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EFFECT OF CARBON NANOTUBES ON MOISTURE ABSORPTION PROPERTIES OF EPOXY LAMINATES

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EFFECT OF CARBON NANOTUBES ON MOISTURE ABSORPTION PROPERTIES OF EPOXY LAMINATES

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SCHOOL OF AEROSPACE AND MECHANICAL ENGINEERING

BY

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Table of Contents

List of Tables

List of Figures

Abstract

There have been conflicting studies for how multi-walled carbon nanotube reinforcement will affect the moisture absorption properties of an epoxy laminate. The carbon nanotubes were meant to act as a hindrance for the moisture absorption by the epoxy laminate. In this thesis, the effects the multi-walled carbon nanotubes have on the moisture absorption properties of an epoxy laminate were studied. The study was done by fabricating a variety of epoxy laminates with differing planar size, thickness, and nanotube content. Composite samples of three different planar sizes (0.75in x 0.75in, 1.00in x 0.75in, 1.25in x 1.25in), three different thicknesses (1.5mm, 1.7mm, 2.0mm), and seven different nanotube weight percentage levels (0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0%, and 3.0%) were used to provide a variety of differences in moisture absorption behavior which was used to develop potential trends. Eight samples for each possible combination were made resulting in 504 total samples for gravimetric experiments. The epoxy laminate samples were dried using a vacuum oven, and then placed in a constant-temperature water bath at 25°C where they were weighed periodically. The scanning electron microscope images showed that the nanotube dispersion differs depending on the nanotube content within the sample. The dispersion proved to be homogeneous for the 0.25% and 0.5% nanotube content samples, and somewhat nonhomogeneous for the 1.5% and 3.0% nanotube content samples. The fracture planes on the epoxy samples progressively became smaller as the nanotube content increased, with 1.5% nanotube content samples being an exception.

The addition of nanotubes resulted in an overall increase in the moisture equilibrium of the epoxy laminate samples. The addition of more nanotube content did

not show a consistent rise in the moisture equilibrium, but the highest moisture equilibriums were seen for the 2.0% and 3.0% nanotube content samples. The through-the-thickness and planar diffusivities showed opposite trends from each other with the planar diffusivity showing an increase until the 1.0% nanotube content samples followed by a decrease in value, and the through-the-thickness diffusivity showed an initial decrease followed by an increase in value. In general, the change of through-the-thickness diffusivity due to the presence of nanotubes was smaller than the change in the planar diffusivity. Hence, this finding would imply that the addition of nanotubes affects moisture absorption through the composite edges more than the planar surfaces.

CHAPTER 1. INTRODUCTION

The addition of multi-walled carbon nanotubes to reinforce an epoxy laminate is expected to have an effect on its moisture absorption properties. Each of the moisture absorption properties (moisture equilibrium, diffusivity, etc.) affects the mechanical properties of the epoxy laminates by altering the amount of moisture within the epoxy at any point. The diffusivity changes the rate the moisture intake through the epoxy laminate, which with the addition of nanotubes could potentially provide obstructions, thus resulting in a lower diffusivity for the epoxy laminate.

The epoxy resin is utilized as the matrix material for a number of composite material products, which has importance because the moisture absorption behavior of composite materials is dominated by the matrix. Composite materials affect many different industries such as aerospace and civil industries. Within the industries composite materials are used, having the physical properties a composite material has, lightweight with high mechanical properties, have a growing importance because anything that reduces these mechanical properties affects the structural integrity of different parts. The long term integrity of the large scale structures or engineered products that affect many people have the utmost importance for the safety of the community. A hindrance to the mechanical properties comes from the moisture within the composite materials. As the moisture level within the composite materials increases the mechanical properties start to degrade, which indicates in the importance of improving the moisture absorption properties by reducing the moisture equilibrium and diffusivity. The addition of any obstruction for the moisture where the moisture diffusion slows to adjust the flow path within the material should reduce the overall diffusivity and may decrease the moisture equilibrium.

1.1. EPOXY RESIN

Mechanical property studies are preceded by moisture absorption experiments because of the degradation of the mechanical properties in epoxy resin from the moisture aging. Different moisture absorption studies have been done with the addition of nanotubes to find the effect of sample thickness and planar sample size has on the moisture absorption properties. Effects such as plasticization and different molecular modification, including degradation and cross-linking, occur through the moisture absorption process of epoxy resin, changing the physical properties of the epoxy [1]. A study showing the differences in moisture absorption and resorption curves reinforces that the moisture absorption process alters the physical properties of an epoxy resin. Experimental moisture absorption data for epoxy resin samples showed that although the diffusivity had changed between the absorption and resorption, the moisture equilibrium level remained unchanged. Following the moisture absorption and desorption process, the resorption curve resulted in a decrease in diffusion coefficient for the epoxy resin samples [2, 3].

Moisture absorption properties are affected by multiple factors, one factor - thickness of the sample - should not result in changing properties. For an epoxy resin sample, there was a critical thickness found for samples to follow Fickian behavior [2]. When the sample becomes too thin, the moisture uptake behavior becomes non-Fickian. This critical thickness value was reported to be around 0.030 inches. The thickness study shows that, for samples with planar size much larger than the thickness, the one-dimensional moisture absorption experimental data results in a similar Fickian moisture uptake during the initial stages. Initial moisture uptake stays consistent regardless of the thickness, but between initial uptake and reaching moisture equilibrium, thickness has an effect on the moisture uptake dynamics. As the sample thickness increases, the moisture uptake more slowly reaches its moisture equilibrium following the initial Fickian uptake [3]. Different neat epoxy resin samples show moisture absorption affects the properties along with showing that the moisture absorption properties stay the same regardless of the thickness, unless the thickness is below a critical range,

The addition of a hardener during the fabrication of an epoxy resin has been tested to see how moisture absorption properties are altered [1]. The study with changing levels of hardener was done for mechanical properties with an additional moisture absorption study that did not reach moisture equilibrium during the study. This study showed little to no change in the moisture absorption with the middle amount of hardener trending higher when the study ended. Increasing the temperature of the environment holding the moisture absorption samples would result in an accelerated moisture uptake, and moisture equilibrium would be more quickly reached.

1.2. ACCELERATED TESTING

Moisture content degrades the mechanical properties of composite materials, because of this moisture absorption experiments are done in combination with mechanical testing. Since the mechanical testing of moisture samples is done at moisture equilibrium, the moisture absorption is often accelerated to reduce the waiting time for mechanical testing. Multiple studies have been done using differing temperatures to find the affect these accelerated testing process have on the moisture absorption [4-10]. Some studies have shown that with the differing temperature, the moisture equilibrium has shown differences [4-6]. Molding compounds of MP8000 (Nitto) and CEL 9220M (Hitachi) went through moisture absorption tests where the relative humidity and the temperature were changed. Moisture absorption of two different molding compounds was studied at different relative humidity and temperature. Unlike many studies where the samples were immersed in water, this study placed the samples in a humidity-controlled environment. 30 and 85°C environments were used where the temperature increase resulted in an increase from 0.21 to 0.35%, and 0.093 to 0.18%, moisture equilibrium and diffusivity, respectively for both compounds [4]. Moisture uptake, done in seawater, with increasing temperature - 26, 35, 45, 55 and 65°C -resulted in a moisture equilibrium decrease from 1.3 to 0.3% [5]. Moisture sorption done with temperatures of 23 and 60°C showed an increase in moisture equilibrium from 2.0 to 2.4%, by weight, reinforcing that an increase in temperature increases moisture equilibrium [6].

Moisture equilibrium level is not always affected by the temperature, but the increasing temperature consistently increases the diffusivity of the samples [7-9]. The changing temperature has shown to either increase or decrease the moisture equilibrium previously, the moisture equilibrium has also been shown to stay constant regardless of temperature change. Moisture equilibrium always has fluctuation through experimentation, but when accounting for error the fluctuations are negligible. Temperature effects on composite samples were studied by using multiple temperature baths where samples were moved from bath to bath throughout the moisture uptake [10]. Three different temperature baths - 10, 40 and 70°C - had a batch of samples starting in each one where groups of the samples were moved from one bath into different temperature baths to show the effect temperature can have on the moisture absorption. Changing the temperature bath of the samples at any point will result in an initial increase in the moisture uptake with increasing or decreasing temperatures. The "reverse thermal effect" takes place when samples are moved from a higher temperature bath to a lower temperature bath where the moisture level increases each time [10]. The importance of keeping a constant temperature throughout moisture absorption was shown by knowing the "reverse thermal effect" can take place. Having a constant temperature environment between the baths and during the mass measurements has importance by limiting the variables changing in an experimental setup.

1.3. MULTI-WALLED NANOTUBES

The multi-walled nanotubes are more commonly used than the single-walled nanotubes. The multi-walled nanotubes have a lower price point than the single-walled nanotubes, making them more cost-effective if large quantities are needed. Conflicting results can be seen when looking for the effect of nanotubes on the moisture absorption properties of composite materials. The addition of multi-walled nanotubes into a composite material has resulted in an increase in moisture equilibrium and diffusivity with increasing quantities of nanotubes [11-13]. Nanotube weight content levels of 0, 0.3, 0.5 and 1.0% show different moisture equilibrium levels. As the nanotube content increases from 0% to 0.5% the moisture equilibrium level increases, but following this step the 1.0% nanotube content samples lowers the moisture equilibrium back to an equal level as the 0.3% nanotube weight content [11]. With nanotube weight contents of 0 and 1.0%, the moisture equilibrium values increase with the addition of nanotubes.

The increase in the nanotube content increased the moisture equilibrium when the samples were placed in distilled water, but when placed in 1.5 wt % brine, the moisture equilibrium decreased with increasing nanotube weight content [12]. The different environments affect the moisture equilibrium in different ways, but in both cases the addition of nanotubes resulted in significant changes.

The moisture absorption studies including multi-walled carbon nanotubes more commonly have shown a decrease in moisture absorption properties of the composite material [14-17]. Studies had a maximum of 2.0% nanotube content by weight, and all showed a decrease in moisture equilibrium with the addition of nanotubes. Constant decreases in maximum moisture equilibrium occur until 1.0% nanotube weight content [14]. The 1.0% nanotube weight content samples result in the lowest moisture equilibrium point, and the 2.0% nanotube weight content samples initially trend lower, but have a higher moisture equilibrium value than the 1.0% nanotube content samples, providing a limit to the benefit of the addition of nanotubes.

Different properties within composite materials also begin to change with the addition of nanotubes, thus suggesting the addition of nanotubes would have considerable effects on composite materials [18-22]. Surface modification of the nanotubes has been studied to see if that will result in a change in moisture absorption properties. Different modifications on the nanotubes result in unchanged moisture absorption properties [18]. The moisture uptake curves of surface modified nanotube epoxy samples constantly cross paths throughout the moisture absorption. The addition of nanotubes positively affects the mechanical properties during dry tests, but if they increase the moisture absorption, the wet mechanical tests will have negative results.

1.4. SINGLE-WALLED NANOTUBES

Single-walled nanotube studies are less common than multi-walled nanotubes, but some studies have been done with the addition of single-walled nanotubes to composite materials [15, 23-26]. Single-walled nanotubes less commonly were used in moisture absorption studies than multi-walled nanotubes. The different types of single-walled nanotubes are more limited than the types of multi-walled nanotubes making the multi-walled nanotubes more desirable for nanotube studies. Comparison in the adsorption properties of singled-walled and multi-walled nanotubes was done. The adsorption differences showed that single-walled nanotubes trended higher than the multi-walled nanotubes making them less desirable for reducing the moisture absorption properties of composite material [15]. Multi-walled nanotube studies typically would have weight percentages of 0% to 3.0% nanotube content maximum, but the single-walled nanotubes were used in less quantity of a maximum weight content of 0.15% [25]. The moisture absorption curves constantly overlap each other throughout uptake when using single-walled nanotubes as reinforcement. The only change in the experiment for this study was the single-walled nanotube content - the size of the samples and temperature of the environment stayed consistent.

1.5. OTHER NANOFILLERS

The multi-walled nanotubes showed conflicting effects on the moisture absorption properties, but other nanofillers more consistently resulted in a decrease in the moisture absorption properties. The inconsistency between results only still occurs with a study where epoxy resin was given Nanomer I.30E organoclay reinforcement [27]. The addition of organoclay into the epoxy resin system increased the maximum moisture equilibrium of the system from 2.5% to 5%. The organoclay was added in 2 parts per hundred (phr) intervals from neat to 10 phr, and with accelerated testing at 80°C the moisture absorption properties were shown to constantly increase the moisture equilibrium level of the material up until 10 phr.

The most common nanofiller addition to epoxy resin samples was nanoclay, which showed a decrease in the moisture absorption properties with the increase in nanoclay weight content [28-30]. The moisture equilibrium level shows a decrease with the addition of nanoclay, but there comes a point when the addition of nanoclay starts to negatively affect the moisture absorption properties. One study had nanoclay weight content from neat to 10% and indicated the maximum reduction of moisture is obtained with the 5% nanoclay. At higher nanoclay content, the moisture equilibrium starts to increase [29]. The study was done using both water and crude oil for the environments the samples were in. In the water environment, the addition of nanoclay affects the moisture absorption properties, but in crude oil the moisture uptake fluctuates more significantly. The diffusivity of the samples with the addition of nanoclay consistently showed a decrease from the neat samples, but not a constant decrease with the increase in nanoclay content. Different nanofillers were also used to study the moisture absorption properties of composite materials, such as nanographene, SN, BN, and SD fillers, and Halloysite nanotubes [31-33]. Each of these nanofillers decreased the moisture equilibrium level of the composite material.

