# Nanomechanics and Testing of Core-Shell Composite Ligaments for High Strength, Light Weight Foams

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## ABSTRACT

Composite nanostructured foams consisting of a metallic shell deposited on a polymeric core were formed by plating copper via electroless deposition on electrospun polycaprolactone (PCL) fiber mats. The final structure consisted of 1000-nm scale PCL fibers coated with 100s of nm of copper, leading to final core-shell thicknesses on the order of 1000-3000 nm. The resulting open cell, core-shell foams had relative densities between 4 and 15 %. By controlling the composition of the adjuncts in the plating bath, particularly the composition of formaldehyde, the relative thickness of copper coating as the fiber diameter could be controlled. As-spun PCL mats had a nominal compressive modulus on the order of 0.1 MPa; adding a uniform metallic shell increased the modulus up to 2 MPa for sub-10 % relative density foams. A computational materials science analysis using density functional theory was used to explore the effects pre-treatment with Pd may have on the density of nuclei formed during electroless plating.

## INTRODUCTION

Metallic foam materials can provide exceptional strength versus density properties that in combination with high specific surface area have a potential to produce catalyst materials, fuel cells, filters, and other applications [1-3]. One of the most important features of foams is the relative density (the density of the cellular structure divided by density of the monolithic material that comprises the whole structure). For example, polymeric foams used for packaging, insulation, and cushioning have relative densities between 0.05 and 0.2 [2]. Metallic foams, in comparison, more commonly have relative densities on the order of 0.2-0.3; this occurs both in bulk form when foams are formed via replication [4] and at the nanoscale when formed via de-alloying [5]. There is a need for foams with metallic surfaces (providing catalyst or filtering properties not viable in polymeric structures) at relative densities closer to those in the open cell polymeric foam regime. In this report metallic foams were manufactured using electrospun polymer fiber networks as a template and then subsequently coated with copper by electroless deposition. This current work used both randomly distributed and aligned PCL networks as a template that can be regarded as open-cell foams, due to material contained in cell edges only [2].

## EXPERIMENT

Fiber mats of PCL were created through electrospinning a solution of 9 wt% PCL in trifluoroethyl alcohol (TFE) in an electrospinning tool with dual control electrodes to enforce fiber alignment [6] as shown in figure 1. The spinneret, control electrodes and collection grid

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were aligned in a horizontal plane to allow any accumulated solution to avoid dripping on the deposition substrate. Both control electrodes are given an offset voltage of ~13 kV, while one electrode is also modulated with a ~0.5 kV amplitude sinusoidal voltage. The spinneret serves as the ground electrode. Fiber deposition is preferentially directed at the electrode with the highest voltage. When the two electrodes alternately become the preferential deposition electrode, aligned fibers are deposited between these two electrodes on the collection grid (or substrate). Without oscillating the voltage randomly oriented fibers are deposited. Fiberglass mesh was placed between electrodes to enable aligned deposition of microfibers onto mechanically robust structures. Cross-hatch patterns were created with subsequent fiber layers by rotating substrates 90° between subsequent depositions. Individual fibers were on the order of 2 µm in diameter.

PCL mats with lateral dimensions of approximately 0.5 x 2.0 cm and a thickness on the order of 0.1 mm were cleaned in an aqueous solution of $NaCO_3$ for 1 minute in an ultrasonic bath and washed with deionized water. The samples were cleaned in an aqueous solution of $NaCO_3$ for 1 minute in an ultrasonic bath in order to remove any hydrophobic contaminates on the surface, followed by washing with deionized water. The samples were then immersed in $NaOH_{(aq)}$ (155 g/L) for 1 minute in order to enhance surface hydrophillicity by partial hydrolysis, rinsed with deionized water again, and immersed in a $PdCl_2$ seeding solution for 5 minutes. The $PdCl_2$ seeding solution is made by dissolving 0.6 g of $PdCl_2$ in 2.7 g of 37% $HCl_{(aq)}$. Without further rinsing each specimen surface was exposed to droplets of $NaBH_4$ solution. The base electroless copper deposition bath, consisting of 15.4 g DI water, 1.64 g $CuSO_4$*$5H_2O$, 1.92 g ethylenediaminetetraacetic acid (EDTA), and 0.52 g of formaldehyde solution (37 wt.% $CH_2O$ in water with methanol) was adjusted to control the pH by adding NaOH to a pH between 11.5 and 12 and maintained at 50 °C. The base bath was a molar ratio of 1:1:1 of Cu, EDTA, and formaldehyde. The time of deposition varied between 6 and 15 minutes, and all specimens were rinsed with deionized water following treatment. Composition of the molar ratio of Cu, EDTA, and $CH_2O$ is noted in the results section, $PdCl_2$, 37% $HCl_{(aq)}$, EDTA, and NaOH were purchased from Sigma-Aldrich, $NaBH_4$ and formaldehyde solution were purchased from Mallinckrodt. The final structure was a nanocomposite foam of metallic shells surrounding a PCL core (Figure 1).

