INTRODUCTION AND BACKGROUND

0.1 Motivation

The main focus of this work, in the broadest sense, is the improvement of the mechanical properties of brittle systems, particularly ceramics. Many ceramic systems have a great deal of potential in numerous industrial applications because of their high thermal and chemical stability. Thermal stability provides such great benefit because it allows for higher engine operating temperatures, which improves engine efficiency and reduces operating costs. This is useful not only in transportation applications, but also in power generation. Even in a well developed country like the United States, 37% of annual energy production still comes from petroleum and another 29% from natural gas, so improving the efficiency of the engines that produce this power would provide significant benefit in terms of cost reduction and output improvement.[1] The chemical stability of ceramics is also a major consideration, as they offer significantly better corrosion resistance than most structural metals and alloys. This corrosion resistance is major benefit, both in the context of operating life as well as cost. The National Association of Corrosion Engineers estimates that the annual global cost of corrosion is around 2.5 trillion US dollars, so any improvements to corrosion resistance that can be made through the implementation of ceramic components would provide significant benefits.[2]

Ceramics offer promising thermal and chemical resilience, but their widespread incorporation into technical applications has long been limited by their mechanical properties, namely a combination of low toughness and high stiffness. Low toughness means that it takes less mechanical energy to propagate a crack through a ceramic than it would through a higher toughness material, such as most metals. This problem is further exacerbated by high stiffness, which means that there is significantly greater elastic energy buildup for a given applied strain. This combination of large energy buildup and poor energy dissipation means that ceramics tend to fail catastrophically and unstably, especially when compared to more ductile metals. This limits not only the potential applications of ceramics, but also the available processing techniques, as conventional shaping techniques like machining cannot easily be used on materials that fracture so readily. Recently however, additional processing techniques have been developed that allow for a greater degree of control over the fabrication of many different materials including ceramics. These processes, now known as additive manufacturing, allow for the fabrication of polymers, metals, and ceramics in a wide array of designs and structures. Because additive manufacturing uses element-by-element construction to produce physical recreations of digital designs, it is possible to create effectively any structure of arbitrary shape. This intersection of brittle systems and additive manufacturing is the focus of this thesis study. The objective of this work is to gain a better understanding of how the design freedom afforded by additive manufacturing might be used to improve the toughness of brittle systems through the implementation of designed composite structures, particularly ones with anisotropic design. Anisotropic design in particular has the potential to produce highly directional toughness behavior that would not be achievable with more traditional composite structures.

0.2 Fundamentals of Brittle Fracture

0.2.1 Griffith Theory

In order to understand the influence of composite structure on fracture properties, it is first critical to understand the fundamentals of fracture, particularly the energetics of fracture. The fundamentals of fracture were first described from an energetic standpoint by A.A. Griffith in 1921.[3] The premise of this work has become the basis of what is now referred to as the Griffith theory of fracture, and it centers on the idea of describing failure of material from the standpoint of thermodynamic equilibrium. In Griffith theory, a continuous, homogeneous, body containing a single crack of length 2C is subject to a far field load, as shown in Figure 0.1.



Figure 0.1: Schematic of the loading configuration used by Griffith to quantify the energetics of fracture.

For this scenario, the total energy in the system U can be broken into a sum of the mechanical energy U_M and the surface energy U_S .

$$U = U_S + U_M \tag{1}$$

The surface energy is the energy associated with the formation of new surfaces due to the formation and propagation of the crack in the body. The mechanical energy is comprised of the elastic energy in the body due to the applied load U_E as well as the energy from the applied load itself U_A .

$$U_{\rm M} = U_{\rm E} + U_{\rm A} \tag{2}$$

A combination of linear elastic fracture mechanics and simple potential energy arguments can readily quantify both U_E and U_A .

$$U_{\rm E} = \frac{1}{2} P \delta \tag{3}$$

$$U_{A} = -P\delta \tag{4}$$

$$U_{\rm A} = -2U_{\rm E} \tag{5}$$

Here, P is the applied far-field load, and δ is the displacement of the body as it deforms due to the applied load. From this point, an application of the Inglis solution for the stress and strain fields in the volume elements around the crack, and integration over the body extending well beyond the crack can produce the following solution for U_M.[4]

$$U_{\rm M} = \frac{-\pi C^2 \sigma^2}{E'} \tag{6}$$

In this solution, C is the half length of the crack, σ is the far field applied stress, and E' is E for the plane stress condition and E/(1 - v) for the plane strain condition, where E is the elastic modulus of the solid body and v is Poisson's ratio.[5]

