

Design of flexible puncture resistant gloves inspired by natural dermal armors

Anqi Lin

A thesis

**Submitted in partial fulfillment of the
requirements for the degree of**

Master of Science

University of Washington

2017

Committee:

Dwayne D. Arola

Guozhong Cao

Program Authorized to Offer Degree:

Materials Science and Engineering

©Copyright 2017

Anqi Lin

University of Washington

Abstract

Title: Design of flexible puncture resistant gloves inspired by natural dermal armor

Anqi Lin

Chair of the Supervisory Committee:

Dwayne D. Arola

Associate Professor, Materials Science and Engineering

Adjunct Associate Professor, Oral Health Sciences

Adjunct Associate Professor, Restorative Dentistry

Materials Science and Engineering

For the purpose of providing protection against potential environmental and physical threats, many animal species have developed hierarchical and heterogeneous biological materials. In turn, scientists and engineers have been inspired by the design of these biological materials and are working to apply this knowledge to develop “biologically inspired” engineered materials and structures. For example, puncture resistant materials are developed to provide protection against needles, thorns and other sharp objects, which may pierce soft flesh. Many natural armors are designed to have high puncture resistance and high flexibility. Unfortunately, these two properties are usually hard to achieve at the same time since most hard materials are also very stiff. In this study, we evaluate the puncture resistance and flexibility of fish scale structures. Elasmoid fish scales possess a unique balance of stiffness, strength and low weight to provide protection against predators and not interfere with locomotion. In this investigation the biological design of fish scales is dissected and then applied to pursue improved material designs for puncture resistant gloves.

Table of Contents:

I Abstract.....3

II Acknowledgement.....5

1. Background.....6

1.1 Learning from Nature: Biomimetics and bioinspiration6

1.2 Biological Protective systems and Engineering.....7

1.3 Fish scales.....8

1.4 Multi-layered Flexible Articulating Armor Design.....10

1.5 Objectives.....10

2. Materials and Methods.....11

2.1 Materials.....12

2.2 Experimental and Methods.....12

2.2.1 Puncture testing.....12

2.2.2 Elastic properties by nanoindentation.....16

2.2.3 Flexural stiffness investigation.....16

2.2.4 Finite element modeling.....15

3. Results and Discussion.....17

3.1 Puncture resistance of commercial protective materials and scales.....17

3.2 Contribution of the individual layers.....19

3.3 Whole scales.....22

3.4 Comparison of flexural stiffness of PC sheets, TPR and each layer of scale.....24

3.6 ANSYS stress distribution modeling.....28

4. Conclusion and future works.....28

4.1 Conclusion.....29

4.2 Future work30

5. References.....32

Acknowledgements:

I am special thankful to my advisor and MSE department professor D. Arola for giving me this great opportunity to work in his biomaterial and mechanical engineering research lab. When I joined your lab last year, I have very limited knowledge with research and biomechanical experience. You teach me how to be a logical researcher and think like an engineer patiently. The most important thing I learned in 2016 is how to achieve the goal step by step. The way to achieve the goal is hard but I need to believe myself. You encouraged me when I was low and punished me when I over-estimated myself. I remembered every advice you gave me and every comment you put underneath my puncture test results. Especially my graphing skills keep improving by following your suggestions. I worked hard to learn how to be a good researcher and I think I worth a graduate degree of material science of engineering now.

I am also thankful for my colleague, my friend Weishi Yan, he encouraged me when I wasn't sure if I still want to insist and finally I made the right decision. He gave me a lot of advice and helped me do better on this research step by step. I am not smart, but I am very lucky that I have such a good friend. The people in Dr. Arola's research lab are very nice to me, Sandra Murica, Dr. Jiawang Song, Alex Stark and Sean Ghod provided a lot of help on my research.

To my parents, grandma and my friend Dingyu Yao, for never questioning my abilities, always supporting my decisions. I am the strongest man on the world because of you guys. Thanks for providing funding for my graduate school tuition at the University of Washington. I can overcome any hardship I meet in the future because the strongest armor for me are you guys.

1. Background

1.1 Learning from Nature: Biomimetic and bio-inspiration.

Biological materials have numerous capabilities that surpass synthetic materials in many aspects such as flexibility, specific strength and toughness and elegance of design. For example, silk (a biological material created by silkworms) usually has better breathability, durability and better heat retention than dacron (a man-made polymer that is usually used on clothes). The idea of taking the advantages of biological materials and applying them to man-made product designs is regarded as “biomimetics” or “bioinspiration”.[1] By definition, biomimetic design is the imitation of the models, systems, and elements of nature for the purpose of solving complex human problems. [1] Over millions of years, plants and animals have developed various functional properties that have the high potential to be applied in biomimetic designs. In recent years, fish scales have received more attention by researchers because they exhibit a unique balance of flexibility, strength and toughness. [2] In this study, we focus on the puncture resistance and complimentary properties of fish scales and pursue the design of compatible synthetic materials for potential application in flexible impact resistant gloves.

As shown in Fig. 1, bioinspiration includes bioinspired structural materials, biomimetic materials for tissue engineering, bioinformatics and artificial intelligence, biomimetic synthesis, as well as bioinspired sensors and actuators in conjunction with conventional science and engineering fields. [3] In the early 14-15th centuries, scale topologies were used in the design of body armor among ancient European countries. The scaled armor design can be considered as one of the most important biomimetic designs and bio-inspired products, which exhibit multifunctional and superior capabilities. Today, the design principles of fish scales are inspiring

flexible armor designs that can achieve a balance between protection and flexibility/mobility, and utilize synthetic man-made material systems.

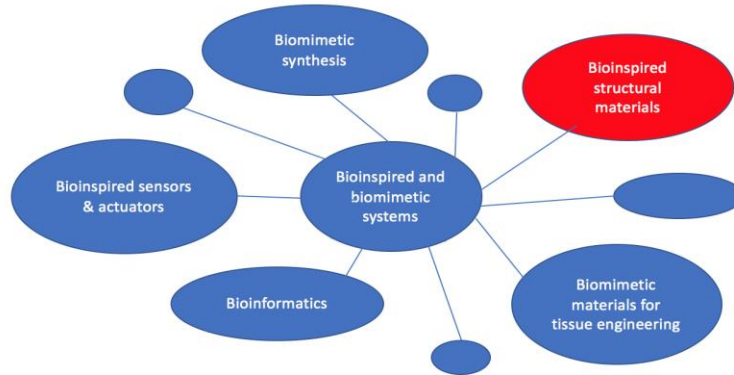


Fig. 1 Bio-inspiration and its related science disciplines

1.2 Biological protective systems and engineering

In nature, many animal species of animals have developed and utilize flexible dermal armors for protection against predators through a process of convergent evolution. For example, fish, alligators, armadillos, turtles, and even butterflies have tiny scales as shown in Fig. 2



Fig. 2 Some species with natural flexible dermal armor; (A) *Aprapaima giga* fish in the Amazon river [4] (B) Alligators [5] (C) Armadillo (Mammalia) [6] (D) Turtles [7] (E) Butterfly wing [8](F) Carp fish (*Cyprinus Carpio*)

During evolution, ancient armored fish were required to increase their swimming speed with enhanced body flexibility to adapt to their more predatory and dynamic environments. [3] Flexibility is also one of the most important properties that is required in puncture resistant glove designs. Fig. 3 shows the body of a carp fish in a state of extreme body curvature and the normal body position. The scales on its body provide protection against threats from the environment but don't impede the movement of its body as necessary for evasion of threats.



