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BINDER EFFECTS DURING COOKOFF OF HMX

Michael L. Hobbs, Michael J. Kaneshige, William W. Erikson
Sandia National Laboratories[*]
Albuquerque, New Mexico 87185 USA

Abstract

We have previously developed a cookoff model for a plastic bonded explosive containing HMX (PBX 9501) [1]. The model was validated with data from six laboratories with scales ranging from 2 g to more than 2.5 kg of explosive. In the current work, we apply the cookoff model to neat HMX and 11 PBX formulations containing HMX (EDC-29, EDC-37, LX-04, LX-07, LX-09, LX-10-0, LX-14, PBX 9011, PBX 9404, PBX 9501, and X-0298) by accounting for the correct HMX mass and adjusting the binder reactivity. The model is verified using one-dimensional time-to-explosion (ODTX) data as well as limited Sandia Instrumented Thermal Ignition (SITI) data.

The success of our PBX 9501 model was attributed to inclusion of an exothermic, pressure dependent reaction for the nitroplasticizer (NP). Temperature excursions in our low-density SITI experiments were modeled by allowing the NP to decompose exothermically within the PBX sample. The temperature excursions were not observed in our high-density experiments. For some of these experiments, we observed binder diffusing to the edges of our samples and decomposing near the highly conductive confinement walls.

We have performed additional experiments with LX-14 consisting of 95.5 wt% HMX and 4.5 wt% Estane® 5702 (a polyurethane thermoplastic). The primary difference between LX-14 and PBX 9501 is the binder composition: 4.5% Estane vs. 2.5% Estane with 2.5% nitroplasticizer. We initially suspected that PBX 9501 would be more reactive than LX-14 due to the energetic binder. Our experiments show the opposite trend. We believe the brittle polyurethane binder in LX-14 retains reactive gases better than the softer binder in PBX 9501 resulting in faster ignition times.

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Introduction

Predicting the response of any energetic material (EM) during an accident, such as a fire, is important for safety analysis and is sometimes referred to as a cook-off analysis. The time-to-ignition, the amount of decomposition gases, the pressurization of the confinement, the state of the degraded EM at ignition, and the violence of reaction are all needed for safety assessments. The current paper is focused on the cookoff of plastic bonded explosives (PBX) containing octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). A list of these explosives and description of the various binders is given in Table 1. The thermicity of the binder from Tarver and Tran [2], the binder oxygen balance, and the binder adiabatic flame temperature determined with the TIGER equilibrium code [3] is also given in Table 1.

Table 1. Various HMX containing explosives (bolded/boxed) and their binders

Acronym	Composition	Binder thermicity [2], binder O_2% [a] ($T_{adibatic}$, 1 bar)[b]
BDNPA/F	bis(2,2-dinitropropyl)acetal/formal (50/50)	-58 (1840 K)
CEF	tris-β-chloroethylphosphate	-81 (746 K)
EDC-29	95 wt% HMX, and 5 wt% polyurethane	Endothermic binder
EDC-37	91 wt% HMX, 9 wt% oil and nitrocellulose	Exothermic binder
Estane®	a polyurethane thermoplastic	-200 (706 K)
FEFO	1,1′-[methylenebis(oxy)]bis[2-fluoro-2,2-dinitroethane]	-10 (2880 K)
HMX	octahydro-1,2,5,7-tetranitro-1,3,5,7-tetrazocine	no binder
LX-04	85 wt% HMX and 15 wt% Viton A	Endothermic binder
LX-07	90 wt% HMX and 10 wt% Viton A	Endothermic binder
LX-09	93% HMX, 4.6% pDNPA, and 2.4 wt% FEFO	Exothermic binder
LX-10-0	95 wt% HMX and 5 wt% Viton A	Endothermic binder
LX-14	95.5 wt% HMX and 4.5 wt% Estane®	Endothermic binder
NC	Nitrocellulose	-24 (2780)
PBX 9011	90 wt% HMX and 10 wt% Estane®	Endothermic binder
PBX 9404	94% HMX, 3% CEF, 3% nitrocellulose	Exothermic binder
PBX 9501	95 wt% HMX, 2.5 wt% Estane®, 2.5 wt% BDNPA/F	Exothermic binder
pDNPA	2,2- dinitropropyl acrylate	-78 (1080)
Viton A	vinylidine fluoride/hexafluoropropylene copolymer	-73 (1345)
X-0298	97.5% HMX and 2.5 wt% Kraton oil	Exothermic binder

[a]The oxygen balance is the degree at which the binder can be oxidized. If binder molecule contains just enough oxygen to form CO_2 from carbon, H_2O from hydrogen, SO_2 from S, etc., the binder will have zero oxygen balance.
[a]Adiabatic flame temperature at 1 bar.

