CHARACTERIZATION OF A THIN FILM COMPOSITE MEMBRANE: FLUORINATED COPOLYMER IN A CARBON NANOTUBE MATRIX

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Project Title: Characterization of a Thin Film Composite Membrane: Fluorinated
                      Copolymer in a Carbon Nanotube Matrix

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ABSTRACT

IDEX Health and Science has created a thin-film composite membrane consisting of a carbon nanotube matrix impregnated with a fluorinated copolymer called Teflon® AF 2400. This membrane is being studied for use in degassing chambers of analytical instruments such as a High Pressure Liquid Chromatography (HPLC) degassing modules. The level of impregnation of the Teflon® in the carbon matrix affects the diffusion properties which are crucial for the performance of the membrane. Scanning Electron Microscopy (SEM) characterization techniques were used to measure the outer Teflon® and the inner carbon matrix layer thickness. The outer Teflon® and inner carbon matrix layer thicknesses ranged from 1.92 to 28.17 microns and 5.07 to 41.70 microns, respectively. Energy Dispersive X-ray Spectrometry (EDS) was used to measure the Teflon® fluorine concentration gradient across the composite membrane. Mechanical tensile testing was also performed on each sample to compare the mechanical properties of the membrane to the initial design parameters. Ultimate Tensile Strength (UTS), Young's Modulus (E), and Percent Elongation were collected for each membrane. IDEX Health and Science used the following processing parameters to create each membrane: (a) Concentration, (b) Density, (c) Time, and (d) Recoat. Statistical analysis indicated that time and recoat had the largest effect on maximum stress at maximum load. The results from SEM imaging, EDS scans, and tensile testing helped determine how well the Teflon® infiltrated the carbon matrix. The interactions between the four processing parameters provided IDEX Health and Science with information to determine the optimal set of processing parameters for generating the ideal membrane.

Key Words: Materials Engineering, Composite, Thin Film, Teflon®, Carbon Nanotubes, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), Mechanical Tensile Testing, IDEX Health and Science, Cal Poly

1. INTRODUCTION

The IDEX Health and Science division of IDEX Corporation focuses on highly engineered fluidics systems and components for analytical instruments. One of their products is a degassing chamber that houses a Teflon® fluorinated copolymer tubing (Figure 1). A solution is passed through the tubing while a vacuum is applied simultaneously to the outside of the tube. By applying a vacuum to the chamber, the gases inside the liquid diffuse through the polymer tube, resulting in a pure liquid sample that can be analyzed by separate instruments (Figure 2).
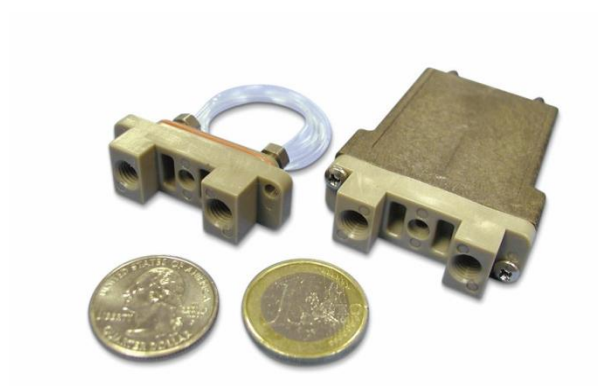
Figure 1. Systec degassing chamber made by IDEX is roughly the size of a quarter or euro. The white Teflon® AF tubing is coiled inside the chamber.
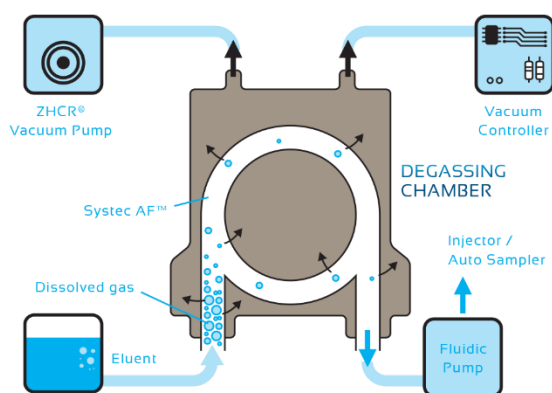
Figure 2. The degassing unit draws an eluent into the degassing chamber and applies a vacuum which separates the dissolved gases from the solution.

Although this simple system is an effective way to separate gases from a solution, it has certain disadvantages, primarily geometric limitations. This degassing chamber must fit inside instruments similar to High Pressure Liquid Chromatography (HPLC) degassing modules and, thus, limits the size of such instruments (Figure 3). IDEX has begun researching a new way to separate gases that would no longer require the chamber and tube system.

The tubes inside the degassing chamber are difficult and expensive to produce. Using a flat copolymer instead of tubes reduces material use, cost, and allows for greater geometric design abilities (Figure 4). A flat copolymer with a thickness range from 1-5μm becomes brittle and cannot be shaped into desired geometries. Therefore, the copolymer must be reinforced with a carbon nanotube paper matrix to create a composite membrane. The combination of the copolymer and the carbon matrix phase (15-25μm thick) increases the ductility of both materials,

allowing for better workability. Additionally, by replacing the tubing with a flat membrane the production and material costs were decreased, allowing the system to be applied in lower cost applications.
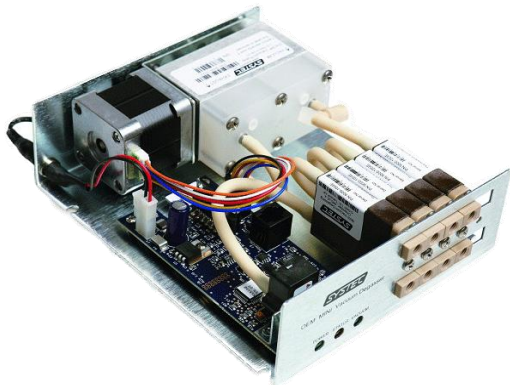
Figure 3. High Pressure Liquid Chromatography (HPLC) degassing module made by IDEX is a small compact unit.
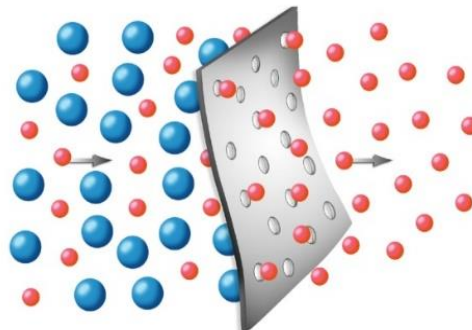
Figure 4. A semi-permeable membrane can separate gases from liquids by diffusion.

