandwiches. The dependence of the sandwich burning rates on the matrix lamina thickness and the quenched surface features are examined to explain the plateau burning rate trends. The results indicate that the two-dimensional coupling of heat feedback from the hot, near-surface parts of the oxidizer/fuel diffusion flamelets is diminished at elevated pressures due to their greater proximity to the burning surface and the corresponding shrinking of their lateral extent.

Introduction

IT has long been recognized that the details of combustion of composite propellants are inherently multidimensional in nature, although one-dimensional models incorporating multiple flames, such as the derivatives of the Beckstead–Derr–Price (BDP) model[1] have been popular. Recent advances have been reported on multidimensional modeling of sandwich and propellant configurations,[2–4] but such efforts are still fraught with difficulties in terms of uncertainties in chemical kinetic mechanisms and parameters and the requirement of large computational resources. Moreover, available results of modeling efforts are still confined to treating simple configurations of oxidizer and binder/fuel and do not as yet pertain to real propellant situations that include the presence of widely different oxidizer particle sizes, action of nanoparticle-size burning rate catalysts and the mechanism of their action, and the possibility of molten microflows of one of the pyrolyzing ingredients, for instance, the binder, on the burning surface. On the other hand, advanced experimental diagnostics have not yet been sufficiently developed for interrogation of the microstructure of combustion zone of composite propellants under high-pressure conditions to clarify its multidimensional details completely, including the complications just mentioned, although some progress has been reported in the recent past.[5–7] In view of this, multiple experimental observations on edge burning of simplified geometric configurations, such as alternating layers of oxidizer and fuel (i.e., sandwiches) and the collective interpretation of such observations continue to be relevant not only to understanding the predominant combustion mechanisms under different conditions, but also to address specific issues of macroscopic propellant combustion behavior. The present work is an example in this context, in that the extension of previous studies on sandwich burning over an expanded pressure range and the associated advancement in the understanding of the details of the combustion zone have been used to explain a plateau trend in the burning rates of sandwiches in an elevated pressure range. The work has prompted examination of propellant compositions for similar plateau burning rate trends, and striking correlations between sandwiches and propellants on such unique burning rate trends have been observed for the first time.

In the present work, burning of sandwiches with slabs of ammonium perchlorate (AP) forming the outer laminas and a matrix of fine AP particles and poly-butadiene acrylonitrile acrylic acid (PBAN) binder comprising the middle lamina is studied over the pressure range of 0.345–13.78 MPa (50–2000 psig). Inclusion of nanoparticle-size ferric oxide catalyst is also considered. This is an extension of past works at this laboratory in the pressure range of 2.07–6.89 MPa (300–1000 psig), wherein sandwiches with the middle lamina made of 1) pure binder lamina,[8] 2) an uncatalyzed matrix of fine AP and binder,[9] and 3) a fine AP/binder matrix with the addition of a nanoparticle-size ferric oxide burning rate catalyst,[10] were tested. Reference 11 summarizes these results in a consolidated manner to a large extent. The results of sandwich burning obtained in the present study and the explanation of propellant burning rate trends reported here can be understood in terms of the background of the insights gained from the past studies referred to earlier. Important aspects of the past studies pertinent to the present work are listed as follows (see Figs. 1 and 2, taken from Refs. 8 and 10, respectively):

1) The burning surface of the outer AP lamina far away from the lamina interface exhibits the self-deflagration behavior of AP, but there is lateral heat loss to the middle lamina in the vicinity of the interface that causes the AP lamina to protrude in that region. Correspondingly, this region exhibits a distinctly smooth appearance on the burning surface, referred to as the "smooth band."

2) The cause for the smooth appearance on the AP surface just referred to is not clear. It is known that the combustion of AP above its low-pressure deflagration limit (LPDL) involves a reactive liquid froth,[12] possibly one or more of its first decomposition products, namely, ammonia and perchloric acid. In the region where excessive heat drain occurs to the middle lamina in the sandwich, the AP lamina might not sustain the usual gas-phase flame, but rather undergoes decomposition due to heating from the oxidizer/fuel (O/F) diffusion flame. It is likely that the decomposition products, existing in molten form, smear the details of surface features in this region, presenting a smooth appearance in the quenched samples, as suggested by P. J. Paul and H. S. Mukunda in private communications in 1995. Such a

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*Postdoctoral Fellow, School of Aerospace Engineering; currently Assistant Professor, Department of Aerospace Engineering, Indian Institute of Technology Madras, Chennai 600036, India. Member AIAA.

†Regent's Professor Emeritus, School of Aerospace Engineering. Fellow AIAA.

‡Senior Research Engineer (retired), School of Aerospace Engineering.

§Associate Professor, School of Aerospace Engineering.

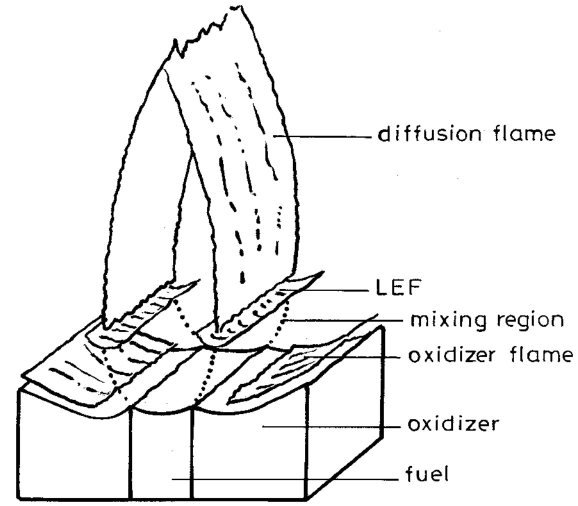


Fig. 1 Combustion zone structure for an AP/HC-binder/AP sandwich.[11]

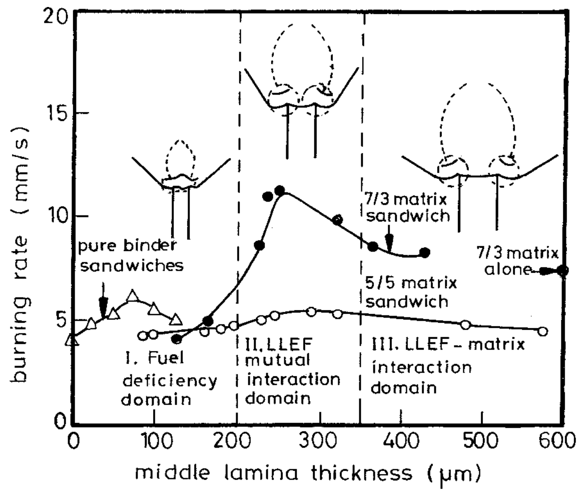


Fig. 2 Typical dependence of sandwich burning rate behavior on matrix lamina thickness for pure PBAN, and uncatalyzed AP/PBAN matrix in the 2.07–6.89 MPa (300–1000 psig) range[10]; data obtained at 3.45 MPa (500 psig).

possibility has not been resolved by means of any experiments designed specifically to investigate this aspect of AP combustion. In further work,[10] and in the present studies, situations have arisen that cause the leading edge of the diffusion flames (LEFs) to be located very close to the burning surface, resulting in a somewhat parched appearance of the region in the AP lamina immediately adjacent to the lamina interface, as detailed later. This region has been referred to as a "dry band."[10] In any of these investigations, the terms smooth band and dry band are used to refer to surface qualities presented in accompanying scanning electron micrographs (SEMs), without further elaboration on what exists in those regions of the surface.

