

Fabrication and Mechanical Characterization of Nano-architected Composites Across Scales and Strain Rates

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Kevin Hiroshi Keesun Nakahara

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Kevin Hiroshi Keesun Nakahara
ORCID: 0009-0003-1901-6176

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ABSTRACT

Transportation, infrastructure, personnel protection, and all other applications requiring dynamic impact resistance drive the demand to develop advanced manufacturing for structural materials that are simultaneously lightweight and superior at energy absorption. Polymer matrix composites (PMCs) are widely used in mechanical applications due to their high strength-to-weight ratios, high stiffness-to-weight ratios, corrosion resistance, and design flexibility. However, these composites often suffer from matrix and interfacially driven failure mechanisms under dynamic compression. Nano-architected materials are an emergent class of metamaterials capable of achieving high-stiffnesses and strengths while also exhibiting high specific energy absorptions under micro particle impacts. Most studies of nano-architected materials focus on periodic lattices geometries or other cellular solids while their use as reinforcements in composites, especially at large-scales, remains limited. Combining the works of nano-architected metamaterials and PMCs, we create nano-architected composites possessing high mechanical energy absorptions under dynamic compression without the need for dense constituent reinforcement materials.

We first explore how nano-architected materials are fabricated at large-scales, and we demonstrate how they can be incorporated with epoxy polymer matrices to create nano-architected composites using molding methods. Subsequently, we characterize these nano-architected composites, showing how changing fabrication parameters can produce various configurations of nano-architecture within samples, and how fabrication limitations can result in defects at multiple scales. Through various quasi-static and dynamic testing methods, we study how nano-architectures deform, fail, and contribute to composite performance — decoupling their effects from defects. Our study shows that while composite performance can be mitigated by defects, increasing the amount of nano-architectures present in composites leads to higher strengths and delayed catastrophic failure. In-situ observations of these tests allow us to directly connect deformation and failure mechanisms to enhanced stress-strain performance. We then use phenomenological modeling to relate mechanical performances across loading rates showing high nano-architected rate sensitivities and verifying the role of nano-architectures in delaying catastrophic failure. Nano-architected performance is compared against classical PMCs reported in literature

demonstrating their high energy absorptions and unique capability to address shortcomings of fiber- and particle-reinforced composites.

Our nano-architected composites offer a new way to toughen polymer matrix composites, utilizing small scale architectures rather than changes to constituent material composition to delay catastrophic failures. These nano-architected composites are a unique demonstration of the capabilities of nano-architectures to perform under high rates, loads, and energies, paving the route to new possibilities for composite design. Our modeling work of nano-architected composite performance shows the potential of these materials to absorb energies through the introduction and control of nano-architected structures.

PUBLISHED CONTENT AND CONTRIBUTIONS

- [1] M. Kagias, T.T. Tran, K. Toniolo P. Nakahara, N.W. Phillips, and J.R. Greer. “Elucidating energy absorption and morphology relationships in scalable nanoarchitected metamaterials with X-ray nano-ptychography and digital twins.” *In Preparation* (2026).
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NOMENCLATURE

IPC. Interpenetrating Phase Composite.

LIL. Laser Interference Lithography.

nIPC. Nano-architected Interpenetrating Phase Composite.

nLPC. Nano-architected Layered Phase Composite.

nTile. Nano-architected Tile.

PMC. Polymer Matrix Composite.

SHPB. Split-Hopkinson Pressure Bar.

Thick nIPC. Thickened Nano-architected Interpenetrating Phase Composite.

Chapter 1

BACKGROUND AND INTRODUCTION

1.1 Background

1.1.1 Classical Polymer-Matrix Composites

Engineering composites are widely used across industries in demanding structural applications due to their ability to achieve combinations of mechanical properties that are unattainable in monolithic materials. While the idea of combining two materials together to attain superior mechanical properties is not new, with early examples being Roman concrete (cement and rocks) or wattle and daub (clay and natural fibers), engineering composites remain as one of the most widely used classes of materials in modern applications because of their adaptable mechanical properties determined by constituent material selection and arrangement [32]. As modern transportation methods increasingly seek structural materials that are lightweight and therefore more energy efficient, metallic structural materials are being increasingly replaced with composites. Generally, engineering composites are comprised of two or more phases of material categorized as either a reinforcement or matrix - reinforcements are typically discrete collections of fibers or particles, shown in fig. 1.1, that are meant to provide load bearing capacity while matrix materials protect and bind reinforcements together transferring stress among discrete reinforcing elements [71]. Since the mechanical properties of engineering composites can vary drastically based upon its constituent material selection, the classification of composites is divided based upon matrix material, reinforcement material, and reinforcement shape [23]. Compared against metal- and ceramic-matrix composites, polymer matrix composites (PMCs) represent the most extensively utilized class due to their low density, ease of processing, low cost, and relatively high stiffnesses and strengths [63]. In PMCs, a polymeric matrix — commonly epoxy, polyester, or vinyl ester — binds together reinforcing phases such as carbon, silica, or clay fibers or particles — typically these reinforcements are several orders of magnitude stiffer and stronger than the surrounding polymer matrix [54, 121]. By simply controlling the ratio of reinforcing and matrix materials, engineers can obtain effective stiffnesses and strengths ranging anywhere between the two constituent material properties, highlighting the inherent flexibility of composite systems to tailor mechanical response across a broad design space [57].

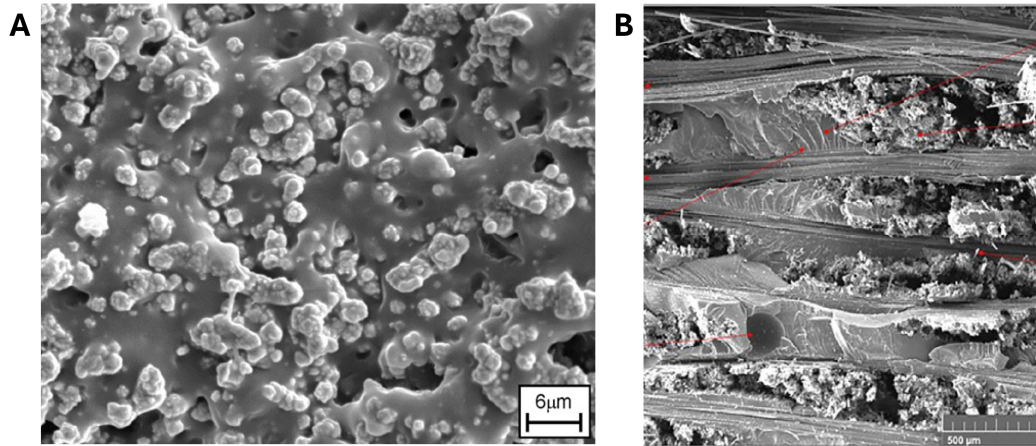


Figure 1.1: Classical polymer matrix composites used across engineering applications like transportation. A) Silicone–Ni type 123 QTC nano-particle composite, reproduced with permission from: [17]. B) Carbon/epoxy plain weave fiber composite, reproduced with permission from: [99].

While estimates of composite properties can be made by taking a rule of mixtures combination of constituent material properties, coupling between these composited phases has been shown to enhance composite stiffness and strength beyond rule of mixtures estimations [23, 32]. To account for coupled effects between matrix and reinforcement phases, rule of mixtures approaches have been further decomposed to incorporate interphase regions which capture enhancements due to coupling at the interface between composited material phases [74]. Further refinements to rule of mixtures approaches can also be achieved to provide less conservative estimations, like the Hashin-Shtrikman bounds [72], of expected composite properties by incorporating more information from constituent material performances - shear modulus in addition to elastic modulus. Additionally, incorporation of reinforcement geometries to rule of mixtures estimations, as shown by Halpin-Tsai [70], can be used to further refine estimations of expected composite properties. These rule of mixtures approaches have been investigated under both elastic [32] and plastic assumptions [49, 107] of deformation demonstrating the utility of this approach for predicting composites performance based upon the underlying constituents.

Despite the advantages afforded by composite materials, the mechanical performance of PMCs is highly dependent on loading mode, with significant differences observed between tensile and compressive behavior [32]. Under tensile loading in fiber composites, deformation is typically reinforcement-dominated, failing through fiber fracture [4] or pull-out [115]. In contrast, compressive loading activates and

combination of matrix-, fiber-, and interfacial-dominated deformation mechanisms, including shear yielding [39], fiber kinking [19], and interfacial instability [61], often resulting in low compressive strengths relative to tension. While fiber composites offer advantages in tension, like crack bridging [10], particle based composites offer advantages in compression, such as reinforcement stability and improved load transfer to the matrix [59]. Despite these advantages, particle-reinforced composites can suffer from matrix cracking [142], particle-matrix debonding [108], void formation and growth [124], particle-induced stress concentrations [92], or matrix shear banding [137]. Additionally, particle-reinforced composites can have too much reinforcement material causing particle agglomeration, which can lead to premature yielding and cracking [59]. Within PMCs, there is an opportunity to enhance compressive performance and increase reinforcement content by replacing fiber- or particle-based systems with other types of reinforcements.

In addition to the differences between tensile and compressive performance in PMCs, loading rates also influence mechanical performance and failure. Quasi-static composite performance has been widely investigated across different material systems, loading conditions, and reinforcement configurations leading to their adoption as structural materials in industries like infrastructure and aerospace [23, 32, 57, 59, 71]. Furthermore, fiber composites are frequently used as lightweight impact energy absorbers in applications from transportation to ballistics. Despite their widespread use, PMC design for dynamic compressive energy absorption remains an active area of research [21, 63, 76, 99]. In these dynamic loading conditions, the matrix largely governs rate-dependent behavior, while the reinforcement phase constrains deformation and enhances stiffness. Consequently, under high-rate loading, fiber-reinforced PMCs often suffer from failures governed through shear lag [18, 63, 95, 96, 119], delamination [21, 109, 113, 158], debonding [63, 95, 119, 145], or matrix cracking [66, 76, 110, 129]. These failure mechanisms mitigate the ability of PMCs to absorb energy under dynamic loading often resulting in low failure strains and sharp drops in loading curves indicative of catastrophic failure. Explicitly designing PMCs for dynamic compressive energy absorption requires consideration of rate-sensitive underlying deformation mechanisms and utilization of reinforcements which suppress catastrophic failures while supporting high loads.

To overcome these challenges, there is growing interest in incorporating architected materials as reinforcements within composite systems. In the following sections

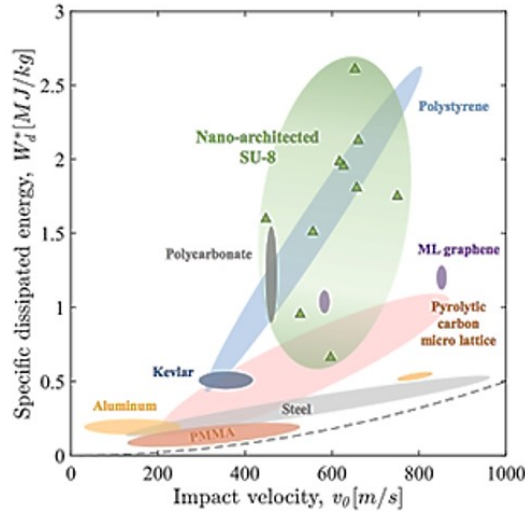


Figure 1.2: High specific energy absorptions in nano-architected polymer lattices under micro-particle impact. Reproduced with permission from: [82].

we will discuss nano-architected materials and how they can be incorporated into composite systems to achieve enhanced mechanical performance.

1.1.2 Nano-architected Materials

Additive manufacturing methods have made it possible to easily fabricate a variety of free standing structures with interconnected elements of arbitrary constructions [89]; these can be periodic lattice structures, stochastic networks, or a balance of ordered and random components [67]. Advances in additive manufacturing technologies have enabled the creation of a new class of materials known as nano-architected materials [141]. Unlike conventional materials, nano-architected materials derive their properties, like high specific strengths [155] and high specific energy absorptions [117], through deformation of interconnected three-dimensional free-standing structures at the nano-scale. Notably, carbon nano-architected materials have shown strengths which approach theoretical maximums set by diamond and graphene [155]. Due to their tremendous standalone properties, nano-architected materials are suitable candidates for use as reinforcements in composite systems.

Over the past decade of research in nano-architected materials, significant effort has been dedicated towards studying the relationship between different unit cell geometries and their resulting mechanical properties [65, 89, 126]. While various levels of stochasticity have been investigated [67], the vast majority of these works have centered around well ordered 3-D space filling beam- or shell- based periodic lattice structures characterized by their unit cell types — octet, kagome, diamond,

kelvin, etc [89]. Canonically, rod-based unit cells are classified as either bending- or stretching- dominated based upon Maxwell's criterion [43] or distinguished by stress-strain performance [89]. More broadly speaking, this delineation refers to how the nano-architected elements carry load, axially (stretching) or flexure (bending). Shell based architectures, on the other hand have been shown to mitigate bending and improve stiffness through improved load redistribution [13, 136] but are susceptible to stress concentrations at junctions resulting in material failures [47, 135]. In both rod- and shell-based architectures symmetry-breaking defects such as strut/wall waviness, varying cross-section, and offset nodes can mitigate the beneficial properties of these systems [97, 103, 135]. More stochastic systems like nano-porous foams [16] and nanolabyrinthine materials [118] or natural cellular materials like bone [98] have been demonstrated to be both resilient to defects and tough. Other tough architectures in nature like nacre and wood have sophisticated hierarchical structures characterized as brick-and-mortar or lamellar arrangements which also do not possess strictly ordered and periodic architectures [106]. These architectures, rather than highly ordered ones, are natural candidates to create high energy absorbing nano-architected composites.

Nano-architected materials are typically fabricated using two-photon lithography [77] which allows control over geometric features with dimensions in the sub-micron range. While these methods demonstrate a facile approach to fabricating these nano-architected materials, the face tradeoffs between feature resolution and overall volume throughput [77]. In recent years, significant efforts have been dedicated to scaling nano-architected material fabrication to high volumes through a variety of approaches like holographic lithography [7, 82], metalens enabled nanolithography [68], multi-photon multi-focus printing [127], and self-assembly [38]. In particular, holographic lithography approaches [82] produce polymeric brick-and-mortar like nano-architectures which exhibit high-specific energy absorptions under dynamic micro-particle impact, fig. 1.2. Under impact, these brick-and-mortar like nano-architectures owe their energy absorption capabilities to combinations of elastic and plastic deformation mechanisms in both the base polymeric material as well as the cellular solid network as whole. This demonstrates the capability of scalable approaches in producing nano-architected materials that outperform monolithic materials like steel, aluminum, and polymethyl methacrylate (PMMA) - further evidence that nano-architected materials are viable candidates for use as composite reinforcements.

While nano-architected materials have been shown to possess desirable energy absorption properties and can now be produced in sufficient volumes for use as composite reinforcements, they have only been tested under μJ energies. Despite, many works studying stress-strain responses of nano-architected materials at quasi-static strain rates, only a small number of works have investigated the energy absorption capability of nano-architected materials under dynamic loading conditions [37, 82, 117] — all of which are at μJ energies using laser induced particle impact testing (LIPIT). While, these materials can adequately accommodate for micro-scale energies, it is uncertain how these performances will scale under larger energies. Considering the scales of energy typical for composite materials used in transportation or ballistics, these materials may be subject to energies on the order of $10^2 - 10^5 J$ — at least 100 million times greater than that of LIPIT testing [87]. With such a vast disparity between energy scales, underlying deformation mechanisms present in these nano-architected materials may change dramatically. Practically, before nano-architected materials can be used as structural materials and energy absorbers in applications with dynamic loading, these materials must be tested with macro-scale energies.

1.1.3 Nano-architected Composite Materials

Nano-architected composites represent an emerging class of materials that integrate the concepts of composite material design with architected structures [7, 8, 11]. In these systems, a three-dimensional nano-architecture is combined with a one or more other material phases to form a composite structure. These nano-architected composites systems typically take the form of interpenetrating phase composites (IPCs) [31], otherwise called co-continuous composites [143], utilizing a combination of load redistribution, interfacial mechanisms, and constituent material effects to attain high-stiffness, strengths and energy absorptions. In particular, nano-architecting metal/ceramic interpenetrating phase composites has been shown to produce high strengths and energy absorption by combining the advantages of IPCs with material size effects [11], shown in fig. 1.3. Similarly to their nano-architected lattice precursors, these systems have only been demonstrated a micro-scales with sample sizes on the order of $5 - 10 \mu m$ and loads below $4N$. Testing these materials in response to loads expected in everyday life, on the order of $10^0 - 10^2 kN$ is essential for demonstrating their utility as structural materials across engineering applications.

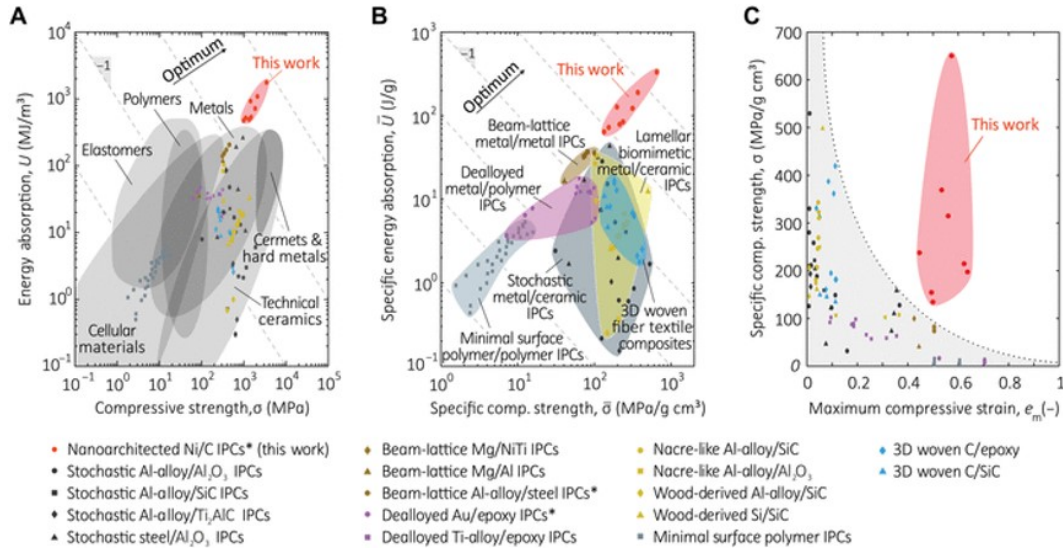


Figure 1.3: Nano-architected nickel/carbon IPCs compared to commercial bulk materials, literature-reported metal/ceramic IPCs, and other architected interpenetrating composites. Compressive strength versus strain energy absorption charts, (A) absolute and (B) specific properties, i.e., property-to-density ratios. The strain energy absorption values correspond to the areas under reported compressive stress-strain curves. (C) Specific strength versus maximum compressive strain chart. Data marked with asterisks (*) have not been tested to high-enough strains to reach fracture or densification. Reproduced with permission from: [11].

Despite the advantages of nano-architected IPCs, the majority of work studying IPC systems has been conducted at larger scales due to fabrication limitations [132]. In recent years, investigations on IPCs have focused on novel material combinations, namely metal-metal [157], ceramic-metal [91], polymer-metal [5], and polymer-ceramic [35] combinations, and topological designs, like triply periodic minimal surfaces, gyroids, octets and kelvin trusses. Despite significant work being dedicated to investigating the quasi-static compressive performance of IPCs, works on their dynamic behavior are limited [53, 130, 153]. Dynamic experimental investigation of polymer-based IPCs are particularly important due to the highly rate-dependent behavior of polymer matrices; these effects are especially prominent for polymer-polymer IPCs [130].

1.2 Thesis Outline

In this thesis we unite the works of PMCs and nano-architected materials by creating polymer-polymer nano-architected composites fabricated with macro-scale dimensions as a means to attain enhanced energy absorptions — exploring the potential of nano-architecture to remedy the failure mechanisms common in PMCs under

dynamic compression. In Chapter 2 we discuss the fabrication and micro-structural characterization of nano-architected composites materials in layered (nLPC) and interpenetrate configurations (nIPC). Here we will cover the fabrication of constituent nano-architectures through laser interference lithography (LIL) as well as their incorporation into composite configurations through two different molding approaches. We then discuss quasi-static mechanical testing of these nano-architected composites, in Chapter 3, from their underlying constituent lattices to macro-scale composite samples. These tests establish a baseline understanding of how nano-architectures deform and contribute to overall performances measured in nano-architected composites. In Chapter 4 we test these nano-architected composites at high-strain rates under split-Hopkinson Pressure bar (SHPB) loading with in-situ high speed imaging and correlate observed stress-strain performance to observed deformation and failure modes. To further understand how nano-architectures are contributing to high strain rate mechanical responses, in Chapter 5 we discuss the results of SHPB testing with in-situ synchrotron radiography. These measurements allow us to visualize deformation and failure on the interior of nano-architected composite samples, establishing a direct observational connection between nano-architected behavior and stress-strain performance. In Chapter 6 we relate stress-strain performances across strain rates using a Johnson-Cook style phenomenological model as well as compare nano-architected composites to classical PMC performances to determine broader trends in energy absorption. We conclude this thesis by then discussing unexplored areas of nano-architected composite design, fabrication, and modeling and remark on future research directions to realize enhanced mechanical properties.

Chapter 2

FABRICATION AND MICROSTRUCTURAL CHARACTERIZATION OF NANO-ARCHITECTED COMPOSITES

2.1 Introduction

To create nano-architected composites at scale, we must bridge the gap between fabrication of classical polymer matrix composites and nano-architected materials. At small scales, nano-architected materials are most commonly fabricated through two-photon polymerization (TPP) or two-photon lithography, in which photo-polymerization is triggered in a confined focal volume of a laser light through nonlinear absorption and patterned in 3-space to create architected structures [101]. Over the past few decades significant work has been done to develop and improve methods to write 3D nano-structures using TPP with high geometric fidelity [77], however, these methods typically involve a tradeoff between speed, feature resolution, and overall samples size [148]. Recently, methods like multi-focus multi-photon printing [127], phase-mask lithography [7], colloidal self assembly [38], 3D nano-lithography [68] and metasurface-based holographic lithography [82] have shown scaling nano-architected fabrication to the macro-scale is achievable at high speeds. In this work we show how one of these techniques, metasurface-based holographic lithography, can be used to create nano-architected reinforcements for PMCs.

Classically, PMCs are comprised of discrete fibers or particles dispersed and bound together in a polymer matrix [71]. In fiber-reinforced PMCs, the reinforcement is first produced as continuous tows, woven fabrics, mats, or chopped fibers through chemical synthesis or extraction from natural materials [121] and is then incorporated into a polymer matrix through methods such as hand lay-up [50], pultrusion [80], resin transfer molding [151], and other molding processes [94, 114]. In particle-reinforced PMCs, the reinforcement can be produced via pyrolysis [46], flame synthesis [140], wet chemical synthesis [133], sol-gel processing [159], plasma synthesis [41], or ball milling [149] and are then dispersed within the polymer matrix through mixing methods such as melt and solution blending [54]. Drawing inspiration from these

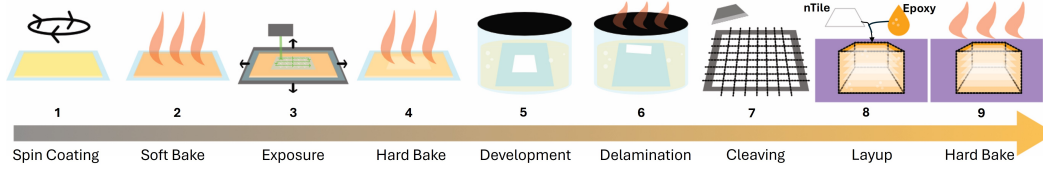


Figure 2.1: Overview of nano-architected composites fabrication process.

classical PMC fabrication techniques, we developed a molding-based fabrication method for creating nano-architected PMCs.

While using architectures as reinforcements phases in composites, commonly referred to as interpenetrating phase composites (IPCs) or co-continuous composites, is a natural direction to develop advanced 3D materials, so far fabrication limitations have prevented these works from achieving nano-scale reinforcements [84, 85, 143, 144, 156]. Only a limited number of studies have demonstrated fully nano-architected interpenetrating phase composites (nIPCs) with co-continuous load-bearing phases [11]. This work discusses how nano-architected materials can be fabricated with macro-scale global sample dimensions and combined with a matrix polymer to create nano-architected composites capable of withstanding macro-scale mechanical loads.

In this chapter, we discuss the fabrication of nano-architected reinforcement materials and their incorporation into nano-architected PMCs. In section 2.2.1 we demonstrate how nano-architected structures are fabricated using a lithography-based interference lithography (LIL) method, allowing the fabrication of large areas of architected material while maintaining fine feature resolution. Details of the underlying geometry and morphology of LIL produced nano-architectures are discussed in section 2.2.2 and modifications to the LIL method to obtain thicker nano-architectures are discussed in section 2.2.3. Sections 2.3 and 2.4 show how LIL produced nano-architectures are used to fabricate nano-architected composites with ambient and vacuum assisted methods. The produced samples were then characterized using nanoCT, shown in section 2.5, to understand defect and nano-architected reinforcement volume fractions and distributions.

2.2 Fabrication of Reinforcements

2.2.1 Laser Interference Lithography Method

Nano-architected sheets with macroscopic global dimensions ($\approx 2.1\text{cm} \times 2.4\text{cm} \times 35\mu\text{m}$) and nano-scale feature resolution ($\approx 500\text{ nm}$) were fabricated using laser

interference lithography (LIL), also called meta-surface mask enabled holographic lithography, as demonstrated by Kagias et. al. (2023) [82]. The LIL fabrication method was developed in the Greer Research Group by Prof. Matias Kagias and Dr. Andrew Friedman in collaboration with Prof. Andrei Faraon and Dr. Tianzhe Zhang. I fabricated and characterized all LIL samples shown in this work. I also extended this method to achieve thicker nano-architected samples, as discussed in section 2.2.3. The fabrication of nano-architected lattice reinforcements is shown schematically in steps 1 – 7 in fig. 2.1. These steps consists of: (1) spin coating photo-polymer (3000 rpm, 60 s), (2) two-step soft bake (65/95 °C, 10/30min, respectively), (3) laser light exposure (shown in fig. 2.2), (4) post-exposure bake (65 °C, 3 min), (5) chemical development (PGMEA and isopropanol), (6) delamination (80 °C in DI water overnight), (7) cleaving LIL sheets into nTiles with a razor blade. For the exposure step, nano-architectures were patterned via 532nm wavelength laser (230–270mW) in green light sensitized SU-8 2050 (Kayaku Advanced Materials, Westborough, MA, USA), a negative-tone epoxy-based photoresist formulated for high-aspect-ratio features.

The resulting nano-architected sheet produced from development (step 5) is shown in fig. 2.3. Figure 2.3(A) shows a photograph of a typical 35 μ m-thick nano-architected sheet produced via this process. Here, the opaque region of the sheet corresponds to the nano-architected material, and the translucent surrounding areas corresponds to monolithic (unpatterned) SU8. Figure 2.3(B–C) Cross-sectional SEM images of the nano-architected region of the sample reveal a well patterned brick-and-mortar like structure with a lateral periodicity of ≈ 900 nm and a vertical periodicity of $\approx 1.62\mu$ m. Beam diameters vary across the sample from ≈ 420 –560nm with overall relative densities (solid volume fraction) of $\rho^* \approx 0.2$ –0.35. To evaluate the geometry of the underlying 3D unit cell present in these nano-architectures, PXCT measurements were performed at the cSAXS beamline of the Swiss Light Source (Paul Scherrer Institute, Villigen Switzerland) utilizing the OMNY instrumentation [73]. Projection data was then reconstructed into 3D geometries and visualized as a unit cell in ImageJ, shown in fig. 2.3(D) [45]. Following step 7, resulting nTiles possess lateral dimensions (L) of $\approx 4 \times 4$ mm² and thicknesses (t_1) of the $\approx 35\mu$ m. These nTiles are directly used for fabrication of nano-architected composites as discussed in sections 2.3 and 2.4.

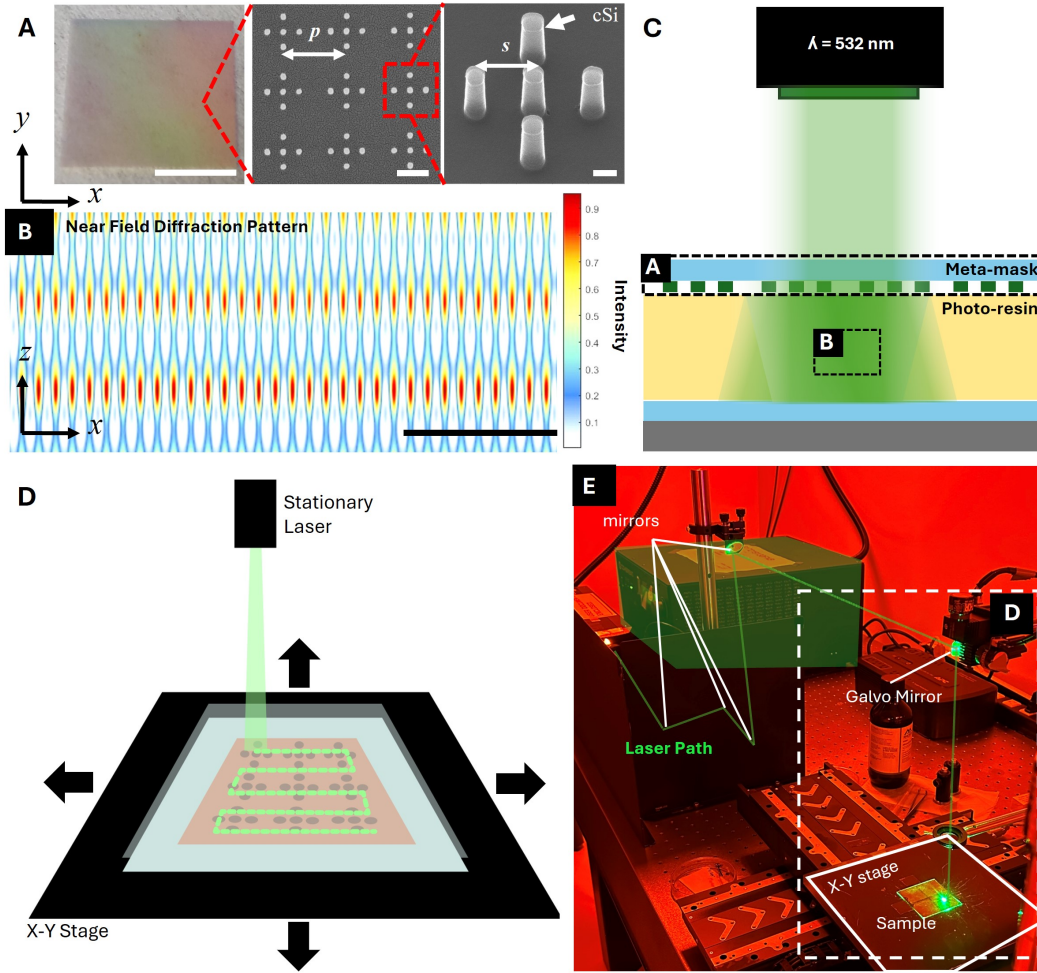


Figure 2.2: Details of the exposure step in the LIL process. A) Metasurface mask used to generate near field diffraction pattern transferred into photoresist. B) Near field diffraction pattern generated by metasurface mask. C) Configuration of laser exposure mediated by the metasurface mask. D) Method for rastering laser over large mask areas using X-Y stage. E) Photograph of LIL laser setup. Scale bars: A) 1cm, i) 450nm, ii) 100nm. B) 10 μ m.