CHAPTER 2. EXPERIMENTAL PROCEDURE

The epoxy laminates were fabricated at three different thicknesses—1.5 mm, 1.7 mm, and 2.0 mm—with the three thicknesses the rate of diffusion was studied to see the effects of the two dimensional moisture absorption properties. Along with the thicknesses there were three planar sizes (0.75in x 0.75in, 1.00in x 0.75in, 1.25in x 1.25in) that changed the ratio of planar area to edge area, allowing for a broad range of tests for the diffusivity differences based on the aspect ratio. The nanotube weight percentage had seven sets (0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0%, and 3.0%). Using a variety of nanotube weight percentages increased the sample size for testing the affect nanotubes have on the moisture absorption properties of the epoxy laminate. With the different amounts of nanotube weight percentage, the dispersion had the potential to differ between each content level, so the dispersion was examined for each nanotube weight percentage. All testing for moisture absorption was done in distilled water at room temperature (25°C).

2.1. DIFFUSION MODEL DEVELOPMENT

The standard representative diffusion model used in moisture absorption studies is the Fickian Diffusion Model. Many moisture absorption studies do follow the Fickian diffusion process, typically within the linear uptake region [34-36]. The addition of another material within the epoxy, carbon nanotubes, can lead to changes in moisture uptake behavior. The moisture diffuses through the material homogeneously in Fickian diffusion, but the addition of nanotubes act as a road block within the epoxy laminate. The 3-D Fickian diffusion model can be displayed as follows:

$$\frac{\partial n}{dt} = D_x \frac{\partial^2 n}{dx^2} + D_y \frac{\partial^2 n}{dy^2} + D_z \frac{\partial^2 n}{dz^2} \tag{1}$$

As Equation 1 above shows, the only material parameters used in Fickian diffusion are the three diffusion coefficients in each of the directions

A three-dimensional anisotropic hindered diffusion model, that is able to cover both Fickian and non-Fickian behaviors, has recently been developed. In the three-dimensional hindered diffusion model there are six different material parameters describing the absorption process: the diffusion coefficient in each of the three dimensions, the maximum moisture equilibrium, γ, the probability per unit time that a mobile molecule will become bound, and β, the probability per unit time that a bound molecule will become mobile. This model is described by the following coupled governing equations.

$$D_x \frac{\partial^2 n}{\partial x^2} + D_y \frac{\partial^2 n}{\partial y^2} + D_z \frac{\partial^2 n}{\partial z^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \tag{2}$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \tag{3}$$

As stated, this model will cover both Fickian and non-Fickian behavior, which can be shown by reducing the gamma term to zero resulting in Equation 2 reducing back to Equation 1. Along with the beta and gamma terms, the n and N terms are defined as the mobile molecules per unit volume and the bound molecules per unit volume, respectively.

2.2. DENSITY STUDY

In combination with the fabrication of the samples, there was a density study of the neat epoxy. This step was necessary to get accurate mass values to have the proper weight percentage of nanotube content within the samples. The density study was done on six different samples of neat epoxy through suspension testing. Suspension testing was done by using a combination of water and glycerin to have an accurate idea of what the density of the fluid was at all times. Initially, the pre-curing density was found by a bulk density calculation using the following formula:

$$\rho_{final} = \frac{\rho_1 m_1 + \rho_2 m_2}{m_1 + m_2} \tag{4}$$

Using Equation 4 with the two density values being the density of EPON 862 (ρ=1.174g/cm^3) and Epikure curing agent w (ρ=1.019g/cm^3), and the mass values for the ratio of the two (1:0.264), respectively, the final density can be calculated.

$$\rho_{final} = \frac{\left(1.174\frac{g}{cm^3}\right)(1\ g)+\left(1.019\frac{g}{cm^3}\right)(0.264\ g)}{(1\ g+0.264g)} = 1.1416\,\frac{g}{cm^3}$$

For the post-cure density, suspension testing was done to find the density of the laminate. Six different 1.0in x 1.0in laminates were cut out. Before the testing was done an approximation was found to give a decent starting place for the mixture. Using an 80cc cup and first zeroing a scale to the weight of this cup then placing the six samples within the cup gave the weight of the samples. Once again the cup with the samples was zeroed to the scale and the cup will be filled with distilled water, which has a density of 1 g/cm^3. Knowing the weight and density of the water, the volume can be calculated and then the remaining portion of the cup will be the volume of the samples. The cup was fully emptied and cleaned, and then the cup was filled with glycerin to find the exact density of the glycerin used in the experiment.

The approximation for the samples was replicated by a mixture of water and glycerin for a volume of 300mL. When the approximate sample density has been replicated by the mixture, each sample was separately placed in the center of the mixture to see if the sample rises, falls, or is suspended in the mixture. If the collective group of the samples sink then more glycerin will need to be added, and water will be added if the samples rise. Between suspension checks there can only be a 1% addition of fluid into the mixture, which equates to 3 mL additions. The 3 mL additions were done while the mixture was being mixed by a magnetic mixer at 500 rpm for 10 minutes. Following the magnetic mixing the mixture was placed in a sonication bath for another 10 minutes. After each suspension check, the 80cc cup was filled with the mixture to get a weight measurement, which calculated a density measurement by knowing the constant volume of the cup. The sample density was limited to the values between the density of the liquid when the samples rose and when the samples sunk. Table 1 shows the mass values of the mixture of distilled water and glycerin within the cup from the mass value of the sample sinking within the mixture and then the mass value from when the sample began to rise within the mixture. Using these two values there will be a potential error in the density measure of 0.0014g/cm^3 making this density calculation correct to the thousandth place. From knowing the volume within the cup, the upper and lower mass measurements can calculate the density of liquid by using the standard relationship between the three:

$$\rho = \frac{m}{V} \tag{5}$$

Once the corresponding density values were found from the mass measurements, the average density was taken from the two values. The average overall density was taken and used as the baseline for the mass calculations for the fabrication of the nanocomposite.

Table 1: Density Suspension Testing Results

Sample	Lower Weight (g)	Upper Weight (g)	Lower Density (g/cm^3)	Upper Density (g/cm^3)	Density (g/cm$^{3)}$
1	100.31	100.42	1.2056	1.2070	1.2063
2	100.42	100.53	1.2070	1.2083	1.2077
3	100.42	100.53	1.2070	1.2083	1.2077
4	100.42	100.53	1.2070	1.2083	1.2077
5	100.11	100.31	1.2032	1.2056	1.2044
6	100.31	100.42	1.2056	1.2070	1.2063
Average	100.33	100.46	1.2059	1.2074	1.2067

2.3. FABRICATION OF NANOCOMPOSITE

The fabrication process used EPON 862 from Miller-Stephenson Chemical Company, Inc., EPIKURE Curing Agent W from Miller-Stephenson Chemical Company, Inc., and Nanoamor regular-length multi-walled nanotubes (MWNT) with 95% purity, outside diameter of 20-30 nm, and a length of 10-30 µm. The combination of EPON 862 and EPIKURE Curing Agent W with a mixing ratio of 1:0.264, by weight, results in the epoxy resin. The EPON 862 and nanotubes were mixed together in a 250 mL high shear blender cup - the nanotubes were poured into the cup first followed by the EPON 862 (130 g). The mixture had the same final mass, but with differing percentages of nanotubes. The cup was placed on a high shear blender and mixed at 1000 rpm for 1 minute followed by 3000 rpm for 3 minutes. The high shear mixing was done to lower the viscosity of the EPON 862, allowing the nanotubes to more easily disperse throughout the mixture. After the high shear mixing was done the mixture was poured into a plastic 250 mL cup. The mixture should be poured until there is 126 g in the plastic 240 mL cup. The high shear blender cup was cleaned using acetone and water.

Sonication of the mixture followed the high shear mixing. The 250 mL cup was placed in an ice bath to go through sonication, done at 42 KHz for one hour pulsing on and off every five seconds. The tip of the sonicator was placed in the center of the mixture. Degassing for one hour followed the sonication to remove the air bubbles and voids from the mixture before mixing the EPIKURE curing agent W. Degassing was done at 25 in Hg. The mixture was reweighed to account for the loss while pouring and sonication, and the curing agent W, at a 0.264:1 ratio with the remaining EPON 862, was added. Before adding the curing agent W the mixture ratio between the EPON 862 and nanotubes remained the same. After adding the curing agent W the mixture was mechanically mixed at 150 rpm for 45 minutes. The first 30 minutes the blade sat in the middle of the mixture followed by 15 minutes of the blade at the bottom of the cup. The movement of the blade improved the uniformity of mixture dispersion. The mixture was degassed for 5 hours at 25 in Hg.

Following degassing, the mixture was poured and cured. The mold used for curing was a 10in by 10in aluminum mold where a 6in by 6in area in the center of the mold was used for cutting samples. The cure cycle began with one hour left in the degassing process. After an hour, the release agent was applied to the aluminum mold and the mixture was poured, and spread evenly. The cure cycle is displayed below:

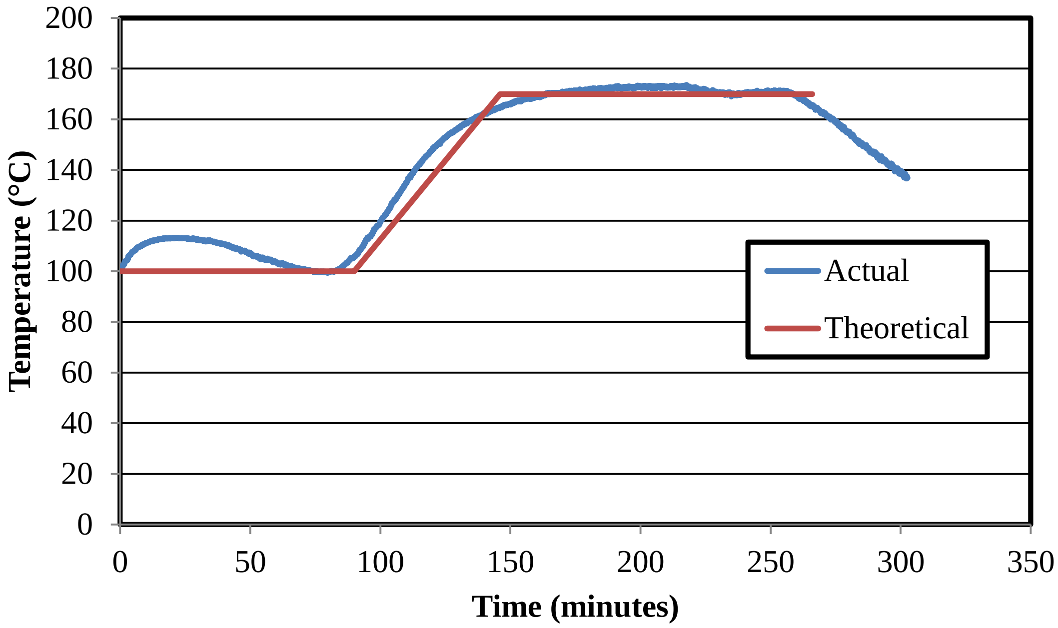

Figure 1: EPON 862/EPIKURE Curing Agent W cure cycle profile

The cure cycle profile is as follows:

- Preheat from 25°C to 100°C for 60 minutes at 1.25°C/min
- Pour the resin mixture
- 1.5 hour hold at 100°C
- Temperature ramp from 100°C to 170°C for 56 minutes at 1.25°C/min
- 2 hour hold at 170°C
- Turn off heating and let the oven cure to room temperature

Figure 1 shows a graphical representation of the cure cycle theoretically along with the actual temperature data obtained from a thermocouple. As the graph shows, the ability for the oven to accurate follow the cure cycle was relatively consistent. At changes from ramping to holding a stable temperature there were the largest differences in the actual and theoretical temperatures. The figure shows an initial temperature of 100°C instead of room temperature. At room temperature the spreading of the mixture along the mold resulted in air bubbles forming. Increasing the starting temperature results in lowering the viscosity, by reducing the viscosity of the mixture to the point where it is easily spread evenly throughout the mold without developing air bubbles will improve the quality of the samples.

2.4. MOISTURE ABSORPTION

The moisture absorption testing was done using a total of 504 samples obtained from a total of 21 molded laminates. Three different planar sizes, three different thicknesses, and seven nanotube weight percentages were used. With the size of the mold being so large all three of the planar sizes can be cut from one mold - using eight samples each. The samples were cut and weighed and then moved into an oven to dry and be weighed periodically until the sample weight remained constant. The samples were placed in jars filled with distilled water and set in a water bath at room temperature (25°C). Periodically the samples were removed, dried on Kimwipes, and weighed to check for changes in the moisture content of the laminate.

During the fabrication of the laminates, there was a 10in x 10in mold placed within an oven that goes through the proper cure cycle. From this larger laminate, the 6in x 6in area in the center of the mold was used for the cutting area of a particular laminate. This area was used to keep the thickness of the samples as consistent as possible. The further away from the middle of the laminate, the larger variance in the thickness because the mixture tried to stay together while being poured in the mold, so less material moved towards the edges.

Figure 2 displays the exact cutting layout that used for each of the laminates that were produced. The cutting layout results in a centralized cutting area where the samples are as closely packed as possible to give thickness uniformity throughout each of the samples. Using this cutting layout, the cutting process was repeatable. This lay out helped following straight cut lines as well as having the blade being used the same way for each of the different laminates.

After the fabrication of all the different laminates is complete, the laminates were then cut into individual samples for each of the different distinctions made previously. Each of the different nanotube weight content samples has a representative image of one of the specific sets below. The first representative image, shown in Figure 3, displays the neat epoxy samples with a planar size of 1.25in x 1.25in and a 1.5mm thickness. As the image shows, the neat epoxy samples are translucent yellow samples.