Fig. 3 The carp fish in normal position (left) and on its extreme body position

1.3 Fish scales

Fish scales serve as a form of natural armor that has been investigated within the last half decade for its unique microstructure and mechanical behavior. With regards to providing resistance to puncture, fish scales have two important functions: (i) they resist penetration and

(ii) redistribute the force from the location of the bite over a much larger area. According to Zhu et al, [8] the whole penetration process can be divided into three stages with progressively increasing penetration depth. Stage I is essentially elastic loading, which terminates with cracking of the external mineral layer; Stage II involves the penetration of collagen; while in Stage III the tip of the indenter completely traverses the scale.

Elasmoid scales are relatively thin and compliant compared to the bony or ganoid scales. [9] As such, Elasmoid scales allow unencumbered and, flexible movement of the fish. In this study, we selected scales from the *Cyprinus carpio* and *Arapaima gigas* for the model scale system to explore for bioinspired design.

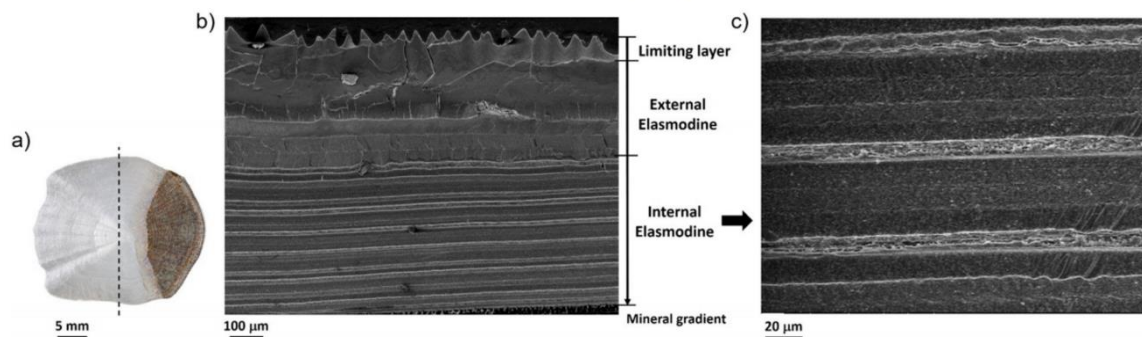


Fig. 4 The hierarchical microstructure of carp scales. [10]

As shown in **Fig. 4**, the structure of elasmoid scales over the cross-section thickness consists of two primary layers. The “limiting layer”, which is the external or outermost layer of the scales, is highly mineralized and composed of hydroxyapatite. The limiting layer in carp fish is thin but stiff. The limiting layer plays a major role in the puncture resistance of fish scales. The other primary layer is the “elasmodine” layer that is composed layers or laminae of unidirectional collagen fibers and apatite mineral. [11] The elasmodine is often divided into two different layers, including the external and internal elasmodine, which are differentiated mostly

by the higher mineral content of the external portion. The microstructure of elasmoid scales is often referred to as a “plywood” structure due to the stacking of the individual lamina of collagen fibers. This structure can also be found in the elasmoid scales of all fish, including the arapaima giga fish scales as well. [12] The diameter of the collagen fibers is generally $\leq 1\mu\text{m}$, and they are constructed of an assembly of fibrils roughly 100 nm in diameter. [9, 13, 14]

1.4 Multi-layered Flexible Articulating Armor Design

This research focuses on using or mimicking the multilayered structures of carp fish scales to pursue a glove design that provides improved puncture resistance over the existing material design, as well as to enable biomechanical flexibility, as shown in **Fig. 3**. A 2-D view of a puncture resistant glove model is shown in **Fig. 5**. In this figure, the finger can be considered as the body of the carp fish. The carrier elastomeric material of the glove can be considered as the elasmidine layer, and a flexible fiber reinforced hard plastics can be considered as the external elasmidine and limiting layer of carp scales. We expect that the top layer of the puncture resistant gloves can provide enhanced puncture resistance and with further engineering can be optimized to increase puncture resistance without penalty of lost flexibility. Additionally, the compliant material in between top layer and finger can achieve a balance between protection and mobility for this puncture protection system.

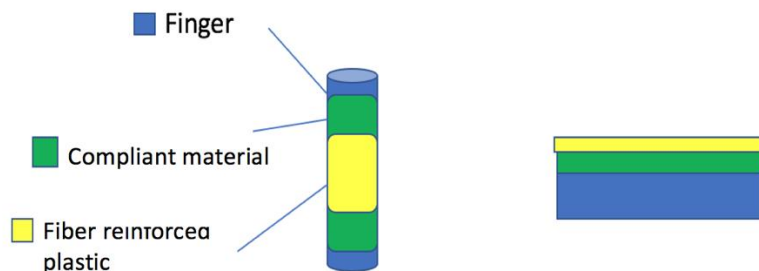


Fig. 5 The 2-D sketch of bioinspired puncture resistant gloves. (Left) the top view of the puncture resistant gloves model. (Right) the side view of the model.

1.5 Objectives

The goal of this project is to explore the principle of bioinspired design of puncture resistant materials from the design and puncture resistance of flexible fish scales. The performance of fish scales and relative puncture resistance of individual layers will be evaluated experimentally. Then, we plan to use the results from the puncture tests to guide the selection of material combinations that can be used to design and develop puncture resistant gloves. The puncture resistant gloves should be inexpensive, comfortable and flexible. More importantly, they should provide an improved puncture resistance when compared to the existing materials. There are three primary goals:

The first goal is to investigate the contribution of the individual layers of fish scales (including the limiting layer, external elasmodine and internal elasmodine) to their puncture resistance and flexibility.

The **second goal** is to investigate if fish scales can provide increased protection to puncture when it is placed on the top of glove materials and to compare it with the results on modern engineering polymers to see which one is better.

The final goal is to analyze the change in stress distribution during a puncture loading of a bio-inspired glove materials that is achieved with the use of fish scales. For this purpose, computational modeling software will be used.

2. Materials & Methods

2.1 Materials

Scales of the *C. carpio* fish for this investigation were obtained from a single farm-raised fish. According to the method introduced by Garrano et al, [9] the scales from *C. carpio* were extracted by using tweezers, rinsed in bleach solution for 2-3 second to remove the bacteria on the surface of scale and rinsed in DI water 5-6 times. After that, the carp scales were submerged into HBSS solution and kept in the fridge. The scales of carp are categorized as cycloid scales and details of these scales are shown in **Fig. 6a**.

