Thermal Shock Behavior of Polymer Bonded Explosive below and above the Viscous Flow Transition Temperature

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Abstract. The effect of initial cooling temperatures on the thermal shock behavior of cylindrical polymer bonded explosive (PBX) was investigated by using a combined acoustic emission (AE) and strain gauge technique in fast air-cooling tests. Dissimilarity was observed below and above the viscous flow temperature ($T_f$) where the PBX exhibited brittle-ductile transition and temperature dependence on material properties. We found that cooling below $T_f$ would lead to fracture with strong AE signals and a linear strain-time response followed by a sharply decline, while above $T_f$ would generate weaker AE events and a non-linear strain history with soften response. A segmented characterization was proposed for the calculation of thermal shock resistance and the corresponding critical fracture temperature difference. This estimation fits well with our experimental and simulation results.

1. Introduction
Plastic bonded explosives (PBX), as typical high explosives (HE), are extensively used in both military and civil applications. Formula design of PBX and subsequent managing are directly influenced by the need to improve the resistance to physical stimuli and insults, which is mainly dominated by their thermo-mechanical properties. In general, it is well known and reported that pressed PBX, specifically those with high wt% crystalline, can be described as low-strength and quasi-brittle materials. This nature consequently contributes to poor resistance to weakening or fracture under a transient thermal shock. The response of PBX subject to thermal condition, as well as mechanical loads, is of equal importance for determining a safe working life.

Up to now, the susceptibility of PBX to thermal stresses has not been well acknowledged. In view of the fact that PBX exhibits temperature sensitivity on physical properties and dependence on constitutive behaviors [1-3], it is more difficult to model thermal damage and fracture. For typical wild conditions, PBX studies have been made to attempt to clarify degradation in continuous high temperatures [4], ratchet growth in thermally cycles [5], and thermal damage in linear thermal gradients [6]. Yet few investigations are issued on PBX response subjected to harsh environment, i.e., a thermal shock during unexpected situations.

Thermal shock which generates thermal stresses sufficient to cause fracture of a material, is one of the most dangerous loading for brittle materials. Since the first calculation of thermal stresses in a cylinder in late 1830s, numerous attempts were made to solve the problem of thermal failure. It turns out that the ability to endure thermal shock is affected by several variables, including, but not limited to, elastic modulus, tensile strength, coefficient of thermal expansion (CTE), thermal conductivity, and specific heat capacity [7]. Efforts were also paid to define and to measure this material property which was named thermal shock resistance (TSR) [8-10]. Now it is possible to use TSR ranking the
performance of thermal fracture for ceramic based materials. But the exploration of thermal shock behavior on PBX is faced with flinty challenge because of its inherent heterogeneity, low-strength, and temperature dependence of physical properties.

The aim of this work is to evaluate the effect of initial equilibrium temperature on the thermal shock behavior of PBX in a rapid cooling experiment. The start temperatures were chosen below and above the viscous flow transition temperature ($T_f$) of the material, respectively, where its thermo-mechanical properties undergo a distinct variance [11]. The results endeavor to testify acoustic emission (AE) and strain gauge combination technology as a diagnostic tool, and provide insight into the governing failure criterions of PBX for finite element method (FEM) advancement.

2. Experiment and Results

2.1. Material and Experiment Setup

PBX employed in this investigation is composed of 95% wt.% octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) held together by a rubber binder. The viscous flow transition temperature ($T_f$) of the rubber, measured ~60°C, is slightly higher than that of the PBX, due to some weak interaction between the HMX and the binder. In manufacture, hot-pressing technology was used for moulding. Cylindrical samples were finally received with 100 mm in diameter and 110 mm in height after finish machining.

Thermal shock experiments were conducted with a fast temperature test chamber. Specimens were first heated from room temperature to a predetermined temperature at 1 °C per minute, then keeping constant for 3 hours, finally cooled till fracture at 10 °C per minute. The preset temperatures were 50 °C and 70 °C, which were just below and above $T_f$, respectively. Both of the two procedures are represented in figure 1.

A home-made T-type thermocouple was used for temperature measurement of the specimen surface and the air. AE sensors and strain gauges were positioned on the cylinder as a fracture signal diagnosis. This technique makes use of the principle that elastic waves will be released and strain distribution will be redistributed with the occurrence of fracture, generating an AE event and a decline on the strain-time curves. It is then possible to determine the fracture time and the corresponding surface temperature by means of the coincident mentioned above. Sampling frequency of temperature and strain gauging was unified to 1 Hz. And a much higher frequency of 20 MHz was applied to AE data collecting. Shown in figure 2 is the layout of three types of sensors.

