MICROFABRICATION OF HIERARCHICAL STRUCTURES FOR ENGINEERED MECHANICAL MATERIALS

by

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Microfabrication of hierarchical structures for engineered mechanical materials

Thesis directed by Prof. Mark P. Stoykovich

Materials found in nature present, in some cases, unique properties from their constituents that are of great interest in engineered materials for applications ranging from structural materials for the construction of bridges, canals and buildings to the fabrication of new lightweight composites for airplane and automotive bodies, to protective thin film coatings, amongst other fields. Research in the growing field of biomimetic materials indicates that the micro-architectures present in natural materials are critical to their macroscopic mechanical properties. A better understanding of the effect that structure and hierarchy across scales have on the material properties will enable engineered materials with enhanced properties. At the moment, very few theoretical models predict mechanical properties of simple materials based on their microstructures. Moreover these models are based on observations from complex biological systems.

One way to overcome this challenge is through the use of microfabrication techniques to design and fabricate simple materials, more appropriate for the study of hierarchical organizations and microstructured materials. Arrays of structures with controlled geometry and dimension can be designed and fabricated at different length scales, ranging from a few hundred nanometers to centimeters, in order to mimic similar systems found in nature. In this thesis, materials have been fabricated in order to gain fundamental insight into the complex hierarchical materials found in nature and to engineer novel materials with enhanced mechanical properties. The materials fabricated

here were mechanically characterized and compared to simple mechanics models to describe their behavior with the goal of applying the knowledge acquired to the design and synthesis of future engineered materials with novel properties.

DEDICATION

To my great family and all my new and old friends.

ACKNOWLEDGMENTS

I want to thank the effort and time of all the members that served in the committee for the defense of this Master's Thesis: Professor Franck Vernerey, Professor Stephanie Bryant and Professor Mark Stoykovich. I am particularly grateful to my advisor, Mark Stoykovich, for his excellent guidance, caring, patience, and providing me with an excellent atmosphere for doing research during these two years.

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CHAPTER 1

1. INTRODUCTION

In nature, materials such as cellulose aggregates in wood, collagen aggregates in tendons, sea shells, cartilage and bones exhibit unique combined mechanical properties. The vast majority of such materials are composites with complex architectural designs and dimensions that span the nano- to macro-scale. Most of these biological materials have evolved intricate micro-architectures that enable them to be highly tolerant to damage and provide them with a hallmark of functionality. They show the best of the properties of their base constituents.

Soft tissues are an example of natural composites. Aggregates composed of collagen molecules are arranged in a way to form basic building blocks named collagen fibrils. Blocks can assemble with numerous levels of organizations with highly specific interconnectivity and architecture forming tissues for specific functions. Interestingly, composites with similar compositions at the macromolecular level can show different properties at the macroscale due to their geometries. Materials that contain structured elements which themselves have structures are known as Hierarchical solids. The hierarchical organizations of such materials at different length scales play an important role in their overall properties.

Aizenberg et. al., in 2005, studied the properties of biosilica in the *sponge Euplectella*. Glass is widely used as a building material in the biological world, despite its brittleness. In their study, seven hierarchical organizations ranging from the nanoscale to the macroscale were identified. The cooperation between the different levels of hierarchy provide the sponge with properties that differ with those of its building blocks (SiOx), showing exceptional flexibility and toughness[1].

Proud et. al., among others, have investigated conch shells due to the great increase in strength shown. Conch shells are constituted of a structure with characteristic length scale in the nanometer regime. They are composed of two building blocks: a mineral crystal and a soft biopolymeric matrix. Even though 95% of conch shells are composed of $CaCO_3$, which is a brittle material, its toughness is 103 times greater than that of monolithic $CaCO_3$. In order to avoid brittle fracture in flaws or defects, the material has evolved to an optimal of maximum toughness that corresponds to a uniform distribution of stress in the material. This state is achieved by sized reduction of the micro-architectures and is known as the flaw tolerance solution[2,3]. Moreover, under uniaxial tensile stress, the soft matrix transfer load between the mineral crystals via shear. This mechanism helps dissipate the stresses concentrated in certain areas of the materials such as flaws.

Kotov et. al., in 2003, developed a pathway to synthesize an artificial analog of nacre and bones. Spontaneous ordering of organic/inorganic layers was achieved by coupling precipitation reactions with self-organizing surfactants. The process resulted in a nanoscale version of nacre with alternating organic and inorganic layers. The mechanical tests showed combined properties of the corresponding building blocks. They found that the ultimate tensile strength and Young modulus of the synthetic analog approached that of nacre and lamellar bones.[4,5,6]

Nature always seems to find new pathways to evolve and adapt to new environments. In this case, besides the brittleness of their building blocks, structural organizations have evolved to tune the mechanical properties of materials by turning weaknesses in to strength and vice versa.

Due to their complexity, however, these hierarchical structures can be difficult to engineer into man-made materials[7,8]. Bio-inspired materials and systems are defined as material systems, structures, and other devices developed through observations of natural phenomena and that reflect the functionality found in nature. They are of high interest and the range of practical applications includes self-cleaning surfaces, adhesives, coatings, and prevention of cracking and fracture in mechanical materials.

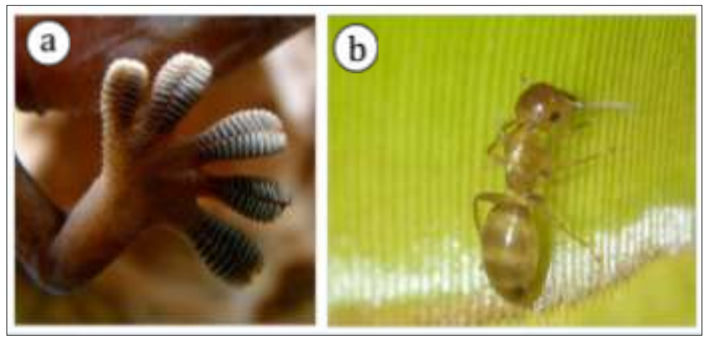

Figure 1.- a) Close up of a gecko's foot on glass. b) Ant trying not to slip from a leaf.

As an example, geckos are able to adhere reversibly to nearly any surface because their feet are covered by millions of fine hairs organized in a hierarchical arrangement that range from the mili- to the nanoscale (see Figure 1a). Artz et. al., developed a bio-inspired material based on this hierarchical structure[9,10,11]. These man-made structures or artificial gecko feet show adhesion strengths approaching those of the gecko and the authors believe their studies will eventually lead to the design of surfaces surpassing their natural counterparts. On the other hand, Speck et. al., in 2013, studied the permanent anti-adhesive biological properties that some surface plants with cuticular folds show in nature (see

Figure 1b). Tests with actual beetles showed that such surfaces can reduce the traction forces by 88% compared to smooth surfaces[12]. These slippery properties serve as an inspiration for scientists to engineer materials with Anti-Stick-Foils that could be later on applied to doorsills and ventilation shafts to reduce the accumulation of dust.

In this thesis, two different bio-inspired materials have been made and characterized. In the short term, the designs and fabrication will provide insight in the fundamentals of composite materials while their characterization will provide useful information for the improvement in their mechanical properties. In the long term, the composite materials fabricated here may be used for targeted structural applications such as lightweight and stiff frames for bicycles, airplane wings, and bridges, as well as coatings with mechanical properties for the protection of flexible and electronic devices.

CHAPTER 2

2. ENGINEERED FISH SKINS FOR APPLICATIONS IN PROTECTIVE COATINGS

2.1 OVERVIEW

Fish skins are attractive structural composites from an engineering perspective due to their multifunctional properties. They offer both protection and flexibility to the fish, and must be compatible with many modes of deformation.

Here we design and fabricate synthetic fish skins consisting of discrete, imbricate scales composed of a photo-patternable polymer covalently attached to a thin, flexible polydimethylsiloxane (PDMS) layer. The small dimensions of the fish scales (70μm x 70μm x 10μm) enable bending to a small radius of curvature which makes them suitable to adapt to different geometries and provides extra flexibility. The flexibility is further enhanced by scales that are only attached to the PDMS from the bottom, providing extra flexibility due to scale rotation. The scales are bent and overlapped, allowing full coverage of the surface upon stretching. The arrays help distribute the load when the material is subjected to indentation and even though some regions can be damaged, the protective film preserves its functionality at the macroscale. The light weight, transparency, composition, and morphology of the device make it optimal for protection in a broad range of products, from flexible/stretchable electronics to body armors. The film has been characterized qualitatively showing great flexibility and stretchability and has shown unique mechanical properties through indentation tests making it a promising protecting layer.

2.2 INTRODUCTION

2.2.1 Fish scales

Scaled skins are hierarchical structures commonly found in the animal kingdom; fishes, lizards, snakes, and even butterflies all exhibit scaled skins. Dermal armor in fish appeared at the beginning of the Paleozoic period about 500 million years ago[15]. At the time, fish skin was more rigid than it is nowadays because fish were more predaceous. With time, fish skins evolved to be less rigid, in order to allow the fish to become lighter weight and more mobile. Depending upon the animal, the scales vary in size, morphology, function and composition of the material, ranging from rigid armor plates to flexible soft ones[1]. These skins consist of discrete, imbricate (i.e., spatially overlapped) scales attached

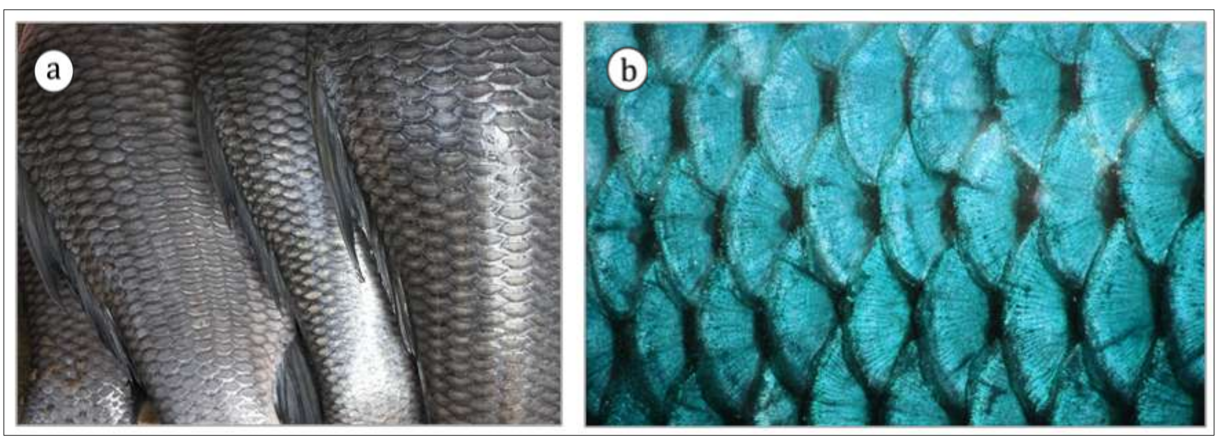

Figure 2.- a) Overview of the fish skin in several fishes. b) Magnified image of real fish scales.

to a flexible dermis layer that can deform with the animal's motion (see Figure 2a and 2b). The scales are generally composed of an outer bony rim supporting a softer cross-ply layer of collagen fibers.

The fish scales help the fish in several ways through their mechanical properties. They provide a body armor to protect fish from attack by predators[2]. Currey et. al., in a review article on mineralized tissues, reported that some fish scales are so tough they cannot be easily fractured even after immersion in liquid nitrogen[3]. The multifunctionality of fish skins has led many scientists to also study their locomotor function[6,7], the structural organization allows the scales to slide past one another and play a critical role in the animal's motion. The hydrodynamics enhance the fish mobility through the water and the scales also have self cleaning capabilities[4,5].

Recent studies performed mechanical tests in fish scales to understand their protective properties against predator attacks[8,9]. Ortiz et. al. studied the mechanical properties of *Polypterus senegalus* ganoid fish scales. Ganoid type scales are composed of a hard and stiff external layer combined with a much tougher underlying dentine layer resulting in a reduction of weight in the fish scale but preserving its mechanical properties[10]. Vernerey et. al. studied the structure and mechanics of theolost type scales that are thinner, more flexible and evolved type of fish scale. In their experiments, the outer fish scales provided a higher resistance to penetration than polystyrene and polycarbonate, polymers mainly used for protective equipment. At the same time, the softer dermis of the fish skin registered lower resistance to penetration than the engineered polymers. This observation emphasizes the important role that structure and architecture of the scale plays in their mechanical properties[11].

2.2.2 Engineering fish skin materials

It is the balance between mobility and rigidity that really fascinates scientists. Interestingly, bio-inspired body armors or materials with "similar" properties, were already engineered by humans many centuries ago. Romans and Japanese samurais already used fish scale type armors in the past (Lorica squamata and Gyorin kozane, respectively). Nowadays, engineered materials with structural configurations similar to those found in fish remain of interest for protective layers or coatings. Available techniques, however, allow the design and fabrication of scales with smaller dimensions, which therefore increases their range of applicability.