In this same manner, the surface energy can also be quantified in terms of material and geometric parameters, though in this case the quantification is more straightforward. For a body of unit width, the energy due to surface formation U_S can be described using the following equation

$$U_{\rm S} = 2(2C\gamma) = 4C\gamma \tag{7}$$

where γ is the free energy of surface formation for the solid body. Reincorporating these into Equation 1 produces a complete description of the energy in the system.[5, 6]

$$U = 4C\gamma - \frac{\pi C^2 \sigma^2}{E'}$$
(8)

Finally, once the energy of the system has been described, the condition for equilibrium is set as $\frac{dU}{dC} = 0$. Differentiating and solving describes the stress at which propagation occurs in terms of the system geometry and properties of the body. This formulation became the basis off which fracture mechanics and the concept of fracture toughness were established.

0.2.2 Stress Intensity Factor

Griffith's description fracture toughness provides a good starting point for homogeneous, isotropic, uniform solids, but it is far from a complete description of the mechanisms of failure within a solid. An alternate description involves the concept of stress intensity factors, which are material prefactors in the stress functions that satisfy the bi-harmonic equation, which is a fourth order differential equation that accounts for the equilibrium conditions of failure, the constraints of Hooke's law, and strain compatibility.[5, 7, 8] These stress intensity factors, which have units of MPa \sqrt{m} , not only depend on the material being fractured, but also the loading conditions under which it failing. There are three different types of loading behavior that are labeled Mode I, Mode II, and Mode III. Mode I is in-plane opening, Mode II is in-plane shear, and Mode III is out-of-plane shear. Diagrams of each of these modes are shown in Figure 0.2



Figure 0.2: Schematics of the possible loading modes for failure by fracture.

Using this nomenclature, the stress field around a crack under far field loading can be described using the form[5]

$$\sigma = \frac{K_{\rm M}}{(2\pi r)^{\frac{1}{2}}} f(\theta) \tag{9}$$

where K_M is the stress intensity factor in Mode M, with M being either I, II, or III, r is the distance from the crack tip, and $f(\theta)$ is a directional cosine function that changes depending on the stress state and coordinate system. This stress intensity factor is not only used to describe the stress state around a crack, but it is also a good method of establishing criteria for material failure. When a far field load is applied, the stress intensity factor increases, and when it exceeds some critical stress intensity factor K_C , the material will fail. This critical stress intensity factor is often referred to as fracture toughness, and it is both mode dependent, and is considered to be a property of the material system. The lowest toughness failure mode is Mode I, so K_{IC} is often used as a reference for the toughness of the material. Quantitatively, fracture toughness magnitudes give a fairly clear picture of why ceramics and other brittle systems are not as mechanically robust as many metal systems. The fracture toughness of a typical ceramic is in the range of 1-10 MPa \sqrt{m} , whereas the toughness of most ductile metals is in range of hundreds of MPa \sqrt{m} .

0.2.3 Nonlinear Behavior

Even with stress intensity factors, however, the description of behavior around the very tip of the crack is not straightforward to describe. This becomes apparent if one considers the form of Equation 9. Regardless of the value of $f(\theta)$, the magnitude of the stress rises to an infinite singularity at the tip of the crack as r approaches 0. This singularity is not a true physical singularity, but rather arises from the fact that the Irwin stress function solutions rely on linear elastic fracture mechanics, and the tip of the crack behaves nonlinearly. This nonlinearity has been addressed in different ways depending on the nature of the material being fractured. The most common approaches to addressing this are the Dugdale model and the Barenblatt model. The Dugdale model, which is most commonly used for metals and ductile systems, describes the region around the tip of the crack as a yield zone containing significant plastic deformation.[9] The Barenblatt model, which is used more commonly to describe ceramics, treats the region near the crack tip as a region of stretched atomic bonds spanning a few nanometers, and these stretched bonds apply a compressive force that slightly closes the tip of the crack, changing its shape.[10] The difference between these two models further emphasizes the disparity in toughness between metals and ceramics, as the energy dissipation from plastic formation is significantly larger than that from the separation of bonds in the cohesive zone, which further elaborates why ductile metals tend to be significantly tougher than ceramics and why additional methods of toughening ceramics through composite structures are so desirable.