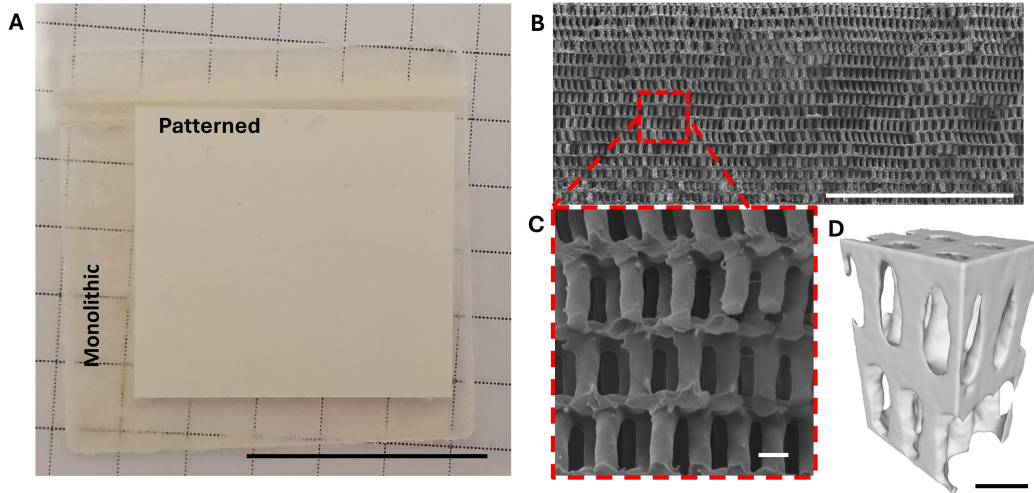


Figure 2.3: Characterization of LIL-produced samples A) Photograph of a sample produced by the LIL process [82]. Opaque rectangle represents nano-architected region. B) Cross-sectional SEM image of nano-architected sample. C) Zoomed in SEM image showing brick-and-mortar nano-architected structure. D) PXCT reconstruction of nanoarchitected unit cell. Scale bars: A) 1.5cm, B) 30 μ m, C) 500nm. D) 1 μ m.

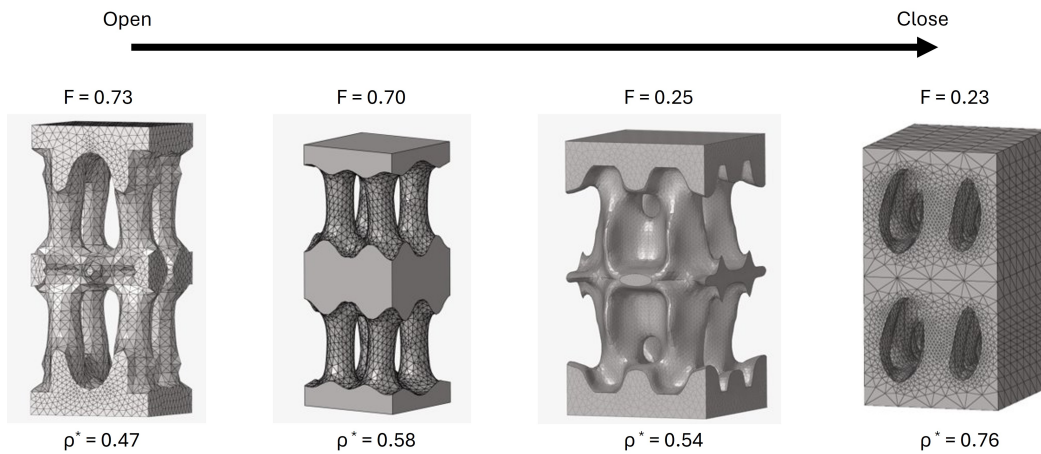


Figure 2.4: Unit cells extracted from LIL produced nano-architected structures. Extracted unit cell morphologies are arranged by shape factor (F) with high values corresponding to open-cell (left) and low values corresponding to closed-cell (right). Measured relative densities of the extracted unit cells are shown below the extracted morphology.

2.2.2 Variation of Underlying Morphology

Across fabricated LIL sheets, nano-architectures exhibit a spatially distributed variation in morphology as a product of complex light interference and spatially controlled polymer cross-linking. Understanding the resulting morphologies of underlying unit cells is critical for understanding nano-scale deformation mechanisms. PXCT measurements of LIL produced nano-architectures, obtained by Prof. Matias Kagias and Dr. Nicholas W. Phillips, recorded more than 30,000 individual unit cells allowing us to identify a bimodal distribution of underlying morphologies. Analysis of the processed PXCT image stacks was performed in collaboration with Pietro Toniolo. Relative densities (ρ^*) and principal curvatures (κ_1, κ_2 - shown in eqs. (2.1) and (2.2)) of unit cells were estimated to quantitatively distinguish between underlying morphologies. Extracted representative unit cells of morphologies varying from open to closed cell are shown in fig. 2.4. Shape factor F , eq. (2.3), is calculated as the angle between principal curvature peaks in the (κ_1, κ_2) plane and $\kappa_1 = \kappa_2$ line normalized by π [81]. High shape factor values correspond to open cell morphologies, whereas low shape factor values correspond close cell morphologies.

$$\bar{\kappa}_1 = \frac{1}{L_{\kappa_1}} \sum \kappa_1(i) \quad (2.1)$$

$$\bar{\kappa}_2 = \frac{1}{L_{\kappa_2}} \sum \kappa_2(i) \quad (2.2)$$

$$F = \frac{1}{\pi} \arccos\left(\frac{\bar{\kappa}_1 + \bar{\kappa}_2}{\sqrt{2}\sqrt{\bar{\kappa}_1^2 + \bar{\kappa}_2^2}}\right) \quad (2.3)$$

Comparing cross-sectional SEM characterization to unit cells characterized with PXCT reveals a large increase in relative density especially in closed cell morphologies. These differences may arise from coupled interactions between optical, chemical, and thermal effects present in during the fabrication process. However, the origin of morphological variation is driven by harmonic mismatches in diffractive light orders generated by meta-surface periodicity and lithographic wavelengths. To mitigate these effects, meta-surface design approaches should be developed to take into account the macroscopic optical behavior rather than aiming to optimizing morphology of a single unit cell [83].

2.2.3 Increasing Thickness of Nano-architected Layers

To increase the thickness of nano-architected layers produced by the LIL method, photoresist and fabrication parameters were adjusted to generate architectures with

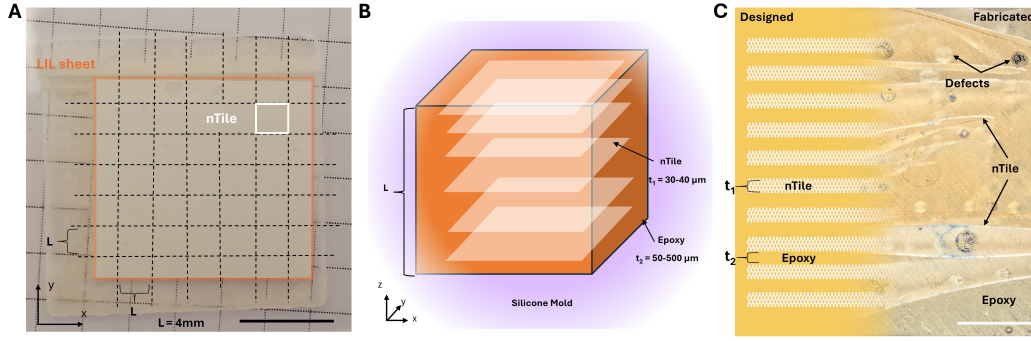


Figure 2.5: Overview of composite sample fabrication starting from nano-architected LIL samples. A) Sample produced by the LIL process divided from a sheet to an nTile. Lateral dimensions of nTiles (L) are 4mm. B) schematic diagram of ambient molding process showing nTiles suspended in matrix epoxy inside a cubic silicone mold. Relative thicknesses of nano-architected (t_1) and matrix epoxy regions (t_2) labeled C) Side-by-side comparison of as designed and as fabricated nano-architected composite samples. nTiles, defects, and matrix epoxy regions are labeled with arrows. Scale bars: A) 1cm, C) 1mm.

over twice the thickness of samples fabricated using the process outlined in section 2.2.1. Photoresist for thick nano-architectures were created from SU-8 2100 (Kayaku Advanced Materials, Westborough, MA, USA) and green light sensitized through the addition of sensitizer H-Nu 470 (Spectra Group Limited, Millbury, Ohio, USA), accelerator H-Nu 254 (Spectra Group Limited, Millbury, Ohio, USA), and solvent cyclopentanone (Sigma-Aldrich, St. Louis, Missouri, USA). In contrast to previously made photoresists, SU-8 2100 based formulations possess higher viscosity which leads to thicker resin layers when spin coated at the same speed [36]. Photoresists made with SU-8 2100 were then spin coated at reduced speeds of 1000 rpm to attain nano-architected sheets with $\approx 90\mu\text{m}$ thicknesses after exposure, thermal treatment, and development. To account for increased resin thicknesses, pre-exposure soft bake durations were increased by 50% and development durations were increased by 100%. These thick nano-architectures possess the same underlying geometries and morphologies as samples produced with the standard LIL method. These thick nano-architected sheets were cleaved into nTiles and used in place of standard thickness LIL produced nTiles in both ambient molding (section 2.3) and vacuum molding (section 2.4) processes to create 22% volume fraction thick nIPCs.

2.3 Nano-architected Composites: Method 1 - Ambient Molding

2.3.1 Ambient Molding Method

Fabrication of nano-architected composites from nano-architected reinforcements produced via LIL method and epoxy thermoset polymers occurs through and the ambient molding process discussed in this chapter. Ambient molding consists of two main steps: (1) layup of matrix epoxy and nano-architected nTiles into cubic silicone molds and (2) overnight hard bake, labeled steps 8-9 in fig. 2.1. This ambient molding method was used to create two different configurations of nano-architected composites, nIPC (interpenetrated nano-architectures) and nLPCs (void nano-architectures). These configurations were achieved using two different diglycidyl ether of bisphenol-A (DGEBA) epoxy systems (1) - for nLPCs, system 2000 resin (Fibreglast 2000) with the 2120 slow hardener, mixed 3:1 by volume, and (2) - for nIPCs, 635 thin epoxy (U.S. Composites) with a non-blushing medium hardener, mixed 3:1 by volume. Prior to integration with nTiles, epoxy resins and hardeners were degassed at ≈ 40 mbar in two steps: separately in a vacuum chamber for 24 hours before mixing and 10-15 minutes after mixing until visible bubble evolution ceased. Mixed, degassed epoxy systems were then used immediately for composite layup to prevent polymer gelling before layup is completed. Silicone molds containing nano-architected composite layups are then hard baked at 80°C in a oven for >24 hours. Figure 2.5 shows details of nTiles cleaved from LIL sheets, expected distributions of nano-architected nTiles within matrix epoxy, and as designed and as fabricated comparisons of sheet distributions and orientations. Depending upon fabricated sample volume fraction as well as nTile migration during successive layup and curing steps, composited nTiles are separated by $t_2 = 50 - 500\mu\text{m}$ of matrix epoxy. Fully cured nano-architected composites are removed from silicone molds and specimen faces were polished with 600-grit (P600) SiC paper on a flat granite slab using light pressure and a figure-eight motion, then rinsed with DI water/isopropanol and air-dried, results of polishing are shown in fig. 2.6. During fabrication, nTiles are also free to bend, twist, and angle stochastically resulting in various distributions, orientations, and curvatures of nano-architected regions produced within samples, shown in 2.6 (B,C). During layup and curing, matrix voids and other defects can arise naturally as the result of resin agitation or gas evolution. These defects are then trapped and solidified into samples after curing resulting in visible voids encased within fabricated nano-architected composites, shown in 2.6(B,C).

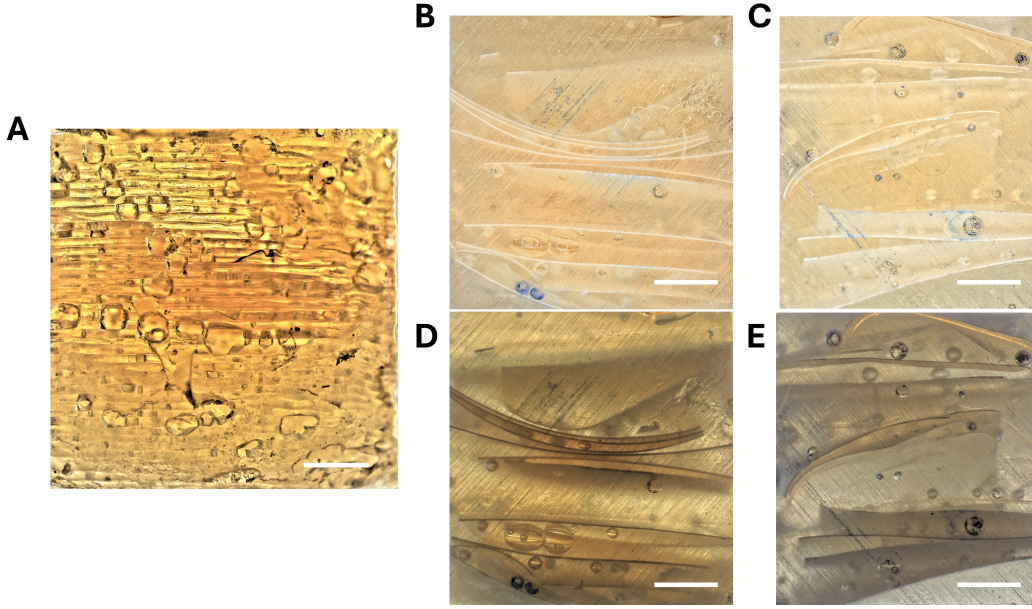


Figure 2.6: Optical microscope image of nano-architected composite samples. A) Sample produced by the ambient molding process before polishing. B) Polished nLPC samples with top illumination C) Polished nIPC samples with top illumination. D) Polished nLPC samples with transmission illumination. E) Polished nLPC samples with transmission illumination. Scale bars: 1mm.

Cubic nLPC and nIPC samples measuring $\approx 4 \times 4 \times 4$ mm were fabricated such that nano-architected volumetric fill fractions can be controlled by the number of nTiles used during the layup process. Volume fractions of nano-architected composite samples ($\lambda_{vf}^{nIPC}, \lambda_{vf}^{nLPC}$) are determined using eqs. (2.4) and (2.5) to account for differing matrix epoxy content resulting from nIPC and nLPC content. Additionally, 22% volume fraction nIPC samples with thick nano-architected regions ($\approx 90 \mu\text{m}$ thick) and half as many nTiles were made by using the modified LIL method discussed in section 2.2.3.

$$\lambda_{vf}^{nIPC} = \frac{n_{nTiles} \rho^* V_{nTile}}{V_{sample}} \quad (2.4)$$

$$\lambda_{vf}^{nLPC} = \frac{n_{nTiles} \rho^* V_{nTile}}{V_{sample} - (1 - \rho^*) n_{nTiles} V_{nTile}} \quad (2.5)$$

For comparability across classical PMC systems, mass fractions ($\lambda_{mf}^{nIPC}, \lambda_{mf}^{nLPC}$) were calculated from volume fractions by normalizing calculated volume fractions by constituent material densities, as seen in eqs. (2.6) and (2.7)

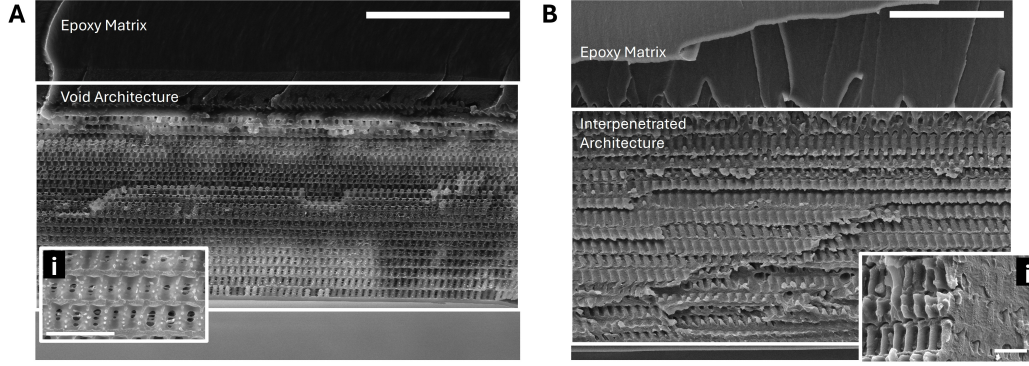


Figure 2.7: Cross-sectional SEM images of nano-architected composites samples. A) nLIPC samples with void architectures. i) Close up SEM image of void architecture. B) nIPC samples with interpenetrated architectures. i) Close up SEM image of interpenetrated architecture. Scale bars: A) $20\mu m$, i) $3\mu m$. B) $10\mu m$, i) $2\mu m$.

$$\lambda_{mf}^{nIPC} = \left[1 + \left(\frac{V_{sample}}{n_{tile}\rho^*V_{nTile}} - 1 \right) \frac{\rho_{matrix}}{\rho_{SU8}} \right]^{-1} \quad (2.6)$$

$$\lambda_{mf}^{nLPC} = \left[1 + \frac{V_{sample} - (1 - \rho^*)n_{nTiles}V_{nTile}}{n_{nTiles}\rho^*V_{nTile}} \left(\frac{V_{sample} - n_{nTiles}V_{nTile}}{V_{sample}} \right) \frac{\rho_{matrix}}{\rho_{SU8}} \right]^{-1}. \quad (2.7)$$

For volume $(\lambda_{vf}^{nIPC}, \lambda_{vf}^{nLPC})$ and mass $(\lambda_{mf}^{nIPC}, \lambda_{mf}^{nLPC})$ filler fraction calculations, n_{nTiles} , ρ^* , ρ_{matrix} , ρ_{SU8} , V_{nTile} , V_{sample} are the number of nTiles used for layup, relative density of the nano-architecture, density of the matrix epoxy, density of SU8, volume of an nTile, and volume of the sample. For the nano-architected samples fabricated and tested in this work n_{nTiles} values of 13, 27, and 55 were used to achieve nIPC volume fractions of 5%, 11% and 22%.

2.3.2 Controlling Interpenetration

As previously mentioned, two configurations of nano-architected composites are achieved by using two different matrix epoxies during fabrication. Cross sectional SEM images of nIPC and nLPC configurations show that nano-architected regions are interpenetrated (nIPC) or void (nLPC), shown in fig. 2.7. nLPC (A) nano-architected regions present with matrix epoxy layered on the top and bottom of the nano-architecture while the surrounded brick-and-mortar structure is void — identical to as produced LIL structures. In contrast, nIPC (B) cross-sections, while still surrounded by matrix epoxy, show nano-architected regions are fully filled and interpenetrated with the matrix epoxy. This stark difference between the nLPC

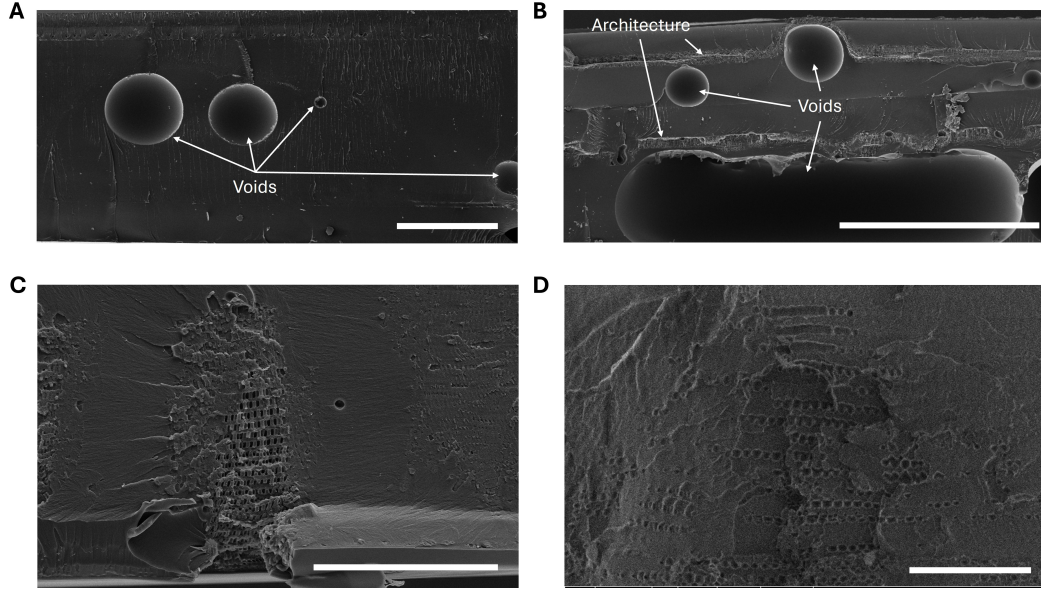


Figure 2.8: Cross-sectional SEM image of defects in nano-architected composites samples. A) Matrix voids. B) Large interlaminar voids caught between nano-architected layers. C) Occluded sections of nano-architectures prevented from interpenetration. D) Occluded cells of nano-architectures producing nano-scale voids. Scale bars: A) 250 μm . B) 500 μm . C) 30 μm . D) 10 μm .

and nIPC configurations is attributed to a large difference in viscosity between constituent matrix epoxy systems (nLPC - 1650 cP, nIPC - 600 cP) which under ambient conditions affects volumetric flux for infiltration (Q) — as seen in Darcy's law eq. (2.8) [134, 139].

$$Q = -\frac{kA\Delta P}{\mu L} \quad (2.8)$$

Here, Q , k , ΔP , and μ are volumetric flux of matrix epoxy, permeability of the architecture, change in pressure over the architected region, and viscosity of the matrix. A and L are the area and length over which the pressure drop is measured. This tells us that flow of the epoxy matrix into the architecture is inversely proportional to matrix epoxy viscosity. Over the pot life of the epoxy, low resin viscosity is critical to achieve interpenetration before epoxy matrix gelling and polymerization cause viscosity to increase drastically.

2.3.3 Architected Region and Matrix Defects

As a result of the ambient molding fabrication process, defects arise at various scales. At the macro-scale, defects appear throughout the matrix in both nIPC

and nLPC samples. These matrix voids form naturally from agitation during the layup process and naturally from solvent off-gassing during the resin curing process. During the layup and curing process, these matrix voids can migrate and deform affecting surrounding architectures not just the matrix epoxy. As the microscale, nIPC samples also possess interpenetration defects where part of the nano-architecture is incompletely infiltrated with the surrounding matrix epoxy, shown in fig. 2.8. These defects in the nanoarchitecture present in a distributed (fig. 2.8(C)) and concentrated manner (fig. 2.8(D)). These defects can be forming due to either fabrication limitations or as a product of the inherent underlying structure of the nano-architected reinforcements. In cases of large concentrated occlusions of architecture, the nano-architected sheets possess an inherently morphologically graded geometry, consequently these architected regions may be blocked from resin flow by a network of closed cell geometries. Defects in the architected areas may also be forming due to a lack of pressure driving voids out of the sample. To mitigate defect formation in samples, the nano-architected composite fabrication method was revised to enable the application of pressure during curing.

2.4 Nano-architected Composites: Method 2 - Vacuum Assisted Molding

2.4.1 Vacuum Assisted Molding Process

To reduce defect density and improve infiltration uniformity, a vacuum-assisted resin transfer approach was developed for the fabrication of nano-architected composites. This method utilizes a pressure gradient generated by a vacuum pump to drive neat matrix epoxy through nano-architected sheets, enabling more complete filling of fine structural features. Nano-architected nTiles produced via LIL method were stacked in a polyvinyl alcohol (PVA) containment, shown in fig. 2.9, which served as a sacrificial holder and flow guide during infiltration. The PVA sample holder was then placed within a resin delivery system consisting of interconnected chambers and microchannels fabricated via digital light processing (DLP) using PR-48 photopolymer resin. This 3D printed enclosure was designed to route resin through the nano-architected layers while maintaining a sealed flow path between inlet and outlet regions. After the PVA holder is loaded into the resin delivery system, degassed matrix epoxy resin was loaded into syringe reservoirs and a vacuum was applied downstream of the sample through outlet channels, establishing a pressure differential across the nano-architected structure. This configuration actively drew the epoxy through the nano-architected sheets, ensuring infiltration occurred through the thickness of the material rather than relying on capillary action. Downstream

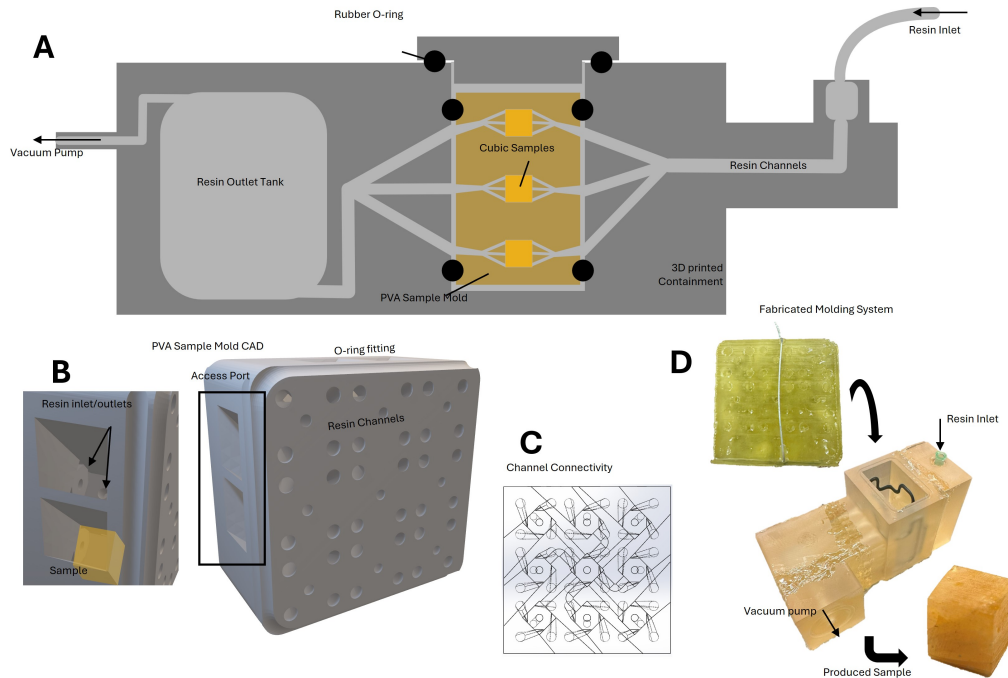


Figure 2.9: Summary of vacuum assisted nano-architected composite fabrication method. A) Schematic diagram of resin infiltration device. B) Poly vinyl alcohol (PVA) sample holder design showing side access ports where nTiles are inserted prior to infiltration. C) Transparent CAD of PVA sample holder showing connectivity of resin channels to cubic sample containers. D) As fabricated images of PVA sample holder, resin delivery system, and produced nano-architected composite sample.

collection chambers captured excess resin and maintained continuous resin flow, preventing stagnation and backflow of voids. Following infiltration, PVA holders are removed from the resin delivery system and suspended in a container of epoxy resin to allow epoxy within PVA mold to gel. After sufficient gelling (≈ 3 hours), PVA holders are removed from the resin container and placed in an oven and hard baked overnight to ensure a fully cross-linked matrix. Following the hard bake, PVA holders are removed by dissolution in an agitated water bath, leaving behind fully infiltrated nano-architected composite samples. These samples are then polished, dimensions and used for mechanical testing. This method allows 9 or more samples to be made concurrently maintaining scalable workflow for rapid production of nano-architected composite samples.

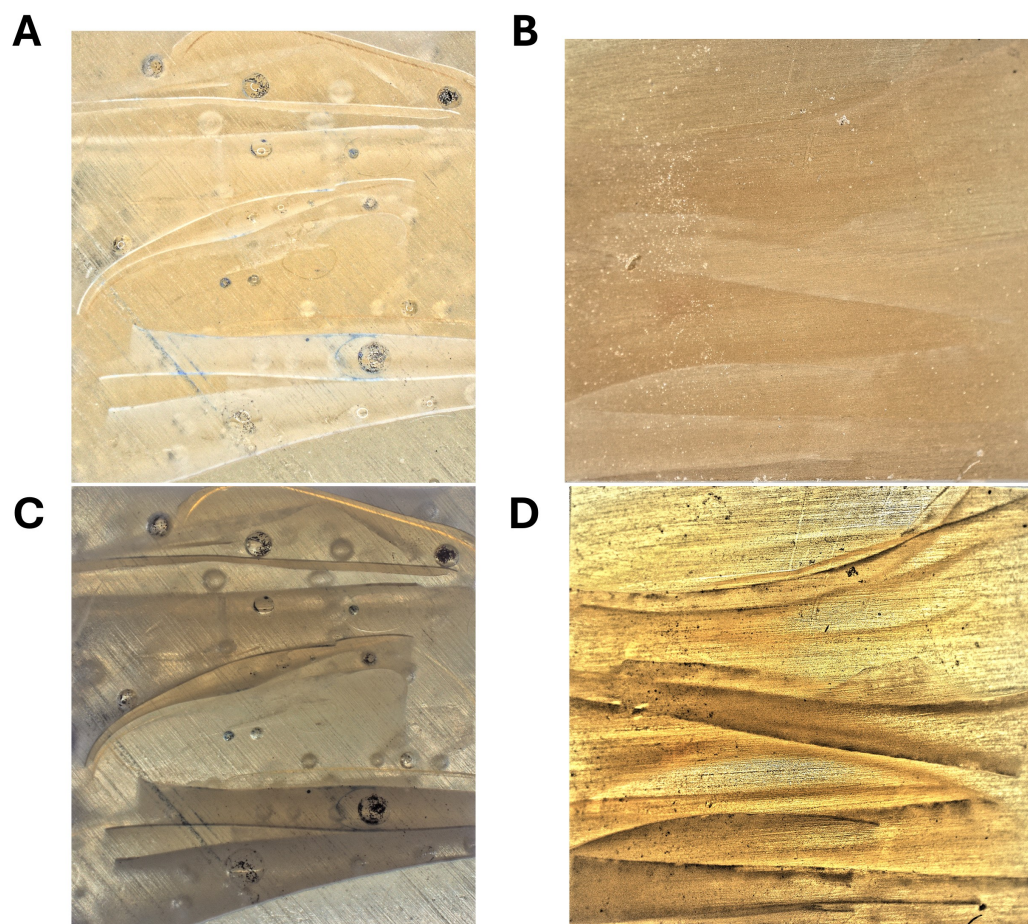


Figure 2.10: Side-by-side comparison of optical microscope images of nIPC samples fabricated with ambient molding and vacuum assisted molding. A) Ambient molded nIPC sample top-down illumination. B) Vacuum molded nIPC sample top-down illumination. C) Ambient molded nIPC sample transmission illumination. D) Vacuum molded nIPC sample transmission illumination.