At the millimiter-scale, Ortiz et. al. engineered a macroscale model composed of a thermoplastic and a silicone rubber to experimentally verify the results obtained from a three-dimensional composite model. In their synthetic material, rigid scales (~100 x 50 x 1 mm size) were embedded into a soft substrate overlapping each other in a certain angle (see Figure 3a and 3b). During the experiments, the scale's angles and overlapping areas were varied over a total of 21 different arrangements. Mechanical tests during different loading modes including indentation, blunt loading and compression were performed on the material. They showed that modifications on the overlapping parameters and angles shifted the flexibility and the protective properties of the composite, through variation in scale bending, scale rotation, and tissue shearing[12].

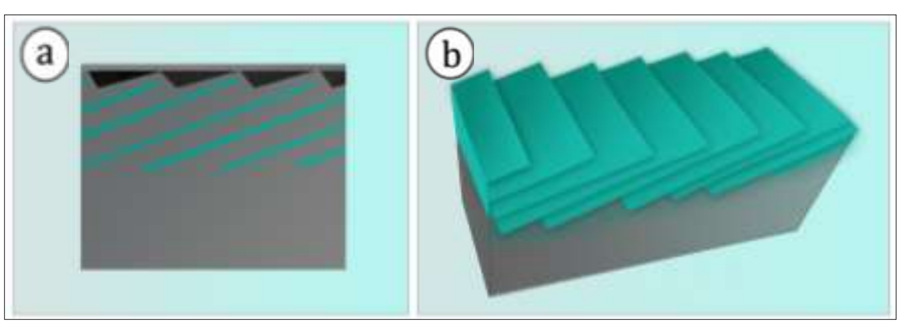

Figure 3.- a) Cross-sectional image of the engineered device b) Perspective image of the engineered device fabricated by Ortiz et.al.

Rogers and coworkers, in 2012, also fabricated a man-made version of the fish scales for use as protection of functional microsystems. Their implementation was at the microscale. They engineered three different types of scales: silicon scales, photonic scales and plasmonic scales with different mechanical and optoelectronic functionalities. Their dimensions were 600μm x 600μm x 4μm. A PDMS slab molded with a square array of posts was used as the flexible substrate. The scales were then transferred to the PDMS using a unique method of dry transfer printing developed by the Rogers group[13,14,15]. In this

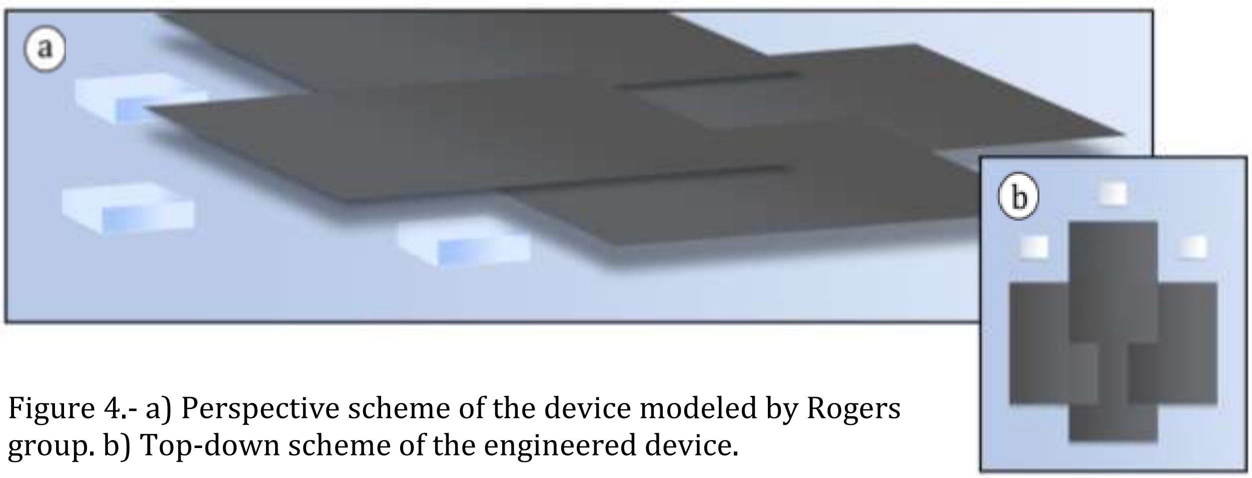

Figure 4.- a) Perspective scheme of the device modeled by Rogers group. b) Top-down scheme of the engineered device.

transfer, the imbricate scales were deposited on top of the PDMS posts one by one parallel to the substrate and overlapped by 100 μm. A reproduction of such device is illustrated in Figures 4a and 4b.

The engineered device was subjected to mechanical tests under different modes of deformation. Tensile stresses were applied and the experiments demonstrated that although the PDMS was elongated by 17% strain, scales overlapped by 100μm were enough to ensure full coverage. This result is beneficial because, in the hypothetical case in which the devices were used in microsystems, protection would be ensured under all modes of deformation[16]. The PDMS substrate was also compressed until it buckled showing enough flexibility to remain in place.

In this chapter, a new method to synthesize microscopic fish scales at the microscale and in three-dimensions has been developed with the aim to achieve similar mechanics to natural fish skin, including exhibiting elastic in-plane deformations and a bending stiffening response. The advantages of engineering fish skin in microscale dimensions include achieving an ultrathin material that is transparent, the ability of the material to be conformally contacted to any curvilinear surface, and compatibility with bending to high curvatures. The engineered material may be used as a protective coating layer for flexible and stretchable electronics, photovoltaics, personal body armor protection, and other applications that require flexibility, durability and wear resistance.

2.3 MATERIALS AND METHODS

2.3.1 Fabrication of fish scales

The microscale fish skins were fabricated using wafer-based fabrication techniques. All lithographic processing, including fabrication of the chrome masks were performed at University of Colorado in the NSF NNIN-sponsored Colorado Nanofabrication Facility. A computer aided drawing package (Clewin 4) was used to layout the analogous structures of the fish scales (see Figure 5). A chrome mask was created using the

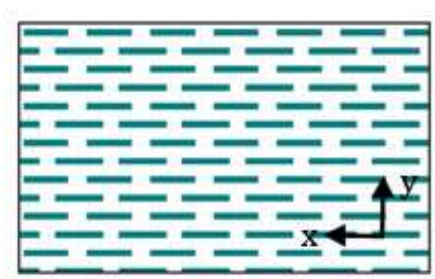

Figure 5.- View of the fish scales computer design. The dimensions of the fish scales are 70 μm wide x 10μm thick with 100μm periodicity in the x-axis and 30μm in y-axis for this specific design

Heidelberg DWL 66FS in order to pattern three-dimensional structures. Silicon wafers were cleaned using a solution of piranha (3 H_2SO_4:1H_2O_2) at 50°C for 20min.

The wafers were dried at 100°C under vacuum for 30min prior to use (Figure 6a). Omnicoat (Microchem) was spincoated at 4000 rpm and heated for 90s at 150°C (Figure 6b). SU8 photoresist (Microchem) was used as the photoresist and spincoated starting from 0 rpm up to 1700 rpm using 5 intervals of 30s each. The wafers were prebaked on the

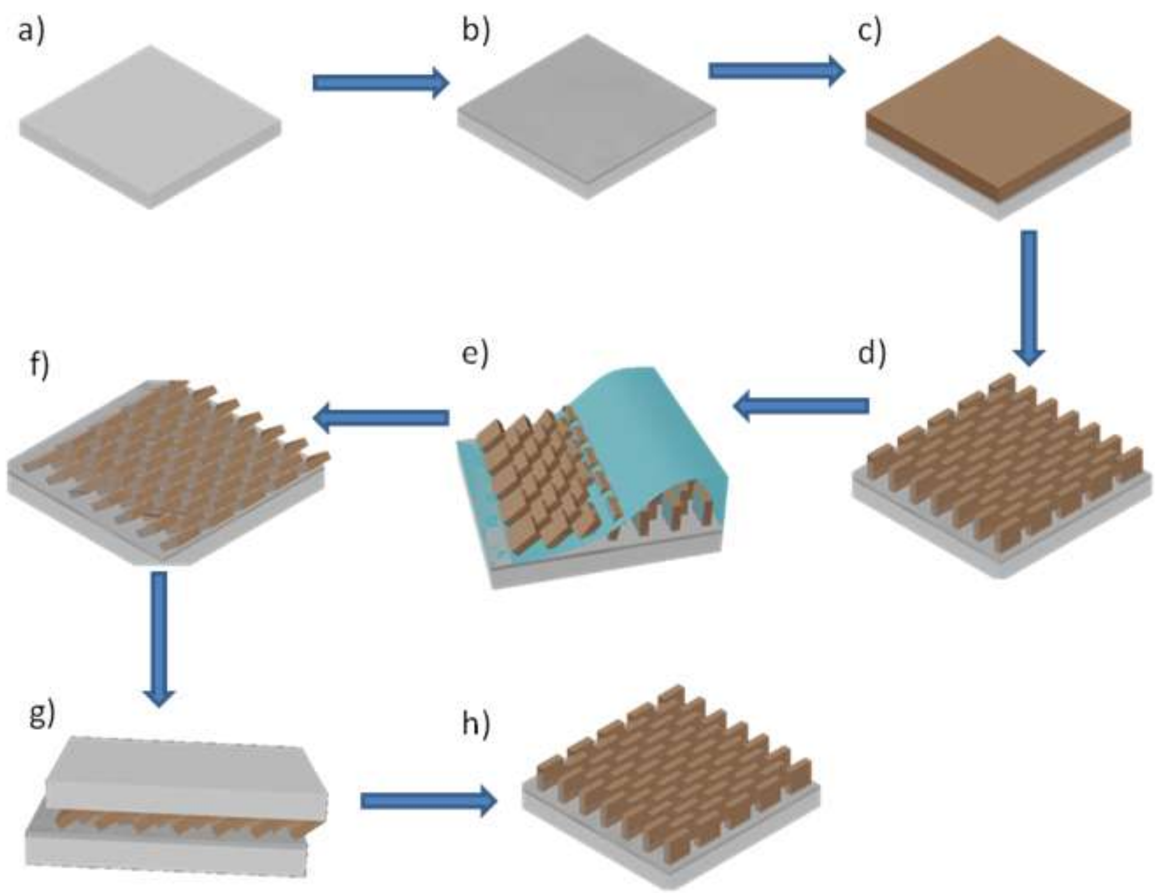

Figure 6.- Engineered material process fabrication. a) plain Si wafer. b) Si wafer with Omnicoat layer. c) Si wafer with Omnicoat and SU8 3010 spincoated on top. d) Patterned SU8 fish scales on top of the Si wafer. e) Drying process used to bend the SU8 scales in the same direction. f) View of the fish scales completely bending showing similar morphology of that observed in fish skin. g) Transfer of the fish scales to a PDMS slab. h) Fish scales acting as a protective, flexible layer on a flexible substrate such as PDMS.

hotplates for 10min at 60°C and 30min at 90°C (Figure 6c). Suss MJB4 Manual Mask Aligner was used for optical lithography through a chrome mask. The wafers were post-baked from 60°C up to 90°C during 25min. The silicon wafers were then immersed in SU8 developer for 7min with mild agitation (Figure 6d). The samples were then rinsed with water and left in the oven at 90°C (Figure 6f). The softer dermis of the fish skin was emulated using PDMS (poly(dimethyl siloxane)). It was prepared by weighing 10 parts of Sylgard 184 pre-polymer and 1 part curing agent. After vigorous mixing, the mixture was left under vacuum for 30min to degas and cured at 80°C for an hour.

The scales fabricated with aspect ratios (height/thickness) of 7 deflected in response capillary forces to generate the imbricate scaled skin structures. The structures collapsed due to capillary forces when rinsing with acetone or water instead of IPA, becoming overlapped scale structures in a single layer.

A new approach was developed in order to transfer the SU8 fish scales from the Si source substrate to a flexible and stretchable PDMS target substrate. Reactive ion etching (March Jupiter III) was used to surface treat the PDMS with nitrogen plasma for 3min. The modified surface was then placed in contact with the bent fish scales on the source substrate and they were left in contact in a hotplate for 1h at 110°C (Figure 6g). PG remover at 80°C was used to detach the fish scales from the Si wafer. After 2min in PG remover, the PDMS was peeled off from the Si wafers with the arrays of fish scales covalently attached. The PDMS samples were rinsed with water and then IPA, and dried in the oven at 90°C (Figure 6h).