HMX cookoff model development at Lawrence Livermore National Laboratories (LLNL), Los Alamos National Laboratory (LANL), and Sandia National Laboratory (SNL) is described by Tarver et al. [4, 5, 2], Henson et al. [6, 7, 8] and Hobbs et al. [1, 9, 10, 11], respectively. More information regarding cookoff modeling of HMX based explosives can be found in these references.

Tarver and Tran [2] modeled cookoff of the PBX explosives in Table 1 by using separate decomposition models for HMX and the various binders. These decomposition models do not include pressure dependency but can differentiate between vented and sealed systems by removing reactive gases from the system. They reported that some binders, as shown in Table 1, decompose endothermically and lengthen the time-to-ignition. Other binders decompose exothermically and shorten the time-to-ignition.

The method used to determine thermicity was not specified by Tarver and Tran [2]. Thermicity might be related to the oxygen balance, which is presented in Table 1 for some of the binder formulations. Zero percent is perfectly oxygen balanced, and the binder is more fuel rich as the oxygen balance decreases below zero. FEFO is close to being perfectly oxygen balanced. The adiabatic flame temperature for some of the binders is also presented in Table 1. Higher adiabatic flame temperatures may also be related to binder thermicity.

We model venting effects by including pressure dependent reaction steps. For example, our PBX 9501 model [1] has five reaction steps that include desorption of water, decomposition of the nitroplasticizer (NP) to form NO_2, reaction of the NO_2 with Estane and HMX, and decomposition of the HMX. The last three steps are assumed to be pressure dependent with the rates multiplied by a normalized pressure raised to a power, e.g. $(P/P_o)^n$, where n is set to zero for vented systems. This method describes complex condensed-phase and gas-phase chemistry. The method also allows interaction of binder decomposition products with HMX.

The porosity, or damage state of the PBX 9501, is specified in our model as either open or closed [1]. Open pore PBXs do not retain all of decomposition gases within the PBX volume; whereas closed pore PBXs retain the decomposition gases. The volume of gas increases in closed pore decomposition via bulk thermal expansion of the PBX and by decomposition of solid into gas. A stress-strain relationship develops as gas pressure in closed pores balances the stress in the solid material that surrounding these pores [12]. Response of closed pore PBXs are sometimes independent of the confinement (vented or sealed) since most of the reactive gases are retained within the PBX. Available gas volume increases in the open pore PBX if the confining structure expands due to pressure or thermal expansion.

In the current work, we apply our PBX 9501 model to the twelve explosives in Table 1, by accounting for the molar volume of HMX in each explosive and adjusting the reactivity of the binder appropriately. Normally our cookoff models are verified using the Sandia Instrumented Thermal Ignition (SITI) experiment. However, SITI data is not available for all explosives listed in Table 1 and results will be compared to LLNL's one-dimensional time-to-ignition (ODTX) data [2]. Predictions of HMX, PBX 9501, and EDC-37 in our SITI apparatus will also be presented along with new data for sealed and vented LX-14 data.

Parameters

Details of the model including all chemical and physical properties can be found in reference [1]. The only parameters changed for each explosive in Table 1 are presented in Table 2. The energetic binder in the PBX was changed to be either reactive or nonreactive by setting the mass fraction of the Estane and NP in the PBX 9501 model to be the same as the binder concentration or to a small number, 0.00001, respectively. A small number was used instead of zero to avoid division by zero during the calculation of the extent of binder reaction. This effect is the same as setting the activation energy for the binder kinetics to a high number. The mass fraction of HMX is consistent with the specific PBX formulation. The molar concentration was determined using the measured bulk density of the given PBX.

