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Surface and Interfacial Influences on the Bulk Responses of Composite Materials – AFOSR Annual Report FY2018

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14. ABSTRACT This report details preliminary results for an effort investigating the relationship between a material's chemical and physical properties. Refinement of new characterization techniques (room temperature inverse gas chromatography of polymer composites and stress and strain curves of single bead inclusion with digital image correlation) are presented. An alternate method to compare surface energy measurement by contact angle goniometry and inverse gas chromatography is detailed. New computational techniques using cohesion zone modeling are detailed. Initial surface and mechanical results of Sylgard 184 and hollow glass beads are considered including initial plans on surface modification to improve modeling efforts are included. Additional research and results are included in the year two and final reports for this effort.					
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ANNUAL LABORATORY TASK REPORT

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Title: Surface and Interfacial Influences on the Bulk Mechanical Responses of Composite Materials – Year Two

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Research Overview:

This research effort is investigating the surfaces and interfaces in heterogeneous energetic formulations and discovering the effects these regions have on the bulk properties of energetic materials (EM), quantifying these effects on mechanical properties and accounting for these effects in the model and design of new materials. This is being accomplished by developing characterization techniques (task 1) capable of elucidating the surface and interfacial properties of EM conglomerates. These materials are also being characterized using a suite of mechanical properties testing (task 2) modified specifically for these materials. These steps are being repeated with materials having measurable surface energy differences. Data obtained from characterization and testing are being correlated (task 3) to distinguish potential relationships between surface and interfacial properties and bulk mechanical properties. At the conclusion of this research effort we will have gained a qualitative and quantitative understanding of the role interfaces play in EM composites and will have a mathematical framework that will aide in creating novel EM formulations with application-driven and tailored mechanical properties.

Surfaces and interfacial characteristics and their effects on standard performance metrics, such as mechanical properties, have increasingly become topics of conversation within the energetic materials community. It is critical to understand these effects in heterogeneous composites as they directly affect a material's agglomeration behavior, process induced disorder, work of cohesion/adhesion, surface chemistry and charging, wettability of surfaces, and powder mixing, flow and segregation. On the macroscale, Figure 1, these features are often the locations of mechanical failures, interesting chemistry, and void formation and contribution to initiation and detonation physics. On the microscale, Figure 2, surfaces and interfaces are the dominant feature of the system. It is clear that there is a need and desire to better understand these features, yet very

little is known about them and their role in influencing bulk characteristics. This gap in knowledge is closing, as new techniques are discovered that are capable of probing these regions, but there remains numerous questions about what surface and interfacial properties are most beneficial to characterize for a given system, how these regions affect bulk properties, and how surface and interfacial properties can be reliably related to historically measured bulk properties and performance characteristics, without having to make and test each formulation iteration individually.

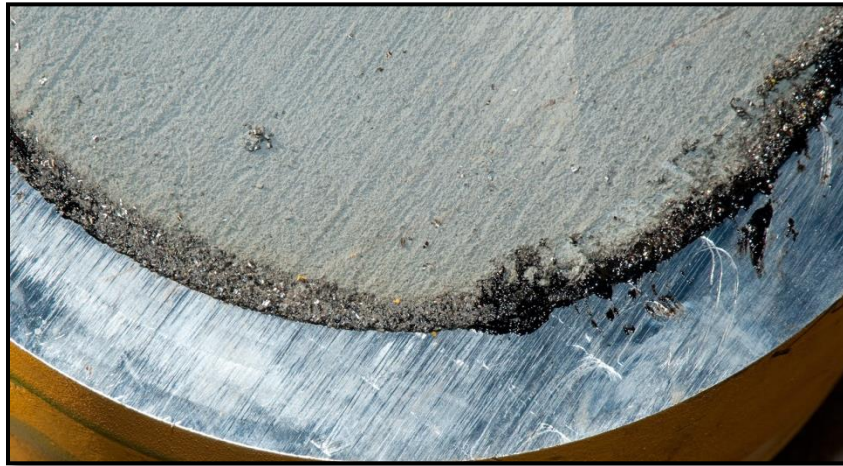


Figure 1. Image highlighting the meso-structures present in a filled high explosive munition. There are a number of interfacial characteristics including boundaries and/or intermixing between the main fill material, liner material and case material.

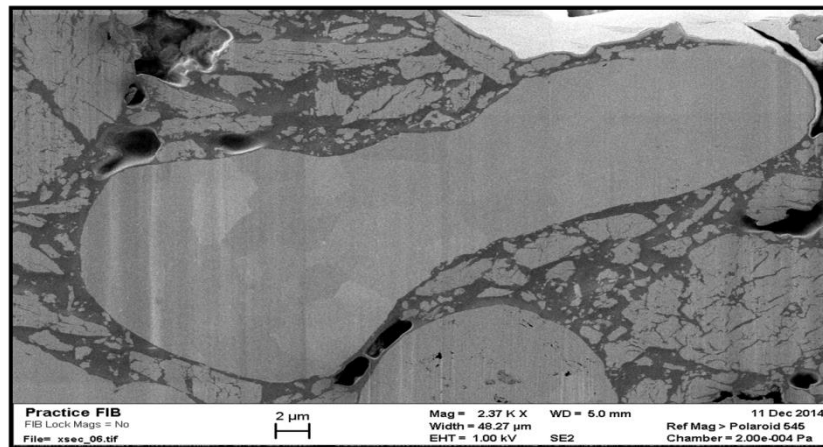


Figure 2. SEM image of an inert simulant energetic formulation. This image shows the various types of surfaces and interfaces present in this heterogeneous composite (composed of 3 different types of particulates, a polymeric binder, various additives and voids).

The Air Force requires munitions items capable of surviving increasingly stressful environments; such as high temperature or pressure. Harsher environments will continue to be a challenge as targets become harder and more deeply buried. Compression during penetration events can lead to premature detonation, or to detonation failure if delamination occurs at the fuze interface and the

material stretches away from the fuze. All materials undergo some degree of ageing during their life cycle. Thermal cycling and ageing can lead to a number of surface and interfacial issues such as delamination and the creation of voids. Ageing can be problematic both on the macroscale and on the microscale. These locations become points for potential material failure and preignition. Voids can be particularly troublesome as they can become hot spots and lead to unintentional initiation points. It is very likely that material interfaces and surfaces also have implications in the overall and inherent sensitivity and safety of energetic materials. Understanding the effects surfaces and interfaces have on an energetic material's bulk characteristics is paramount to being able to remain agile in the face of tomorrow's warfighting needs.

It is unknown how the chemistry of the interface (on the micro- or macroscale) affects the strength of the interface or how both affect the bulk properties of current energetic material formulations. This area of research is ripe for discovery and innovation. Once a basic understanding is obtained, it will be possible to explore modification of surfaces and interfaces in order to design materials with more desirable bulk properties. Moving forward, there is a need for resilient materials as tomorrow's warfighting needs are unknown. Obtaining a fundamental understanding of interfacial features and their performance effects will enable DoD and DOE scientists and engineers to meet those future needs.

A Note on Personnel

This effort lost modeling and simulation support in March 2017, due to the task 3 team lead moving onto another position. This occurred just as the experimental data from task 1 and 2 were complete and before any major modeling efforts were made by the task 3 team. Fortuitously, AFRL/RWML's Computational Team, led by Angela Diggs, was able to step in. Sushilkumar Koundinyan and Michael Nixon have created and made significant progress on the development of a model capable of capturing the experiments being performed in tasks 1 and 2. They have over 30 years of experience in building models similar to the one being developed herein and are a welcome addition to the team. As a result, the energetic materials portion of the overall lab task has been removed in order to meet the goals and deliverables within FY19. Final deliverables still remain a predictive modeling effort that incorporates surface and mechanical properties characterization data and will have been revised with additional surface modified materials.

Technical Summary of FY17 Progress:

1 Surface and Interfacial Characterization

1.1 *Surface and Interfacial Characterization Goals and Objectives*

The purpose of the first task of this research effort is to broaden the general understanding of the properties and characteristics of surface and interfacial regions within heterogeneous mixtures. In order to meet task goals, the following objectives are being addressed. A flexible methodology is being developed based upon existing inverse gas chromatographic (IGC) methods that is capable of providing surface and interfacial properties of a diverse range of materials; particularly glass beads and silicone binder systems. Properties of interest include surface energies (dispersive and specific), works of adhesion and acid/base character. Once the methodology is firmly established, there will be a systematic build-up from homogeneous particulate materials (Sylgard 184 silicone binder system and hollow glass beads of a single particle distribution with and without modified surfaces – within the scope of this three-year effort) to other two-component simple systems and then to multi-component heterogeneous mixtures of increasing complexity. Through observation of the systematic differences between a single component material and the more complex mixture, a more thorough understanding of the effects of each individual component on the overall heterogeneous mixture can be elucidated. This task will produce a series of materials with well characterized surface and interfacial properties which can then be studied for their effects on bulk mechanical properties of interest (including relationships and correlations) and for inclusion into current modeling and simulation efforts.

Major technical challenges include (1) sample preparation methods - exposure of surface and interfacial regions of interest in samples, (2) ensuring IGC measurements are of the surface and not bulk properties and (3) relating the surface and interfacial properties of a raw or simplistic material to those of the more complex system. These challenges are being addressed through (1) exploration of a number of sample preparation techniques including columns and thin films, studying the differences between as-cured surfaces exposed to different environments (air, nitrogen or Teflon), mechanical exposure of the interior of a sample (scalpel, microtome, etc.) vs. the exterior of a sample, and comparison of IGC findings to standard contact angle goniometer measurements as found in literature. Some materials interact with the probe molecules so strongly that they enter the material bulk and can interfere with other probe molecule retention times or provide characteristics of the bulk instead of the surface. This can be overcome by (2) closely monitoring signal/ time curves for signs of strong interactions, adjusting temperature, flow rate, probe concentration and at times eliminating particularly troublesome probe molecules.

1.2 *Material Preparation*

Initial material preparation looked at a number of binder systems of interest. A clear, two-part binder system was preferred for mechanical analysis of interfaces about particles. Hydroxyl-terminated polybutadiene binder (HTPB), epoxy and polydimethylsiloxane (PDMS) were all considered. PDMS, commercially available as Sylgard 184, was selected as the preliminary material due to its cost effectiveness, easy mixing/casting properties and short cure times. Sylgard 184 is composed of a 10:1 mixture of resin to curative and produces a reliable and repeatable casting and cure. Additional attractive features of Sylgard 184 are that laboratory scale samples can cure overnight at room temperature or on the order of a few hours at elevated temperatures (~60-100 °C), sample preparation does not involve hazardous isocyanates, unlike the HTPBs and resulting material is more flexible than its epoxy counterparts (preferable for an initial study).