2.4.2 Architected Regions and Matrix Defects

Samples produced through vacuum assisted molding were imaged using a Keyence VHX-X1 Optical Microscope (Keyence, Osaka, Japan) and compared to samples fabricated using the ambient molding method, fig. 2.10. Comparing the optical microscope images of the samples produced through the two fabrication methods shows that the vacuum assisted process results in fewer matrix voids. To further probe differences in the underlying architecture, nIPC samples produced with the vacuum assisted fabrication method were fractured and mounted on SEM stubs for cross-sectional analysis of the underlying microstructure. Figure 2.11 shows that close-up inspection of the architected regions revealing complete interpenetration of the underlying architecture. SEM imaging also revealed the persistence of some

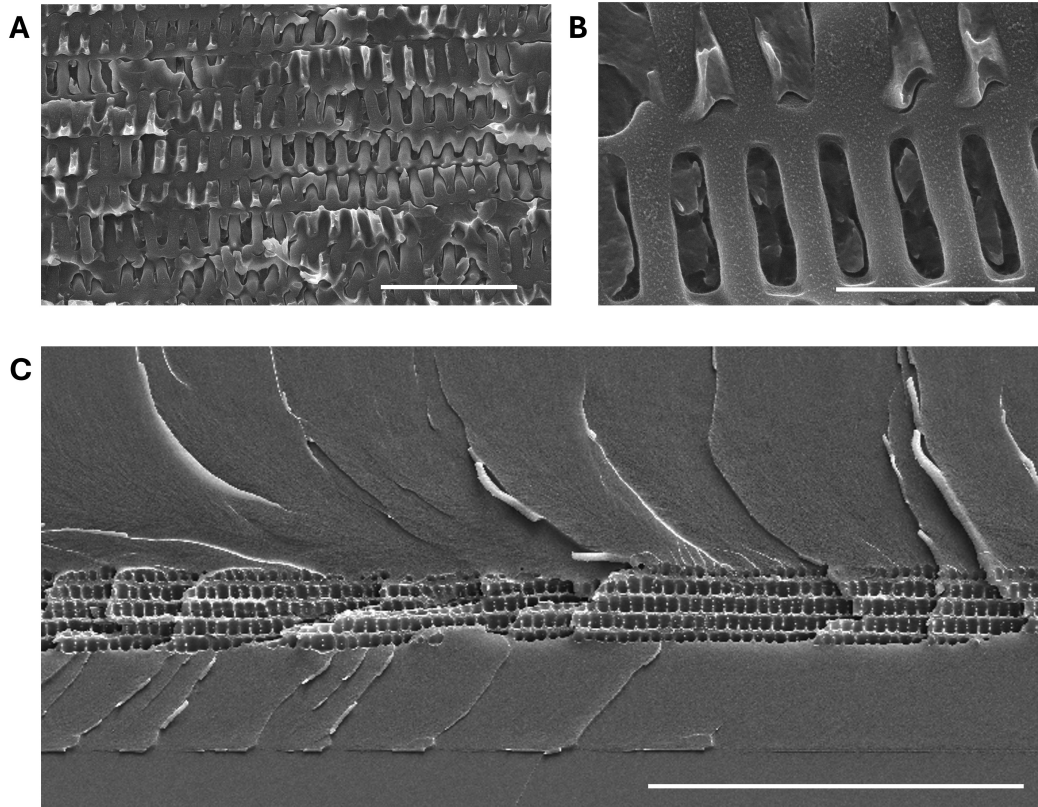


Figure 2.11: Cross-sectional SEM images of nIPC samples fabricated with vacuum assisted molding. A) Architecture well interpenetrated with matrix epoxy. B) Close up image of architecture and matrix epoxy filling nano-architected void space. C) Defect in vacuum molded nIPC sample caused by closed cell morphologies occluding matrix epoxy flow.

matrix voids trapped between layers of nano-architectures. These trapped voids played a significant role in determining observed stress-strain performance inducing early failure within composite samples when present. These voids are the result of the morphologically graded nano-architecture producing volumes of architecture fully occluded from resin flow.

2.5 Computed Tomography Reconstructions

2.5.1 Reconstruction and Segmentation Method

To obtain a more detailed measure of defects present from ambient and vacuum molding processes, X-ray nano-computed tomography (nanoCT) was performed at to resolve the distribution and infiltration quality of the nano-architected composite samples, shown fig. 2.12. All nanoCT measurements were performed in collaboration with Prof. Matias Kagias at Lund University. Obtained datasets were then processed into image stacks using a script developed by collaborator Robin Kruger.

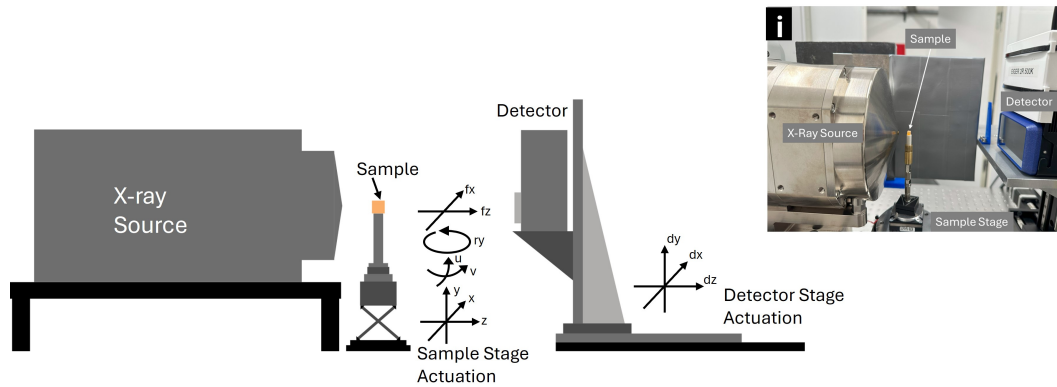


Figure 2.12: Schematic diagram of nanoCT setup used to obtain 3D reconstructions of nano-architected composite samples. i) Photograph of actual nanoCT setup with sample mounted for measurement.

Tomographic datasets were acquired by rotating the sample about a single axis while collecting a series of radiographic projections [48]. For each scan, approximately 1,800–3,200 projections were collected over a 360° angular range. Exposure times ranged from 2–20 s per projection, resulting in total scan durations between approximately 1 and 17 hours, depending on the resolution and signal-to-noise ratio. The X-ray source was operated at an accelerating voltage of approximately 60 kV to provide sufficient penetration through the polymer matrix while maintaining contrast between phases.

High geometric magnification was employed to achieve sub-micron spatial resolution. The source-to-sample distance was typically on the order of 1.5–10 mm, while the sample-to-detector distance ranged from approximately 100–400 mm. This configuration resulted in effective voxel sizes of approximately 300 nm to 1.6 μm , enabling resolution of broad nano-architected layers but not underlying features. To enhance contrast in the low-density polymer system, propagation-based phase contrast imaging was utilized. By selecting an appropriate propagation distance, phase shifts induced at material interfaces were converted into detectable intensity variations, improving visualization of internal features and interfaces that exhibit weak absorption contrast.

The acquired projection data were processed prior to reconstruction to remove artifacts and improve image quality. Flat-field normalization was first applied to correct for spatial variations in detector response and X-ray beam intensity. Defective or noisy pixels were identified using thresholding and statistical deviation criteria and replaced using median-filter-based interpolation. The center of rotation (CoR) was

determined by reconstructing trial slices with varying alignment offsets and selecting the configuration that minimized reconstruction artifacts. Ring artifacts, arising from detector inhomogeneities, were reduced using sinogram-based filtering techniques. To correct for small mechanical or thermal drift during long acquisition times, projection images were aligned using cross-correlation-based image registration, and sub-pixel shifts were applied across the dataset.

For datasets exhibiting significant phase contrast effects, phase-retrieval algorithms were applied to convert phase variations into quantitative intensity contrast. This reduced edge-enhancement artifacts while improving contrast within the polymer matrix. In some cases, mild sharpening (e.g., unsharp masking) was applied following phase retrieval to recover high-frequency features attenuated during processing.

Three-dimensional reconstructions were performed using the Feldkamp–Davis–Kress (FDK) algorithm, a filtered back-projection method for cone-beam geometries. Reconstruction was implemented using GPU-accelerated solvers, enabling efficient conversion of projection data into volumetric representations. Alignment parameters, including center of rotation and tilt corrections, were iteratively refined to minimize geometric distortions in the reconstructed volume.

The final output of the reconstruction process consisted of a three-dimensional image stack, where each slice represents a cross-sectional plane of the sample. These slices were stored as a sequence of 2D grayscale images, with voxel intensities corresponding to the reconstructed X-ray attenuation (and phase contrast contribution, when applicable). The resulting volumetric datasets enabled direct visualization of nano-architected unit cells, assessment of infiltration uniformity, identification of voids and defects, and generation of three-dimensional renderings for subsequent qualitative and quantitative analysis.

2.5.2 Comparing the Ambient Molding and Vacuum-Assisted Method

Representative reconstructed volumes for neat epoxy, ambient molded, and vacuum assisted molding are shown in fig. 2.13. Obtained image stacks from nanoCT were cleaned using Dragonfly3D and applying a 2D 2x2 median filter applied slice by slice in plane with architectures, slices orthogonal to filtering were then segmented using a local upper Otsu threshold and manual corrections. Segmented reconstructions of matrix epoxy, defect void space, and architected regions were then analyzed to determine defect and architected volume fractions and categorize defect types. Reconstructed volumes of neat epoxy samples show no defects throughout

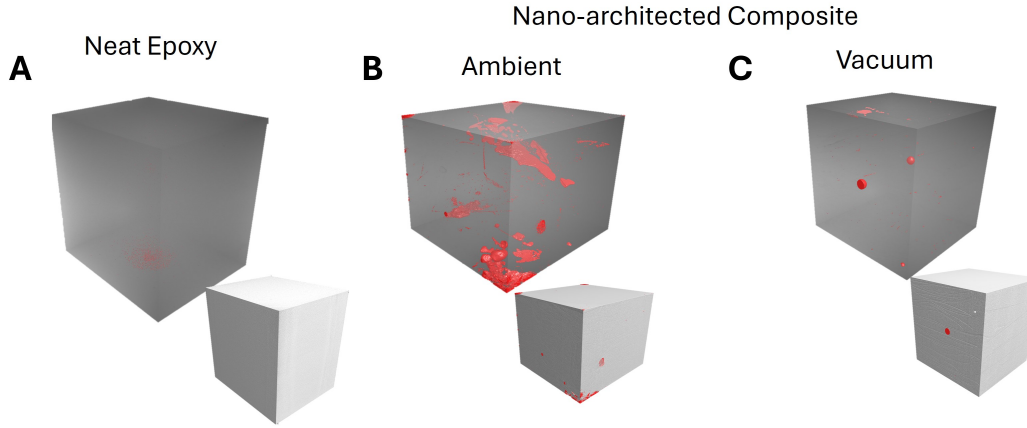


Figure 2.13: Representative nanoCT reconstructions of neat epoxy (A), ambient molded nIPC sample (B), and vacuum molded nIPC sample (C). Defect volumes are highlighted in red.

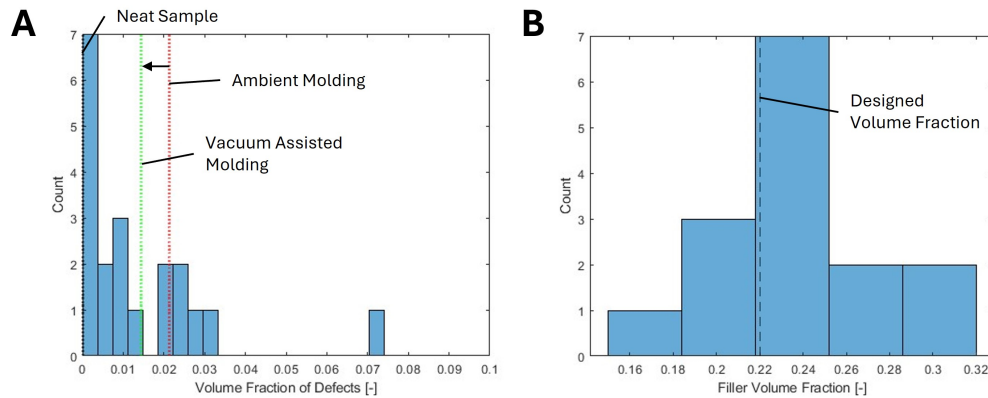


Figure 2.14: Histograms of (A) defect volume fractions and (B) Volume fraction of nano-architected regions.

the reconstructed volumes - as expected. Samples made from ambient molding possessed large matrix bubbles, inter-laminar voids trapped between architected layers, and incomplete interpenetration. Samples fabricated via vacuum-assisted molding also possessed large matrix bubbles, inter-laminar voids and incomplete interpenetration but at significantly reduced volume fractions, shown in 2.14(A). As a result of switching from ambient to vacuum-assisted molding methods, defect volume fractions were greatly reduced. Volume fractions of architected regions were also evaluated from segmented nanoCT reconstructions confirming designed 22% nIPC samples possessed $\approx 22\%$ volume fraction of nano-architecture, shown in 2.14(B).

2.6 Summary and Conclusions

In this chapter, we have discussed the fabrication and characterization of nano-architected composites from the nano-scale to the macro-scale. Summarizing the work discussed in this chapter:

- Fabrication and characterization of macro-scale polymer samples with nano-architected features via laser interference lithography (LIL).
- Fabrication and characterization of macro-scale polymer-polymer composite samples with nano-architected reinforcements.
- Revised fabrication method and characterization of macro-scale polymer-polymer composites with interpenetrated nano-architected reinforcements.

In section 2.2.1 we showed how nano-architected structures are fabricated using the LIL approach. Section 2.2.2 details how these LIL produced architectures possess an inherently morphologically graded architecture and section 2.2.3 shows how thicker layers of nano-architected material may be produced by changing fabrication parameters. Section 2.3 and section 2.4 show how nano-architected material produced by LIL can be then turned into a bulk composite material with macro-scale dimensions. These nano-architected composites may be produced in two different configurations (nIPC and nLPC) depending upon the viscosity of the matrix epoxy, shown in section 2.3.2, and varying volume fractions of reinforcements may be achieved by increasing the number of nTiles used in the molding processes. Section 2.5 evaluates the differences between nano-architected samples fabricated with different molding methods, showing vacuum molded samples possess far fewer defects overall and expected volume fractions.

This work shows that not only can LIL produce nano-architected materials at macro-scales but these nano-architectures can then be used to fabricate bulk composite materials in a scalable manner with high throughput. Although ambient molding methods show fabricated composites possess high volumes defects, vacuum-assisted molding proved effective in removing the majority of these defects. This approach to fabricating nano-architected materials represents a new direction for fabricating and characterizing the effects of small scale architectures in polymer composite materials. Samples produced through these methods can be readily tested using standardized bulk mechanical characterization techniques previously unrealistic due to fabrication limitations and limited load capacities of nano-architected materials.

In the following chapters we will discuss how these composites performed under compressive mechanical loads from quasi-static to dynamic strain-rates.

QUASI-STATIC MECHANICAL TESTING

3.1 Introduction

The mechanical performance of nano-architected composites is strongly influenced by the underlying structure of both the reinforcement and matrix phase. Classically, PMCs utilize fiber- or particle- based reinforcements bound together by the polymer matrix [71]. These systems have been widely studied over the past few decades showing parameters like filler fraction [55], size [78], distribution [62], shape [55], orientation [113], and weave patterns [158] affect composite mechanical properties. Composite performance with architected reinforcement phases have not been as widely investigated especially as architected feature resolution approaches the nano-scale [132]. Further work investigating the effect of reduced reinforcement feature size has been prevented from reaching nano-scales due to fabrication limitations imposing a tradeoff between attainable feature resolutions and overall sample sizes [148]. A limited number of works have shown composite systems with micro- or nano-architected features have produced desirable mechanical properties, however these works mainly focus on quasi-static loading rates and small scale loading $\leq 4N$.

Since composites properties are heavily influenced by underlying constituent material properties, significant effort has been dedicated to relating composite compositions and material selection to measured bulk composite performance [57, 71]. Classically, composite properties can be estimated by taking a rule of mixtures combination of constituent material properties either assuming equal stress or strain distribution among the reinforcement and matrix phases [32]. These iso-stress (Reuss bound) or iso-strain (Voigt bound) serve as upper and lower bound estimates of expected composite properties. Critically, these estimations superpose reinforcement and matrix deformation neglecting coupling between these composited phases [74, 132]. Coupling between matrix and reinforcements has been shown to enhance composite stiffness and strength beyond rule of mixtures estimations [23, 32]. To account for coupled effects between matrix and reinforcement phases, rule of mixtures approaches have been further decomposed to incorporate interphase

regions which capture enhancements due to coupling at the interface between composited material phases [74]. Further refinements to rule of mixtures approaches can also be achieved to provide less conservative estimations, like the Hashin-Shtrikman bounds [72], of expected composite properties by incorporating more information from constituent material performances — shear modulus in addition to elastic modulus. Additionally, incorporation of reinforcement geometries to rule of mixtures estimations, as shown by Halpin-Tsai [70], can be used to further refine estimations of expected composite properties. These rule of mixtures approaches have been investigated under both elastic and plastic assumptions [49, 107] of deformation demonstrating the utility of this approach for predicting composites performance based upon the underlying constituents. In this work we will use the rule of mixtures to decompose measured stress-strain responses and investigate how nano-architected reinforcements contribute to collective composite performance.

In addition to composition and material selection, loading conditions also strongly influence quasi-static performance of composite materials and their constituents. Differences between tensile and compressive performance of both monolithic constituents [88] and composite configurations [52] have been demonstrated and linked to shifts in underlying deformation mechanisms resulting from changes in loading direction. Furthermore, reinforcement phases with anisotropy, like fiber [105], oriented particles [56], or architected composites [132], have been shown to induce anisotropy in their composites, emphasizing the importance of both loading direction and sample orientation on measured composite properties. Under tension, fiber based composites are particularly favorable as stiff and strong fibers accommodate high tensile loading before failure [121] as well as bridge cracks [10] and pullout of the matrix [115] as failure progresses. These tensile advantages are also why fiber composites perform well under penetration or bending testing. However, under compression, fiber reinforcements buckle/kink or nucleate failure [19] before appreciable compressive loadings are reached limiting the ability of the reinforcement to enhance composite performance. Particle composites, in contrast, perform favorably under compressive loadings, however fabrication limitations typically prevent these systems from reaching high reinforcement volume fractions [59]. Architected composites, with fully inter-connected reinforcement phases, offer improved compressive performance as they will not suffer from agglomeration and both reinforcement and matrix phases are continuous and load bearing in compression [132]. In this work we will investigate how nano-architectures deform under

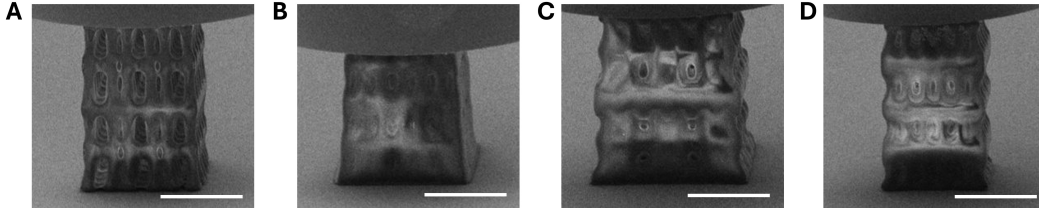


Figure 3.1: Images of unit cells extracted out of PXCT measurements and reproduced at a microscale via TPP 3D printing for compression testing. A) Open cell morphology, $F=0.73$. B) Open cell morphology, $F=0.70$. C) Closed cell morphology, $F=0.25$. D) Closed cell morphology, $F=0.23$. Scale bars: $20\mu m$.

compressive quasi-static loads and how those deformation mechanisms influence overall composite properties.

As a natural consequence of using nano-architected reinforcements for macro-scale composite materials, scalability of nano-architected properties and deformation mechanisms becomes essential to understanding observed mechanical responses. To this point, the scaling of properties from nano- and micro-scales to bulk performances are mainly computational or analytical projections of performance using scaling arguments [12] with a select few demonstrating these properties experimentally [7]. While some works have investigated the effect of micro-scale architectures on bulk composite performance, fabrication limitations have prevented these efforts from reaching nano-scales [24]. As advances in additive manufacturing enable fabrication of high volumes of architected reinforcements with increasingly smaller features, nano-architected composites provide a tremendous design space spanning geometries across scales of structural hierarchy allowing engineers to design for composite properties unburdened by the restrictions typically found in discrete fiber or particle systems [19, 59]. This work represents a first step towards realizing polymer composites with nano-architected reinforcements. In the following chapter we investigate nano-architected composite performance under quasi-static compression and indentation to elucidate the link between nano-architected deformation to an macro-scale performance.

3.2 Fabrication and Testing Methods

3.2.1 Fabrication of Samples

Samples for micro-scale compression testing, shown in fig. 3.1, were fabricated on a Nanoscribe professional GT. Silicon chips of 1 cm^2 were spin coated (10 s at 500 rpm and 30 s at 3000 rpm) with SU8 2050. The spin coated chips were soft

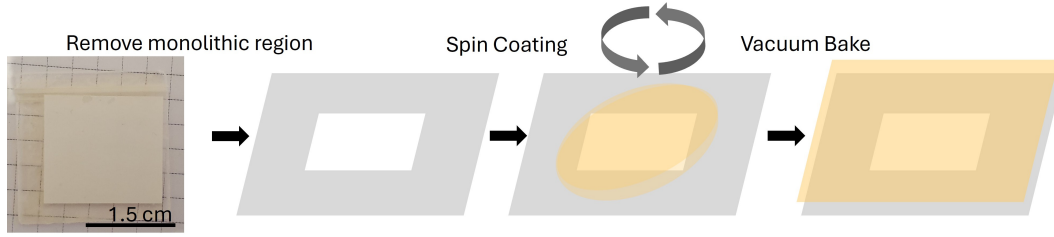


Figure 3.2: Fabrication process for indentation samples containing a single nano-architected layer starting from LIL sheet.

baked for 10 min at 65 deg C and a further 30 min at 95 deg C. 63x lens was used for the printing. The laser power was 3% (of 100 mW), the scanning speed 50 $\mu\text{m/s}$, hatching and slicing distances of 0.25 μm each. After printing the samples were post exposure baked for 3.5 min at 65 deg C and left to cool down on the hotplate for another 3 min. Once cooled down to room temperature, the samples were submerged in Propylene glycol methyl ether acetate (PGMEA) for 20 min and sequentially transferred to IPA for 1h. Finally, the samples were air dried prior to mechanical testing.

For indentation testing, thin film nano-architected composite samples were fabricated using a modified ambient molding technique, shown in fig. 3.2. Following fabrication of nano-architected reinforcements via the LIL method, nIPC and nLPC samples were fabricated by spin coating with their respective neat matrix epoxies. Samples were then hard baked overnight to create thin film samples with a bottom layer of 30–40 μm of nano-architecture and $\approx 100 - 150 \mu\text{m}$ of matrix epoxy on top. Samples were subsequently tested under quasi-static indentation to determine mechanical performance. Samples for quasi-static compression were fabricated using the standard ambient molding technique discussed in 2.3.

3.2.2 Micro-scale Compression Testing

In-situ uniaxial compression experiments were performed by the FT-NMT04 In-Situ SEM Nanoindenter (FemtoTools AG) mounted in a FEI Versa 3D dual-beam microscope. All measurements were performed using a FT-S20'000 Microforce Sensing Probe (FemtoTools AG) with a 100 μm -diameter diamond flat punch tip. The displacement rate was to result in strain rates $\dot{\epsilon} \approx 10^{-3} \text{s}^{-1}$. Force and displacement were recorded at 40 Hz and converted into true stress-strain data using sample dimensions and assuming incompressibility. These tests were carried out in collaboration with Dr. Thomas Tran and Pietro Toniolo.

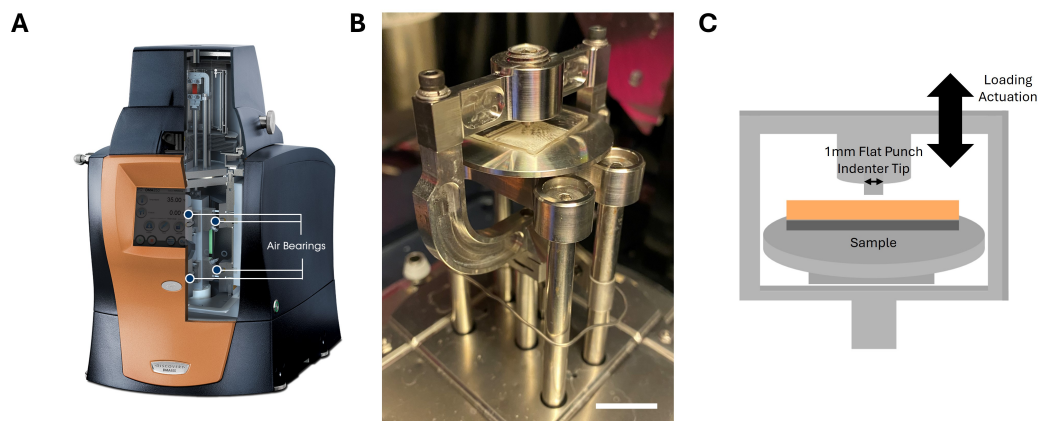


Figure 3.3: Testing setup of indentation testing. A) Dynamic mechanical analysis machine actuated with air bearings. B) Photograph of indentation testing setup with 1mm flat punch and nIPC sample. C) Schematic diagram of indentation setup showing how load is applied to the sample. Scale Bars: B) 1cm.

3.2.3 Indentation Testing

setup and testing conditions Quasi-static indentation experiments were performed using a Discovery DMA 850 (TA Instruments, New Castle, DE, USA) equipped with a 1mm diameter flat punch indenter to characterize the mechanical response of the nano-architected composites and their constituent materials, shown in fig. 3.3. All samples were prepared with nominally flat, parallel top and bottom surfaces to ensure uniform contact during indentation. Prior to testing, indentation of blank glass substrates was performed and used to eliminate substrate, machine and platen compliance during data processing. Additionally, the indenter tip was aligned normal to the sample and a small preload force (<0.1 N) was applied to establish initial contact and define the zero-displacement reference. Indentation tests were conducted in displacement control at various indenter displacement rates to obtain nominal specimen strain-rates of $10^{-3} s^{-1}$. The applied displacement and corresponding measured force were recorded continuously throughout loading and converted to stress-strain using the projected contact area of the indenter and the sample thickness.

Following indentation testing, samples were cleaved to reveal the cross-section of one of these indentation sites post-yield. The post-mortem sample was then sputter coated with 9nm of platinum using a 208HRD Cresington HV Turbo sputter coater (Cresington Scientific Instruments Ltd., Watford, UK) prior to imaging.

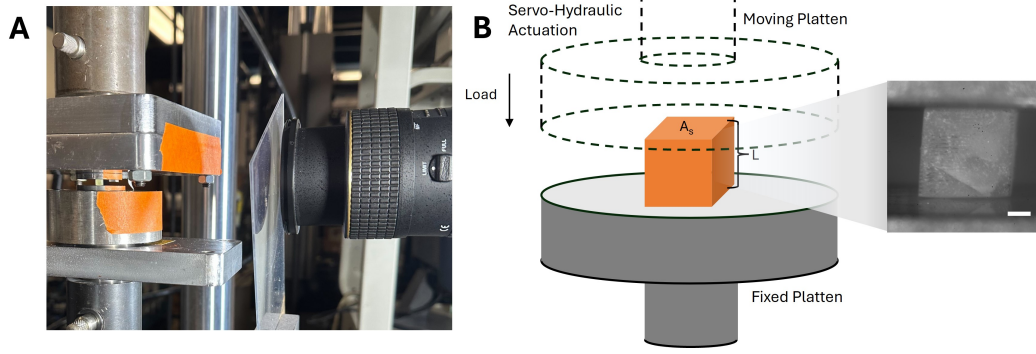


Figure 3.4: Quasi-static compression setup (MTS machine). A) Photograph of MTS machine setup with sample loaded for compression testing. B) Schematic diagram of the quasi-static testing setup showing image of a sample before testing. Scale bar: B) i) 1mm.

3.2.4 Quasi-Static Compression Testing

$$E^{Voigt} = (1 - \nu f)E_m + \nu f E_f \quad (3.1)$$

$$E^{Ruess} = \frac{E_m E_f}{(1 - \nu f)E_m + \nu f E_f} \quad (3.2)$$

Quasi-static compression test were carried out on neat matrix epoxy and 5%, 11%, and 22% fill fraction nLPC and nIPC samples on a servo-hydraulic materials testing system (MTS, model 319.25) at various overhead displacement rates to obtain nominal specimen strain-rates of $10^{-3} s^{-1}$, shown in fig. 3.4. These tests were carried out in collaboration with Dr. Barry Lawlor in the Ravichandran Lab. Deformation data was obtained from the crosshead displacement transducer and corrected to eliminate machine and platen compliance during data processing. Load cell and displacement data are then converted to stress-strain curves for mechanical analysis. The resulting stress-strain curves were used to extract stiffness and yield behavior. Two-material composite system properties, like stiffness, can be estimated by a rule of mixtures (either Voigt iso-strain or Reuss iso-stress) of the constituent components, eqs. (3.1) and (3.2).

3.3 Results and Discussion

3.3.1 Micro-scale Compression Testing

To evaluate the impact of different observed morphologies, extracted open and closed ($F = 0.70$ and $F = 0.25$) unit cells of comparable relative densities ($\rho = 0.54$ and

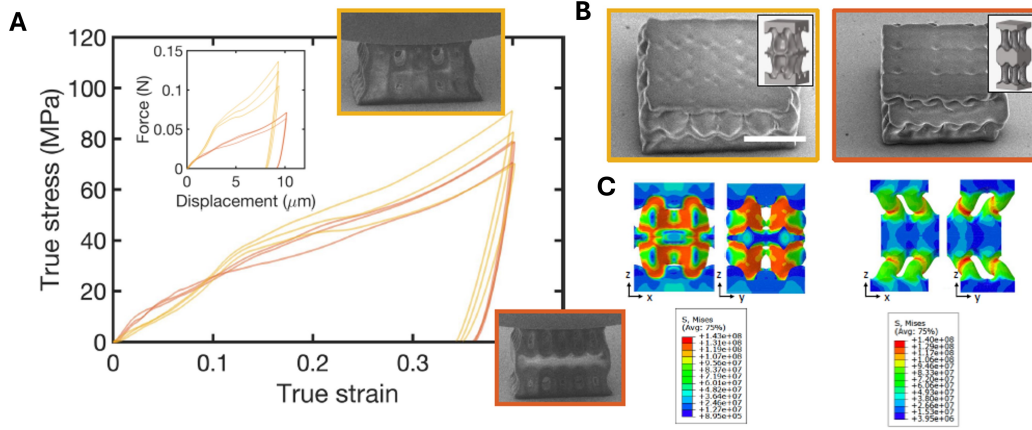


Figure 3.5: Microscale-mechanical characterization of LIL unit cells. A) Stress-strain response of open cell (orange) and closed cell (gold) morphologies of equivalent relative densities (0.58 and 0.54, respectively). B) Post-mortem images of compressed unit cells showing distributed failure (gold) and layer by layer collapse (orange). C) FEA of closed and open unit cell morphologies showing stress distribution corresponding to deformation modes observed in in-situ compression experiments. Scale bar: B) $10\mu\text{m}$.