Table 2. Changed PBX 9501 parameters in [1] to mimic given PBX.[a,b]

PBX	Initial bulk density, ρ_{bo}, kg/m^3	Mass percent			
		HMX	Sorbed gases[c]	BDNPA/F	Estane
EDC-29	1771	95	0.5	2.25	2.25
EDC-37	1795	91	0.5	4.25	4.25
HMX	1767	99.498	0.5	0.001	0.001
LX-04	1865	85	0.5	7.25	7.25
LX-07	1860	90	0.5	4.75	4.75
LX-09	1778	93	0.5	3.25	3.25
LX-10-0	1830	95	0.5	2.25	2.25
LX-14	1830	95.5	0.5	2	2
PBX 9011	1740	90	0.5	4.75	4.75
PBX 9404	1797	94	0.5	2.75	2.75
PBX 9501	1787	95	0.5	2.25	2.25
X-0298	1725	97.5	0.5	1	1

[a] Binder assumed to have same reactivity as BDNPA/F and Estane.
[b] Non-reactive binders mimicked by setting BDNPA/F and Estane percent to 0.001%
[c] Sorbed gases are assumed to be water.

ODTX results

The one-dimensional time-to-explosion experiment (ODTX) considers a 1.27-cm diameter sphere of explosive confined by two aluminum anvils using a hydraulic press with a holding pressure of 1500 bars. The two cylindrical anvils, with two hemispheres machined to accommodate the spherical PBX, are preheated to a given temperature. The ignition time is recorded as the time the anvils are closed to the time the anvils mechanically fail, typically by thermal ignition of the explosive. Details of the ODTX experiment can be found in references [2, 4].

Figure 1 shows a comparison of the measured and calculated ignition times for the explosives listed in Table 2. Measurements from [2] are represented as spheres. Two calculations are shown for each of the ODTX test as either a solid line or a dashed line. The ignition time represented by the solid line was determined by assuming the binder does not react. The ignition time represented by the dashed line was determined by assuming the binder has the same reactivity as the binder in PBX 9501. The mass of the binder was also set to match the binder mass in the given explosive.

Most of the ODTX data are bounded by the two calculations with the calculations performed with the non-reactive binder being the overall best fit to the data. This is especially true for the explosives with Viton A as the binder as shown in Fig. 1.D, 1.E, and 1.G. Several of the explosives with the more energetic binders are fit better by assuming the binder is reactive as shown in Fig. 1.F and 1.J.

The PBX 9501 model with the nonreactive binder fits the data better than the model with the reactive binder. This may seem odd since the model was specifically developed for PBX 9501. We have observed in our SITI experiments that the binder has a larger volume change due to thermal expansion than the volume change in the HMX. As the high-density explosive heats, the energetic plasticizer is extruded to the edges of the explosive. The exothermic energy is quickly dissipated by the conductive aluminum anvils making the effect of the energetic binder negligible for these high-density pressings. This phenomenon does not happen for lower density pressings where binder kinetics sometimes dominate the response. In lower density pressings, the PBX can accommodate the additional expansion of the binder as the binder can expand into the initial pore space.