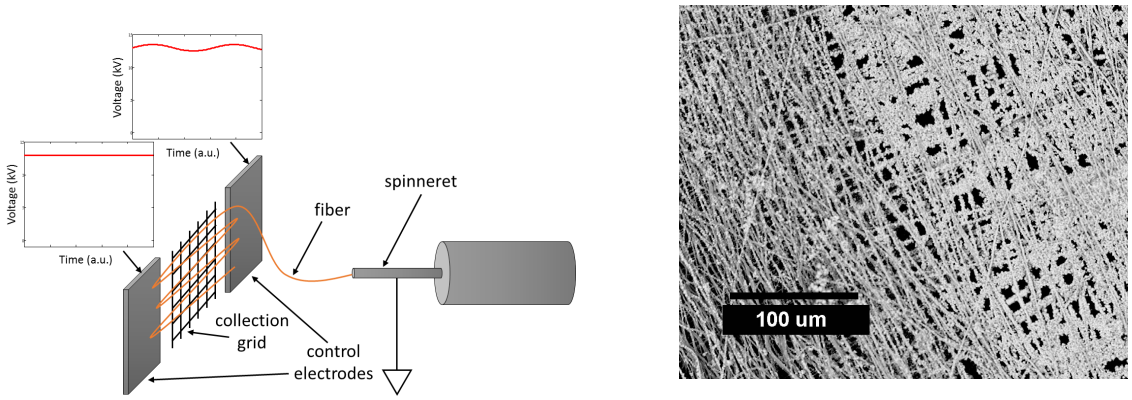


Figure 1. Schematic dual electrode electrospinning system (left). Both collection electrodes are held at approximately ~13 kV with one electrode modulated with an additional floating ~0.5 kV sinusoidal voltage. A fiberglass collection grid is used to collect the mat between the two control electrodes; the mat is then removed from the grid, and fibers coated with shells of metal (right).

The mechanical properties of the nanocomposite foam were assessed using flat punch nanoindentation tests on a Hysitron Triboindenter 950 system using a 100.57-µm diameter flat

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punch (the flat was machined on a 60° conical tip). The ≈0.1 mm thick mats were then secured to a metal base using commercial double side tape; while for many stiff materials this will lead to added compliance for this class of low density foams the compliance of the adhesive should not dramatically impact the measured properties. Elastic modulus and hardness of the foams were evaluated using a single-step nanoindentation, comprising a 60-second loading and unloading segments, and a 15-second hold. The maximum depth for the analysis was chosen to be 2 μm to ensure multiple fibers in the foam were contacted and to minimize any variation in sensing the surface while still remaining far from the adhesive and substrate. Between four and eight indents were carried out on each of the samples over areas with highest relative densities in areas that had similar densities when visualized via optical microscopy. The modulus and hardness was determined using a conventional unloading slope analysis assuming a constant diameter of 50.25 μm. Hardness and modulus were defined using the methods of Oliver and Pharr. [7] To quantify variations in relative density across the sample, the relative density was measured using image analysis of the fibers characterized using scanning electron microscopy and correlated to the resulting properties.

The density functional theory calculations were conducted within the generalized gradient approximation (GGA) by Perdew-Burke-Ernzerhof [8] as implemented in Vienna ab initio simulation package[9,10], in a similar computational setting as we used in previous studies.[11] A single strand of hydrolyzed PCL is modeled in a periodic boundary cell (17.26 Å × 25 Å × 25 Å), where the eigenvalues are evaluated at a gamma-centered *k*-point, using the kinetic energy cutoff of 500 eV. The London dispersion correction devised by Grimme is used.[12] The role of Cu deposited, Pd-implanted hydrolyzed PCL is evaluated by comparing the energy difference during deposition with and without the metal deposited PCL as a catalyst.