2.3.2 Mechanical characterization

Indentation mechanical tests were performed in order to quantify how much protection and puncture resistance the engineered fish skin material provides to the underneath substrate. In these tests, a tip of 35μm in diameter applied a load to a specimen clamped in a sample holder until it was punctured (see Figure 7b.). Figure 7 shows a typical load-displacement curve for PDMS.

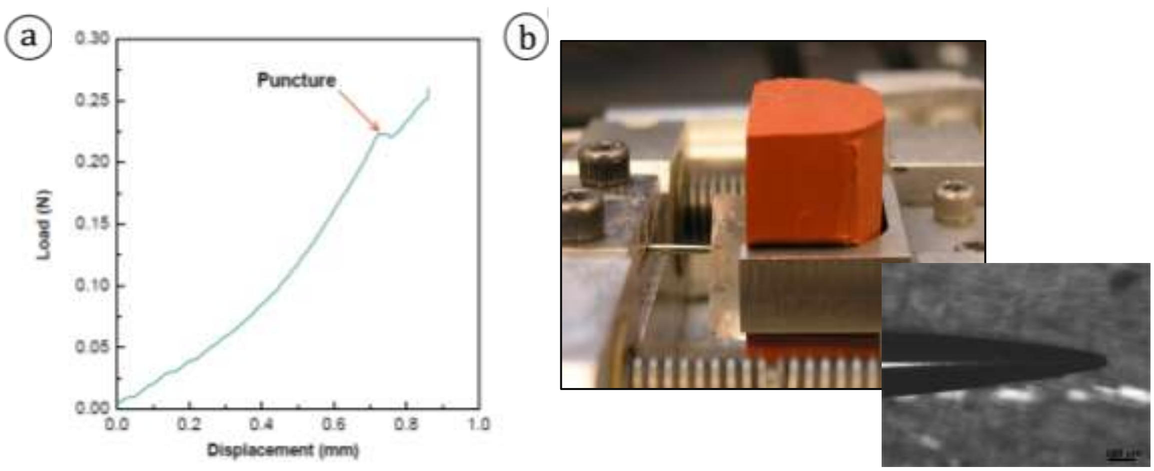

Figure 7.- a) Typical load-displacement curve of plain PDMS (1:10 ratio). b) Image of the tip puncturing the PDMS

2.4 RESULTS AND DISCUSSION

2.4.1 Understanding the mechanics

The fish scales fabricated in this thesis attempted to replicate, in so much as possible, similar mechanics to those of real fish skins. Vernerey and Barthelat studied the mechanics of real fish skins considering the stiffness and constitutive material of the scales, the mechanical interactions between scales and their attachment to the substrate, as well as the scale morphology, shape, size, and spatial deformation. Qualitative aspects from their observations and models were implemented in this thesis as a reference and starting point for the fabrication of fish scales. When considering the applications of the engineered layers for protection in flexible and stretchable electronics, three main mechanical functions should be considered.

Tensile and compressive forces. The devices fabricated in flexible microsystems are exposed to external forces like tensile stresses. Conventional protective layers such as fibers, metals and plastics are stiff but present low elasticity at the microscale level which make them unsuitable for protection at this scales. On the other hand, the engineered scales will be attached to the underneath substrate individually as observed in real fish (see Figure 8b). Because of this conformation, the scales will be able to slide one pass another upon stretching preserving the structure once the load is removed. Moreover, the scales overlap each other providing full coverage at different elastic deformations of the substrate up to a certain extent (see Figure 8c). The scale-overlap is a parameter that could be tuned depending on the fabrication approach and scale design. The conformation of scales allows the substrate to compress as well. In this case, the scale overlap increases and the interaction between scales stabilize the substrate to avoid buckling (see Figure 8a).

Figure 8.- Engineered scales morphology upon in plane a) compression b) unstressed c) tension

Flexibility. Fish-skins are highly flexible, exhibit considerable deformation during locomotion, and can interact hydrodynamically during both propulsion and maneuvering. Fish take advantage of their scales to enhance their motion by stiffening different regions of skin as a function of curvature.

Here, the skins engineered for protection need to be flexible because they will be subjected to tensile and compressive forces. The way the scales are attached to the dermis layer is a key point to provide flexibility. There are two different modes in which the scales can deflect: rotation of the scales and scale bending (see Figure 9a and 9b, respectively).

Figure 9.- a) Scale rotation b) Scale bending

In the engineered material, the fact that the scales are attached to the substrate at the bottom only, allows them to rotate relatively freely providing them extra flexibility. The extent to which a scale rotates is related to the stiffness of the substrate and the interaction strength of the scales with the substrate. In addition, the scales also bend upon substrate flexing, resulting in the stiffening of the layer (see Figure 9b). The scales start breaking apart once the bending is too high. The Young modulus of the scales, the scale overlap, and scale thickness are key factors affecting the flexibility of the device. Layers with a higher overlap or that are thicker will be less flexible.

Puncture resistance. Fish skin provides resistance to penetration (see Figure 10). In the Figure 10a, indentation applies to a soft substrate which results in a low force required to penetrate through the tissue. Figure 10b hypothesizes an indentation applied on one scale placed on top of the soft substrate. The scale is stiffer than the former case and the force necessary to penetrate is much higher than case 10a. Finally, in Figure 10c, the scales cooperate together bending and rotating cooperatively, and dissipating the force applied over a large area. The force necessary to penetrate is higher and the needle displacement for a given applied stress is lower compared to those illustrated in Figures 10a and 10b. Figure 10d describe the mechanical behavior expected in the three different cases.

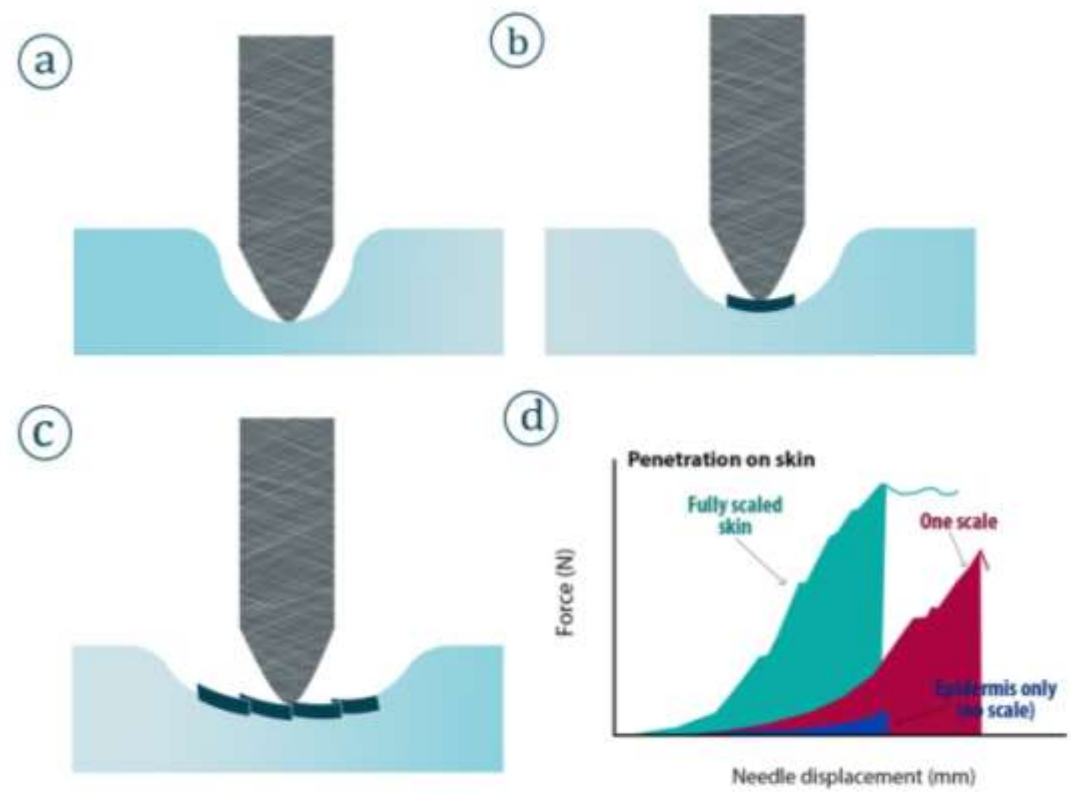

Figure 10.- a) Indentation test applied to plain substrate. b) Indentation test applied to a single scale. c) Indentation test applied to a series of overlap fish scales. d) Indentation force vs displacement for the 3 case scenarios.

When an indentation force is applied, the scales effectively dissipate the load across the skin. However, according to the overlapping configuration in which the scales are fabricated, the load does not dissipate equally in all directions (see Figure 11). In fact, it is anticipated that there will be a difference in deformation along the regions that support the load.

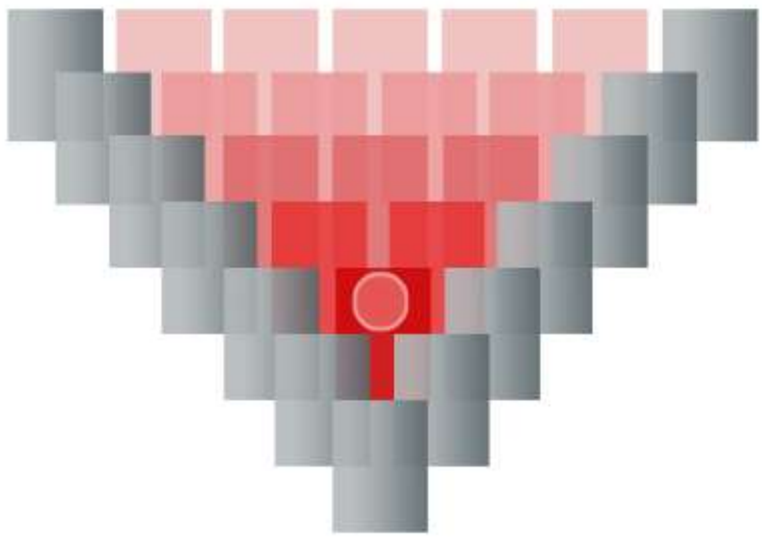

Figure 11.- Top down scheme of the engineered device. The regions in red represent the force dissipated from puncture resistance.

2.4.2 Microfabrication

The dimensions of the engineered device have been a key point on its fabrication. Structures of few hundred microns in size accomplished the properties desired by providing flexibility and a high number of organized structures. At the same time, the scales were big enough as to be able to manipulate them. A microfabrication processing was developed and the engineered material was manufactured in the Colorado Nanofabrication Laboratory.

Mask designs. The first step in the fabrication process was to generate a mask design from which thousands of scales could be reproduced at a time. The first design had to be simple and would provide an orientation for which should be the initial dimensions and whether the processing was well oriented or not. A series of rectangles were designed in series as a proof of concept (see Figure 12). The first structures were 25µm width and with periodicities ranging from 30 to 40µm. Also, 50µm width structures were fabricated with periodicities ranging from 50 to 100µm.

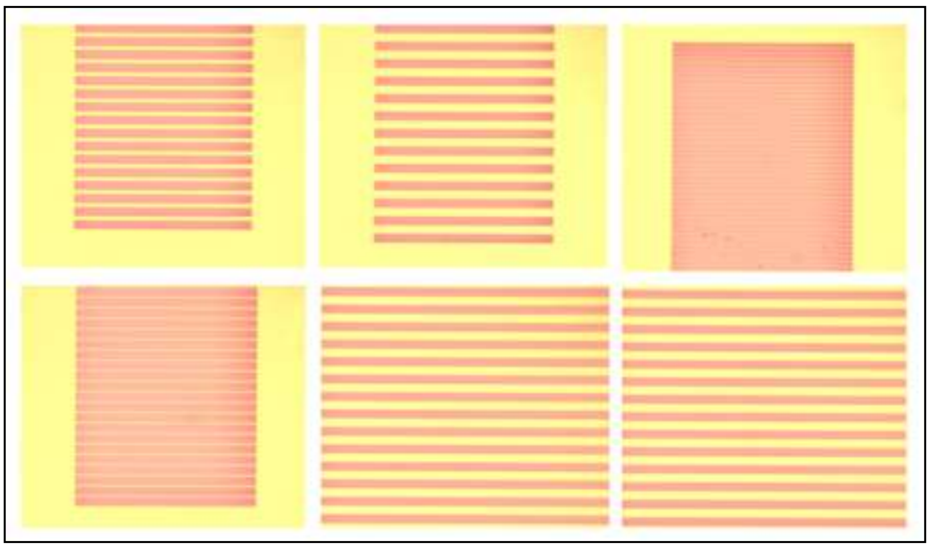

Figure 12.- Initial morphologies for the fish scales using different widths, periodicities and heights.

Additional designs with different dimensions and periodicities were explored so that the best design could be found. All the designs retained the same overall morphologies as the ones found in real fish skins. Figure 13 show some of the designs used during the process and the schematics show the different dimensions.