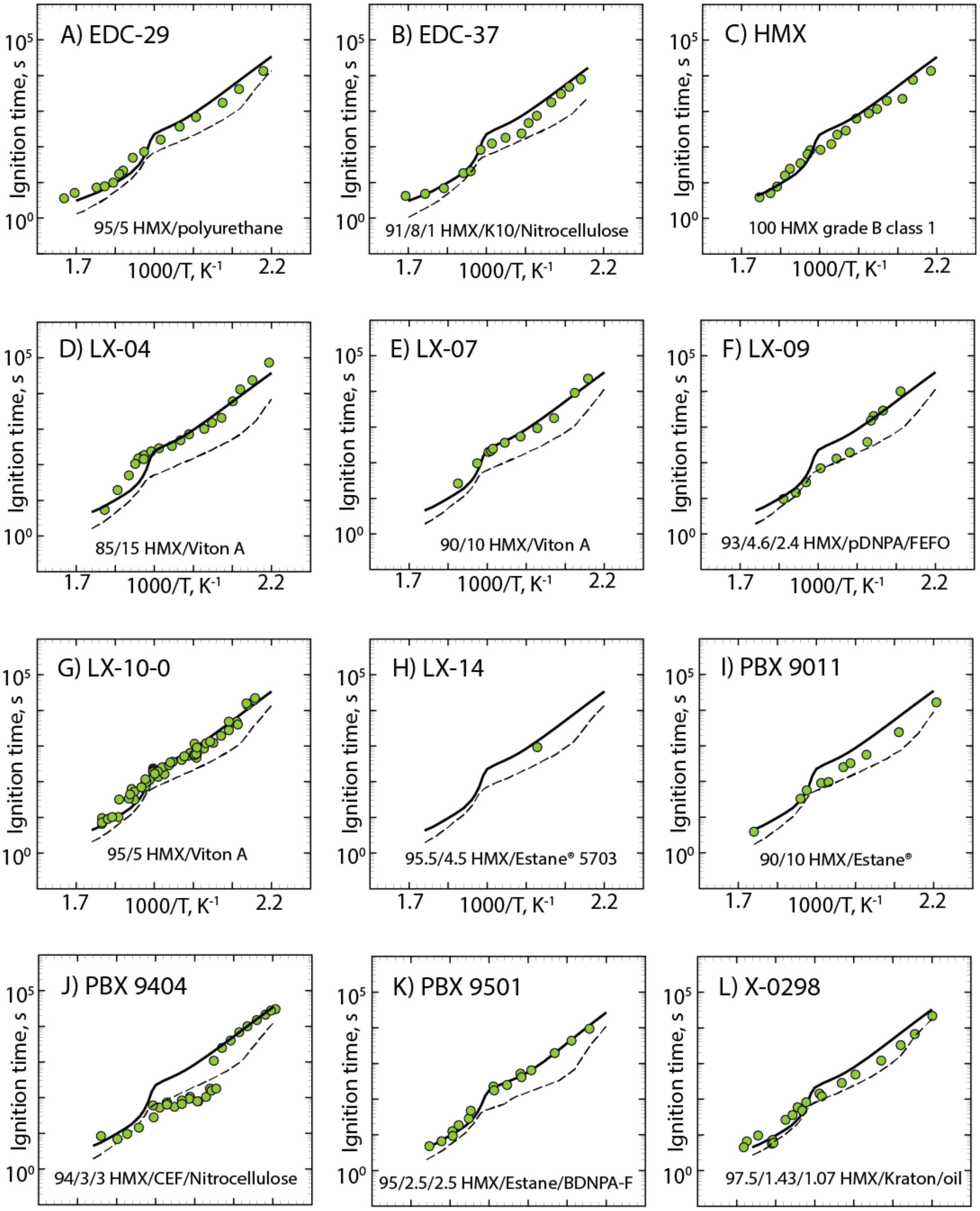

Figure 1. Comparison between measured (symbols) [2] and predicted (lines) ignition times using the PBX 9501 model [1] with parameters in Table 2. The solid line was predicted without allowing the binder to react. The dashed line was predicted by assuming the binder has the same reactivity as the binder in PBX 9501.

SITI results

Figure 2 presents two different schematics of the Sandia Instrumented Thermal Ignition (SITI) experiment with 1) a small ullage space (Fig 2.A) and 2) a large ullage space (Fig 2.C). Figure 2.B shows the thermocouple locations within the center of the 2.54 cm diameter by 2.54 cm tall right circular cylinder of PBX. Figure 2.D shows two images taken with a borescope on two of the PBX 9501 sealed SITI experiments, run #445sb and run #428sb.