## RESULTS AND DISCUSSION

The architecture of the coated foams, shown in figure 2, ranged from conformal coatings to thicker, island like growth. Table 1 lists the fabrication conditions and resulting properties measured during this work. Indentation of a foam (or any material with surface porosity) means that the assumption of a uniform solid makes the contact mechanics inherent in the original Sneddon model an approximation. The 2 μm penetration depth using a perfectly oriented 60° cone would add ≈4% to the contact area over the flat punch assumption in a perfectly plastic material, and less in a perfectly elastic material (the two boundary cases). Figure 3 shows these indentations exhibit significant elastic recovery, and so it seems the flat punch approximately is not a significant source of bias in the measurement. Alignment between the tip and the sample would need to be within ≈1° to ensure contact over the entire flat punch, and errors resulting in a decrease in real contact area of over 10% in area would occur for tilt of 2°. However given uncertainty in the initial contact due to the surface topography of the structures, our assessment of relative tilt can be described by the standard deviation in the indentations. Since a tilted surface will hit random peaks or valleys in the foam, it may be expected that a tilted surface would show more variation and a significantly lower hardness (the real area would be less than the calculated area, so the calculated hardness would be lower than expected). Inspecting Table 1 shows similar coefficients of variation (standard deviation over mean); therefore for the purposes of this report the relative values appear to be consistent between samples, and relative differences should be reflective of the material property rather than a sample to sample testing bias.

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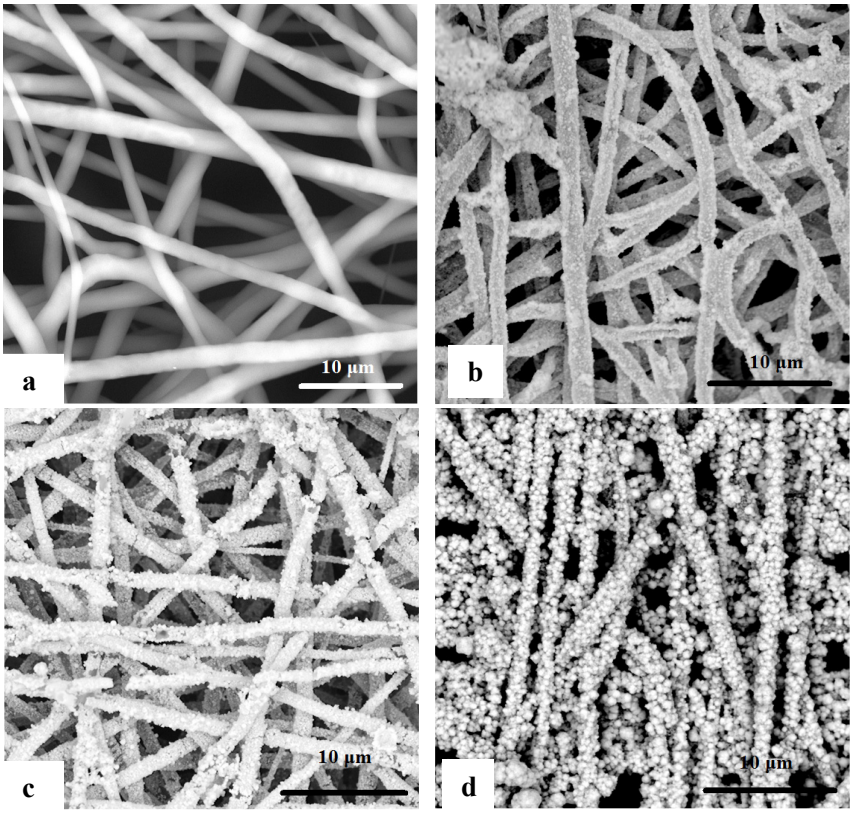


Figure 2. Scanning electron micrographs of Cu coated PCL foams formed via electrospinning and subsequent electroless deposition. The fabrication conditions for each sample is listed in Table 1, a)sample 7, b) sample 1, c)sample 4, and d)sample 8). All scale bars noted are 10 µm.

**Table 1:** Processing conditions and properties measured on Cu coated PCL foams

| Sample | Plating bath conditions (T, t, Cu:EDTA:$CH_2O$ molar ratio) | Hardness, kPa | Elastic modulus, MPa | Relative density | Average fiber diameter, µm |
|---|---|---|---|---|---|
| 1 | 50°C, 9 min, 1:1:1 | 34 ± 8 | 1.9 ± 0.4 | 0.09 | 1.38 ± 0.18 |
| 2 | 50°C, 9 min, 0.75:1:1 | 33 ± 8 | 1.7 ± 0.3 | 0.09 | 1.59 ± 0.50 |
| 3 | 50°C, 9 min, 1.25:1:1 | 12 ± 6 | 0.9 ± 0.3 | 0.08 | 1.47 ± 0.48 |
| 4 | 50°C, 6 min, 1:1:1 | 15 ± 5 | 0.8 ± 0.2 | 0.06 | 1.35 ± 0.19 |
| 5 | 50°C, 15 min, 1:1:1 | 7 ± 2 | 0.4 ± 0.1 | N/A | 3.00 ± 1.00 |
| 6 | no Cu coating | 5 | 0.5 | 0.06 | 1.44 ± 0.42 |
| 7 | no Pd pretreatment & Cu coating, 9 min, 1:1:1: random foam | 0.14 ± 0.02 | 0.03 ± 0.01 | 0.09 | 2.00 ± 0.50 |
| 8 | 50°C 12 min, 1:1:1 on oriented foam | 1.5 ± 1.0 | 0.09 ± 0.05 | 0.14 | 1.40 ± 0.30 |