For the filler phase, we considered beads of various compositions (glass, various metals and polymer). All solid samples had void, settling and density issues at all particle sizes. Void issues were addressed through heat treatment. Settling and density issues were not able to be overcome through any temperature or mechanical means using the chosen polymer matrix. For this reason, glass beads were chosen because they are both cost effective and readily available in low density, high strength, and hollow forms. 3M hollow glass beads were chosen exclusively because they were within our budget and time constraints. The particle sizes are severely limited (under 75 μm) and we will need to identify alternate particulates (likely polymer based depending on viscosity and cure rate of the binder system) for future sample series. Using Sylgard 184 and 3M hollow glass beads (22 μm and 60 μm), density was confirmed to be consistent for all sample configurations used in this study; including standard dogbones, thin/thick films, pucks, and other molded samples. Maximum hollow glass bead volume percentage, while retaining consistent, workable sample properties, was 45%. Sylgard 184 and 3M hollow glass bead (22 μm or 60 μm particle sizes, at 80% pore size distribution) samples within this study contain 5%, 15%, 25%, 35% or 45% glass beads by volume.

Surfaces were modified by hydroxylating the surface and removing any processing residuals through acid (or base washing). In the first case, 80 g of glass beads were combined with 2 L of 1.2 M HCl, allowed to stir at 90 °C for 2 h then washed several times with deionized water, dried at 70 °C overnight then washed with acetone and dried for 24 h. In the second case, 80 g of glass beads were combined with 2 L of 1.0 M NaOH, allowed to stir at 90 °C for 2 h then washed several times with deionized water, dried at 70 °C overnight then washed with acetone and dried for 24 h. Initial testing has shown an increased cohesive affinity in these modified beads. Additional modifications are being considered, particularly the use of small quantities of hydrocarbon rich organosilane molecules, to decrease cohesive properties in the modified materials.

1.3 Method Development and Preliminary Results

IGC allows numerous surface phenomena to be quantified to include the total surface energy (γ_s), dispersive surface energy component (γ_s^d), specific surface energy component (γ_s^{sp}), work of cohesion and adhesion (W_C , W_A), heats of sorption (ΔH), acid or base constants (K_a or K_b), partial solvation parameters based on quantum mechanical analysis, Hildebrandt solubility parameter, crosslink density, diffusion coefficient, chemisorption and physisorption affinity and specific surface area (SA_{BET}) determinations from adsorption and desorption isotherms.¹⁻¹⁰ Bulk properties which can be determined from IGC include the glass transition temperature (T_g), solubility parameter, polymer cross-linking and diffusion coefficient.¹⁰

This task will utilize IGC to develop a methodology capable of measuring surface and interfacial properties for a wide variety of sample types. IGC is a chromatography technique in which the material to be investigated is present as the stationary phase and small quantities of well understood probe molecules, in an inert carrier gas (He), are used as the mobile phase; probe molecules include a series of non-polar alkanes (hexane, heptane, octane, nonane, decane and undecane) and polar molecules (acetone, tetrahydrofuran, ethyl acetate, acetonitrile, chloroform).¹¹ At infinite dilution, adsorption of probe molecules is independent of the surface coverage, does not include lateral interactions of probe molecules and results in a linear isotherm as described by Henry's Law. This experimental mode probes the highest energy sites on a material's surface.¹² Retention times from the resulting Gaussian peak maximums are used to calculate retention volume, V_N , by:²

$$V_N = \frac{j}{m} F(t_R - t_0) \frac{T}{273.15K}; \quad j = \frac{3}{2} \left[\frac{(P_{in}/P_{out})^2 - 1}{(P_{in}/P_{out})^3 - 1} \right] \quad (1)$$

Where j is the James-Martin compression correction factor, m is the sample mass, F is the exit flow rate at 1 atm and 273.15 K, t_R is the retention time of the adsorbing probe from the peak max, t_0 is the dead time as determined from methane, T is the column temperature in K, and P_{in} and P_{out} are the inlet and outlet pressures, respectively. The greater the value of V_N , the greater the affinity of the probe molecule for the investigated material's surface.

The dispersive surface energy, γ_s^d , can be found experimentally by injection of a series of alkane probe molecules and finding the slope of a plot of $RT \ln V_N$ vs. $a \gamma_L^d$, according to the following equation:^{2, 13-14}

$$RT \ln V_N = 2N_A (\gamma_s^d)^{1/2} a (\gamma_L^d)^{1/2} + constant \quad (2)$$

Where R is the gas constant, N_A is Avogadro's number, a is the cross-sectional area of the probe molecule and γ_L^d is the surface tension of the probe molecule. Or alternatively, in the Dorris and Gray approach, by plotting $RT \ln V_N$ vs. c-number (from the alkane series) and using the contribution of a methylene group in the free energy of adsorption, $\Delta G_{CH_2}^\circ$, from:¹⁵

$$-\Delta G_{CH_2}^\circ = N_A a_{CH_2} 2\sqrt{\gamma_{CH_2} \gamma_s^d} + constant \quad (3)$$

The specific surface energy (polar component), γ_s^{sp} , contain both dispersive and specific components and are be found by adding the polar probe V_N values to the above plot (Equation 2) and measuring their distance from the straight line formed by the alkane probes. The difference found is equivalent to the specific component of the free energy of desorption, ΔG_{sp}° , according to:²

$$\Delta G_{sp}^\circ RT \ln V_N - RT \ln V_N^{ref} \quad (4)$$

Specific surface energy can also be calculated by exploration of the acidity and basicity of a material using acidic and basic polar probes through the van Oss concept:^{3, 16-17}

$$\Delta G_{sp} = 2 N_A a_m \left((\gamma_L^+ \gamma_s^-)^{1/2} + (\gamma_s^+ \gamma_L^-)^{1/2} \right) \quad (5)$$

Where a_m is the surface coverage, γ_s^+ and γ_s^- are the acid and base parameters for the surface and γ_L^+ and γ_L^- are the electron acceptor and donor parameters of the probe molecule. Once the acid and base parameters are understood, the specific surface coverage can then be obtained by:^{3, 18-20}

$$\gamma_s^{sp} = 2 (\gamma_s^+ \gamma_s^-)^{1/2} \quad (6)$$

Adsorbate (material a) and substrate (material b) interactions and interfacial shear strength can then be calculated using the dispersive surface energies and acid base parameters for the materials. Work of adhesion, W_{ADH} , can be derived by:²¹⁻²³

$$W_{ADH} = 2 (\gamma_a^d \gamma_b^d)^{1/2} + 2 (\gamma_a^+ \gamma_b^-)^{1/2} + 2 (\gamma_b^+ \gamma_a^-)^{1/2} \quad (7)$$

Up until this point, all experiments and calculations described occur within the infinite dilution regime (10^{-3} to 1 mg probe molecules).²⁴ Infinite dilution experiments (IGC-ID) take place within the Henry's Law region of the adsorption isotherm and probe the most highly energetic sites in a material which allows for very high sensitivity.

Measurements at finite concentration (IGC-FC) provide complimentary information as probe molecules interact with all sites on the surface.¹² Through investigating materials in this regime, lower surface energy sites and concentration of sites at each energy level can be probed and results are more comparable to the average surface energy measurements found in contact angle goniometry (CAG). Surface energy heterogeneity in a material is an important property in understanding the energy across an entire material. As previously discussed, injection of a series of alkane and polar probe molecules at the same molar concentration (surface coverage) can give both the dispersive and specific surface energies at that surface coverage. Repetition over a range of probe molecule concentrations (finite concentration) gives a surface energy profile for a material (a distribution of surface energies as a function of surface coverages). Integration of each point of the profile and plotting surface energy (γ_s^d or γ_s^{sp}) vs. percentage of surface coverage will give surface energy distributions which allow for evaluation and comparison of surface energy heterogeneity.^{13, 18, 20, 25-27}

The current set-up at RWME utilizes a refrigerating incubator system separate from the IGC system that provides for greater temperature control (down to 5 °C from 35 °C), makes use of a thin film cell (easier sample preparation but the longer column length has repercussions on resolution) and has allowed for the surface property measurements of challenging samples with very strong interactions with probe molecules.

1.3.1 Surface Energy Characterization Results

Sylgard 184 and 3M hollow glass bead (22 μ m or 60 μ m particle sizes, at 80% pore size distribution) samples within this study contain 5%, 15%, 25%, 35% or 45% glass beads by volume. Each sample was analyzed by IGC at infinite concentration to obtain surface energy (total, dispersive and specific components) using a series of probe molecules (polar – ethanol, chloroform, ethyl acetate, acetone, acetonitrile and nonpolar – hexane, heptane, octane, nonane, decane, undecane). Preliminary analysis entailed identification of peaks, minimizing tailing and ensuring the full peak is captured at various molar concentrations. Figure 3 shows the resulting chromatogram for a sample with 22 μ m glass beads at 25% vol. with ethyl acetate as the probe molecule at various molar concentrations (infinite concentration mode) at 23 °C. Figure 4 shows the same sample with heptane as the probe molecule. As shown, all samples show peak tailing with thin film cell samples having more significant tails (due to the longer path column length) and peak maximum was used for all calculations. All samples were synthesized and measured on three separate occasions, using the thin film cell in refrigerating incubator and the internal glass column.