2.2. Thermal Shock Behavior of the PBX

Depicted in figure 3 are representative signal curves for cylinders cooled from 50 °C. Figure 3a shows the temperature and strain history starting from the heating point, in which TE indicates the temperature of environment. In the first stage the surface of the specimen was heated, creating an increasing compression strain. It reached a minimum about -500 με at 1934 s, with corresponding
temperature ~38 °C, when the cylinder got a largest temperature difference. Note that there was an interval of time after the environmental temperature growth being stopped at about 1800 s. Then the temperature gradient disappeared and the compression was relieved to nearly zero stress during the following thermostatic control process.

![Figure 3](image)

**Figure 3.** Measurements of the specimen cooled from 50 °C: (a) temperature and strain signals throughout the experiment; (b) strain and AE signals during fracture.

Figure 3b presents the combination of AE and strain signals during the cooling period. It can be observed that the positive temperature difference gives rise to a linearly increasing tension strain and generates small number of low-amplitude acoustic events. A free fall is following when the strain runs close to 600 με, which is equivalent to its failure strain. Simultaneously, several AE events with amplitude up to 90 dB, are detected just prior to this point, indicating a strong elastic wave occurrence. The evolution of strain and AE together suggest that the PBX lead progressively to damage but rapidly to fracture (at 12880 s) by what seems to be a macroscopic crack. It is then easy to determine that the corresponding temperature on the cylinder surface is 37.5 °C via figure 3a. That means the PBX geometry can critically endure a temperature difference of 12.5 °C when it is cooled from 50 °C.

Results of specimens cooled from 70°C are plotted in figure 4. As observed in figure 4a, we obtain similar behavior in the heating stage, whereas they differ in strain signals when the environmental temperature keeps invariable. There is still a local minimum of compression strain at about 3130 s, with a corresponding surface temperature ~53.7 °C. Due to heat conduction, the temperature gradient is decreasing but the absolute temperature is increasing. The ongoing stress-relieving is arrested at 5639 s, as temperature T1 meet 64.1 °C (i.e., higher than the viscous transition temperature T_f), followed by a downgrade on thermal strain. This dissimilarity, contrast to previous figure 3a, is primarily ascribed to the increased viscosity that conduces irreversible deformation. When the temperature passes through T_f, the polymer in PBX starts to flow and the ability of deformation rises rapidly with elevated temperature. Meanwhile softening develops from surface to inner of the specimen which leads to increasing CTE at the same direction. It is therefore no surprise that strain is on the decline after 5693 s and will not return back to zero, as illustrated by figure 4a.

![Figure 4](image)

**Figure 4.** Measurements of the specimen cooled from 70 °C: (a) temperature and strain signals throughout the experiment; (b) strain and AE signals during fracture.
Figure 4b depicts AE and strain signals captured in test-2 from cooling to thermal failure. Unlike curves in figure 3b, the strain-time relationship exhibits evident nonlinearity before it increases to a peak at 17791 s. Note the latter softening response is quite different from the sharply decline shown in figure 3b. The results also demonstrate that much fewer AE events appear in this time period and no signals stronger than 60 dB take place from the very start of the maximum point. As discussed above, the PBX is presently in viscous flow state at 70 °C. It is valid for us to obtain a ductile fracture after considering the strain history and the low-amplitude AE events. Using figure 4a we can easily calculate the current temperature on the specimen surface is 53 °C, suggesting the critical temperature difference is 17 °C under the initial shock temperature of 70 °C.

3. Discussion

3.1. FEM Comparison

In an effort to better understand the PBX response, a 2D finite element (FE) model is implemented in ABAQUS to simulate a thermal shock test on cylindrical specimens. Material properties adopted here are partial temperature related, all derived from experiment in order to achieve a thermal-elastic response, as shown in table 1. The density, Poisson’s ratio are taken as constants, assigned 1845 kg·m⁻³ and 0.33, respectively. A partitioned quadrilateral structural mesh was assigned using CAX4T elements for temperature-displacement coupled conditions. The size of the mesh in the boundary layer is 0.1 mm and inner the cylinder is equal to 0.5 mm, according to the magnitude of the temperature gradient. Heat boundary conditions include convection, with heat transfer coefficient, h, of 23. Environmental temperatures are the same as figure 1.

| Temperature (°C) | 15 | 25 | 35 | 45 | 55 | 65 | 75 |
|------------------|----|----|----|----|----|----|----|
| Elastic modulus (GPa) | 12.28 | 10.68 | 10.94 | 9.20 | 5.12 | 2.27 | 1.02 |
| Heat conductivity (w·m⁻¹·k⁻¹) | 0.473 | 0.463 | 0.454 | 0.445 | 0.437 | 0.429 | 0.421 |
| Specific heat (J·kg⁻¹·k⁻¹) | 969 | 1003 | 1036 | 1069 | 1102 | 1135 | 1169 |
| CTE (10⁻⁵·k⁻¹) | 4.374 | 5.743 | 5.678 | 5.466 | 5.715 | 6.059 | 5.303 |

Shown in figure 5 are the computed temperature-time histories compared with experimental curves. The sampling point is located at the center of the cylindrical side face. It can clearly be seen that the simulation shows good agreement with the measured data. Results also demonstrate that during cooling the specimen undergoes a great decrease at limited time, resulting in a remarkable temperature difference between the center and outside, and causing considerable tensile thermal stress.