The question to consider is how a fluorinated copolymer in a carbon matrix separates gases from a solution. To answer this question, the science of diffusion, permeability, and selectivity must be reviewed.

1.1 Diffusion

Currently, IDEX Health and Science uses a diffusion test to determine how well nitrogen and oxygen diffuse through the composite membrane. Diffusion is determined by Fick's First Law of Diffusion (Eq. 1) which is used to solve for the diffusion coefficient, D (Eq. 2). [1] The diffusion coefficient indicates the speed at which a species diffuses through one another.

$$J = -D\left(\frac{\partial \phi}{\partial x}\right) \qquad \text{[Eq. 1]}$$

where

        J is the diffusion flux [(amount of substance) per unit area per unit time]
        D is the diffusion coefficient diffusivity in dimensions of [length^2 time^{-1}]
        ϕ (for ideal mixtures) is the concentration per unit volume
        x is the thickness of the membrane

Calculation of the diffusion coefficient is done according to:

$$D = D_0 e^{\frac{-E_A}{RT}} \qquad \text{[Eq. 2]}$$

where

        D is the diffusion coefficient

        D_o is the maximum diffusion coefficient (at infinite temperature)

        E_A is the activation energy for diffusion in dimensions of [energy (amount of substance)$^{-1}$]

        T is the temperature in units of [absolute temperature] (kelvins or degrees Rankine)

        R is the gas constant in dimensions of [energy temperature^{-1} (amount of substance)$^{-1}$]

The driving force from a mixture of gases is described by Dalton's law of partial pressures which states that the sum of the partial pressures of individual gases is equal to the total pressure exerted by the gas mixture. The rate at which a gas or vapor passes through a polymer is governed by three processes: (1) absorption of permeating species at the polymer surface (2) diffusion of molecule through the polymer (3) desorption of permeating species from the polymer surface.

After reviewing the general principles of diffusion, the diffusion interactions between carbon nanotubes and polymers must be reviewed and considered for the application of products produced by IDEX Health and Science.

1.2 Material Choice: Permeability and Selectivity

A key factor that must be taken into consideration when choosing a polymer is the relationship between permeability and selectivity. Permeability is the ability of a membrane to allow gasses to pass through. This value is represented by the permeability coefficient, P_a, defined as the trans-membrane pressure difference, (p_2-p_1), and thickness, l, normalized by steady-state gas flux, N_a [5].

$$P_a = \frac{N_a * l}{p_2 - p_1} \qquad \text{[Eq. 3]}$$

This value must be experimentally determined and is often referred to as a material property.

In conjunction with permeability, selectivity is another material property that must be considered. Gas selectivity is the ratio of permeability coefficients of two gases, $\alpha_{a/b}$, (P_a/P_b), where P_a is the permeability of the more permeable gas and P_b is the permeability of the less permeable gas in the binary gas pair. [6] An ideal membrane would have both a high permeability and selectivity (Figure 5).
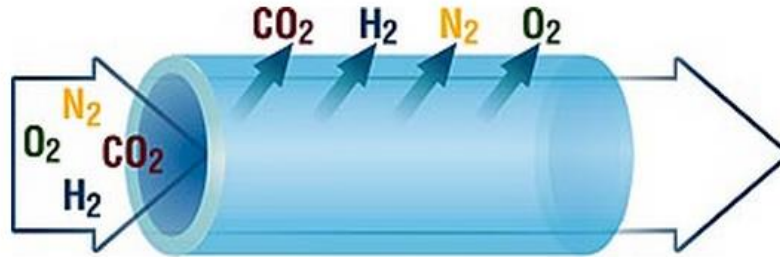
Figure 5. Schematic representation of the permeability and selectivity. Certain gases are selectively removed from the liquid by diffusion through the membrane.

The material chosen, as well as processing conditions for a material can alter the selectivity. [7] If a membrane is porous, selectivity will be low because any gas can pass freely from one side to the other (the material must act as a pure cast membrane). A pure cast membrane is characterized as having no pores. It is assumed that impregnating the sample does not alter the pure cast membrane properties. In order for the design to perform as required, there can be no pores in the sample.

A high permeability would result in minimal material being needed (minimizing cost) to achieve diffusion, while high selectivity would remove very specific gasses, yielding a high purity liquid. The relationship between these two material characteristics is represented by a tradeoff curve (Figure 6). [8] Permeability and selectivity have an inverse relationship. The specific needs of the product must be closely considered to determine where along the trade-off curve the best materials fall.
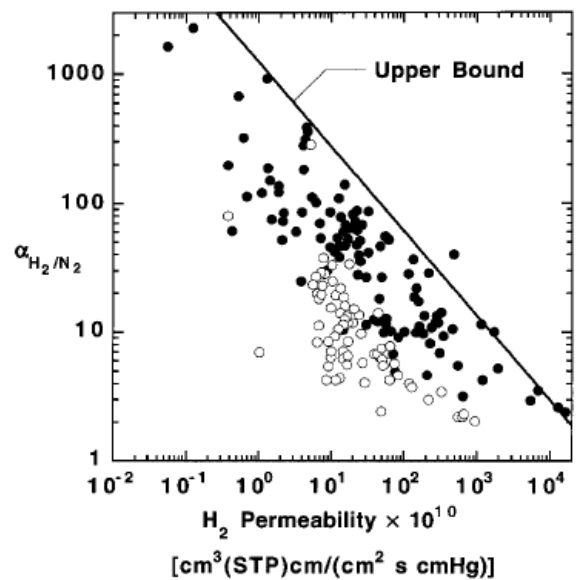
Figure 6. Trade-off Curve showing the inverse relationship of permeability and selectivity of various membranes. The Upper Bound is the upper limit for this give-and-take relationship.[8]

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1.3 Carbon Nanotubes

Carbon nanotubes have been studied for diffusion of gases across a membrane. The permanence of CH_4/H_2 has been predicted using simulations. [3] Carbon nanotubes have extremely rapid gas diffusion rates compared to other nonporous materials. The permeability and selectivity trade-off curve for the carbon nanotube membrane was studied and the transport properties of molecules adsorbed inside the carbon nanotubes was not high compared to similar materials. This is most likely due to the smoothness of the carbon nanotubes on the atomic scale. These carbon nanotubes show promise as gas separation membranes but there are still challenges to overcome. The results from this study shows that for certain elements carbon nanotubes can be used as the means for diffusion but the selectivity of the carbon nanotubes is not good enough for IDEX's product. The nanotubes may be able to separate elements of vastly different sizes but IDEX requires a material with a much higher degree of selectivity.