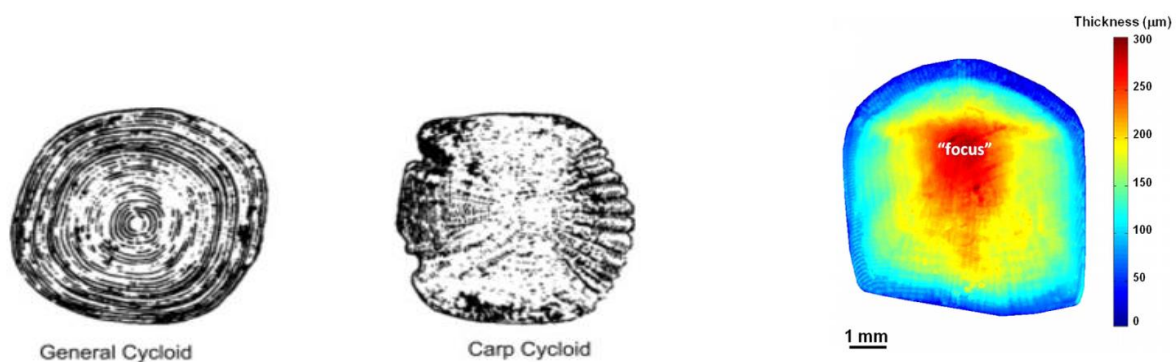


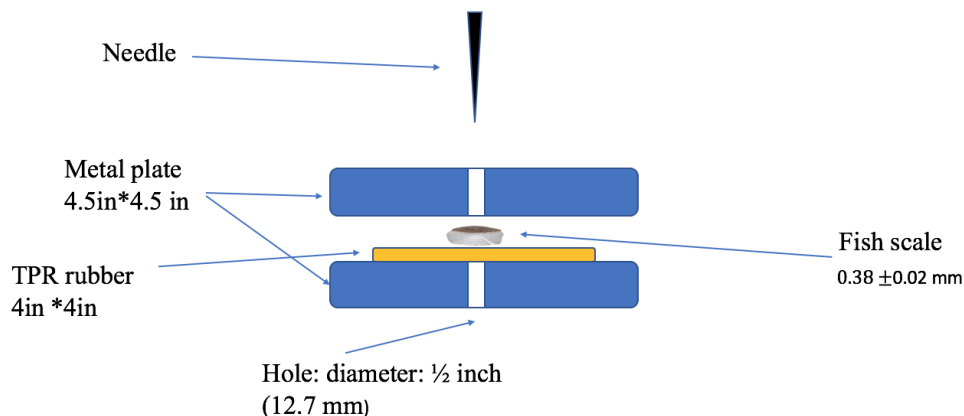
Fig. 6a. (left) Types of cycloid scales. [9] **b.** Carp scale with thickness indicated by different colors [15]

The thermoplastic rubber (TPR) substrate was ordered from Qingdao Seven King Industrial Company through Alibaba.com. The TPR was obtained in sheet form with roughly 3 mm thickness. In order to grip the TPR specimens under the metal plate on the fixture, we cut the TPR substrate into 100mm x100 mm squares to fit the size of the experimental fixture. A polycarbonate sheets (PC) sheet with thicknes of 0.39 mm was directly ordered from [msdirect.com](https://www.msdirect.com). The sheet was cut into section of roughly 26mm x 26mm.

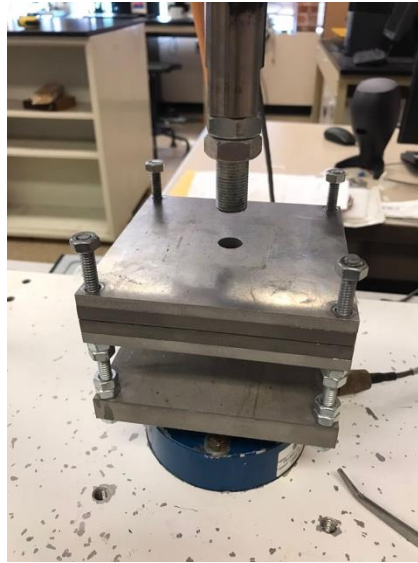
2.2 Experimental Methods

2.2.1 Puncture testing

Earlier work showed that the puncture resistance of fish scales is site dependent. This spatial variation can be explained by changes thickness across the scales and possibly by other scale features, for example differences in mineral content and layer thickness across the scale. [15] To be consistent across all portions of the evaluations, the puncture tests performed on scales were all conducted within the “focus” area of the scales. That also enabled comparison with the results reported in previous studies. [15 Zhu et al 2013] Although it is believed that fish scales play an important role on the protective capacity of fish skin, the effectiveness of scales placed on top or integrated within glove materials is not clear. The experimental setup and procedures used for the evaluation followed the procedures defined by ASTM standard D-3763-02 for puncture testing. The load and displacement to puncture were evaluated for each of the materials evaluated. The tip radius of the steel puncture needle is consistent with that described in the ASTM standard, with 40 μm tip radius of curvature and with an inclination of 26 degrees; the tip the geometry was evaluated using microscope. As shown in **Figure 7b**, the specimens, including carp scales and selected polymers, were gripped in a custom fixture and placed in between two metal plates with a 12 mm hole in the center.



a. 2-D schematic diagram of the experimental arrangement for puncture testing



b. Steel plate and screws to clamp the sample in middle of the plate.

Fig.7 Puncture testing experimental arrangement.

The ramp rate for all puncture testing was 0.05 mm/min. To compare with the results of puncture resistance of polycarbonate sheets, we selected 5 scales obtained from the middle part of the carp fish that have similar thickness with the PC sheets; the PC sheet thickness is 0.38 mm, and the average carp scales thickness was 0.38 ± 0.02 mm in focus area. Puncture tests were conducted on a total of five samples for each material, and the maximum load and energy to puncture were determined. The substrates evaluated include TPR rubber, scales and TPR+ scales in stacked arrangement. The energy to puncture was calculated by using the integral of area under the load-displacement curve. A one-way statistical analysis of variance (ANOVA) was used to determine whether a significant difference exists between data sets. If the p value is less than 0.05, a significant difference between the data sets does exist. If the p value is larger than 0.05, we cannot conclude that a significant difference exists. [16]

To investigate the contribution of the individual layers of fish scales (including the limiting layer, external elasmodine and internal elasmodine) to the total puncture resistance and flexibility, a needle was used to separate the internal elasmodine from the carp scales. The needle was inserted in between the internal elasmodine and mineralized layer (a combination of external elasmodine and limiting layer). The internal elasmodine was separated from the mineralized layers, by simple tearing. For the purpose of separating external elasmodine from mineralized layer, we taped the mineralized layer on a double-sided tape and grind on a piece of 800 um abrasive grinding paper. Approximately, 0.03mm thickness was removed, which is the typical thickness of limiting layer.

2.2.2 Elastic properties by nanoindentation

Nanoindentation tests were performed on the internal elasmodine and mineralized layer of carp scales to determine the elastic modulus for each layer. Results are reported in Murcia et al. [11] Briefly, selected scales were cross-sectioned, mounted in epoxy resin and then polished to mirror finish as necessary to obtain a smooth and flat surface. The elastic modulus and hardness were determined directly from the indentation load and displacement measurements obtained during indentation. [17] In a previous study by Yang et al, [18] nanoindentation tests performed on ganoid scales have showed that the modulus and hardness exhibit spatial variations through the thickness, which appears related to the distribution of mineral. [11,18] The results can be used on the finite element model and ANSYS stress distribution modeling.