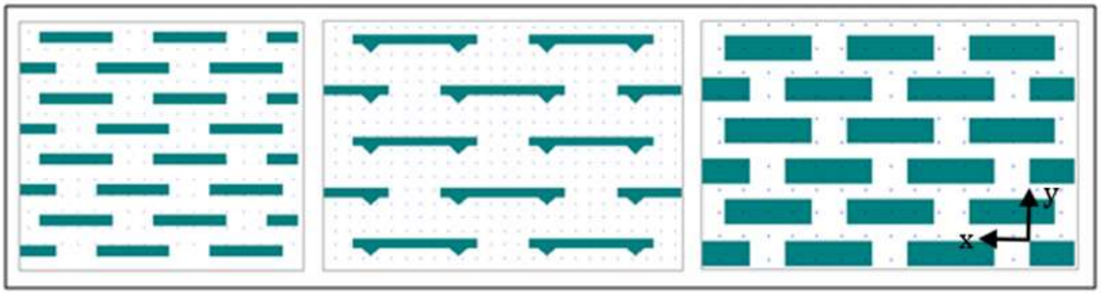

Figure 13.- Example of different dimensions used for the fabrication of fish scales. Thicknesses of 5-30µm, 70 µm in height, 50-70 µm periodicities in the y-direction and 100 µm periodicities in the x-direction were studied.

Optical Lithography Processing. In optical lithography, a photosensitive polymer (also named as photoresist) is exposed selectively to a radiation source in order to produce a pattern on a substrate. For the purposes of this thesis, the selection of the scale size was not affected by the limitations of the equipment since the scales dimensions ranged from 5 to 70 microns and the resolution of the patterns in optical lithography can go down to 1 micron. The photoresist used was SU-8(3010). It is an epoxy-based negative (cross-links upon exposure) photoresist. Because it is very viscous, it is ideal to produce structures with high aspect ratios. It is also a stiff polymer when cross-linked (an elastic Young's modulus of 2-4 GPa approximately) making it an ideal candidate for the production of the fish scales. The fabrication process began with the creation of three-dimensional structures.

The SU8 usually presents more difficulties than other photoresists in terms of its processing and patterning. A key step in the lithographic patterning of the scales is the soft bake step (pre-bake). The soft baking times are different for each specific SU8 thicknesses and the process should be optimized each time. For SU8 film thicknesses ranging from 70 to 80 µm that were spin coated, the hotplate was set to 65°C for 5min and ramped up 3 times until 90°C using intervals of 3min. Once at 90°C, the sample was heated for 30min.

Heating the photoresist at 65°C is recommended because it helps to create an even layer (it avoids having thicker layers at the edges). In addition, without a sufficient prebake step, the photoresist sticks to the mask during the exposure step.

The exposure dose for patterning SU8 also varies depending upon the thickness of the photoresist. In the experiments, the optimal dose necessary was found to be 175mJ/cm2. In terms of optimizing the process, optical filters can be used to eliminate UV radiation below 350nm and, therefore, obtain more vertical sidewalls.

Another key step in the lithographic process of the fish scales is the Post-baking. The wafers were post-baked from 60°C up to 90°C for 25min. Two minutes after the wafers were heated, the structures patterned were visible by eye, otherwise the exposure dose was too low. The postbaking step is critical in the fabrication of the fish scales in order to be able to control the aspect ratios.

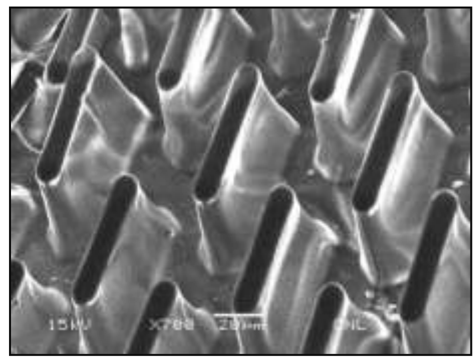

Figure 14.- SEM image of 70 μm SU8 fish scales perpendicular to a Si substrate.

Finally, the SU8 patterns were developed by immersion in developer for 7min. When rinsing with IPA or acetone, if the SU8 is underdeveloped a white film is observed. Oppositely, an overdeveloped photoresist may lead to deadhesion or detachment from the substrate. Figure 14 is an SEM image showing the conformation of the fish scales fabricated on a Si substrate. The scales are perpendicular to the substrate. The next step was to bend the fish scales in the same direction so that they overlap to each other without falling apart. Prior experiments based their methodology on applying mechanical forces tangential to the wafer. The forces were initially applied with plain PDMS because, since it is an elastomeric polymer, it would not damage the scales in the process. A more sophisticated procedure consisted on applying a PDMS roller through the substrate so that the fish scales would bend sequentially (Figure 15a).

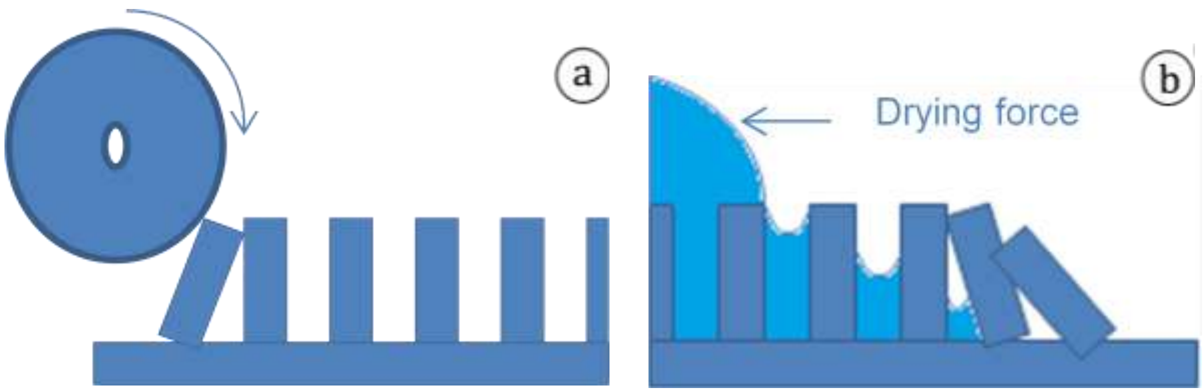

Figure 15.- a) Mechanical approach for the deflection of the scales. b) Deflection of the fish scales based on the drying forces.

The mechanical approach for scale deflection did not show success among the different dimensions that were tried. A second approach consisted of modifying the aspect ratios and post baking times, and using surface tensions in order to bend the fish scales en masse (see Figure 15b). The approach was accomplished through spontaneous pattern collapse caused by large capillary forces via the drying of high surface tension solvents such as water. Even though there is not absolute control for the scales to bend in a specific direction, the direction is homogeneous over macroscopic areas (see Figure 16).

PDMS substrate and transfer process. The fish scales were designed and fabricated to be used as a protection in flexible and softer substrates. PDMS was chosen as the substrate to represent the soft dermis of fish skin, because it has a Young modulus of about 2-4 MPa compared to the 2-4 GPa of the SU8 scales, it is a widely utilized polymer, and it can be

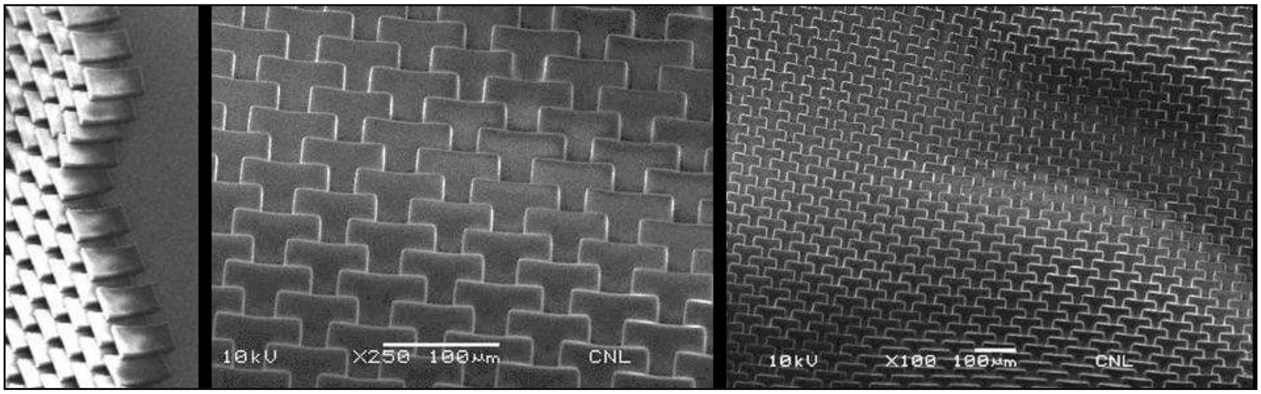

Figure 17.- The figure show 70µm x 70µm x 10µm scales overlapped offering full coverage of the surface. a) Edge of the area of coverage. b) Scales overlap c) Large area of scales in a non-flat surface. Images taken with LV-SEM.

easily processed and prepared. In addition, the fact that it can be molded in different shapes and that its Young modulus can be easily tuned, by changing the ratio between the elastomer base and the curing agent, makes PDMS attractive as the underlying substrate for the synthetic fish skin materials.

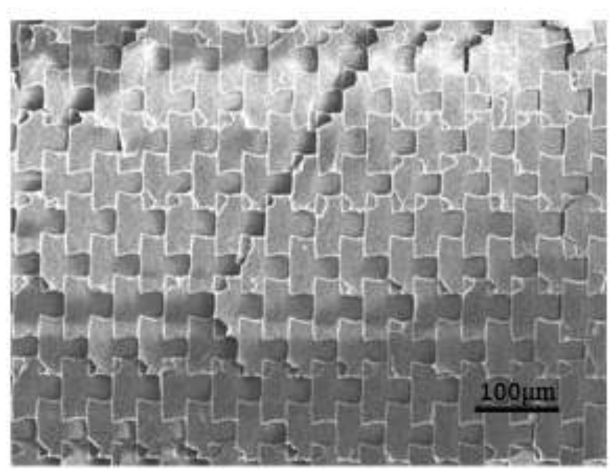

Figure 16.- SEM image of SU8 fish scales transferred to PDMS.

The attachment of the scales to the substrate is also important. One objective of the procedure developed in this thesis was to bond the scales from the bottom of the PDMS and, at the same time, provide them with sufficient rotational mobility (see Figure 17). The transfer using a chemical bond between the SU8 structures and the PDMS simultaneously transfers thousands of fish scales over large areas. The scales shown in the Figure 18 replicate the shapes of the fish scales, being able to cover fully large areas of the substrate without gaps. The scales can be fabricated with high regularity and perfection over macroscale areas (>1mm²). Furthermore, the ultrathin skins show good conformal contact with the flexible substrates and maintain structure under deformation. Fig. 18, for example, shows the skin covering some small, irregular waves or ripples in the substrate.

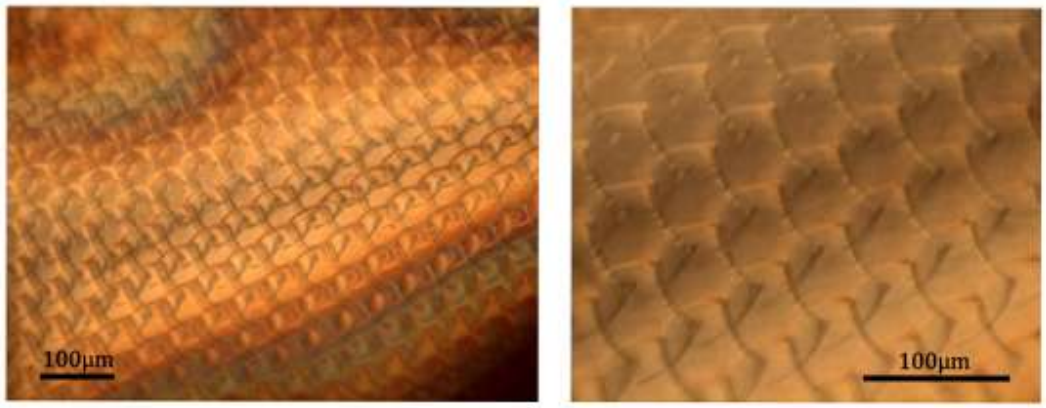

Figure 18.- Images of fish scales transferred to a flexible substrate. They can adapt to many different surfaces

2.4.3 Mechanical characterization of synthetic fish skins

Mechanical characterization has been executed to provide information about the efficiency of the engineered material in replicating the behavior of natural fish skins. Indentation tests were performed to verify whether the fish scales provided resistance to

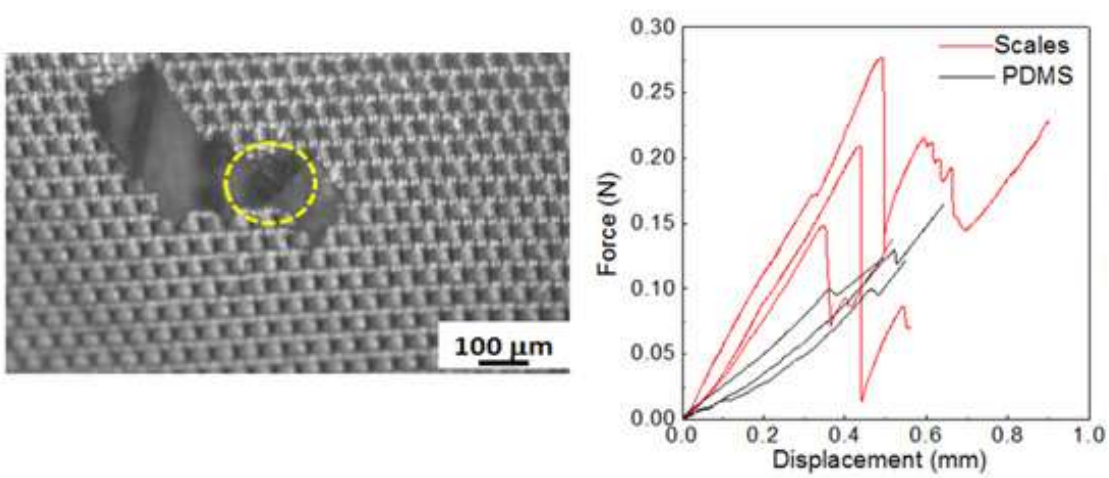

Figure 19.- a) Optical micrograph of the region of scales after puncturing b) Indentation test showing force versus displacement.

penetration.