1.4 Fluorinated Copolymer

Polymers are preferred for gas separation due their inherent resistance to many different types of solvents. Instruments such as HPLC degassing modules that use a degassing chamber inject varying types of solvents which require a material that can resist most solvents. By using polymers, a wide range of solvents can be injected into the system without damaging the degassing membrane. Fluorinated copolymers are also used due to their position on the trade-off curve (Figure 6). They present the ability to maximize both permeability and selectivity, reducing the time required for the diffusion of gasses, while ensuring the proper gasses are being removed from a solvent.

Gu-Gon Park studied the effects of various amounts of Polytetrafluoroethylene (PTFE), most commonly known as Teflon®, on air permeability and pore diameter. [4] The mean pore diameter and permeability were recorded using an Automated Perm Porometer (Figure 7). As the PTFE content increases the permeability decreases and as the permeability decreases the selectivity increases according the trade-off curve (Figure 6). PTFE can be used for gas separation and as the PTFE content increases the selectivity increases as well making PTFE a viable option for IDEX's use.
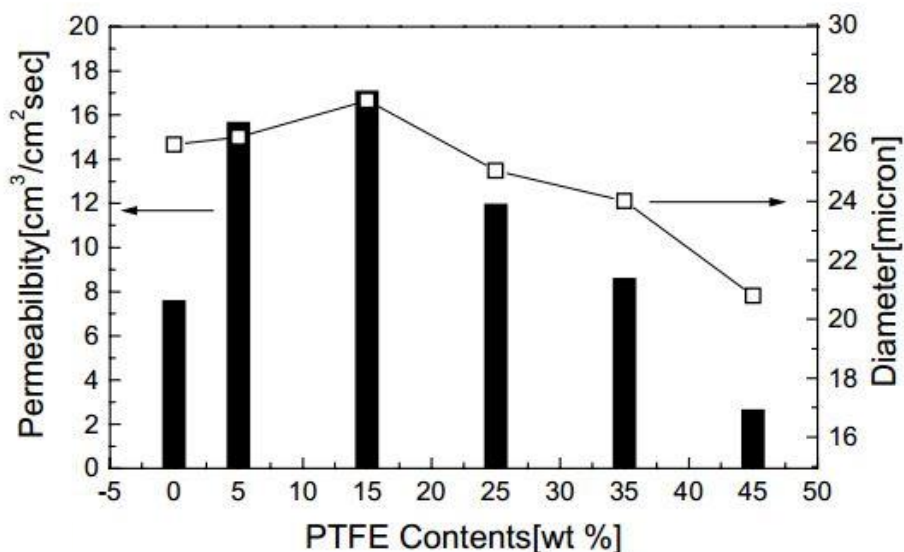
Figure 7. Effect of PTFE content on the air permeability and pore diameter.[4]

In addition to chemical resistance, polymers are also used due their ability to adhere to a variety of geometric designs. The copolymer is very ductile, allowing for use in applications that use non-traditional shapes, such as tubing. By choosing a fluorinated copolymer, IDEX Health and Science can create a product that has many design considerations, and can be marketed to a wide variety of customers using varying solvents in their specific applications.

1.5 Relevance

By studying previous literature and carefully considering the products' needs, IDEX selected Teflon® AF as the material for the gas diffusion membrane. However, as a small film membrane the Teflon® AF becomes brittle. A carbon nanotube matrix enforces the copolymer increasing the toughness and ductility of the membrane.

Measuring the thickness of the outer layer fluorinated copolymer of the composite membrane leads to an understanding of how material permeability can be altered. A thicker coating requires more material during production and alters the permeability of the desired composite membrane.

To gain a complete picture of the composite membrane, the carbon matrix thickness was measure. The thickness of this layer correlates to the processing conditions that adhere the copolymer to the carbon matrix. During processing, the thickness of the composite may vary due to the combination of processing parameters.

Determination of a fluorine concentration gradient is also useful in determining the adherence of the copolymer to the carbon matrix. For cost concerns related to processing, it is desirable to use the least amount of Teflon® AF possible. Since the copolymer becomes brittle as thickness decreases, adherence to the reinforcing carbon matrix is critical. A strong adherence level is desirable for the development of processing conditions that produce a variety of shapes and design iterations for application purposes.

By analyzing the following three different aspects of the membrane a complete characterization of the membrane can be obtained: (a) outer Teflon® AF and inner carbon nanotube matrix thicknesses, (b) fluorine concentration gradient across membrane, and (c) mechanical properties. Combining the characterization of the membrane with the diffusion rates provided insight into which processing parameters led to optimal membrane characteristics.

2. TEST PROCEDURE

2.1 Design of Experiment

Eighteen (18) samples were produced by IDEX with the following varying processing parameters: (a) Teflon® AF 2400 concentration (%), (b) carbon nanotube paper density (g/m^2), (c) ultrasound exposure time (min), and (d) recoat (Table I). Each sample was sectioned and imaged using Scanning Electron Microscopy (SEM) on low vacuum mode. The image was used to measure three different cross sectional layer thicknesses: the two outer Teflon® AF layers and the inner carbon nanotube matrix. The layer thicknesses for each sample were recorded and used to show how well the Teflon® AF penetrated the carbon nanotube matrix.

Table I. Design of Experiment Sample Variation Completed by IDEX Health and Science

Sample	Processing Parameters			
	Concentration	Density	Time	Recoat
	%	GSM	min	
1 - 24	2.5 : 3.75 : 5	1.97 : 3.59 : 5.22	30 : 135 : 240	Yes : No

Additionally, Energy Dispersive X-Ray Spectroscopy (EDS) was performed on each sample using INCA software to confirm the penetration levels of the Teflon® AF. Five points across the cross section of each sample were scanned. The points were numbered as follows: outer Teflon® AF layer (1, 5), and carbon nanotube matrix layer (2, 3, and 4) (Figure 8). The amount of

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Teflon® AF in each sample was mapped to determine how well it had infiltrated the carbon nanotube matrix. The level of infiltration was determined by the amount of fluorine present in the center of the sample.
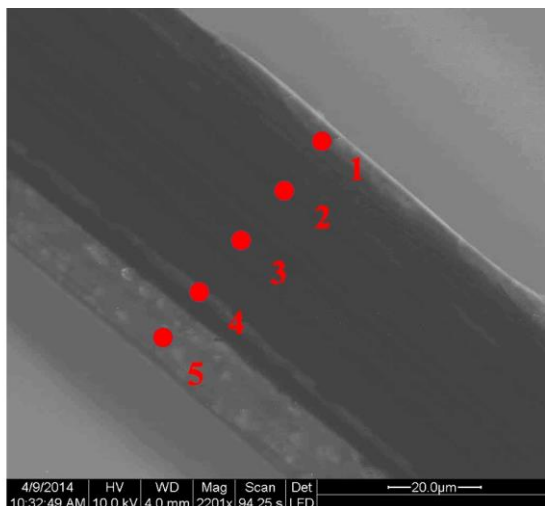
Figure 8. The points of interest for EDS analysis were the outer fluorinated copolymer layer (1, 5), diffusion region between Teflon® AF and carbon matrix (2, 4), and center of the carbon matrix (3).