Figure 5. Comparison of temperature-time lots: (a) cooling from 50 °C; (b) cooling from 70 °C.

Figure 6 indicates the evolution of the thermal stress at the side center of the cylinder surface. When
the specimen is cooled, a thermal stress generates and increases significantly with the corresponding temperature. We also notice immediately that the increasing is linearly when specimen is cooled from 50 °C and nonlinearly when cooled form 70 °C. At the same time, the strength of the PBX is exponentially increasing with decreasing temperature. On the basis of the first strength criterion, fracture will occur as long as the thermal stress exceeds the strength. It is easily calculated from figure 6 that the fracture temperature is 39.6 °C and 54.6 °C, respectively, which keeps well with the values in test-1 and test-2.

Figure 6. Comparison of the simulated stress and tested strength: (a) cooling from 50 °C; (b) cooling from 70 °C.

3.2. Thermal Shock Resistance Analysis

TSR estimation, introduced by investigators as a material property of ceramic materials, is another method to assess the behavior under thermal shock. Among all unsteady heat transfer state, heat flow with constant \( h \) is the simplest condition that approximates general thermal environments. The most attention has been paid to this case in literatures including this paper. Following Kingery [10], a second thermal shock resistance is defined as:

\[
R = \frac{\sigma_f(1-\nu)}{E\alpha k} \tag{1}
\]

in which \( E \) is elastic modulus, \( \alpha \) is CTE, \( \sigma_f \) is the strength of the material, \( \nu \) is Poisson’s ratio, \( k \) is thermal conductivity. The corresponding critical temperature difference of fracture, \( \Delta T_f \), is expressed by

\[
\Delta T_f = R \cdot S \cdot \frac{1}{\delta h} = R' \cdot \frac{1}{(\gamma \delta) h} \tag{2}
\]

where \( S \) is called a shape factor, \( \delta \) is a characteristic length for heat transfer, \( \gamma \) is a ratio related to biot number.

Based on Bradshaw’s work [12], \( \gamma \) is equal to 0.25, indicating the critical fracture temperature difference to be

\[
\Delta T_f = \frac{\sigma_f(1-\nu)}{0.25 \delta h E\alpha k} \tag{3}
\]

As discussed above, thermal and mechanical parameters in equations (1) and (3) are practically temperature dependent. Taking this into consideration, the two equations should be functions of the current temperature on the specimen surface. If we notice the fact that \( \nu \) and \( h \) are insensitive to temperature over the selected range, the following modification has to be introduced to equation (3) from the suggestion of Li [13]
\[ \Delta T_f = \frac{1 - v}{0.25\Delta h} \cdot \frac{\sigma_f(T_0 - \Delta T_f) k(T_0 - \Delta T_f) \cdot \varepsilon_f}{E(T_0 - \Delta T_f) \alpha(T_0 - \Delta T_f)} \]  

where \( T_0 \) is the initial cooling temperature.

Based on our experimental work [14] and table 1, the expressions of parameters in equation (4) can be fitted as follows. Here the temperature limitation is 35-70 °C.

It is thus clear that equation 4 is an implicit expression with independent variable \( \Delta T_f \). When \( T_0 \) is set to 50 °C, the solution would be about 11.02 °C, which accords well with the result in test-I. There is, however, an unreasonable answer of 11.17 °C when \( T_0 \) approximates 70 °C. As a matter of fact, the solution becomes relatively low as long as the initial-value of \( T_0 \) exceeds \( T_f \). That is to say, for the investigated PBX, this modelling is not suitable above the viscous flow transition temperature.

3.3. A Modification above the Rubber Transition Temperature

At first TSR was only brought up for the approach of thermal stress fracture in brittle materials. In the interest of calculation, the temperature difference causing stresses equal to the tensile strength of the material is employed. This method is acceptable to most brittle ceramics, especially those physical constants can be generally taken as independent of temperature. Yet for the given PBX, which is not just sensitive to temperature but also behaves a brittle-ductile transition around 60 °C, the treatment of strength criterion may be not that rigorous. This explains why, at the point of 70 °C, a solution cannot be obtained from equation (4).