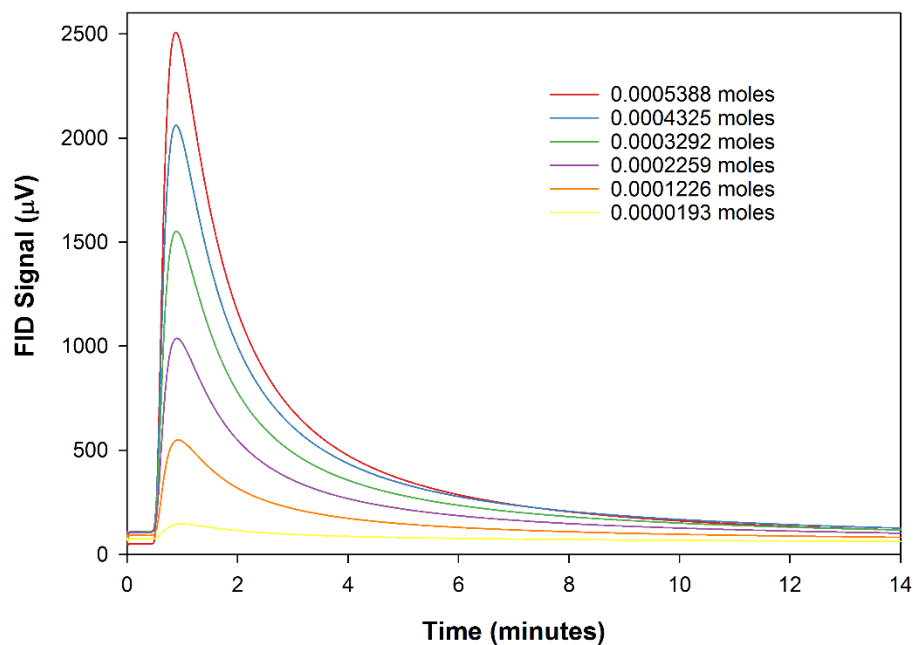


Figure 3. Retention times of a series of infinite concentration injections of the polar probe molecule ethyl acetate with a Sylgard 184 and 22 μm glass bead composite thin film

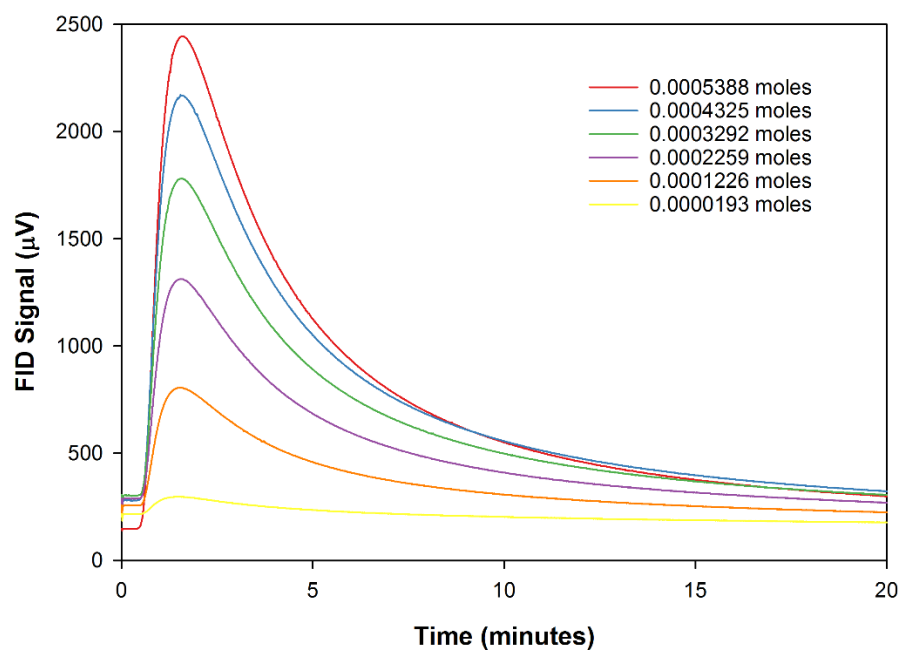


Figure 4. Retention times of a series of infinite concentration injections of the nonpolar probe molecule heptane with a Sylgard 184 and 22 μm glass bead composite thin film

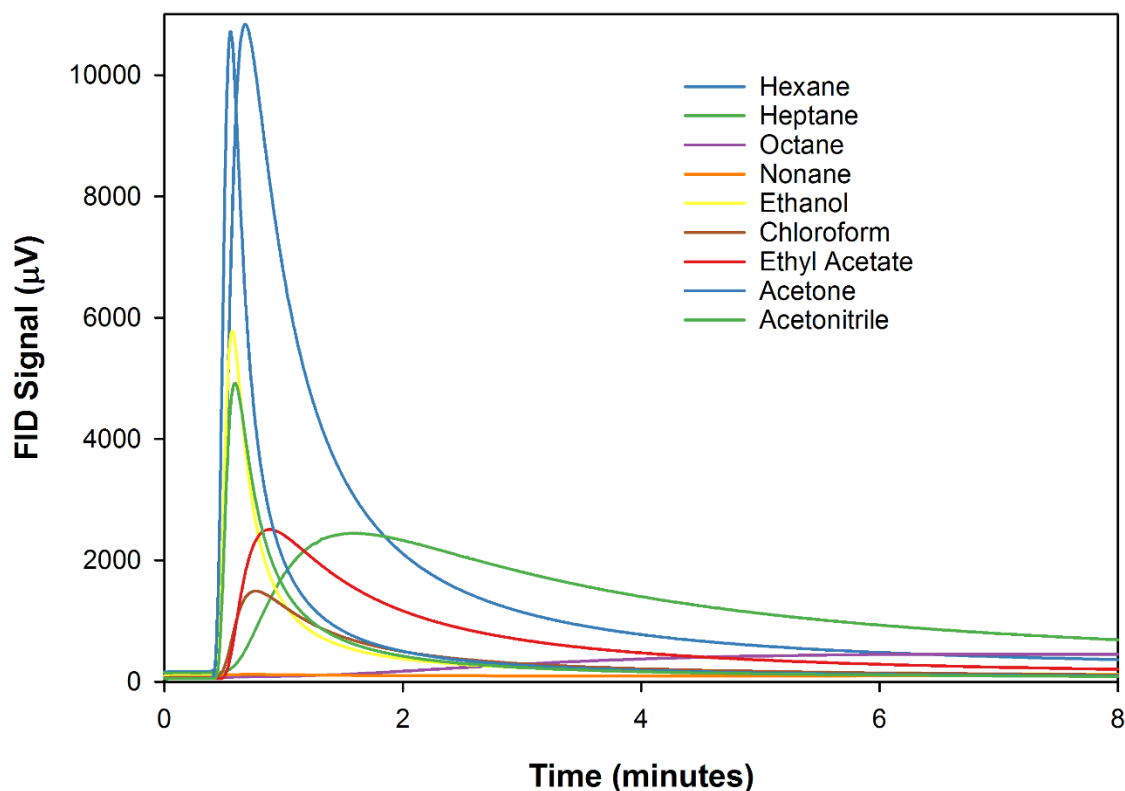


Figure 5. Retention times of all polar and nonpolar probe molecules, at the highest infinite dilution concentration, for a Sylgard 184 and 22 μm glass bead composite thin film

Surface energy values are calculated, as previously discussed, based on the pulse injection results at very small concentration of probe molecules at very low surface coverages (typically less than 0.01%). This allows for the probe molecule concentration to be linearly dependent on the injection concentration and ideally result in symmetrical and Gaussian peaks. Figure 5 shows the 22 μm glass beads at 25% vol. sample with all of the probe molecules run at their highest molar concentrations. Care was taken to ensure the peaks were significantly separated from the methane peak (used as dead time measure, not included in image), that the peak maximums were clearly distinguishable and probe molecules were eluted completely between subsequent runs.

Surface Energy Determination for Sylgard 184 and 22 μm beads (25%vol)

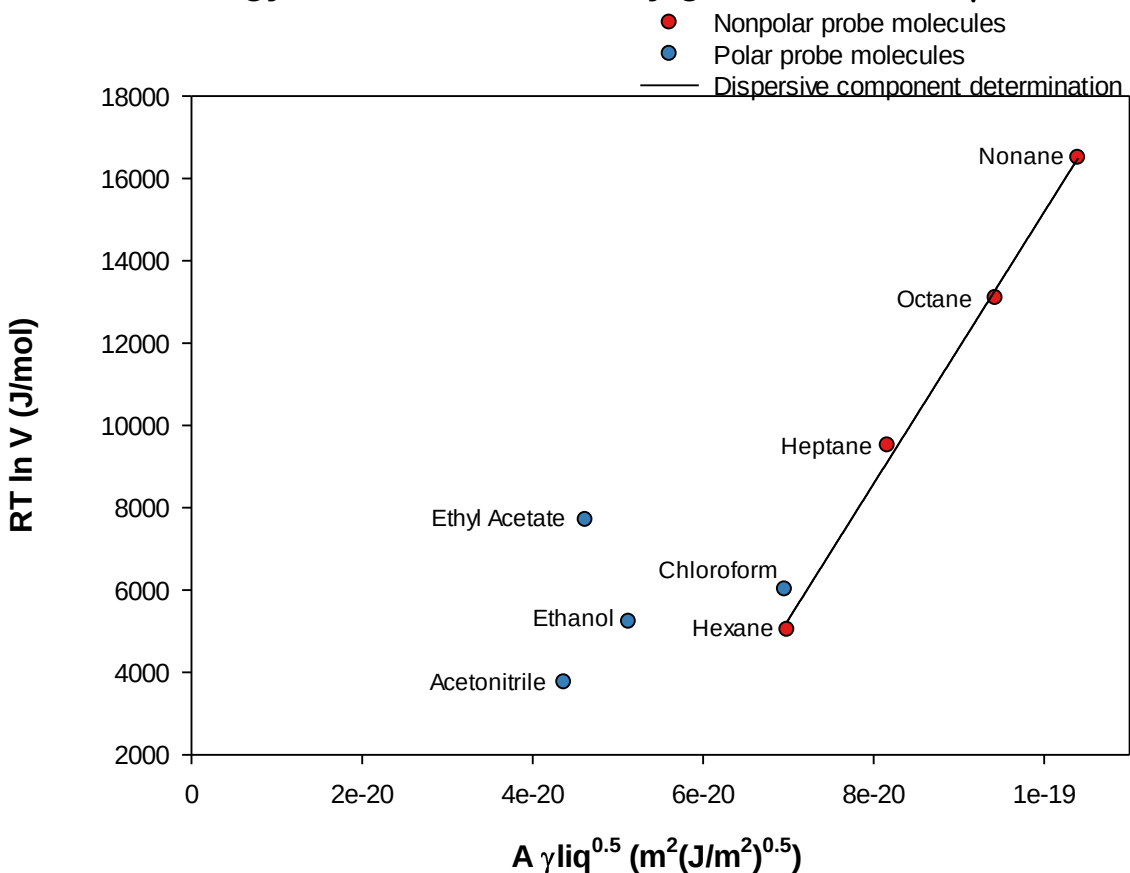


Figure 6. Surface energy determination for a Sylgard 184 and 22 μm glass bead thin film sample. The dispersive (nonpolar) component is calculated from the slope of the regression line and the specific (polar) component from the y-distance to the regression line.