3) The O/F diffusion flame is aligned along the stoichiometric surface in the gas-phase mixing fan anchored to the lamina interface, but it is not fully diffusion limited in the near-surface region. The LEF propagates in a premixing field, allowing chemical kinetics to play an important role.

4) The LEF has a certain lateral extent on the fuel-rich and oxidizer-rich sides of the stoichiometric surface, which is governed by a) the stoichiometry of the gases emerging from the laminas on either side of the interface and b) the proximity of the LEF to the burning surface.

5) The burning rate variation with the binder lamina thickness shows a peak around 50–75 μm for pure binder sandwiches, indicating a two-dimensional coupling in the heat feedback to the burning surface from the hot, near-surface LEFs. For small values of the binder lamina thickness, the system is too fuel lean to enable adequate heat release, and, for large thicknesses, the coupled effect of the adjacent LEFs is weakened.

6) When fine AP particles are mixed with the binder in the middle lamina, the LEFs in the mixing fan anchored to the lamina interface edge are designated as lamina LEFs (LLEFs), to distinguish them from LEFs that could possibly be attached to the fine particles, depending on their size and the pressure,[13] resulting in particle-attached LEFs (PLEFs).[9] With fine AP particles in the matrix lamina at a mass ratio level of AP/PBAN = 5/5, the peak in the sandwich burning rate variation with the middle lamina thickness appears at a large-thickness value of around 250–275 μm because the AP particles act as a diluent in the matrix. However, the LLEFs get closer to each other as the stoichiometric surfaces above the lamina interfaces move inward, and the lateral extent of the LLEFs are extended on the fuel-rich side due to the addition of the AP particles in the matrix. The AP/PBAN = 5/5 matrix does not sustain burning by itself.

7) When the addition of fine AP particles in the matrix is increased to the 7/3 level, the matrix is flammable by itself. As a consequence, there is a substantial rise in the burning rate peak with variation in the matrix lamina thickness. It is expected that the 7/3 matrix burns mostly in a premixed flame with fine AP particles of 10-μm size over the midpressure range of 2.07–6.89 MPa (300–1000 psig) (Ref. 13). This flame "canopies" the matrix and connects the fuel-rich sides of the adjacent LLEFs on the burning surface of the sandwich. In the limit of large-matrix lamina thickness, the sandwich burning rate asymptotically tends to a value somewhat greater than the matrix burning rate when tested alone. This indicates an interactive effect between each of the LLEFs and the matrix flame, as depicted in Fig. 2.

8) When a nanoparticle-size ferric oxide burning rate catalyst is added to the AP/PBAN = 5/5 matrix, it burns by itself in a smoldering fashion and with a weak pressure dependence, but the AP/PBAN = 7/3 matrix shows a substantial increase in the burning rate with the addition of the catalyst. The burning rates of the sandwiches with either matrix show a dramatic increase with the addition of the catalyst, but the peak in their variation with the matrix lamina thickness are not as pronounced as that in the case of the uncatalyzed sandwiches, particularly with the AP/PBAN = 7/3 matrix. In interpreting these observations, it is noted that the enormous increase in the density of AP/binder contact lines in the matrix affords active sites for the catalyst to participate in surface-layer reactions. As a consequence, the gas-phase flame complex is brought closer to the burning surface. The greater proximity of the LLEFs to the burning surface results in a parched appearance of the AP lamina immediately adjacent to its interface with the matrix, as opposed to a smooth appearance in the uncatalyzed case, referred to earlier.

Note that Fig. 1, retained from Refs. 8, 9, and 11, shows the stoichiometric surface arising from the AP/binder interfacial edge, as opposed to what is argued by Buckmaster et al.,[14] based on flux balance boundary conditions at the burning surface. It will be seen in the context of the present study that this detail is not that important in interpreting the observations at elevated pressures.

When the observations and conclusions noted are adapted to better understand the present results at elevated pressures, it is possible to explain plateau burning rate trends observed at these pressures, mostly within the considerations of the details of the gas-phase flame complex in the combustion zone. The explanation is seen as one of the mechanisms that contribute to plateau burning rate trends in composite propellants. One of the other prominent mechanisms is related to binder melt flow on the burning surface and its effect on the decomposition and deflagration of fine and coarse AP particles in the propellant.[15–18] In this regard, the choice of PBAN as the binder in the present study is quite fortuitous, although it is not considered a contemporary choice for composite propellants. PBAN has long been considered a dry binder in that its thermal decomposition is preceded by very little melting,[16] and, hence, samples with that binder have been reported to be "well-behaved."[19] Therefore, it has been possible in the present context to explain the plateau burning trends based on the gas-phase combustion details clearly, without any ambiguity relating to the details of surface-layer processes such as binder melt flow effects.

Experimental

The present study employs two types of experiments: 1) burning rate measurements based on combustion photography and 2) examination of quenched samples in the SEM. These experiments are routine in propellant combustion research, and are detailed elsewhere.[20,21]

Two types of samples are studied in the present work. One set of samples consists of sandwiches, whereas, in another series of tests, a family of bimodal propellants is tested. The fine AP used in all of the samples in this study was supplied by K. J. Krauetle of the U.S. Naval Air Warfare Center, China Lake, California. It is found to be in the size range of 10–20 μm, and is designated as "10-μm AP." All test samples in the study contain PBAN binder. The binder is made of PBAN prepolymer (64.14%), di–octyl adipate (DOA) plasticizer (15%) and epoxy curing agent (20.86%), the percentages in parentheses being mass proportions. The burning rate modifier used is designated as "Pyrocat," a nanoparticle-size ferric oxide powder; it is the same as that used in Ref. 10.

Three types of sandwich samples are considered. They differ primarily in the matrix composition. The two uncatalyzed matrices have fine AP and binder in the mass ratio of 7/3 and 5/5. In comparison, the stoichiometric O/F mass ratio for the AP/poly-butadiene combination is approximately 9/1. The catalyzed matrix has fine AP and binder in a mass ratio of 7/3, and the catalyst at the level of 1% of the matrix by mass. The matrix lamina thickness in the sandwich tests is varied in the range of 100–600 μm.