$\rho = 0.58$) were fabricated at a micro-scale and subsequently mechanically tested under in-situ quasi-static compression ($\dot{\epsilon} = 10^{-3}$), results are shown in fig. 3.5(A-B). Under compression, open unit cells exhibited layer-by-layer collapse, typical for architected materials in compression, while closed unit cells exhibited a more stochastic and distributed collapse of the architecture. While observed in-situ deformation modes were distinct for open (layer-by-layer collapse) and closed cell morphologies (distributed failures), stress-strain responses are virtually the same. Finite element analysis (FEA) was conducted on the same extracted unit cells and compared against in-situ SEM images of compressed unit cells, confirming the experimentally observed layer-by-layer collapse and distributed failure are a result of stress concentrations and stress distribution inherent to the tested morphologies, results are shown in fig. 3.5(C). Despite widely varying morphologies and deformation modes across unit cells, similarities in compressive quasi-static stress-strain response suggest nano-architected structures produced by the LIL method are agnostic to these differences at quasi-static strain rates. As these structures are tested dynamically and incorporated into nano-architected composites, deformation modes are expected to shift away from quasi-static observations as strain rate effects and composite load redistribution influence the way nano-architected structures carry load. Although this investigation into unit cell morphology in LIL produced nano-architectures provides a baseline understanding of deformation mechanisms inherent

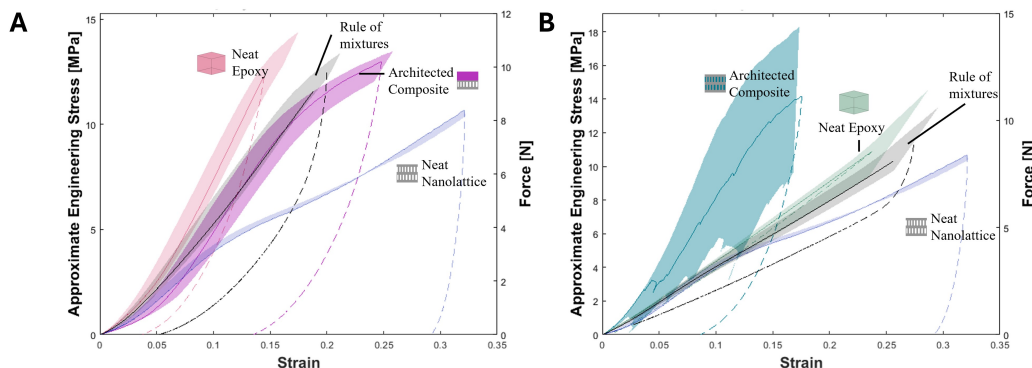


Figure 3.6: Approximate engineering stress-strain curves from indentation testing. A) nLPC and constituent material performances — neat epoxy and nano-architected responses. B) nIPC and constituent material performances — neat epoxy and nano-architected responses.

to the underlying structure, significant work is necessary to scale and translate these insights into macro-scale bulk nano-architected composite systems. Nevertheless, as nano-architected fabrication and tomographic characterization capabilities mature, real-time observation of deformation across length- and rate-scales will enable physical links between nano-scale unit cell geometry and morphology to macro-scale bulk stress-strain performance.

3.3.2 Indentation Testing

Approximate engineering stress-strain performances are shown in fig. 3.6 for quasi-static indentation testing of both nIPC and nLPC composites and their constituent materials. For nLPC samples, shown in fig. 3.6(A), composite responses follow a rule of mixtures combination of neat constituent performances. In contrast, nIPC samples, shown in fig. 3.6(B), exhibit a better than rule of mixtures response where the composite performance is unbound by the neat constituent material performances. Across nIPC indentation tests, a wide variety of stress-strain behaviors were observed. While some samples exhibited a smooth linear elastic region followed by a non-linear transition towards yield, many samples exhibited sharp drops in stress corresponding to localized failure — driven by either cracking or cellular collapse. To further understand the observed stress-strain performance, indentation samples were cleaved and mounted on SEM stubs and indentation sites were examined via cross-sectional SEM.

Images of post-mortem nIPC indentation samples are shown in fig. 3.7. Examination of the edge of these indentation sites show that interpenetrated nano-architectures

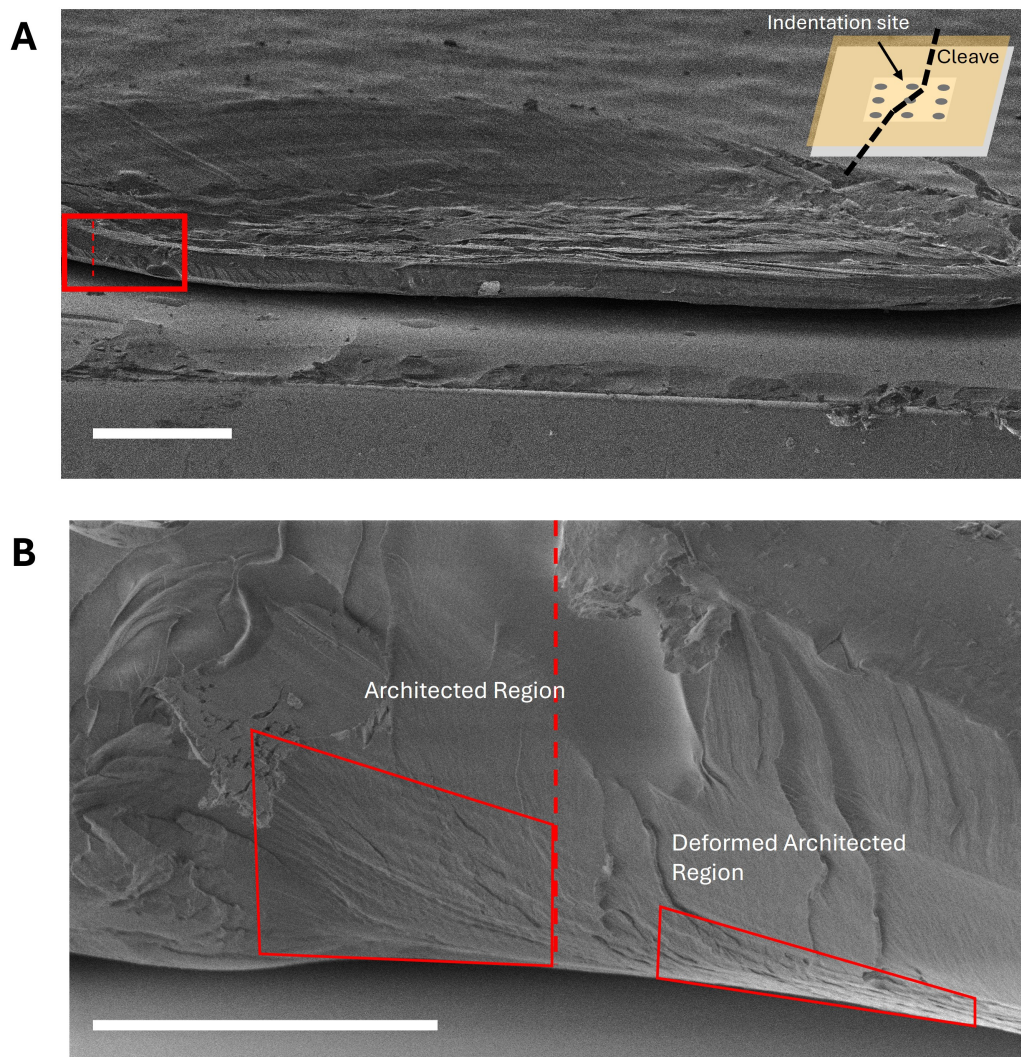


Figure 3.7: Post-mortem cross-sectional SEM images of a cleaved indentation site. A) Indentation site. B) Close up SEM image of deformed underlying architecture showing the difference between architecture below and adjacent to the indentation. Scale bars: A) $100\mu\text{m}$. B) $30\mu\text{m}$.

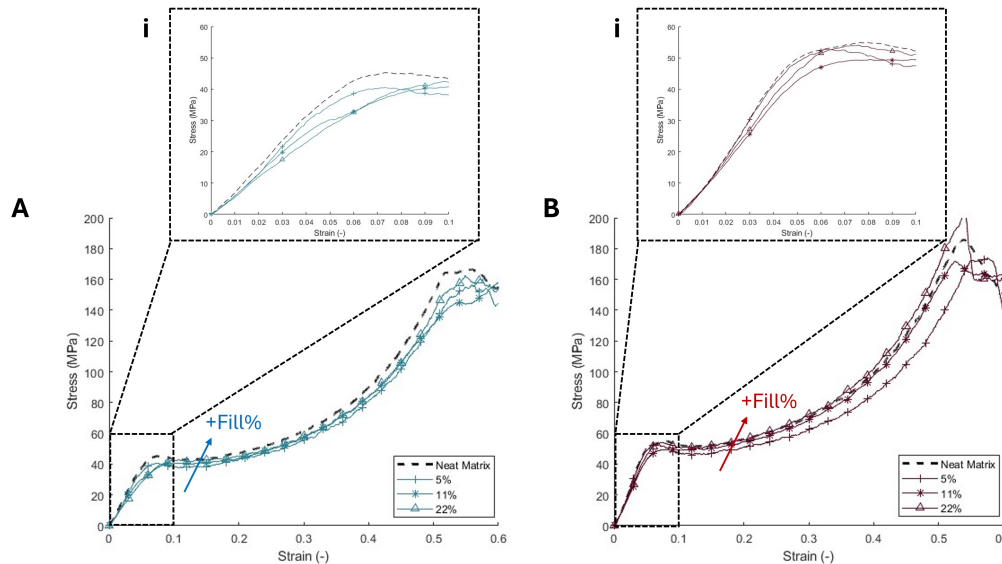


Figure 3.8: Quasi-static compression stress-strain responses. A) nIPC responses for neat matrix epoxy, 5%, 11%, and 22% fill fractions. i) Close up view of elastic and yield behavior. B) nLPC responses for neat matrix epoxy, 5%, 11%, and 22% fill fractions. i) Close up view of elastic and yield behavior.

undergo significant plastic deformation underneath the flat punch indenter. However, directly adjacent to the indentation site, architected regions show a tapered region of deformed architecture indicating that the nIPC composite indentation response induced cellular collapse under the indenter while also deforming nano-architectures outside the projected flat-punch area. The combination of stress-strain data and post-mortem imaging suggests nIPC configurations offer enhanced stiffness and strength through collective deformation of the nano-architecture and the matrix epoxy interpenetrated into the architecture. Since these tests were carried out under indentation rather than compression, boundary effects may also play a role in the observed enhancement to stress-strain performance as nIPC nano-architectures distribute deformation to the areas surrounding the indenter, not just under the flat punch.

3.3.3 Quasi-Static Compression Testing

To isolate the compressive response in nano-architected composite samples, quasi-static compression tests were conducted on both nIPC and nLPC samples across fill fractions (5%-22%). Stress-strain performances for nano-composites and their neat matrix epoxies are shown in fig. 3.8. Inset images, fig. 3.8(A,B)(i), show a close up view of the elastic and non-linear transition regions of the stress-strain curves used to extract mechanical properties. Extracted quasi-static mechanical properties

Sample	Stiffness (MPa)	Yield Stress (MPa)	Yield Strain (-)	Plateau Stress (MPa)
Neat nLPC epoxy	1049.7	54.26	0.07	51.82
5% nLPC	1060.5	52.32	0.07	46.76
11% nLPC	886.2	49.26	0.08	49.26
22% nLPC	937.5	53.55	0.08	50.97
Neat nIPC epoxy	808.1	45.16	0.08	42.98
5% nIPC	735.8	40.18	0.07	37.85
11% nIPC	692.4	37.54	0.07	40.18
22% nIPC	602.3	41.11	0.09	42.14

Table 3.1: Table of mechanical properties extracted from quasi-static compression testing on MTS machine

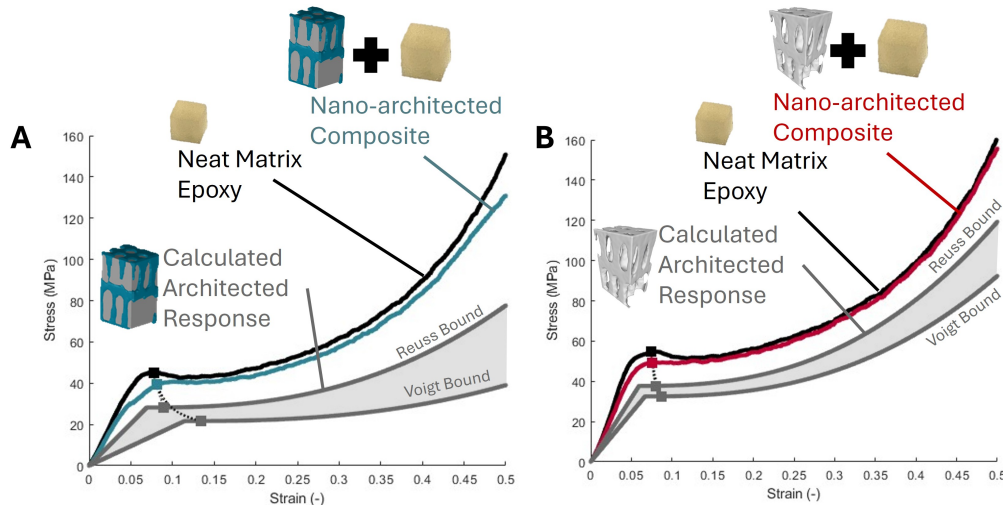


Figure 3.9: Extraction of nano-architected quasi-static stress strain response for 11% filler fraction systems assuming a rule of mixtures combination of constituent responses. A) nIPC system. B) nLPC system.

are shown in table 3.1. Stiffnesses were extracted by taking the slope of the linear region and yield was determined using a 2% strain offset. Plateau stresses were then determined by taking the average stress over a 0.1 strain window immediately following yield. Notably, comparing extracted nano-architected composite properties to their respective neat matrix epoxy constituents shows tested nano-architected composites are weaker and more compliant across volume fill fractions.

Using an iso-stress (Reuss) and iso-strain (Voigt) rule of mixtures bound, nIPC, nLPC and their neat matrix epoxy responses are used to extract a range of approximate nano-architected responses. Calculated architected response are plotted against measured composite and matrix epoxy responses in fig. 3.9. By rule of

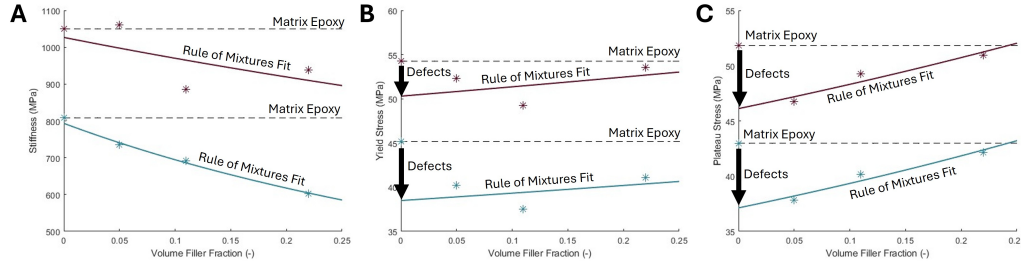


Figure 3.10: Plots show a rule of mixtures fit of nano-architected composite performance across volume fraction for: A) Stiffness. B) Yield Stress. C) Plateau Stress. Extracted mechanical properties and fitted rule of mixtures are shown for both nIPC system (blue) and nLPC system (red). Mechanical properties for neat epoxies are extrapolated from fitted data showing a defect mediated decrease from the measured neat epoxy value.

Ruess Rule of Mixtures	nLPC Matrix	nLPC Nano-architecture	nIPC Matrix	nIPC Nano-architecture
Stiffness (MPa)	1026.7	648.2	793.4	327.3
Yield Stress (MPa)	50.30	63.33	38.49	48.87
Plateau Stress (MPa)	46.11	84.65	37.13	84.99

Table 3.2: Table of mechanical properties determined from Reuss rule of mixtures fit of mechanical properties of nano-architected composites across filler volume fractions.

mixtures, nano-architected reinforcements for both nIPC and nLPC configurations are calculated as weaker and more compliant than the surrounding matrix epoxy. These calculations, however, do no account for matrix defects observed in nano-architected composite samples but not observed in neat matrix epoxy samples.

To account for defects introduced by the ambient molding of nano-architected composites, a Reuss (iso-stress) rule of mixtures was fitted to the extracted mechanical properties using a least-squares regression across filler volume fractions, results are shown in fig. 3.10. Fitted rule of mixtures stiffness values show good agreement with stiffnesses extracted from measured neat epoxy responses. Fitted strengths, for both yield and plateau stress, were lower than strengths extracted from measured neat epoxy responses. This discrepancy is the result of matrix voids causing stress concentrations within the surrounding matrix causing premature failure and lower extracted strengths. By accounting these defects, the fitted rule of mixtures shows nano-architected regions are more compliant but stronger than the matrix epoxy containing defects. Fitted stiffnesses and strengths of the matrix and reinforcing nano-architecture for nIPC and nLPC systems are tabulated in table 3.2.

Comparing the calculated nLPC nano-architecture strengths for both rule of mixtures approaches to reported strengths of LIL nano-architectures (42.40 ± 5.55 MPa [81]) and SU-8 (108.4 ± 10.0 MPa [150]) shows these two approaches span a range of plausible strengths attributable to the underlying nano-architecture. Performing rule of mixtures calculations assuming defects do not influence measured composite strengths underestimates nano-architected strengths while fitting the rule of mixtures to nano-architected responses with defects approximates nano-architected strength to fall between the reported strength of LIL structures and strength of SU-8 micro-pillars (constituent photo-polymer). Full decoupling of the effects of defects and nano-architectures in nano-architected composites will require either revisions to the fabrication process to eliminate defects or full field imaging capable of measuring stress and strain states present at the nano-architected scale.

3.4 Summary and Conclusions

In this chapter, we showed how fabricated nano-architected composites with different configurations of nano-architected reinforcements (nIPC and nLPC) perform under quasi-static loading. To summarize the key takeaways from the quasi-static testing:

- Micro-scale quasi-static compression testing showed open and closed cell LIL architectures (polymer reinforcement only) possess similar stress strain responses despite differing deformation modes. These results are confirmed through agreement between experimental and computational deformation modes and stress-strain responses.
- Quasi-static flat punch indentation testing of nano-architected composite samples (nLPC and nIPC) shows interpenetrated nano-architected composite (nIPC) configurations exhibit a better than rule of mixtures response. Post-mortem SEM imaging shows indentation sites with enhanced performance concentrate deformation to architected regions.
- Quasi-static compression testing of nano-architected composite samples (nLPC and nIPC) shows that both composite configurations exhibit stress strain responses that are similar to their respective neat matrix epoxy response. In both cases the neat matrix epoxy is slightly stronger and stiffer than the composite samples.
- Applying the rule of mixtures by either directly solving for properties or by fitting performances across volume fraction reveals the composite fabrication

introduces matrix defects which inhibit the matrix strength contribution to composite performance. Accounting for these defects, we show good agreement between rule of mixtures estimations of nano-architected performance, and reported literature values of equivalent architected systems.

These quasi-static test elucidate the role of nano-architected reinforcements in composite deformation and performance. In section 3.3.1 we fabricated and compressed unit cells of LIL nano-architecture showing that despite differences in observed unit cell morphologies and deformation modes, stress-strain performance is similar in unit cells possessing the same relative density. Unit cell deformation was also observed in post-mortem images of indentation testing in section 3.3.2. Indentation tests showed that nIPC configurations, possessing interpenetrated nano-architectures, exhibit better than rule of mixture performance while nLPCs performed very similar to rule of mixtures estimations of composite performance. Under compression, results, shown in section 3.3.3, both nIPC and nLPC samples possessed significant defects which caused composites to perform worse than neat epoxy samples without defects. Rule of mixtures calculations of architected reinforcement performance without accounting for effects serve as a lower bound estimate of nano-architected contributions to composite performance. Performing rule of mixtures fits to nIPC and nLPC performances revealed the effect of defects on neat matrix epoxy strengths. Extrapolated nano-architected strengths from these rule of mixtures fits fall between reported performance of other LIL nano-architectures and base SU-8 material properties.

These quasi-static investigations of nano-architected composite responses serve as baseline of understanding for mechanical performance. Broadly, these tests show the rule of mixtures is an effective estimate of quasi-static compression performance in nano-architected composites. Importantly, defects in nano-architected composites play a large role in mitigating measured composite performances. As loading conditions are shifted to dynamic regimes the impact of these defects is expected to worsen as dynamic effects and stress concentrations will cause failures to propagate within composite samples. Decoupling the effect of these defects from nano-architected composite performance is essential to understanding the advantages offered by nano-architected reinforcements. Following chapters will detail how cutting edge in-situ imaging methods combined with revisions to nano-composite fabrication methods enable isolation of deformation linked to enhanced nano-architected composite performances under dynamic loading.

IN-SITU HIGH-RATE COMPRESSION EXPERIMENTS

4.1 Introduction

The characterization of nano-architected composites under high strain-rate loading is essential for determining their viability as structural materials particularly when applications require high energy absorptions. Relative to quasi-static, when composites are loaded at high strain-rates underlying deformation modes shift as rate-dependent material properties and failure mechanisms affect the measured response [131]. For PMCs and polymer-based architected materials alike these effects are particularly pronounced due to the inherent rate-sensitivity of polymer materials [132]. Dynamic compression testing of classical PMCs has been widely investigated over the past few decades in both fiber- and particle- reinforced systems [9, 22, 34, 44, 66, 78, 79, 86, 92, 95, 100, 102, 104, 108, 110, 111, 113, 119, 124, 137, 142]. For particle-reinforced PMCs, mechanical testing reveals underlying deformation characterized by interfacial debonding [55, 108], matrix failure [137, 142], particle-induced stress concentrations [92], and void growth and compaction [124]. Fiber-reinforced systems exhibit fiber kinking [19], fiber–matrix debonding [63, 95, 119, 145], and delamination [21, 109, 113, 158]. These mechanisms, while heavily affected by the rate sensitivity of the underlying constituent materials, is also heavily dependent upon composite fabrication method, defects, reinforcement type, amount, and distribution [19, 40]. This is by no means an exhaustive review of factors that may influence measured mechanical performances as there are a wide variety of loading, sample, and environmental conditions that may also play a role. Nevertheless, studies of dynamic compression of classical PMCs emphasize the importance of linking underlying deformation and failure modes to measured dynamic properties. In this chapter, we will use in-situ high-speed imaging as well as post-mortem scanning electron microscopy (SEM) to contextualize recorded stress-strain data linking observed mechanical performances to observed underlying mechanisms.

While there are a wide variety of works investigating the dynamic compressive behavior of classical polymer matrix composites, the dynamic compressive response of architected composite materials, particularly nano-architected composites, is not

as well explored [132]. In contrast to classical polymer matrix composites, architected PMCs possess interconnected networks of load bearing reinforcements. Consequently, architected PMC deformation is governed by modes available to the reinforcement structures as well as the compatibility of that deformation with the surrounding matrix. Similarly to classical PMCs, factors like geometry, constituent materials, coupling between reinforcements and architecture, as well as fabrication methods may influence observed deformation modes and measured mechanical properties [132]. While dynamic compressions of architected structures have been explored for standalone large structures [146], exploration of bare nano-architectures layered into a composite have not. Furthermore, while some have investigated the dynamic compressive response of interpenetrated architected composites [131], those with interpenetrated nano-architected reinforcements have not been reported. Due to fabrication limitations, macro-scale testing of nano-architected materials has been very sparsely investigated - particularly at high loads and high energies. While the novelty of incorporating architected reinforcements possessing a large separation of scales (100s nm features to mm sample size) into composites presents a unique opportunity to investigate enhanced mechanical performances, it also presents a significant challenge in characterizing underlying deformation across scales. In this chapter we investigate how varying volume fill fractions and distribution in two separate configurations of nano-architected reinforcements affects the measured dynamic compressive composite performance. In conjunction with in-situ observations of underlying deformation modes, these performances provide a baseline understanding of the advantages and disadvantages of incorporating nano-architectures into composite materials comparing them against classical PMC performances reported in literature.

4.2 Samples and Testing Methodology

4.2.1 Specimen Fabrication

Nano-architected samples were fabricated according to the ambient molding method discussed in section 2.3 in both nIPC and nLPC configurations for filler volume fractions 0% (neat matrix epoxy), 5%, 11%, and 22%. Figure 2.6 shows a sample lineup of nIPC and nLPC samples across fill fractions fabricated for split-Hopkinson pressure bar (SHPB) testing. Additionally, 22% nIPCs with thick nano-architectures were fabricated using the same ambient molding process and reinforcements fabricated according to section 2.2.3. To obtain comparable stress-strain responses with classical PMC systems, 22% volume fraction carbon fiber composite samples were

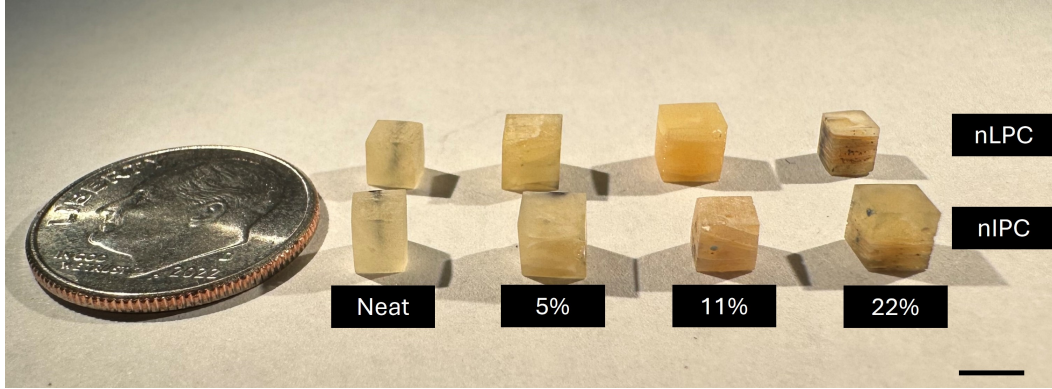


Figure 4.1: Sample lineup of neat matrix epoxy, nLPC and nIPC samples across filler fractions tested under split-Hopkinson pressure bar compression. Scale bar: 4mm.

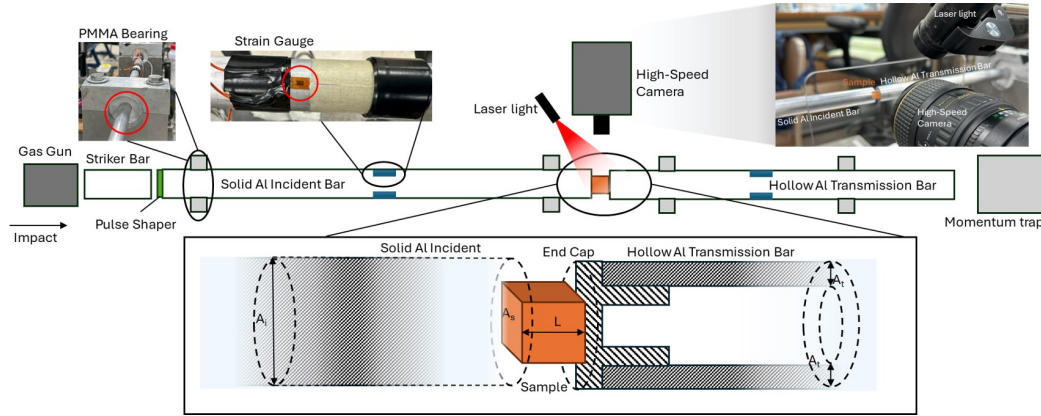


Figure 4.2: Schematic diagram of split-Hopkinson pressure bar setup.

also fabricated using the ambient molding method. Carbon fiber prepreg 3K 2x2 twill weaves were obtained from Fibreglast Developments Corporation (Brookville, Ohio, USA) and used for composite fabrication with the same ambient molding process used to fabricate nano-architected composite samples — replacing LIL produced nano-architected sheets as the reinforcement.

4.2.2 High Strain-Rate Testing Methodology

High strain-rate mechanical compression nano-architected composites was performed using a split-Hopkinson Pressure Bar (SHPB) apparatus at $\approx 4 \times 10^3 s^{-1}$ [123]. SHPB test were carried out in collaboration with Dr. Bary Lawlor in the Ravichandran Lab. Figure 2 shows a schematic diagram of the SHPB setup used in this work consisting of a solid striker (7075 aluminum), solid incident (7075 aluminum), and hollow transmitted (6061 aluminum) bars with Micro-measurements

EA-06-062AQA-350/LE strain gauges (1/2 bridge circuit) attached to both the incident and transmitted bars. Striker, incident, and transmitted bars measured 19.05mm in diameter and 0.45m, 1.83m, and 1.83m in length, respectively. Samples were mounted between incident and transmitted bars with a thin layer of petroleum jelly such that the planar reinforcement regions are oriented parallel with the bar end surfaces and orthogonal to the impact direction. Gauge data was recorded via Vishay 2310B signal conditioning amplifier and 2.5 GHz Tektronix DPO 3014 digital oscilloscope and analyzed with eqs. (4.1) to (4.3) according to conventional one-wave SHPB analysis with a hollow transmitted bar to obtain the stress-strain responses [27].

$$\epsilon(t) = \frac{c_0}{L} \left(1 - \frac{A_i}{A_t}\right) \int_0^t \epsilon_i(\tau) \partial\tau - \frac{c_0}{L} \left(1 + \frac{A_i}{A_t}\right) \int_0^t \epsilon_r(\tau) \partial\tau \quad (4.1)$$

$$\sigma(t) = \frac{A_0}{A_s} E \epsilon_t(t) \quad (4.2)$$

$$\dot{\epsilon}(t) = -\frac{2c_0}{L} \epsilon_r(t) \quad (4.3)$$

Examples of outputted strain gauge data are seen in fig. 4.3(A). Extracted strain-time and stress-time data using eqs. (4.1) and (4.2) are shown in fig. 4.3(B-D), respectively. Force balance between input and transmitted bars is plotted in fig. 4.3(E) showing equilibrium conditions are satisfied throughout the compressive response. Stress and strain time histories are parametrically plotted with respect to time to attain stress-strain curves. Recorded SHPB stress-strain responses of tested composites and neat matrix epoxies are shown in section 4.3.

4.2.3 In-situ High-speed Image Correlation

During SHPB experiments, a Shimadzu HPV-X2 camera with a 100 mm Tokina AT-X Pro lens illuminated with a Cavitar Cavilux Smart Laser (20ns incoherent pulses) was used to capture in-situ high-speed video of the dynamic compression event (128 images, 500,000 fps). Oscilloscope delays (170-175 μs) were adjusted such that image acquisition and compressive loading begin simultaneously triggered by the incident strain gauge signal. In-situ images were then correlated to compressive strains by matching image time stamps and numbers to strain-time data.