Plotting the nonpolar probe molecules (blue), fitting a regression line and also plotting the polar probe molecules (red) allows one to calculate, Figure 6. The regression line slope gives the dispersive component of surface energy and the distance between the regression line and the polar probe molecules will give the specific components to surface energy. Acidic (or basic) polar probes will also provide the acidic (or basic) component of the polar or specific component to surface energy.

Table 1. Surface energy values for series of Sylgard 184 and K20 (60 μm) or K42HS (22 μm) hollow glass beads

Sample (mJ/m^2)	γ^{total}	γ^{d}	γ^{ab}	Sample (mJ/m^2)	γ^{total}	γ^{d}	γ^{ab}
Sylgard 184	84.54	79.78	4.76	Sylgard 184	84.54	79.78	4.76
60 μm beads	55.48	44.38	11.10	22 μm beads	85.64	62.11	23.53
60 μm 5% (vol)	75.02	70.37	4.64	22 μm 5% (vol)	81.95	77.18	4.76
60 μm 15% (vol)	74.99	71.30	3.69	22 μm 15% (vol)	84.90	80.41	4.49
60 μm 25% (vol)	75.26	71.66	3.60	22 μm 25% (vol)	78.32	74.86	3.46
60 μm 35% (vol)	79.74	75.47	4.27	22 μm 35% (vol)	74.49	70.98	3.51
60 μm 45% (vol)	75.68	71.25	4.43	22 μm 45% (vol)	74.04	69.99	4.06

Table 1 has the total (γ^{total}), dispersive (γ^{d}), and specific or polar (γ^{ab}) components of surface energy for the raw materials and samples included in this study, thus far. Each of the bead sizes (22 μm and 60 μm) has 5 different volume fractions (5, 15, 25, 35 and 45%). Also included are Sylgard 184 and each of the beads on their own. Of interesting note is that the 60 μm glass bead samples do not vary significantly one from another while the 22 μm bead samples may. It was difficult to determine any real conclusions due to the instrument variation in the early samples. Those samples are being added as additional data point to the end of the study in order to draw more firm conclusions.

The 60 μm beads have a surface energy of approximately 30 mJ/m^2 lower than that of the Sylgard 184 while the 22 μm beads were approximately the same as the Sylgard system. During sample preparation and mixing, the 60 μm beads separated and were much more difficult to get into solution. It was interesting that such a small difference in energies created such large processing challenges.

Current efforts are focused on completing measurements for the third replicate series, quantifying and further minimizing instrumental and user error and moving onto the modified sample measurements.

1.3.2 Contact Angle Goniometer Comparative Study

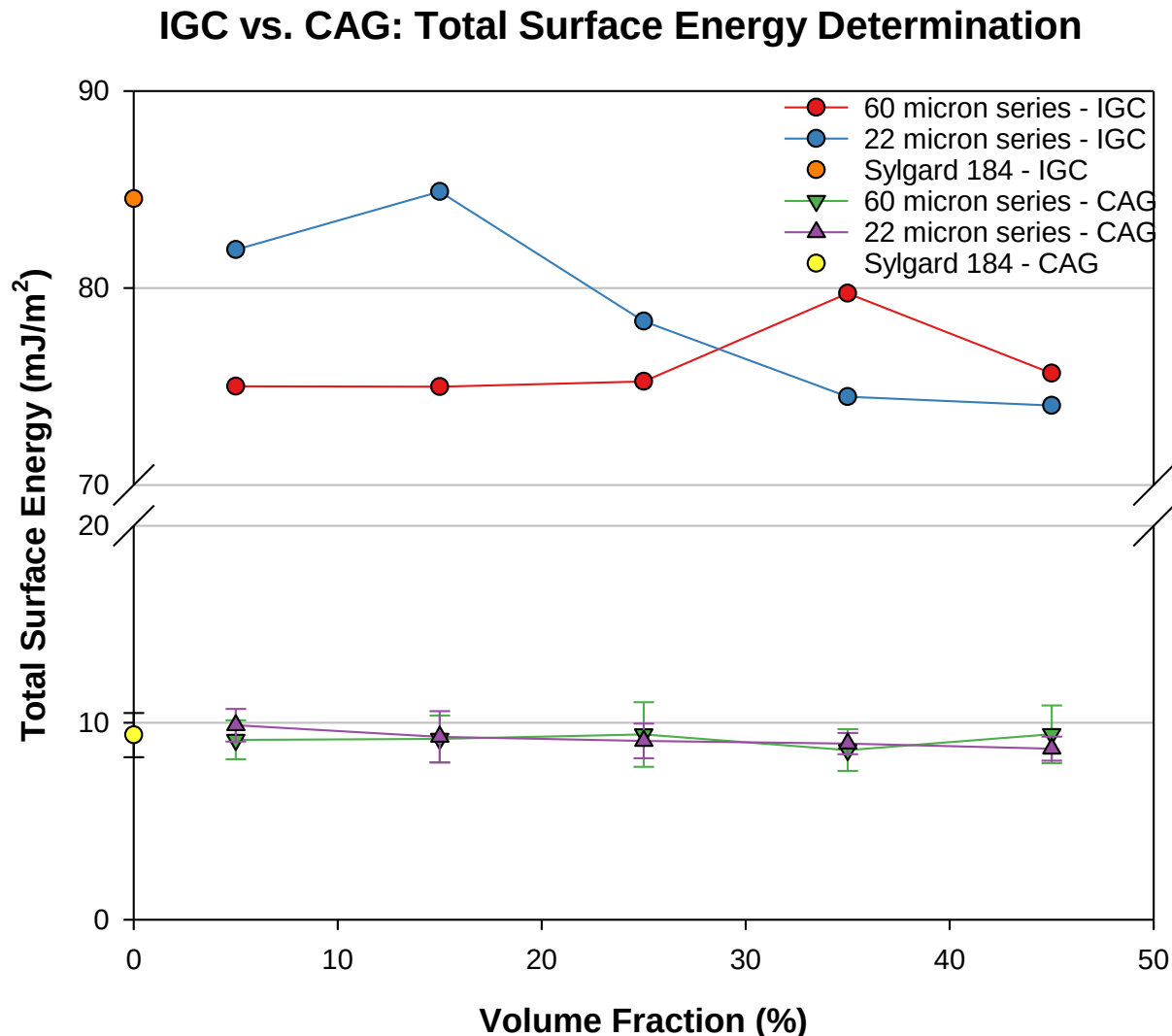


Figure 7. Total surface energy values for Sylgard 184 and glass bead (60 µm and 22 µm) samples at various glass bead volume fractions as determined from IGC and CAG analysis. Sylgard 184 at 0% volume fraction is included for comparison (orange dot).

A brief study was completed in which the samples used in this study were also measured using CAG. CAG is the standard measurement technique for surface energy of flat samples but has numerous downfalls, needing pristinely clean and flat samples being one of the more significant. Surface energy values of samples from both IGC and CAG were plotted in Figure 7. There is a very stark contrast in IGC and CAG values, as expected, because IGC at infinite dilution probe only the high surface energy sites of a surface while CAG gives a local average. While values vary largely, trends amongst the samples seem to follow along with one another within the two methods. In order to better compare these disparate instrumental methods, probing and quantifying all sites by IGC is required.

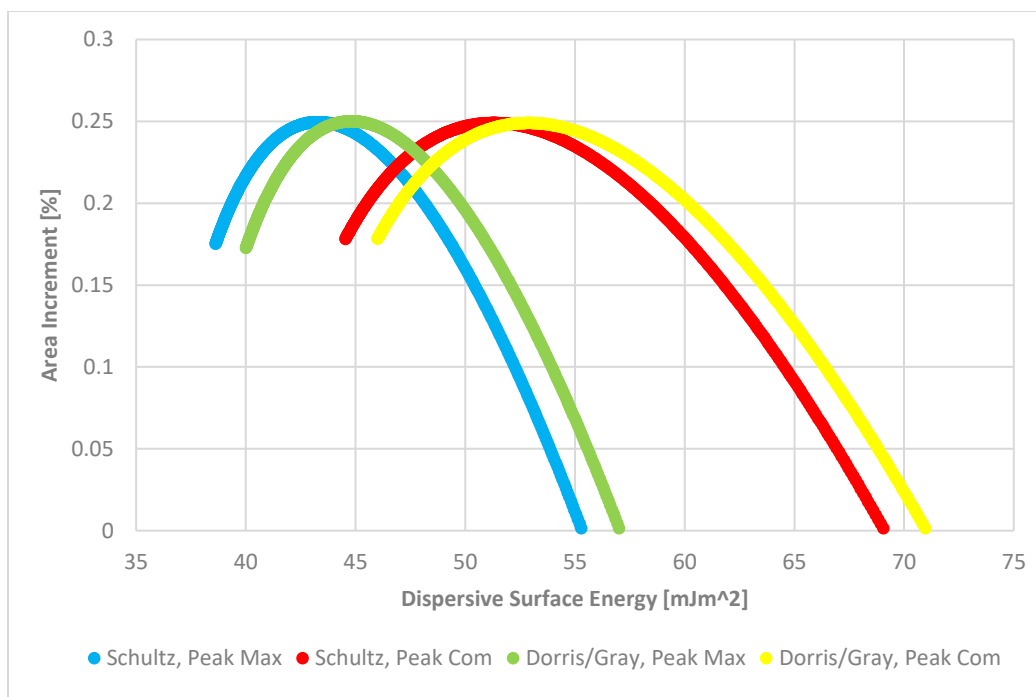


Figure 8. Surface Energy Heterogeneity profile for an unrelated sample using IGC-FC using Schultz or Dorris and Gray analysis techniques at peak maximum (Peak Max) or peak computed (Peak Com)

Surface energy heterogeneity profiles are performed by using IGC at finite concentration. This mapping technique allows one to obtain a total surface energy value by integrating over the entire surface while retaining information unique to the IGC – high energy site quantity and energy values. This method is significantly more complex and requires the derivation of an adsorption isotherm and retention volume over a vast range of probe molecule concentrations. Figure 8 shows the dispersive surface energy profile (energy values and area increment %) for an unrelated sample using peak maximum or peak commuted values in the Schultz or Dorris and Gray techniques. This study will always use peak maximum due to the lack of symmetry in some peak families, previously shown. Figure 9 shows surface energy heterogeneity mapping with γ^{total} , γ^{d} and γ^{ab} values. This technique gives a wealth of information in a single measurement - surface coverages, dispersive, specific, acidic, basic and total contributions to surface energy.