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Figure 3 shows the typical range of load depth curves of the flat punch indentation of (in this case for sample 4); both uniform loading curves as well as "jerky" flow are observed; it is possible that the jerky flow is indicative of joint fracture. In all cases the residual impression depth is a small fraction of the overall indentation depth, suggesting the elastic loading of the foam is still dominated by stretching or bending rather than significant realignment of fibers relative to one another. Figure 4 shows the relationship between the relative density of the foam and the resulting hardness and modulus; for the conditions where relatively uniform metallic coatings were created, the modulus scales with density to the third power. Specifically excluded from this figure are foams where island growth dominated the morphology. This is significantly higher than one would expect from classical cellular solids models [2][3], which would more likely exhibit a squared, rather than cubed, relationship. It is possible that this is not due to enhanced behavior in modulus at relatively high densities but instead is driven by artificially low values of stiffness at low relative densities. The foam may not exhibit fixed joints but instead may have significant sliding of ligaments relative to one another.

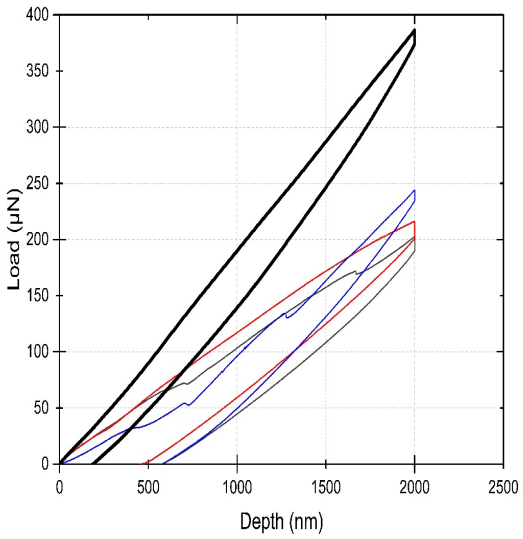


Figure 3. Typical flat punch load depth curves of metal coated PCL foams.

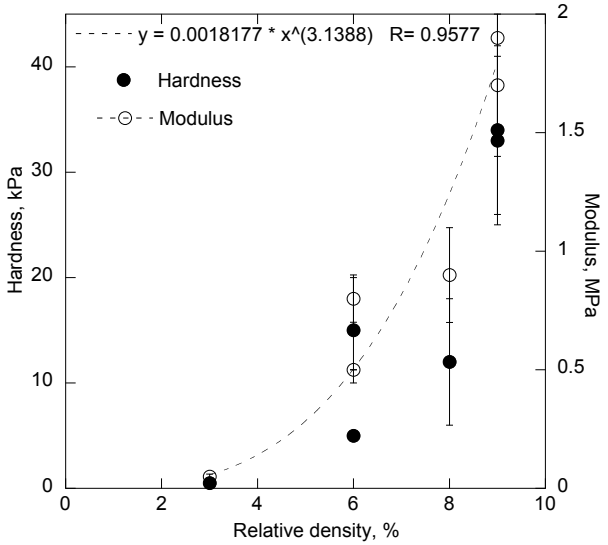


Figure 4. Hardness and modulus as a function of relative density of metal coated fibers for foams.

To explore the viabiliy of future enhancement of the electroless coating, a DFT simulation showing the relative impact of the Pd to the Cu deposition proces on PCL was carried out. Figure 5 shows the simulation cell and the reaction processes. When Pd is present the adsorption energy of the Cu metal is more than 1 eV lower than the solution state. This suggest that the concentration of nuclii will be controllable via alterning either the surface energy (through the use of surfactants) or by future modifications of the Pd concentration of the pre-treatment.