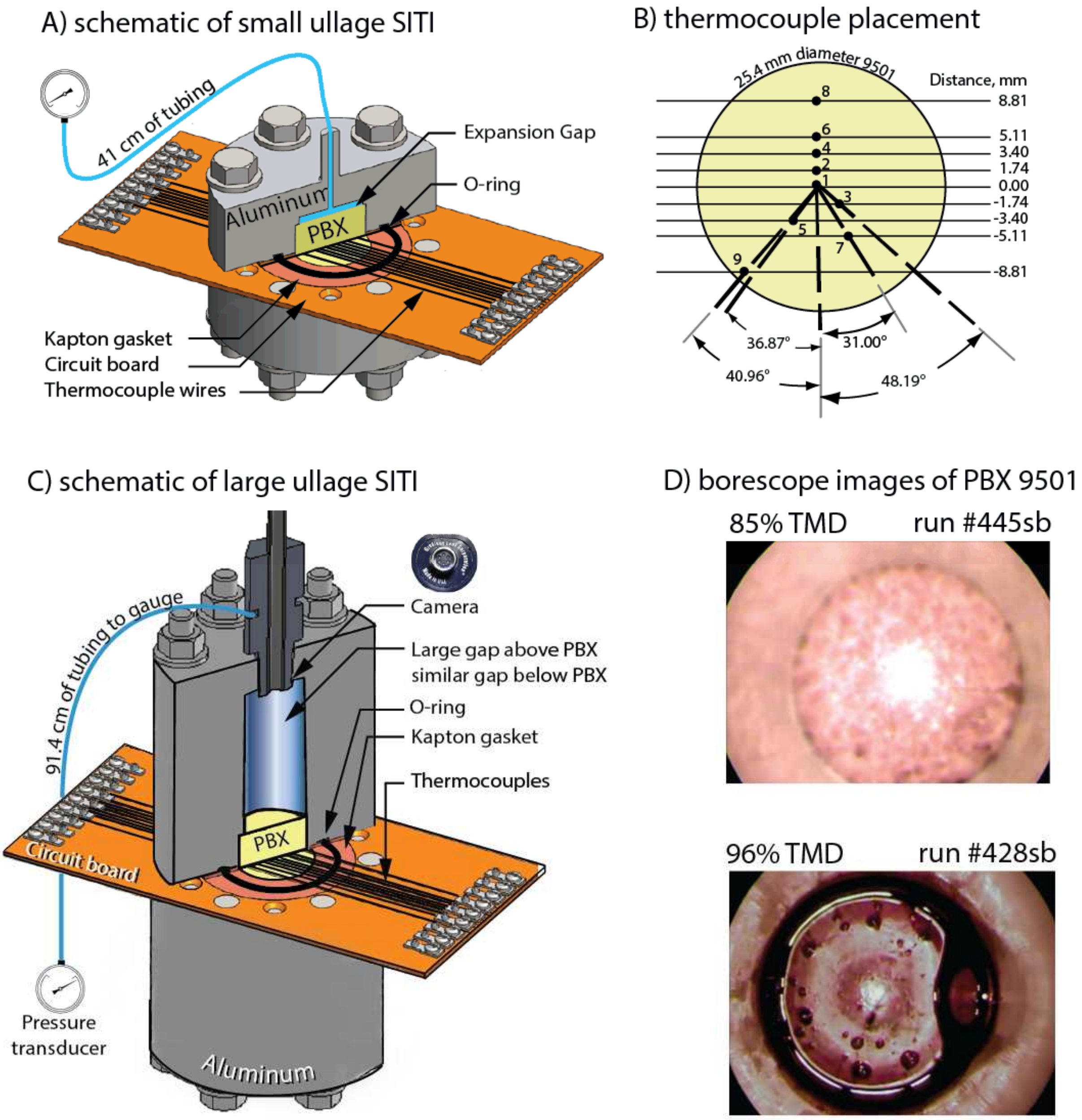

Figure 2. Schematic, thermocouple placements, and borescope images of PBX 9501.

Run #445sb is a sealed large ullage SITI PBX 9501 experiment at a density of 1582 kg/m^3, which is 85% of the theoretical maximum density (TMD). Run #428sb is a sealed large ullage SITI PBX 9501 experiment at a density of 1779 kg/m^3 or 96% TMD. We believe the dark liquid on the edges of the PBX for run #428sb is extruded nitroplasticizer (NP). None of the NP is extruded in the lower density pressing shown in Fig. 2.D. Extrusion of the NP to the edges of the ODTX experiment may explain why the reactive binder does not affect ODTX results, as it does in the SITI experiment at lower densities.

Normally, our cookoff models are verified using SITI experiments. However, SITI data for most of the explosives listed in Table 1 are not available. Nevertheless, we have some data for HMX acquired in 2004-2005 [10], EDC-37 acquired in 2007, PBX 9501 acquired in 2015 [1], and LX-14 acquired in 2016-2017. Our most extensive SITI study was with PBX 9501 where we investigated the effects of density and confinement (vented and sealed configurations with different ullages).