2.2.3 Flexural stiffness investigation

Glove materials must be flexible. The ideal puncture resistant gloves should achieve better protection with good comfort and better dexterity. Investigating the flexural stiffness (bending stiffness) is another important metric of this project. Based on definition, flexural

stiffness is the resistance of a member against bending deformation. [19] In this study, we used the V-shape indenter for the flexural properties test by applying load on the center of a specimen prepared with rectangular geometry of 20 mm* 5 mm. The specimen was placed on top of a hole approximately 13 mm in diameter and the scale was indented with ramp rate of 0.05 mm/min.

The flexural stiffness (κ) of a beam can be expressed as the load over the deflection of the beam.

$$\kappa = F/w \text{ [19]}$$

Here, “F” represented the load (units in Newton) applied on the beam while “w” is the deflection (units in mm). Lower flexural stiffness (κ) results in better compliance of the material. The flexural stiffness for each layer of carp scales, glove materials, and engineering polymers was determined.

2.2.4 Finite element modeling

In this investigation, a finite element model was developed to develop a better understanding of the benefits of using scales in puncture resistant gloves. A commercial software was used for this effort. The version of ANSYS we used in this study was the version. The objective of the ANSYS modeling was to explore the change in stress distribution achieved by the addition of scales placed on top of a rubber substrate, and the increased resistance to puncture and damage of the materials beneath. In addition, deformation of the TPR rubber that occurs during puncture can also be modeled by using ANSYS software. In this study, we developed models including the typical thickness of TPR rubber that is applied on puncture resistant gloves in the fingers region, which is approximately 3mm thickness. On the top of TPR rubber, the scales, including the IE, EE and LL layers by using the Poisson ratio and elastic modulus obtained by nanoindentation.

3. Results and Discussion

3.1 Puncture resistance of commercial protective materials and scales

One of the primary functions of fish scales is to provide protection against environmental and predator attack. [15, 20, 21] For example, carp scales should provide resistance to damage associated with attack from predators that may involve puncture. However, it should be understood that the carp fish used for this evaluation have no real eminent threat except for that from man as they are raised under captivity for food.

The effectiveness of scales to resist puncture was explored by conducting puncture tests on carp scales, TPR substrate, and carp scales overlaid on top of a TPR substrate, which serves as a typical glove material. [8] The results are shown in **Fig. 8**. The origin of the graph is where the sharp contact happened which indicate the puncture needle starts contacting the material under puncture. The load then increases until the needle punctures through the sample. The drop in load indicates the maximum load to puncture and the area under the curve is recorded as the maximum energy to puncture. From **Fig. 8**, we can see the TPR rubber has much lower load to puncture than carp scales, as well as lower energy to puncture. The complete results of average load and energy to puncture of carp scales, TPR substrate, and carp scales overlaid on top of a TPR substrate are shown in **Fig. 9 and Table 1**.

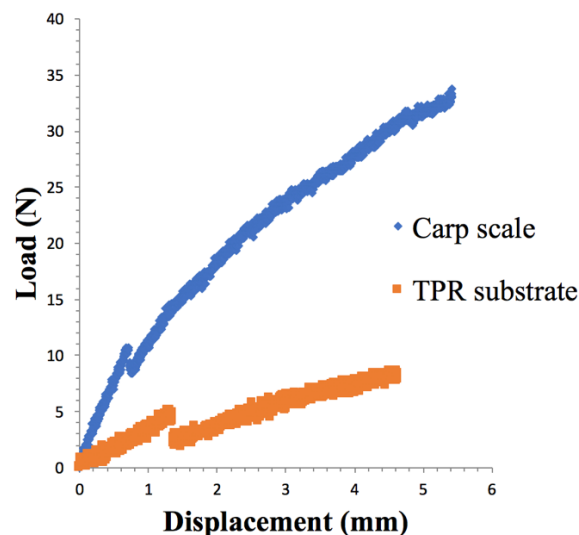


Fig. 8 Typical load vs displacement curve obtained from the results from puncture test

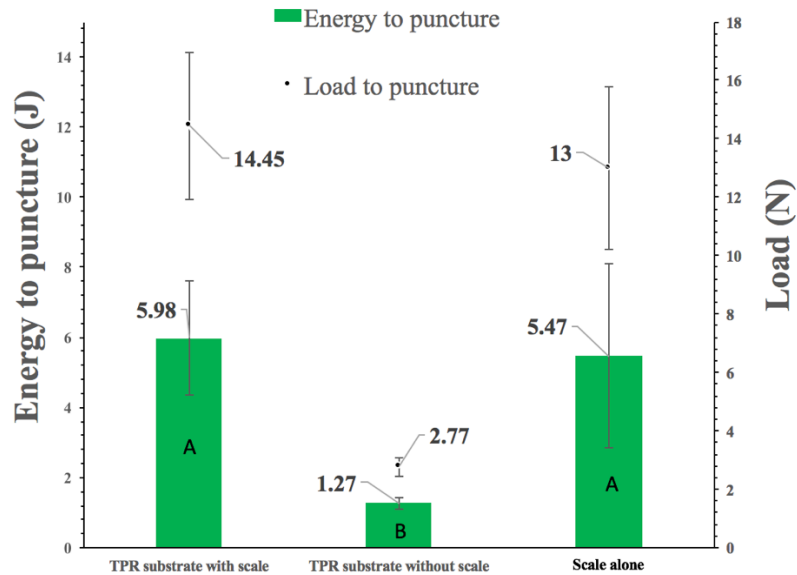


Fig. 9 Load and energy to puncture on glove material with and without carp scale on top and scale alone

Table 1. Average maximum load and energy to puncture for carp scale and rubber with scale, without scale and scale alone.

	Average maximum load (N)	Standard Deviation	Energy to puncture (J)	Standard Deviation	p^{α} 0.05
TPR with scale	14.45	2.51	5.98	1.64	A
TPR without scale	2.77	0.32	1.27	0.17	B
Carp scale alone	13.00	2.78	5.47	2.39	A

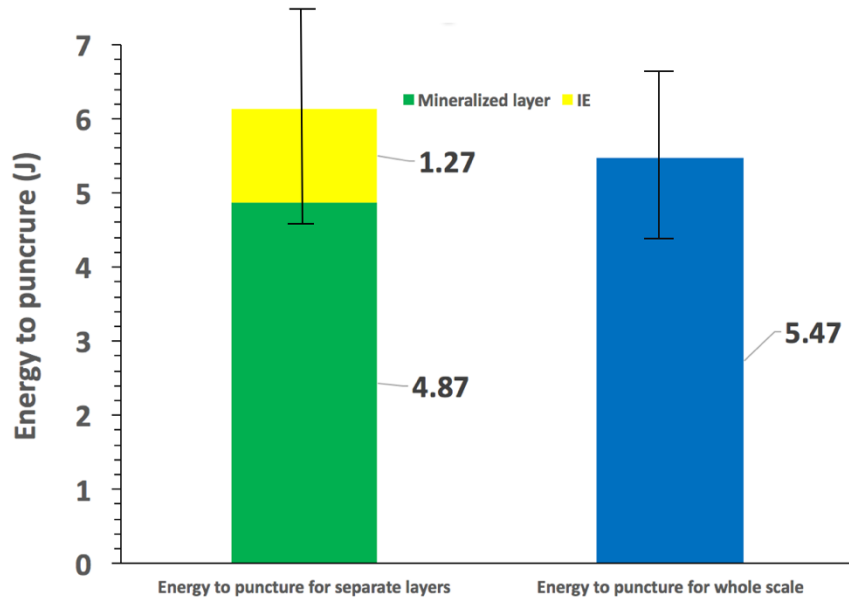
*Groups with same letter are not significantly different.