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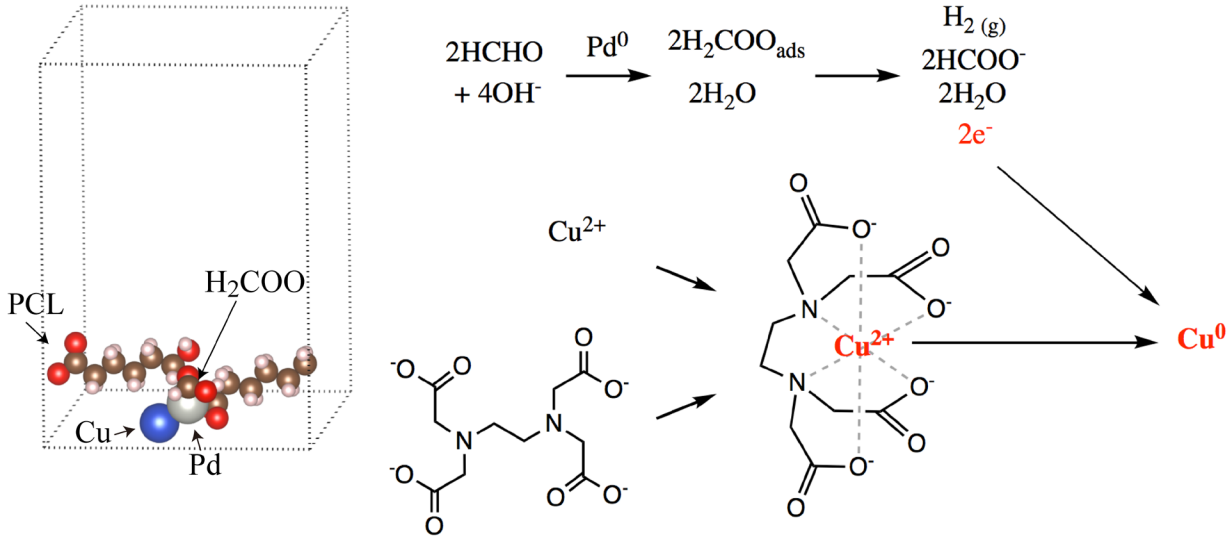


Figure 5. DFT simulation cell and reaction pathway for $Cu^{2+}$ to Cu deposition on PCL in the presence of EDTA and $CH_2O$. Pd catalyzes the reaction. Without Pd present the adsorption step is not spontaneous with a total energy difference of +0.4 eV; however, with Pd present there is ~1 eV energy decrease of the total energy, meaning the reaction can be exothermic.

## CONCLUSIONS

The mechanical strength and stiffness of fabricated metallic-polymer composite core-shell nanowires is dependent on the morphology and structure of the foam. Samples with a more uniform copper coating had superior mechanical properties. The hardness and elastic modulus tend to be higher for samples with higher relative densities, but this requires a uniform or conformal coating. In general, metallization of sub-10 % dense electrospun mesh/foams is viable. A 100x increase in mesh stiffness possible with ~100 nm layer coatings on a PCL foam. Future work is needed to refine the scaling laws for this class of cellular solids to determine if the composite foam consistently follows a fixed joints condition rather than a sliding and bending mechanism during deformation.

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## REFERENCES


[1] M.F. Ashby, L.J. Gibson, *Cellular Solids* 2nd ed. (Cambridge University Press, Cambridge 1999) pp. 175-217.
[2] M.S. Hossain, B. Shabani, J. Power Sources 295, 275 (2015)
[3] S.T. Kolaczkowski, S. Awdry, T. Smith, D. Thomas, L. Torkuhl, R. Kolvenbach, Catal. Today 273, 221 (2016).
[4] C. San Marchi, A. Mortensen, Acta. Mater. 49, 3959 (2001).
[5] Y. Sun, K.P. Kucera, S.A. Burger, T.J. Balk, Scripta Mater. 58, 1018 (2008).
[6] J.D. Beisel, J.P. Murphy, J.M. Andriolo, E.A. Kooistra-Manning, S. Nicolaysen, O. Boese, J. Fleming, W. Nakagawa, J.L. Skinner, J. Vac. Sci. Tech B, 34, 06KG02 (2016).
[7] W.C. Oliver, G.M. Pharr, J. Mater. Res. 19, 3 (2004)
[8] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[9] G. Kresse, J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
[10] G. Kresse, J. Furthmuller, Comp. Mater. Sci. 6, 15 (1996).
[11] C.E. Kim, R.M. Rahimi, T.L. Maxwell, T.J. Balk, D.F. Bahr, Scripta Mater. 136, 33 (2017).
[12] S. Grimme, J. Anthony, S. Ehrlich, H. Krieg, J. Chem. Phys. 132, 154104 (2010).


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