0.2.4 J-Integral

To more completely describe the energetics of fracture in a manner that can account for both the linear elastic behavior further from the crack tip as well as the nonlinear behavior closer to the tip of the crack, J. Rice developed an integration method for evaluation of toughness from an energetic standpoint.[11] This integral, known as the J-integral, does not describe fracture toughness in the manner previously discussed, but rather describes the release rate of mechanical energy in the system due to propagation of the crack. The J-integral is shown the equation[5, 11]

$$J = -\frac{dU_M}{dC} = \int \mathcal{U}dy - \overline{T} \bullet \left(\frac{d\overline{u}}{dx}\right) ds$$
(10)

where \mathcal{U} is the strain energy density, y is direction of the far field load, \overline{T} is the traction vector on the curve defined in relation to the outward normal vector, \overline{u} is the displacement vector, x is the direction of crack growth, and s is the contour around the crack. Although the faces of the crack itself are traction free, the value of the



Figure 0.3: Schematic of J-integral contour around the crack tip.

J-integral with respect to the nonlinearity of the crack tip depends on the region of the solid body over which the contour is taking with respect to the tip of the crack. If the J-integral contour is taken in the near vicinity of the crack tip, it will capture the influence of the cohesion zone or plasticity zone, depending on the material system.[5] In this way, the J-integral is able to capture either the linear or nonlinear behavior of the crack, depending on its location. This contour integral can also be manipulated algebraically to create an area integral, with the only additional constraint being that the integral must be over a domain with a Lipschitz boundary.[11] As previously mentioned, this J-integral provides an energetic description of toughness, but relationships again developed by Irwin can relate this energetic description to the critical stress intensity factors previously discussed.[7]

$$J = \mathcal{G}_{C} = \frac{\left(K_{C}\right)^{2}}{E'}$$
(11)

Here, E' is E for the plane stress condition and E/(1 - v) for the plane strain condition. With the use of this J-integral, a complete description of toughness can be obtained for any brittle system, even those with heterogeneous composite structures.

0.3 Composite Toughening Mechanisms for Brittle Solids

With clearly establish methods for measuring and describing the toughness of a material or composite system, it is important to understand how that toughness can be affected and increased, especially for brittle systems. In the context of microstructure, toughening mechanisms can be broken into two groups: those that toughen by changing the direction or geometry of the crack, and those that toughen by shielding the crack through interactions either in front of the crack tip or in the crack wake.[5]

0.3.1 Toughening by Crack Deflection

Geometric toughening effects can come in several forms, but one of the most common forms is found in the fracture of brittle polycrystalline materials. Because grain boundaries have higher energies that vary based on the orientation mismatch of the grains on either side of the boundary, it is often energetically favorable for a crack to travel at different angles along grain boundaries to take advantage of these higher energy domains. The result of this is that, depending on the orientation of loading, the crack may either twist out-of-plane or deflect in-plane to fracture in the most energetically favorable manner based on the arrangement of crystals in the material. This effect has been seen in numerous crystalline ceramics materials as including structural ceramics such as alumina.[5, 12] The influence of higher energy domains can be seen not only at grain boundaries, but also at the interfaces between dissimilar materials. When a crack arrives at the interface between dissimilar materials, if the interface is low enough toughness compared to the homogeneous materials on either side, it can often be favorable for the crack to propagate along the interface instead of travelling directly through into the second material.[13]

Geometric toughening can also manifest in composite structures with inclusions or dispersoids scattered in them. When a second phase of inclusions or heterogneities is present in a material, cracks can sometimes be forced to travel around these inclusions in order to continue propagation, depending on the residual stress state and the relative stiffness and toughness of the matrix with respect to the inclusion. The shape and aspect ratio of these inclusions can have an influence on the extent to which the crack is deflected. The influence of inclusion shape and arrangement on the tilt and twist deflection behavior of a crack was explored for several common inclusion geometries by Faber and Evans.[14] The investigation explored how the aspect ratio, angle of orientation, and spacing of plates, rods, and spherical particles could influence the magnitude of the tilt and twist deflection shape, spacing,

and aspect ratio, the presence of residual stresses can also influence crack behavior. One of the earliest and clearest demonstrations of this was by Davidge and Green, who dispersed thoria spheres into melts of glasses with different thermal expansion coefficients.[15] As a result, when the glasses cooled, the residual stress fields around the thoria spheres would vary depending on the coefficient of thermal expansion of the glass with respect to the thoria. If the glass had a lower coefficient of thermal expansion than the thoria, the thoria spheres would have tensile residual stresses, and the crack would be attracted to the spheres, but if the glass had a higher coefficient of thermal expansion than the thoria, the spheres would be in compression, and the crack would deflect around the spheres instead.[15]