Figures 3.A and 3.B present a comparison between measured (symbols) and predicted (lines) ignition times for both vented and sealed HMX pressed to 85% TMD in the SITI apparatus shown previously in Figure 1.A. The vented model predictions were made by setting the pressure exponents in the model to zero. The predictions in Fig. 3.A were made using the HMX parameters presented in Table 2. The predictions in Fig. 3.B were made in an *ad hoc* manner using the concentrations given in Fig. 3.B, which correspond to a material having 8 wt% reactive binder with kinetics similar to PBX 9501 binder kinetics. The 8% was chosen to get a better data match to the neat HMX when using the PBX 9501 model. The *ad hoc results* in Fig. 3.B suggest that our PBX 9501 model could be improved to be more specific to HMX.

Figure 3.C shows measured and predicted outer boundary temperature and the center temperature of the HMX for test #356s. Test #356s was sealed and the data point representing ignition time is labeled in Fig. 3.A and 3.B. The measured and predicted pressure is also presented in Fig. 3.C. This comparison shows that the thermal conductivity used in the HMX model should probably be higher near and above the HMX β-to-δ phase change temperature.

Only a few SITI experiments were performed with EDC-37. Figure 3.D shows the measured and predicted temperatures for EDC-37 run #58. This run was sealed, but the measured pressure indicates that the pressure tubing may have clogged. The measured ignition time for the EDC-37 test was closer to the model prediction using a non-reactive binder. The predicted pressure indicates that the confinement may have failed before thermal ignition since the SITI apparatus usually only holds pressure to 2500 to 5000 psig (17.2-34.4 MPa).