Five bimodal PBAN propellants are tested, with one of them (mix 5) containing the burning rate catalyst. The catalyst is added at the level of 1% of the fine AP/binder matrix in the propellant by mass. Four of the propellant formulations have a fine AP/binder matrix with O/F ratio at the 7/3 level, including the catalyzed propellant. The fifth formulation contains fine AP/binder matrix in the O/F ratio of 5/5 (mix 4). Coarse AP is added in all of the formulations to take the total AP/binder ratio by mass to 87.5% in the propellant. The coarse AP size in the three uncatalyzed propellant formulations with O/F ratio of 7/3 in the matrix is varied at size levels designated as 200 μm (180–212 μm) in mix 1, 300 μm (300–355 μm) in mix 2, and 400 μm (355–425 μm) in mix 3. The ranges in the parentheses denote the size ranges of openings in standard sieves used to segregate the particles. The 300-μm AP is used in the remaining two formulations. The propellant compositions tested in this study are summarized in Table 1. All of the AP samples used in the study, namely, the fine AP, the coarse AP of different sizes, and that used to prepare the slabs for sandwiches, are not conditioned with any anticaking agent such as tricalcium phosphate.

All samples are tested for burning rate measurements by combustion photography in the pressure range between 0.345 and 13.78 MPa (50–2000 psig). The pressure is monitored with the help of regularly calibrated Bourdon gauges with resolutions of 0.035 MPa (5 psig) in the 0–0.345 MPa (0–50 psig) range, 0.069 MPa (10 psig) in the 0.345–2.07 MPa (50–300 psig) range, and 0.345 MPa (50 psig) in the 2.07–13.78 MPa (300–2000 psig) range. The combustion chamber is pressurized with nitrogen, a slight amount of which is vented through a choked orifice (needle valve) during burning of samples. The venting flow is maintained at dynamic head levels of 0.035–0.069 MPa (5–10 psig), monitored with a differential pressure Bourdon gauge with a resolution of 0.0069 MPa (1 psig). The venting serves the dual purpose of maintaining the pressure in the combustion chamber constant during sample burning, and of clearing the optical windows of any smoke that might obscure the viewing of the burning event.

Burning rates are obtained by noting the location of the burning surface of the sample along the direction of flame propagation in successive frames of video images, and fitting a straight line to the loci plotted as a function of time with a correlation coefficient >99.9%. The slope of the straight line adjusted for the magnification of the images gives the burning rate of the sample. At least 50% of the tests are repeated, and the repeatability of the data is within 5%.

The focus of the quench tests is on sandwiches, in the elevated pressure range, with specific attention paid to the pressure levels at 10.34 MPa (1500 psig) and 13.78 MPa (2000 psig). The accuracy in pressurization in these experiments is the same as in the combustion photography experiments, as detailed earlier.

Results

Sandwich Studies

Burning Rates

Figures 3 and 4 show the variation of the burning rates of sandwiches with the matrix lamina thickness at different pressures. In Fig. 3, comparison is made of uncatalyzed sandwiches with different matrices, namely, AP/PBAN = 5/5 and 7/3. Data at 2.07, 3.45, and 6.89 MPa (300, 500, and 1000 psig) are taken from Ref. 9. In Fig. 4, sandwiches without any catalyst and with 1% Pyrocat in an AP/PBAN = 7/3 matrix are compared. Whereas the uncatalyzed data at 2.07, 3.45, and 6.89 MPa (300, 500, and 1000 psig) are from Ref. 9, as before, the data with the catalyst at these pressures are from Ref. 10. The AP self-deflagration rates at different pressures are shown along the left ordinate and the burning rates of matrices that undergo self-sustained burning at a given pressure are shown in the right ordinate in both of these plots. The uncatalyzed

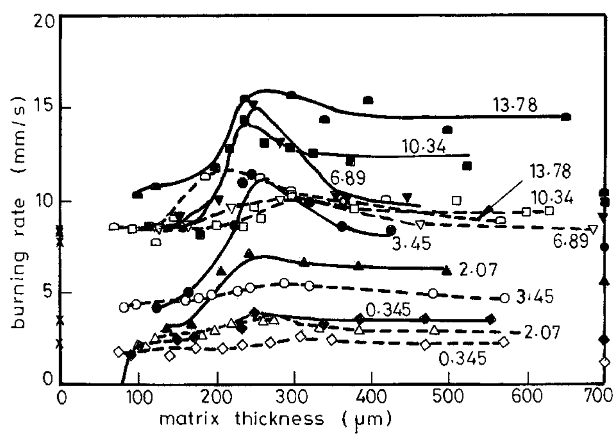


Fig. 3 Dependence of burning rate on matrix lamina thickness for uncatalyzed sandwiches with AP/PBAN = 7/3 (filled symbols and continuous lines) and 5/5 (open symbols and broken lines) matrices at different pressure levels (values noted in megapascal); burning rates of pressed AP are shown on the left ordinate and those of matrix burning alone on the right ordinate lines.

Table 1 Propellant compositions tested in the present study

Mix no.	% Binder	Coarse AP Size, μm	Coarse AP %	% Fine AP	% Pyrocat	Coarse AP/ fine AP	Fine AP/ binder	% Total solids
1	12.50	200	58.33	29.17	——	66.66:33.34	70:30	87.50
2	12.50	300	58.33	29.17	——	66.66:33.34	70:30	87.50
3	12.50	400	58.33	29.17	——	66.66:33.34	70:30	87.50
4	12.50	300	75.00	12.50	——	85.71:14.29	50:50	87.50
5	12.45	300	58.09	29.05	0.42[a]	66.66:33.34	70:30	87.55

[a]Proportion in propellant: 1% in matrix, as in the sandwich samples.

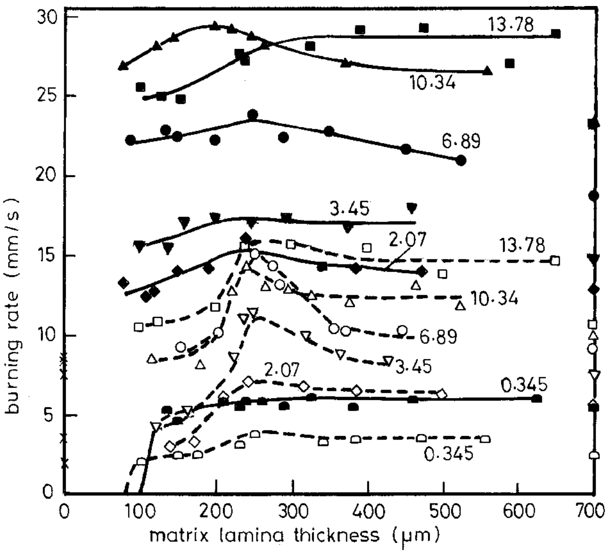


Fig. 4 Dependence of burning rate on matrix lamina thickness for sandwiches with uncatalyzed (open symbols and broken lines) and 1% Pyrocat-catalyzed (filled symbols and continuous lines) AP/PBAN = 7/3 matrices at different pressure levels (values noted in megapascal); burning rates of pressed AP are shown on the left ordinate, and those of matrix burning alone on the right ordinate lines.

AP/PBAN = 5/5 matrix self-sustains burning only at 0.345 MPa (50 psig) in the range tested. The sandwich burning rates are logically expected to approach the AP self-deflagration rate at each pressure level as the matrix lamina thickness approaches zero. However, at 0.345 MPa (50 psig), where AP does not exhibit self-deflagration (with the initial temperature of the sample being room temperature), the sandwiches fail to burn to completion at a finite nonzero value of the matrix lamina thickness. This is indicated by the curve falling to the abscissa for the AP/PBAN = 7/3 (uncatalyzed and catalyzed) sandwiches in Figs. 3 and 4. The sandwiches with AP/PBAN = 5/5 matrix did not exhibit such self-quenching in the range of matrix lamina thickness tested.