Fish scales of 10 µm in width and 50 µm periodicity were engineered on top a PDMS substrate (1:10) and tested mechanically by indentation. Statistical data showed that the force necessary to indent a substrate containing fish scales was 0.20±0.10N while the force necessary to indent plain substrate was 0.10±0.04N. The Figure 19a shows the conditions of the scales after puncturing. The scales break apart when the load applied is too high. Because the scales are attached individually to the surface and not to each other, only localized regions of the scales break apart upon puncture instead of the entire skin.

The scales were able to double the force necessary to puncture the substrate showing a similar behavior as of that in real fish skins. It is possible to increase the sizes and thicknesses of the fish scales in the microfabrication process to achieve much higher resistance to puncture at the cost of flexibility. The values obtained in the resistance to puncture are not intrinsic of the material properties but the configuration of the material, the substrate holding the protective layer underneath and the type of tip that is being use. Because of that, in order to optimize the designs presented in this thesis it is necessary to apply them to a specific application so that an optimized material can be fabricated.

2.5 CONCLUSIONS

Biological materials continue to be a source of inspiration for scientists and engineers because they exhibit unique mechanical properties. However, there is still a lack of understanding behind their functionality and they can be difficult to replicate. In this chapter, a bio-inspired, engineered material based on the structures found in real fish skin has been designed and fabricated at the microscale to provide an ultrathin, flexible material.

The engineered material has been characterized and shows enhanced resistance to puncture on PDMS substrate. Moreover, the scales are lightweight, their small size makes them incredibly flexible, they can cover macroscopic areas, and may provide robustness, durability and wear resistance to a variety of surfaces. The artificial fish skin is thus uniquely positioned as an engineered material for coatings and protecting flexible/stretchable electronic devices since, unlike many other continuous or rigid protective coatings, can be applied on fabrics, elastomers, and other substrates that at present are rarely used for electronic materials since they lack mechanical robustness and durability. Future work will focus on measuring the flexibility of the material and finding an optimal balance between the flexibility and resistance of the material for targeted applications.

CHAPTER 3

3. HIERARCHICAL COMPOSITES FOR TOUGHNESS AMPLIFICATION

3.1 OVERVIEW

In the quest to design materials with enhanced toughness and strength, understanding this fundamental mechanical response is essential. The macroscopic behavior of the material is a consequence of all the components, structures, and interactions that constitute the material at the micro- and nano-scale. Modifying the structural hierarchy at the microscopic level can dramatically enhance the energy dissipation (toughness) provided that there is an efficient cooperation between adjacent scales. This idea has been the focus of interest of many scientists and engineers for many years. Different analogical and mathematical models have been developed over the last decades, but not many describe the links existing between different levels of hierarchy. The models also have not been validated and properly tested because of the difficulty in fabricating well-defined hierarchical systems.

In this chapter, microfabrication techniques (e.g., lithography, dry etching, metal depositions) have been applied to manufacture a material with different levels of hierarchy through which a crack is propagated. The objective is to test how different populations of voids or inclusions at different scales affect the overall fracture toughness of the material. Also, we have studied how materials can change their mechanical behavior when interacting with materials with different properties. The results will serve as proof-of-concept for the development of a fracture model and will provide a fundamental understanding of why and how toughening arises in hierarchical and composite materials.

3.2 INTRODUCTION

3.2.1 Hierarchical structures affect toughness in ductile and quasi-brittle fracture

Crack initiation and propagation are essential to the fracture of materials. Flaws may initially appear as cracks, voids and other defects in the processing, fabrication, or service of a material/component. When a material that contains a crack is under stress, the crack will propagate when it is energetically favorable to do so (Griffith theory).

In ductile fracture, the propagating crack moves slowly and is accompanied by a large amount of plastic deformation. This phenomenon is complex and difficult to describe because it includes heterogeneous and nonlinear materials behaviors (e.g., plasticity, damage, fracture). The amount of plastic deformation before fracture and especially the deformation region determine the fracture toughness of the material. The key to toughness is a good combination of strength and ductility. Therefore, the material toughness can be enhanced by increasing the size of the region undergoing plastic deformation (for a given material and material strength).

In brittle fracture, the cracks propagate with relatively little plastic deformation and there is low energy absorption before fracture. In order to make brittle materials serviceable for engineering applications, their properties can be modified by the addition of particle aggregates. The correspondent composites show quasi-brittle behavior, desirable because it provides a significant energy absorption capability to a material that does not yield plastically.

In quasi-brittle fracture, a crack propagating through the material dissipates energy. In the case of ductile fracture, apart from the cracking, there is an extra effect in the region around the crack that suffers plastic deformation. This region is known as the crack process zone and, in the absence of voids, the size of this region is dictated by the characteristic length scale (around a micron for metals) arising from crystallographic dislocations (see Figure 20a)[1,2,3]. One approach that can be used to magnify the crack process zone and, as a consequence, to increase the toughness in materials in ductile fracture is to take advantage of structural hierarchies. For instance, if a population of voids is added to a metal containing a crack, if there is strong cooperation between the voids and the dislocations, the size of the process zone can be significantly amplified (see Figure 20c). If the same idea is applied to materials with "N" cooperative levels of microstructure, the material toughness should increase because the crack process zone would be maximized since the energy that the material can dissipate is higher (see figure 20d).

This phenomenon has repercussions in quasi-brittle fracture and can help explain why biological materials constituted of brittle building blocks show ductile properties at a macroscale[4,5]. Thus structural hierarchy can enhance energy dissipation provided that there is an efficient cooperation between adjacent scales[6, 7, 8, 9].

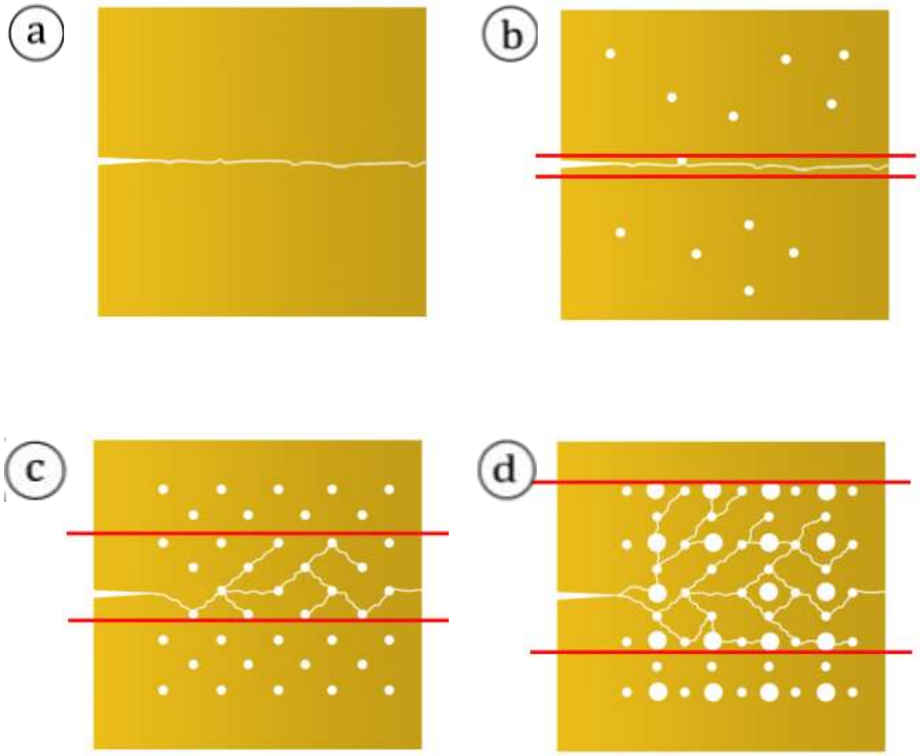

Figure 20.- a) A schematic of a crack propagating in a homogeneous material b) A crack propagating in a material with some population of voids. The red lines show the process zone. c) A crack propagating in a surface with a dense population of cracks. The red lines show the process zone. d) the process zone increases when an extra level of hierarchy is applied.

3.2.2 Modeling

Biological materials such as bones are composed of brittle building blocks arranged in specific structural organizations across dimensional scales. At the same time, such organizations are covered with a matrix of soft materials such as proteins and other biopolymers. Both the hierarchical structures present in the materials and the interactions between the structures/matrix seem to play a role in the materials toughness. Measuring the separate impact that both components have on the material toughness can be difficult.

Due to that, very little research has focused on understanding these effects and the fundamentals have been explained by few theoretical models.

Buehler et. al., in 2011, developed a computational model based on continuum mechanics to predict the stiffness, strength and toughness of a material with different levels of hierarchy. The model was applied to different situations. First, two different silica-based materials were defined and served as the building blocks for structures with two levels of hierarchy: a bulk silica (very stiff and brittle, properties similar to those found in biocalcite) and a nanoporous silica (soft and tough, bone-like structure). Two materials with different morphologies were designed with the initial building blocks using the same volume fraction in both materials. The first material had the bulk silica as the matrix and the nanoporous silica was embedded within the matrix. The second material had the opposite configuration. A stress-strain response from these materials showed significant differences in the mechanical properties of the material such as stiffness, fracture strength, toughness and the defect-tolerance[10].

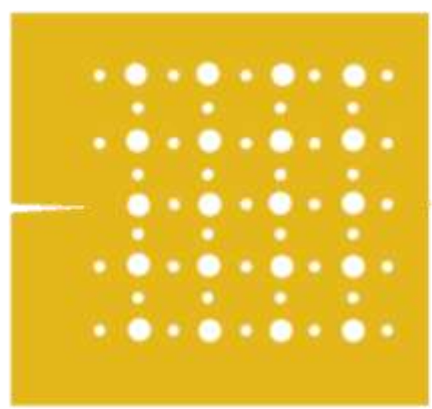

Figure 21.- Schematic of a hierarchical structure designed for the study of fracture mechanics.

Here experiments have been designed to study the role of structural hierarchy on the mechanics of fracture. The objective is to capture the key features of a hierarchical microstructure, including nonlocal effects at the various scales, the cooperation between adjacent scales and the emerging properties of the system, as well as the effect that the matrix can have on the material properties (analogous to the protein/silica relationship observed in bones). This chapter details a simple case in which a porous metal contains two different levels of hierarchy (see Figure 21). In future work, a close integration between modeling and fracture experiments across the microstructure scales will help provide a fundamental understanding of fracture mechanisms in hierarchical materials. Here, standard microfabrication processes were used to create materials with different levels of hierarchy with a high level of accuracy that can be duplicated easily. Qualitative experimental tests serve as a proof-of-concept and subsequent experimentation should lead to a model that can predict the relationship between a given hierarchical microstructure and fracture toughness so that materials with enhanced fracture resistance may be designed and synthesized.

3.3 MATERIALS AND METHODS

3.3.1 Metal sheets hierarchically structured by microfabrication

An engineered material composed of a hierarchical structured metal layer encapsulated in a polymer sheet has been fabricated in this study. All lithographic processing, including fabrication of the chrome mask and the deposition of metals were performed at University of Colorado in the NSF NNIN-Sponsored Colorado Nanofabrication Facility. The populations of inclusions in the metal sheet were fabricated using wafer-based microfabrication techniques. A computer aided drawing package (Clewin 4) was used to design and layout the hierarchical organizations, sizes of the arrays and the initial cracks. A chrome mask was created using the Heidelberg DWL 66FS in order to pattern three-dimensional structures.