The average values for the maximum load and energy to puncture for the three material systems are listed in **Table 1**. According to these results in **Table 1**, the carp scales have greater resistance to puncture than the TPR rubber alone, and that they cause a significant increase in the resistance to puncture of the TPR substrate when placed on top. Based on the results of the single factor ANOVA analysis, the difference in the maximum load and energy to puncture both have

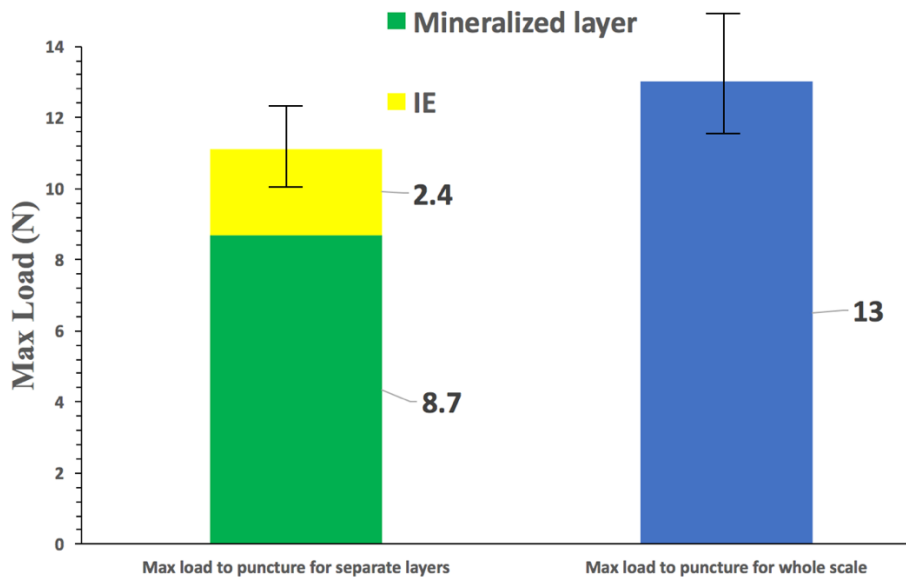
significant increases after applying a carp scale on top compared to results of just the TPR substrate. The average energy to puncture was increased from 1.27 Joules to 5.98 Joules, which corresponds to an increase over 350%. Interestingly, the maximum load increased from 2.77 N to 14.45 N, an increase of over 400 %. Results of the statistical analysis using ANOVA show that the p value of the two sets of data is 0.0047, ($p < 0.05$). Therefore, based on the results of the puncture test, we believe that a fish scale overlaid structure can significantly increase the puncture resistance property of gloves.

3.2 Contribution of the individual layers

One of the primary goals of this study was to evaluate the contribution of the individual layers to the total puncture resistance of fish scales. In order to achieve this goal, carp scales were selected from middle part of the fish with the same thickness ($0.38\text{mm} \pm 0.02\text{mm}$), for consistency, with the puncture test performed on the whole carp scales. As shown in **Fig. 4**, fish scales are composed of three discrete layers including the internal elasmodine, external elasmodine and a limiting layer. The limiting layer is the most external layer of a fish scale. It is the last part of the scale to develop [22] and promotes a downward diffusion of minerals to the underlying elasmodine layer. [23] The internal elasmodine was separated from the mineralized layers, by simple tearing with needles. Thereafter, puncture tests were performed on the internal elasmodine and the mineralized layers separately. Resulting from that work is summarized in terms of the load and energy to puncture in **Fig. 10**. The average of these results are listed in **Table 2**.



a. Energy to puncture of whole scale with summation of each layer in scale



b. Load to puncture of whole scale with summation of each layer in scale.

Figure 10. Comparison of energy and load to puncture of whole carp scale with sum of each layer.

Table 2 . Average maximum load and energy to puncture for IE and mineralized layer of carp scale compared to the whole scale.

	Average maximum load (N)	Standard Deviation	Energy to puncture (J)	Standard Deviation
1.Internal elasmidine	2.40	0.38	1.28	0.48
2.Mineralized layer (LL+EE)	8.70	1.65	4.87	2.25
3.Carp scale alone	13.0	2.78	5.47	2.39

*Groups with same letter are not significantly different.

As evident in **Fig. 10a**, the sum of the energy to puncture of the internal elasmidine mineralized layer is approximately equal to that of the whole scale. According to results of statistical analysis, there is no significant difference ($p>0.05$). Clearly evident, the mineralized layer is the major contribution to the energy to puncture. Also evident in **Fig. 10b**, the max load to puncture for the separate layers is slightly lower than the whole scale. Based on results of the statistical analysis, there is no significant difference ($p>0.05$). Thus, the summation of contributions from the individual layers of the fish scale to the energy and load to puncture is not significantly different from these results for the whole scale. That implies that the interface between the internal and external elasmidine does not contribute significantly to the puncture resistance. Overall, the largest contribution to the scales is the external mineralized layer. Additions to glove materials to increase puncture resistance should be modeled after the mineralized layer.

3.3 Whole scale

After identifying that the largest contribution of energy and load to puncture is the external mineralized layer, it is important to explore what part of that layer provides the most resistance to

puncture. To answer this question, the experimental set-up used in the previous experiments was adopted, but now on scales in which the low and high mineralized regions were separated. These portions of the scales were placed on top of the TPR substrate and the puncture resistance was examined. The energy to puncture for individual layers of carp scale was obtained by using the average energy to puncture of that layer on TPR substrate subtracting the energy to puncture of the TPR substrate. alone The results are shown in **Fig. 11** and listed **Table 3**.