Three important features are noted in Figs. 3 and 4 regarding the data at elevated pressures [10.35 and 13.78 MPa (1500 and 2000 psig)] relative to those obtained earlier at lower pressures [2.07, 3.45, and 6.89 MPa (300, 500, and 1000 psig)]:

1) The peak burning rates of sandwiches at elevated pressures are approximately around the same lamina thickness range of 250–275 μm, as in the case at lower pressures.

2) The peaks grow significantly between 2.07 and 6.89 MPa, particularly for the AP/PBAN = 7/3 matrix sandwiches, as pointed out earlier, but begin to weaken as the pressure is increased to 10.34 and 13.78 MPa (1500 and 2000 psig). That is, the dependence of the burning rate on the matrix lamina thickness is weaker at higher pressures, particularly with the AP/PBAN = 7/3 matrix.

3) The peak burning rates (around lamina thickness 250–275 μm) increase only marginally between 6.89 and 13.78 MPa (1000 and 2000 psig), although the increase in the burning rate of sandwiches with relatively thick matrix lamina (>400 μm) is proportionate with the increase in pressure.

Although the present study was not originally intended to explore the pressure dependence as carefully as that on the matrix lamina thickness, the preceding observations suggest plateau burning rate trends with variation in pressure for specific matrix lamina thickness ranges. To explore this aspect clearly, the preceding burning rate data are replotted in Figs. 5 and 6 as a function of pressure for different ranges of matrix lamina thickness, in the customary log–log scale. In Fig. 5, the trends for sandwiches with the uncatalyzed matrices with fine AP/PBAN = 7/3 and 5/5 are compared, whereas in Fig. 6, the trends for the sandwiches with the catalyzed and uncatalyzed AP/PBAN = 7/3 matrices are compared. The following observations can be made:

1) The matrix burning rates (when the matrix burns by itself) do not show any plateaus.

2) The sandwich burning rates show significant plateaus in the 6.89–13.78 MPa (1000–2000 psig) range.

3) The extent of the plateau (low-positive, zero, or negative pressure exponent) depends on the matrix lamina thickness in an interesting manner. Plateaus are sure to arise for thin laminas (~100 μm), become prominent for optimally thick laminas (corresponding to maximum burning rates, 250–275 μm), but diminish for very thick laminas, particularly for sandwiches with the AP/PBAN = 7/3 matrices.

4) With the 5/5 matrix, plateaus were present in the whole range of matrix lamina thickness all of the way up to the thick lamina limit, whereas with the 7/3 matrix, the thick lamina sandwiches did not show any significant plateaus, as mentioned in item 3.

5) Sandwiches with 1% Pyrocat in the AP/PBAN = 7/3 matrix also exhibited plateaus in a manner similar to their uncatalyzed counterparts, except for an overall increase in the burning rates at all pressures.

6) Note that the pressure range of plateaus exhibited by the sandwiches coincides with a somewhat low exponent exhibited by the AP self-deflagration rate, designated as "Regime II" by Boggs.[20] However, note that all of the sandwich burning rate curves are above the AP self-deflagration rate curve in this pressure range, indicating that the AP lamina far away from the lamina interface does not control/determine the sandwich burning rate. This is unlike the burning of pure binder sandwiches at elevated pressures, where the AP lamina far away from the lamina interface leads the burning surface and, hence, determines the burning rate of the sandwich.

Surface Features

Quench tests were conducted on sandwiches at 10.34 and 13.78 MPa (1500 and 2000 psig), and the quenched surfaces were viewed in the SEM for comparison with surface features reported in the 2.07–6.89 MPa (300–1000 psig) range.[9] The SEM examination of quenched surfaces of the catalyzed sandwiches did not yield much information, even at lower pressures,[10] because the region in and around the matrix lamina of the sandwich burned so fast as to leave a deep V-shaped crevice that was too difficult to view through in the SEM. This situation is practically unaltered in the present work at elevated pressures also.

Figures 7–9 show micrographs of quenched surfaces of sandwiches. Whereas Figs. 7 and 8 show comparisons of surface features at 10.34 and 13.78 MPa (1500 and 2000 psig) of sandwiches with 250–275 μm thick laminas of AP/PBAN = 7/3 and 5/5 matrices, respectively, Fig. 9 shows surface features of sandwiches with thin (200-μm) and thick (460-μm) laminas of the AP/PBAN = 7/3 matrix at 13.78 MPa (2000 psig). The latter are to be viewed along with Fig. 7a. The following overall observations can be made:

1) The point of maximum regression on the surface profile is almost coincident with the lamina interface edge in these tests, more so as the pressure is increased (comparing Figs. 7a and 7b or Figs. 8a and 8b), when the AP content is greater (comparing Figs. 7a and 8a or Figs. 7b and 8b), and as the matrix lamina thickness is increased beyond the thin range, that is, <200 μm (comparing Figs. 9a, 7a, and 9b). By contrast, at lower pressures, the point of maximum regression on the burning surface profile is usually away from the lamina interface in the AP lamina.[9] The region in the AP lamina in between the interface and the point of maximum regression is usually protruded and exhibits a smooth appearance, namely, the smooth band[8] mentioned earlier.

2) The smooth band is usually wavy on the outer side (away from the lamina interface) as it weaves into the frothy and porous sites of AP self-deflagration. In the present case, this wavy edge almost coincides with the lamina interface edge, as noted in item 1, resulting in the existence of the smooth band only in patches along the breadth of the sample. The tendency of a sample to exhibit this behavior is in the order mentioned earlier.

3) In patches on the AP lamina immediately adjacent to the lamina interface edge where the surface features are appreciably different from those of AP self-deflagration, there exists a dry quality. This feature was noted at lower pressures only for the case of catalyzed sandwiches.[10] In fact, even for uncatalyzed sandwiches at lower