Figure 4 shows the samples with a nanotube weight content of 0.25% of planar size 1.0in x 0.75in and thickness of 2.0mm. These samples quickly changed coloring to a deep black color because of the nanotubes, a trend that continues for all of the samples containing nanotubes. Figure 5 through Figure 9 shows the samples for the nanotube weight contents 0.5%, 1.0%, 1.5%, 2.0% and 3.0% , in that order. Each of the figures shows the samples with a similar coloring regardless of the nanotube content within them. The only samples with noticeable defections were the 1.5% nanotube content samples displayed in Figure 7, where small surface marks are shown.

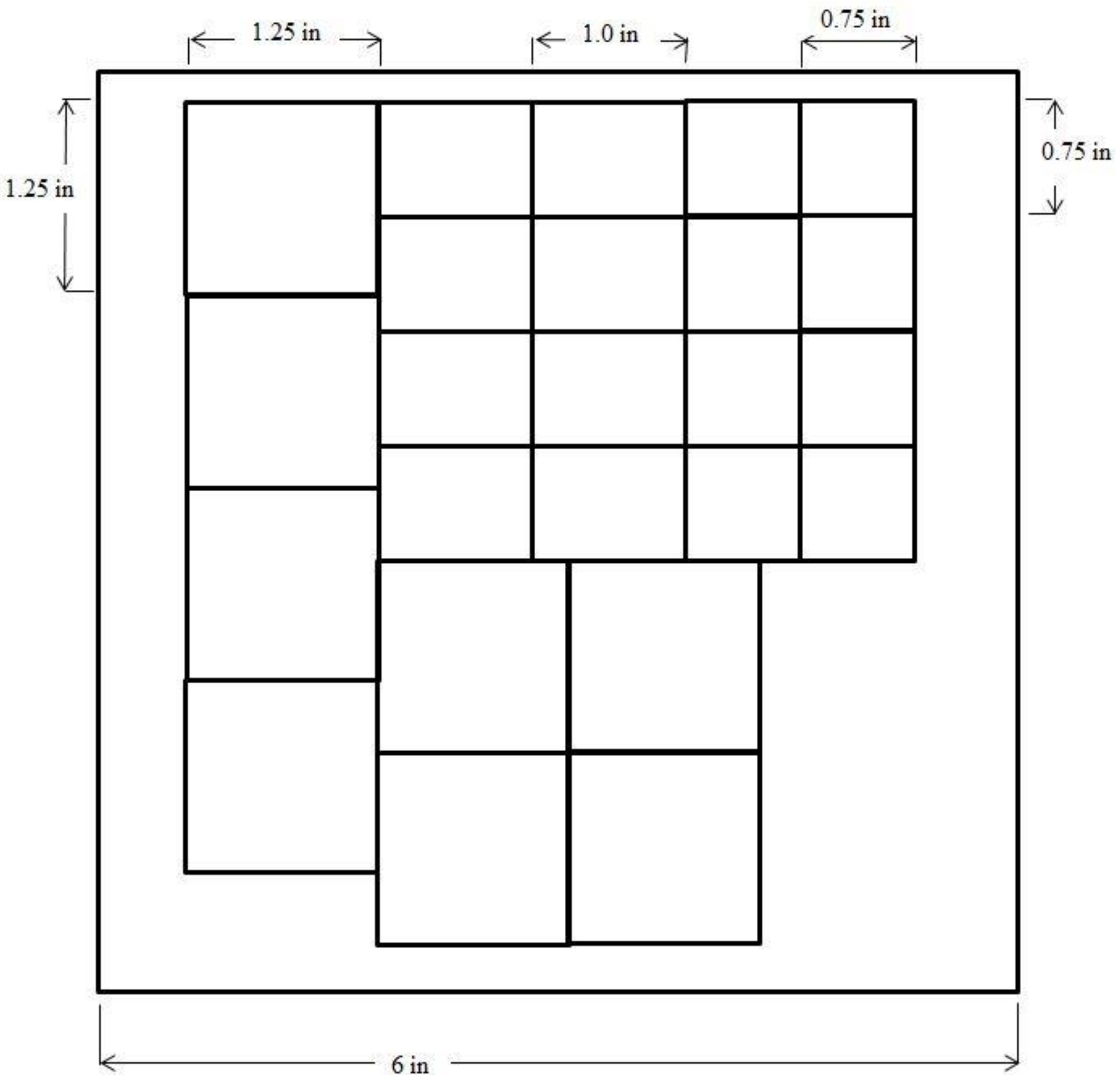

Figure 2: Cutting layout for the samples from a 6in x 6in cutting area of the full laminate

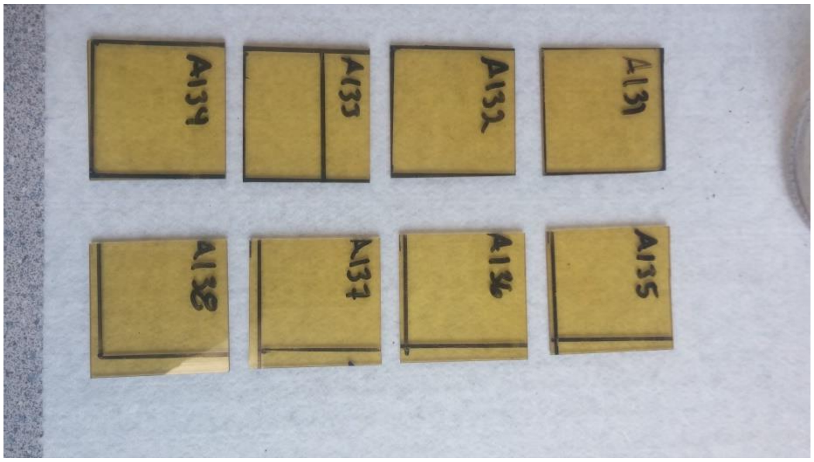

Figure 3: Neat 1.25in x 1.25in planar size 1.5mm thickness samples

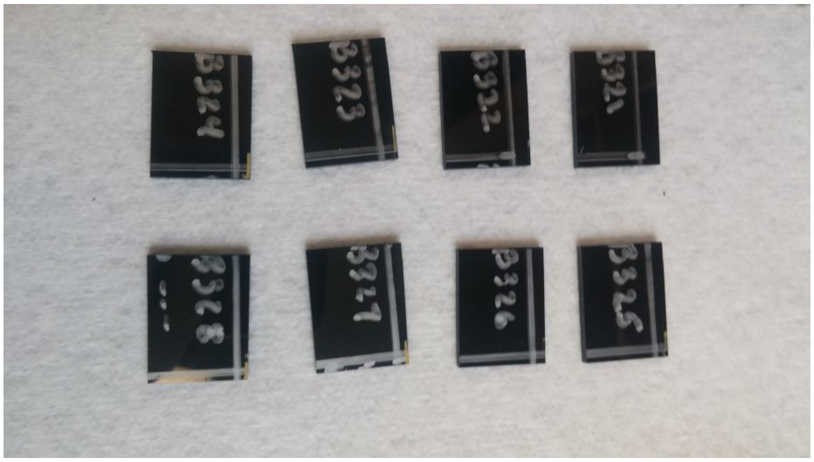

Figure 4: Samples with 0.25% nanotube weight content 1.0in x 0.75in planar size 2.0mm thickness

Figure 5: Samples with 0.5% nanotube weight content 1.0in x 0.75in planar size 2.0mm thickness

Figure 6: Samples with 1.0% nanotube weight content 1.0in x 0.75in planar size 2.0mm thickness

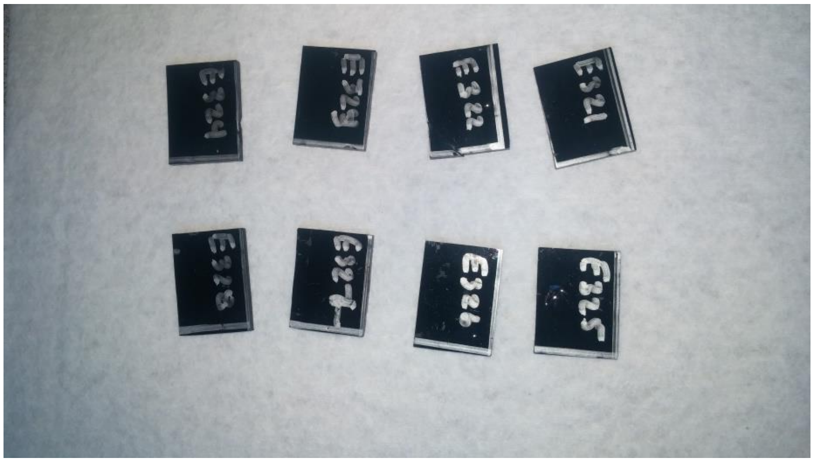

Figure 7: Samples with 1.5% nanotube weight content 1.0in x 0.75in planar size 2.0mm thickness

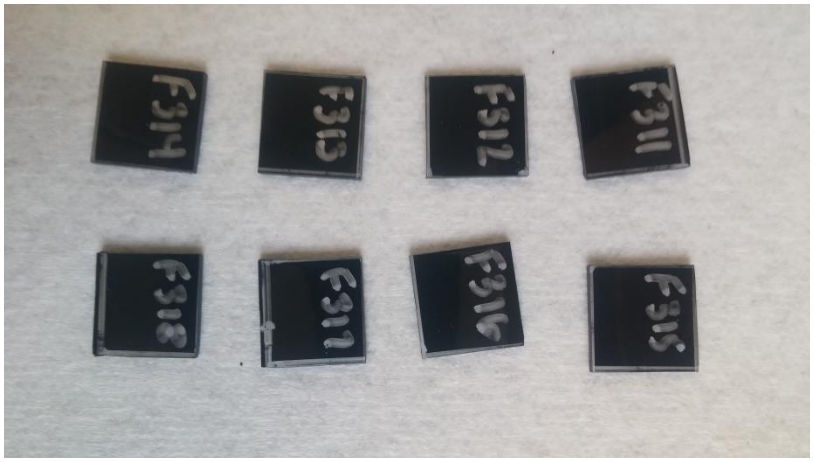

Figure 8: Samples with 2.0% nanotube weight content 0.75in x 0.75in planar size 2.0mm thickness

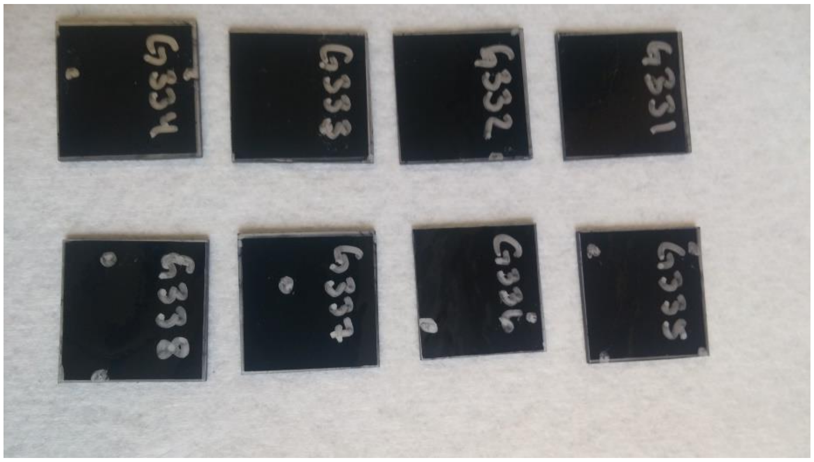

Figure 9: Samples with 3.0% nanotube weight content 1.25in x 1.25in planar size 2.0mm thickness

Figure 10 shows a representative image of the differences in planar size between each of the samples. The particular case shown below has the neat samples with a thickness of 1.5mm at each of the different planar sizes to show the differences in a clear way. As shown the three different planar sizes in comparison to the edges will provide an effective difference in each of the cases helping to show the edge effects of moisture absorption.

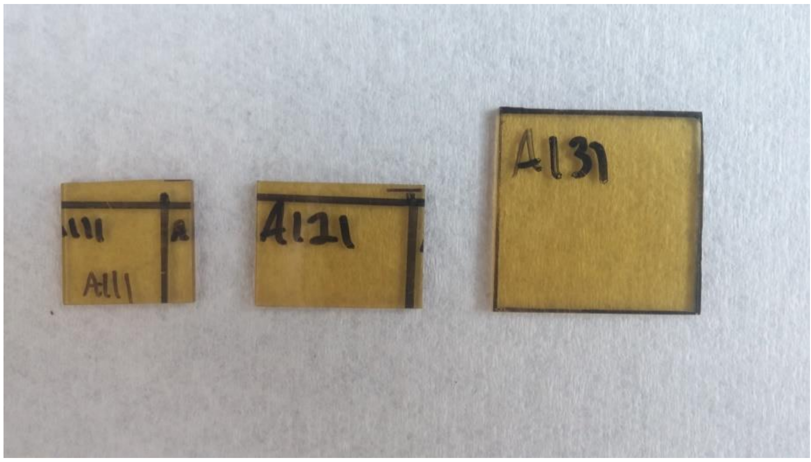

Figure 10: Neat 1.5mm thickness samples planar size comparison

2.6. RECOVERY OF MOISTURE ABSORPTION PARAMETERS

The recovery of the moisture absorption parameters was done by using an approximate solution to the three-dimensional hindered diffusion model, and adapting that into a numerical solution where the experimental data can be used in a program and ran until an accurate representation of the moisture parameters (M_∞, D_z, D_{planar}, γ and β) are found.

$$M(t) = \frac{4}{\pi^{\frac{3}{2}}}\left(\frac{\beta}{\beta+\gamma}\right)M_\infty\sqrt{t}\left[\sqrt{\frac{\pi^2 D_x}{L^2}+\frac{\pi^2 D_y}{W^2}+\frac{\pi^2 D_z}{h^2}}\right] \quad , \qquad 2\gamma, 2\beta \ll K\ , t < \frac{0.7}{K} \tag{6}$$

$$M(t) = M_\infty\left[1-\left(\frac{\gamma}{\beta+\gamma}\right)\exp[-\beta t]\right] \quad , \quad 2\gamma, 2\beta \ll K\ , t \gg \frac{1}{K} \tag{7}$$

Equations 6 and 7 are representative of the model approximations. These model approximations are made based on the original equations along with assumptions made about how the moisture absorption is taking place. These equations are making the assumption that initially all the sites which will absorb moisture are free of any molecules and the first molecules to penetrate this area are considered to initially be unbound. Additional assumptions are made that after a long period of time the diffusivity no longer affects the moisture absorption and the absorption will, instead, be governed by the small non-Fickian effects, β and γ, due to the fact that with small β and γ would suggest the molecules take a long time to change from being unbound to bound, or bound to unbound.