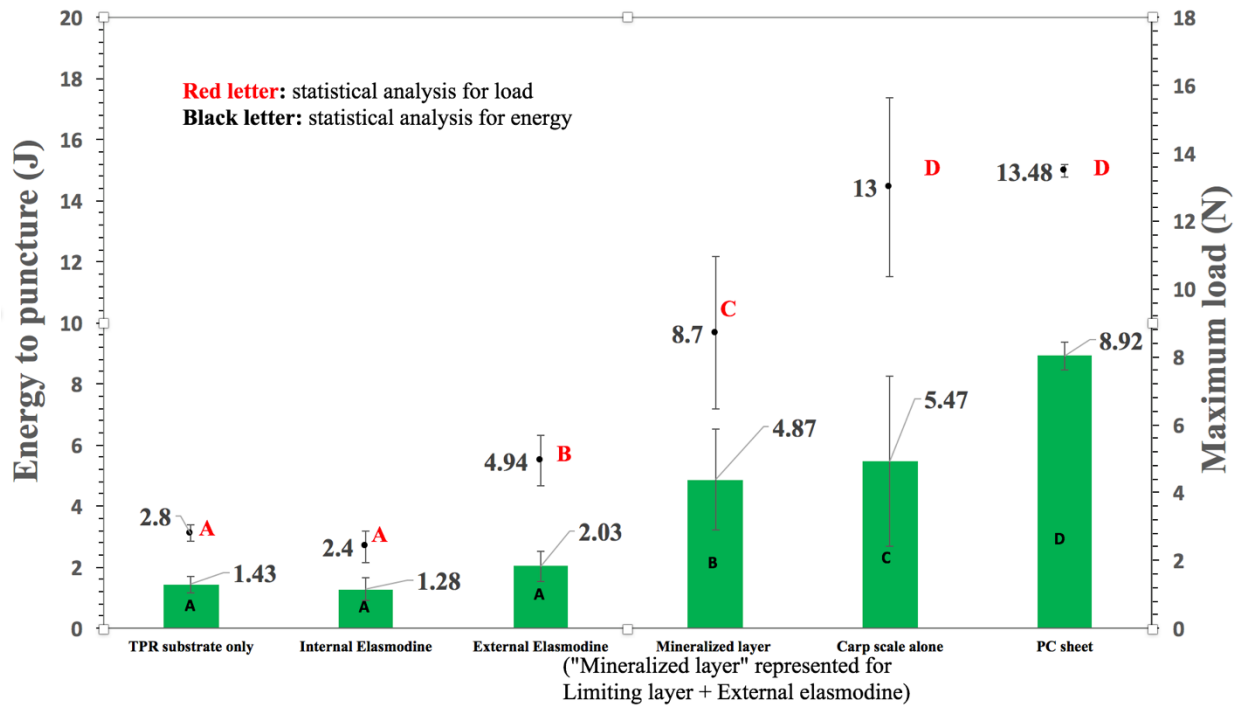


Fig. 11 The max load and energy to puncture for TPR substrate with addition of specific layers of carp scales.

Table 3. Average maximum load and energy to puncture for each individual layer of carp scale, TPR substrate, and engineering polymer (PC sheets).

	Average maximum load (N)	p^{α} 0.05	Standard Deviation	Energy to puncture (J)	Standard Deviation	p^{α} 0.05
1.TPR substrate	2.80	A	0.28	1.43	0.23	A
2.Internal elasmodine	2.40	A	0.38	1.28	0.48	A

3.External elasmodine	4.94	B	0.51	2.03	0.75	A
4.Mineralized layer (LL+EE)	8.70	C	1.65	4.87	2.25	B
5.Carp scale alone	13.0	D	2.78	5.47	2.39	C
6. Polycarbonate (PC) sheet	13.48	D	0.17	8.92	0.45	D

*Groups with same letter are not significantly different.

According to the results presented in **Table 3**, each of the three layers of the fish scales contributes to the puncture resistance. However, the puncture resistance achieved by each of the layers is different. Recall from the results of individual layer summation principle, we know that the energy to puncture of the entire carp scale can be estimated from the energy to puncture of the individual layers combined. However, the energy to puncture of the limiting layer may not be achieved by actual tests since we were not able to separate the limiting layer from the external elasmodine. Therefore, we applied the individual layer summation principle to use the energy to the puncture of mineralized layer (external elasmodine and limiting layer) minus the energy to the puncture of external elasmodine to estimate the energy to puncture of the limiting layer alone. By dissecting the scales and evaluating each layer it is found that the limiting layer has the greatest puncture resistance (in terms of critical load), followed by the external elasmodine and then the internal elasmodine. Overall, the largest contribution to puncture resistance is the mineralized portion (including the limiting layer and external elasmodine). The combination of these two layers contributes over 95% of the energy required to puncture on average. These results are consistent with previous evaluations.

According to previous studies on the microstructure of fish scales, [9, 10, 24] the limiting layer is composed of calcium carbonate or calcium apatite, varying across the different fish species. The external elasmodine layer is composed of unidirectional collagen fibers reinforced

with apatite mineral. [10] The individual lamina of the external elasmodyne are thicker in comparison to those of the internal elasmodyne, which is attributed to the higher mineral content. [24] As shown in **Fig. 10**, the puncture resistance of external elasmodyne is better than that of the internal elasmodyne, which indicates that the reinforcement provided by the mineral plays an important role in dissipation puncture energy. It appears that the mineral platelets resist the movement/sliding of the collagen fibrils.

Due to the interesting performance achieved by the addition of scales as an overlay to the TPR rubber, a comparison of puncture resistance of fish scales with thin polycarbonate sheets was performed. Polycarbonate is a typical modern engineering polymer that is commonly applied for protective gear such as sports goggles, safety glasses, protective covers...etc. [8] Based on the results of ANOVA single factor analysis, the specific load of whole carp scales and thin polycarbonate sheets was not significantly different. For the load to puncture, the difference in average is less than 5%. These results are consistent with similar measurements reported by Bathelat et al, [8]. The load to puncture of carp scales is comparable to that of PC sheets with the same approximate thickness.

3.4 Comparison of flexural stiffness of PC sheets, TPR and each layer of scales

Table 4 shows the average flexural stiffness of the individual layers of the carp scales. By dissecting the scales and evaluating each layer separately it was found that the internal elasmodyne layer has the greatest flexibility, followed by the external elasmodyne, and the mineralized layer (including the EE and LL). Compared to the whole carp scale, the flexural stiffness of the PC sheet is much significantly greater. However, in comparison to the current

TPR glove material, carp scales are not as flexible as TPR, and based on the ANOVA single factor analysis, the difference is also significant ($p < 0.05$).

Table 4. Average flexural stiffness (K) comparison of each layer in carp scale with TPR substrate and PC sheet

	Average flexural stiffness K (N/mm)	Standard Deviation	Average thickness (mm)	Standard Deviation	$p^{\alpha} 0.05$
Whole scale (Carp)	4.85	0.63	0.38	0.0055	A
Mineralized layer (LL+EE)	4.94	0.61	0.35	0.0055	A
Polycarbonate (PC) sheets	9.82	0.17	0.39	0.0	B
TPR rubber	2.20	0.23	3.18	0.0	C
External elasmordine (EE)	2.37	0.44	0.17	0.0182	C
Internal elasmordine (IE)	0.31	0.052	0.19	0.0192	D

*Groups with same letter are not significantly different.

The flexural stiffness of the EE, IE and mineralized layer of the carp scales are all different. As expected, the mineralized layer is the stiffest, followed by the external elasmordine and internal elasmordine. Unfortunately, the limiting layer can't be separated so the results do not include the limiting layer. The specific energy to puncture is calculated by using the energy to puncture over the average thickness of the material. Similarly, the specific flexural stiffness is calculated by dividing the average flexural stiffness by the thickness of that material. The reciprocal is the specific flexibility (or compliance). These two quantities were used to construct an Ashby chart including the specific energy to puncture and specific flexural stiffness for each material. These results are listed in Table 5 and plotted in Fig. 12. The average energy to puncture and the flexural stiffness have been normalized by the thickness to account for the differences in thickness between the different materials. The PC sheets and TPR substrates both have uniform thickness so the standard deviation for the thickness of these two are equal to zero.