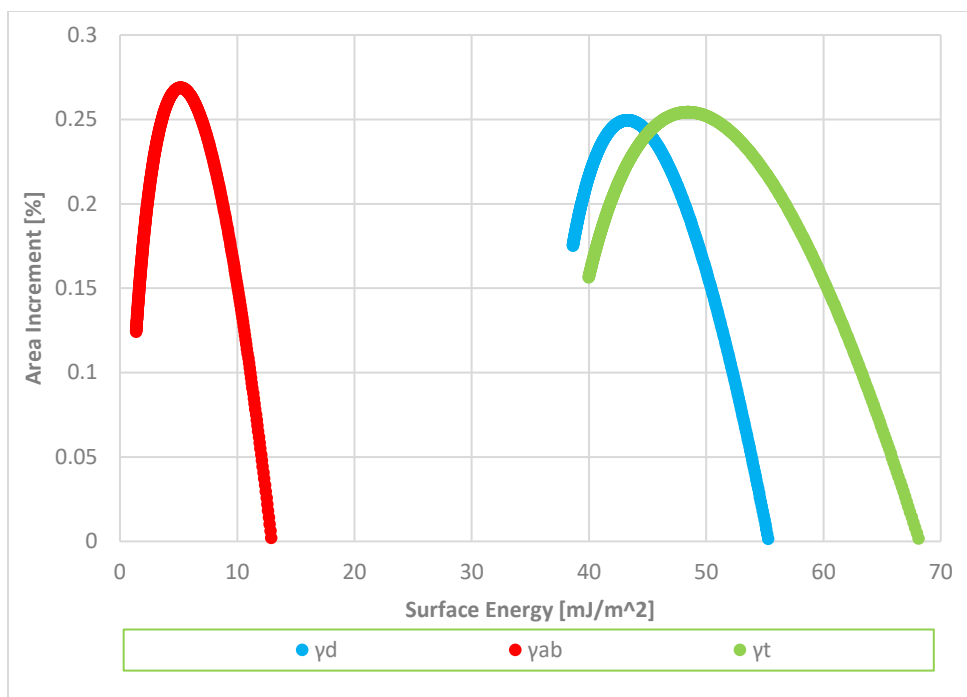


Figure 9. Surface Energy Heterogeneity profile for an unrelated sample using IGC-FC using Dorris and Gray analysis techniques at peak maximum (Peak Max)

Table 2. Surface Energy Heterogeneity profile analysis results for an unrelated sample showing surface coverages, dispersive, specific, acidic, basic and total contributions to surface energy

Analysis Results - γ_{ab} γ_s γ_t [mJ/m ²]					
n/nm	γ_d	γ_{s+}	γ_{s-}	γ_{ab}	γ_t
0.0436	53.01662	3.021617	10.95521	11.50694	64.52357
0.2349	49.52455	1.801402	6.893327	7.047738	56.57229
0.4262	44.06557	1.21933	3.988618	4.410642	48.47622
0.6174	40.05279	0.926552	2.059191	2.762569	42.81536
0.8087	38.97095	0.791254	0.918127	1.704666	40.67562
1	39.90868	0.748855	0.810101	1.557752	41.46643

Current efforts are focused on completing acrylic and graphite measurements by CAG and IGC in addition to including all Syglard 184 samples in these calculations of total surface energy of samples. Obtaining this information would allow one to be able to more accurately compare surface energy values between IGC and CAG but show the wealth of information the IGC can obtain in addition to being able to analyze powders and other non-standard material configurations.

1.3.3 Wetting

Wetting is a significant phenomenon in the processing of heterogeneous energetic formulations. After discovering the challenges associated with a 30 mJ/m² difference between the binder and particulate within this study, efforts have begun to evaluate organosilica molecules with functional groups of energies similar to components to be mixed. Concentrations as small as 1% by volume were able to visibly and remarkably improve the processability of dual component systems. FY 19 efforts will look to further this understanding so that high solids loading formulations can be facilitated.

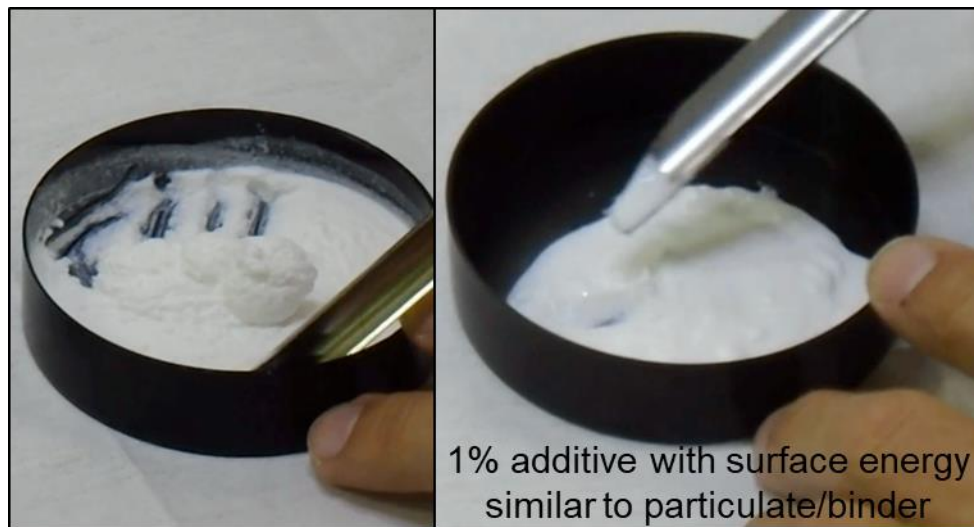


Figure 10. Wetting behavior of materials is a consequence of surface energy - adding small quantities (1% vol.) of additives with surface energy values similar to that of dissimilar materials (particle/ binder), significantly improves particle wetting behavior as seen in these images

1.4 Plans for FY19

Research plans for FY19 Surface and Interfacial Chemical Properties Characterization include:

- Additional method development (hardware additions to minimize error, finite concentration analysis, surface modification of glass beads) with Sylgard 184 and modified 3M hollow glass beads will be completed;
- All samples are undergoing replicate measurements to elucidate instrumental and random error in non-traditional set-up and validate method in comparison to traditional contact angle measurements;
- Analysis approval for energetic particulates by IGC is underway in order to further study and transition wetting improvement results for AFRL/RWME's Energetic Materials Processing team;
- Surface energy heterogeneity mapping has been added as parameter of study as a result of the comparative study with contact angle goniometer.

2 Mechanical Properties Studies

2.1 Mechanical Characterization Overview

The goal of the mechanical characterization task is to measure interface debonding strength in polymer bonded explosives. This feeds into the overall goal of the Laboratory Task of correlating interfacial mechanical properties with interfacial chemistry by providing deterministic and stochastic measurements of interface debonding strength.

In this work, measurement of interface debonding strength is accomplished in two ways – implicitly and explicitly. In the implicit approach, bulk properties measured on a family of hyper engineered composites where composition variables such as filler volume fraction, filler particle size, filler particle surface chemistry, etc. are well-controlled and characterized and then constructing correlations between bulk properties and composition details. With the implicit approach, we hope to elucidate the effect of surface chemistry on particle-binder interface strength as well as the effect of particle-binder interface strength on bulk composite properties. In the explicit approach, we will attempt to directly measure particle-binder interface strength by way of targeted mechanical experiments which control the stress and strain state such that the mechanical load at an interface can be directly quantified. This report summarizes the to-date experimental data for the explicit approach.

2.2 Mechanical Characterization Methodology

To better understand and characterize the mechanical state of the binder at the moment of delamination, experiments were conducted to determine the spatially mapped strain state of a highly idealized delamination scenario. In order to accomplish this task, tensile test samples were constructed consisting of a single spherical particle embedded within a binder material as depicted in Figure 11. To induce a global stress condition on the sample, a tension force was applied to the sample in a single direction, as in a typical “tensile test.” A pattern of small tracking particles were placed within the sample to quantify the strain state of the binder material with the use of commercial digital image correlation (DIC) software, a camera and appropriate supporting optics. The spatial distribution of the stress state of the binder material can then be inferred from the known global loading condition of the sample and local strain measurements. This information can be collected up to and throughout the delamination process, which can be determined through visual inspection of the collected images, also depicted in Figure 11. Specific accomplishments of the development of this experimental method follows.

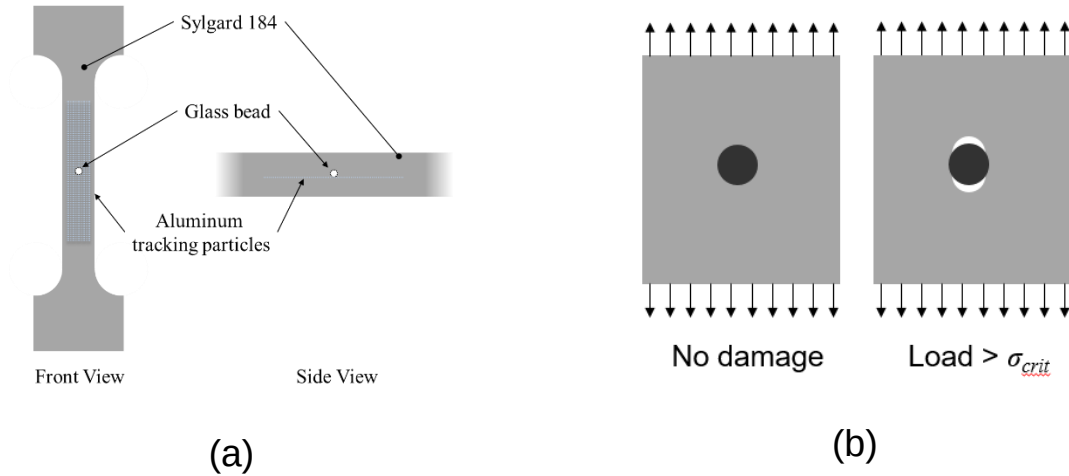


Figure 11. (a) Front view of composite dogbone with embedded glass bead and digital image correlation speckle pattern. (b) Sketch of local microstructure immediately before and after debonding

2.2.1 Sample Production

JANNAF standard dog-bone tensile samples were constructed from a castable material in a layered approach in order to properly embed the particle of interest as well as the tracking particles for use in DIC.²⁸ Dow Corning Sylgard 184 silicone elastomer was mixed in a 10:1 base to curative ratio by mass and used for the binder material of all samples. The highly transparent nature of the material allowed for the observation of the translation of the particles within the sample throughout the experiment. An initial layer of Sylgard 184 was poured into a dog-bone shaped mold to a height of approximately 6.35 mm and cured at 100 °C for 30 minutes. A thin layer of binder was then applied to the partially cured surface and a spherical glass particle was placed in the middle of the sample such that the thin layer of binder was level with the mid-plane of the particle. The sample was then cured for an additional 30-minute cycle at 100 °C. A layer of small tracking particles was then applied to the surface of the new cure layer and the mold was then filled to the full mold height of 12.70 mm. The sample was then subjected to a final cure cycle at 100 °C for 30 minutes. The sample was released from the mold and excess binder was trimmed. The sample construction process is summarized in Figure 12.