Lastly, mechanical tensile testing was completed to determine the relative strength of each sample. The mechanical properties of each sample were compared to the processing parameters used to create the sample to determine if the parameters had a significant effect on the mechanical performance of the membranes.

3. TEST PROTOCOL

The material was be sectioned into a 5 cm x 1 cm samples by placing the membrane under a scoring jig and scoring with a scalpel (blade #10) along one side of the slot. The scored edge was labeled for imaging (Figure 9).

3.1 Scanning Electron Microscopy

The sample was adhered in a looped pattern so as to provide ample cross sectional surface for imaging (Figure 10). Copper tape was used to adhere the sample to the mount. The sample was mounted carefully to avoid wrinkles with the scored edge face up (Figure 11). SEM imaging was performed in low vacuum mode under the following conditions: 100.00 Pa, 10.00

KV, and spot size 4. The Standard Operation Procedure (SOP) for imaging with the SEM was used to locate a portion of the cross section which allowed for clear differentiation between layer thicknesses (Figure 12).
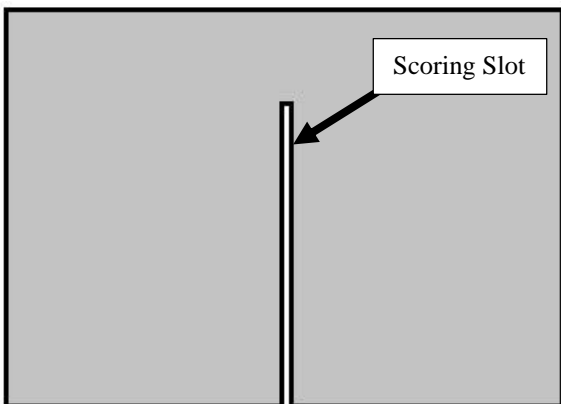
Figure 9. Schematic of jig design used to score the membrane to create a clean cut for imaging the cross section.
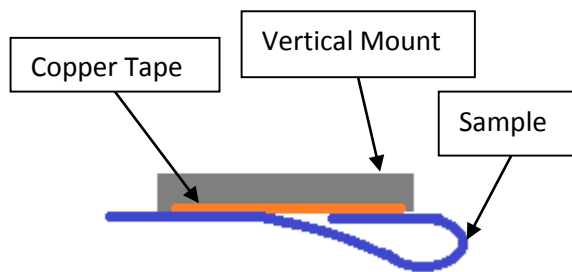
Figure 10. Looped mounting pattern was used to provide a large cross sectional surface area for viewing and imaging with the SEM.

Figure 11. A sample mounted using double sided copper tape and a looped technique.
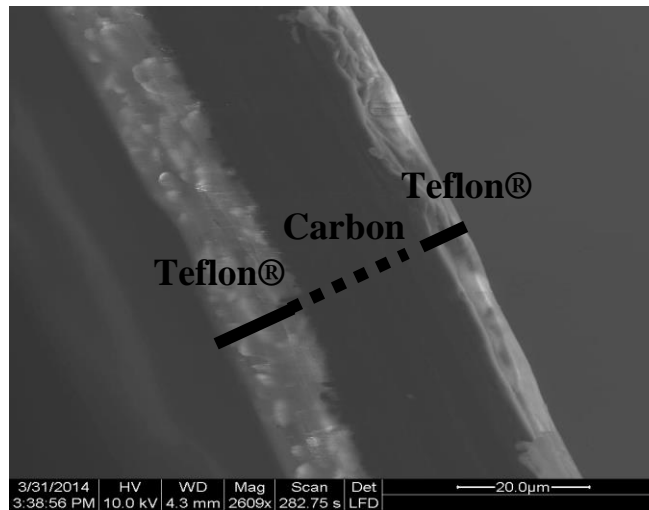
Figure 12. The outer Teflon® AF layers (solid black line) can be distinguished from the carbon nanotube matrix (dotted black line) by a difference in color and texture.

3.2 Energy Dispersive X-Ray Spectroscopy

Each sample was imaged and Photoshop® was used to measure the outer and inner layer thicknesses. Energy Dispersive X-Ray Spectroscopy (EDS) was then preformed on each sample by following the Standard Operation Procedure (SOP) for EDS with INCA software. During analysis the process time was set to ensure a dead time of 12-25%. Five (5) points of interest were selected across each membrane to trace the fluorine and oxygen present at each location

(Figure 13). Oxygen was analyzed as a secondary indicator of polymer penetration, as fluorine and oxygen are the only two elements present that clearly identify the polymer coating, and not the carbon matrix.
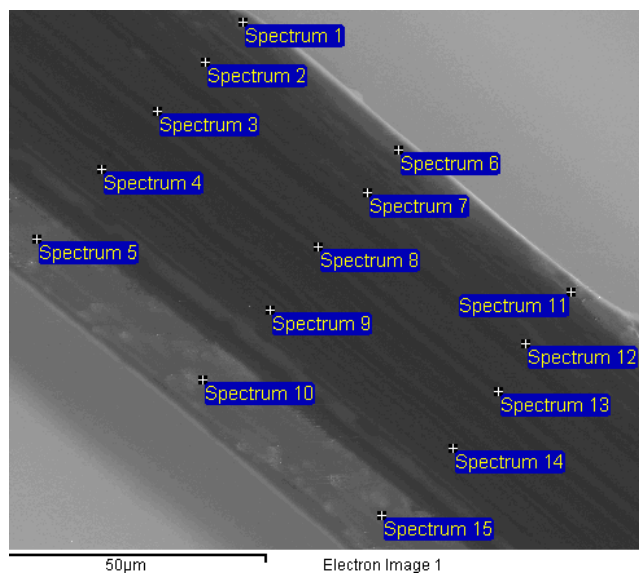
Figure 13. Locations of scan points for EDS analysis to trace the major elements (carbon, fluorine, oxygen) present in the different layers.

Five (5) spectra were collected along three (3) separate lines for each membrane sample. The averages of the corresponding spectrum data points were used to create an Excel® line plot of each element with respect to spectra position. This clearly provided a concentration gradient of Carbon, Oxygen, and Fluorine across the cross section of each membrane.