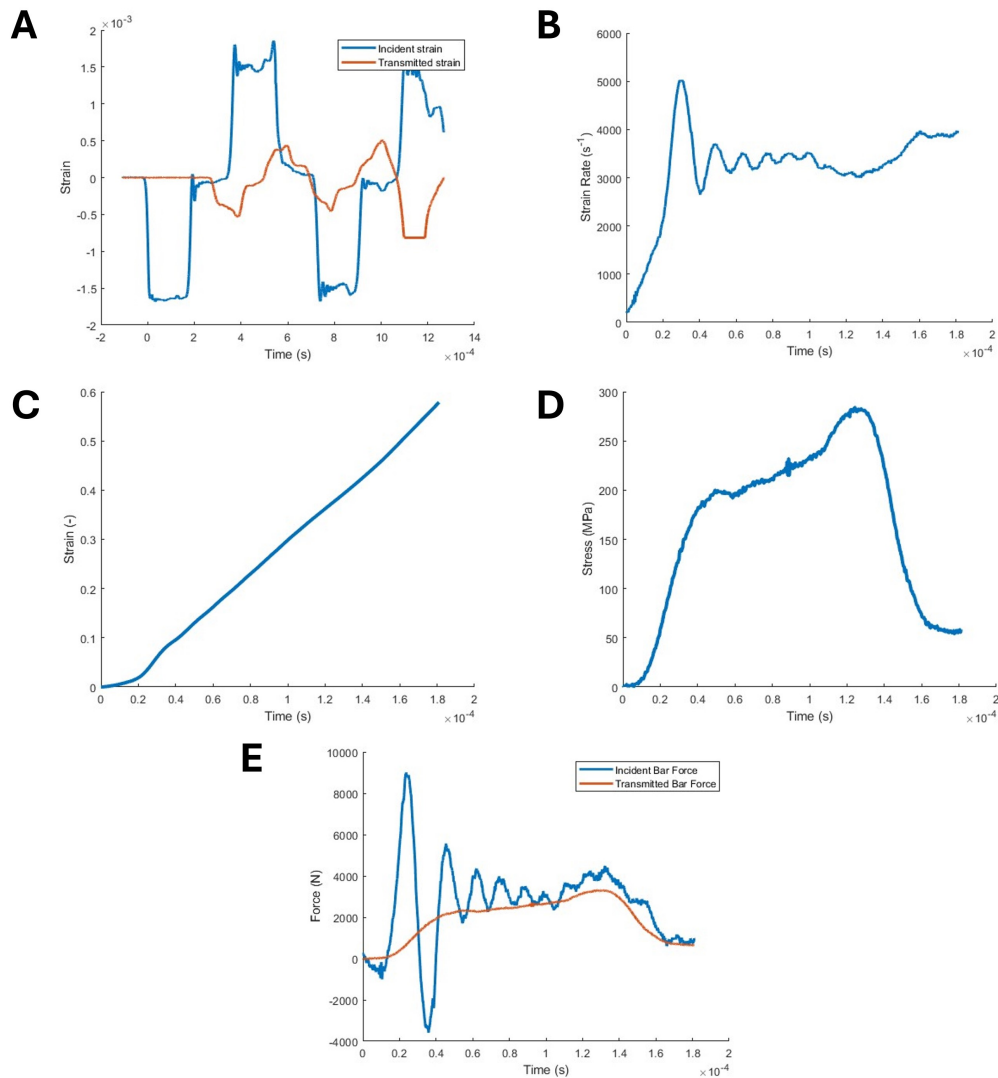


Figure 4.3: Representative split-Hopkinson pressure bar waveform analysis curves. A) Strain gauge responses calculated from oscilloscope signals. B) Strain rate time response. C) Strain time response. D) Stress time response. E) Force equilibrium between incident and transmitted bars.

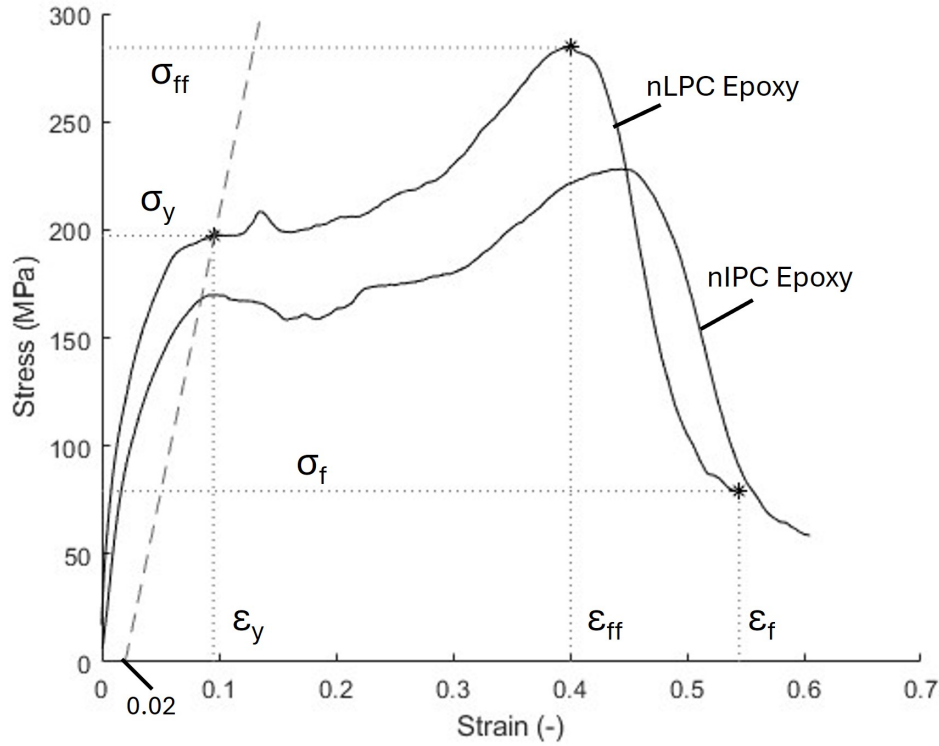


Figure 4.4: Representative split-Hopkinson pressure bar stress-strain responses of neat epoxy with key points yield (σ_y, ϵ_y), first failure ($\sigma_{ff}, \epsilon_{ff}$), and failure (σ_f, ϵ_f) identified.

4.3 Results and Discussion

4.3.1 High Strain-Rate Experiments on nIPCs and nLPCs

Representative stress-strain curves for SHPB compressions of neat matrix epoxy are shown in fig. 4.4. Figure 4.4 shows yield (σ_y, ϵ_y), first failure ($\sigma_{ff}, \epsilon_{ff}$), and failure (σ_f, ϵ_f) points taken from the nLPC neat epoxy response. These points will be used in the following sections for comparison of in-situ images of dynamic compressive responses. Here, yield points were determined base upon a 2% strain offset. Figure 4.5 shows the complete set of neat matrix epoxy responses recorded from SHPB testing for (A) nIPC and (B) nLPC systems with representative curves highlighted in black. These representative neat epoxy responses are used as a baseline reference to which nano-architected composite responses are compared. Overall, neat epoxy responses, shown in fig. 4.5, exhibit typical stress-strain behavior for polymers under compression with deformation. Generally these responses are characterized by the following deformation sequence: (1) elasticity, (2) yielding, (3) stress plateau, (4) strain hardening and barreling, and (5) catastrophic failure.

Sample	Stiffness (GPa)	Yield Stress (MPa)	Yield Strain (-)	Plateau Stress (MPa)
Neat nLPC epoxy	2.00	197.27	0.10	198.96
5% nLPC	2.14	122.33	0.12	-
11% nLPC	2.09	154.40	0.08	-
22% nLPC	1.43	138.74	0.10	-
Neat nIPC epoxy	1.86	169.74	0.10	161.74
5% nIPC	1.97	144.18	0.09	-
11% nIPC	1.86	217.93	0.13	217.40
22% nIPC	1.43	205.10	0.14	211.84
22% thick nIPC	1.89	181.08	0.13	175.16
22% Carbon Fiber	3.18	190.17	0.08	-

Table 4.1: Table of mechanical properties extracted from dynamic compression testing on SHPB apparatus

Sample	First Failure Stress (MPa)	First Failure Strain (-)	Failure Stress (MPa)	Failure Strain (-)
Neat nLPC epoxy	284.30	0.40	79.00	0.54
5% nLPC	121.95	0.12	25.57	0.34
11% nLPC	154.23	0.09	28.94	0.32
22% nLPC	124.99	0.20	45.88	0.34
Neat nIPC epoxy	227.69	0.45	58.54	0.61
5% nIPC	141.96	0.10	24.01	0.29
11% nIPC	219.11	0.31	105.70	0.45
22% nIPC	288.52	0.41	67.52	0.56
22% thick nIPC	169.45	0.46	78.55	0.59
22% Carbon Fiber	185.63	0.12	5.20	0.35

Table 4.2: Table of mechanical properties extracted from dynamic compression testing on SHPB apparatus

nIPC samples with filler volume fractions ranging from 5% to 22% were tested under SHPB loading and their stress-strain responses are shown in fig. 4.6. nIPC responses are plotted against neat matrix epoxy performance (black - -) and all recorded responses are shown in grey while representative curves are highlighted in blue. In-situ high speed images of samples under SHPB loading corresponding to representative stress-strain curves are shown in fig. 4.7. Across the tested volume fill fractions, nIPCs exhibited a wide range of responses ranging from early catastrophic failure to enhanced performance depending upon nano-architected fill fractions and presence of defects. Extracted mechanical properties of nIPC samples are collected and reported in tables 4.1 and 4.2. Increasing nano-architected volume fractions in

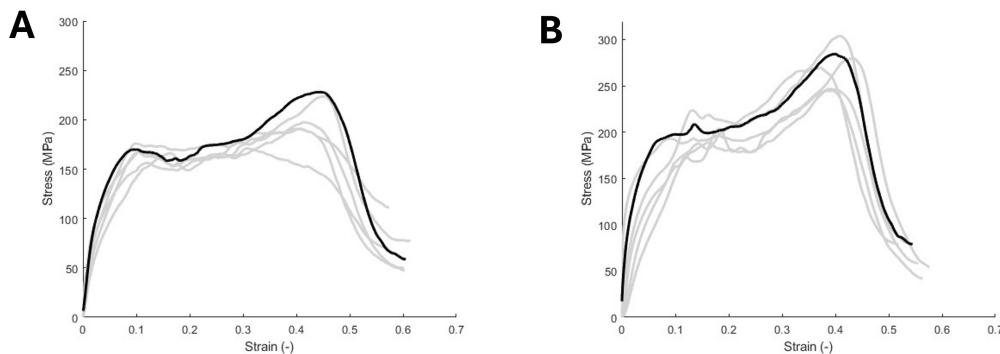


Figure 4.5: Split-Hopkinson pressure bar stress-strain responses of neat epoxy with representative curves shown in black. All responses are reported (grey). A) nIPC neat matrix epoxy responses. B) nLPC neat matrix epoxy responses.

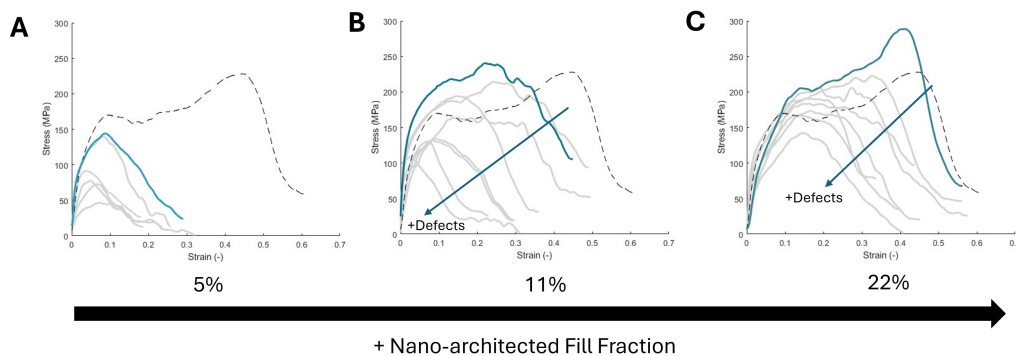


Figure 4.6: Split-Hopkinson pressure bar stress-strain responses of nIPCs across fill fractions: A) 5%. B) 11%. C) 22%. Representative curves used for mechanical properties (blue), compared against neat matrix epoxy responses (black - -) and all responses are reported (grey). B-C) Grey nIPC responses represent defect affected performances.

nIPC samples from 5% to 11% results in a 74 MPa higher yield stress and increasing volume fractions from 5% to 22% increases yield stress by 61 MPa. Both 11% and 22% nano-architected volume fractions outperformed the neat matrix epoxy system yield stresses by 28% and 21%, respectively. Additionally the 22% nIPC stress at initiation of catastrophic failure is 147 MPa higher than the 5% sample and 61 MPa higher than that of the neat matrix epoxy (27% increase). Overall, increasing nIPC fill fractions resulted in improved stress-strain performance.

At 5% volume fractions, shown in fig. 4.6(A), nIPCs exhibit early catastrophic failures characterized by decreases in stress-strain curves at stresses and strains equal to or below the yield point of the neat matrix epoxy. These early failure points in the stress-strain data correspond to cracking events identified on in-situ images by

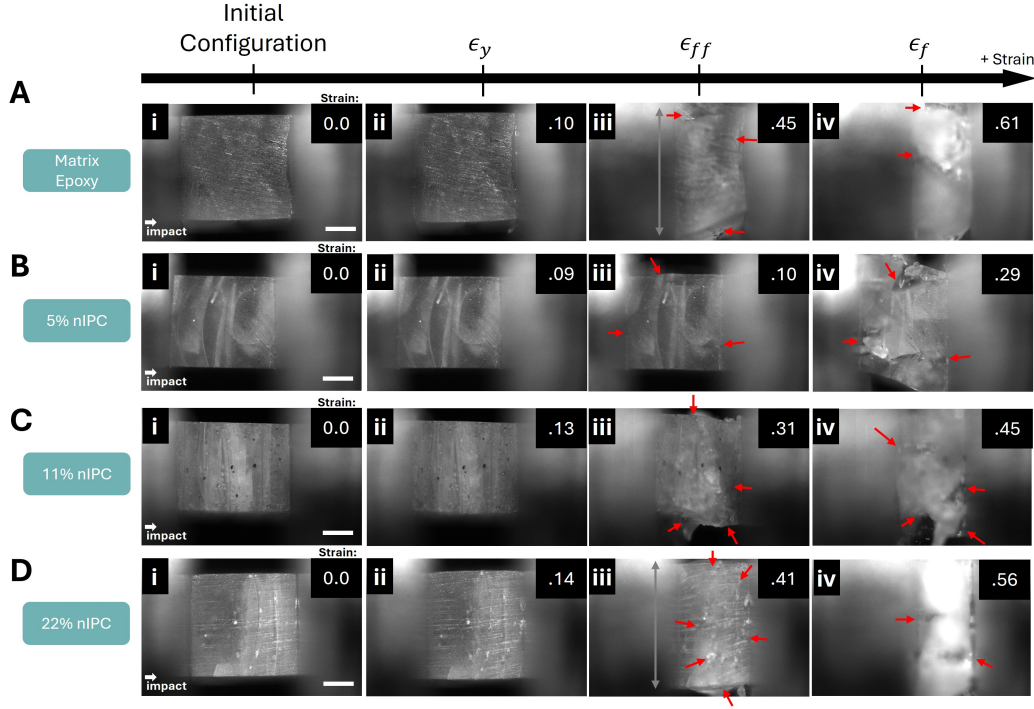


Figure 4.7: In-situ high speed images of split-Hopkinson pressure bar compression of nIPCs across fill fractions: (A) neat matrix epoxy, (B) 5%, (C) 11%, and (D) 22% fill fractions. Failure points are highlighted by red arrows and grey arrows show lateral expansion from Poisson effect. Scale Bars: 1mm.

red arrows in fig. 4.7(B-iii). In contrast to neat epoxy responses, 5% nIPCs possess early cracking events which propagate quickly around features corresponding to nano-architected regions. These early catastrophic failures may be the result of stress concentrations caused by defects introduced by the ambient molding process, however, the proximity of these failure events to the nano-architected regions suggests nano-architectures may also play a role in inducing these early failures.

Increasing nIPC volume fractions to 11%, shown in fig. 4.6(B), resulted in the partial mitigation of these early catastrophic failures with some samples exhibiting yield and plateau behavior exceeding that of the neat matrix epoxy. While early catastrophic failures were still observed in some 11% nIPCs, in-situ images, shown in fig. 4.7, suggest enhanced nano-architected composite performance is the result of a high amount of local cracking failures building up within the sample prior to the onset of catastrophic failure (sharp decrease in stress-strain response). Similarly to 5% nIPC cracking events, these local failures accumulate near architected regions, however, in the case of enhanced performance, these failure events are prevented from propagating to catastrophic failure. This suggests that a critical amount of nano-architecture

is required to enable local crack arrest. The spread of measured performances in 11% nIPCs is a result of the variable distribution of nano-architected regions in fabricated samples with some possessing concentrations of nano-architected regions capable of enabling arrest mechanisms and some with nano-architectures too sparsely distributed to prevent catastrophic crack propagation. Figure 4.7(C) shows an example of a 11% nIPC with a high concentration of nano-architecture in the middle of the sample capable of enabling local crack arrest. Figure 4.7(C-iii) shows the accumulation of local cracking near these concentrated nano-architectures prior to catastrophic failure.

Raising nIPC fill fractions to 22%, shown in fig. 4.6(C), also shows a range of stress-strain responses but, in contrast to 11% nIPCs, these responses tend to exhibit enhanced performance rather than early catastrophic failure. Notably, 22% nIPCs possess a combination of elevated stress relative to neat epoxy as well as failure strains approaching that of the neat epoxy. Looking at the in-situ images of 22% nIPC deformation, shown in fig. 4.7(D), reveals localized cracking accumulating throughout the sample, similar to 11% nIPCs, but in this case, these local cracking events do not inhibit lateral expansion and barreling resulting in high failure strains. Previously, nIPC responses at lower volume fractions resulted in a change in deformation modes relative to the neat matrix epoxy where responses were largely characterized by cracking inhibiting lateral expansion within the samples. For 22% nIPCs, global sample deformation modes mimic that of the neat matrix epoxy while, locally, cracking mechanisms characteristic of nIPC samples across fill fractions are distributed throughout the sample. While cracking events are typically associated with failure, in these cases, they act as a competing mechanism against matrix polymer deformation. When these cracking events are arrested, the polymer matrix is forced into higher states of stress as the arrested cracks prevent polymer regions from deforming collectively in response to loading. Elevated stress-strain responses are attributed to this complex competition between localized cracking and polymer deformation mechanisms. Notably, this competition is enabled by interpenetrated nano-architected reinforcements which delay catastrophic failure and prevent cracking events from coalescing.

nLPC stress-strain performance is shown in fig. 4.8 for nano-architected volume fill fractions varied from 5% to 22%. nLPC responses are plotted against neat matrix epoxy performance (black - -) and all recorded responses are shown in grey while representative curves are highlighted in red. In-situ high speed images of

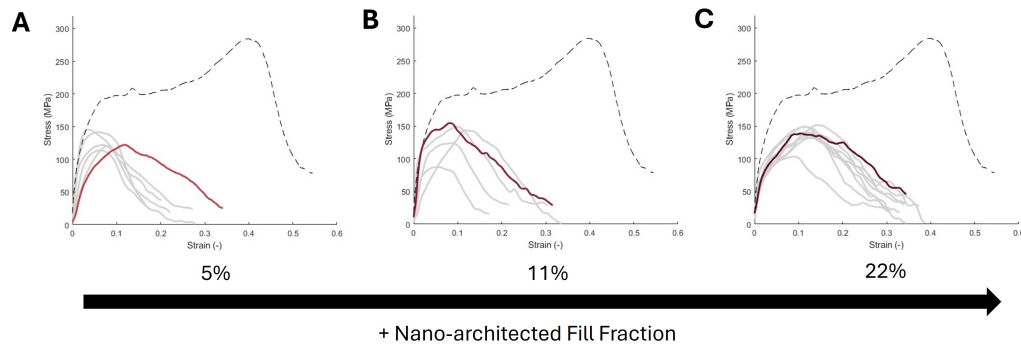


Figure 4.8: Split-Hopkinson pressure bar stress-strain responses of nLPCs across fill fractions: A) 5%. B) 11%. C) 22%. Representative curves used for mechanical properties (red), compared against neat matrix epoxy responses (black - -) and all responses are reported (grey).

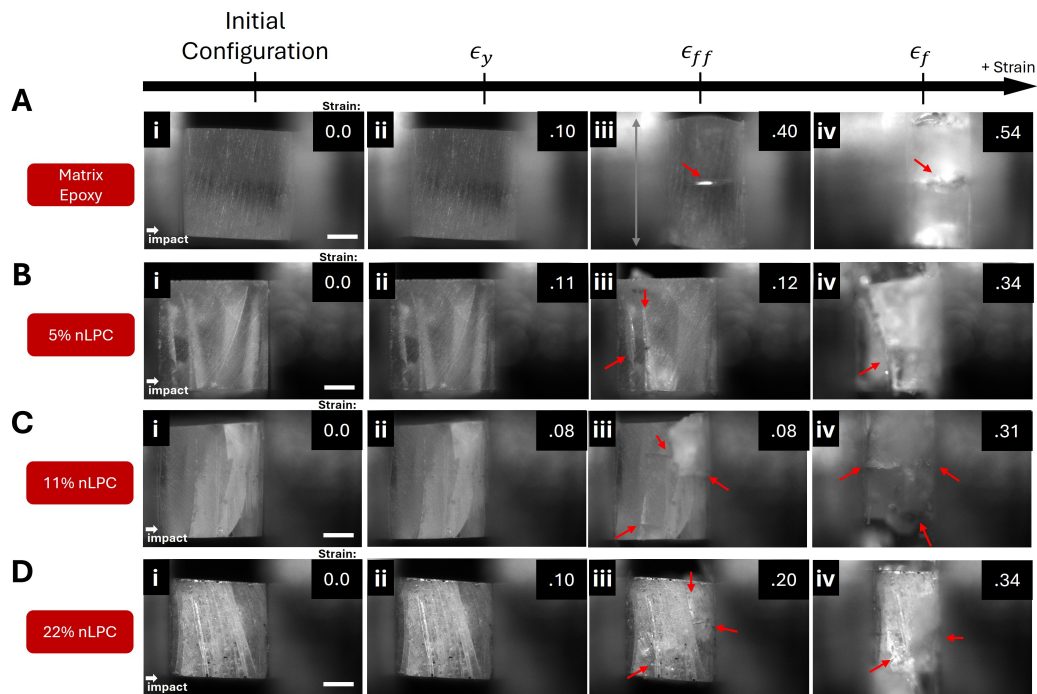


Figure 4.9: In-situ high speed images of split-Hopkinson pressure bar compression of nLPCs across fill fractions: (A) neat matrix epoxy, (B) 5%, (C) 11%, and (D) 22% fill fractions. Failure points are highlighted by red arrows and grey arrows show lateral expansion from Poisson effect. Scale Bars: 1mm.

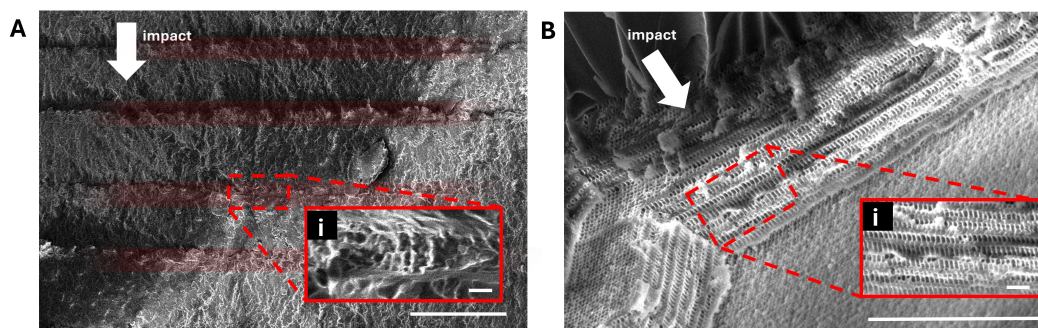


Figure 4.10: Post-mortem SEM images of particles collected from split-Hopkinson pressure bar compression of (A) nIPC and (B) nLPC samples. A) nIPC sample fragment with nano-architected regions highlighted in red. i) Closeup SEM image of nano-architected region with localized deformation and damage. B) nLPC sample fragment containing void nano-architected region with large planar regions of fracture. i) Closeup SEM image of intact nano-architecture. Scale Bars: A) $40\mu\text{m}$, i) $3\mu\text{m}$. B) $30\mu\text{m}$, i) $2\mu\text{m}$.

samples under SHPB loading corresponding to representative stress-strain curves are shown in fig. 4.9. Across the tested volume fill fractions, nLPCs exhibited early catastrophic failure with minimal changes in stress-strain behavior with increasing nano-architected fill fractions. Extracted mechanical properties of nLPC samples are collected and reported in tables 4.1 and 4.2. Increasing nano-architected volume fractions in nLPC samples from 5% to 11% results in a 32 MPa higher yield stress and increasing volume fractions from 5% to 22% increases yield stress by 16 MPa. Early catastrophic failure in nLPCs generally resulted in yield and catastrophic failure stresses at least 30% lower than that of the neat matrix epoxy system.

While nIPCs only exhibit early catastrophic failure at low volume fractions, nLPCs categorically exhibit early failure. Looking at the in-situ images, shown in fig. 4.9, nLPCs experience cracking localized around nano-architected regions which are quickly propagated throughout the sample. This deformation is observed across fill fractions for all nLPC samples tested suggesting these early catastrophic failures are driven by the layered configuration of nano-architecture and matrix epoxy.

To further investigate underlying mechanisms present in nIPC and nLPCs, post-mortem SEM imaging, shown in fig. 4.10, was performed on samples fragments collected from SHPB apparatus following dynamic compression. SEM images of nIPC samples, shown in fig. 4.10(A), show deformation concentrated in nano-architected regions. Figure 4.10(A-i) shows a closeup of one of these deformed nIPC nano-architected regions where the underlying structure no longer resembles

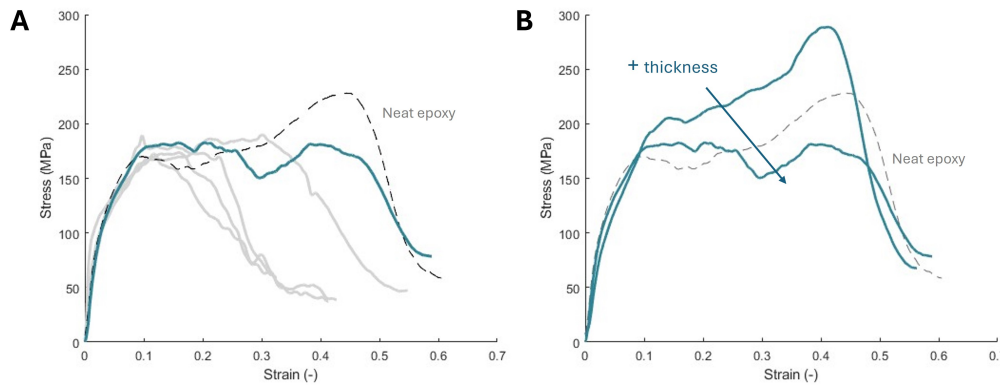


Figure 4.11: Split-Hopkinson pressure bar stress-strain responses of (A) 22% thick nIPCs and (B) Comparison of 22% nIPCs with differing distributions of nano-architecture. Neat matrix epoxy response (black - -) all thick nIPC responses reported (grey).

an orderly architecture suggesting significant cracking and plastic deformation has occurred. Furthermore, the thickness of the post-mortem nano-architecture is significantly reduced ($\approx 70 - 80\%$) and the surrounding matrix surfaces also show highly textured surfaces suggesting tortuous crack propagation during failure. In contrast, SEM images of nLPC samples, fig. 4.10 (B), reveal large sections of undeformed nano-architectures with large planar fracture regions extending through the architecture. Despite undergoing dynamic compression, nano-architectures, expected to collapse at low loads [82], appear virtually unaffected by the loading. This suggests that rather than inhibit catastrophic failure, these void nano-architected regions provide little resistance to crack propagation — explaining why all nLPC samples exhibited early catastrophic failure regardless of fill fraction.

4.3.2 Changing the Distribution of Nano-architectures

In order to probe the effect of the distribution of nano-architectures on the stress-strain performance and observed deformation, 22% nIPC samples with thick nano-architected regions were fabricated using the ambient molding method, section 2.3, and LIL sheets possessing twice the thickness of standard ones, section 2.2.3. These thick nIPCs, possessing half the number of layers as standard thickness nIPCs of equivalent volume fractions, were tested under SHPB loading and stress-strain curves are reported in fig. 4.11(A) with mechanical properties tabulated in tables 4.1 and 4.2. All recorded stress-strain responses are reported in grey with a representative curve highlighted in blue. Thick nIPC samples exhibit yield stresses and stress

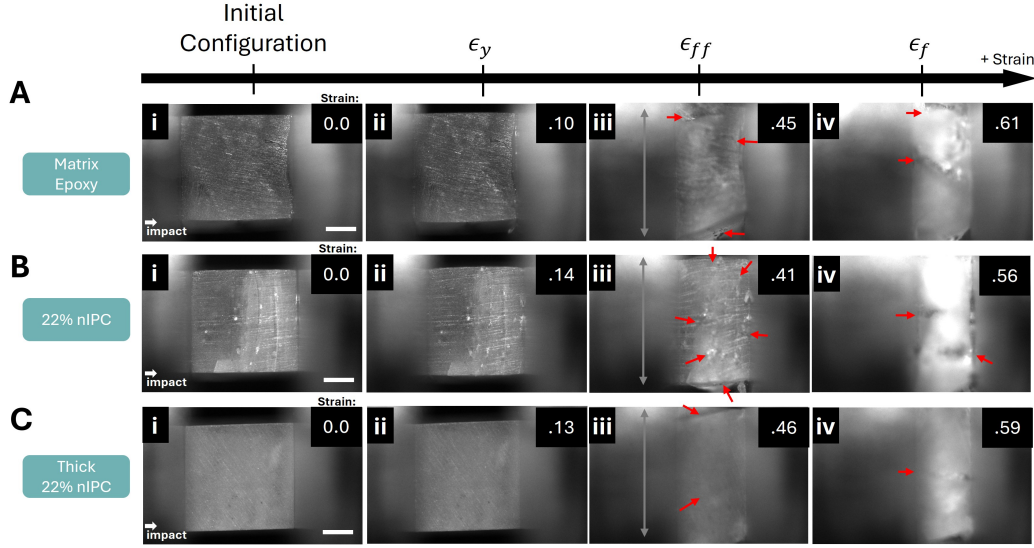


Figure 4.12: In-situ high speed images of split-Hopkinson pressure bar compression of nIPCs with differing distributions of nano-architecture. (A) neat matrix epoxy, (B) 22% standard nIPC, (C) 22% thick nIPC. Failure points are highlighted by red arrows and grey arrows show lateral expansion from Poisson effect. Scale Bars: 1mm.

at catastrophic failure initiation 24 MPa and 119 MPa lower than nIPCs with standard thickness nano-architected regions. This difference can be seen by comparing stress-strain responses in fig. 4.11(B). While thick nIPCs did not show improvements in stress, they exhibited failure strains ($\epsilon_f = 0.59$) approaching that of the neat epoxy system ($\epsilon_f = 0.61$). This suggests nano-architected volume fraction influences failure strains but is not strictly determinate of stress performance.

In-situ high speed images of the dynamic compressions are shown in fig. 4.12(C) juxtaposed against neat epoxy and standard thickness 22% nIPC responses. Comparing observed deformation behavior, all three of the responses compared in fig. 4.12 exhibit lateral expansion, however, in contrast to standard nIPCs, thick nIPCs do not show as much of a build up of localized failure throughout the sample. This suggests these arrested cracking events, present in standard nIPCs, are necessary for enhancements in stress performance.

