A temperature-mapping molecular sensor for polyurethane-based elastomers

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A temperature-mapping molecular sensor for polyurethane-based elastomers


1Research Department, Naval Surface Warfare Center, Indian Head, Maryland 20640, USA
2Department of Physics, Naval Postgraduate School, Monterey, California 93943, USA
3Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106, USA

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We present a crosslinked polyurethane elastomer featuring a thermochromic molecular sensor for local temperature analysis. The thermochrome is a modified donor-acceptor Stenhouse adduct (DASA) that was dispersed homogeneously into the polymer blend in minuscule amounts. Rapid temperature jump measurements in a pyroprobe and impacts in a Hopkinson bar show that the DASA has suitable kinetics for detecting localized temperature increase following impact or rapid heating. The thermochrome retains a signature of the peak temperature in the elastomer, allowing post-mortem mapping of micron-scale temperature localization in materials such as explosive and propellant composites. We demonstrate the concept by using the kinetics of the DASA activation to determine peak temperatures reached during bullet perforation of the polyurethane.

Localized temperature sensing in polymers is of critical importance in composites such as armors, solid rocket motors, and explosive formulations. Impact and shock loading can lead to micron-scale temperature increases that are critical for understanding the safety of these materials, but have proven very difficult to observe experimentally due to their small size and rapid time evolution. In the case of common polymer-bonded explosives, which typically contain explosive crystals embedded in a binder such as urethane-crosslinked polybutadiene, in-situ measurement of the temperature without disturbing the micro- and mesoscale mechanical properties is quite challenging. Thermochromic polymers which use microencapsulated leuco dyes or liquid crystals have been widely studied, but cannot give spatial resolution throughout the polymer and can themselves introduce undesirable defects. A method that could analyze microscale temperature localization post-mortem after an impact or shock-loading event with submicron spatial resolution and no alteration of local mechanical properties is highly desirable.

Herein, we report a modified polymer binder system that maps temperature localization by means of an integrated thermochromic photoswitch (thermophore). The thermophore shows promise for quantifying spatially resolved temperatures in the polymer binder of explosive composites. A donor-acceptor Stenhouse adduct (DASA) inverse photoswitch was embedded in hydroxyl-terminated polybutadiene, in the Hopkinson bar of this PBXN-110 mock formulation of a new photochromic molecule based on the donor-acceptor Stenhouse adduct recently synthesized by Read de Alaniz and coworkers. The molecule is shown in Figure 1(a) and behaves as an inverse photoswitch. The closed, colorless form is zwitterionic and upon heating opens to a conjugated, colored system. Sustained visible light reconverts back to the colorless form. A DASA variant with a dioctyl secondary amine donor and a Meldrum’s acid acceptor was synthesized and found to solubilize readily into HTPB with desirable cyclization kinetics. In this work, we study dioctyl-DASA integrated into neat HTPB as well as an inert simulant of PBXN-110, a prototypical polymer-bonded explosive formulation. High-rate compression in the Hopkinson bar of this PBXN-110 mock formulation with DASA/HTPB (see the supplementary material) showed that the high strain-rate response was consistent with the previous literature, and the DASA had not significantly altered the dynamic mechanical properties. Additional information on the synthesis and properties of DASA variants can be found in Ref. 8 and additional information on the formulations in this paper can be found in the supplementary material.

The DASA kinetics were measured with a CDS Analytical Pyroprobe 5000 capable of heating samples at 20°C/ms in a 1/4 in. pyroprobe boat. After heating, samples were kept in the dark and the optical absorbance was immediately measured with an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. The deactivated samples

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A. McEachen, S. Helmy, J. Read de Alaniz, and J. P. Hooper, b) Electronic mail: jphooper@nps.edu.