Silicon wafers were cleaned using a solution of piranha (3 H_2SO_4 – 1 H_2O_2) at 50°C for 20min. The wafers were dried at 100°C in vacuum for 30min prior to use. NR71 photoresist was spincoated starting from 0 rpm up to 2000 rpm using 3 intervals of 30s each (2μm layers were created, see Figure 22/1). The wafers were prebaked for 60s at 150°C. The Suss MJB4 Manual Mask aligner was used for optical lithography through the chrome mask. The samples were exposed for 2min and then post-baked at 100°C for 60s. The silicon wafers with the NR71 were immersed in RD6 developer for 15s with mild agitation. The samples were then rinsed with DI water and left in the oven at 90°C for 2hr. The samples, already patterned the microstructures, were exposed to an O_2 plasma treatment for 20s using the March Jupiter III RIE at 1Torr. The reactive sputter system was used to deposit 400nm of Cu metal on the photoresist-patterned wafer. The conditions at which the metal was sputtered were: 40sccm argon, $3x10^{-3}$Torr and 120W. The samples were sonicated with acetone for 15min to do the lift off. Finally, the samples were dried in the oven at 90°C for 2hr (see Figure 22/2).

In order to transfer the metal sheets to a flexible substrate, an uncured polymer (superglue) coated on the entire surface and was left in the oven for 24hr at 40°C (see Figure 22/3). In a template stripping procedure, the polymer was then peeled from the substrate along with the copper layer (see Figure 22/4). The polymer was then coated on the other side with an additional layer of polymer and cured at 40°C for 24hr.

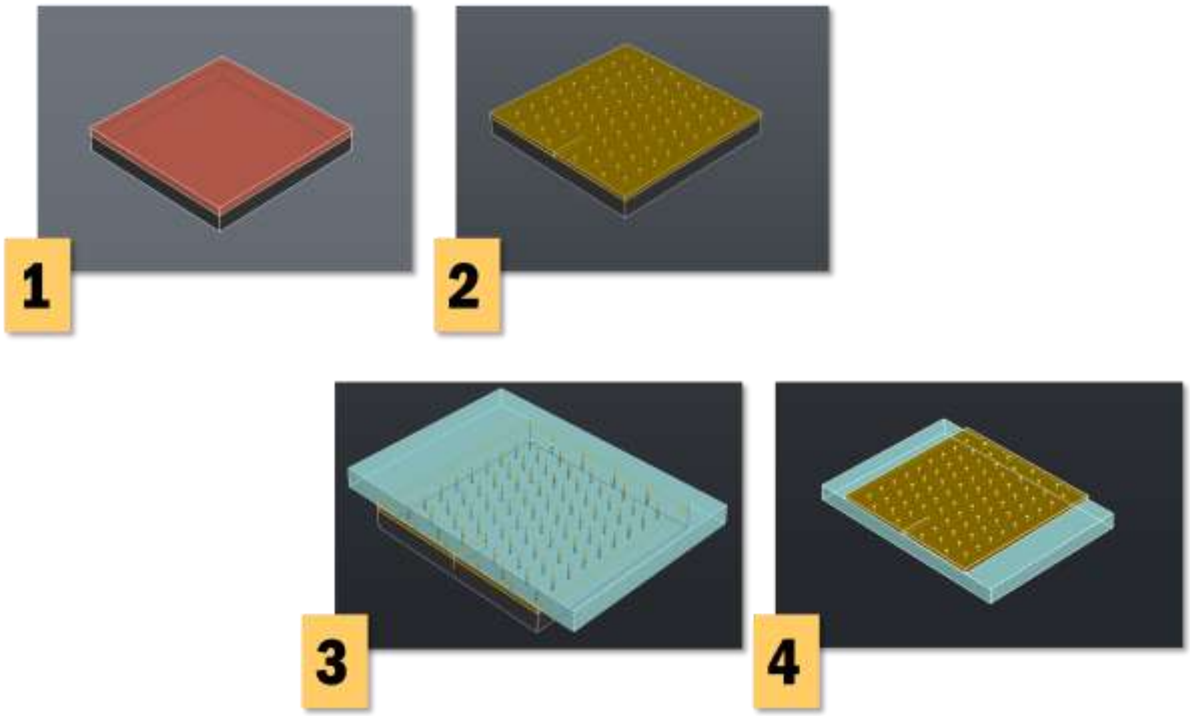

Figure 22.- Schematic showing different steps in the fabrication process. 1) NR71 photoresist covering a Si-wafer. 2) A 400nm thick copper layer is patterned on top of the Si-wafer. 3) The template stripping process for transfering microfabricated Cu onto a superglue support. 4) A copper layer transferred to a soft polymer, ready to be mechanically tested.

3.3.2 Mechanical characterization

A metal may possess satisfactory toughness under static loads but may fail under dynamic loads or impact. As a rule ductility and, therefore, toughness decrease as the rate of loading increases. Temperature is the second variable to have a major influence on material toughness. As the temperature is reduced, the ductility and toughness also decrease.

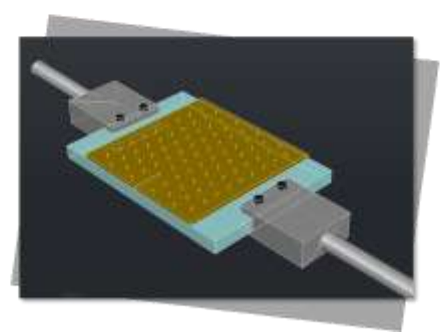

Figure 23.- Schematic of the mechanical test executed.

Dynamic Mechanical Analysis (DMA) was the tool selected to perform the experiments. It is a technique that is widely used to characterize a material's properties as a function of temperature, time, frequency, stress, atmosphere or a combination of these properties (see Figure 23). Experiments were performed controlling the force to a certain strain at a fixed temperature of 120°C and with a load rate of 1N/min.

3.4 RESULTS AND DISCUSSION

The models found in literature explaining the mechanics of fracture are based on observations from biological materials found in nature. When studying the hierarchical organizations observed in such biological materials, there is no control over the pore size and the morphology of the sample, there are variations in densities in the material, and several initial cracks may exist. The samples also are not ideal for mechanical testing since they have different shapes and the stress directions cannot be completely controlled. It is because of these challenges that the conclusions extracted from such studies can be sometimes vague. Here an engineered material consisting of a patterned layer of copper embedded in a polymer was fabricated for the study of different parameters found in composite biological materials that seem to have an effect on their mechanical properties such as brittleness, ductility, strength and toughness.

3.4.1 Engineered composite materials designs

The initial designs consist of a metal sheet embedded with populations of polymer inclusions at different scales. An initial crack was patterned into the metal sheet to concentrate stresses and control the region that would start fracturing first (see Figure 24). It was chosen to fabricate the systems by following a photolithographic process because it enables the fabrication of multiple levels of hierarchy in a single metal sheet, for example inclusions with diameters spanning 4 orders of magnitude from 1 to 1000 μm. Also, the systems can be designed as desired and with high levels of reproducibility. Different designs were microfabricated in order to test the effect that volume fraction, diameter of inclusions, number of different inclusions and periodicities have in the micro-cracking and thus the process zone. Table 1 shows the configurations that were designed.

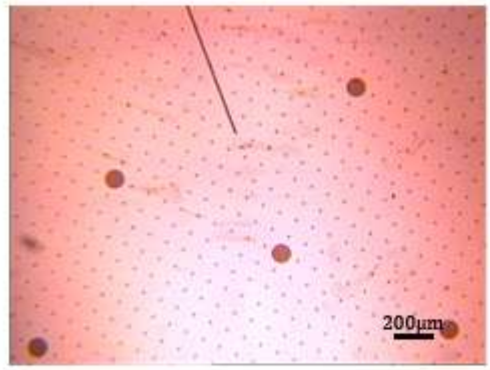

Figure 24.- Optical image of a hierarchical organization for the study in fracture mechanics in Cu metal sheets.

Sample	Volume fraction	Number of inclusions	Diameter of inclusions	Periodicities
A1	0.25%	1	10μm	100μm
A2	0.25%	1	100μm	1000μm
B1	1%	1	3μm	28μm
B2	1%	1	3μm	IRREGULAR
C	2.60%	2	10/100μm	100/1000μm
D1	4%	1	3μm	10μm
D2	4%	1	3μm	IRREGULAR
E1	7%	1	3μm	10μm
E2	7%	1	3μm	IRREGULAR
D1	21%	2	3/10μm	20μm
D2	21%	1	3μm	5.7μm
D3	21%	1	10μm	19.3μm
E1	40%	1	10μm	14μm
E2	40%	2	3/10μm	14.6μm
E3	40%	1	3μm	4.2μm

Table 1.- Different systems designed and fabricated for the experimentation

3.4.2 Deposition of the metal sheets

Once the Si wafer was patterned with the desired features, a metal film was deposited. The metal deposition techniques considered were electroplating, reactive sputtering and thermal evaporation. Each of the modes provided advantages and drawbacks. In electroplating, really thick metal films could be deposited. However, the control of the thickness was not accurate and the surfaces resulting were rough instead of being smooth (see Figure 25). In the thermal evaporation, the metal layers deposited were less porous than in the reactive sputtering and the metal did not attach to the photoresist side walls as well, thus facilitating the subsequent lift off process. However, the process was more tedious, expensive and the deposition batches were limited to ~200 nm thick films (depending upon the metal deposited). Finally, the reactive sputter system was found to be the best tool to use for the experiments. It allowed the deposition of thicker films than in the thermal evaporation process and the surface was smooth. In the process, an inert gas such as Argon is used to sputter the target (a high purity metal plate) from which the sputtered ions fly from the target and impact and coat the Si substrate[11].

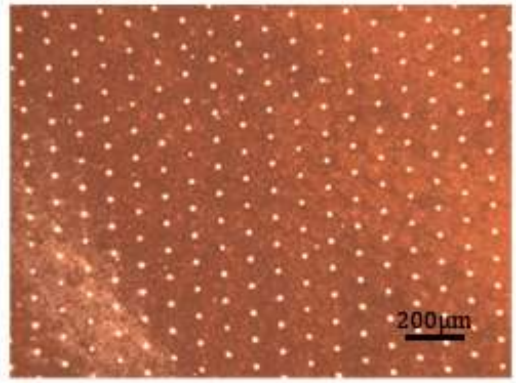

Figure 25.- Cu metal sheet fabricated using electroplatting techniques

The metals studied in the deposition were aluminum, gold, and copper. All of them are broadly used in the field of microfabrication for electronics. The experiments performed with aluminum showed that it bonded too well to the silica wafer and so it was difficult to transfer it to a flexible substrate once patterned. At the end, copper was the material selected for the system because it was cheaper than gold and it did not adhere as strongly to the Si substrate as did the aluminum.

3.4.3 Template stripping

The copper sheet with the desired populations of voids was fabricated. However, the metal layer did not provide information by itself and the Si substrate was too stiff to perform mechanical tests on it. Thus the metal layer had to be transferred to a softer polymer. By doing so, the sample could be stretched elastically to the desired strains and the behavior of the metal could be observed. The process was designed to produce a patterned layer sheet of copper immersed in a transparent polymer. The most challenging part of the transfer printing process was to achieve a metal layer completely free from cracks and defects (see Figure 26), which was achieved over 1cm^2 areas[19,20,21].

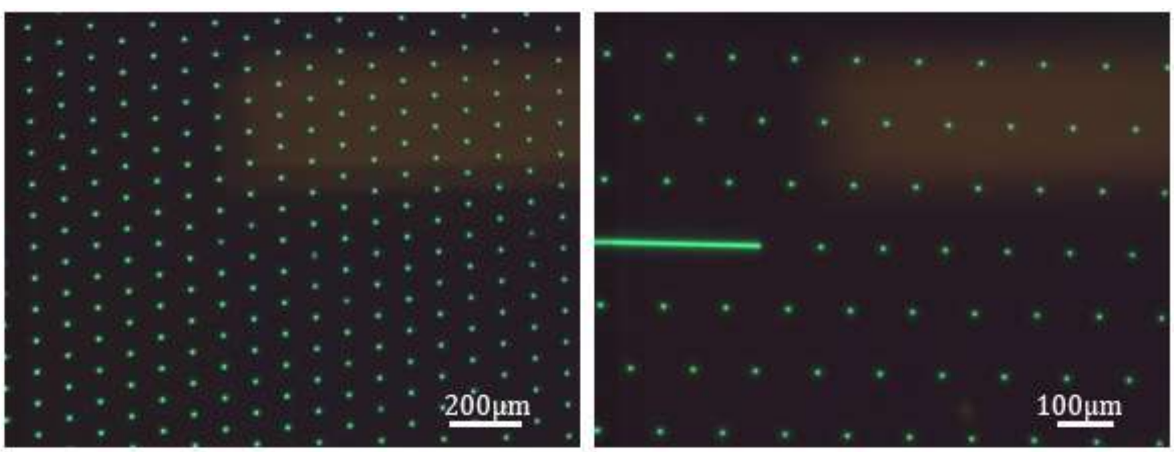

Figure 26.- Two images in a transmitance mode show the patterned layer sheet of copper immersed in a transparent polymer.