4.3.3 High Strain-Rate Experiments on Classical PMCs

While a number of literature sources report SHPB compression of classical PMCs like carbon fiber [66, 95, 119], few report stress-strain performances of samples with equivalent volume fractions to tested nano-architected composite systems explored

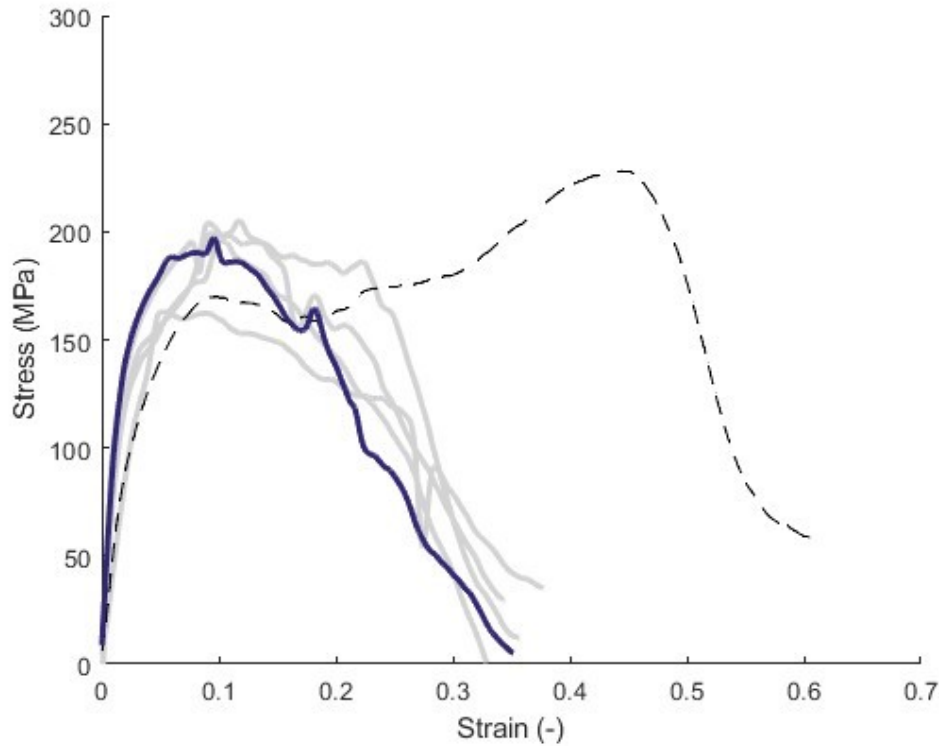


Figure 4.13: Split-Hopkinson pressure bar stress-strain responses of 22% carbon fiber samples fabricated using ambient molding process. Neat matrix epoxy responses (black - -) all carbon fiber composite responses reported (grey).

in this work. To compare nano-architected composite performance to that of carbon fiber PMCs at equivalent volume fractions, carbon fiber samples were fabricated at 22% volume fraction using the ambient molding method. Carbon fiber samples were then tested under SHPB compression ($\dot{\epsilon} \approx 4 \times 10^3 s^{-1}$) with in-situ high speed imaging. Stress-strain responses are reported in fig. 4.13 with mechanical properties tabulated in tables 4.1 and 4.2, and in-situ images shown in fig. 4.14 compared against neat matrix epoxy and 22% nIPC responses. Looking at the recorded stress-strain performance, carbon fiber samples were 71% stiffer and 12% stronger than neat matrix epoxy but failed catastrophically post-yield at low plastic strains. While similar to previously observed early catastrophic failures, in-situ images reveal interfacially dominated failures concentrated between carbon fiber reinforcements and neat epoxy regions. This interfacial failure is consistent with carbon fiber failure mechanisms commonly reported in literature stemming from large differences in constituent material properties localizing deformation at the interfaces within the composite [63, 102, 110, 113, 119]. While these carbon fiber

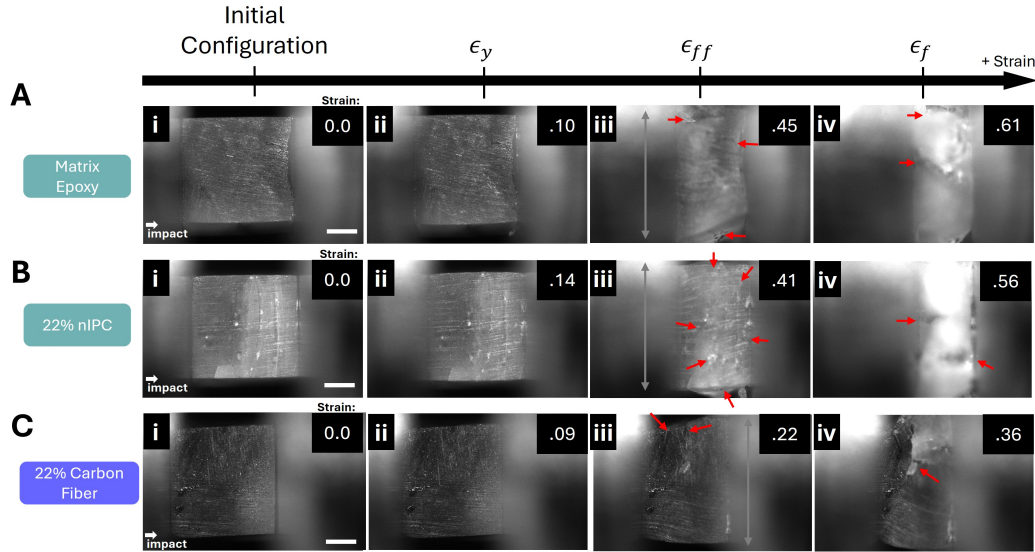


Figure 4.14: In-situ high speed images of split-Hopkinson pressure bar compression of 22% carbon fiber composites compared against neat epoxy and nIPC deformation. (A) neat matrix epoxy, (B) 22% nIPC, (C) 22% carbon fiber composite. Failure points are highlighted by red arrows and grey arrows show lateral expansion from Poisson effect. Scale Bars: 1mm.

samples were stiffer (3.18 GPa) than nIPCs (1.43-1.97 GPa), they exhibited yield stresses and failure strain 7% and 38% lower than that of 22% nIPC, respectively.

4.3.4 Comparing Nano-architected Composite Energy Absorption to Classical PMCs

Dynamic energy absorption is particularly important for structural materials undergoing dynamic loads. To evaluate the energy absorption of nano-architected composites tested in this work, strain energy absorptions are calculated via direct integration of the reported stress-strain curves from section 4.3.1. Calculated strain energy absorptions of nIPCs across tested volume fill fractions are: 26.5 MJ/m³ (5%), 86.6 MJ/m³ (11%), 107 MJ/m³ (22%). Calculated strain energy absorptions of nLPCs across the same volume filler fractions are: 27.6 MJ/m³ (5%), 30.4 MJ/m³ (11%), 35.2 MJ/m³ (22%). Specific energy absorptions are calculated by normalizing strain energy absorptions by sample densities. Specific energy absorptions for nIPCs across volume filler fractions are: 23.9 J/g (5%), 77.9 J/g (11%), 95.3 J/g (22%). For nLPCs specific energy absorptions are: 26.1 J/g (5%), 31.0 J/g (11%), 43.3 J/g (22%). Figure 4.15 shows strain energy absorptions and specific energy absorptions measured in this work compared to other particle and fiber based

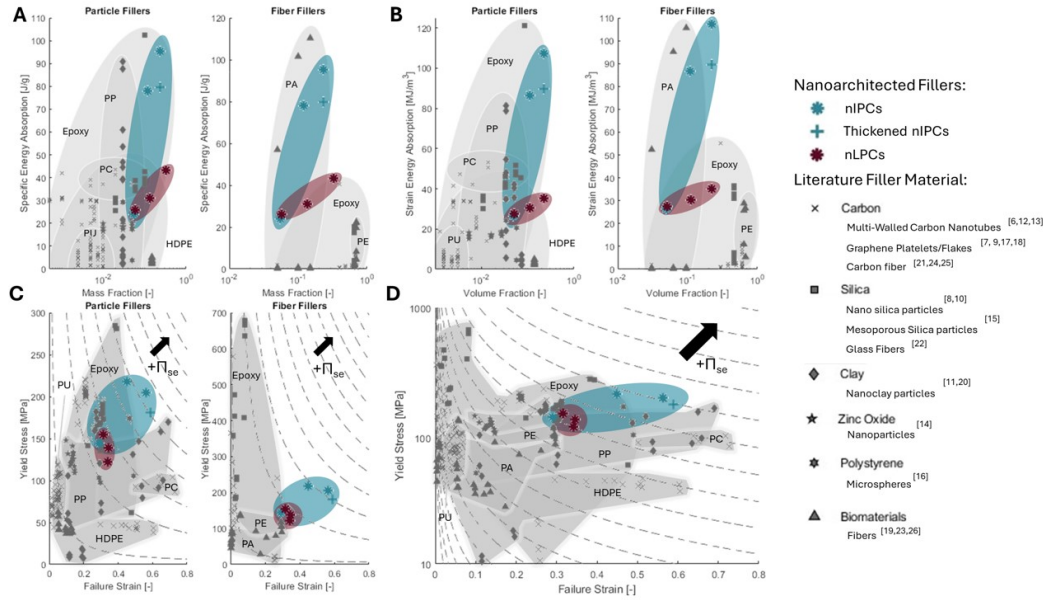


Figure 4.15: Plots compare measured nIPC and nLPC energy absorptions to reported literature values from compressive SHPB testing at nominal strain rates on the order $\dot{\epsilon} \approx 10^3 s^{-1}$. Literature values are grouped by composite matrix materials with markers denoting differing reinforcement materials. Matrix material abbreviations are as follows: epoxy, high-density polyethylene (HDPE), polyurethane (PU), polypropylene (PP), polycarbonate (PC), polyester (PE), polyamide (PA). (A) Specific energy absorptions and (B) strain energy absorptions are plotted against particle and fiber composite systems across various (A) mass and (B) volume fractions. (C) Comparison of yield stress and failure strains for particle and fiber composites. (D) Comparison of yield stress and failure strains for all reviewed literature sources. (C,D) (---) Lines denote increasing strain energy absorptions assuming yield stress is constant till failure strain.

composites reported in literature [9, 22, 34, 44, 66, 78, 79, 86, 92, 95, 100, 102, 104, 108, 110, 111, 113, 119, 124, 137, 142]. All reviewed data was collected on a SHPB apparatus at nominal strain rates on the order of $\dot{\epsilon} \approx 10^3 s^{-1}$. Composite systems reported in literature are grouped into bubbles based upon polymer matrix material and marker symbols based upon the reinforcing filler materials. Across literature documenting particle composites, 22% volume fraction nIPCs are among top performers in both specific energy absorption (6.4% lower than nano-silica particle composites — outperforming all others) and strain energy absorption (11.5% lower than nano-silica particle composite — outperforming all others) [9, 22, 34, 44, 78, 79, 86, 92, 100, 104, 108, 111, 124, 137, 142]. For literature documenting fiber composites, 22% volume fraction nIPCs are among top performers in both specific energy absorption (13.9% lower than cellulose fiber composites and 2.3x

higher than carbon fiber composites) and strain energy absorption (1.4% higher than cellulose fiber composite and 1.9x higher than carbon fiber composites) [66, 95, 102, 110, 113, 119]. Examining reviewed improvements in composite dynamic compressive energy absorptions through comparisons of reported yield stress and failure strain, reveals nIPC performance possesses a unique combination of moderate yield stress and high failure strain. Figure 4.15 (C) shows yield stress vs. failure strain of nano-architected composite samples plotted against reported particle and fiber composite literature values. Among reviewed particle composite literature, many studies demonstrate the capacity to increase yield stress with increasing rigid particle filler fractions [34, 44, 78, 79, 86, 100, 104, 108, 111, 124, 137, 142]. Only graphene reinforced nano-particle systems demonstrated the ability to increase yield stress and maintain failure strain while increasing rigid filler fractions [34, 86]. Considering reviewed fiber composites, all works show a low tolerance for high strain compression, instead attaining increased energy absorptions through increasing yield stresses [95, 102, 110, 113, 119]. High volume fractions of fiber fillers were not found to be advantageous to energy dissipation as fiber composite failure is interfacially or matrix driven through debonding/delamination and matrix cracking. nIPCs show the uncommon ability to maintain yield stress at high failure strains with increasing filler fractions. Figure 4.15 (D) shows yield stress vs. failure strain of nano-architected composite samples plotted against dynamic compressive performances in all reviewed composite systems. nIPCs exhibit a combination of yield stresses and high failure strains comparable to top energy absorbers like silica-epoxy and cellulose-polyamide composites through the introduction of architecture.

4.4 Summary and Conclusions

In this chapter, we investigate the dynamic compressive performance of nano-architected composites under SHPB loading. To summarize the findings in this chapter:

- Samples with matrix defects failed early and catastrophically.
- Layered nano-architected reinforcements do not inhibit crack propagation.
- Interpenetrated nano-architected reinforcements induce higher yield and plateau stress than neat matrix epoxy samples while also achieving comparable failure strains due to crack inhibiting mechanisms introduced by the nano-architecture.

- Thickening interpenetrated nano-architected layers while maintaining the same reinforcement volume fraction resulted in stress-strain performance similar to that of neat epoxy. The distribution of reinforcements affects yield and plateau strengths while reinforcement volume fraction affects failure strain.
- SHPB testing of carbon fiber PMCs fabricated via the ambient molding method exhibited early catastrophic failures where failures were concentrated at the interface between fiber reinforcements and matrix epoxy — consistent with reported literature on similar systems.
- Interpenetrated polymer-polymer nano-architected composites (nIPCs) are among top dynamic energy absorbers — outperforming systems reinforced with denser, stiffer, and stronger materials.

Both nIPC and nLPC stress-strain behavior and observed sample deformations are discussed in section 4.3.1 across nano-architected reinforcement volume fractions. These tests reveal that high volume fractions of interpenetrated nano-architectures enhance composite stress-strain performance beyond that of neat matrix epoxy. In these samples, cracking competes with polymer matrix deformation modes producing enhanced mechanical performance in nIPCs. Changing the distribution of nIPC reinforcements, discussed in section 4.3.2, mitigates this competition of mechanisms resulting in lower yield and plateau stress but maintains high failure strains — confirming high volume fractions of interpenetrated nano-architectures delays the onset of catastrophic failure. In contrast, in nLPCs exhibit early catastrophic failures for all samples tested. In these cases, void nano-architected regions do not resist cracking events allowing catastrophic failure to occur at low strains. Similarly, carbon fiber samples, discussed in section 4.3.3, exhibit early failures concentrated at interfaces between fiber reinforcements and surrounding matrix regions demonstrating the unique ability of nIPCs to arrest cracking failures under dynamic compression. Comparing nano-architected composite performances to dynamic compression of classical PMCs reported in literature in section 4.3.4 revealed nIPCs are among top energy absorbing composite systems. While some nIPCs demonstrated the mechanical advantages of reinforcing composites with nano-architecture, many samples exhibited performances mitigated by defects. As discussed in sections 2.3 and 2.3.3, these defects are the result of the chosen fabrication method and persist at multiple scales within the samples. To address these shortcomings, fabrication methods

were revised and vacuum-assisted molding was used to produce samples for testing in section 5.3. Despite defects, these initial dynamic compression experiments serve as the first investigation of nano-architected composites under high strain-rates and peak loads demonstrating the utility of nano-architectures as dynamic energy absorbers. In the following chapter, we will perform SHPB testing focused on observing deformation and failure within nIPCs to explain how enhancements to stress-strain performance arise from underlying mechanisms.

Chapter 5

IN-SITU HIGH-RATE COMPRESSION EXPERIMENTS WITH SYNCHROTRON ULTRA-HIGH-SPEED X-RAY RADIOGRAPHY

5.1 Introduction

While nano-architected composites provide a unique opportunity to design for desirable combinations of mechanical properties through control of structures across length scales, the same separation of scales also poses a challenge to characterization efforts relating underlying deformation mechanisms to macro-scale performance. Furthermore, linking deformation to mechanical properties under dynamic loading conditions makes characterization challenging across time scales in addition to length scales. Classically, mechanical properties and underlying deformation mechanisms were related through a pre- and post-mortem imaging of samples using changes sample features from testing to back out underlying mechanisms [19, 23, 32]. As in-situ imaging and real-time observation of mechanical phenomena has been enabled by advancements in digital imaging technologies, it has become possible to directly link mechanical performance to underlying deformation mechanisms induced by sample design [152]. In recent decades, advances to high-speed cameras capable of obtaining hundreds of thousands or even millions of images per second has enabled temporal resolutions sufficient to characterize dynamic phenomena like unstable crack propagation and ballistic impact events [33]. While current technologies are sufficient for capturing the temporal evolution of dynamic phenomena present in high-rate mechanical test, as shown in section 4.3, establishing a direct link between nano-architected deformation modes and measured mechanical properties requires high-temporal resolution in addition to high resolution, wide fields of view, and spatial resolution in 3D. Combining high temporal and spatial resolutions requires a combination of cutting edge technologies. In this chapter we investigate dynamic deformation and failure within nano-architected composites using in-situ imaging techniques with high spatial and temporal resolutions pushing characterization efforts to the very edge of what is possible with today's technologies.

In many cases, in-situ imaging is limited to surface level observations using techniques like digital image correlation to quantify observed deformation. These

techniques utilize optical image acquisition methods which prevent resolution of features beyond half the wavelength of light used for measurement [42]. Practically, in-situ imaging of deformation is not typically limited by optical limitations but rather difficulties arising from tracking motion through time [93]. To correlate sequences of images to observed deformation, scientists and engineers commonly use speckle patterns, or fine patterns of dots, in order to track and resolve deformation events thereby limiting spatial resolution to how fine you can apply speckling patterns to samples. Other imaging techniques, like electron microscopy, may be capable of high resolutions ($< 1\text{ nm}$) but impose other requirements for image acquisition (samples must be conductive and under vacuum). In-situ imaging of polymer deformation with resolutions on the order of hundred of nanometers often requires incredibly delicate and expensive instrumentation and even those methods are restricted to surface level observations. Previously, characterization of the interior of samples was conducted through destructive processes in which sections of material are sequentially removed and imaged. Advances in tomographic imaging techniques using X-rays, advanced detectors, and powerful lab-scale light sources have enabled 3D visualization of sample interiors with high resolution ($< 1\mu\text{m}$) [48]. In-situ imaging of dynamic deformation events using 3D imaging methods requires synchrotron light sources with high intensities and short photon bursts in order to obtain through thickness information with high temporal resolution [33]. In this chapter we perform split-Hopkinson pressure bar compressions with in-situ synchrotron radiography in order to obtain real-time observations of dynamic deformation and failure events throughout composite volumes. This work allows us to link deformation and failure mechanisms observed throughout tested nano-architected composite samples to recorded stress-strain performances providing insight into why nano-architected reinforcements induce enhanced performance in composites at dynamic loading rates.

5.2 Samples and Testing Methodology

5.2.1 Specimen Fabrication

Samples for SHPB were fabricated using both the ambient molding process from section 2.3 and the vacuum-assisted molding process discussed in section 2.4. Representative samples of each tested configuration (neat matrix epoxy, 22% ambient molded nIPC, 22% vacuum molded nIPC - only standard thickness sample shown, 22% carbon fiber hybridized composite, and 22% aramid fiber hybridized composite) were imaged with a Keyence VHX-X1 Optical Microscope, shown in fig. 5.1.

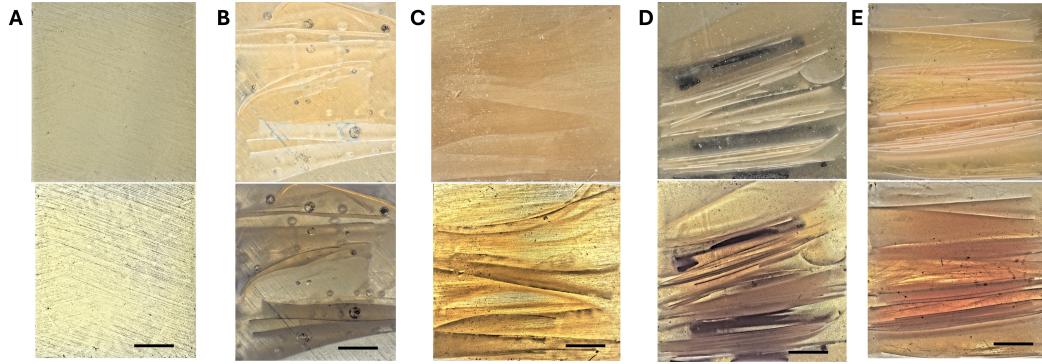


Figure 5.1: Optical microscope images of samples tested under split-Hopkinson pressure bar compression. Top images are with top-down illumination. Bottom images are with transmission illumination. A) Neat epoxy. B) Ambient molded 22% nIPC. C) Vacuum molded 22% nIPC. D) Vacuum molded 22% hybridized carbon fiber composite. E) Vacuum molded 22% hybridized aramid fiber composite. Scale Bars: 1mm

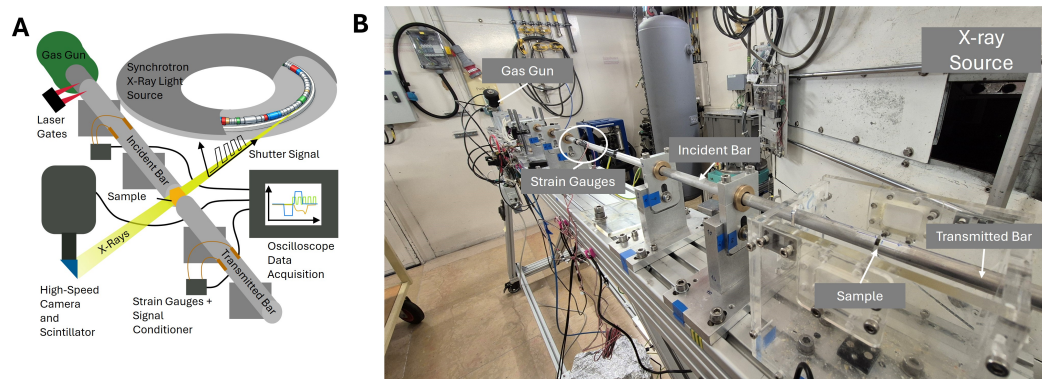


Figure 5.2: Details of split-Hopkinson pressure bar setup. A) Schematic diagram of SHPB setup with in-situ synchrotron radiography. B) Photograph of actual setup at the European Synchrotron Radiation Facility.

Notably, hybridized fiber/nano-architected composite samples reinforced with 22% volume fraction interpenetrated nano-architecture and 22% fiber reinforcement were fabricated for SHPB testing using the vacuum-assisted molding method section 2.4. Carbon fiber hybridized samples we made from 3K 2x2 twill weaves obtained from Fibreglast Developments Corporation while aramid fiber hybridized samples were made from 200GSM 2x2 Twill Weave Kevlar fabric obtained from Fibreglast Developments Corporation. Nano-architected nTiles produced via LIL and purchased fiber weaves were integrated into layups consisting of ≈ 6 layers of fiber reinforcements each separated by 7 – 8 layers of nano-architecture.

Synchrotron X-ray Radiography

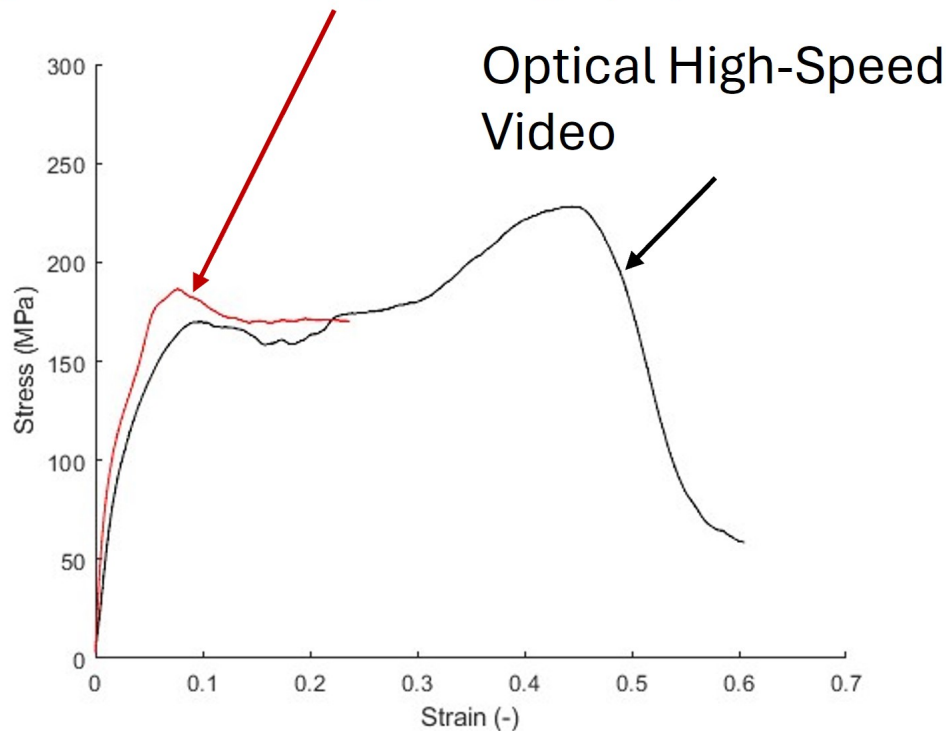


Figure 5.3: Split-Hopkinson pressure bar stress-strain responses of neat matrix epoxy shown for optical high-speed imaging (black) and synchrotron radiography (red). Matrix epoxy responses for in-situ radiography show polymer embrittlement and incomplete stress-strain responses due to shortened striker bar.

5.2.2 High Strain-Rate Testing Methodology

Dynamic compression experiments were performed using a custom 6061 aluminum split Hopkinson pressure bar (SHPB) system integrated with synchrotron X-ray phase contrast imaging at beamline ID19 of the European Synchrotron Radiation Facility (ESRF) [33]. SHPB setup was designed and constructed by ESRF beamline scientists and I fabricated custom bars for nano-architected composite testing. All SHPB measurements were taken in collaboration with Prof. Matias Kaggias and Dr. Bratislav Lukic. The system consists of a gas-gun-driven striker (400mm), incident bar (1300 mm), and transmitted bar (1100 mm) all with 12.7 mm diameter aligned coaxially, with specimen placement at the X-ray beam intersection. Samples were mounted between incident and transmitted bars with a thin layer of petroleum jelly such that the planar reinforcement regions are oriented parallel with the bar end surfaces and orthogonal to the impact direction. We used a hollow transmitted bar with an inner diameter of 6.6 mm (about half the outer diameter) with 6061

aluminum caps press fit on either side matching the setup used by Chen et. al. [27]. Micro-measurements C2A-06-125LW-350 strain gauges (1/4 bridge circuit) were attached to both the incident and transmitted bars to record the incident, reflected, and transmitted waves, allowing reconstruction of stress–strain response under the standard one-dimensional SHPB assumptions [123].

The SHPB system was mounted perpendicular to the synchrotron X-ray beam within the ID19 hutch. High-flux synchrotron radiation generated by two U-32 type undulators within the synchrotron storage ring enabled imaging of optically opaque specimens during dynamic loading. Transmitted X-rays were converted to visible light using a LYSO:Ce single crystal scintillator and recorded using a Shimadzu HPV-X2 camera (128-256 images at 880,000 fps). High-speed imaging with synchrotron X-ray illumination provided ultra-high temporal resolution with wide fields of view ($\approx 2 \times 3\text{mm}^2$) sufficient to resolve rapid deformation and failure processes present in dynamic compression of nano-architected composites.

5.2.3 In-situ High-speed Image Correlation

Synchronization between mechanical loading and imaging was achieved using a trigger derived from the incident bar strain signal and synchronized with the synchrotron bunch structure. A delay generator was used to align camera acquisition with the arrival of the stress wave at the specimen, ensuring that the full deformation sequence was captured. The resulting datasets consist of time-resolved radiographic image stacks acquired simultaneously with strain gauge signals, enabling direct correlation between macroscopic stress–strain response and internal deformation mechanisms such as densification, crack initiation, and crack propagation.

5.3 Results and Discussion

High strain-rate compression of samples was carried out on nIPC samples fabricated using both ambient molding and vacuum assisted molding methods. Stress-strain data was obtained from strain gauge signals using the same process outlined in section 4.2.2. The following sections present and discuss the results of SHPB testing with in-situ X-ray radiography for each of the tested sample configurations.

5.3.1 High Strain-Rate Experiments on Ambient Molded nIPCs

Stress-strain responses and in-situ radiographs of the dynamic compression of an nIPC sample fabricated using the ambient molding method from section 2.3 are shown along with the neat matrix epoxy response in figs. 5.4 and 5.5. Samples

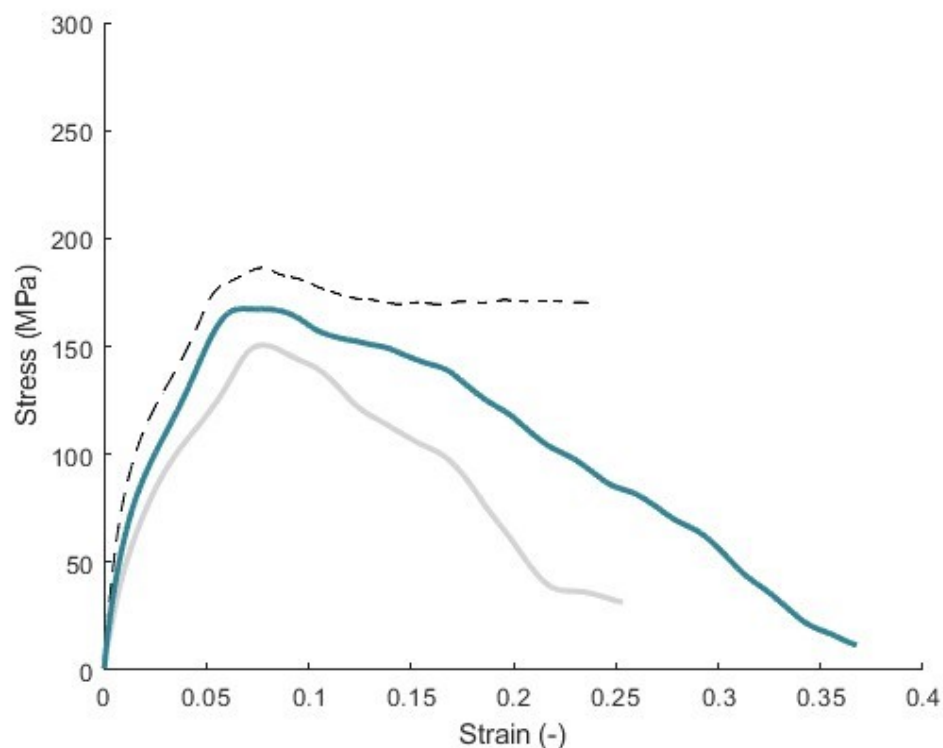


Figure 5.4: Split-Hopkinson pressure bar stress-strain responses of ambient molded 22% nIPCs compared against neat matrix epoxy (black - -) and other ambient molded 22% nIPC response shown in grey.

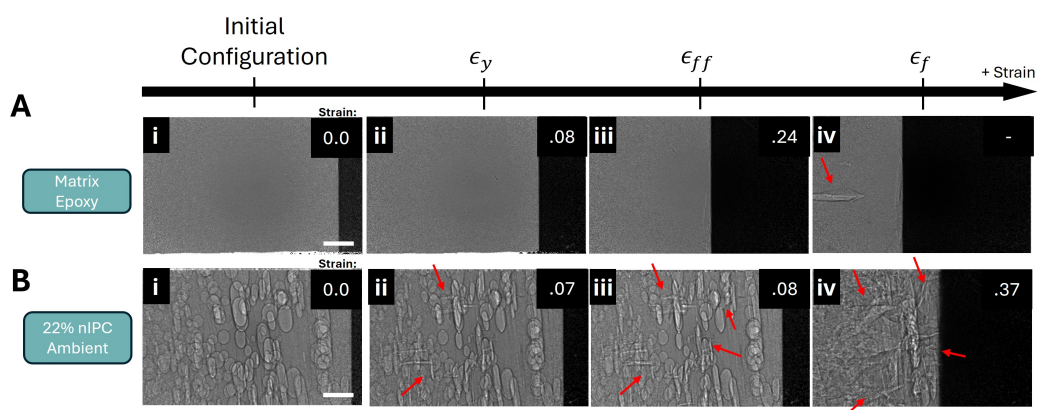


Figure 5.5: 2D in-situ synchrotron radiographs of split-Hopkinson pressure bar compression of (B) ambient molded 22% nIPCs compared against (A) neat matrix epoxy. Failure events are highlighted by red arrows. Scale bars: $500\mu m$.