During the process of recovering these moisture parameters multiple steps were involved to insure accuracy. With the obtained results for each given nanotube weight content, there are three different planar sizes along with three different thicknesses. The data was combined to six different graphs for each nanotube content level: constant planar size of 0.75in x 0.75in, 1.0in x 0.75in and 1.25in x 1.25in with differing thicknesses; constant thickness of 1.5mm, 1.7mm and 2.0mm with differing planar size. For each of the individual graphs four separate runs went through the numerical solution code. These different runs were done in order to validate the data and show the accuracy of how the numerical solution compares to the experimental data. All three curves on the specific graph were run together resulting in the moisture parameters for that unique graph. The other three runs were done in different combinations of running two curves at once and using those recovered parameters to validate the third curve. Each of these graphs three curves should theoretically possess the same moisture parameters because the material and nanotube content levels will not be changing, just the area through which the moisture can move through will be changed.

2.7. PREPARATION OF SEM IMAGES

The scanning electron microscope images were taken from fractured samples prepared for the moisture absorption experiments. One sample of 1.0inx 0.75in planar size, 2.0mm thickness was used for SEM imaging for each nanotube weight content. These samples were fractured using three point bending. Each of the samples was sputter coated, applying a conductive layer to the sample, and placed under the SEM. Images were taken at several different magnifications, but 500x, 5,000x and 10,000x are primarily used to show multiple clusters, single clusters and individual nanotubes, respectively. Comparing the images for different nanotube weight contents will show the fracture surfaces, nanotube dispersion, and void content.

CHAPTER 3. RESULTS AND DISCUSSION

3.1. SCANNING ELECTRON MICROSCOPY IMAGES

The images from the scanning electron microscope will help understand the dispersion state, presence of microvoids, potential internal defects, and fracture surface morphology of the samples with the addition of nanotubes. Initially as-received multi-walled carbon nanotubes were investigated. A number of SEM images were taken at 500x, 5,000x and 10,000x magnification showing a group of nanotube clusters, multiple individual nanotube clusters and the individual nanotubes, respectively. Figure 11 through Figure 13 display these different magnifications in the same location within the group of nanotubes. The central point of Figure 11 was magnified to show the closer look in Figure 12 and Figure 13. These images display how the nanotubes look under these different magnifications without being embedded or damaged in any way.

Figure 14, Figure 15 and Figure 16 show the SEM images from the sample with nanotube content 0.25% by weight. Figure 14 displays an image with magnification of 500x. From this figure the fracture surfaces are clearly shown along with small nanotube clusters and no void content. The nanotube clusters are small because of the nanotube content only being 0.25%, along with the dispersion being more effective. The nanotube clusters can be seen as small, light grey impurities. One of the nanotube clusters can be seen in the center of Figure 14, which is also shown in Figure 15 and Figure 16 at higher magnifications. The size of the nanotube cluster at the order of 1-2 μm can be seen in Figure 15. The fracture surfaces from the 5,000x magnification curve around the nanotube cluster. Individual nanotubes around the cluster are noticeable from Figure 16.

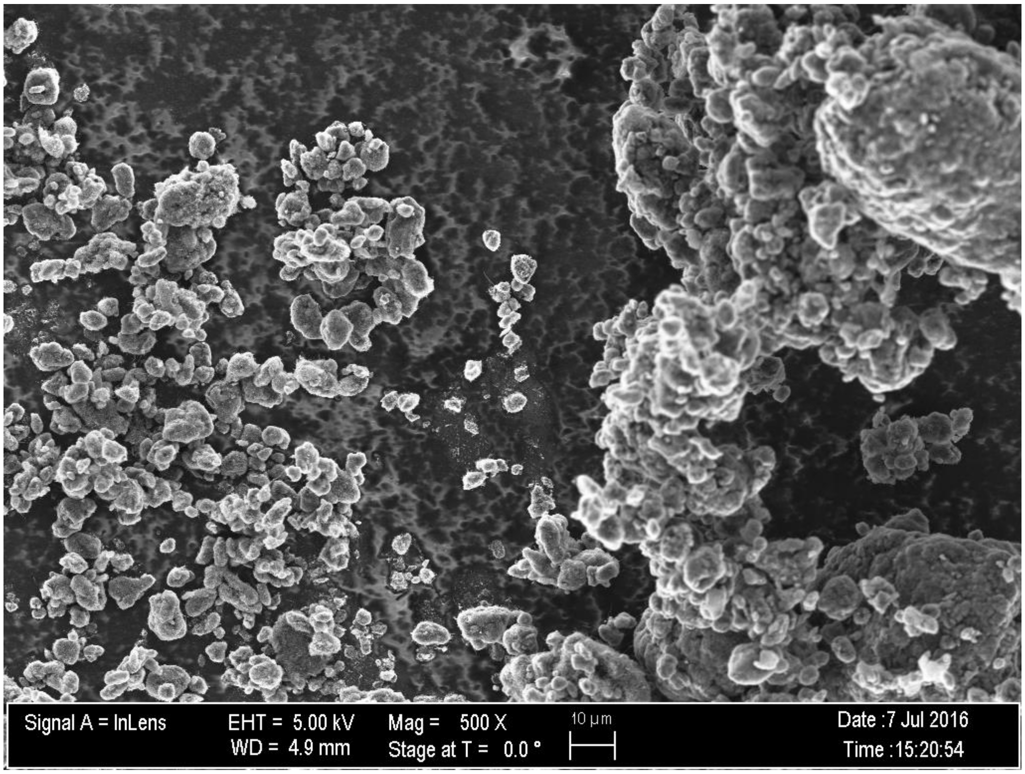

Figure 11: MWCNTs as received 500x magnification

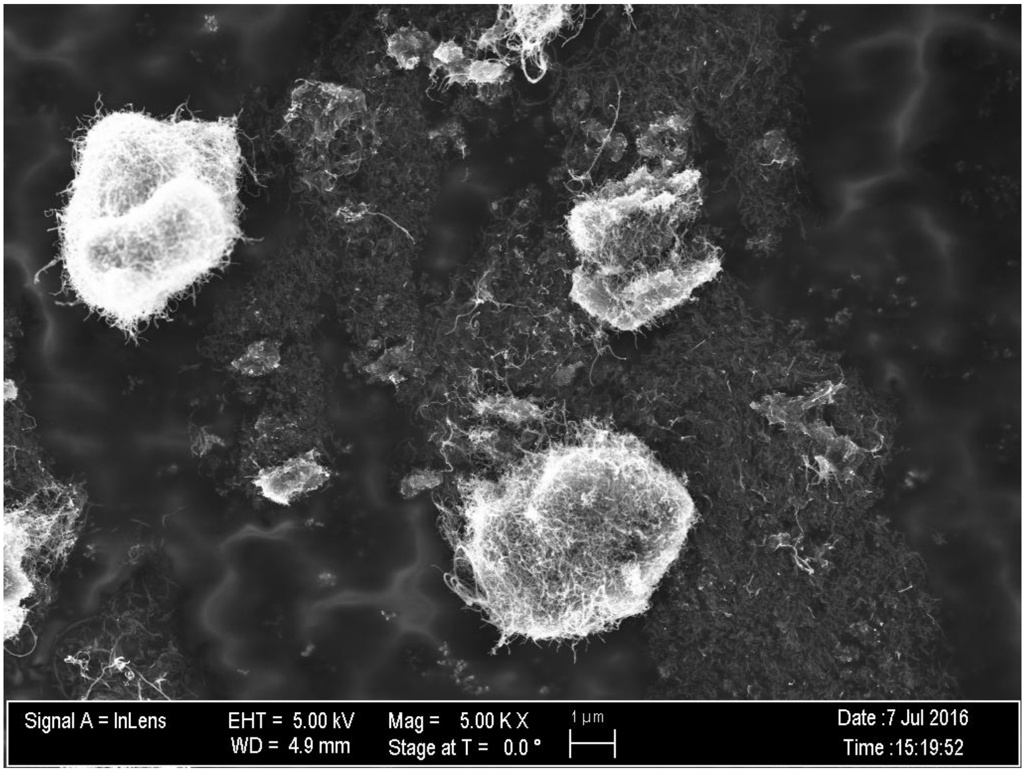

Figure 12: MWCNTs as received 5,000x magnification

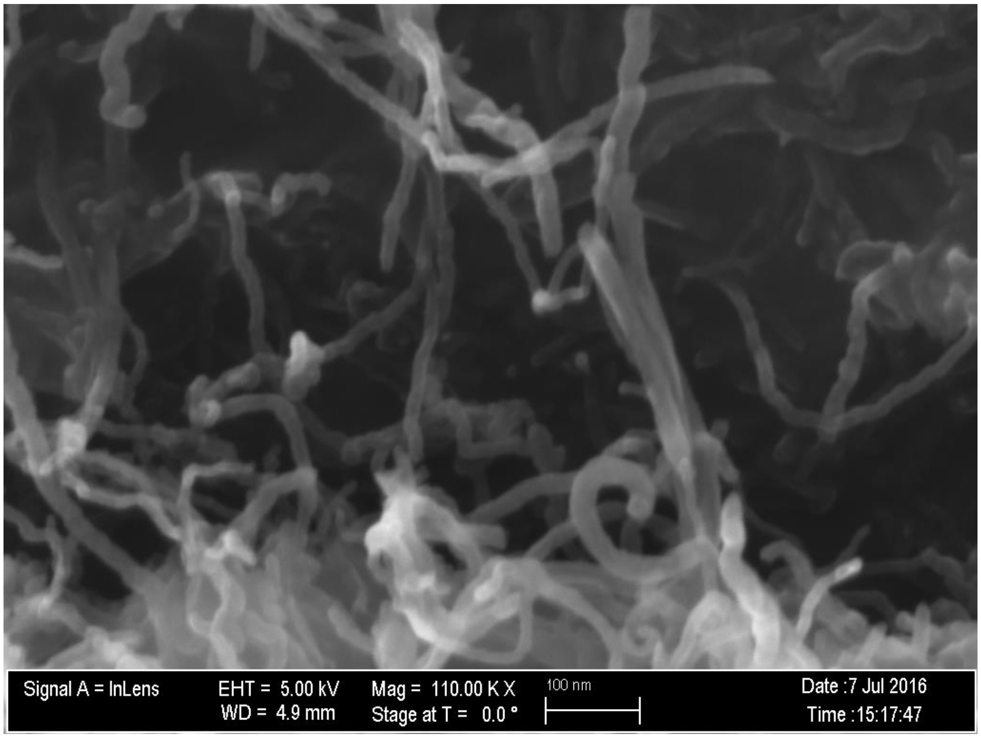

Figure 13: MWCNTs as received 110,000x magnification

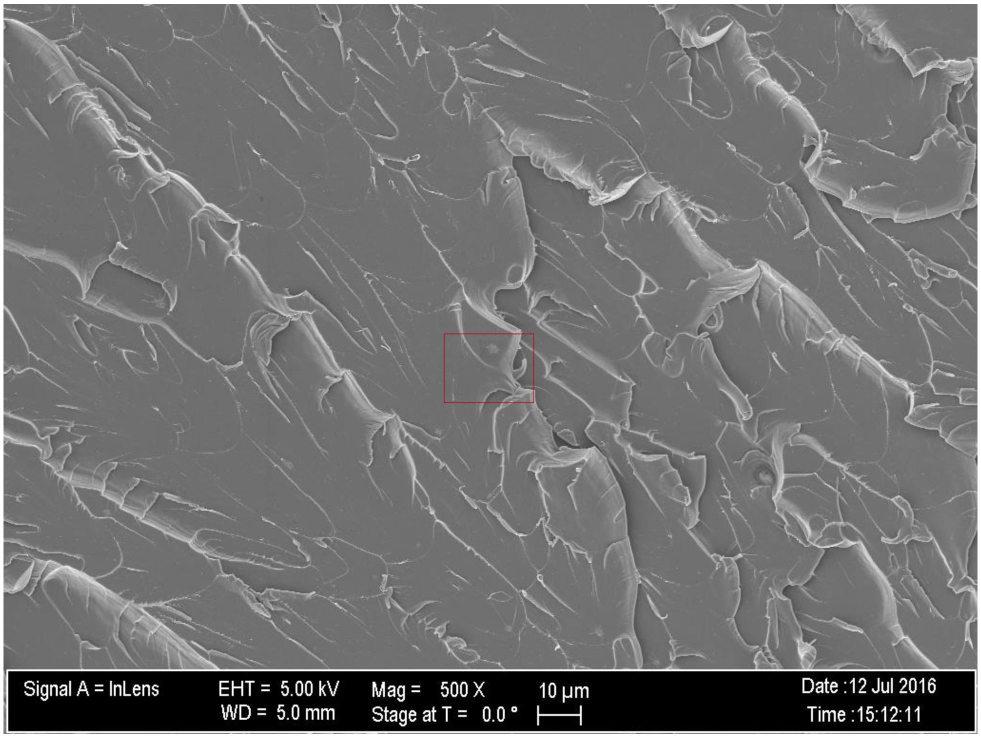

Figure 14: SEM images for 0.25% nanotube weight content sample 500x magnification