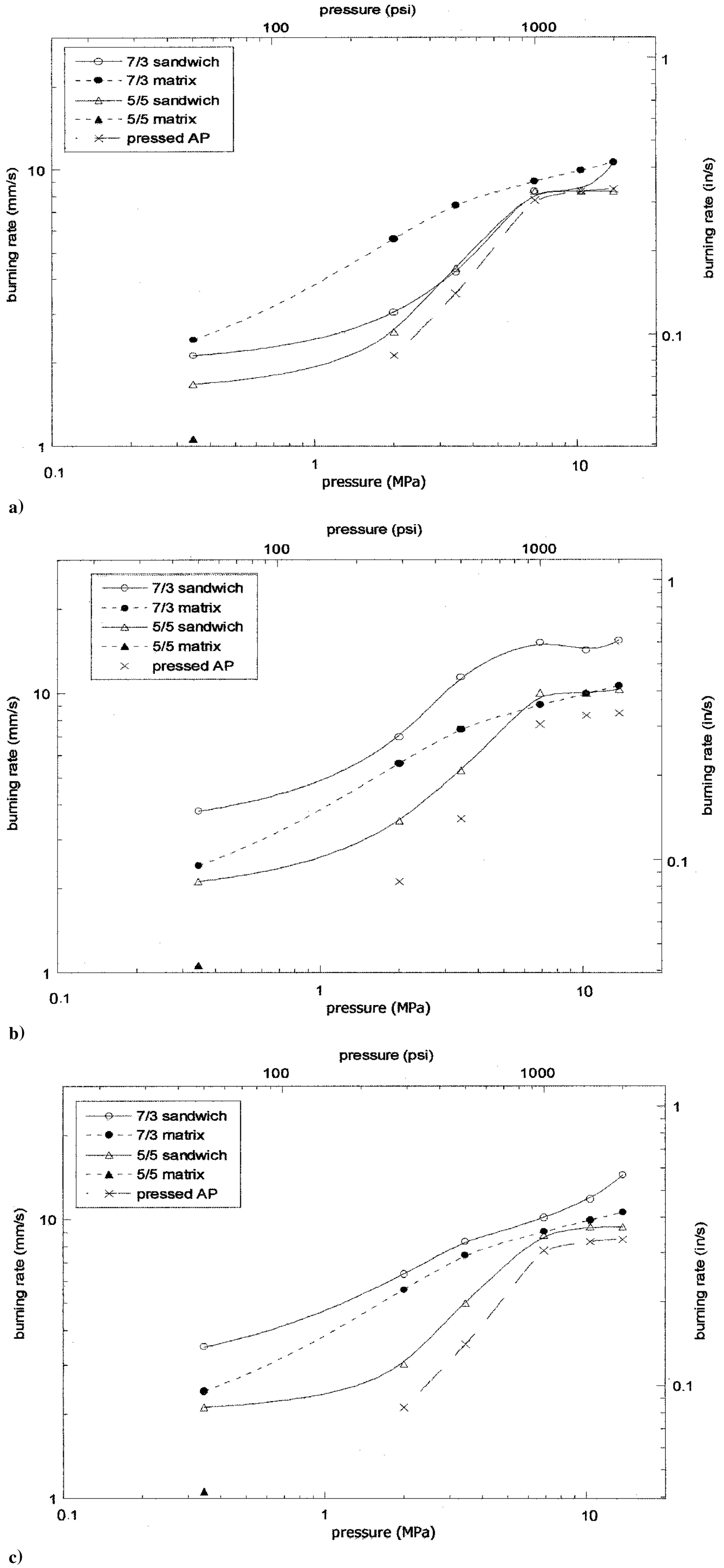


Fig. 5 Pressure dependence of burning rates of sandwiches with AP/PBAN = 5/5 and 7/3 matrices of different lamina thickness ranges: a) 100–200, b) 250–275, and c) >400 μm.

pressures, a dry region is discernible along the point of maximum regression in the AP lamina a slight distance away from the lamina interface edge, an aspect not highlighted in the previous studies.

4) Specific attention is drawn to the thin lamina sandwich quenched at 13.78 MPa (2000 psig) seen in Fig. 9a, which exhibits a distinct region of smooth band (not quite dry), with the point of maximum regression well in the AP lamina, similar to the quenched surfaces at lower pressures for most lamina thickness values. This is in contrast to the other cases as described in item 3.

5) There is a sporadic presence of fine AP particles in the matrix lamina with their burning surfaces exposed, with froth and pores, more or less all of the way across the matrix lamina thickness, particularly under conditions of high pressure [13.78 MPa (2000 psig)], high AP content in the matrix (AP/PBAN = 7/3), and/or matrix lamina thickness greater than 200 μm. See Figs. 7a, 7b, 8a, and 9b, for example. This is an evidence of the possibility of occurrence of PLEFs. PLEFs were noticed in earlier studies only in the case of 33.5-μm AP particles in an AP/PBAN = 7/3 matrix lamina at 6.89 MPa (1000 psig), and that, too, only along the lamina interface edge.[9] In general, the presence of fine AP particles in the matrix lamina have been noticed in the form of mounds in a relatively smooth covering of the binder all of the way across the matrix burning surface, which has been taken to signify burning in a premixed flame.

Propellant Burning Rates

To verify if the plateau burning rates observed in the sandwiches in the elevated pressure range are really witnessed in propellant burning, high solids-loading propellants were formulated and tested in this study. Variations in the coarse AP size, the amount of fine AP in the matrix, and the addition of the burning rate catalyst are included in the formulations. Figure 10 shows the burning rates of all of the five propellant formulations tested in the present study, in the pressure range of 0.689–13.78 MPa (100–2000 psig). Four of these formulations indicated plateau burning in the 6.89–13.78 MPa (1000–2000 psig) pressure range. Only the propellant with the 200-μm