Sample	Stiffness (GPa)	Yield Stress (MPa)	Yield Strain (-)	Plateau Stress (MPa)
Neat nIPC epoxy	3.80	186.31	0.08	169.71
Ambient nIPC	3.12	167.28	0.07	-
Vacuum nIPC Defect Dominated	3.09	131.64	0.03	-
Vacuum nIPC Plateau Dominated	3.37	205.21	0.08	194.09
Vacuum nIPC Peak Dominated	5.52	250.97	0.07	181.43
Thick nIPC Defect Dominated	4.49	134.58	0.05	-
Thick nIPC Plateau Dominated	2.41	173.48	0.09	154.61
Hybrid CF nIPC Defect Dominated	5.49	149.46	0.04	-
Hybrid Aramid nIPC Defect Dominated	3.71	149.64	0.05	-

Table 5.1: Table of mechanical properties extracted from dynamic compression testing on SHPB apparatus

fabricated with the ambient molding method posses a significant amount of defects as seen in the in-situ radiographs and confirmed by nanoCT reconstructions shown in section 2.5. These voids concentrated in the matrix epoxy cause stress concentrations throughout the sample which then causes cracks to form between voids coalescing to catastrophic failure. This crack formation and propagation at low strains results early failures at stresses and strains beneath that of the neat matrix epoxy. This behavior is consistent with the defect dominated behavior discussed in section 4.3, confirming defects in the matrix epoxy as a source of early failures and mitigated stress-strain performance in previous SHPB experiments.

5.3.2 High Strain-Rate Experiments on Vacuum Molded nIPCs

To reduce the presence of matrix voids and other defects, nIPC fabrication was revised according to section 2.4. Stress-strain responses and in-situ radiographs of the dynamic compression of vacuum molded nIPC samples are shown along with the neat matrix epoxy response in figs. 5.6 and 5.7. The recorded stress-strain responses for vacuum molded nIPCs are categorized as plateau dominated, peak dominated, and defect dominated responses.

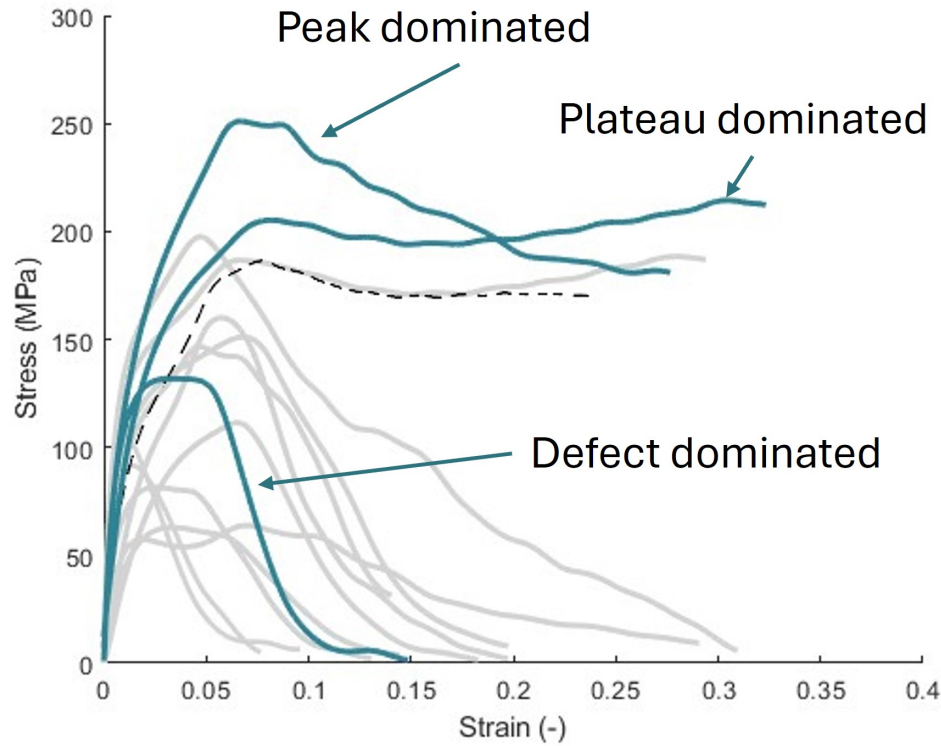


Figure 5.6: Split-Hopkinson pressure bar stress-strain responses of vacuum molded 22% nIPCs compared against neat matrix epoxy (black - -) and other vacuum molded 22% nIPC response shown in grey. Stress-strain responses are categorized as either plateau, peak, or defect dominated.

Plateau dominated stress-strain responses, seen in fig. 5.6, exhibit yield stress ($\sigma_y = 205.21$ MPa) that is sustained post-yield $\approx 10\%$ higher than that of the neat matrix epoxy ($\sigma_y = 186.31$ MPa). For plateau dominated nIPC responses, failure initiates at higher strains than what is recorded by SHPB strain gauge data, however in-situ radiographs provide insights into failure mechanisms present at high strains. Figure 5.7(B) shows no visible cracking throughout the sample similar to the observed deformation in neat matrix epoxy suggesting deformation is largely dominated by matrix deformation. At high strains, plateau dominated nIPCs nucleate cracks on the exterior of the sample as a result of Poisson effect expansion similar to neat epoxy samples. In contrast to neat epoxy samples, in nIPCs cracks are pinned and arrested as they encounter the nano-architected regions, indicated by red arrows in fig. 5.7(B). Rather than propagating towards the interior of the nIPC samples, as in the neat matrix epoxy samples, the crack at the top of the radiograph shows a jagged cracking front with textured features within the cracked region unable to progress deeper into the sample, indicating tortuous cracking causing crack arrest.

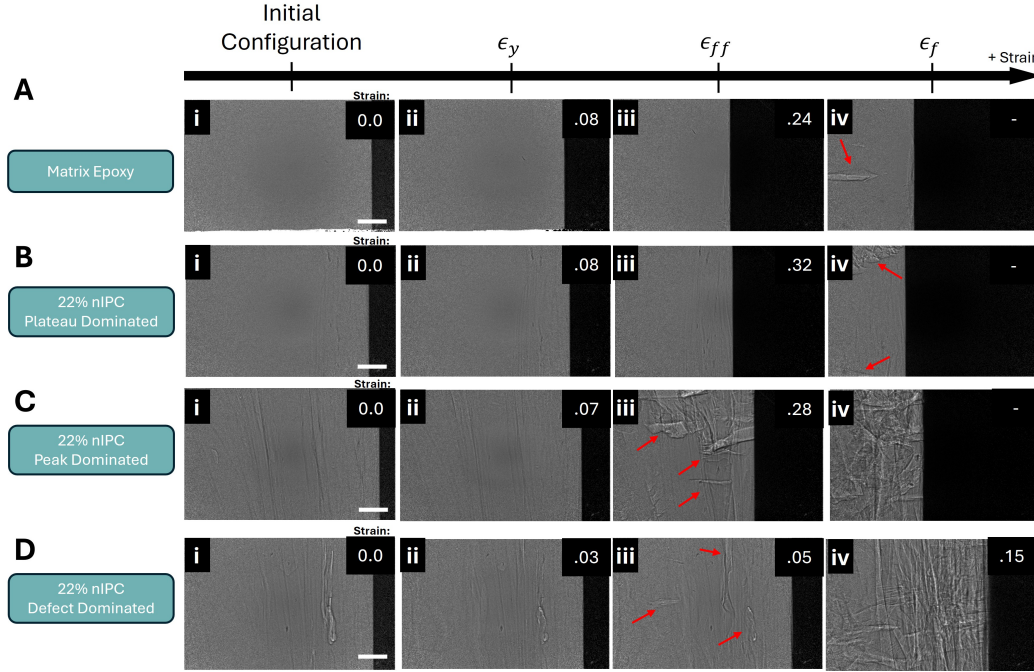


Figure 5.7: 2D in-situ synchrotron radiographs of split-Hopkinson pressure bar compression of (B-D) vacuum molded 22% nIPCs compared against (A) neat matrix epoxy. Rows correspond to: B) Plateau dominated. C) Peak dominated. D) Defect Dominated. Failure events are highlighted by red arrows. Scale bars: 500 μm .

At the bottom of the radiograph, we see behavior characteristic of crack pinning. In this case, the crack front expands towards the nano-architected regions halting as the crack tip meets the nano-architected region - subsequently the crack begins to expand as higher strains are reached while the crack tip remains fixed. This deformation process of matrix deformation and Poisson expansion leading to exterior crack propagation arrested by nano-architectures is similar to the deformation previously observed in 22% nIPCs with thickened layers, shown in fig. 4.12. The observed crack pinning and crack arrest mechanisms observed under in-situ synchrotron radiography are possible explanations for the previously observed delay in catastrophic failure as seen in fig. 4.11. While this plateau dominated vacuum molded nIPC sample possesses nano-architected regions that are thinner (40 μm rather than 80 μm) than 22% nIPCs shown in fig. 4.12, its nano-architected regions are tightly concentrated together toward the right side of the sample. The overall distribution and concentration of nano-architecture rather than thickness of individual nano-architected regions is crucial for activating crack arrest and pinning mechanisms responsible for high failure strains.

In contrast to plateau dominated responses, peak dominated responses in vacuum molded nIPCs exhibit deformation concentrated in and around nano-architected regions beginning shortly after yield. Peak dominated behavior, shown in fig. 5.6, is characterized by a yield stress ($\sigma_y = 250.97$ MPa) far higher than the neat epoxy ($\sigma_y = 186.31$ MPa) followed by a steady decay in stress with increasing strains. Similar to plateau dominated responses, ultimate failure occurs at strain higher than what is recorded by strain gauge data but in-situ radiographs lend insight into deformation and failure modes at higher strains. Figure 5.7(C) shows in-situ radiography of a peak dominated response. In this case, cracking initiates at the top of the radiograph, shortly after yield, along groupings of nano-architectures in the middle of the sample. These cracks then initiate a branched cracking pattern which spreads toward the right side of the sample. After the initial cracking event, crack tips around the nano-architecture are pinned causing these cracks to expand and bow while cracking initiates in other areas of sample from load redistribution. This peak dominated deformation process, corresponding to the accumulation of cracking surrounding nano-architected regions accompanied by crack pinning, arrest, and load redistribution was only observed for SHPB experiments with synchrotron in-situ radiography. The elevated yield stress observed in the peak dominated response is the result of a combination of polymer embrittlement induced by synchrotron radiation and strain-rate sensitive nano-architected regions confining matrix deformation leading to crack initiation around nano-architected regions. Although cracking initiates post-yield, crack pinning, arrest, and load redistribution are able to prevent catastrophic crack propagation.

Switching from ambient molding to vacuum molding of nIPC samples successfully reduces the presence of defects, as seen in the x-ray radiographs and confirmed by nanoCT reconstruction shown in section 2.5. However, a large number of nIPC samples exhibited early catastrophic failures despite this change to fabrication methods. These early catastrophic failures occur as a result of defects that remain despite vacuum assisted molding. In-situ radiographs of a representative response of one of these defect dominated responses is shown in fig. 5.7(D) demonstrating the effect these remaining defects have on the observed deformation. Here, the defect dominated response results from a slender inter-laminar void trapped between architected regions. At low strains ($\epsilon \approx 0.03$) the void collapses and nucleates cracking in the surrounding matrix and nano-architecture which is quickly driven to catastrophic failure. Interestingly, defect dominated responses in vacuum molded samples experienced more severe early failures (21% lower yield stress and 57%

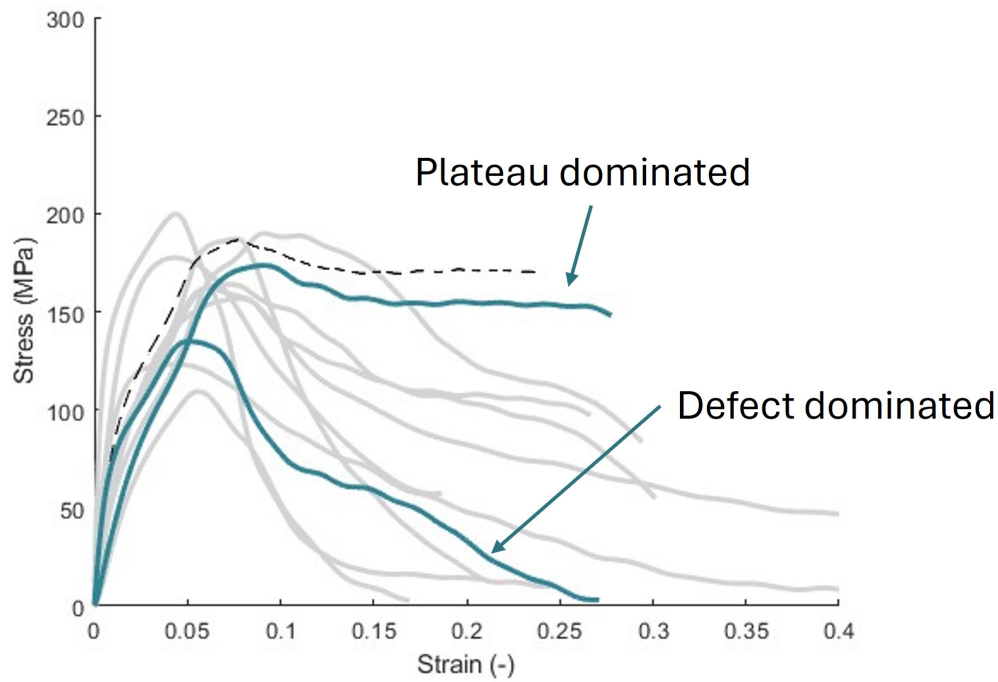


Figure 5.8: Split-Hopkinson pressure bar stress-strain responses of vacuum molded 22% thick nIPCs compared against neat matrix epoxy (black - -) and other vacuum molded 22% thick nIPC responses shown in grey. Stress-strain responses are categorized as either plateau or defect dominated.

lower failure strains) than that observed in the ambient molded samples from section 5.3.1. While matrix voids and other defects cause stress concentrations and crack nucleation, they also provide some resistance to crack propagation resulting in a more tortuous progression to catastrophic failure. This can be seen by comparing the post yield decay in stress-strain data between ambient molded nIPCs, fig. 5.4, and defect dominated vacuum molded nIPCs, fig. 5.6. Comparing the distribution of stress-strain responses between 22% volume fraction nIPCs shown in fig. 5.6 to those shown in fig. 4.6 shows the reduction of defects results in a sharper difference between stress-strain responses affected and unaffected by defects. The contrast between responses affected and unaffected by defects highlights the defect sensitivity of nIPCs, particularly when polymer embrittlement is expected to affect the observed mechanical responses, as seen in fig. 5.3.

Similar to previous SHPB testing, 22% volume fraction nIPCs with thicker nano-architected regions were fabricated and tested to determine the effect of nano-architected distribution on stress-strain performance and observed deformation modes, results are shown in fig. 5.8. Stress-strain responses for 22% vacuum molded

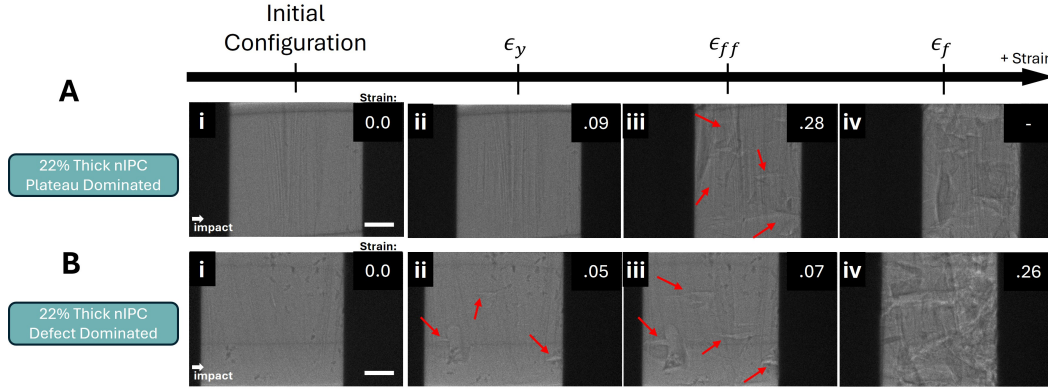


Figure 5.9: 2D in-situ synchrotron radiographs of split-Hopkinson pressure bar compression of vacuum molded 22% nIPCs. Responses are categorized as: A) Plateau dominated. B) Defect Dominated. Failure events are highlighted by red arrows. Scale bars: 1mm

thick nIPCs are categorized as either plateau dominated or defect dominated. For the plateau dominated response, yield stress ($\sigma_y = 173.48\text{MPa}$) and plateau stress are 6.9% lower than that of the neat epoxy ($\sigma_y = 186.31\text{MPa}$). This stress-strain response is similar to the plateau dominated responses observed in other vacuum molded nIPCs with thinner nano-architected regions, fig. 5.6(B), as well as the plateau dominated responses in ambient molded nIPCs with thick nano-architected regions, fig. 4.12. However, in-situ radiographs, seen in fig. 5.9, show plateau dominated failures occur as a result of accumulated cracking around nano-architected regions, matrix deformation, crack arrest, and crack pinning. This progression of deformation is distinct from other plateau dominated responses due to the accumulation of cracking concentrated around nano-architected regions throughout the sample. In this case, the resulting stress-strain responses have lower yield and plateau stress. Putting the accumulation of cracking and diminished yield and plateau stress in context with the even distribution of nano-architected regions reveals tight groupings of nano-architectures are necessary for plateau dominated responses with elevated yield stress.

Vacuum molded thick nIPCs also exhibit defect dominated responses. These defect dominated stress-strain responses show early catastrophic failures occurring at stresses and strain lower than that of the neat matrix epoxy — consistent with other defect dominated responses previously discussed. In this case, in-situ radiographs show small voids and particulate debris trapped within the matrix nucleate and

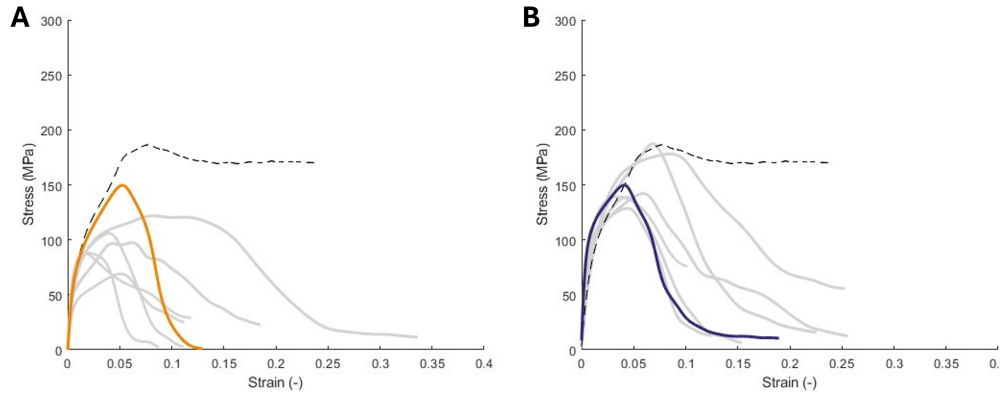


Figure 5.10: Split-Hopkinson pressure bar stress-strain responses of vacuum molded 22% hybridized nIPCs compared against neat matrix epoxy (black - -) and other vacuum molded 22% hybridized nIPC responses shown in grey. A) Aramid fiber hybridized nIPC. B) Carbon Fiber hybridized nIPCs. Stress-strain responses are characterized as defect dominated.

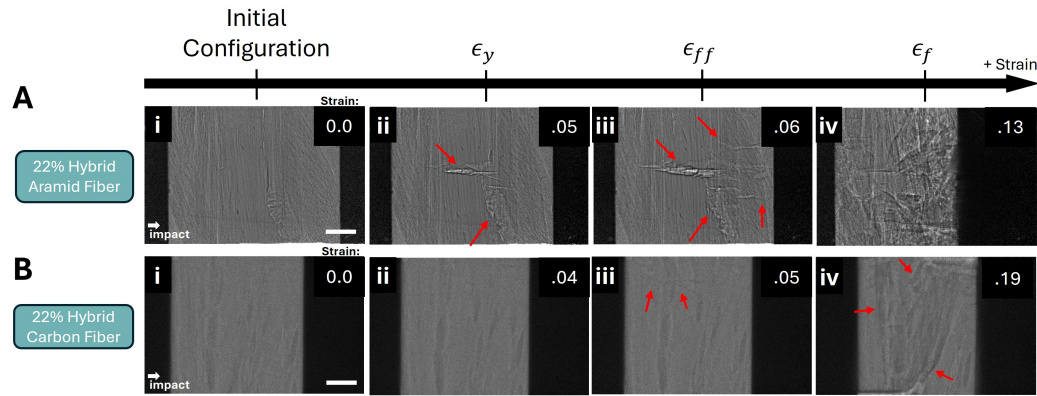


Figure 5.11: 2D in-situ synchrotron radiographs of split-Hopkinson pressure bar compression of vacuum molded 22% hybridized nIPCs. A) Aramid fiber nIPCs. B) Carbon fiber nIPCs. Failure events are highlighted by red arrows. Scale bars: 1mm.

cracks at low strains ($\epsilon = 0.05$) which then quickly propagate to catastrophic failure ($\epsilon = 0.26$)

5.3.3 High Strain-Rate Experiments on Hybridized nIPCs

In pursuit of further improvements to stress-strain performance, nano-architected reinforcements were combined conventional carbon and aramid fiber reinforcements to create hybridized nIPCs, results of SHPB testing are shown in fig. 5.10. Stress-strain results show early catastrophic failures occur at stresses and strains equal to or below that of the neat matrix epoxy across all hybridized nIPC samples. In-situ radiographs show failures concentrate at the interfaces between matrix epoxy and

fiber reinforcements, shown by the red arrows in fig. 5.11. This interfacial failure mechanism between stiff and strong reinforcements and the surround matrix polymer is well documented in fiber-reinforced PMC literature [57, 63, 71]. While literature documents composite hybridization as a commonly used method to improve load transfer between fiber-reinforcements and the surrounding matrix [18], SHPB testing shows the introduction of nano-architectures to fiber reinforcements is insufficient to suppress failures at these interfaces. While nano-architectures have been observed to provide crack arrest and pinning mechanisms, activation of these toughening mechanisms requires judicious control over distribution and location of nano-architectures. Enhanced performance in hybridized nIPCs requires improvements to fabrication methods where nano-architectures are directly integrated with fiber-reinforcements such that matrix epoxy is not mediating load transfer between fiber reinforcements and nano-architectures.

5.4 Summary and Conclusions

In this chapter, results of SHPB testing with in-situ synchrotron radiography of nIPCs and hybridized nIPCs are discussed and compared against previous SHPB testing in section 4.3. Summarizing the conclusions that can be drawn from this work:

- Matrix defects are observed to cause early catastrophic failure.
- Revised fabrication of nIPCs reduced the presence of matrix defects but did not eliminate defect dominated nIPC responses. Remaining defects, present in both matrix and nano-architecture, can cause early catastrophic failure.
- Enhanced yield and plateau stress in nIPCs was observed in both peak and plateau dominated responses. Peak dominated responses showed early tortuous cracking concentrated around bunches of nano-architected reinforcements while plateau dominated responses delayed crack initiation to high strains.
- Interpenetrated nano-architected regions act as crack inhibitors — particularly when nano-architected regions are tightly grouped together.
- SHPB testing of thickened nIPCs further confirmed the distribution of nano-architected regions affects composite strength performance.
- Adding nano-architected reinforcements to layups of classical PMCs like carbon fiber and kevlar results in early catastrophic failure.

While the use of synchrotron radiation for in-situ observations induces slight changes to stress-strain performance due to radiation effects, these through thickness visualizations paired with stress-strain data provide insight into underlying nano-architected composite deformation mechanisms under dynamic compression. Section 5.3.1 discusses how cracking and defects in nIPCs fabricated with ambient molding result in early catastrophic failures. SHPB results and observations from samples fabricated with vacuum-assisted molding are discussed in section 5.3.2 showing peak, plateau and defect dominated responses. In-situ radiographs of these samples reveal differing distributions of nano-architected regions result in early stress peaks, caused by deformation localized around nano-architected regions, or plateaus, caused by matrix deformation and cracking impeded by nano-architecture. While the majority of nano-architected matrix defects we removed through revisions to fabrication methods, defect dominated responses persisted due to remaining matrix voids or imperfections in interpenetration present within the nano-architecture. Furthermore, confirming previous SHPB results, changing the distribution of nano-architectures did not result in improved yield and plateau stresses. While these samples possess plateau dominated stress-strain responses exhibiting crack arrest and pinning behaviors, this distribution of nano-architected regions did not enhance stress-strain performance beyond that of neat epoxy. Although interpenetrated nano-architectures demonstrate the ability to impede cracking and delay catastrophic failure, section 5.3.3 shows incorporating these nano-architectures into layups with fiber reinforcements (hybridized nIPCs) does not offer resistance to interfacial failure mechanisms.

While these tests provide direct observations of how nIPCs interfere with cracking mechanisms and produce elevated stress-strain responses, further improvements to both fabrication and characterization methods are necessary to fully understand the link between nano-architected deformation and enhanced performance. Presently, the LIL fabrication method cannot precisely control produced nano-architected morphologies nor can they control the distribution, orientation, and location of nano-architectures within nIPC samples. Furthermore, improvements to in-situ observation techniques are necessary to visualize and quantify nIPC deformation and failure in 3-dimensions and finer resolutions. Addressing these shortcomings will enable a deeper understanding of how nano-scale deformation and macro-scale performance are related.

Chapter 6

DISCUSSION OF DEFORMATION MODELS, ENERGY ABSORPTION, AND DISSIPATION

6.1 Introduction

While prior chapters have established the role of architecture in governing stress-strain responses and failure modes under both quasi-static and dynamic loading, this chapter quantifies how these observed rate-dependent behaviors differ across loading regimes. In PMCs, a number of different approaches have been investigated to relate composite design parameters, such as reinforcement volume fractions, feature aspect ratios, or reinforcement orientations, to expected composite stress-strain performance. Previous chapters have shown how Voigt and Reuss rule of mixtures bounds may be used to compose composite responses from the sum of its constituents. These approaches can be further refined, as demonstrated by Hashin-Shtrikman [72], Halpin-Tsai [70], or Eshelby-Mori-Tanaka [122], but do not take into account rate affected changes in constituent properties or deformation modes and require additional information about constituent material behavior. Efforts to capture rate or time effected mechanisms in PMCs commonly employ Maxwell or Prony series style lumped element models capable of expressing time-dependent viscoelastic behavior [147]. Alternative models of the viscoelastic behavior of polymers may also be formulated as constitutive laws and used in conjunction with governing equations to determine stress states and deformation in structures, however, their use is limited due to practical limitations [147].

Beyond elasticity, a variety of different approaches have been used to describe polymer plasticity. Methods like J_2 , Johnson-Cook, or Druker-Prager plasticity [14], are commonly adapted from metal plasticity to determine yield and plastic behaviors in PMCs. Additionally, other phenomenological models, such as Eyring [51], Arruda-Boyce [3], or Bergstrom-Boyce [15], have been used to capture viscoplastic flow and entropic deformation. Practically, efforts to model PMC deformation have centralized around implementation to finite element models in commercially available software [14]. Most commonly composite performance is modeled in FEA using constituent properties and cohesive models [1, 20, 138]. However, these computational efforts often require a precise understanding of micro-structures to

capture failure behavior — sometimes involving multi-scale frameworks if there are large separations of scales [58, 60]. For this reason, simple phenomenological models like Johnson-Cook are used to homogenize composite performance [154]. In this chapter, we apply Johnson-Cook plasticity to model the stress-strain performance of nano-architected composites across rate-scales. These models are then compared across nano-architected volume fractions to quantify the changes in deformation and failure induced in their composite configurations.

While experimental studies of classical PMCs and architected materials commonly report energy absorptions calculated from stress-strain data, comparisons of energy absorptions under dynamic loading conditions are rarely compiled and compared in Ashby-style plots — common practice under quasi-static loading [6, 128]. Comparison of dynamic stress-strain responses is particularly challenging as properties like energy absorption are frequently a product of various loading or underlying sample conditions which are not well represented by simple categorizations of composite material systems [63, 123]. Despite these challenges, as PMCs are increasingly used as structural materials across engineering applications undergoing dynamic loading, there is a strong need to identify performance trends to inform composite material design. In this chapter we review and compare PMC performance [9, 22, 34, 44, 66, 78, 79, 86, 92, 95, 100, 102, 104, 108, 110, 111, 113, 119, 124, 137, 142] measured under SHPB loading ($\dot{\epsilon} \approx 10^3$) across material systems, and reinforcement volume fractions to understand if high yield strengths or high failure strains produce high energy absorption.

6.2 Strain-Rate Scaling of Mechanical Properties

$$\sigma_t = \sigma_e(1 - \epsilon_e) \quad (6.1)$$

$$\epsilon_t = \ln(1 - \epsilon_e) \quad (6.2)$$

To quantify the effects of filler fraction, configuration and strain rates, stress-strain data was first converted to true stress-strain using eqs. (6.1) and (6.2). $\sigma_t, \sigma_e, \epsilon_t, \epsilon_e$ are true stress, engineering stress, true strain, and engineering strain, respectively. All models and reported material properties in the following chapter are calculated using true stress-strain data.

$$\sigma = (A + B\epsilon_{pl}^n)(1 + C\ln(\frac{\dot{\epsilon}}{\dot{\epsilon}_{ref}})) \quad (6.3)$$

The Johnson–Cook model (JC) is a phenomenological model that has been widely adopted to describe the rate-dependent plasticity of polymers [15] and polymer matrix composites [154] due to its simplicity and ability to capture trends in strain hardening and strain-rate sensitivity. Equation (6.3) shows the isothermal form of the JC model where σ , ε_{pl} , $\dot{\varepsilon}$, and $\dot{\varepsilon}_{ref}$ are true stress, plastic strain, strain rate, and quasi-static strain rate. A , B , C , and n are fitting parameters. The following studies have sought to improve the JC model by modifying or replacing terms with polynomial or power functions [25, 26].

$$\sigma = \sigma(\varepsilon_{pl})(1 + C \ln(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{ref}})) \quad (6.4)$$

$$\sigma(\varepsilon_{pl}) = A + B_1\varepsilon_{pl} + B_2\varepsilon_{pl}^2 + B_3\varepsilon_{pl}^3 + B_4\varepsilon_{pl}^4 + B_5\varepsilon_{pl}^5 + B_6\varepsilon_{pl}^6 \quad (6.5)$$

Here, we replace the first term of the classical JC model with a polynomial function to ensure good capture of stress-strain behavior, shown in eqs. (6.4) and (6.5). To characterize the changes in plastic stress-strain performance across sample and loading conditions, we fit this modified Johnson-Cook model to the nano-architected composite mechanical responses reported in previous chapters. Here, the two terms of the modified JC model are fitted independently. For the first term, we perform a nonlinear least-squares fit of the modified polynomial function, shown in eq. (6.5), to the stress-strain data post yield at both low and high strain-rates. The fitted values of A and $B_1 \sim B_6$ for quasi-static and high-rate responses are reported in tables 6.1 and 6.2. For the second term, constant C is determined by solving eq. (6.6) at the yield point using the previously fitted result of the first term.

$$C = (\frac{\sigma}{\sigma(\varepsilon_{pl})} - 1) / \ln(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_{ref}}) \quad (6.6)$$

The fitted values of C are reported in table 6.3. This method for fitting the JC-form model to stress-strain data across strain rates has also been used to fit other material parameters such as stiffness [28, 40].