0.3.2 Toughening by Crack Shielding or Bridging

Going beyond geometric effects that influence crack path direction, composite systems can also be toughened by mechanisms that shield the crack and prevent propagation by either creating stress relief or a compressive closing force ahead of the crack tip or in the crack wake. These shielding mechanisms come in many different forms, and many of them involve composite structures with either multiple phases or non-homogeneous microstructure in the environment around the tip of the crack. The most common mechanisms for shielding in front of the crack tip are microcrack cloud formation, phase transformation, and the presence of a ductile or compliant second phase. [5] Microcrack clouds provide toughening by forming a dilation zone in front of the crack tip that increases compliance and reduces the overall stress available in front of the crack to drive propagation forward.[16] The most common form of phase transformation shielding is in zirconia-based systems, originally developed by Garvie et al., where a stabilizing agent, which is usually an oxide ceramic such as yttria, ceria, or magnesia, can help produce a metastable tetragonal phase that changes to monoclinic phase when exposed to the the stress fields created by crack propagation. [17] This phase change also creates an increase in volume, which produces compressive stresses that push the crack tip closed, making propagation more difficult.

Toughening of ceramics can be achieved not only through interactions with the crack tip, but also by bridging the crack interface in the wake of propagation, which prevents the crack from opening further and slows growth.[5] This type of interface bridging technique can be achieved with whisker reinforcement, fiber reinforcement, or even with frictional effects from grains that bridge the crack interface. Many particle and fiber reinforced composites achieve higher toughness through this interface bridging

mechanism. However, for many brittle fiber reinforced composites, the presence of fibers alone is not sufficient to see toughness improvement, but rather the interface between the fibers and matrix must be carefully designed to maximize toughening. If the fiber and matrix are too strongly bonded, the crack will simply fracture the fiber in the same manner as the matrix, and propagation will be relatively unhindered. Similarly, if the bonding between the matrix and fiber is too weak, the fiber will be readily debonded and pulled from the matrix, again providing little resistance to the propagating crack. However, if the interface is chosen to be sufficiently weak to allow for some debonding, but sufficiently strong to prevent complete pullout, the crack will deflect when it encounters the fiber, causing debonding, but then the fiber will ultimately have to be ruptured and pulled out in order for propagation to continue. This combination of debonding followed by rupture and pullout produces significantly higher toughening, especially in brittle systems with fiber reinforcement. The role of this carefully balanced interface on fiber mechanical response was first explored in detail by Marshall et al., and it is the reason that fiber compositions in ceramic composite systems must be carefully chosen, even though the introduction of fibers into a matrix is relatively straightforward.[18]

0.3.3 Limitations of Conventional Composite Toughening Space

All of the toughening mechanisms that have been discussed thus far have been explored in great detail across numerous material systems and have provided a great deal of toughness improvement for different technical ceramics. However, almost all of them share one common limitation, and it is not a material limitation, but rather a processing one. Almost all of the toughening mechanisms established rely on a combination of traditional ceramic and glass processing techniques and thermodynamics to achieve higher toughening. Polycrystalline interactions are controlled by the size and shape of grains, which are limited by the crystal structure and processing parameters during sintering or ceramic formation. Dispersoids and secondary phase particles are dispersed randomly throughout the any matrix in which they are used, because they must be added either directly into a glass melt or via an intermixing of particles before sintering. Additionally, the shapes of different dispersoids and second phase particles is limited by crystal structure and available processing techniques, which is why most dispersoids are relatively simple shapes like spheres, plates, and rods. These limitations of randomly dispersed particles and phases whose structure is governed by crystallization or solidification thermodynamics means that the composite space is relatively constrained from the

standpoint of design. On one hand, this random dispersion can be convenient. For example, the description of volume fraction of secondary phase is only meaningful when the secondary phase is randomly and uniformly distributed throughout the matrix such that the structure is effectively homogeneous. On the other hand, this is also a significant limitation because it represents an overall lack of complete processing control. Beyond uniform microstructural changes, the design of composite systems cannot be readily tailored for specific purpose. The one exception to this is fiber reinforcement, where, if the fibers are laid manually, different weave patterns can be achieved for different orientations, but even in this case, manual laying of fibers is time consuming, and the precise positions of individual fibers still cannot be readily controlled. In general, what this means is that most conventional composite theory has been built around these processing limitations, so once new processing methods are introduced, new design space becomes accessible.