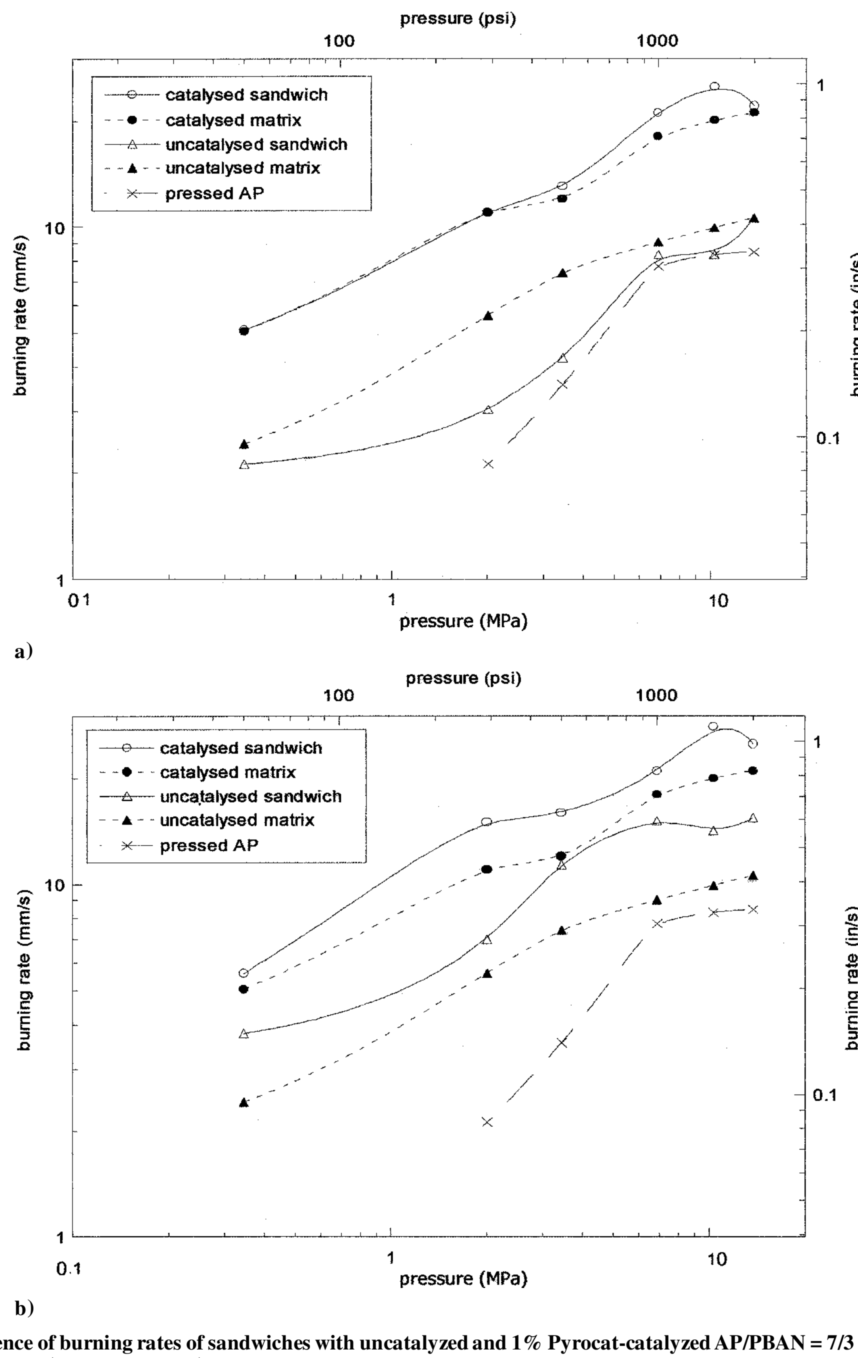
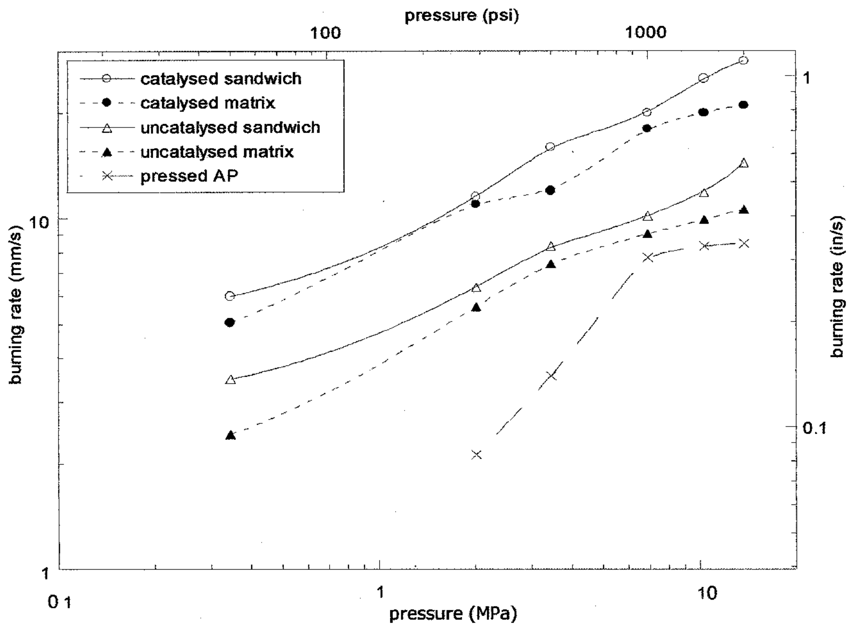


Fig. 6 Pressure dependence of burning rates of sandwiches with uncatalyzed and 1% Pyrocat-catalyzed AP/PBAN = 7/3 matrices of different lamina thickness ranges: a) 100–200, b) 250–275, and c) >400 μm.



c)

Fig. 6 Pressure dependence of burning rates of sandwiches with uncatalyzed and 1% Pyrocat-catalyzed AP/PBAN = 7/3 matrices of different lamina thickness ranges: a) 100–200, b) 250–275, and c) >400 μm (continued).

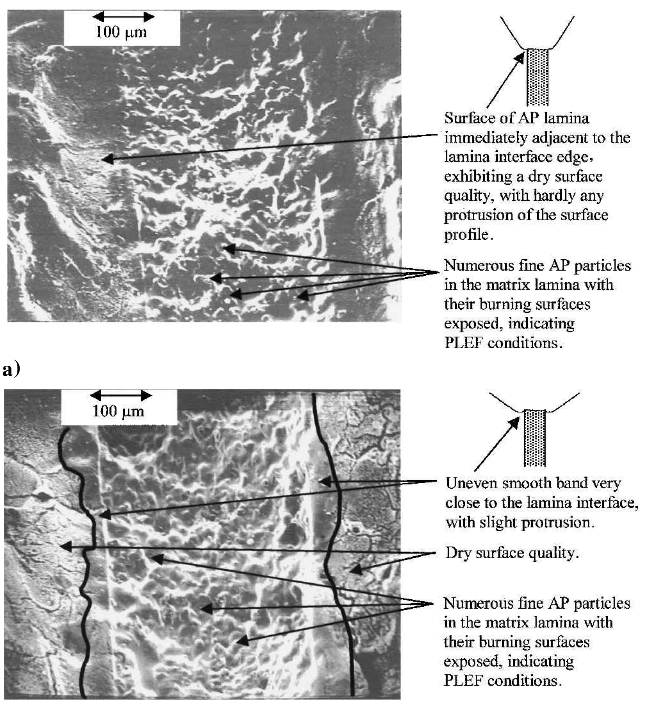


Fig. 7 SEM images of surface features of sandwiches with AP/PBAN = 7/3 matrix of lamina thickness 250–260 μm, quenched at a) 13.78 MPa (2000 psi) and b) 10.34 MPa (1500 psi).

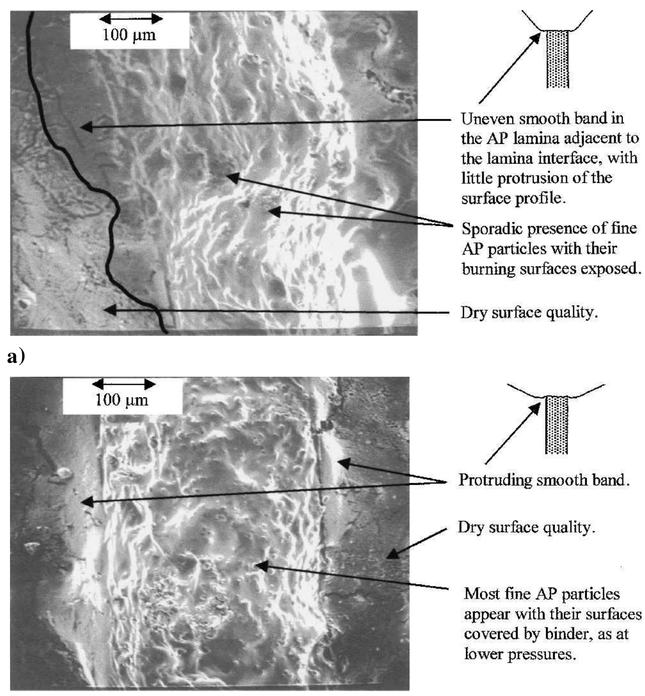


Fig. 8 SEM images of surface features of sandwiches with AP/PBAN = 5/5 matrix of lamina thickness 240–270 μm quenched at a) 13.78 MPa (2000 psi) and b) 10.34 MPa (1500 psi).

coarse AP (fine AP/PBAN = 7/3), that is, mix 1, did not show any plateau burning rate trend.