3.3 Tensile Testing

Tensile testing was conducted according to specifications listed in the ASTM D882-12. Three tensile test samples labeled A, B, and C were created from each of the original membrane samples by using a scalpel and the jig. Each tensile test sample was cut to 0.5 in. x 3 in. A sample of the pure carbon matrix was also tested as a control. Roller grips and an Instron® tensile test machine with a 500 N load cell and a strain rate of 0.5 mm/min were used for all tests. Each sample was mounted in the grips with a 1.63 in. gauge length which allowed enough material to be properly gripped. Each test was completed until fracture. The Young's modulus, Ultimate Tensile Strength (UTS), and percent (%) elongation was recorded for each tensile test sample.

4. RESULTS

4.1 Layer Thicknesses

SEM analysis provided cross sectional images of each sample which were exported to Photoshop® for completing thickness measurements. The pixels of the SEM scale bar was converted to microns and used to measure the total thickness of each membrane sample. The thicknesses ranged from 18.04 µm to 68.42 µm (Figure 14). The two outer Teflon® AF layers and inner carbon matrix layer were also measured using the same technique (Figure 12). While each composite membrane sample consisted of three distinct layers, the thicknesses of each layer varied between samples. The outer Teflon® AF layers, ranged from 1.85 µm to 21.43 µm and the carbon matrix layer ranged from 5.06 µm to 41.72 µm. The large degree of variance between layer thicknesses was a result of the processing parameters used to manufacture the membranes.
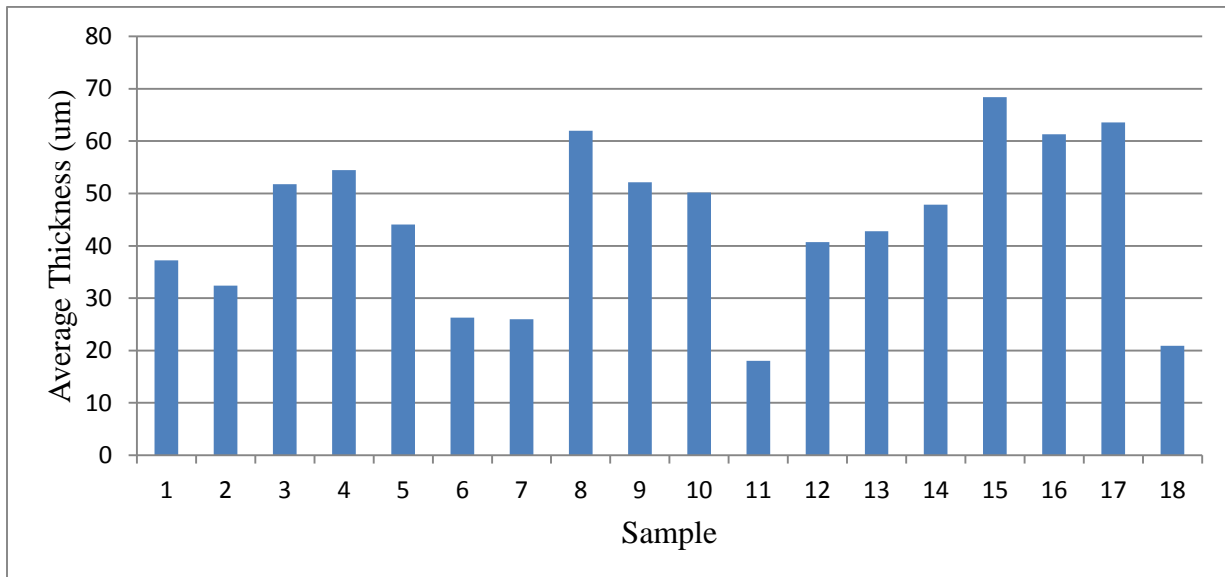
Figure 14: Total membrane thickness measurements from SEM images. Sample 14 and 11 were 68.42 µm and 18.04 µm thick, respectively. The individual layers within each membrane were also measured and recorded using the same technique.

4.2 Fluorine Gradient

EDS analysis was used to trace the fluorine present across each membrane. As discussed earlier, five (5) spectrum points were taken over the cross section of each sample and the three (3) spectra lines were averaged to achieve representative values (Figure 13). The averaged values were then plotted to identify the trend of fluorine concentration across the sample. In general

each sample followed the expected pattern with high levels of oxygen and fluorine present toward the outer Teflon® AF layers. A gradual decrease of these elements occurred at points toward the center where a high level of carbon was present do to the carbon matrix that was used to create the composite membrane (Figure 15). The different design parameters led to different levels of polymer penetration resulting in samples with differing levels of fluorine.
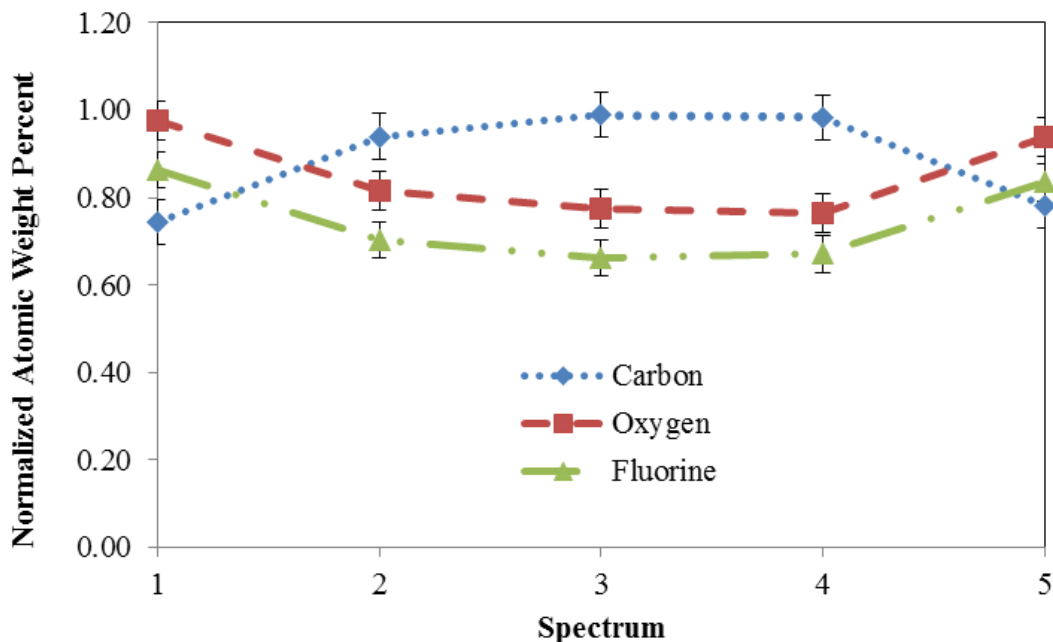
Figure 15. Normalized weight percent's for the fluorine, carbon, and oxygen content across the cross section of a thin film Teflon and carbon matrix composite. Spectrum three represents the center of the membrane proving that the outer fluorine layer has penetrated into the center of the sample.