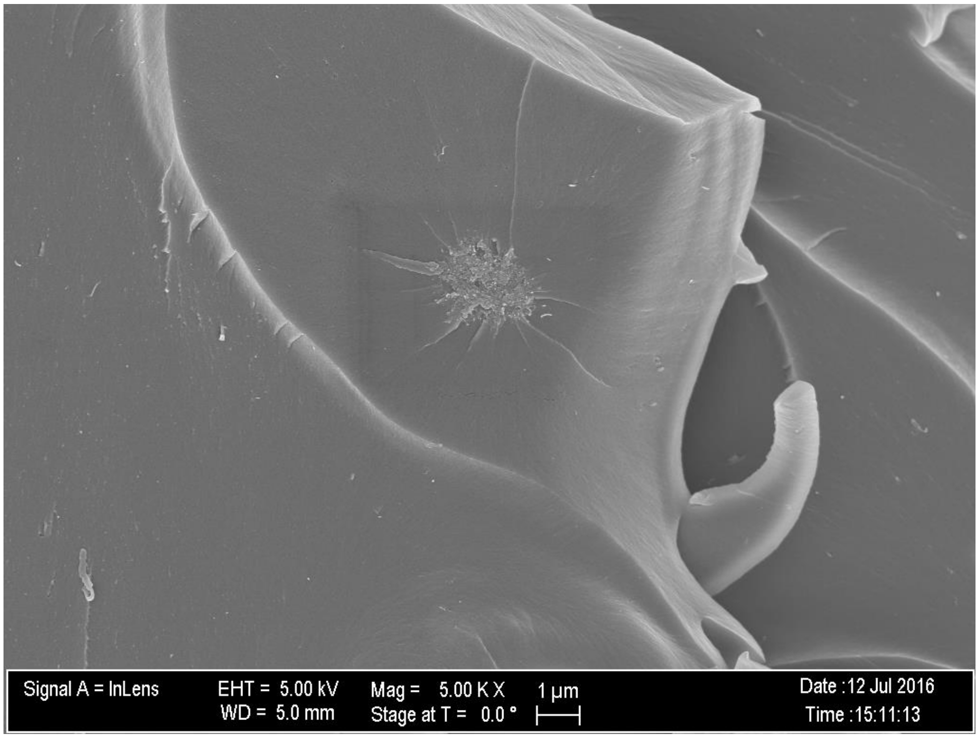

Figure 15: SEM images for 0.25% nanotube weight content sample 5,000x magnification zoomed in from Figure 14

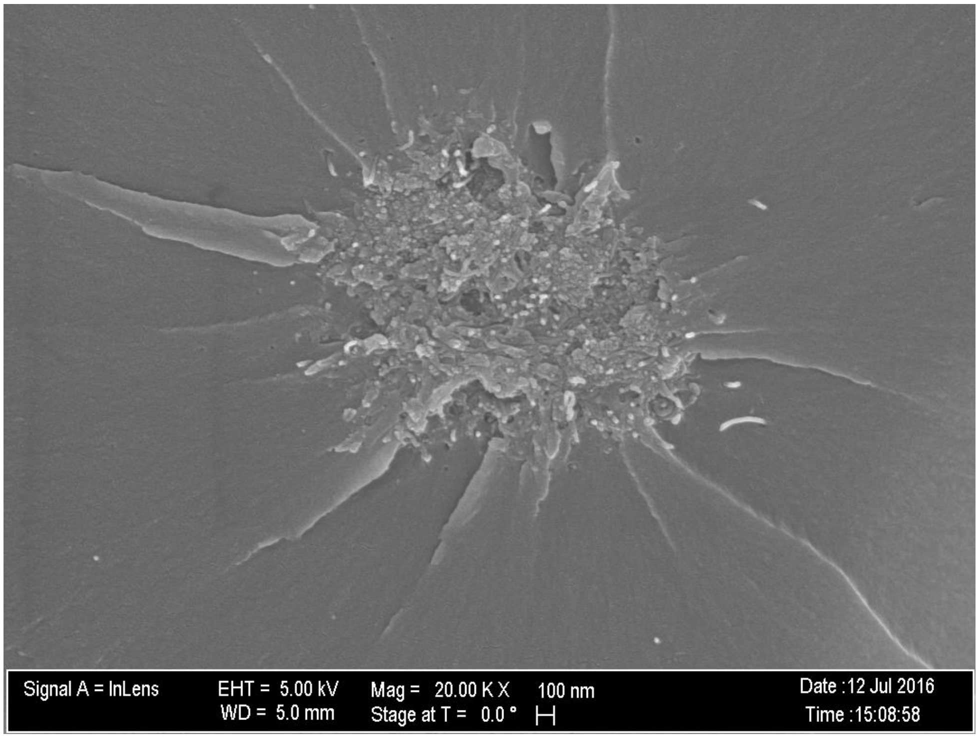

Figure 16: SEM images for 0.25% nanotube weight content sample 20,000x magnification zoomed in from Figure 15

Figure 17 through Figure 19 show images from the 0.5% nanotube weight content sample. The nanotube clusters in Figure 17 are similarly sized to the clusters from the 0.25% nanotube content sample. The nanotube clusters are more difficult to see because with increasing the nanotube content the fracture surfaces became smaller, resulting in more points of fracture within the image. The nanotube dispersion for the 0.5% nanotube content samples was homogeneous because the clusters are small and spread out equally. A closer look at the nanotube clusters for 0.5% nanotube content can be seen in Figure 18 and Figure 19. Figure 18 shows the nanotube cluster on the fracture surfaces making the cluster appear slightly more dispersed than the cluster in the 0.25% nanotube content sample. The 20,000x magnification view of the nanotube cluster makes it clear that the cluster being placed on a fracture results in many loose individual nanotubes instead of the closely knit cluster from Figure 16.

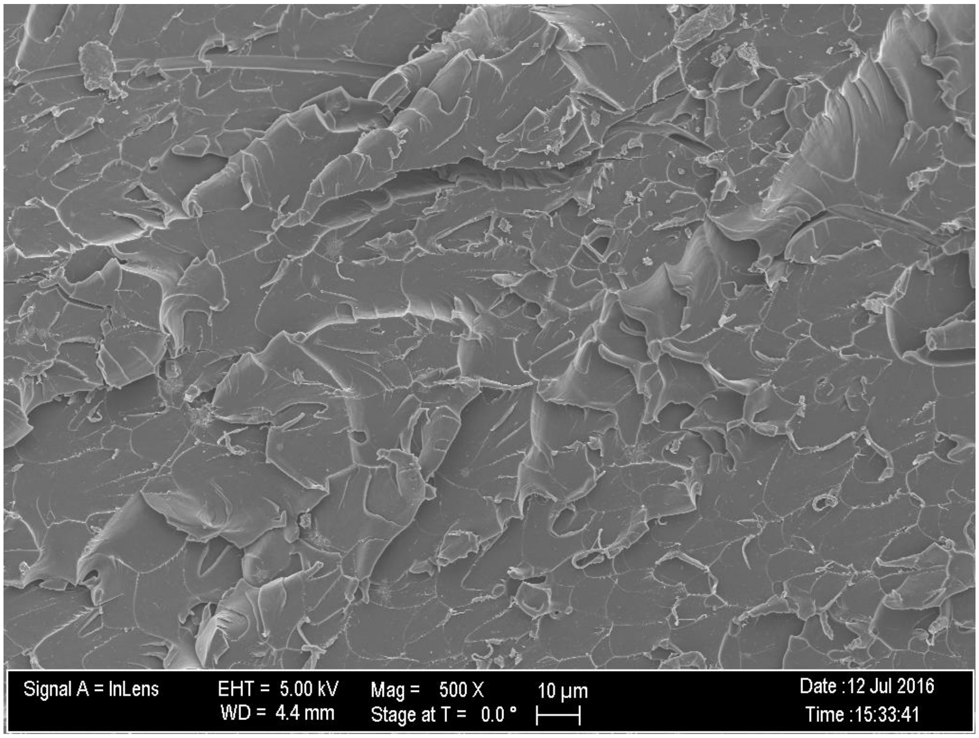

Figure 17: SEM images for 0.5% nanotube weight content sample 500x magnification

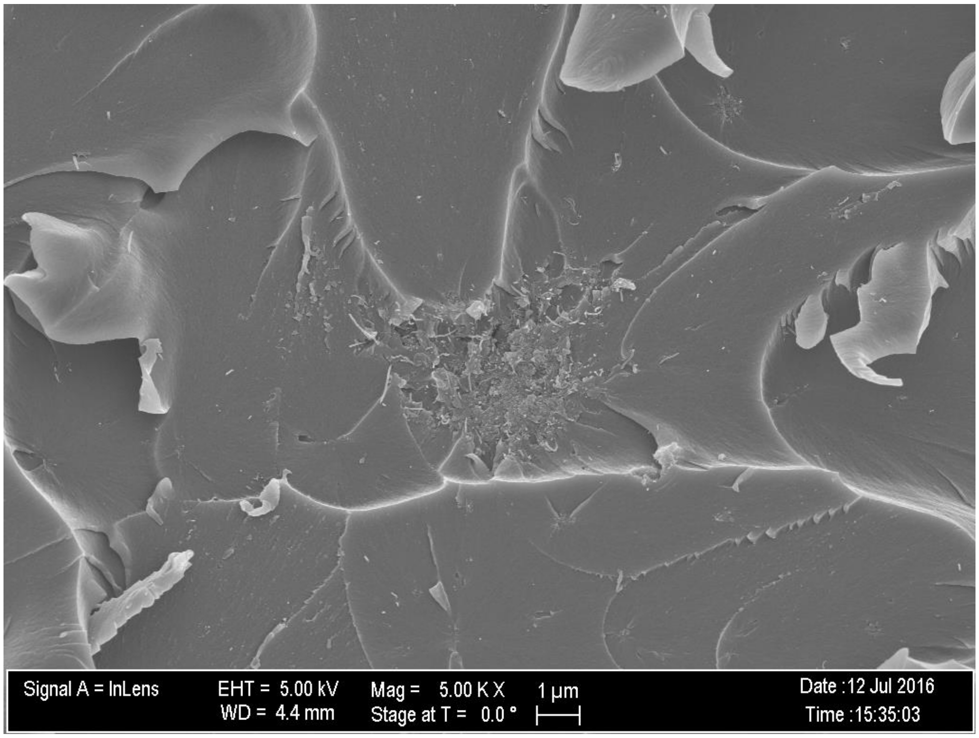

Figure 18: SEM images for 0.5% nanotube weight content sample 5,000x magnification zoomed in from Figure 17

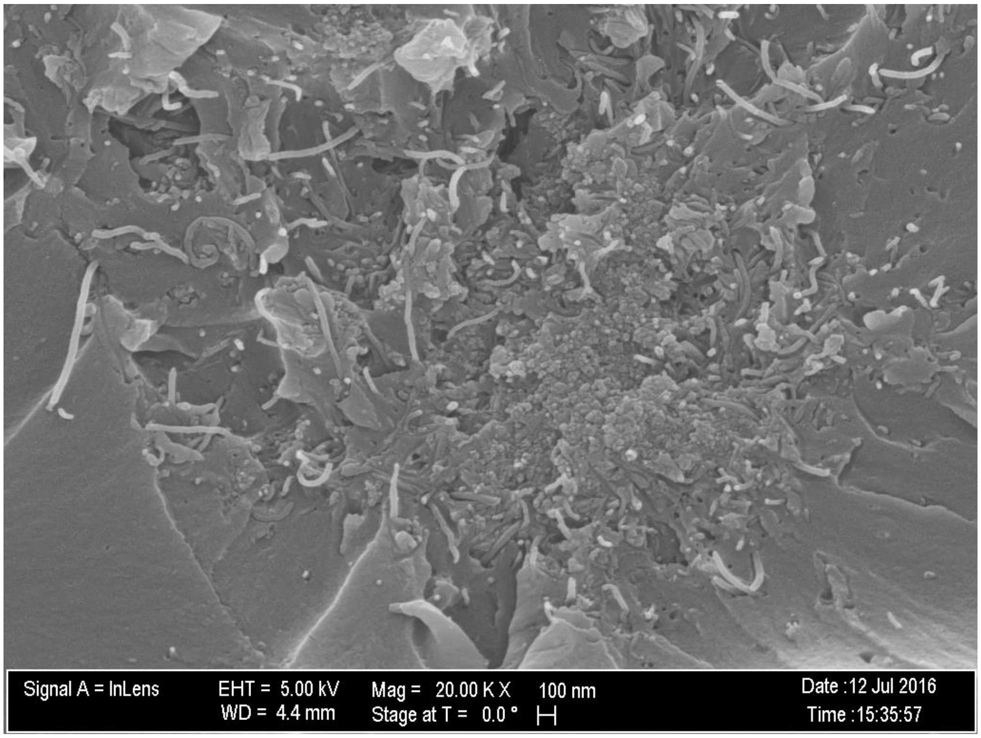

Figure 19: SEM images for 0.5% nanotube weight content sample 20,000x magnification zoomed in from Figure 18

The 1.0% nanotube weight content sample SEM images are shown in Figures 20, 21, and 22. The lowest magnification, 500x, continues to show no voids within the sample. The nanotube clusters are becoming much more noticeable with the nanotube content increasing to 1.0%. The larger clusters continue to stay relatively evenly spaced, but starting to become nonhomogeneous compared to the lower nanotube content samples. Fracture surfaces continue to grow smaller with the increase in nanotube content. The nanotube content increase results in the epoxy samples becoming more brittle. Nanotube clusters in Figure 20 appear closer together than those in previous figures. With the clusters being closer together, Figure 21 displays multiple clusters at once. Unlike previous samples, the 1.0% nanotube content sample shows little individual nanotubes; instead the cluster stays compact even along the edges. Figure 22 shows 20,000x magnification of the edge of a nanotube cluster. The edge of the cluster lands along a fracture, but the nanotubes appear to stay grouped together instead of having many individual nanotubes fraying.