Discussion

In this section, we examine the effect of increase in the pressure in the 6.89–13.78 MPa (1000–2000 psig) range on the combustion zone of the sandwiches with the different matrices tested in this study, to explain the results collectively presented in the preceding section, including the propellant burning rates.

At the outset, note that the fine AP/binder matrices considered in the present study undergo a diverse set of burning conditions: 1) The uncatalyzed 7/3 matrix undergoes self-sustained burning over the entire pressure range tested and most probably burns in a premixed flame at all pressures, with sporadic exceptions in the 10.34–13.78 MPa (1500–2000 psig) range. 2) The uncatalyzed 5/5 matrix does not burn by itself in the whole test pressure range, except at 0.345 MPa (50 psig). 3) The catalyzed 7/3 matrix undergoes an enormous amount of interfacial near-surface exothermic reactions, with unclear implications on its gas-phase flame structure. In all of these cases, the LLEFs are rate controlling because the sandwich burning rates are different from the self-deflagration rates of the matrix and the AP laminas. Hence, the focus of this discussion is

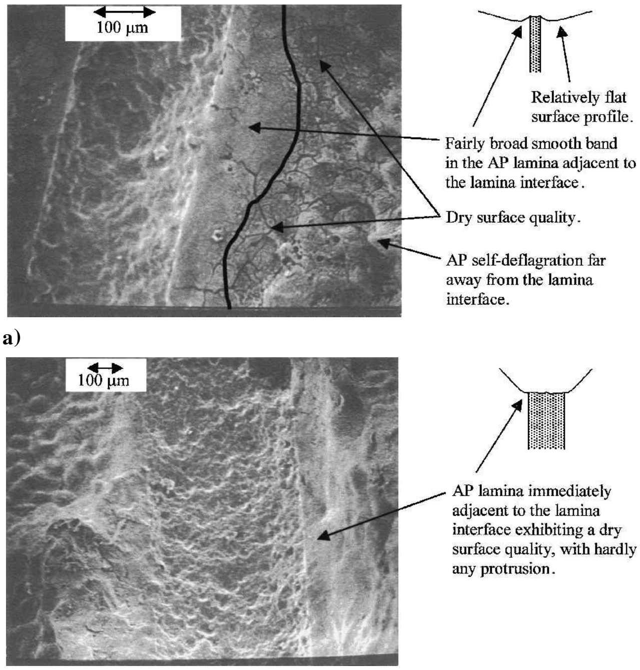


Fig. 9 SEM images of surface features of sandwiches with AP/PBAN = 7/3 matrix with lamina thickness a) 200 and b) 460 μm, quenched at 13.78 MPa (2000 psi).

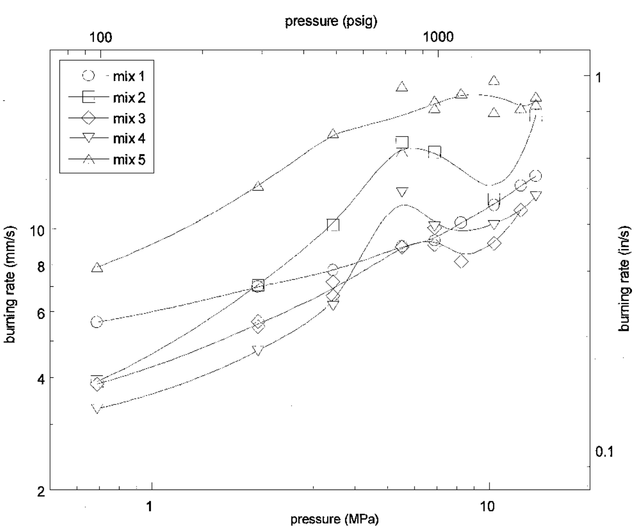


Fig. 10 Burning rate trends of the five bimodal propellant mixes tested in the present study.

primarily on the LLEFs, particularly their response to increases in pressure.

As the pressure is increased in the aforementioned range, the flame complex moves closer to the burning surface, as indicated by the appearance of PLEFs even on 10-μm AP particles in the matrix.[13] Two important consequences of the LLEFs moving closer to the surface with increase in pressure are as follows:

1) The heating of the burning surface by the LLEFs becomes highly localized around the vicinity of the lamina interface edge, with the result that the two-dimensional coupling between them is greatly reduced, except in quite thin matrix lamina sandwiches. This results in the weaker peaks of the sandwich burning rate variation with matrix lamina thickness at higher pressures. The burning rate is, however, sensitive to the lamina thickness in the thin lamina limit, where the fuel supply is inadequate for appreciable heat release in the LLEFs, despite the possibility of intense coupling in the heat feedback from them. For this reason, the burning rate of the sandwich in the thin lamina limit is even lower than the matrix rate when tested alone and almost coincides with the AP self-deflagration rate (above the latter's LPDL) in the entire test pressure range (Figs. 5a and 6a).

2) The lateral extent of the LLEF reduces as it witnesses increasingly nonpremixed reactants in a shrinking mixing fan originating from the burning surface.

The preceding scenario can be deduced from the decreased smooth band thickness in the AP lamina and the shift of the point of maximum regression in the burning surface profile toward the lamina interface edge as pressure is increased (Fig. 7a).

The LLEF standoff distance is governed by a heat balance between its chemical heat release and the two-dimensional heat feedback to the burning surface. A scenario of decreasing LLEF standoff and shrinking lateral extent with increase in pressure indicates an increasingly locally nonadiabatic situation in that the heat loss to the surroundings increase, whereas the chemical heat release itself may be decreasing due to the LLEF shrinkage. This would cause the advancement of the LLEF toward the burning surface to cease with increase in pressure at some pressure level. This situation appears to prevail in the case of the sandwiches with thin lamina (<200 μm) of the AP/PBAN = 7/3 matrix. This can be seen from the fairly wide smooth band, with actually a somewhat smooth appearance, and the location of the point of maximum regression in the burning surface profile being a finite distance away from the lamina interface edge (Fig. 9a). In this case, the fuel deficiency due to the thin lamina results in reduced heat release rate at the LLEF and causes it to stay a little distance away from the burning surface even when the pressure is increased. This results in burning rate trends that exhibit a somewhat plateau trend in the elevated pressure range (Fig. 5a).

On the other hand, when the matrix lamina thickness is sufficiently large (250–275 μm), the available fuel supply enables increased heat release rate with increase in pressure, causing the LLEF to move closer to the burning surface than it would with a thin matrix lamina (noted in item 1). This is supported by the observation of near coincidence of the point of maximum regression with the lamina interface in the burning surface profile and the replacement of the smooth band in that region by a dry appearance (Fig. 7a). The accompanying shrinkage of the LLEF results in a reduced contribution to the heat feedback from the LLEF region itself, but an increasing contribution from the near-surface parts of the outer diffusion flame. This results in somewhat of a plateau in the burning rate variation with pressure for the sandwiches with the aforementioned matrix lamina thickness, particularly with the AP/PBAN = 7/3 matrix (Fig. 5b). The competition between the LLEF and the outer diffusion flame at elevated pressures has been assumed on the basis of the BDP model itself early on,[1] but not on the basis of the multidimensional structure of the LLEF as considered here.