4.3 Mechanical Properties

By comparing Young's modulus, UTS, and percent elongation of each sample, the relative toughness of the respective samples was determined. Representative bar charts were created for each mechanical property. The bar chart for UTS indicated that sample 10 had the highest UTS while the pure carbon paper had the lowest UTS (Figure 16). Similarly, pure carbon paper had the highest percent elongation. The properties of the pure carbon paper were expected due to the ductility it adds to the brittle copolymer. In terms of Young's modulus, sample 10 and 2 had the highest and lowest respective values.
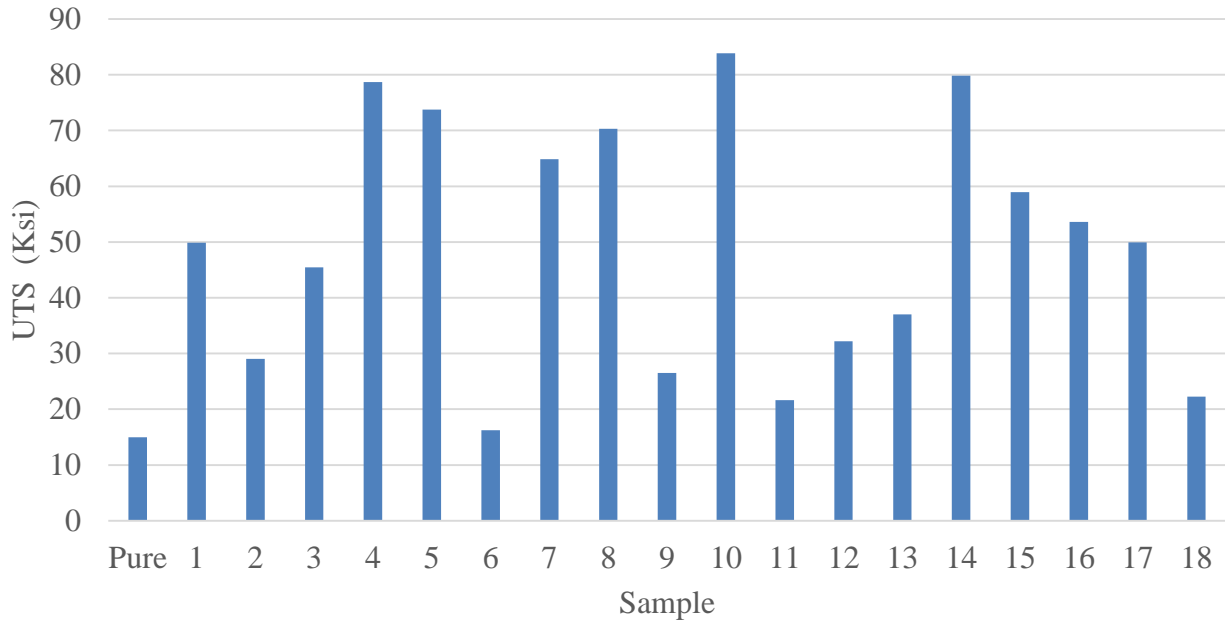
Figure 16: UTS results from tensile testing. Sample 10 and the pure carbon matrix had a UTS of 83.88 Ksi and 14.99 Ksi, respectively

5. ANALYSIS

5.1 Layer Thickness

Due to the variance in total copolymer and total membrane thickness between samples, a thickness ratio was developed in order to normalize the data from the SEM image layer measurements (Eq. 4). This allowed for more useful comparisons to be made between samples. In terms of minimizing production cost, it was assumed that minimizing the copolymer thickness would provide the optimal sample.

The thickness ratio was derived by using the following equation:

$$Thickness\ Ratio = \frac{Total\ Copolymer\ Thickness}{Total\ Membrane\ Thickness} \qquad \text{[Eq. 4]}$$

Sample 7 had the smallest thickness ratio and sample 1 had the largest. The results collected from these measurements were given the IDEX Health and Science to be used in conjunction with the EDS and tensile testing results for determining the optimal membrane.

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5.2 White Light Interferometry

White Light Interferometry (WLI) was used to verify the sample thickness values collected from the SEM image measurements. WLI creates a topographical map highlighting the different layers and topographical changes across the membrane (Figure 17). The scans collected using WLI verified the SEM thickness measurements but also presented an unexpected discovery. WLI revealed valleys and trenches in the cross section of the membrane despite the flat images taken with the SEM. This was attributed to the cutting technique used to score each sample and, therefore, ion beam milling should be used to produce a cleaner cut. Cal Poly unfortunately does not have the capabilities for ion beam milling which made this a limitation that could not be overcome.
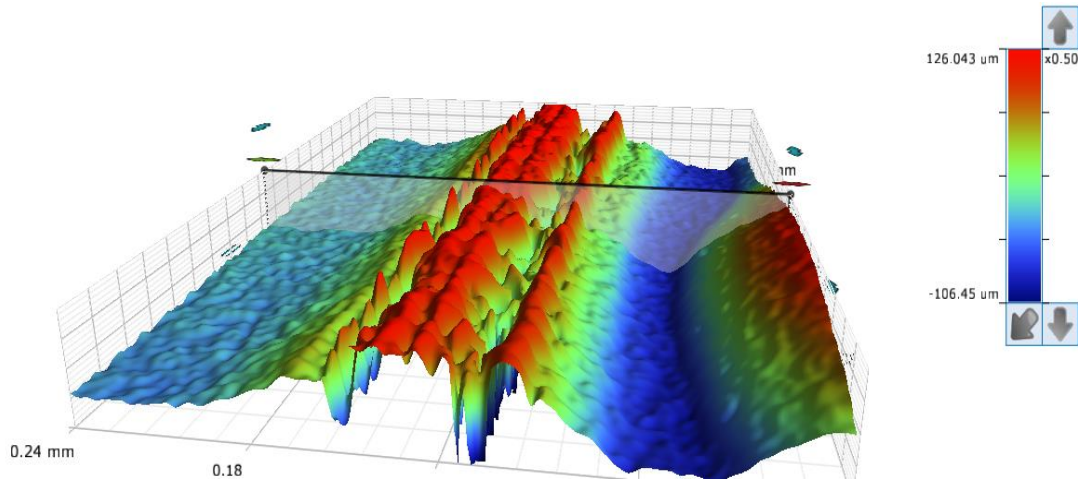
Figure 17. A topographical White Light Interferometry (WLI) image of the cross-section of sample 8 indicated height differences via color representation. The rough edge may be a result of the cutting technique used on the sample.