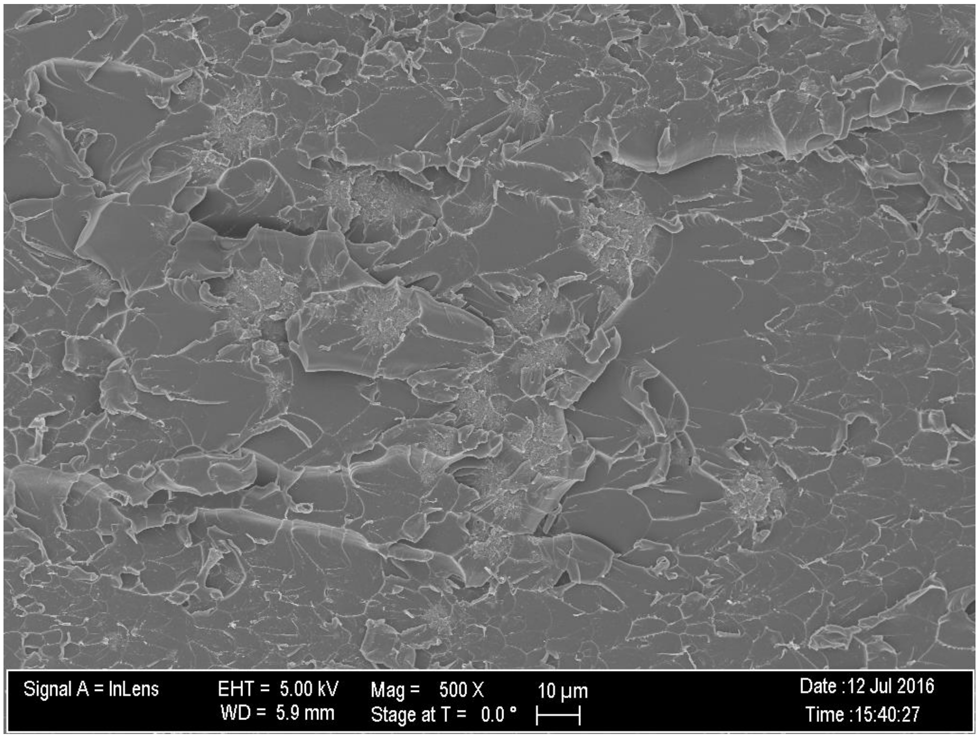

Figure 20: SEM images for 1.0% nanotube weight content sample 500x magnification

The samples with 1.5% nanotube weight content have a fracture surface much different than the previous weight contents. In Figure 23 the 1.5% nanotube weight content sample SEM image for 500x magnification is shown. The nanotube clusters have both large clusters along with smaller clusters surrounding the larger one. The fracture lines shown in Figure 23 are sporadic appearing more as folds than the shattered look of previous figures. The smaller nanotube clusters in Figure 23 match the size of the 1.0% nanotube weight content nanotube clusters, which makes the comparison with the large cluster easier to see. Significant differences in the appearance of the 1.5% nanotube content sample compared to the other samples should result in noticeable differences in moisture properties.

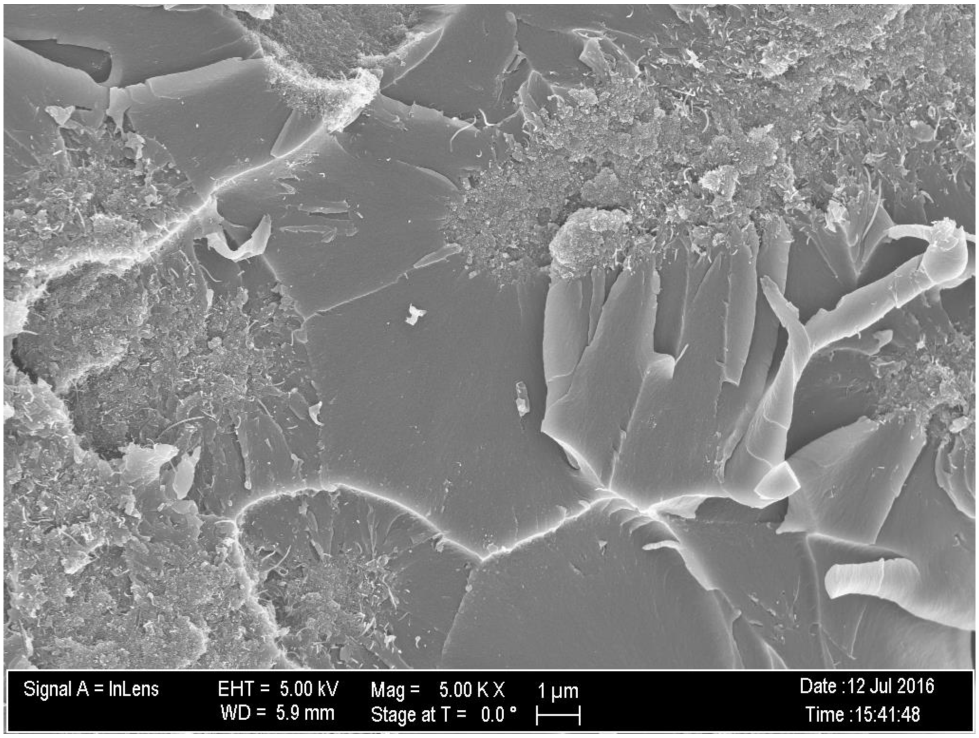

Figure 21: SEM images for 1.0% nanotube weight content sample 5,000x magnification zoomed in from Figure 20

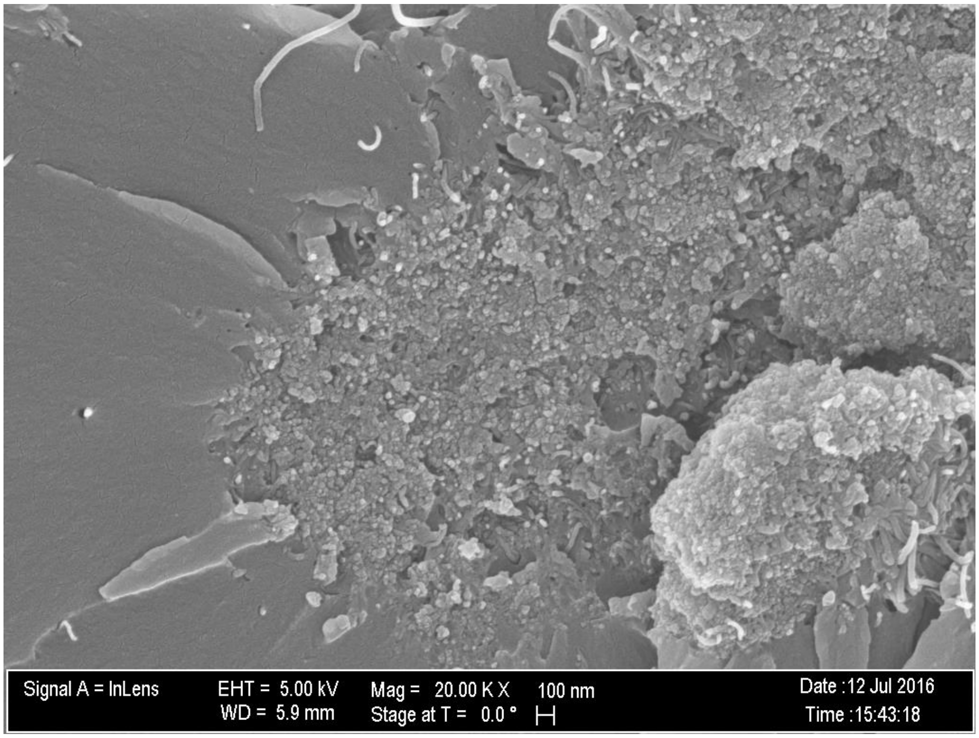

Figure 22: SEM images for 1.0% nanotube weight content sample 20,000x magnification zoomed in from Figure 21

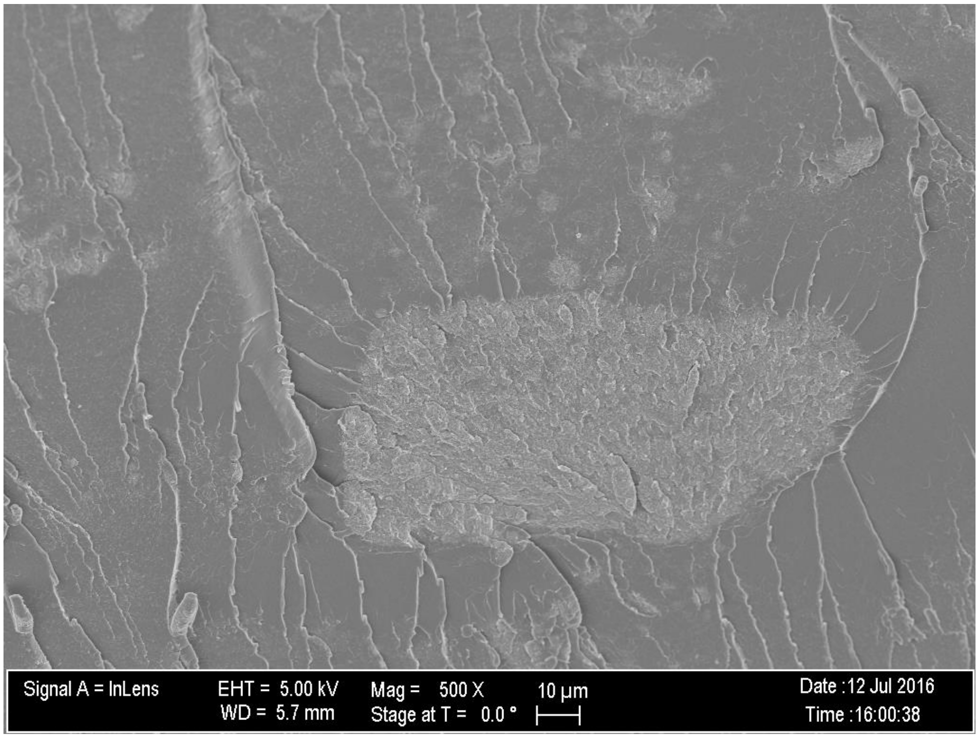

Figure 23: SEM images for 1.5% nanotube weight content sample 500x magnification

The dispersion of nanotubes within the sample continues to become less homogeneous, which would skew the results further. The images continue to reinforce that no voids are present within the samples through fabrication. Figure 24 and 25 show a magnified view of the smaller clusters around the large cluster. The nanotube clusters in Figure 24 are less pronounced than the other nanotube content level samples. Individual nanotubes are shown in Figure 25 where the magnification of the 1.5% nanotube weight content sample is at 20,000x. The surface of the sample shown in Figure 25 has many of the nanotubes still embedded. Nanotube clusters continue to show the same appearance in the different nanotube content samples.

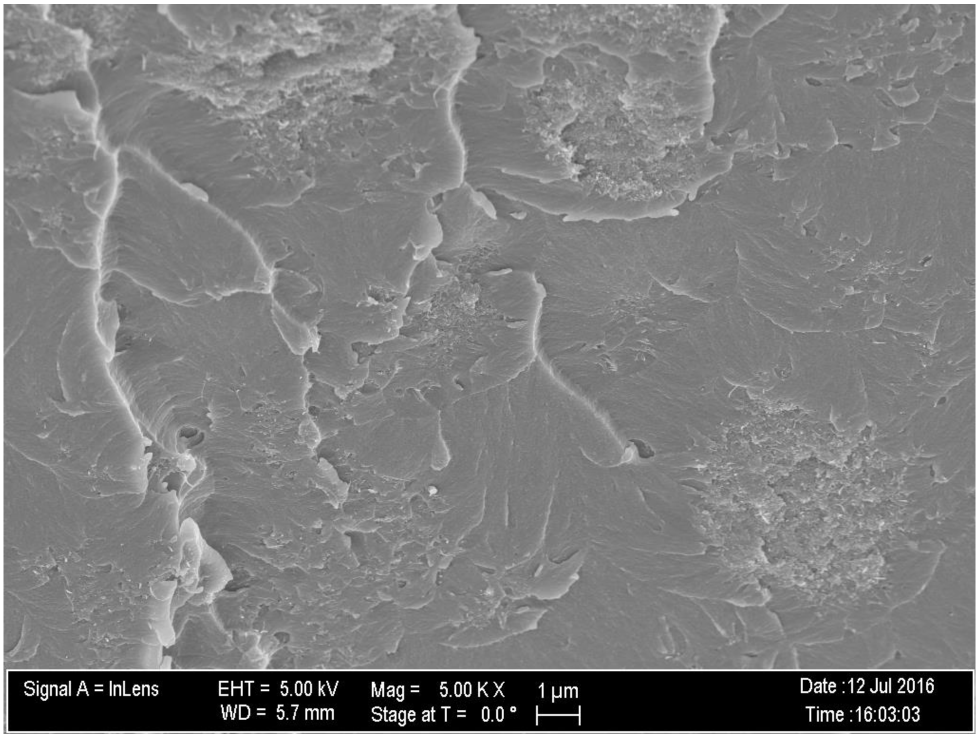

Figure 24: SEM images for 1.5% nanotube weight content sample 5,000x magnification zoomed in from Figure 23