Table 5. Ashby chart of specific average energy to puncture (J/mm) over the reciprocal of specific flexural stiffness $1/(K/mm^2)$

	Reciprocal of specific flexural stiffness $1/(N/mm^2)$	Specific puncture resistance (J/mm)
Whole scale (Carp)	0.078	14.39
Mineralized layer (LL+EE)	0.071	13.91
Polycarbonate (PC) sheets	0.040	22.87
TPR rubber	1.445	0.450
External elasmodine (EE)	0.072	11.94
Internal elasmodine (IE)	0.613	6.73

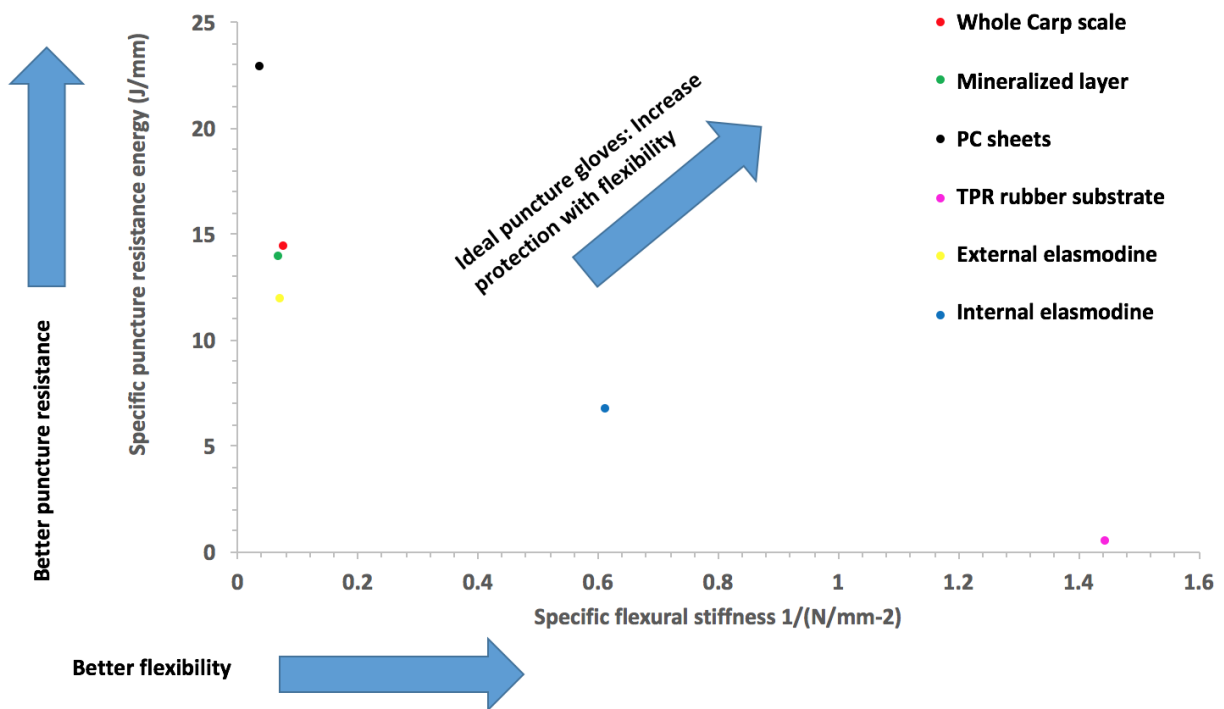


Fig.12 An Ashby chart describing puncture resistance in terms of the flexibility. The chart is used to show material design space for better glove material to achieve better puncture resistance and dexterity.

When evaluated in terms of an Ashby chart presentation, the fish scales have the best performance on flexibility and puncture protection properties than TPR substrate or PC sheets. Compared to the TPR rubber, fish scales have much better puncture resistance in terms of both the load and energy to puncture; when comparing with the PC, although the specific energy to puncture is slightly higher for scales, carp scale is less stiff than PC sheets. The results substantiate that applying a layer of fish scale on top of the puncture resistant gloves are promising.

3.6 ANSYS stress distribution modeling

The results of nanoindentation showed that the elastic modulus of the internal elasmodine and limiting layer are 0.45 GPa and 20 GPa, respectively. The typical elastic modulus for TPR rubber substrate is 0.05 GPa. In the simulations, a 200 N point load was applied at the outer surface of the substrate, which consisted of the TPR substrate with or without the carp scale covering. The stress on the bottom surface of the TPR was recorded. The results of the finite element analysis is shown in **Fig. 13** We expected that when applying point load on top of the TPR substrate, the maximum load transfer to the bottom should decrease. It's evident that after applying the fish scale layer on top, the stress at the bottom of the TPR substrate is distributed over a larger area and the maximum stress is lowered. The maximum stress is decreased by over 20% . Hence, the stress transferred to the finger by the reinforced “glove model” provides improved protection to the fingers.

More importantly, the maximum stress transfer to the bottom of the TPR substrate also indicated the protection of fish scale. **Fig.13** has shown the stress distribution on the bottom side of the surface. The stress is recorded from the puncture origin to the edge of the model. The maximum stress significantly decreased by over 20% that once again approve the protection function for fish scales.

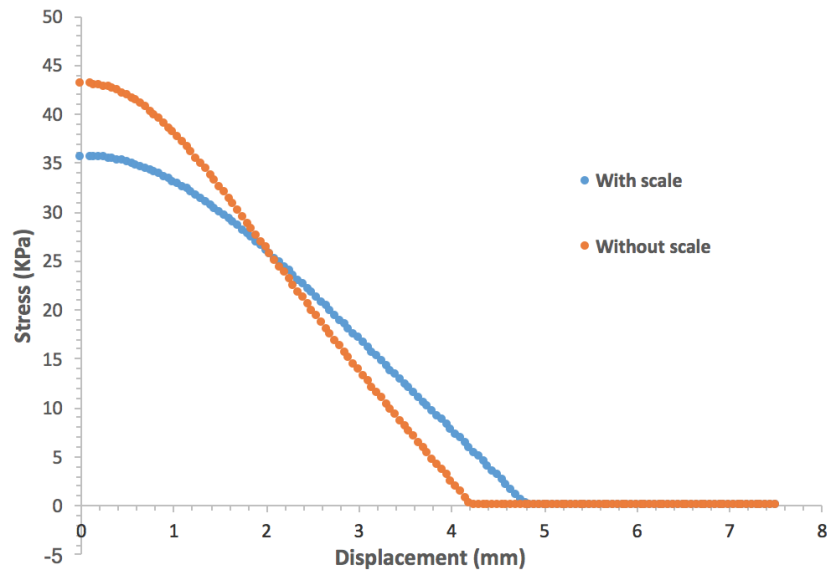


Fig. 13 The stress distribution on the finger in ANSYS simulation.

4. Conclusion and Future work

4.1 Conclusion

According to the puncture tests performed on the carp scales, the energy to puncture for the whole scale is approximately equal to the summation of the individual layers. The largest contribution to the scales is the external mineralized layer (a combination of the limiting layer and external elasmodine layer). But when evaluated individually, the limiting layer makes the largest contribution to puncture resistance, followed by the external elasmodine and lastly internal elasmodine. The limiting layer and external elasmodine sum to over 90% of the total puncture

resistances. Therefore, additions to glove materials to increase puncture resistance should be modeled after the mineralized layer.

The experimental evaluation also showed that the fish scale achieves a combination of protection to puncture and flexibility that exceeds that of modern engineering polymers including polycarbonate (an engineered plastic for protection) and thermoplastic rubber (a current glove materials). Thus, the scale topology could be used in designing flexible puncture resistant gloves. With the scale placed as a layer on top of the glove material, both the energy and load to puncture have significantly increased. In addition, the maximum stress transferred to a “finger model” was decreased and the stress was distributed over a larger area with the present of fish scales on top of puncture gloves.