Table 6.1: Quasi-static Johnson Cook first term fitting parameters

Sample	A	B_1	B_2	B_3	B_4	B_5	B_6
nIPC Matrix Epoxy	30.95	207.34	-1836.55	7028.74	-12364.21	10838.51	-3946.03
5% nIPC	30.50	109.40	-1064.29	4560.99	-8832.22	8583.96	-3431.42
11% nIPC	27.88	189.46	-1554.70	5559.69	-8609.55	6058.22	-1620.97
22% nIPC	27.90	237.26	-2099.33	8238.33	-15239.87	14025.06	-5250.34
nLPC Matrix Epoxy	42.16	129.11	-1267.09	5106.64	-9393.36	8939.13	-3640.11
5% nLPC	42.29	76.95	-1388.79	7693.47	-18395.30	20673.90	-8843.20
11% nLPC	37.73	142.53	-1046.37	3139.70	-3394.94	1109.16	36.92
22% nLPC	42.99	18.67	239.64	-2568.00	8779.36	-10963.39	4475.90

Table 6.2: High strain-rate Johnson Cook first term fitting parameters

Sample	A	B_1	B_2	B_3	B_4	B_5	B_6
nIPC Matrix Epoxy	127.14	738.45	-8359.00	34025.03	-61650.84	49569.84	-14318.43
5% nIPC	102.10	1268.88	-18817.56	98475.42	-314559.02	645140.07	-614529.48
11% nIPC	178.34	363.87	-5241.41	36280.31	-135700.52	230701.62	-143782.99
22% nIPC	128.02	1358.05	-13507.04	55249.81	-101818.29	79182.64	-19077.09
nLPC Matrix Epoxy	158.88	656.73	-9974.29	54228.35	-124487.04	118702.38	-36848.95
5% nLPC	94.98	412.29	23267.35	-1031469.61	11689095.21	-54681741.26	93115365.05
11% nLPC	113.08	311.25	9725.53	-221947.38	1326828.86	-3293231.57	3001782.55
22% nLPC	96.05	1403.85	-18566.69	80456.49	-150708.88	78161.80	60398.97

Sample	C
nIPC Matrix Epoxy	0.2045
5% nIPC	0.1537
11% nIPC	0.3544
22% nIPC	0.2346
nLPC Matrix Epoxy	0.1832
5% nLPC	0.0817
11% nLPC	0.1306
22% nLPC	0.0807

Table 6.3: Johnson Cook rate scaling parameter

The influence of strain-rate on the stress-strain response is expressed through fitting parameter C where higher values correspond to higher rate sensitivity. Figure 6.1 shows the effect of increasing filler volume fraction on yield stress and stiffness for both nIPC and nLPC samples. Rate sensitivities for stiffness are calculated using eq. (6.6) replacing stresses, σ and $\sigma(\epsilon_{pl})$, with stiffnesses, S and S_{ref} , the stiffnesses at high strain-rates and quasi-static strain-rates, respectively.

Across nIPC and nLPC fill fractions, all report equal or higher stiffness rate sensitivities compared against the neat matrix epoxy, shown in fig. 6.1(A-B). Out of the four volume fractions tested across rates, 11% nIPCs and nLPCs were most rate sensitive in stiffness with no clear correlation with increasing filler fractions. For yield stress rate sensitivity, only 11% and 22% filler volume fraction nIPCs were higher than that of the neat matrix epoxy. The apparent low rate sensitivity of all other samples is indicative of early failure at high strain rates reflecting performance dominated by defects rather than the composites itself. Additional testing of nIPCs and nLPCs at various filler fractions and strain rates will help to establish a strong quantitative link between nano-architected fill fractions and yield stress and stiffness rate sensitivities.

6.3 Cracking and Energy Absorption

$$\Delta\sigma = \sigma^{hr}(\epsilon_{pl}) - \sigma^{qs}(\epsilon_{pl})(1 + C \ln(\frac{\dot{\epsilon}^{hr}}{\dot{\epsilon}^{qs}})) \quad (6.7)$$

To understand the changes in deformation induced by low (MTS machine) and high strain rate testing (SHPB), we use eq. (6.7) to compare the fitted responses of the JC model across strain rates. Critically, while the implemented modified JC model is able to capture overall plastic stress-strain performance, there are a large difference

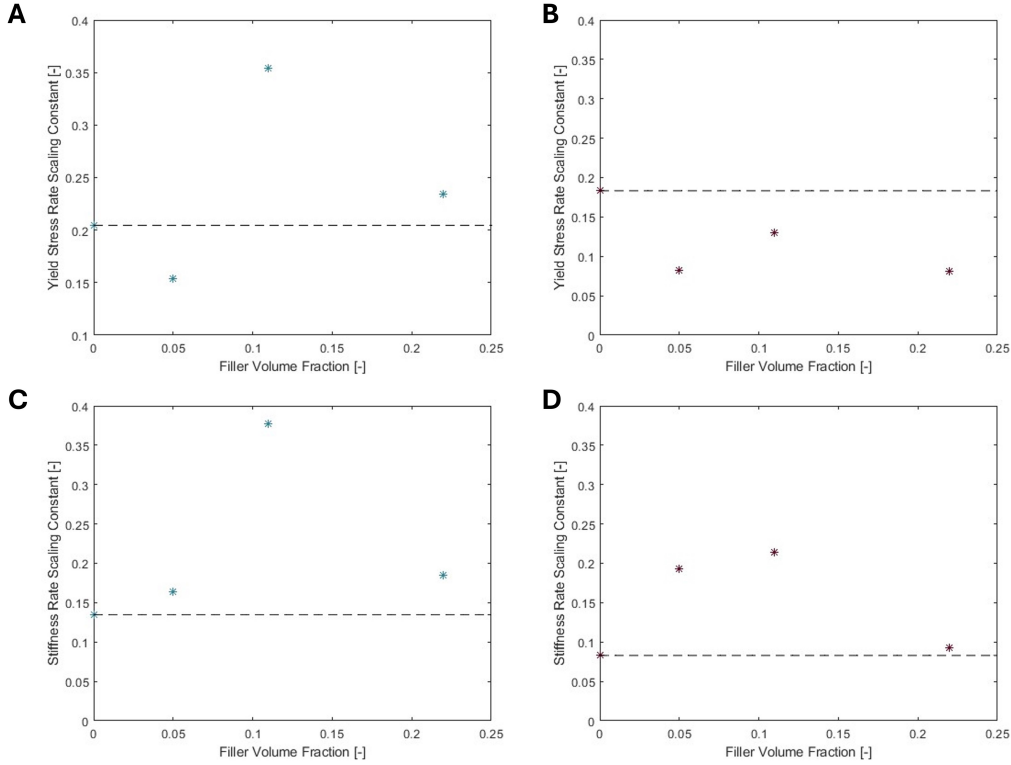


Figure 6.1: Plots show a comparison of (A,B) yield stress and (C,D) stiffness strain rate scaling across nano-architected composite volume fractions. (A,C) show rate scaling behavior for nIPCs. (B,D) show rate scaling for nLPCs.

in fitted values of A and $B_1 \sim B_6$ between quasi-static and high strain-rate data. These differences represent changes to the stress-strain behavior inherent to changing testing apparatus and inducing rate affected deformation modes. To account for these changes, eq. (6.7) calculates the difference in stress strain performance which is then normalized by the rate scaling constant C and plotted in fig. 6.2.

Here, $\Delta\sigma/C$ is a relative damage parameter which represents the increase in viscoplastic and cracking deformation as a function of plastic strain normalized by strain-rate scaling. Sharp increases in the damage parameter indicate the onset of catastrophic failure. Figure 6.2(A) shows nLPCs exhibit high amounts of damage at low plastic strains across all fill fractions when compared against the neat matrix epoxy. This is indicative of early catastrophic failure initiating and propagating at low strains. Higher filler volume fractions in nLPCs correspond to a higher plastic strains before the onset of catastrophic failure. Figure 6.2(B) shows nIPCs suppress damage to much higher plastic strains particularly at high filler volume fractions. At 5% filler volume fraction nIPCs exhibit early catastrophic failure indicated by the sharp rise in damage at low plastic strains. At 11% filler volume fraction nIPCs

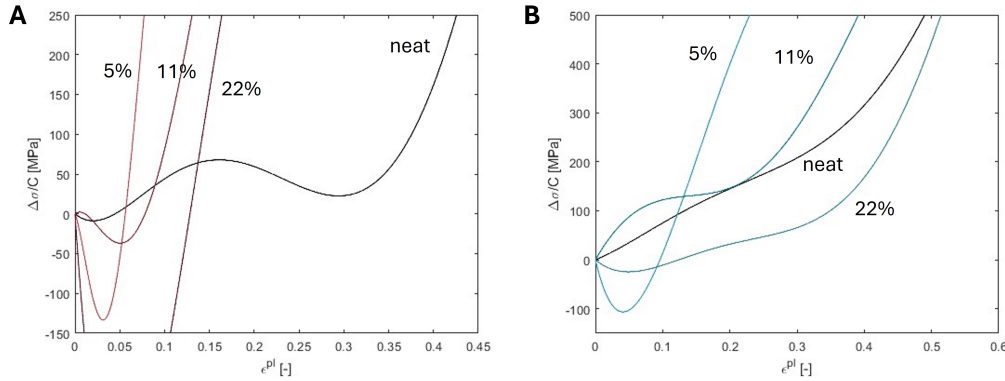


Figure 6.2: Plots show a comparison of damage accumulated with increasing plastic strain plotted across neat epoxy and increasing volume fraction of nano-architected fillers for (A) nLPCs and (B) nIPCs.

behave similarly to neat, but fail catastrophically at lower plastic strains. However, at 22% filler volume fraction, nIPCs outperform neat samples, suppressing the damage parameter by $\approx 80\%$ at low and moderate plastic strains ($\varepsilon_{pl} \leq 0.4$). At $\varepsilon_{pl} \approx 0.4$, 22% nIPCs begin to accumulate damage at a much faster rate than the neat samples as they progress to catastrophic failure. Damage parameter values for nIPC and nLPC samples across fill fraction show increasing nano-architected filler volume fractions leads to damage suppression and a delay in the onset of catastrophic failure in agreement with observed stress-strain data. Interestingly, in-situ images of dynamic compressions of nIPC and nLPC samples show increasing nano-architected volume fractions increases the accumulation of cracking prior to the onset of catastrophic failure. Together, the damage parameter calculations and in-situ observations suggest crack arrest, crack pinning and load redistribution work against crack initiation and propagation to elevate post-yield and plateau stress while delaying catastrophic failure to higher plastic strains.

6.4 Comparing Energy Absorption Across Composites

Due to their widespread use in transportation, aerospace, and other applications expected to undergo dynamic loading, strain energy absorptions are commonly reported for novel PMCs. In many cases, these energy absorptions are calculated by integrating quasi-static stress-strain responses and plotting them across material densities or strengths in an Ashby-style plot. While this has been done extensively for quasi-static loadings, dynamic energy absorptions are not commonly collected and compared due to difficulties accounting for differences in testing conditions. Figure 6.3 shows a 3D Ashby style plot for dynamic strain energy absorption plotted

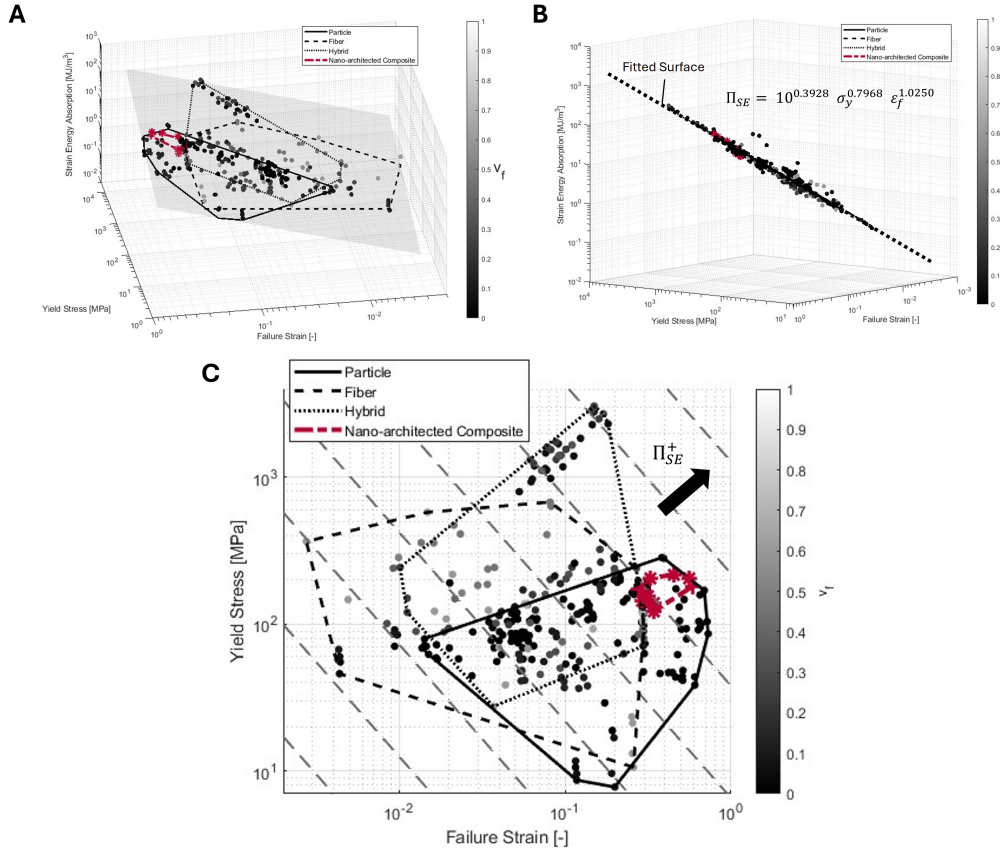


Figure 6.3: Plots show a comparison of energy absorption (Π_{se}) vs. yield stress and failure strain across PMCs of different configurations (particle, fiber, and hybrid) and volume fraction (grayscale) with nano-architected composites (red) plotted against literature values. A) Overview of data fitted to a power-law strain energy function of yield stress and failure strain (grey plane). B) In-plane view of fitted plane and literature data showing good agreement with fitted plane. C) Out-of-plane view of reviewed literature values, dotted lines (grey) represent increasing strain energy absorptions while dotted lines (black) divide data by configuration.

against yield stress and failure strains. Here, dynamic compressive responses for composites tested under SHPB loading at nominal strain-rates of $10^2 - 10^4$ are collected and compared [9, 22, 34, 44, 66, 78, 79, 86, 92, 95, 100, 102, 104, 108, 110, 111, 113, 119, 124, 137, 142]. While, minor strain-rate effects are expected over this range of strain-rates, fig. 6.3 provides an overview of how dynamic energy absorption scales across yield stress and failure strain in PMCs across reinforcement classes and filler volume fractions.

$$\Pi = K \sigma_y^n \epsilon_f^m \quad (6.8)$$

To quantify the scaling of strain energy absorption with yield stress and failure strain, we assume a power-law relationship shown in eq. (6.8). Taking the logarithm transforms this expression into a linear form in log space, which allows the parameters k , n and m to be obtained via linear least-squares regression on the log-transformed data. Fitted values for k , n and m are $10^{0.3928}$, 0.7968 and 1.0250, respectively. Here, n and m are scaling parameters for yield stress and failure strain and k is a fitting parameter. The fitted values of scaling parameter n reveals, across PMCs, increasing yield stresses results in a worse than linear scaling ($n = 1$) of strain energy absorptions reflecting a tendency for PMCs to embrittle as higher yield stresses are obtained through strain-rate effects or changes to the PMC composition. Contrarily, fitted values of m show a slight better than linear scaling of strain energy with increasing failure strains meaning PMCs can be toughened to higher failure strains without significant losses of yield or plateau stresses. Overall, this signifies increased strain energy absorptions in novel PMCs are most effectively obtained by high failure strains rather than high yield stresses.

Looking at the distribution of particle-reinforced, fiber-reinforced, or hybridized PMCs in eq. (6.8) shows the different methods by which each class of PMC absorbs energy. Fiber-reinforced systems possess high yield stresses but lack high failure strains. Contrarily, particle-reinforced systems show high failure strains but are unable to attain the high yield stresses found in their fiber-reinforced counterparts. Hybridized systems, combining two or more reinforcing phases, strike a balance between fiber- and particle- reinforced systems - achieving both high yield stress and high failure strains. Surprisingly, there is no apparent trend in strain energy absorptions with respect to volume fractions signifying how a reinforcement phase is incorporated with the polymer matrix and other reinforcements is more important than how much reinforcement is added.

Comparing nIPC and nLPC responses to other reported PMCs performances shows nano-architected composite systems have similar yield stresses and failure strains as top strain energy absorbing particulate composites. However, unlike particle-reinforced PMCs nano-architected composites do not experience issues with particle agglomeration signifying further gains to performance may be achieved with higher volume fractions of nano-architectures. Additionally, while possessing lower yield stresses, nano-architected composite systems are as good or better than fiber-reinforced PMCs at absorbing strain energy due to their high failure strains. While eq. (6.8) suggests hybridization of nano-architectures with a fiber reinforced system

may lead to further gains in strain energy absorption, testing shows simply integrating fiber reinforcements into the nano-architected layups does not realize the high yield stress high yield strain performance present in some hybridized systems. In-situ radiographs of the hybridized nano-architected samples show failures concentrated at the interface between fiber reinforcements and the surrounding matrix epoxy limiting the nano-architected ability to suppress catastrophic crack propagation. Further revisions to the fabrication of hybridized nIPCs is necessary to realize performance gains seen in other reported hybridized systems.

6.5 Summary and Conclusions

In this chapter, we discuss modeling of nano-architected composites and general trends across PMC mechanical performance. Summarizing the work discussed in this chapter:

- We used a Johnson-Cook plasticity model to capture strain-rate dependent post-yield nano-architected composite behavior. nIPCs possess higher than neat rate sensitivities for stiffness and yield stress.
- Using a normalized damage parameter we show interpenetrated nano-architectures delay catastrophic failures and suppress damage to high plastic strains — with 22% nIPCs outperforming neat samples.
- Across composite literature (constituent materials, reinforcement type, and volume fraction), dynamic energy absorption can be estimated through yield stress and failure strain. While nano-architected composites perform similarly to top-performing nano-particle composites, they can attain much higher reinforcement volume fractions.

In section 6.2, nano-architected performances are modeled across strain rates using Johnson-Cook plasticity. The phenomenological models are then used in section 6.3 to show how increasing fill fractions of nIPCs results in delayed catastrophic failure. Finally, the energy absorption of nano-architected composites is compared across classical and hybridized PMCs reported in literature. 3-d plots show nano-architected composites behave most similarly to top performing nano-particle reinforced composites - possessing moderate yield strengths and high failure strains. As a general trend across PMC literature, strain energy absorption is enhanced most effectively through prolonged failure strains rather than elevated yield stresses. This

trend articulates a tendency for embrittlement in PMCs at high yield strengths suggesting PMC reinforcements should emphasize mitigation of matrix and interface failures rather than elevated reinforcement properties.

Chapter 7

SUMMARY AND FUTURE WORK

7.1 Summary

Nano-architected composites were fabricated with varying filler fractions (5–22%) in both layered (nLPC) and interpenetrating (nIPC) configurations. These specimens, with nominal dimensions of $4 \times 4 \times 4 \text{ mm}^3$ and characteristic feature sizes on the order of $\approx 500 \text{ nm}$, represent one of the first efforts to systematically characterize nano-architected composites at macroscopic length scales. Quasi-static and dynamic compression experiments (with loads on the order of 1–10 kN) were conducted to investigate the role of strain rate, filler fraction, and architectural distribution on stress–strain behavior.

Under quasi-static loading, both nIPC and nLPC systems exhibit reduced stiffness and strength relative to the neat epoxy matrix, with low sensitivity to filler fraction. Applying rule of mixtures bounds to determine the role the nano-architecture in producing these responses shows accounting for defects is necessary to extract nano-architected reinforcement strengths in agreement with those reported in literature. In contrast, high strain-rate experiments coupled with in-situ high-speed imaging reveals a variety of deformations and failures. At low filler fractions (5%), both architectures undergo premature catastrophic failure at stresses and strains below matrix yield. However, at higher filler fractions ($\geq 11\%$), nIPCs exhibit enhanced stiffness, strength, and energy absorption under dynamic loading.

At high strain-rates, nano-architected composites demonstrate pronounced rate sensitivity. In particular, nIPCs with high volume fractions ($\geq 11\%$) exhibit higher strain-rate scaling than the neat epoxy in both stiffness and yield stress and show a delayed onset of catastrophic failure, with damage accumulating over larger plastic strains as filler fraction increases. In-situ high-speed radiography further reveals two distinct deformation modes in nIPCs: (i) peak-dominated responses associated with early, tortuous crack propagation centered around nano-architected regions, and (ii) plateau-dominated responses characterized by sustained load-bearing at large plastic strains with deformation concentrated in the polymer matrix and cracks pinned and arrested by nano-architectures. Competing mechanisms of polymer deformation

and tortuous cracking enable elevated yield and plateau stresses depending upon the distribution, orientation, and location of nano-architected regions within nIPCs.

High-rate testing also reveals the configuration of nano-architectures within the composite, interpenetrated (nIPCs) or layered (nLPCs), is critical for mitigating early failures. Across all filler fractions, nLPCs exhibited early catastrophic failure at stresses and strains below the yield stress and strain of the neat matrix epoxy. In contrast, only 5% nIPCs exhibited early catastrophic failure similar to that of the nLPCs. Post-mortem SEM images of nLPCs reveals layering of nano-architected regions do not provide resistance to crack propagation, instead allowing fracture to freely propagate through architected regions. On the other hand, post-mortem SEM images and in-situ radiography images of nIPCs under dynamic compression show interpenetrated architectures compress significantly throughout the sample and induce tortuous matrix cracking, crack pinning, and crack arrest leading to enhanced stress-strain performance.

Architectural distribution plays a critical role in governing mechanical response. Increasing the thickness and spacing while reducing the number of nano-architected regions in nIPCs produces a plateau-dominated behavior with plateau stresses approximately equal ($\pm 8.8\%$) to that of the neat matrix. In contrast, nIPCs with the same nano-architected volume fractions but twice as many sheets produced a plateau dominated response with yield 10–21% greater and plateau stresses 14–31% greater than that of the neat epoxy. Furthermore, in-situ radiography of nIPCs showed that tight groupings of nano-architectures induce crack pinning, and arrest while more distributed nano-architected regions induce tortuous crack propagation. This highlights the importance of composite parameters—such as architected region spacing, size, and distribution—in determining yield and post-yield behavior.

When benchmarked against conventional composite systems tested under similar SHPB conditions, nIPCs rank among the highest-performing energy-absorbing materials. This superior performance arises from a unique combination of high post-yield plateau stresses (rare in particulate composites) and large failure strains (typically limited in fiber-reinforced systems) demonstrating the potential of nano-architected designs to overcome traditional trade-offs in composite materials.

7.2 Future Work

7.2.1 Improvements to Fabrication

Although, significant efforts in this work were dedicated to revising nano-architected fabrication methods using vacuum assisted molding, shown in section 2.4, further control of nano-architected structures is necessary. As optical microscopy images of vacuum molded nIPCs in fig. 5.1 show, molding methods do not sufficiently control the location, distribution, and orientation of nano-architected regions within nIPC samples. Work in classical fiber- and particle-reinforced composites shows how reinforcements are arranged and within composites has a strong influence on measured mechanical properties [57, 71]. Fabrication of nano-architectures with significant thicknesses ($\geq 100\mu m$) will increase control over nano-architected distributions while simultaneously reducing the tendency for architected regions to change shape and migrate during the fabrication process. Nano-architected reinforcements with greater thicknesses will also reduce the number of sheets necessary to achieve high volume fraction loadings making it easier to manipulate and control locations and orientations of nano-architected regions during fabrication. As truly volumetric methods of fabricating nano-architected materials are made possible by advances to additive manufacturing methods [68, 127], matrix regions will be evenly distributed throughout reinforcements eliminating the presence of monolithic matrix regions within composites - maximizing the advantages provided by nano-architectures.

Furthermore, cross-sectional SEM, fig. 2.7, and tomographic visualizations of defects present in vacuum molded samples, fig. 2.13, show defects persist in both matrix and nano-architected regions within samples. While the reduction of matrix defects can be achieved by adapting currently existing injection molding or autoclave fabrication techniques used for classical composites, reduction of nano-architecture scale defects will require significant improvements to large scale meta-mask fabrication methods [83, 116]. Particularly, mitigation of occluded or closed unit cells within nano-architectures is essential to ensure complete interpenetration of matrix phases into nano-architectures.

7.2.2 Effect of Architectural Variation

The field of nano-architected materials has been devoted to exploring how underlying geometries and structures create observed mechanical performances. These works span different classes of periodic unit cells, incorporate structural hierarchy, explore unusual and stochastic topologies and even draw inspiration from natural micro- and nano-structures [65, 126]. While the design space of these nano-architected

materials is widely studied for cellular solids, this design space is not nearly as well investigated for architected interpenetrating phases composites, particularly with nano-scale features [11, 132]. This is largely a fabrication limited problem as architected materials possessing micro-scale features are readily producible through low-cost additive manufacturing approaches, while those possessing nano-scale features and appreciable sample volumes are bespoke manufacturing setups requiring extensive expertise to design, setup, operate and maintain [68, 82, 90]. As these methods become commercially available, nano-architected IPCs of various unit cell geometries a topologies will likely be produced and studied under a wide variety of loading conditions filling out the property design space.

Among the directions nano-architected variations may take, those capable of achieving multiple scales of structural hierarchy are particularly interesting. Across natural materials, underlying structures are frequently divided across length scales exhibiting complex combinations of structures which collectively result in favorable macro-scale performance [112]. While nano-architected cellular solids communities draw inspiration from porous natural materials like bamboo or bone, engineers designing the next generation of nano-architected composites may draw inspiration from nacre or teeth [69]. While it is uncertain if these bio-inspired approaches represent fully optimized combinations of structures across scales, the variety of differing natural structures serve as an example of vast design space afforded by architected control over orders of hierarchy. Practically, hierarchy in composite materials has been an academic pursuit as hierarchical arrangements of fibrous and particulate reinforcements have not proven to provide advantages in properties which outweigh the efforts required to produce them at scale [29, 120]. Nevertheless, as additive manufacturing approaches bridge the gap between nano-scale feature resolution and macro-scale material production, nano-architected composite designs possessing optimized orders of structural hierarchy and artificial constituent materials promise combinations of mechanical properties which may revolutionize the materials that compose the world around us.

While significant work is required to both realize and characterize the property space available to nano-architected composite materials, there is a strong tendency within reported literature to study either periodic or stochastic arrangements of reinforcements with fewer works are dedicated to studying the space in between these extremes [89]. This tendency naturally arises as a design constraint of space filling unit cells which forces engineers to either incorporate imperfections or release

control over underlying structures [67]. This duality presents interesting potentials within composites materials as architected reinforcements allow for more intentional incorporation of stochasticity within composite reinforcements. Furthermore, characterizations of natural materials shows that biological systems are neither perfectly ordered nor entirely stochastic [69] — motivating exploration of semi-ordered/semi-stochastic arrangements of composite reinforcements. As fabrication methods of nano-architected composites mature, more significant efforts should be devoted to studying nano-architected reinforcements possessing a balance of order and stochasticity.

7.2.3 Effect of Reinforcement Material

While this work has focused on the fabrication and characterization of a polymer-polymer composite system, there are a wide variety of material systems and combinations that should be explored in nano-architected composite configurations. Typically, classical composites are designed with reinforcement and matrix materials with widely disparate properties, like carbon and epoxy or ceramics and metal alloys [57, 71]. Due to fabrication and time limitations, this work has been restricted to polymeric reinforcements, however, a number of works have shown these polymer nano-materials can be converted to carbon, metallic or ceramics using chemical and thermal processes [125, 127]. Under micro-scale testing conditions combinations of metal and ceramic systems have been shown to possess a combination of high energy absorptions and specific strengths due material size effects and co-continuous load bearing architectures [11]. Converting polymeric reinforcements into metals and ceramics will enable engineers to use material size effects to unlock unique properties within reinforcements at the nano-scale [64]. Realizing these nano-architected structures at the macro-scale while maintaining high resolution features and minimizing defects is an enormous challenge as scalable additive approaches each come with a unique set of design limitations. While nano-lattices may promise to deliver on combinations of lightweight high-stiffness and strength materials [126], nano-architected composites utilizing these same structures as reinforcements may enable high toughness and energy absorption which enable these materials to be used in more demanding applications requiring impact resilience and long life cycles.

Although reinforcement phases within composites are classically thought to be the primary load bearing elements within composites, matrix materials are of equal importance as they enable load transfer and prevent stress concentrations from

causing failure within the composite [57]. Selecting compatible combinations of matrix and reinforcement materials has been a central focus in composites as certain combinations may induce synergetic composite performances which are better than the sum of their parts [75]. Ideally, engineers would be able to select and combine desired reinforcement and matrix materials at will, however, fabrication limitations bias composite material selection towards matrix materials which may be easily integrated with reinforcements without producing defects. This has been one of the reasons why thermo-set epoxy polymer matrix composites have achieved widespread use throughout engineering applications [63]. As shown in this work, integrating matrix phases with architected materials present unique challenges in mitigating defects across scales. These challenges are amplified as engineers seek to combine nano-architectures with arbitrary matrix materials beyond thermo-set polymers. Therefore, as additive approaches for producing nano-architected reinforcements are improved, significant efforts should also be dedicated towards integrating these architectures with matrix materials, without defects, in order to maximize the performance of nano-architected composites.

7.2.4 Experimental and Computational Methods

Ideally, characterization of deformation and failure within nano-architected composites would occur across time and length scales allowing for both visualization of nano-architected dynamic feature deformation as well as macro-scale fields of view of dynamic global sample deformation. Today this capability does not exist. Advanced characterization efforts, like nanoCT, frequently require a tradeoff between feature resolution or wide fields of view using scanning or rastering methods to compensate for these limitations by increasing the time necessary for these measurements [48]. While using more powerful light sources or more complex imaging methods can help to reduce these tradeoffs [33], these setups are rare combinations of capabilities which still do not possess the set of capabilities necessary to visualize dynamic processes with high resolution at small scales and wide fields of view in 3-dimensions. While these capabilities will be expanded as engineers continue to improve upon characterization methods and instrumentation, computation may provide a lower path of resistance to attaining understanding of these multi-scale dynamic events.

Over the past few decades, mechanical engineers have relied increasingly upon computational tools to determine expected mechanical performances for unique loading and sample geometries. Finite element analysis (FEA) of quasi-static elastic

behaviors in composites is standard practice while modeling the failure and damage evolution within these materials is a complex endeavor [2]. The parallel use of computational tools in conjunction with experimental testing has allowed engineers to understand deformation and failure within materials despite being unable to visualize these events in 3-dimensions and in real-time [81]. While this work has focused on explicit observation of deformation within experimentally tested samples, simulating these events with FEA will reduce the necessity and complexity of these in-situ observations. The combination of multi-scale computational frameworks and custom FEA solvers offers a promising direction for computational methods to fill the gaps of existing experimental characterization methods [30]. With advances to machine learning based inverse design tools [127], developing these computational efforts may also allow engineers to judiciously explore the vast design space afforded to nano-architected composite materials — unlocking the full potential of these materials to meet the demands of industrial applications.

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