B. P. Mason and M. Whittaker contributed equally to this work.

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were baselined inside the pyroprobe quartz boat before any UV-Vis data were taken. Fluorescence measurements were recorded at the mesoscale using a confocal inVia Raman microspectrometer (Renishaw) with a 514 nm Ar ion solid state laser. High-rate compression studies were performed on DASA/HTPB as well as mock formulations using a 3/4 in. split Hopkinson pressure bar. Additional details on the experimental methodology can be found in the supplementary material.9

The thermophore activates readily under heating, converting to a bright pink form (Figure 1(e)) with a broad absorption peaked at 544 nm. We used fluorescent microscopy to determine the rate of DASA deactivation under light. Figure 1(b) shows the basic emission spectra from a single point on the sample at ambient conditions (with the DASA closed) and in the activated state after heating at 120°C for 30 min. There is a distinct emission peak centered at 570 nm arising from the photoswitch. Reconversion kinetics were measured on a 2.2 mm thick cylindrical sample of 10 mm in diameter placed 11 cm from a 26 W fluorescent light. Following heating at 120°C for 30 min, fluorescence maps were taken on an identical smooth, featureless region of the sample every 2 h of direct light exposure. The maps were averaged to give a mean number of counts at 570 nm. The exponential reconversion of the photoswitch is shown in Figure 1(c) and has a decay constant of 34 h. This value will naturally depend on sample size, light intensity, and other factors, but, in general, the HTPB/DASA materials will retain their signature for several days if kept out of intense direct light and in a cool environment. Following approximately 80 h of light exposure, the sample was reheated at 120°C for 30 min and an additional map was taken as indicated by the dashed line in Figure 1(c). Some portion of the DASA appears to have been damaged by photobleaching over this long exposure time in direct light, but this does not affect the measurements of the initial activation such as we report here.

To quantify the DASA activation beyond a visual indicator, we mapped the fluorescent emission on the surface of recovered fragments using a confocal microspectrometer. This technique provides a means of capturing fluorescence variation on the micron scale in a quantitative fashion. A 514 nm Ar-ion laser was used at a very low power density (<200 W/cm²) to excite the DASA sample, and maps were made collecting the emission as the sample was translated beneath the optics to form a spatial map.

Maps of the fluorescent emission show highly uniform activation at the 100 nm scale following bulk heating (Figure 2(e)/Figure 2(f)), confirming that there are not widespread agglomerates of the DASA. Mapping at ambient conditions showed no spatial variation, and the mean background counts at 570 nm was approximately 75 with a typical standard deviation of around 15 counts. We then performed fluorescent mapping before and after high-rate Hopkinson bar impact on prepared cylindrical samples of 10 mm in diameter and 5 mm thickness. False-color maps were generated using the number of counts at 570 nm. A 20× objective was used on the spectrometer, which provided a reasonable resolution while allowing large portions of the sample to remain in focus.

![FIG. 1.](image1.png)

![FIG. 2.](image2.png)
Analysis of recovered fragments showed small regions of intense activation, orders of magnitude above the background. In many cases, these regions could be seen visually in an optical microscope. Figures 2(a)–2(d) show two typical examples of recovered HTPB/DASA fragments along with a fluorescent map of the emission intensity. Figures 2(a) and 2(b) show activation in an inert mock of the plastic bonded explosive PBXN-110 using sugar in place of explosive crystals. Activation is observed at the boundaries of the sugar granules.

Quasistatic loading has no effect on the photoswitch. A 10 mm diameter, 10 mm tall cylinder of HTPB/DASA was compressed in an Instron load frame at a rate of approximately 1 x 10^-4 s^-1 until widespread sample failure. No sensor activation was observed in these samples, consistent with a purely thermal response.

Quantitative measurements with the thermophore require knowledge of the kinetics of the thermally induced photocyclization process. Fig. 3 shows the absorption kinetics of the dioctyl-DASA thermophore at several temperatures. The molar attenuation coefficient for the photoswitch was measured in the uncrosslinked, HTPB prepolymer to be 55 000 M^-1 cm^-1 and this value was used to convert absorbance into a concentration. The kinetics are well described by a zeroth-order Arrhenius expression, and the corresponding Arrhenius plot is given in Fig. 3(b). The activation energy is 23 kcal/mol with a prefactor of 4.23 x 10^10 M/s.