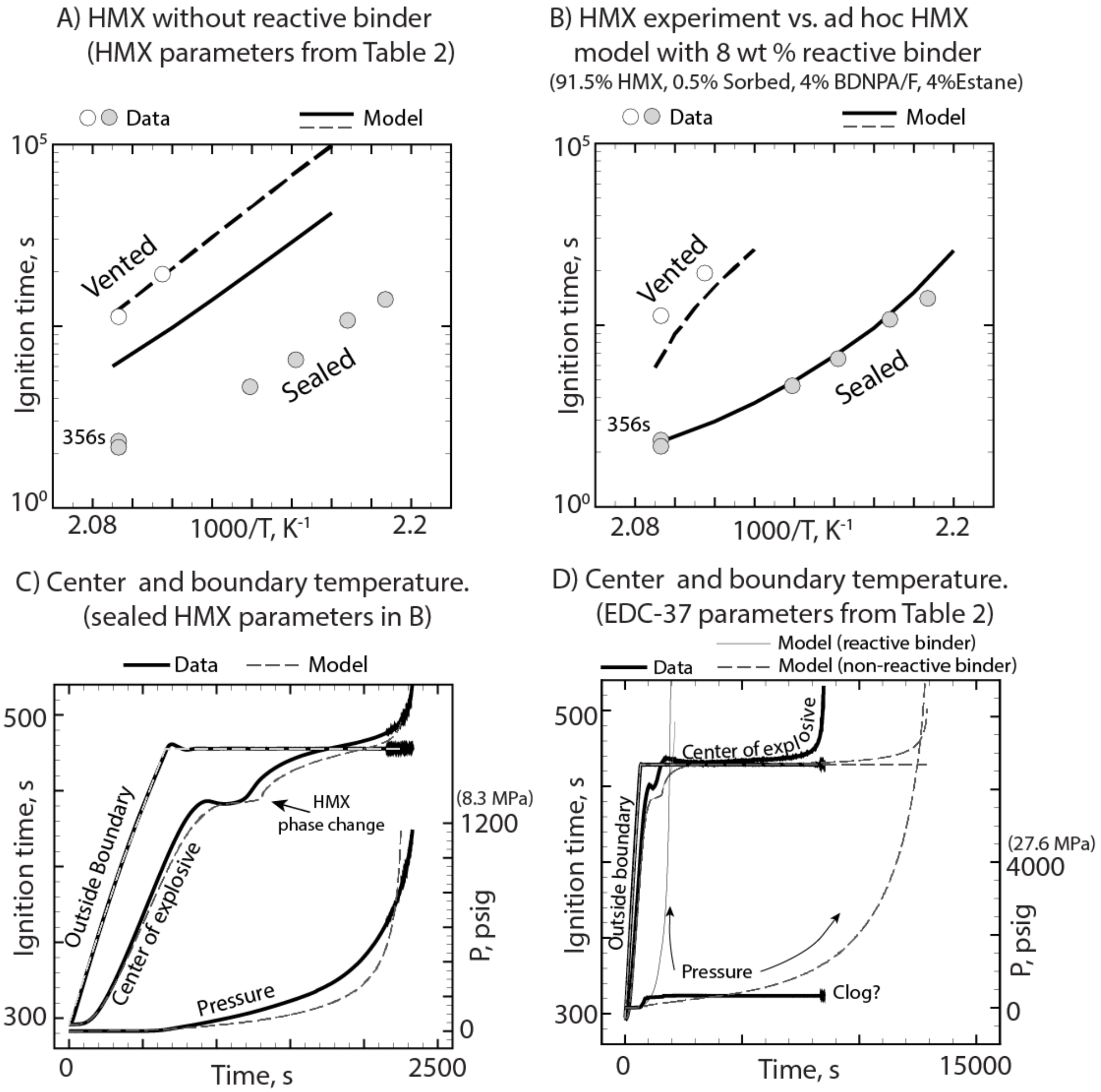

Figure 3. Measured and predicted ignition times for HMX using A) parameters from Table 2 and B) assuming the PBX is composed of HMX with an 8% binder with the same reactivity as Estane and BDNPA/F. The center and boundary temperature are presented for C) HMX and D) EDC-37.

Figures 4.A and 4.B show measured and calculated ignition time for both vented and sealed low density PBX 9501 (860 kg/m^3) and LX-14 (850 kg/m^3), respectively. Figure 4.C and 4.D show predicted and measured temperatures for PBX 9501 runs 413s and 414v, respectively. The "s" and "v" in these run numbers indicate the confinement level of the explosive (i.e. sealed or vented). Figures 4.E and 4.F present a comparison of measured temperature and pressure in PBX 9501 and LX-14 with the same set point temperature of 478 K.