4.2 Future work

Shear thickening solid materials include most thermoplastic polymers, especially at temperatures greater than the glass transition. These materials, and interesting topologies, can be realized by the 3-D printing technique. The 3-D printing approach is an important customization manufacturing process which enables small quantities of customized goods to be produced at relatively low costs. [25] In general, 3-D printing techniques and processes are built on a layer by layer basis through a cross section view of the product. Because of this, the complex structure such as scale armor can be manufactured much easier than the traditional manufacturing process to permit experimental exploration. From **Table 6**, the advantage of 3-D printing and mass customization have generally each been used for producing different kinds of materials. In the future, we can apply zirconia coating (one kind of ceramic protective coatings) on the external of the puncture resistant gloves as a model for the limiting layer.

Table 6. A comparison of mass customization and 3-D printing [25]

<u>Characteristic</u>	<u>Mass Customization</u>	<u>3-D Printing</u>
Manufacturing Technology	Based on pre-assembled modular parts in different combinations or delayed differentiation.	Automated manufacturing based on CAD software and additive manufacturing.
Supply Chain Integration Requirements	Need for highly-integrated supply-chain management to ensure right goods at right times from multiple supplies.	Uses readily available supplies available from multiple vendors.
Economic Benefits	Ability to produce custom products at relatively low prices. Low inventory risk. Improved working capital management.	Ability to produce custom products at relatively low prices. Low inventory risk. Improved working capital management.
Range of Products	Computers; watches; windows; shoes; jeans.	Prototypes; mockups; replacement parts; dental crowns; artificial limbs.

The 3-D printing technique is suitable for developing customized products in small quantities and economically. In the future, we want to apply the test results found on fish scales to explore the design of protective materials and strategies of more and more sports protection gear, such as helmets, knee pads and protection vests. Considering the knee/elbow pad, as the size and shape of people’s knees/elbows are also unique. A customized protective pad can effectively reduce the possibility of injury and give greater protection from sudden impact. The gloves can also be manufactured based on laser or NMR scans for measuring the length of fingers, size of palms, and thickness of hands. In the future, the 3-D printing technique can customize the shape of the gloves for each of the worker so that the industrial bio-inspired gloves can fit each individual.

5. Reference:

- [1] Julian V, Bogatyreva O, Bowyer A and Pahl AK. Biomimetics: it's practice and theory. Journal of the royal society 2006; Vol 3, issue 9.
- [2] Murcia S, Lavoie E, Linley T, Devaraj A, Alex Ossa. E and Arola D. The natural armors of fish: A comparison of the lamination pattern and structure of scales. Elsevier 2016.
- [3] Song J. Multiscale Materials Design of Natural Exoskeletons: Fish Armor. Massachusetts Institute of Technology 2011.
- [4] Tomek. Giant Arapaima. Zppchat.com. 2013. Accessed 14 May 2017. Available at: <https://www.zoochat.com/community/media/giant-arapaima-arapaima-gigas.243630/>
- [5] Emery D. Alligators in the sewers of New York. Getty images News. 2017. Accessed 14 May 2017. Available at: <https://www.thoughtco.com/alligators-in-the-sewers-3298849>
- [6] Sartore J. Armadillos. National Geographic photo ark. National Geographic.com. Accessed 14 May 2017. Available at: <http://www.nationalgeographic.com/animals/mammals/group/armadillos/>
- [7] Busby C. Welcome to the world. National Geographic.com. 2015. Accessed: 19 May 2017. Available at: <http://yourshot.nationalgeographic.com/photos/6932267/>
- [8] Zhu D, Ortega CF, Motamedi R, Szewciw F, Vernerey F, Barthelat F. Structure and mechanical performance of a “modern” fish scale. Journal of the Adv Eng Mater 2012; pp. B185–B194
- [9] Garrano AMC, La Rosa G, Zhang D, Tay FR, Niu L, Majd J and Arola D. On the mechanical behavior of scales from Cyprinus Carpio. Journal of the Mechanical Behavior of Biomedical Materials 2012; 7: 17-29.

- [10] Murcia S, Yahyazadefar M and Arola D et al. Effects of polar solvents on the mechanical behavior of fish scales. 2016 Master Sci Eng C mater Biol Appl.61, 23-31
- [11] Murcia S, McConville M, Li GH, Ossa A, Arola D, Temperature effects on the fracture resistance of scales from *Cyprinus carpio*. *Acta Biomater*. 2015. 14, 154-163
- [12] Torres FG, Le Bourhis E, Troncoso OP, and Llamaza J. Structure-property Relationships in *Arapaima Gigas* Scales Revealed by Nanoindentation Tests. 2013.
- [13] Zimmermann EA, Gludovatz B, Schaible E, Dave NK, Yang W, Meyers MA and Ritchie RO, Mechanical adaptability of the Bouligand-type structure in natural dermal armour, *Nat* 2013. Commun. 4- 2634.
- [14] Dastjerdi AK, Barthelat F. Teleost fish scales amongst the toughest collagenous materials, *Journal of the Mechanical Behavior of Biomedical Materials* 2015; 52: p 95-107.
- [15] Zhu D, Szewciw L, Vernerey F and Barthelat F. Puncture resistance of the scaled skin from striped bass: collective mechanisms and inspiration for new flexible armor designs. *Journal of the Mechanical Behavior of Biomedical Materials* 2013; 24: 30-34
- [16] Martz E. What Can You Say When Your P-Value is Greater Than 0.05? The minitab blog. 2015. Accessed: 27 April 2017.
- [17] Oliver WC, Pharr GM. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *Journal of Materials Research*, 2004; 19: 3-20
- [18] Chen PY, Schirer J, Simpson A, Nay R, Lin YS and Yang W. Predation versus protection: fish teeth and scales evaluated by nanoindentation. *Journal of Mater Res* 2012; 26: 1-12
- [19] Mishra M. What is flexural stiffness. *Quora.com*. 2016. Accessed: 27 April 2017.

- [20] Meyers MA, Lin YS, Olevsky EA, Chen PY. Battle in the Amazon: Arapaima versus Piranha *Advanced Engineering Materials* 2012; pp. B279–B288.
- [21] Yang W, Chen IH, Gludovatz B, Zimmermann EA, Ritchie RO, Meyers MA Natural flexible dermal armor *Advanced Materials* 2013; 25: pp. 31–48
- [22] Le Guellec D, Morvan-Dubois G and Sire JY. Skin development in bony fish with particular emphasis on collagen deposition in the dermis of the zebrafish (*Danio rerio*). *Int J Dev Biol* 2004; 48: pp. 217–232
- [23] Sire JY, Akimenko MA. Scale development in fish: a review, with description of sonic hedgehog (shh) expression in the zebrafish (*Danio rerio*). *Int J Dev Biol* 2005; 48: pp. 233–248
- [24] Lin YS, Wei CT, Olevsky EA and Meyers MA, Mechanical properties and the laminate structure of Arapaima gigas scales, *Journal of mechanical behavior of Biomaterials* 2011; 4: 1145–1156.
- [25] Berman B. 3-D printing: The new industrial revolution. *Business Horizons* 2012; 55: 155-162.