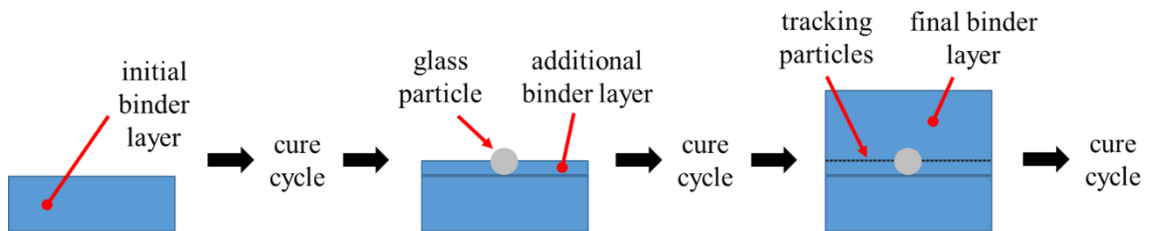


Figure 12. Illustration of the layered approach to construct dog-bone samples of Sylgard 184 with an embedded spherical glass particle and pattern of tracking particles

The quality of the placement of the spherical glass particle and the surrounding plane of tracking particles were evaluated with the use of a Zeiss Discovery V12 stereoscope. The glass particles were examined to ensure their placement at the middle of the dog-bone shape, as well as at the mid-plane of the sample. The plane of tracking particles were also checked for proper placement at the mid-plane of the glass particle and subsequently, the mid-plane of the sample. In order to allow for suitable observation of the delamination event, glass particles with a nominal diameter of 2.00 and 0.65 mm were used in the samples.

2.2.2 DIC Pattern Application

It is well known in the field of DIC that the success of the strain field measurement is highly sensitive to the application of the tracking pattern. To address this issue, a number of different tracking particles were used in a series of initial samples in order to select a suitable tracking pattern. Particle types of (1) commercially available DOMINO powdered sugar, (2) aluminum particles (25 μm nominal particle size), (3) commercially available Lexmark C736H1KG printer toner, (4) carbon black, and (5) dyed polyethylene beads were evaluated.

After samples were constructed using these particle types for tracking patterns, high resolution images of the embedded glass particle and tracking pattern were captured using a Zeiss Discovery V12 stereoscope. These images were then digitally expanded such that a set of images of 100 to 150% uniform expansion were created for each sample. These images were then used to evaluate the quality of the DIC algorithm strain calculation result to the known artificially expanded patterns. An example series of a set of digitally expanded images are presented in Figure 13.

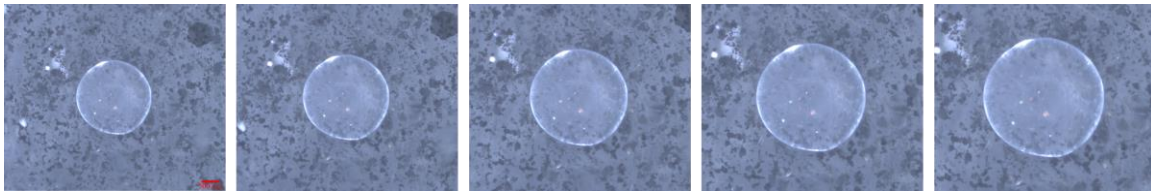


Figure 13. A set of digitally expanded tracking patterns of carbon black tracking particles in Sylgard 184 surrounding an embedded glass bead

2.2.3 Experimental Methods

A MTS Exceed E42.503 (5 kN) load frame was used to apply a constant velocity extension and measure a continuous tensile load to the sample and was controlled by MTS TestSuite Elite software. The extension of the load frame cross head was held at a constant rate of 0.5 mm/s in order to apply a constant global engineering strain rate to the sample. The glass particle and surrounding tracking pattern was imaged with the use of a Point Grey Grasshopper 2 camera with a resolution of 2048 by 2048 pixels. A Rokinon 2.8/14 mm optical lens was used in concert with the camera to capture highly detailed images of the region of interest which corresponds to a field of view of approximately 10 by 10 mm with an approximate standoff distance of 0.5 m. Illumination of the sample was supplied by the use a Visual Instrumentation Corp. 900420 LED module lamp.

Due to the load frame configuration, the load is applied to the sample with the controlled displacement rate of an upper grip while the lower grip is held stationary. This configuration subsequently results in a displacement of the glass particle nominally equal to one half of the displacement of the crosshead controller of the load frame. This behavior in turn makes it difficult to continuously observe the glass particle and surrounding tracking pattern at high resolution. In order to counter this effect, the camera was mounted to a Thorlabs LTS150 motorized stage in the vertical direction and controlled with Thorlabs Kinesis software. The displacement of the stage was then programmed to travel at a constant rate equal to one half that of the travel rate of the crosshead controller.

The images were captured using Point Grey FlyCapture 2 software and the loading conditions were measured such that the imaging and loading information of the sample were recorded as a function of common time. The images were then analyzed in Correlated Solutions VIC2D digital image correlation package to measure the evolving strain field over time for each sample. The delamination event of the glass bead is also observed in the images such that the global loading conditions and local strain field near the particle are known at the moment of debonding.

2.2.4 Evaluation of Effects of Multiple Cast Layers and DIC Pattern

It is expected that the effect of the multiple layered samples will result in mechanical behavior that is not identical to samples created without layers or “cold joints”. To evaluate this effect, samples were specifically produced with no glass particles or tracking patterns using the same layered process as previously listed. These samples will be tested under tensile loading as previously described and the global stress-strain curve and ultimate strength will be compared to results from samples produced of a single, complete casting process. This comparison will illuminate the significance of the multiple layers on the effect of the bulk mechanical behavior of the sample. Additionally, the effect of the presence of the tracking particle will also be compared to “blank” samples with the presence of all layers. This result will indicate the magnitude of the effect of the tracking particles on the bulk mechanical behavior of the sample.

2.3 Mechanical Characterization Results

2.3.1 Evaluation of sample construction technique

Figure 14 shows stereoscope images of the glass bead for a dogbone with a carbon black embedded DIC pattern. From these images, we see that the embedded speckle pattern is near the midplane of the glass bead, which gives us confidence that the measured strain fields will be in or very near the plane where delamination begins.

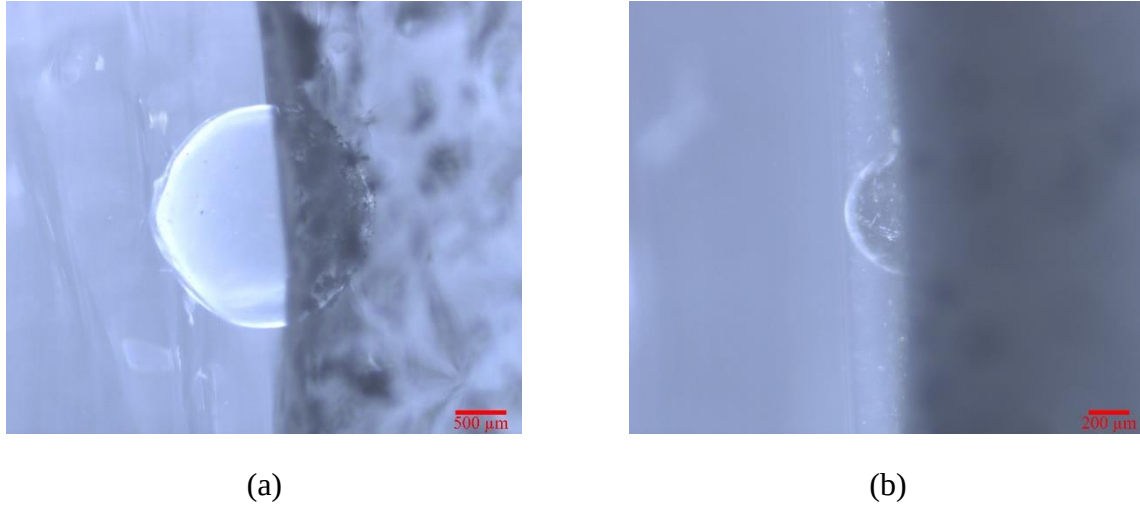


Figure 14. Side view stereoscope images of the dogbones with carbon black (a) and laser printer toner (b) DIC patterns

2.3.2 *Nondestructive evaluation of embedded speckle patterns*

As mentioned in the previous section, to evaluate the viability of some of the materials used to create the embedded DIC speckle patterns, microscope images were obtained and an artificial biaxial expansion was imposed. The expansion was imposed by creating a series of images where each image was slightly stretched and then cropped down to match the original image size. This series of images was then fed into the DIC algorithm from which the 2D strain tensor was computed. Figure 15 shows the DIC results for the artificial expansion of the carbon black embedded speckle pattern. Figure 16 shows the DIC results for the artificial expansion of the laser printer toner embedded speckle pattern. In both figures, the first principal strain is plotted and from the figures we see that the strain field is uniform within the resolution of the numerical algorithm for the given speckle patterns. These strain values correspond very well to the amount of expansion introduced by artificially expanding the images, giving high confidence in both carbon black and laser printer toner as embedded speckle pattern materials.