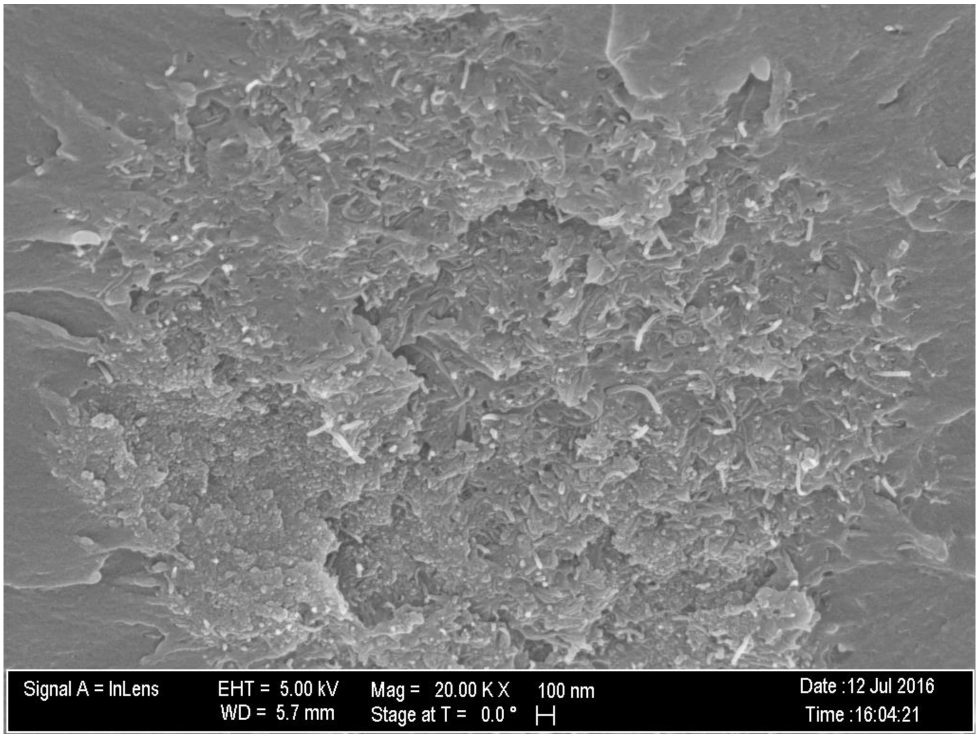

Figure 25: SEM images for 1.5% nanotube weight content sample 20,000x magnification zoomed in from Figure 24

Figure 26 displays the SEM images of the 2.0% nanotube weight content samples at 500x magnification. The fracture surface returned to the trend interrupted by the 1.5% nanotube weight content. The difference in the fracture surface suggests that the 1.5% nanotube weight content samples will not follow the same moisture absorption trends as any of the other samples. Along with the fracture surface changing, the nanotube cluster size is comparable to the 1.0% nanotube weight content samples. The decrease in size with increasing nanotube content means improved nanotube dispersion from the 1.5% content sample.

Multiple nanotube clusters are shown in Figure 27 for the 2.0% nanotube weight content samples at 5,000x magnification. Nanotube clusters begin to get more loosely connected in Figure 27 and Figure 28. The nanotubes appear to be protruding from the surface similarly to how the nanotubes looked when they were not embedded in a sample. The similarity to the "as received" nanotubes could suggest the dispersion process did not disrupt the clusters that were mixed during the fabrication process. Increasing the magnification to 20,000x from 5,000x results in the image shown in Figure 28. Figure 28 reinforces that the nanotube clusters are coming off the surface in these images. The individual nanotubes along the edge of the nanotube cluster are becoming more clearly shown with the increased nanotube content. The nanotube clusters are defined with no small clusters just outside of the large clusters.

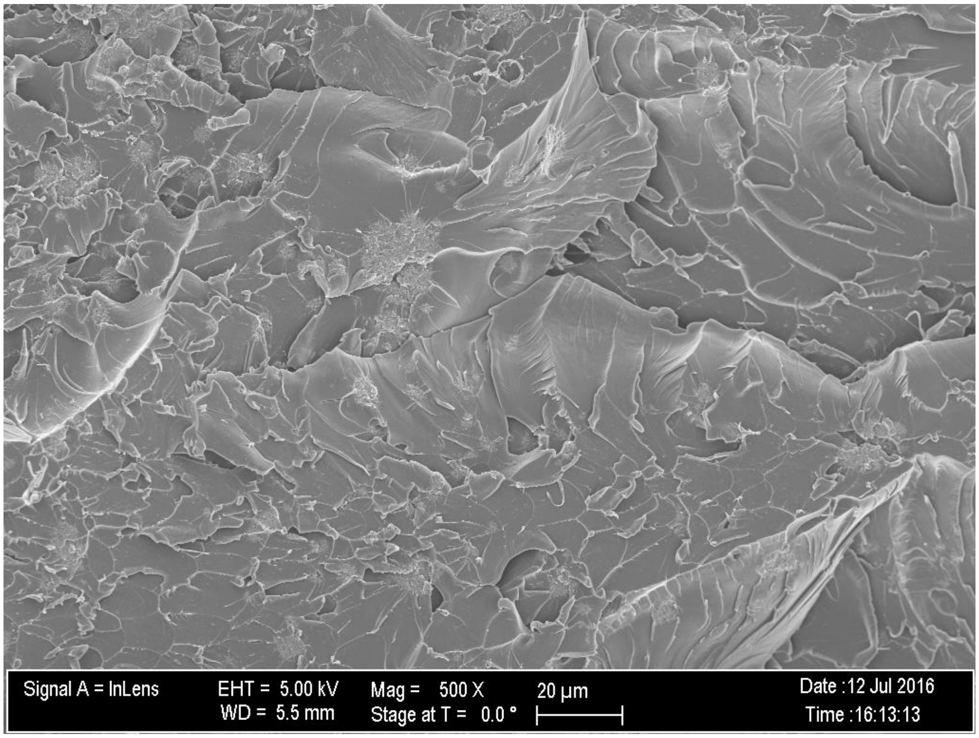

Figure 26: SEM images for 2.0% nanotube weight content sample 500x magnification

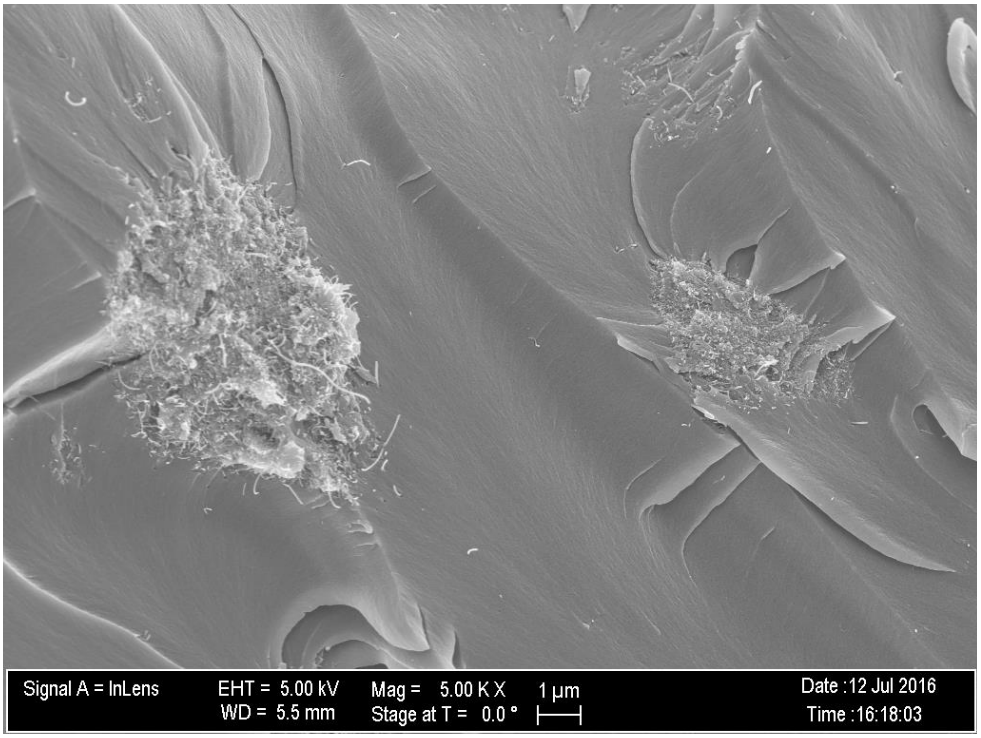

Figure 27: SEM images for 2.0% nanotube weight content sample 5,000x magnification zoomed in from Figure 26

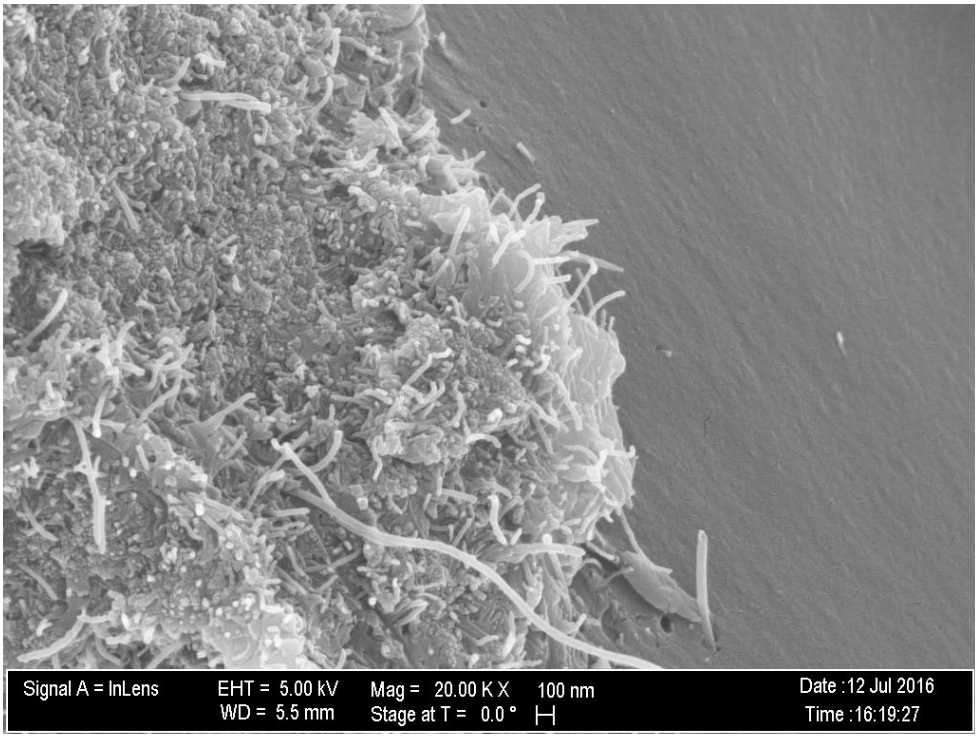

Figure 28: SEM images for 2.0% nanotube weight content sample 20,000x magnification zoomed in from Figure 27

Increasing the nanotube content level to 3.0% resulted in a similar fracture surface to the 2.0% content sample. Small fracture planes within the sample cause a shattered fracture structure. Throughout the image the nanotube clusters are seen similarly in size and dispersion to the 2.0% content samples. A larger cluster appears towards the top left corner of Figure 29, but other than that the clusters are similarly sized to other samples. Figure 30 displays multiple small nanotube clusters. These clusters appear along fracture lines, and on top of the fracture. The lower center nanotube cluster lies on a fracture that displays the nanotubes at multiple layers. The 20,000x magnification in Figure 31 shows the nanotube cluster with multiple layers. The surface where the fracture did not happen looks similar to other nanotube content samples, but along the multiple layers many individual nanotubes are protruding.