3.4.4 Mechanical testing

The initial experiments focused on the crack growth when applying Mode I tensile stresses perpendicular to a pre-fabricated crack. The material was tested at different strains (1%, 2%, 5%, 10%, 20%, 30%) until the crack propagated through the metal layer. An interaction between the populations of inclusions at different scales were desired and predicted to lead to the formation of micro-cracks along the metal sheet layer. The materials with different hierarchies were fabricated in the same sample so that identical stresses were applied.

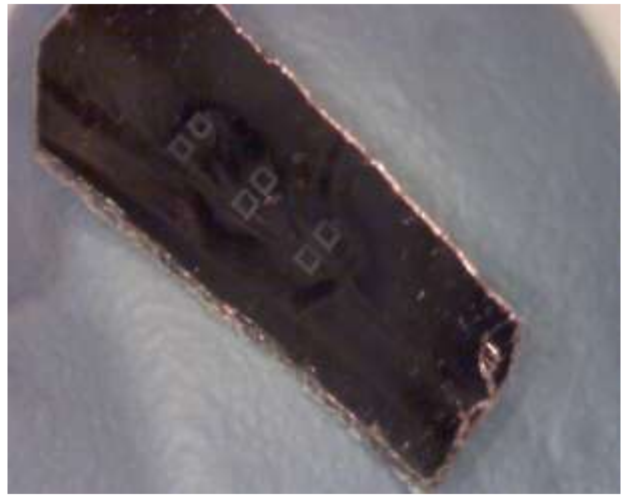

Figure 27 The image show a finger holding a sample of copper embedded in a polymer ready to be tested. The three square arrays shown correspond to the patterned regions that will be used for the research.

3.4.5 Mechanical testing using the DMA

The first experiments were tested with samples type B, D and E (see Table 1). The square arrays had only one level of hierarchy and the volume fractions were below 7% in all the cases (see Figure 27). Figures 27a and 27b show two different arrays before any stress is applied. On the other hand, Figures 27c and 27d show the samples after the application of tensile forces perpendicular to the propagating crack. Strains up to 25% were necessary in order for the crack to grow suggesting a ductile fracture mode. It seems that, although the cracks are not completely straight, they try to follow the easiest path to fracture. The reason no micro-cracking is observed is because the mode of fracture is totally ductile. Even though there are no cracks, the inclusions seem to have an effect in the directionality of the crack somehow. For example, it can be seen in Figure 27c that the crack propagates from inclusion to inclusion.

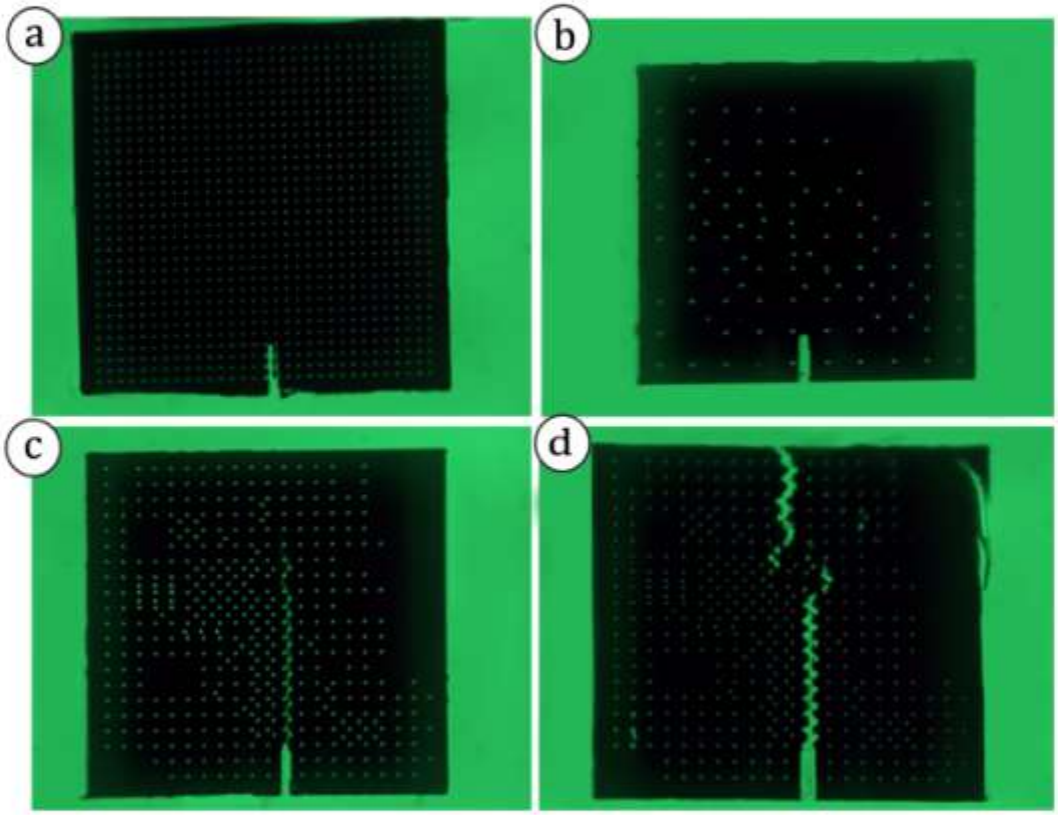

Figure 28 Images in transmission mode show 400 nm Copper layer embedded in a polymer with a low volume fraction of inclusions (<7%). a) Homogeneous array of 3μm inclusions. b) Non-homogeneous array of 3μm inclusions. c) A crack propagates through a non-homogeneous array after perpendicular stresses are applied d) A crack propagates through a non-homogeneous array after perpendicular stresses are applied (same configuration as in c)

Tensile deformation in metals layers surpassing 25% strains without failure are not intrinsic properties of the metal. The experimental observations suggest that there is a strong influence of the polymer encapsulating to the metal layer. The fracture of copper films differs depending upon the substrate to which it is attached. Literature reports show freestanding or polymer-supported copper fracturing at strains of 1%-2%. More recent articles show copper films on a polyimide substrate that can be stretched to strains exceeding 10% and up to 50% without rupture[12-18]. The interaction between the metal and the polymer layer seem to have an effect in the properties of the metal by making it more ductile than expected. These kinds of behaviors have already been observed in nature before. Bones for example, are made of a combination of a mineral component (brittle) and an organic protein component (ductile). A composite of brittle and ductile materials is formed that is tough and has outstanding properties. It might be then, that not only the hierarchical structures found in biomaterials are responsible for their properties, but also the interactions and bonds created between materials with different properties at small scales.

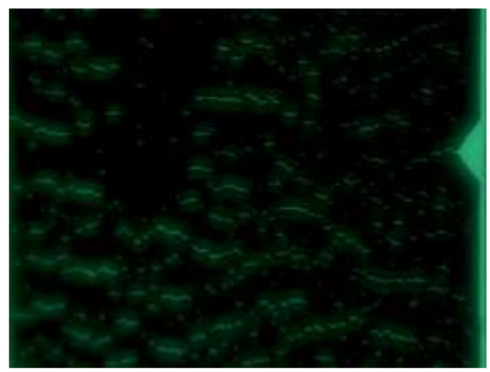

Figure 29 Copper layer embedded into the polymer without inclusions after stresses applied perpendicular to the initial crack.

Another fact that seems to reaffirm the hypothesis is the observations from the cracking affecting the copper layer with no voids or inclusions in Figure 28. In a typical ductile fracture the cracks usually are localized in a certain region. In this case though, it seems that there is micro-cracking all over the sample. It seems that the sample micro-cracks without the presence of inclusions. In theory, a copper layer with such properties should be able to dissipate more energy than a layer with a conventional behavior. Subsequent experiments involved the experimentation with squarre arrays with higher volume fractions (20% and 40%). The responses from the experiments were similar to those found at lower volume fractures.

Figure 29a and 29b shows 40% volume fraction copper layer that contain two different populations of voids. The images in the reflecting mode show high plasticity, the small inclusions seem to elongate and undergo plastic deformation to try to minimize the localized stresses.

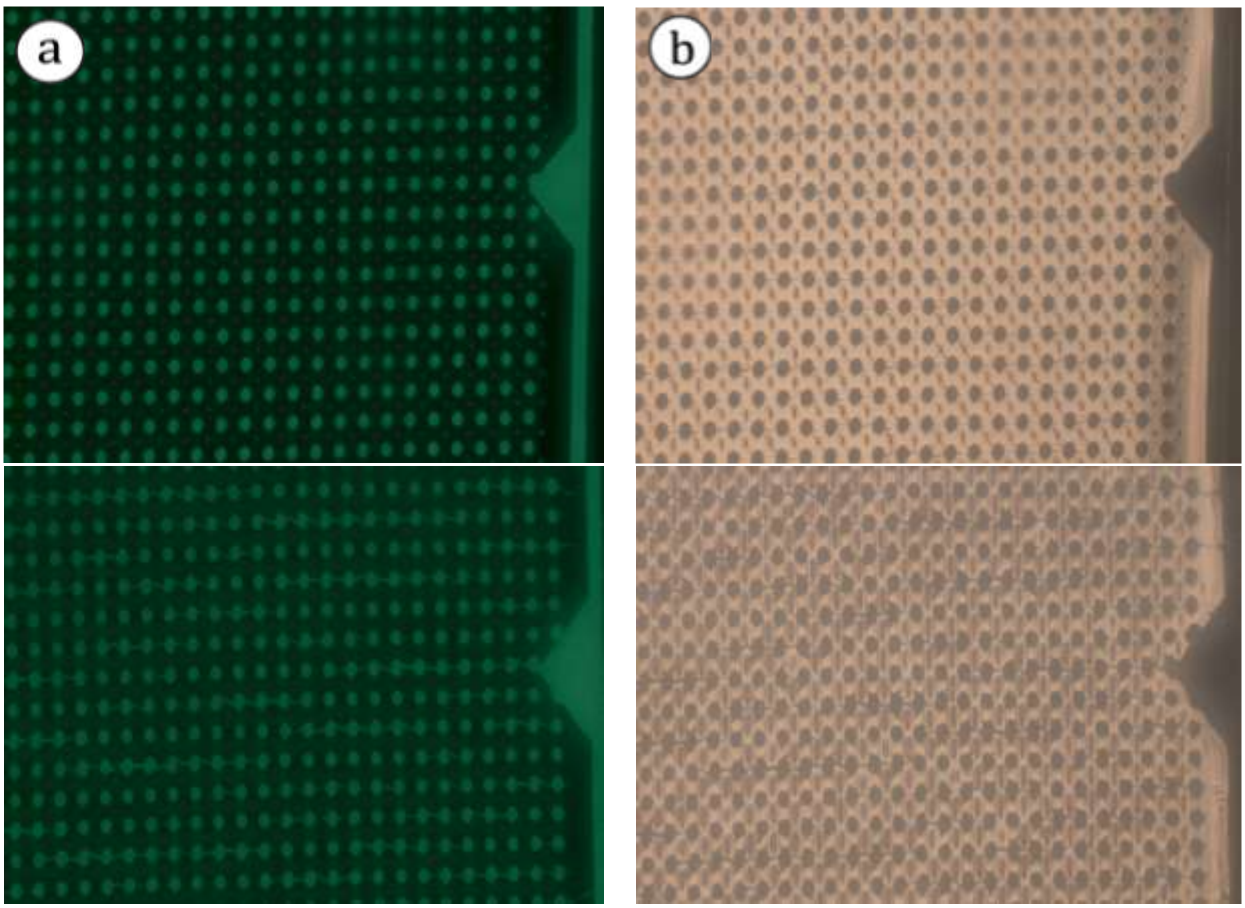

Figure 30 a) Transmission mode picture of a 20% volume fraction metal layer with two levels of hierarchy before tensile deformation. b) Reflective mode picture of a 20% volume fraction metal layer with two levels of hierarchy before tensile deformation. c) Transmission mode picture of a 20% volume fraction metal layer with one levels of hierarchy after DMA testing. d) Reflective mode picture of a 20% volume fraction metal layer with one levels of hierarchy after DMA testing.

Figures 29c and 29d show the metal layer fracturing parallel to the initial crack. There seem to be still a strong dependence with the delocalized cracks forming along the sample. However, comparing the sample with an early one in which there was no inclusions (see Figure 28) the cracks are more directional due to the presence of the inclusions. This occurs probably because the 20% volume fractional of inclusions reduced the strength of material in certain directions.