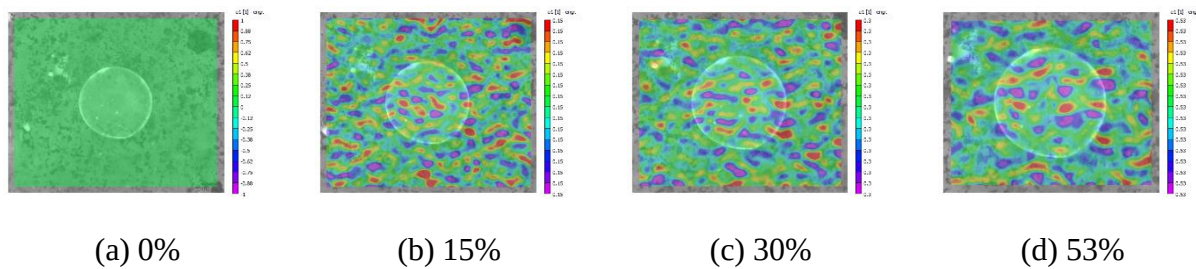


Figure 15. First principal strain for carbon black artificial expansion. Values shown below images correspond to the x-y averaged mean strain with an uncertainty below 1%

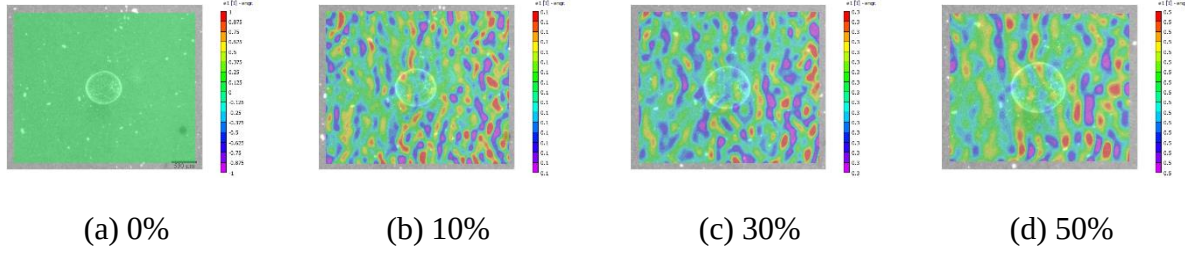


Figure 16. First principal strain for printer toner artificial expansion. Values shown below images correspond to the x-y averaged mean strain with an uncertainty below 1%

2.3.3 Destructive evaluation of embedded speckle patterns

As mentioned in the previous section, samples were constructed using aluminum, powdered sugar, carbon black and laser printer toner as materials for the embedded speckle pattern. We have shown through artificial biaxial extension of the stereoscope images that carbon black and laser printer toner are viable embedded speckle pattern materials. In this section, we will present the DIC results from the destructive tension tests that were performed on the sample with aluminum and laser printer toner speckle patterns.

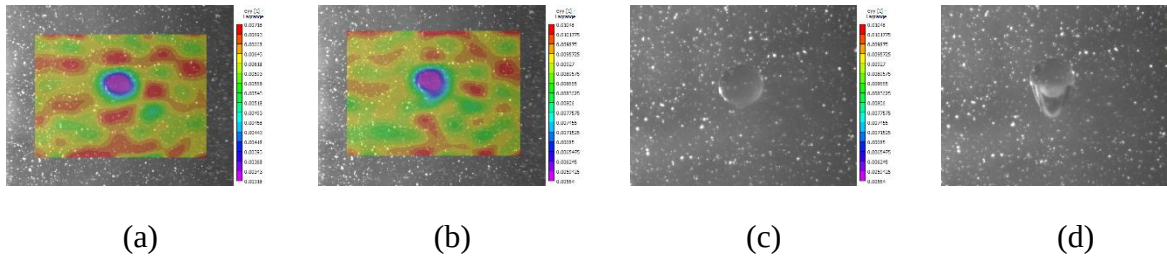


Figure 17. Strain in vertical direction for dogbone with embedded aluminum DIC speckle pattern. Images (a) and (b) show the strain field very early on in the experiment. Images (c) and (d) are subsequent frames much later in the experiment

Figure 18 shows the DIC results for the dogbone with aluminum tracking particles. For this test case, the DIC numerical algorithm worked well early in the test, but due to light reflection from the aluminum particles, the algorithm began having issues due to too much change in the speckle pattern from frame to frame. Ultimately, we were not able to capture the strain field the moment before and at the point of delamination.

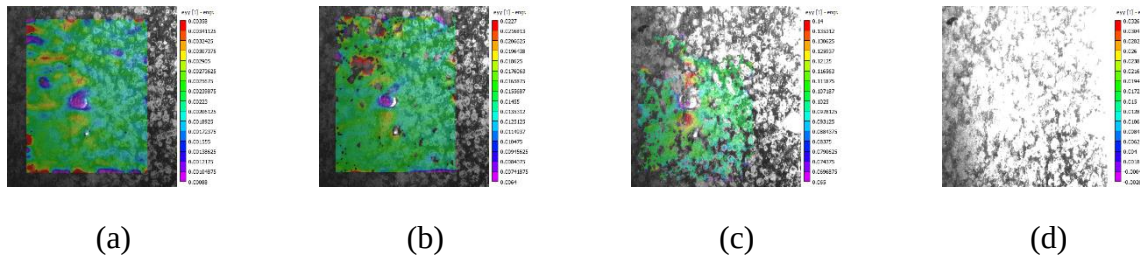


Figure 18. Strain in vertical direction for dogbone with embedded printer toner DIC speckle pattern. Images (a) and (b) show the strain field very early on in the experiment. Images (c) and (d) are subsequent frames much later in the experiment.

Figure 18 shows the DIC results for the dogbone with laser printer toner tracking particles. For this test case, the DIC algorithm generated strain fields very early on in the experiment, but due to lighting issues began to fail as the experiment progressed. Images (a), (b) and (c) were taken within the first 25% of the experiment and image (d) was taken at approximately 75% of the way through the test. We suspect that by adding a diffuser to our light source we will be able to eliminate or minimize this effect.

2.4 Plans for FY19

Research plans for FY19 Mechanical Properties Characterization include:

1. Final Evaluation of Tracking Particles for DIC

This task includes collecting stereoscope images for samples constructed using the remaining speckle pattern materials (powdered sugar, aluminum, polyethylene beads) as well as destructive tension tests with DIC imaging. A down-selection will be made based upon the quality of the DIC results.

2. Full Production of Standard Test Samples

Once the previous task is completed, a full suite of samples will be produced which will allow us to measure the strain field around embedded glass beads of various sizes and correlate the failure strain field to the global stress state.

3. Production of Surface Modified Particle Samples

A set of dogbones will be produced for which the embedded glass beads will have had various surface treatments to alter the work of adhesion. This will provide a means of measuring the sensitivity of the debonding strength to the work of adhesion. The result of this is essentially a correlation between debonding strength and surface chemistry.

4. Collect Statistical Representation of Sample Results

Due to the stochastic nature of sample preparation, a statistically significant number of samples will be produced which will allow us to bound our results with data-based uncertainty quantification.

Overall, this effort will lead to support the overall goal to characterize the relationship between surface energy and interface strength via computational efforts (i.e. parametrized cohesive zone model as a function of surface energy).

3 Modeling and Simulation

3.1 Overview

The goal of this year's effort was to determine appropriate material model parameters to accurately simulate the decohesion of a particle embedded in a matrix material under tensile loading. The initial simulations model a single glass bead embedded in a tensile specimen made of Sylgard 184 silicone. All simulations use the explicit Lagrangian FE code, EPIC. The EPIC code (Elastic Plastic Impact Computations) is a Lagrangian explicit finite element code developed by Dr. G.R. Johnson *et al.*, currently with the Southwest Research Institute.^{29, 30} It takes advantage of the fact that triangular or tetrahedral element formulation is better suited to represent the severe distortions than is the traditional quadrilateral or hexahedral finite difference methods.^{31, 32} However, EPIC does offer both quadrilateral and hexagonal element structures that are suitable for the large but not severe distortions occurring in the tests performed under this study.³³

EPIC has internal mesh generators for a range of simple shapes, but it also allows the user to import a mesh generated externally. The geometries and meshes for this study were generated by Cubit and exported in the EXODUSII format compatible with the EPIC mesh reader.³⁴

An important feature of the EPIC code is the capability to import user models for strength, equation of state (EOS), damage or cohesive interface models. The cohesive interface model is a key element in this study in that the objective is to include surface energy data from Task 1. Using the experimental data from Task 2, the goal is to develop or modify currently available models to capture the experimental behavior.

3.2 Material Modeling

3.2.1 Sylgard 184

Sylgard 184 is a lightly cross-linked, highly flexible isotropic elastomer. It has been widely studied in the literature.

In our review, there is no model that can accurately predict the strength behavior of Sylgard 184 from low to high strain rate. Long and Brown performed the most comprehensive study of Sylgard 184.³⁵ They use the frequency domain master curve of oscillatory shear to parameterize a Universal Polymer Model, which is used as the primary polymer viscoelastic strength model in the Sandia's Sierra Mechanics Simulation suite. The model is validated by comparing the results to cyclic tension and compression tests out to moderate strains of 40% and 20% at room temperature.

Capturing thermodynamic behavior for Sylgard 184, represented in hydrocodes using an equation of state model, is particularly difficult due to lack of simple, static experimental methods for acquiring PVT data for polymer materials at high pressures. Dattlebaum *et al.* uses a novel approach to determining static EOS for polymers using high-pressure diamond-anvil cells coupled with optical microscopy and image analysis.³⁶ The isothermal data was fitted to various empirical equations of state such as 3rd order Birch-Murnaghan, Tait, Vinet and Sun forms. In addition, the static data is converted to shock data and a particle velocity-shock velocity fit is also presented. The fit is shown to match well with experimentally measured shock velocity-particle velocity data presented by Marsh.³⁷

In order to parametrize the traction-separation model chosen for this work, one must properly model the strength behavior of Sylgard 184 within the range of the experiment. Thus, we will first

simplify the analysis to elastic behavior and add more complexity as needed. There can be significant variations between the Sylgard 184 used in these tests when compared to those used by Sandia National Labs. Hence, we intend to calibrate an appropriate model using the data presented in Task 2 and compare it to data presented by Long and Brown.³⁵ The EOS can effectively be ignored in the beginning of the analysis, as there is little evidence that there is large pressure, density, or temperature variation in the dogbone tensile tests presented in Task 2. If this scenario changes, the EOS behavior of Sylgard 184 can readily be taken from literature as shown above.

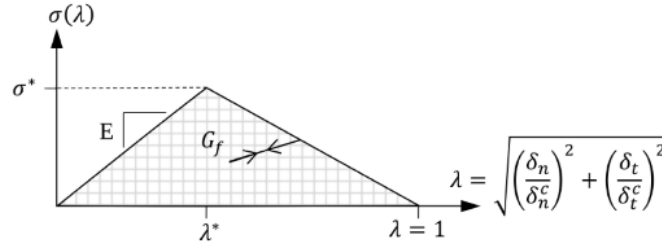
3.2.2 Glass Bead

Deformation of the glass bead is not significant under the conditions tested. This is clearly evident from the preliminary results shown in Task 2. There is not enough stress or strain concentration in the glass bead to incorporate a strength model for the glass bead. Hence, for all simulations the bead is modeled as a rigid body.