To determine local temperatures from a measured DASA concentration, a model for the thermal history must be assumed. In this work, we use a simple piecewise function

\[ T(t) = \begin{cases} 
T_o \left( \frac{T_{max} - T_o}{\tau} \right)^{\frac{t}{\tau}} & 0 < t < \tau \\
T_o + (T_{max} - T_o) \exp \left( -\frac{\pi(t - \tau)}{\delta^2} \right) & \text{else}.
\end{cases} \]

(1)

Here, \( T_{max} \) is the peak temperature, \( T_o \) is the ambient temperature, \( \tau \) is a characteristic time for the temperature rise based on details of the impact event, and \( \delta \) is a characteristic length scale over which the temperature has reached roughly \( T_{max} \). \( \alpha \) is the thermal diffusivity of the HTPB, \( \alpha = k/\rho c_p \), where \( k \) is the thermal conductivity, \( \rho \) is the density, and \( c_p \) is the specific heat capacity. This form approximates a rapid thermal increase over a time \( \tau \), followed by thermal conduction to return to ambient temperature. Activation of the thermophore can occur both during the initial heating as well as during the cooling period. For a measured concentration \( c_{exp} \), the peak temperature \( T_{max} \) is then found numerically from the relationship

\[ c_{exp} = \int A \exp \left( -E_a/RT(t, T_{max}) \right) dt. \]

(2)

To demonstrate this approach, we performed several bullet impact experiments on our thermochromic HTPB; Figure 4(a) (Multimedia View) shows a frame from high-speed video and Figures 4(b) and 4(c) show two post-mortem samples with visual DASA activation. Immediately following the shot, samples were cooled in a freezer and carefully sliced for absorption measurements. Test cuts confirmed no additional activation of the DASA during the cutting process.

Figure 4(d) shows the peak temperatures around the path of a 7.62 mm NATO bullet that impacted the HTPB at 800 m/s moving from bottom to top in the image. Temperatures were calculated from Eq. (2) using \( \delta = 20 \mu m \) based on size measurements of the highly activated regions in fluorescence maps of the shot channel. \( \alpha \) was set to 36 \( \mu s \), equal to the duration of the bullet’s contact with a given point along the penetration channel. The absolute temperature scale is quite sensitive to the choice of \( \delta \) in this simple model, in part because the very low thermal diffusivity of HTPB (1 x 10^-7 m^2/s) means that considerable activation of the DASA occurs during the cooling period. For example, at typical observed concentrations observed in Fig. 4, doubling the value of \( \delta \) to 40 \( \mu m \) reduces the estimated maximum temperature by approximately 18°C. Over the range of relevant sizes and concentrations observed here, the calculated temperature scales approximately as

FIG. 3. (a) Concentration as a function of time following fast pyroprobe heating of a HTPB/DASA sample. (b) The activation rate constants \( k \) as a function of inverse temperature. Fit line is to a zero-order Arrhenius expression \( dc/dt = A \exp(-E_a/RT) \).

FIG. 4. Images of pure polyurethane samples before (a) and after (b) bullet perforation (50 cal.) and with 5.56 mm caliber (c). Calculated peak temperatures around a 30 cal. rifle bullet penetration channel are shown in (d). (Multimedia View) [URL: http://dx.doi.org/10.1063/1.4940750.1]
$T_{\text{max}} \propto \delta^{-\frac{1}{2}}$. Relative temperature variations between points, however, are only weakly affected by the specific choice of $\delta$. The calculated temperatures with the experimentally based value of $\delta$ fall in the range 124 to 180°C; these rely on transmission absorption measurements that are averaged over an area roughly comparable to the dark circles in Figure 4(d). These temperatures are consistent with the lack of thermal degradation of the HTPB itself, which generally begins above 190°C. Temperatures on the right hand side of the sample are slightly higher due to the precession of the bullet. A cork-screw pattern can be seen in the full sample as the nose of the bullet give precesses moving through the polymer.

In conclusion, we have incorporated a donor-acceptor Stenhouse adduct thermophore into polyurethane to act as a microscale sensor of localized temperature increase. This photoswitch integrates readily into the non-polar elastomer environment and switches thermally to a conjugated state with a distinct visible and fluorescent signature. We fabricated pure HTPB gumstocks and an inert explosive warhead simulant of PBXN-110 and showed that the localized mesoscale temperature localization was observable with this material following high-rate impact. We used rapid heating in a pyroprobe to measure the DASA activation kinetics and combined this with a thermal history model to measure peak temperatures in a sample that had been perforated by high-velocity projectiles. The high solubility of the photoswitch and its molecular scale means that the limiting factor on the resolution is the optics on the confocal spectrometer; with a technique such as near-field scanning optical microscopy, nanoscale resolution could be obtained. The small weight percent of photoswitch required and its negligible effect on mechanical properties indicates that the thermochromic HTPB could serve as a drop-in replacement in explosives and rocket motors that could “self-report” the peak local temperature at the microscale.

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