0.4 Improved Processing Control Through Additive Manufacturing

On of the most promising ways that the processing space for brittle composites can be expanded is through the implementation of additive manufacturing. Traditional manufacturing techniques where a component is shaped, cut, or machined from a larger section of material would be classified as reductive manufacturing. In additive manufacturing however, each component is assembled from smaller portions of material that are combined into the exact shape of the desired part. This not only reduces waste, but allows for significantly more complex designs than traditional manufacturing would permit.

0.4.1 3D Printing

One of the most prevalent and widely used subsets of additive manufacturing is the field of 3D printing. Printing, in this case, is used to describe the deposition of material in a pattern dictated by a digital design. The nature of this deposition can vary widely depending on the material and process being used. The most common forms of 3D printing are direct ink writing, binder jetting, direct laser melting, selective laser sintering, and stereolithography. Direct ink writing is exactly as its name describes, where the ink material is extruded through a nozzle and written into the desired shape based on a digital design. This is most commonly done with low melting point plastics, but can also be done with preceramic polymers, ceramic slurries, and even living cellular material.[19, 20] The biggest limitations of this technique are that it demands careful rheological control of inks to ensure extruded

materials are stiff once they leave the nozzle, and the surface quality of parts formed by extrusion is dictated by the size and shape of the nozzle. Binder jetting, though less common, is similar in principle to direct ink writing. However, instead the material itself being extruded through a nozzle, the material, typically powder, is deposited layer by layer onto a bed, and binder is extruded through the nozzle to hold the powder together in select regions, forming the desired component.

Direct laser melting, also called direct metal laser sintering, is a layer-by-layer powder deposition technique similar to binder jetting, but it is typically done only with metal powders. Instead of gluing these powders together with binder, a high energy laser is used to heat up and locally melt the metal powders to form them into a single solid part.[21] With this technique, it is challenging both to avoid directionally dependent properties due to laser orientation as well as to achieve densities comparable to those seen in forged metals, but recently it has attracted great interest for its potential with nickel superalloys used in complex turbine components for aerospace and energy applications.[22] Selective laser sintering is similar in function to direct laser melting, but instead of using metal powders, it typically uses ceramic powders. The limitations of selective laser sintering are also very similar to those of direct laser melting, in that it is difficult to achieve ceramic densities comparable to those gotten with traditional powder sintering techniques.

Stereolithography The final 3D printing technique to be discussed is stereolithography, which is of particular focus because of its versatility and applicability to the materials investigated in this work. Stereolithography is a 3D printing technique that uses ultraviolet (UV) light to polymerize material in specific regions based on a pattern dictated by a digital design. In the case of laser stereolithography or two-photon polymerization, the UV light is introduced through a laser, and in the case of digital light processing, the UV light it introduced through a projector. Regardless, of the exposure method used, light-based techniques offer high resolution across multiple length scales because they can take advantage of precise and well-controlled optical techniques originally developed for lithography patterning of silicon microdevices.[23] For this reason, components fabricated with stereolithography typically have good surface quality and feature resolution.

In addition to the optics, the material chemistry used in stereolithography is also based off systems originally developed for the patterning of silicon. Many of the earliest resins developed for stereolithography rely on acrylate polymer chemistry to form solids under UV light, similar to many of the photoresists used in traditional lithography patterning.[23] This acrylate polymerization is actually free radical polymerization, similar to that seen in many catalyst driven polymerization processes, but here the source of the free radical is a photoinitiatior that reacts with UV light of a certain wavelength range to produce free radicals. These radicals attack the acrylic endgroups of the multifunctional acrylate polymers present in the resin, causing them to polymerize into a cross-linked network. In the case of resins used in stereolithography, a photoinhibitor is also added to absorb either excess UV light or excess free radicals, depending on the polymer system being used. Finally, many resins also incorporate a compound for scavenging excess oxygen, which is known to inhibit polymerization.