5.3 Fluorine Impregnation

A trade-off curve was used to compare the thickness ratio to the concentration of fluorine present in the center of each sample (Figure 18). The curve falls along the bottom edge because the optimum sample would maximum properties while maintaining a low amount of polymer coating to reduce material cost. Samples 3 and 9 contained the highest levels of fluorine in the center while still minimizing the polymer thickness ratio. These samples represent the best adhesion of the polymer, due to highest amount of fluorine detected at the center, while still reducing material usage and thus material cost. Although, sample 7 falls along the bottom of the

trade-off curve because it had the smallest thickness ratio, it did not have the largest fluorine concentration at the center of the membrane. In fact, sample 7 contained the lowest levels of fluorine in the center of the membrane meaning high levels of polymer penetration did not occur during the processing of this sample.
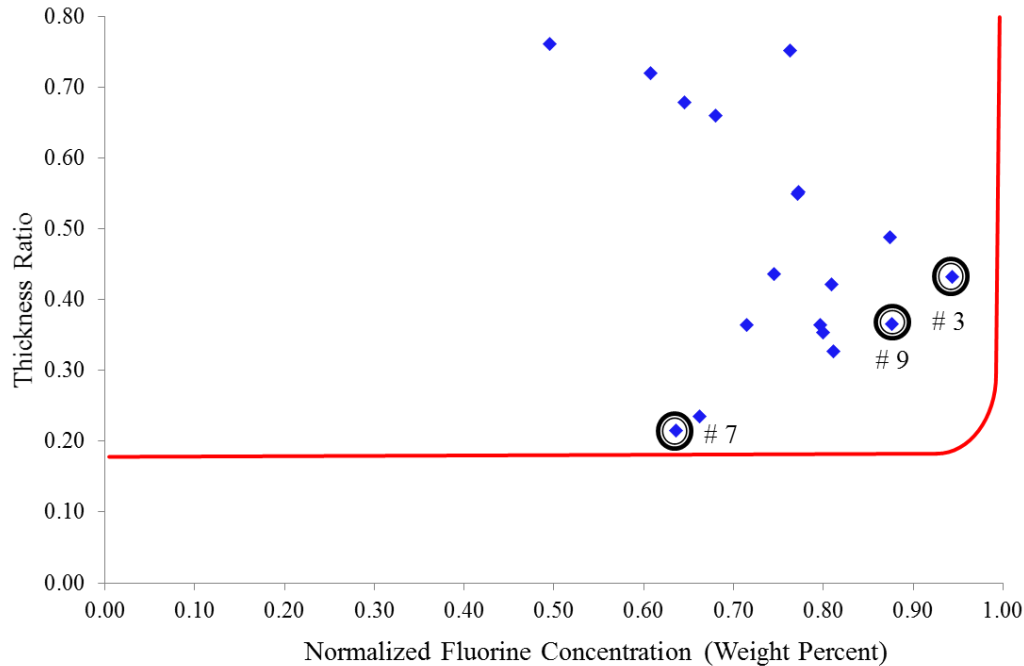
Figure 18. Trade-off curve for fluorine concentration at the center of the sample and the thickness ratio. Sample #9 and #3 both have the highest levels of fluorine and small thickness ratios.

The effect of each processing parameter was determined using statistical comparisons of the fluorine present in the center of each sample. A 95% confidence interval was used for all analysis. The main effect statistics show that recoating had little effect on polymer penetration into the carbon nanotube matrix (Table II). Exposure time had the greatest effect on polymer penetration while concentration had a significant effect but GSM had minimal significance.

Table II. Effect of Processing Parameters on Fluorine Concentration at the Center of the Membrane

Manufacturing Parameter	P-Value
Concentration	0.003
GSM	0.070
Recoat	0.591
Time	0.000

Analysis of the statistics revealed that while the main components of concentration and GSM were identified, there were also interactions between the variables. 2-way and 3-way interactions were determined using Minitab® Software (Table III). Due to these interactions further testing should be conducted to determine what parameter has the greatest effect on fluorine concentration in the center of the sample.

Table III. Interaction Between Processing Parameters and Corresponding P-Values

Interaction	P-Value
Concentration*GSM	0.006
GSM*Recoat	0.026
Concentration*Recoat*Time	0.000

Error bars in Figure 15 show that the levels of fluorine vs. oxygen never overlap, revealing a true gradient between the two elements. A possible artifact of the gradient could be that the fluorine levels do not follow true smooth transitions. A step gradient could occur, but would be obscured by the excitation volume of the electron beam during testing. EDS results were taken to show the estimated excitation volume, and revealed an area of 1-2 microns. While this region was large enough to smooth any step gradient in fluorine levels, it was determined to be of minimal consequence for the scope of this project. Any step gradient in fluorine levels would occur on the submicron scale, which was not sufficient to warrant further investigation.