As figured above, deformation of the PBX above 60 °C is transformed into elastic-plastic because of thermal softening. It has been demonstrated that a critical strain criterion is more reasonable than a strength criterion to state tensile failure of temperature related conditions [15]. Therefore we employ here the failure model that the tensile strain caused by a temperature difference equal to the fracture strain, to describe the thermal shock phenomenon in test-2. The modified critical fracture temperature difference is

\[ \Delta T_f = \frac{(1 - v) \cdot \varepsilon_f(T_0 - \Delta T_f)}{\alpha(T_0 - \Delta T_f)} \]  

where \( \varepsilon_f \) is failure strain of the PBX shown in table 2.

| Table 2. Fitting functions for material properties in equation (4). |
| --- |
| Parameter | Expression | Unit |
| \( \sigma_f(T) \) | \( 6.49469 - 6675.57e^{-6} \exp(0.102T) \) | MPa |
| \( \kappa(T) \) | \( \frac{1}{0.866381 + 4.338e^{-3}(T + 273.15)} \) | W/m°C |
| \( E(T) \) | \( 12.86292 - 0.02652T - 0.00137T^2 - 6.79943e^{-6}T^3 \) | GPa |
| \( \alpha(T) \) | \( -5.55 + 1.169T - 4.291e^{-2}T^2 + 6.59e^{-3}T^3 - 3.51e^{-6}T^4 \) | \( 10^{-5} \)/°C |
| \( \varepsilon_f(T) \) | \( -1.32052 + 0.05017 - 4.2355e^{-4}T^2 \) | % |

Now let \( T_0 \) be 70 °C, equation (5) leads to the solution \( \Delta T_f \approx 17.16 °C \), significantly closer to the result of test-2 than equation (4). Combining with the two equations we achieve an integrated approach to calculate the fracture temperature difference without the limitation of the initial cooling temperature. Shown in figure 7 are the \( \Delta T_f - T_0 \) relationship and its comparison to experimental and simulated results.

One general observation is that the fracture temperature difference of the PBX increases with an increasing initial cooling temperature. It is a reflection of combined effect of material properties contained in equations (4)-(5). We note that the relation between \( \Delta T_f \) and \( T_0 \) is linear below 50 °C, while it shows nonlinearity from 50 °C to 70 °C. This inconsistency may be attributed to the nonlinear
performance, mainly, to the considerably improved ductility.

Another observation comes from the data discrepancy determined from different methods. The ranking of $\Delta T_f$ in the order from small to large, is respectively by simulation, by the proposed model, and by experiment. It is seen that specimens in experiment can suffer a larger fracture temperature difference. We suggest the first reason might be that the applied thermal condition is not a mathematically thermal shock and visco-elasticity is neglected in our analysis. Moreover, the heating procedure in experiment provides a chance to relieve part of residual internal stress, which may result in an enhancement effect on its tensile strength. Since our paper is a very first beginning on the assessment of thermal shock behavior to energetic materials, this has currently not been performed on the PBX.

![Fracture temperature difference via initial cooling temperature and its comparison to simulated and experimental data.](image)

**Figure 7.** Fracture temperature difference via initial cooling temperature and its comparison to simulated and experimental data.

4. Conclusion
Herein, a combined AE-strain gauge technique was employed to characterize the thermal shock behavior of cylindrical PBX in a fast air-cooling test. Different initial temperatures above and below the viscous flow temperature $T_f$ were conducted to our experiments at a unified cooling rate (10 $^\circ$C/min). Thermal fracture behavior of the PBX showed initial temperature dependent, that it fractured at 37.5 $^\circ$C and 53 $^\circ$C when it is respectively cooled from 50 $^\circ$C and 70 $^\circ$C.

A transition from brittle to ductile exists around the viscous flow temperature where the thermal-mechanical properties vary obviously. Initial temperature below $T_f$ will lead to strong AE events and to a linear strain-time response followed by a sharply decline, while initial temperature above $T_f$ will generate lower AE signals and a non-linear strain history with soften segment.

When estimating thermal shock resistance and critical fracture temperature difference of the PBX, we must take into account not only the temperature sensitivity of thermal-mechanical performances, but also the alteration of its failure model. Our study suggests that a segmented formulation, dominated by stress below $T_f$ and by strain above $T_f$, will coincide well with experimental and simulated results. The authors believe that this modification will be serviceable for the formula design and managing of PBX and other explosives.

Acknowledgments
The authors appreciate the financial support from National Natural Science Foundation of China under Grant No. 21805257 and No. 11902304. Special thanks go to Zhiqiang Feng (ICM, CAEP) for the help on experiments.

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