Although acrylate chemistry is the basis for many of the resins used in stereolithography, it can also be used as a fabrication method for many other material systems. Through either functionalization or the incorporation of polymers with acrylate side chains, stereolithography can be used to directly fabricate components made of preceramic polymer, which can be converted into ceramics through pyrolysis, although shrinkage and the effects of volatilization of organics must be considered.[24–26] Additionally, ceramic particles can be dispersed into acrylate polymer systems at relatively high concentrations and then used for printing, with the acrylate polymers acting as a binder to hold the powders in place.[27] The challenges that arise with this approach are that the introduction of ceramic powders changes the photosensitivity and cure depth of the acrylate resin, and burnout and sintering must be carefully performed to properly remove all unwanted binder phase.[28–32] Ceramic structures can also be achieved with stereolithography by more indirect means. For example, acrylate polymer structures produced using two photon have been used as scaffolds for the fabrication of truss structures composed of alumina formed through atomic layer deposition.[33] All of these examples clearly show the potential of UV polymerization through stereolithography as a new processing method for the precision fabrication of brittle composite structures, both in acrylate polymers as well as in ceramics.

0.5 New Toughening Methods Through Improved Processing

The significant improvements to additive manufacturing in recent years have greatly expanded the available design space for brittle composite systems by introducing a degree of control that was not previously available. Instead of having to rely on random dispersions of heterogeneities or toughening phases, it is now possible to control both the structure and position of inclusions or toughening phases. This change may seem subtle, but it is surprisingly disruptive as characterization of inclusions can no longer be driven by topology, as inclusions are no longer constrained to topological groups like spheres, plates, and rods. For this reason, different approaches need to be taken to understand how this new processing control can be fully utilized to create tougher composite materials.

Some attempts have been made to better explore the possibilities available for improving toughness through composite design with additive manufacturing, but these have been somewhat limited due to both the vastness of the design space as well as the challenges associated with properly describing brittle fracture of composite systems. From a numerical standpoint, attempts have been made to use tools like machine learning on voxel-based systems to maximize the toughness of a composite system around a known crack location.[34] However, these types of studies are somewhat limited because they fix the location of the crack in space and do not consider how the trajectory of crack propagation will change as the structure of the composite changes. In general, fracture analysis that considers the full trajectory of the crack is relatively challenging because considering all possible crack paths is very numerically intensive and the constantly changing boundary conditions due to the discontinuity created by the crack means that the system must be fully re-evaluated at every propagation step. To address this, variational approaches have been used to which treat the crack as phase field, which is then constrained to behave similarly to a discontinuity in the material.[35–37] This approach of treating the crack as a damage phase greatly reduces the computational load required to analyze fracture, and makes it much easier to analyze brittle failure in more complex structures. This variational phase field model has been used as a basis for several different fracture analyses, which have shown that composite toughness can be improved through both elastic contrast as well as toughness contrast, and that the shape and arrangement of inclusions in a structure can be chosen to dramatically minimize the volume fraction of inclusion phase needed to achieve comparable or greater toughening than could be achieved through conventional composite processing.[38–40] Despite these promising numerical analyses, experimental verification of these potential toughening mechanisms is relatively limited. The influence of material contrast in 3D printed layered structures has been demonstrated both in the context of toughening due to the presence of elastic contrast as well as the influence of this elastic contrast and layer orientation on the renucleation and propagation of the crack through the structure.[41, 42] Beyond these studies, little has been done to investigate the effect of designed composite structure on fracture behavior in additive manufactured material systems in the context of inclusion arrangement, design, or anisotropy.

0.6 Objective

The objective of this work is to gain a better understanding of how the design freedom afforded by additive manufacturing might be better utilized to achieve higher toughness brittle composites. This work will focus on how designed structures can affect fracture behavior, what kind of material contrast is needed to achieve higher toughness, and how anisotropic structures might be used to improve toughness beyond what is possible with conventional processing techniques. This investigation will begin by using brittle photopolymers to explore the mechanisms that govern fracture in these designed composites. Chapter 2 will focus on how inclusion structures, both isotropic and anisotropic, can be used to affect the propagation behavior of a crack by means of elastic modulus contrast. Chapter 3 will extend this exploration of brittle polymers to consider how anisotropic structure can influence both crack nucleation and propagation in structures referred to as "fracture diodes". The investigation then transitions into how similar toughening techniques might be implemented in ceramic systems, where achieving high toughness behavior is much more challenging. Chapter 4 explores the potential of heterogeneous structure in a model layered ceramic system, muscovite mica. Finally, Chapter 5 completes the extension into additively manufactured ceramics by exploring the effect of different truss structure elements on the failure mechanics of ceramics produced from preceramic polymer. Overall, the findings from this study will help inform composite design of brittle systems of different failure scenarios, which will further expand the available methods for the fabrication of tougher ceramic systems for numerous technical applications.

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