For very large matrix lamina thickness, the fuel supply from the matrix to each of the LLEFs is quite adequate, and, hence, the LLEF continues to get closer to the burning surface with increase in pressure. This is observed from the minimal smooth band thickness and the coincidence of the point of maximum regression in the burning surface profile with the lamina interface (Fig. 9b). The two-dimensional coupling of the LLEFs in terms of heat feedback and reactant supply is lacking, even at low pressures with thick matrix lamina, and continues to be so in the elevated pressure range. Over the whole pressure range, the LLEF contributes to an increase in the sandwich burning rate over the matrix burning alone (with the AP/PBAN = 7/3 matrix), by greater proximity and local heating in the vicinity of the lamina interface edge. This is termed as the LLEF/matrix interaction in Fig. 2, and it prevails as the pressure is increased over the entire pressure range tested for the sandwich with this matrix (Fig. 5c). At elevated pressures, the contribution to the local heating may also be from the near-surface parts of the outer diffusion flame.

In the case of the sandwiches with the AP/PBAN = 5/5 matrix lamina, the LLEFs are farther apart due to the increased fuel richness of the matrix, and, moreover, the lateral extent of the LLEFs is smaller than with the other matrix tested, particularly because the matrix does not sustain burning by itself. This results in reduced coupling between the LLEFs even at low pressures [$\leq$6.89 MPa

(1000 psig)] when compared to the case with the 7/3 matrix. In this situation, the competing contribution of heat release from the outer diffusion flame with that from the LLEFs in determining the burning rate results in a weaker pressure dependence of the burning rate of the sandwiches at elevated pressures, regardless of the matrix lamina thickness (Fig. 5).

On the other hand, in the case of the catalyzed sandwiches, it was pointed out in Ref. 10 that the flame complex is located very close to the burning surface relative to the uncatalyzed case, even at low pressures [<6.89 MPa (1000 psig)], due to exothermic heating of the reactant gaseous species resulting from the catalysis of condensed-phase or heterogeneous reactions along the fine AP/binder contact lines in the burning surface layer of the matrix. This situation results in close location of the LLEFs to the burning surface, with the concomitant shrinking of their lateral extent and the two-dimensional coupling of heat feedback. The major effect of the close proximity of the flame complex to the burning surface is an overall increase in the burning rate over the uncatalyzed samples under all conditions, as pointed out earlier. Therefore, the burning rate trends with pressure variation follow those for the uncatalyzed sandwiches, as explained earlier (Fig. 6). In addition, the effect of the LLEFs being closer to the surface is that the interaction between the adjacent LLEFs becomes weaker at a lower pressure than in the uncatalyzed case, when the matrix lamina thickness is adequately large for such an interaction. Accordingly, look at Fig. 6b; the slope in the sandwich burning rate curve with the catalyzed matrix is steeper in the 2.07–3.45 MPa (300–500 psig) range as opposed to a similar trend with the uncatalyzed matrix at a higher pressure range of 3.45–6.89 MPa (500–1000 psig). The subsequent plateau in the elevated pressure range [10.34–13.78 MPa (1500–2000 psig)] is also additionally related to the LLEF shrinkage and predominance of the near-surface parts of the outer diffusion flame.

The crucial dependence of plateau burning on the coarse AP size in the case of propellants points to the role of the spacing between the coarse AP particles on the burning surface (mix 2 and 3, as opposed to mix 1, all with the AP/PBAN = 7/3 matrix). The spacing between the coarse particles governs the extent of three-dimensional coupling in the heat feedback between adjoining LEFs on these particles. In the formulation with 200-μm coarse AP particles, the closest distance between the particles is large relative to the case with larger particles at the same mass fraction, although the number of particles is large. This is particularly so with the fine AP content being high, at 70% in the matrix, given that the total solids loading is fixed. The relatively large spacing between the coarse particles in mix 1 is not conducive for coupling between the LEFs on adjacent coarse particles for an appreciable rise in the burning rate at low pressures, followed by a plateau trend at elevated pressures, as in the case of sandwiches with a 250–275 μm thick matrix lamina.

Finally, note that the plateaus in these sandwiches and propellants are not related to binder melt flow, based on the following considerations: 1) The binder used is PBAN, considered to be a "low-melt" binder since of the times of pure binder sandwich testing in the late 1970s and early 1980s, based on symmetric burning of sandwiches and SEM observations with that binder,[19] as mentioned earlier. 2) The pressure range of plateaus is high enough to cause doubt as to whether or not there may be any significant binder melt layer in the first place, with most binders. 3) Earlier studies with a catalyst have indicated that 1% Pyrocat in the matrix is considerably high enough to "wash out" any anomalous effects thought to be caused by binder melt.[10] When it is taken into account that sandwiches with Pyrocat also exhibited plateaus in the same pressure range as the uncatalyzed ones in the present study, these plateaus are not likely to be related to melt flow. 4) These plateaus are not related to crossing of any midpressure extinction boundaries of the corresponding matrices in the pressure range in question (cf. Ref. 16). The extinction domains are, in turn, considered to be related to binder melts in ways that are not clear yet.

Conclusions

AP/PBAN sandwiches with fine AP particles in the matrix, and with or without a Pyrocat ferric oxide burning rate catalyst, are tested in a wider pressure range, between 0.345–13.78 MPa (50–2000 psig), than those reported previously. Burning rate trends of the sandwiches are analyzed as a function of matrix lamina thickness and pressure. SEM examination for features of the burning surface quenched at 10.34 and 13.78 MPa (1500 and 2000 psig) is also performed for different AP contents and thicknesses of the matrix lamina. In the elevated pressure range of 6.89–13.78 MPa (1000–2000 psig), the leading-edge portion of the O/F diffusion flamelets anchored at the interface of the AP lamina and the matrix of fine AP and binder tends to approach the burning surface with increases in pressure. The standoff distance is dictated by the availability of sufficient fuel for appreciable heat release in the leading-edge portion; for thin-matrix lamina, the approach may be limited, whereas for larger laminas, the lateral extent of the leading-edge flame diminishes as it approaches the surface. The diminishing extent of the leading-edge flame is accompanied by reduced contribution of heat feedback from that zone, and the heat contribution from the near-surface parts of the outer diffusion flame may become significant. The overall effect is to produce plateau burning rate trends under many conditions tested, except for large lamina of matrices with appreciable fine AP content. These trends are supported by plateau burning rate trends in the same pressure range exhibited by propellants with bimodal AP size distribution containing the same matrices as tested in the sandwiches. The plateau trends are dependent on the size of the coarse AP particles for the propellant formulation with a high fine AP content in the matrix, much as the case with the influence of the matrix lamina thickness in the sandwiches.

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