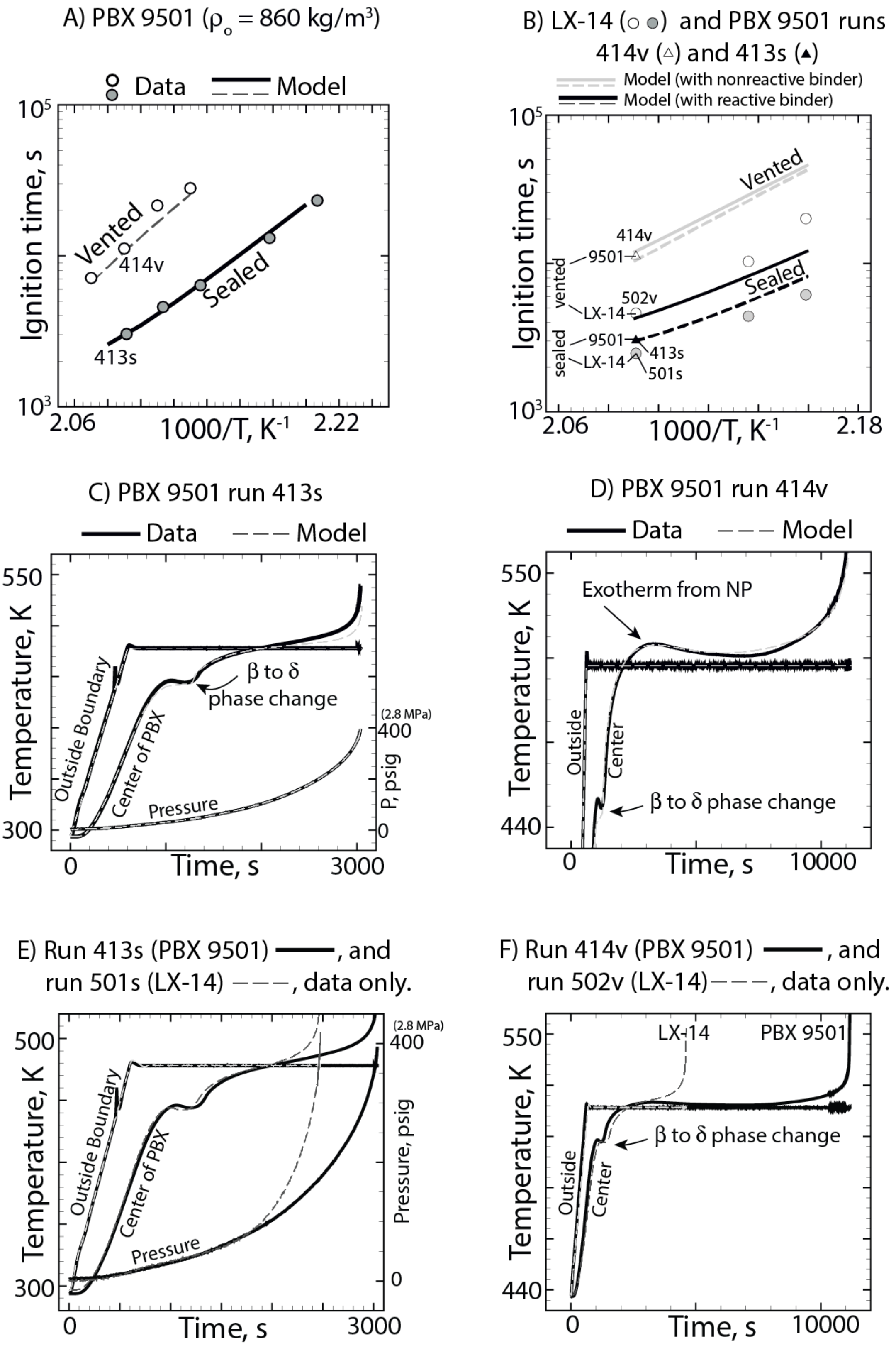

Figure 4. A) Ignition times for PBX 9501, B) temperature and pressure for sealed PBX 9501 run 413s, C) temperature for vented PBX 9501 run 414v, D) ignition times for LX-14 with two PBX 9501 data points for comparison, E) temperature and pressure for run 413s (PBX 9501) and 501s (LX-14), and temperature for run 414v (PBX 9501) and 502v (LX-14).

Predictions in Fig. 4.A were made assuming the PBX 9501 binder was fully reactive. The dashed line in Fig. 4.A represents a vented prediction obtained by setting the pressure exponents in the rate expressions to zero [1]. Predictions in Fig. 4.B were made by assuming the binder was either non-reactive (solid lines) or had the same reactivity as the binder in PBX 9501 (dashed lines). Two of the PBX 9501 runs are plotted in Fig. 4.B to show that the LX-14 ignites sooner than the PBX 9501 at the same temperature. This trend of increased reactivity of LX-14 over PBX 9501 was observed in all our LX-14 experiments. We believe the tough polyurethane binder in LX-14 retains reactive gases better than the softer binder in PBX 9501 resulting in faster ignition times. Future work should test this hypothesis by doing similar experiments with the LX-14 particles ground to a smaller particle distribution.

Summary and conclusions

We have used our PBX 9501 model to investigate cookoff behavior of a variety of plastic bonded explosives containing HMX. The model was applied to the various explosives by accounting for the 1) density, 2) amount of HMX, and 3) reactivity of the binder in each explosive. The binder kinetics were assumed to either have the same reactivity as the binder in PBX 9501 or were non-reactive. All other properties, such as thermal conductivity and specific heat, were assumed to be the same as used in the PBX 9501 model [1].

The model with "reactive" and "non-reactive" binder assumptions were applied to 12 explosive formulations in the ODTX configuration and compared to data. Good agreement with the ODTX data was obtained using the inert binder assumption for HMX based explosives with a Viton binder (LX-04, LX-07, LX-10-0). The non-reacting binder assumption also matches the ODTX data for fully pressed PBX 9501. At high densities, the thermal expansion of the binder causes the binder to extrude to the outer edge of the explosive wherein the reaction energy is quickly dissipated to the vessel walls and does not affect the ignition time. For lower density pressings, the binder is fully reactive and does not extrude out of the explosive. Extrusion in PBX 9501 was visually observed in the SITI experiment with a borescope.

We observed higher reactivity LX-14 with an Estane binder when compared to PBX 9501 with a reactive binder composed of Estane and a nitroplasticizer. We believe the higher reactivity is associated with gas phase reactions that occur within the LX-14. The gases are retained within the LX-14 by the tough Estane® binder. In PBX 9501, the gases can escape from the explosive since the plasticizer allows the binder to flow as observed by several other investigators [13, 14, 15].

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