5.4 Tensile Testing

Trade-off curves comparing each mechanical property (Young's modulus, UTS, and percent elongation) vs. the thickness ratio were created for analysis. The trade-off curve for UTS vs. thickness ratio highlights that while sample 7 had the smallest thickness ratio it also maintained high strength (Figure 19). However, because sample 10 was significantly stronger and had an average thickness ratio it provided to be the better option in terms of this property. This trade off-curve highlights the need to determine the most important property before optimal processing parameters can be selected.
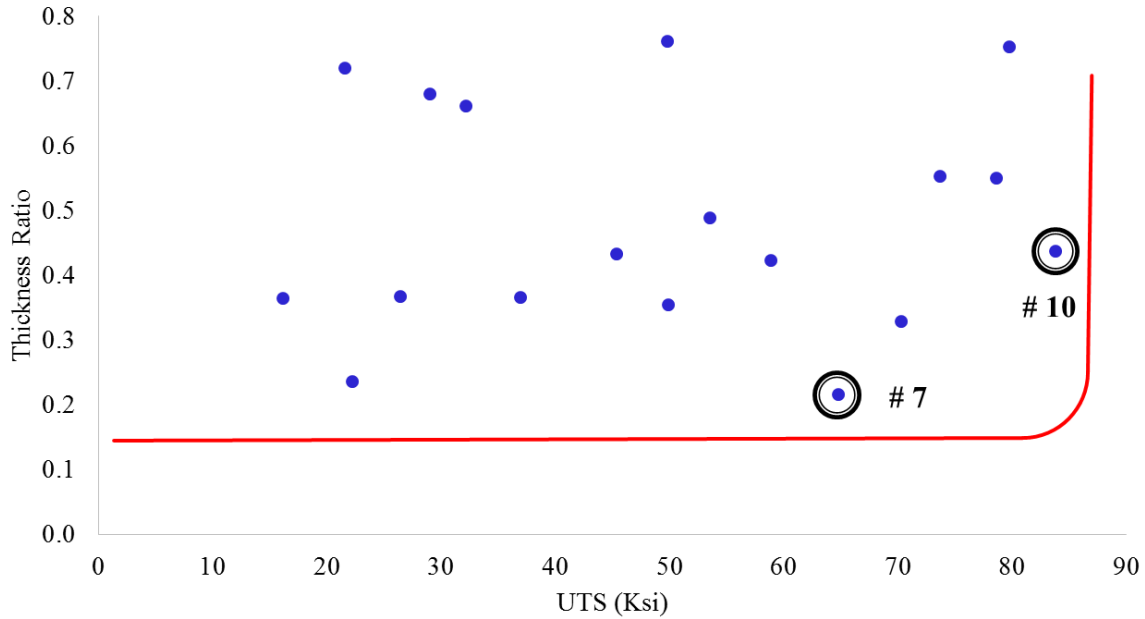
Figure 19. Trade-off curve comparing the UTS to the thickness ratio. The ideal sample would contain a small thickness ratio to reduce polymer use and material costs while maintaining high strength levels.

The design parameters used to create each sample were considered to determine which parameters have the greatest effect on each mechanical property. The results were similar for Young's modulus, UTS, and percent elongation. Using a confidence interval of 95% during statistical analysis, concentration, GSM, and time all showed a significant impact on the strength and toughness of the membrane. Recoat did not have a significant impact (Table IV).

Table IV. Effect of Processing Parameters on Young's Modulus of the Composite Membrane

Manufacturing Parameter	P-Value
Concentration	0.001
GSM	0.000
Recoat	0.329
Time	0.002

6. CONCLUSION

SEM, EDS, and mechanical tensile testing were conducted on 18 uniquely processed samples created by IDEX Health and Science. By characterizing each membrane, results and analysis provided IDEX Health and Science with information of the relative effect each processing parameter had on each membrane. SEM analysis was used to measure the three distinct layers across the cross section of each membrane. A thickness ratio comparing the outer

copolymer layers to the inner carbon nanotube matrix layer was used to for normalized analysis. The small thickness ratio of sample 7 indicated less polymer use during production which yielded lower material use and cost. The mechanical properties of each sample was determined through tensile testing. Young's modulus, UTS, and percent elongation values were used to create trade-off curves comparing the mechanical property in question to the thickness ratio. Each curve was used to determine the "ideal" sample for each parameter. Sample 7 falls along the bottom of every trade off curve, due to this sample having the smallest overall thickness ratio of all the samples.   Sample 10 had an overall higher UTS and Young's modulus, while sample 4 had a higher percentage of elongation. EDS analysis traced the fluorine present over the cross section of each membrane, and determined the fluorine levels present in the center of each sample. Fluorine in the center of the sample was an indication that the polymer penetrated the inner carbon matrix and that the adhesion between the polymer and matrix had been optimized. This also indicates that the diffusion region is maximized, correlating to ideal polymer adhesion. Samples 3 and 9 contained highest levels of fluorine while minimizing polymer use (Table V).

Table V. Comparison of Optimal Samples with Respect to Characteristics and Processing Parameters

	Max. Thickness Ratio	Min. Thickness Ratio	Percent Elongation	UTS and Modulus	Fluorine Concentration
Parameters	**# 1**	**# 7**	**# 4**	**# 10**	**# 3**
Time (min)	30	240	135	240	240
Density (g/m^2)	5.22	5.22	3.59	5.22	1.97
Recoat	Yes	No	Yes	Yes	No
Concentration (%)	2.50	2.50	3.75	5.00	5.00

Statistical analysis revealed that there are 2-way and 3-way interactions, and all the parameters will have some level of interaction. While the main effects are easily identifiable, the interactions between processing parameters cannot be ignored. Due to the various interactions between parameters, there was not an ideal set of processing conditions that will maximize all the material properties that were analyzed. Table V was presented to IDEX and proprietary processing conditions must be determined in order to maximize the material property that is deemed most important.

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8. APPENDIX I: SAFETY PROTOCOL

Operation of Scanning Electron Microscope (SEM) – The SEM works on the principles of using electrons to produce an electrical signal that is converted to an optical image. During the process there is residual radiation emitted from the microscope, potentially causing a radiation hazard. Current standards dictate that radiation produced from an SEM may not exceed 0.5mR at 5cm from the unit. Due to current insulating technology to safeguard against radiation leakage, there is no personal monitoring device required when using the SEM[9].

Liquid Nitrogen – Liquid nitrogen was used in conjunction with the imaging technique of Energy Dispersive Spectroscopy (EDS). Liquid nitrogen must be poured into a dewar attached to the SEM. This presents the hazard of:

1) <u>Falling from a ladder</u>: this hazard was mitigated by having a second person support the person on the ladder, ensuring that the ladder would not move and the person would not fall.

2) <u>Cryogenic Burns</u>: When handling liquid nitrogen the appropriate gloves (cryogenic rated) must be used in conjunction with long pants, closed toed shoes, long sleeves, and protective face shield. This safety precautions drastically reduced the chance of receiving cryogenic burns while handling liquid nitrogen[2].

3) <u>Oxygen Depletion</u>: Pouring liquid nitrogen can result in spillage which produces an excess of nitrogen gas in the immediate area. This increase in nitrogen gas can cause oxygen depletion, posing a potential hazard for the users in the immediate area. While pouring liquid nitrogen, all doors must remain open to ensure proper ventilation of nitrogen gas that may evolve from spills[10].

Sample Cutting Instruments – The samples to be tested must be cut to size with sharp blades. The close proximity to blades and the user's hands presents a hazard with cutting fingers/hands. Proper protective gloves must be worn in conjunction with safety glasses to mitigate this safety concern.

Working Late Hours – Some of the work done on this project was completed be during non-traditional working hours (8am-5pm) due to equipment scheduling conflicts. The nighttime hours provide a safety concern with lack of concentration. There was always a team present in any laboratory environment and as soon as any user felt fatigued, work was immediately stop until the next day.