3.2.3 Cohesive Model

Cohesive zone element models (CZM) regard damage, in particular fracture, as a continuing phenomenon, where the separation between elements takes place across an extended crack ‘tip’ and is resisted by cohesive tractions. Kregting described these models in detail as part of his report. A brief summary is provided in this report.³⁸ CZM elements describe the cohesive forces that occur when material elements are being pulled apart, and do not represent any physical material. Thus, the CZM elements are placed between continuum elements. When damage growth occurs, these CZM elements open in order to simulate crack initiation or crack growth. Since the crack path can only follow these elements, the direction of crack propagation strongly depends on the presence of CZM elements, implying the crack path is mesh dependent. Therefore, the severity of this problem is reduced as mesh resolution increases. The complexity of CZM models increases in two dimensions, since tractions can occur in normal and shear directions. Traction-separation laws define the description of the failure behavior. These relations describe the tractions as a function of separations and determine the constitutive behavior of cohesive zone models. There are many different types of traction separation laws and they all exhibit similar global behavior. As the cohesive surface separates, the traction first increases until a maximum is reached, and subsequently the traction decreases to zero, which results in complete separation. This holds for both the normal and the shear directions. A schematic example of a traction-separation curve is shown in Figure 19. There are a number of factors that play an important role in the resulting failure behavior. For example, the energy needed for separation is represented by the area under the traction separation curve. The initial stiffness associated with the CZM has a large influence on the overall elastic deformation and should be very high in order to obtain realistic results. It is understood that the form of the traction-separation models plays a significant role in the macroscopic mechanical response of the system. This exponential model by Xu and Needleman provides smooth traction-separation curves and may therefore be more stable than discontinuous models, such as the bilinear model.³⁹

For our problem, the bilinear traction-separation model is used as a first attempt at modeling decohesion of the bead and Sylgard. The parameters will be optimized to reproduce the location and timing of decohesion based on imagery from the tests. The results will provide guidance on the need for more advanced models.



Model parameters include:

$$\rho, \delta_n^c, \delta_t^c, \delta_n^*, \sigma^*$$

Figure 19. Bilinear traction-separation based model

3.3 Computational Mesh

All simulations are carried out in half space with a single plane of symmetry using constant strain tetrahedral elements. But, before proceeding further, a mesh resolution study must be performed. The necessary output variables, such as strain rate and strain field data, should converge for a mesh to be considered valid. This is particularly necessary to make sure the results using cohesive zone model is captured well. Hence, a mesh resolution analysis was conducted using the gage section of the test specimen without the glass bead. A sample mesh resolution analysis is presented in Figure 20. The minimum mesh resolution required to achieve convergence is chosen for further simulations presented here. We plan to perform a similar mesh resolution study in the future with embedded glass bead in the next fiscal year.

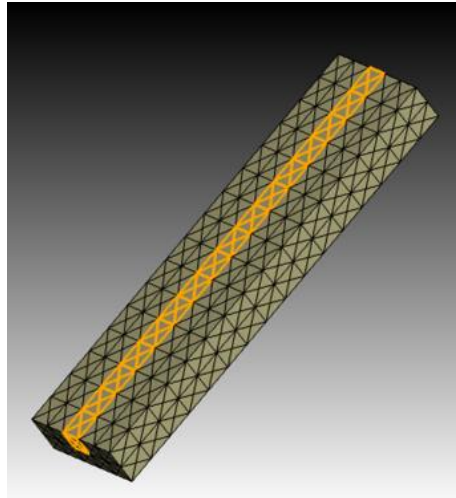


Figure 20. Mesh resolution study

3.4 Simulation Results

3.4.1 Full tensile test simulation

It is important to understand the behavior of Sylgard 184 independently before proceeding further to do the embedded glass bead simulations. It is also essential to match the homogeneous Sylgard

184 tensile simulations to experimental data for accurate modeling validation. Hence, we performed 3-D tensile simulations with only the Sylgard test specimen (no embedded bead) at various loading conditions within the range of experimental apparatus. A sample simulation of homogeneous Sylgard 184 is presented in Figure 22. As mentioned before, the Sylgard model used in these simulations is a simple linear elastic model. While the overall qualitative behavior of the specimen is captured well, a comparison to actual experimental study will be done in the next fiscal year.

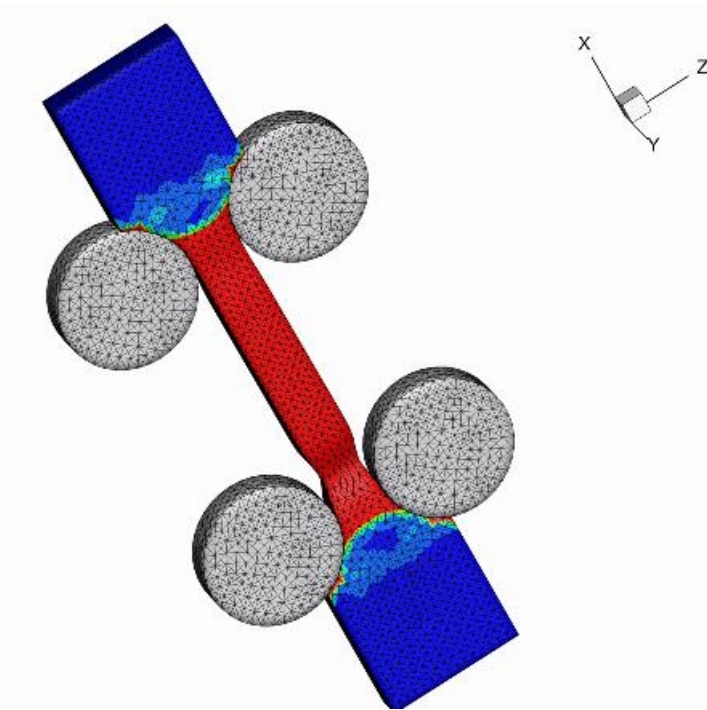


Figure 21. Simulation of Sylgard test specimen

3.4.2 Gage length simulation with embedded bead

Simulations of the gage region with a single glass bead were done with cohesive elements at the interface between the bead and binder. An initial guess for parameters was made based on literature (presented in the sections above) and previous tests results shown in Task 2. These were adjusted until the simulations best matched the test data. The results, Figure 22, show that the simulation is able to capture decohesion of glass bead from the surrounding binder. The tensile rate used in this simulation is arbitrary, as it does not reflect any particular experimental analysis. Once again, we were able to show qualitatively similar behavior between the experiments and simulations. However, there are still several steps that must be performed before a full comparison between experiments and simulations are performed. After finalizing the appropriate material model for Sylgard 184, we hope to iterate on the strain field and decohesion parameters to match the experimental setup. In addition, this method will be extended to various tensile rates and the dependence on tensile rate on decohesion will be shown in future effort. For now, we have established confidence in our methodology and our simulation tools to perform the necessary calculations to match the experimental results.

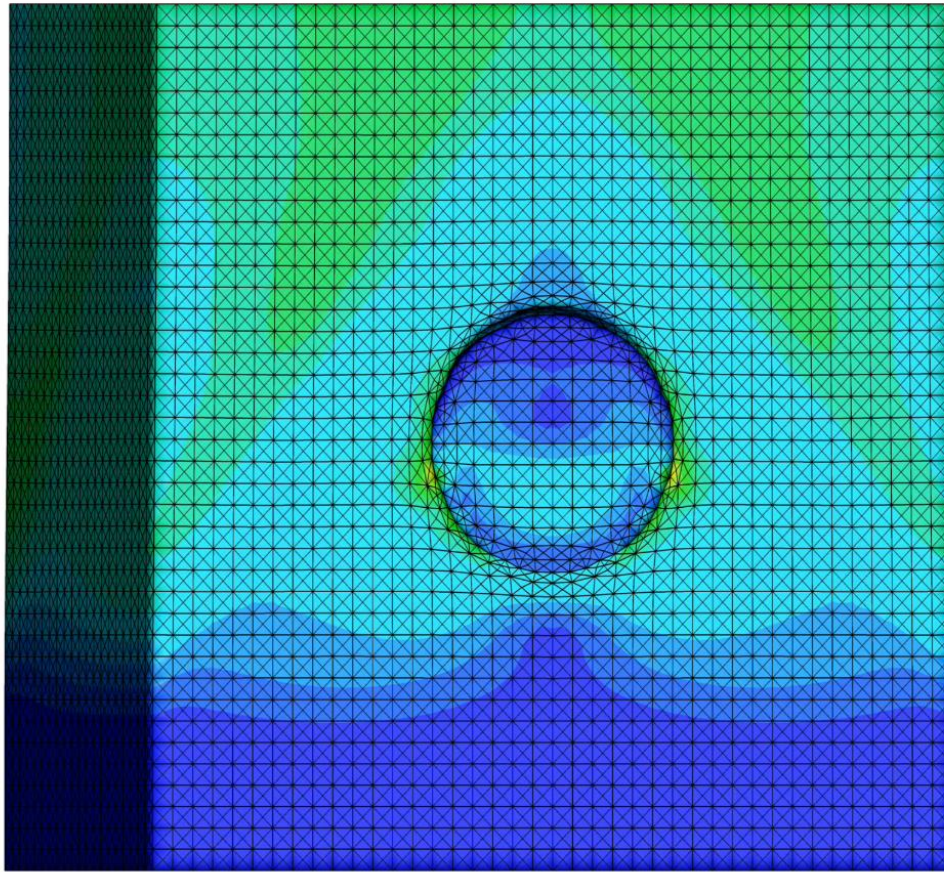


Figure 22. Gage region simulation

3.5 Plans for FY19

Research plans for FY19 modeling and simulation include:

- Compare homogeneous Sylgard 184 tensile data measurements to simulation data
- Finalize material model of Sylgard 184 to match closely with experimental data
- Set up simulations that accurately match the experimental loading/configuration variations included in Task 2
- Generate an iteration procedure that efficiently changes the input parameters to produce simulations results that match the experimental data.
- Correlate cohesive model parameters to surface energy data from Task 1
- Identify updates to the proposed cohesive model based on data from Tasks 1 and 2

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ACRONYMS

CAG	contact angle goniometry
CZM	cohesive zone elements
DIC	digital image correlation
EM	energetic materials
EOS	equation of state
HTPB	hydroxyl-terminated polybutadiene binder
IGC	inverse gas chromatographic
IGC-FC	IGC at finite concentration
IGC-ID	IGC infinite dilution
PDMS	polydimethylsiloxane

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