3.5 CONCLUSIONS

Here a material composite of hierarchical microstructure metal layer embedded in a polymer has been fabricated and mechanically characterized. Different geometries were experimentally tested using tensile strains with controlled loads rates and temperatures to try to qualitatively measure the impact that different inclusions have in amplifying the process zone around a propagating crack. However, the mechanism of propagation was observed to be completely ductile. All the stages of ductile fracture were observed starting from an initial deformation of the inclusions, nucleation of voids, micro-void growth, coalescence, and final fracture. The inclusions seem to have an effect on the fracture process and we would expect to have similar effects on the dissipation energy. This observed behavior differs from the original gids of the project, in which a brittle behavior in the propagation of the crack would arise.

The metal layer was able to withstand outstanding strains of 25% without fracture upon testing. The behavior seems to be a consequence of the bonding at these scales between the polymer and the metal. The same phenomenon has been reported in the literature, in which the strength of the bond between layers seems to have a direct effect upon the mechanical properties of the material. For instance, metals poorly bonded to adjacent surfaces show fractures at strains no larger than 5% while metals strongly bonded to polymer surfaces can hold strains up to 50% without fracture. Similar analogies can be found in nature as it happens with the interactions between the inorganic and organic materials in bones, which provide them with great toughness.

Future work will focus on the study of surface interactions between layers in order to be able to control the ductile/brittle response of the layered materials. Moreover, mechanical tests will be performed to achieve a brittle fracture mode in order to observe micro-cracking and be able to see the effect arising from the different hierarchical organizations that were fabricated into the material. In order to be able to achieve a more brittle fracture different parameters will need to be tuned such as the bonding between layers, the rate of stress loading and temperature of the DMA characterization. The final objective would be to have insight about the impact that hierarchical organizations and interactions between composites have in the biological materials and to engineer materials with enhanced properties for targeted applications.

4. BIBLIOGRAPHY

Chapter 1: Introduction

[1] Aizenberg, J. "Skeleton of Euplectella Sp.: Structural Hierarchy from the Nanoscale to the Macroscale." *Science, 309* (2005): 275-78.

[2] Williamson, D.M., and W.G. Proud. The Conch Shell as a Model for Tougher Composites. Thesis. University of Cambridge.

[3] Hou, D. "Conch Shell Structure and Its Effect on Mechanical Behaviors." *Biomaterials, 25*.4 (2004): 751-56.

[4] Kotov, Nicholas A., Zhiyong Tang, Sergei Magonov, and Birol Ozturk. "Nanostructured Artificial Nacre." *Nature Materials* (2003)

[5] Kotov, Nicholas A., Paul Podsiadlo, and Amit K. Kaushik. "Ultrasong and Stiff Layered Polymer Nanocomposites." *Science, 318.*80 (2007)

[6] Kotov, Nicholas A., Paul Podsiadlo, and Ellen M. Arruda. "LBL Assembled Laminates with Hierarchical Organization from Nano- to Microscale: HIgh-Toughness Nanomaterials and Deformation Imaging." *Acs Nano, 3*.6 (2009)

[7] Vernerey, Franck, Wing Kam Liu, et al. "Multi-length Scale Micromorphic Process Zone Model." *Computational Mechanics, 44.*3 (2009): 433-45.

[8] Smith, N. "An Introduction to Hierarchical Systems Theory." *Computers & Electrical Engineering, 1*.1 (1973): 55-71.

[9] Northen, Michael T., Christian Greiner, et al. "A Gecko-Inspired Reversible Adhesive." *Advanced Materials, 20*.20 (2008): 3905-909.

[10] Greiner, Christian, Eduard Arzt, and Aránzazu Del Campo. "Hierarchical Gecko-Like Adhesives." *Advanced Materials 21*.4 (2009): 479-82.

[11] Boesel, Luciano F., Christian Greiner, et al. "Gecko-Inspired Surfaces: A Path to Strong and Reversible Dry Adhesives." *Advanced Materials, 22*.19 (2010): 2125-137.

[12] Prum, B., R. Seidel, H. F. Bohn, and T. Speck. "Plant Surfaces with Cuticular Folds Are Slippery for Beetles." *Journal of The Royal Society Interface, 9*.66 (2011): 127-35.

Chapter 2: ENGINEERED FISH SCALES FOR APPLICATIONS AS PROTECTIVE LAYERS

[1] Bruet, Benjamin J. F., Juha Song, Mary C. Boyce, and Christine Ortiz. "Materials Design Principles of Ancient Fish armour." *Nature Materials, 7*.9 (2008): 748-56.

[2] Arciszewski, Tomasz, and Joanna Cornell. "Bio-inspiration: Learning Creative Design Principia." *Springer-Verlag Berlin Heidelberg* (2006): 32-53.

[3] Currey, John D. "The Design of Mineralised Hard Tissues for Their Mechanical Functions." *The Journal of Experimental Biology, 202* (1999): 3285-294.

[4] Sudo, Seiichi, Koji Tsuyuki, et al. "A Study on the Surface Shape of Fish Scales." JSME *International Journal Series C, 45*.4 (2002): 1100-105.

[5] Youngblood, Jeffrey P., and Nancy R. Sottos. "Bioinspired Materials for Self-Cleaning and Self-Healing." *MRS Bulletin, 33* (2008): 732-41.

[6] Hebrank, Mary R. "The Mechanics of Fish Skin: Lack of an "external Tendon" Role in Two Teolosts." *The Biological Bulletin, 171* (1986): 236-47.

[7] Hebrank, Mary R. "Mechanical Properties and Locomotor Functions of Eel Skin." *The Biological Bulletin, 158* (1980): 58-68.

[8] Song, Juha, Christine Ortiz, and Mary C. Boyce. "Threat-protection Mechanics of an Armored Fish." *Journal of the Mechanical Behavior of Biomedical Materials, 4* (2010): 699-712.

[9] Chen, Po-Yu, Jeffrey Schirer, et al. "Predation versus Protection: Fish Teeth and Scales Evaluated by Nanoindentation." *Journal of Materials Research, 27.*01 (2012): 100-12.

[10] Bruet, Benjamin J. F., Juha Song, Mary C. Boyce, and Christine Ortiz. "Materials Design Principles of Ancient Fish armour." *Nature Materials, 7*.9 (2008): 748-56.

[11] Zhu, Dej et al. "Structure and Mechanical Performance of a ‘‘Modern’’ Fish Scale." *Advanced Biomaterials, 13*

[12] Browning, Ashley, Christine Ortiz, and Mary C. Boyce. "Mechanics of composite elasmoid fish scale assemblies and their bio inspired analogues." *Journal of the Mechanical Behavior of Biomedical Materials, 19* (2013): 75-86.

[13] Rogers, J. A., H. C. Ko, et al. "Arrays of Silicon Micro/Nanostructures Formed in Suspended Confi Gurations for Deterministic Assembly Using Flat and Roller-Type Stamps." *Small Journal, 7* (2011): 484-91.

[14] Kim, S., et al. "Microstructured Elastomeric Surfaces with Reversible Adhesion and Examples of Their Use in Deterministic Assembly by Transfer Printing." *Proceedings of the National Academy of Sciences, 107*.40 (2010): 17095-7100.

[15] Meitl, Matthew A., et al. "Transfer Printing by Kinetic Control of Adhesion to an Elastomeric Stamp." *Nature Materials, 5*.1 (2005): 33-38.

[16] Kim, Seo, et al. "Imbricate Scales as a Design Construct for Microsystem Technologies." *Small Journal, 8* (2012): 901-06.

Chapter 3: HIERARCHICAL COMPOSITES FOR TOUGHNESS AMPLIFICATION

[1] Rice, J. R., and D. M. Tracey. "On the Ductile Enlargement of Voids in Triaxial Stress Fields." *J. Mech. Phys. Solids, 17* (1969): 201-17.

[2] Tvergaard, Viggo. "On Localization in Ductile Materials Containing Spherical Voids." *International Journal of Fracture, 18* (1980)

[3] Tvergaard, Viggo. "Influence of Voids on Shear Band Instabilities under Plane Strain Conditions." *International Journal of Fracture, 17*.4 (1981): 389-407.

[4] Thiel, Brad L., Keith B. Guess, and Christopher Viney. "Non-periodic Lattice Crystals in the Hierarchical Microstructure of Spider (major Ampullate) Silk." *Biopolymers, 41*.7 (1997): 703-19.

[5] Gao, Huajian. "Application of Fracture Mechanics Concepts to Hierarchical Biomechanics of Bone and Bone-like Materials." *International Journal of Fracture, 138*.1-4 (2006): 101-37.

[6] Vernerey, Franck, Wing Kam Liu, Brian Moran, and Gregory Olson. "Multi-length Scale Micromorphic Process Zone Model." *Computational Mechanics, 44*.3 (2009): 433-45.

[7] Vernerey, Franck, Wing K. Liu, and Brian Moran. "Multi-Scale Micromorphic Theory for Hierarchical Materials." *Journal of the Mechanics and Physics of Solids* (2007)

[8] Vernerey, F., W. Liu, B. Moran, and G. Olson. "A Micromorphic Model for the Multiple Scale Failure of Heterogeneous Materials." *Journal of the Mechanics and Physics of Solids, 56*.4 (2008): 1320-347.

[9] Vernerey, Franck, Wing Kam Liu, Brian Moran, and Gregory Olson. "Multi-length Scale Micromorphic Process Zone Model." *Computational Mechanics, 44*.3 (2009): 433-45.

[10] Sen, Dipanjan, and Markus J. Buehler. "Structural Hierarchies Define Toughness and Defect-tolerance despite Simple and Mechanically Inferior Brittle Building Blocks." *Scientific Reports* (2011)

[11] Anders, André. "A Structure Zone Diagram including Plasma-based Deposition and Ion Etching." *Thin Solid Films, 518*.15 (2010): 4087-090.

[12] Li, Teng, Zhenyu Huang, Z. Suo, Stéphanie P. Lacour, and Sigurd Wagner. "Stretchability of Thin Metal Films on Elastomer Substrates." *Applied Physics Letters, 85*.16 (2004): 3435.

[13] Xiang, Yong, Teng Li, Zhigang Suo, and Joost J. Vlassak. "High Ductility of a Metal Film Adherent on a Polymer Substrate." *Applied Physics Letters, 87*.16 (2005): 161910.

[14] Lacour, Stéphanie Périchon, Sigurd Wagner, Zhenyu Huang, and Z. Suo. "Stretchable Gold Conductors on Elastomeric Substrates." *Applied Physics Letters, 82*.15 (2003): 2404.

[15] Kim, Hyun-Joong, Chulwoo Son, and Babak Ziaie. "A Multiaxial Stretchable Interconnect Using Liquid-alloy-filled Elastomeric Microchannels." *Applied Physics Letters, 92*.1 (2008): 011904.

[16] Lu, Nanshu, Xi Wang, Zhigang Suo, and Joost Vlassak. "Metal Films on Polymer Substrates Stretched beyond 50%." *Applied Physics Letters, 91*.22 (2007): 221909.

[17] Kim, D.-H., J.-H. Ahn, W. M. Choi, H.-S. Kim, T.-H. Kim, J. Song, Y. Y. Huang, Z. Liu, C. Lu, and J. A. Rogers. "Stretchable and Foldable Silicon Integrated Circuits." *Science, 320*.5875 (2008): 507-11.

[18] Ring, Terry A., Paul Feeney, David Boldridge, Jaishankar Kasthurirangan, Shoutian Li, and James A. Dirksen. "Brittle and Ductile Fracture Mechanics Analysis of Surface Damage Caused During CMP." *Journal of The Electrochemical Society, 154*.3 (2007): H239.

[19] Im, Hyungsoon, Si H. Lee, Nathan J. Wittenberg, Timothy W. Johnson, Nathan C. Lindquist, Prashant Nagpal, David J. Norris, and Snag-Hyun Oh. "Template-Stripped Smooth Ag Nanohole Arrays with Silica Shells for Surface Plasmon Resonance Biosensing*." Acs Nano, 5* (2011): 6244-253.

[20] Nagpal, P., N. C. Lindquist, S.-H. Oh, and D. J. Norris. "Ultrasmooth Patterned Metals for Plasmonics and Metamaterials." *Science, 325*.5940 (2009): 594-97.

[21] Chanda, Debashis, Kazuki Shigeta, Sidhartha Gupta, Tyler Cain, Andrew Carlson, Agustin Mihi, Alfred J. Baca, Gregory R. Bogart, Paul Braun, and John A. Rogers. "Large-area Flexible 3D Optical Negative Index Metamaterial Formed by Nanotransfer Printing." *Nature Nanotechnology, 6* (2011)