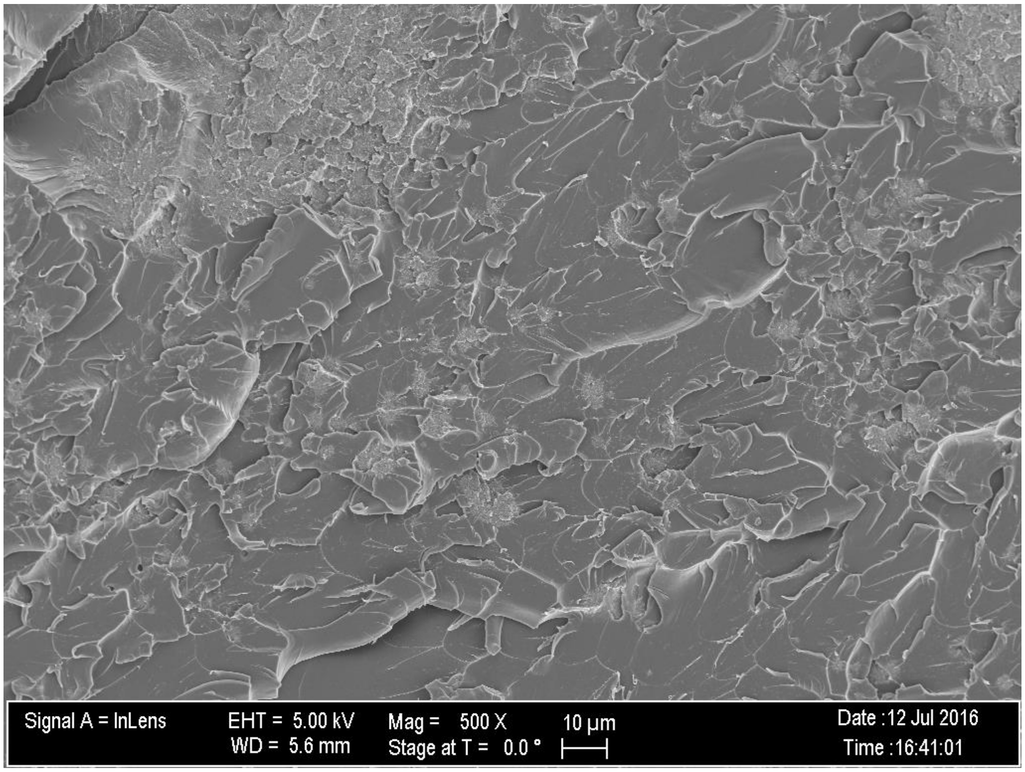

Figure 29: SEM images for 3.0% nanotube weight content 500x magnification

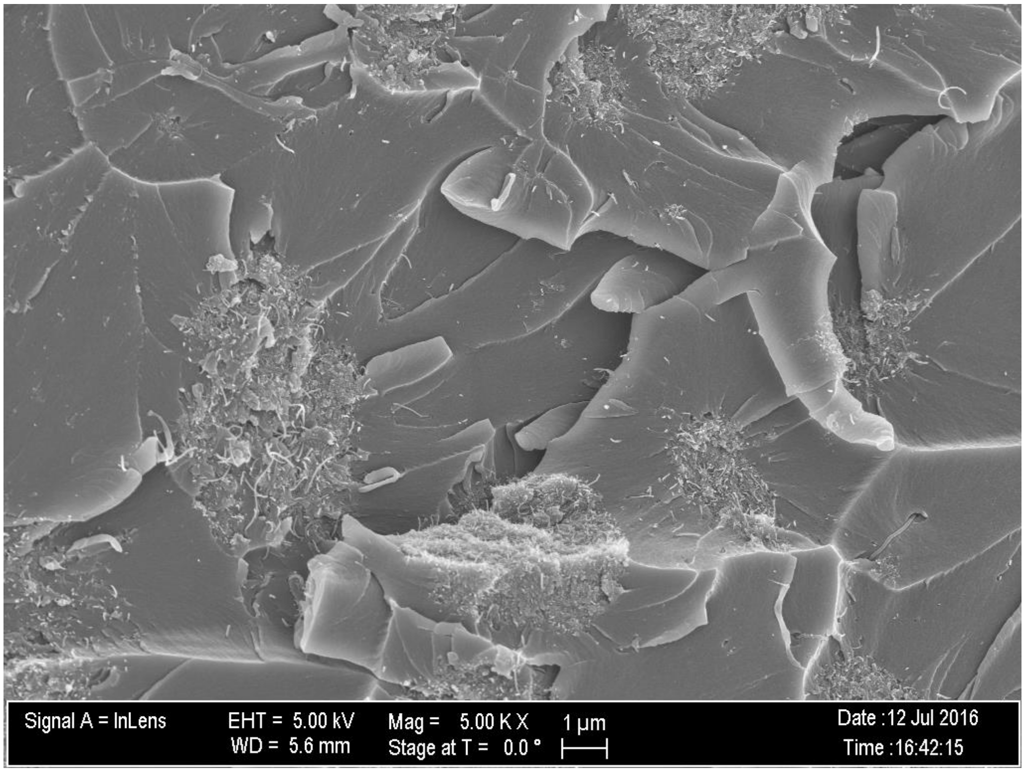

Figure 30: SEM images for 3.0% nanotube weight content 5,000x magnification zoomed in from Figure 29

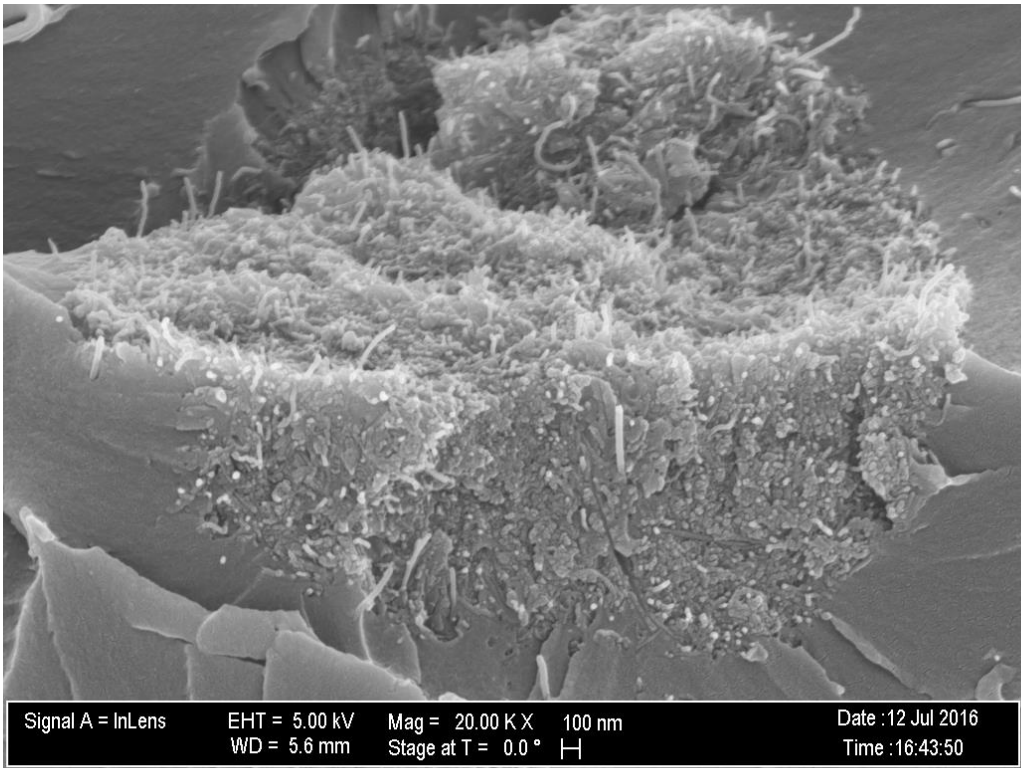

Figure 31: SEM images for 3.0% nanotube weight content 20,000x magnification zoomed in from Figure 30

All of the SEM images proved that through the fabrication process no microvoids were developed within the samples. The nanotube dispersion progressively became less homogeneous as the nanotube content increased, except for the 1.5% nanotube content sample. The nanotube dispersion for the 1.5% nanotube content sample appeared noticeably worse than the other samples. The fracture planes had a decreasing size with the increasing nanotube content, resulting in the sample surface appearing more shattered.

Each of the SEM images displayed was obtained from samples that had gone through the full moisture absorption process. Figure 32 through Figure 34 show a comparative dry sample image with nanotube weight content 2.0%. The effects the presence of moisture has on the fractured surface structure of the samples can be clearly seen in Figure 32, which represents the 500x magnification image for samples with

2.0% nanotube weight content. The fracture lines appear more closely to the 1.5% nanotube weight content samples, which stuck out from the rest of the bunch within the previous images. The similarities between the dry sample fracture and the 1.5% nanotube content sample fracture could suggest the 1.5% sample resisted moisture more than the other samples resulting in a similar fracture to dry samples. The fracture lines consistently follow a similar direction instead of having a shattered effect where fractures occur in all directions. Many of the fracture lines seem to come directly out of the large nanotube cluster shown within the image.

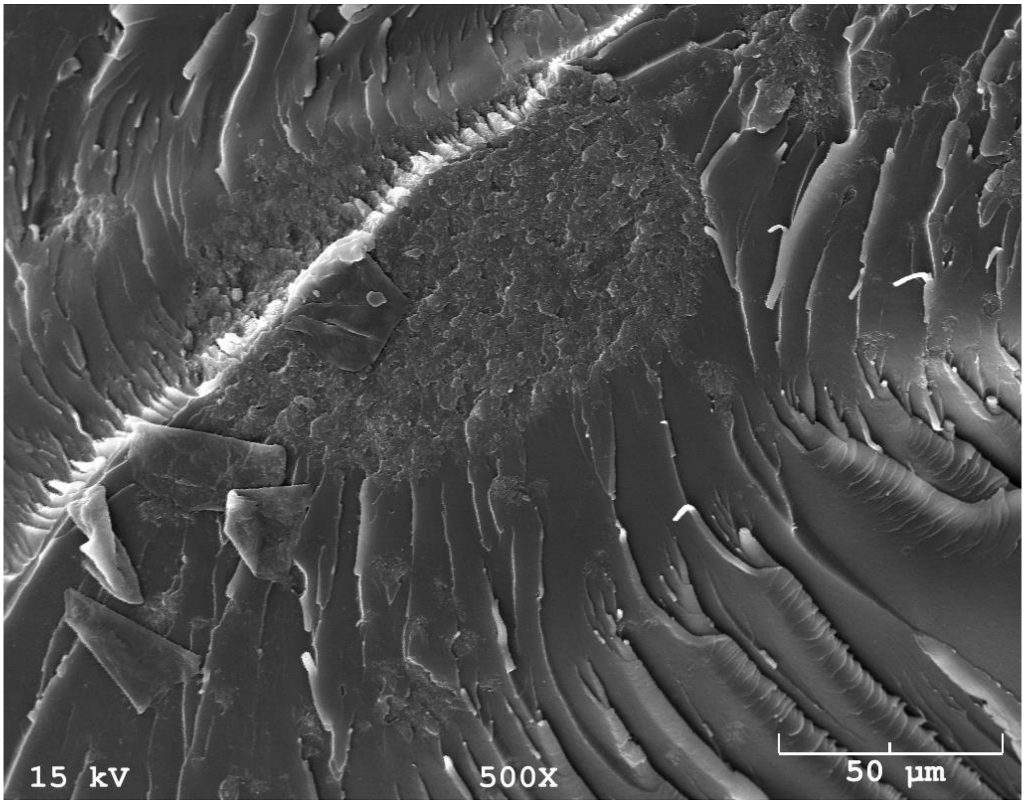

Figure 32: SEM images for dry 2.0% nanotube weight content 500x magnification

Figure 33 displays the zoomed in image of Figure 32 where the magnification is 5,000x instead of 500x. The more magnified image can be compared to images of similar magnification to see how the fractured surface differs in the dry samples. The closer magnification continues to show the changes in the fracture surface where the fractures occur in a more uniform fashion in comparison to the samples that have reach moisture equilibrium. This trend would be expected because the sample did not have its mechanical properties degraded through the moisture process so the randomness of the fracture would be more unexpected.

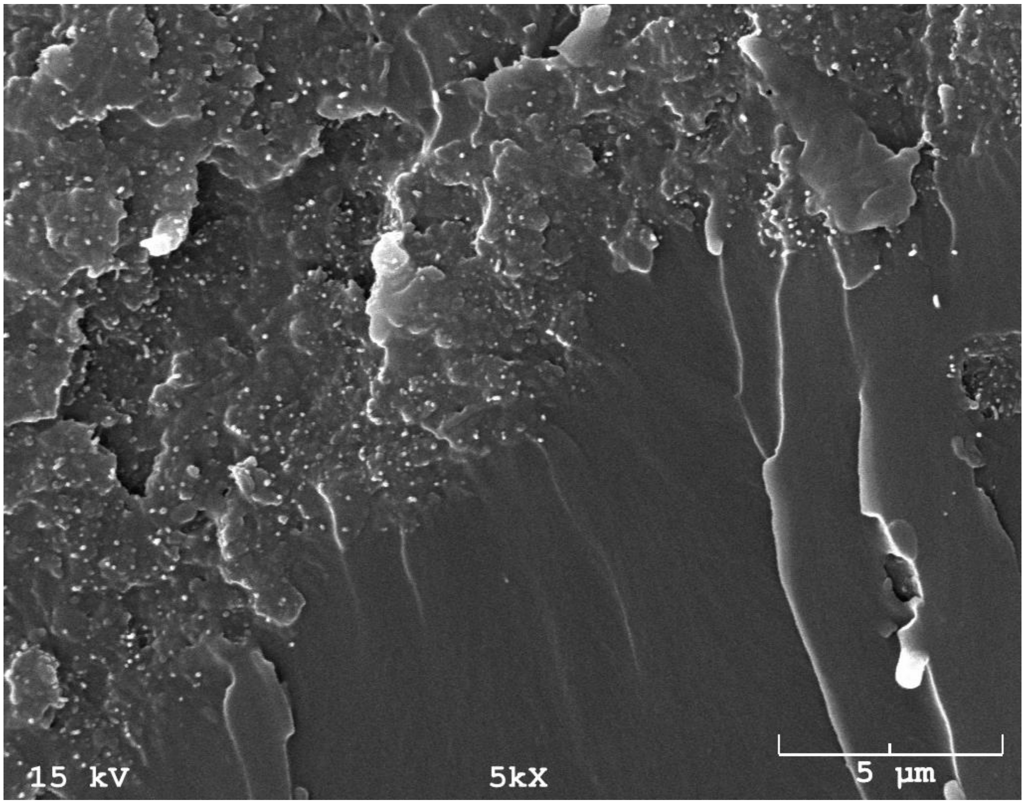

Figure 33: SEM image for dry 2.0% nanotube content sample magnification 5,000x zoomed in from Figure 32

The nanotubes are clearly still seen within the images, but the dispersion would not be different because the sample is dry, so the fractured surface is the important factor to be examined.

Figure 34 displays the zoomed in imaged of Figure 33 for a magnification of 20,000x. At 20,000x magnification the fractured surface is more difficult to see because of how close to a single point is being shown in the image. Figure 34 does show noticeable differences from Figure 28, which is the same nanotube content percentage. The surface of Figure 34 shows many lighting changes, which represents a change of elevation under SEM because the electrons on the surface are closer to the microscope. The change in elevation shows the break did not as cleanly fracture as the moisture sample, which can be seen from the previous images as well.

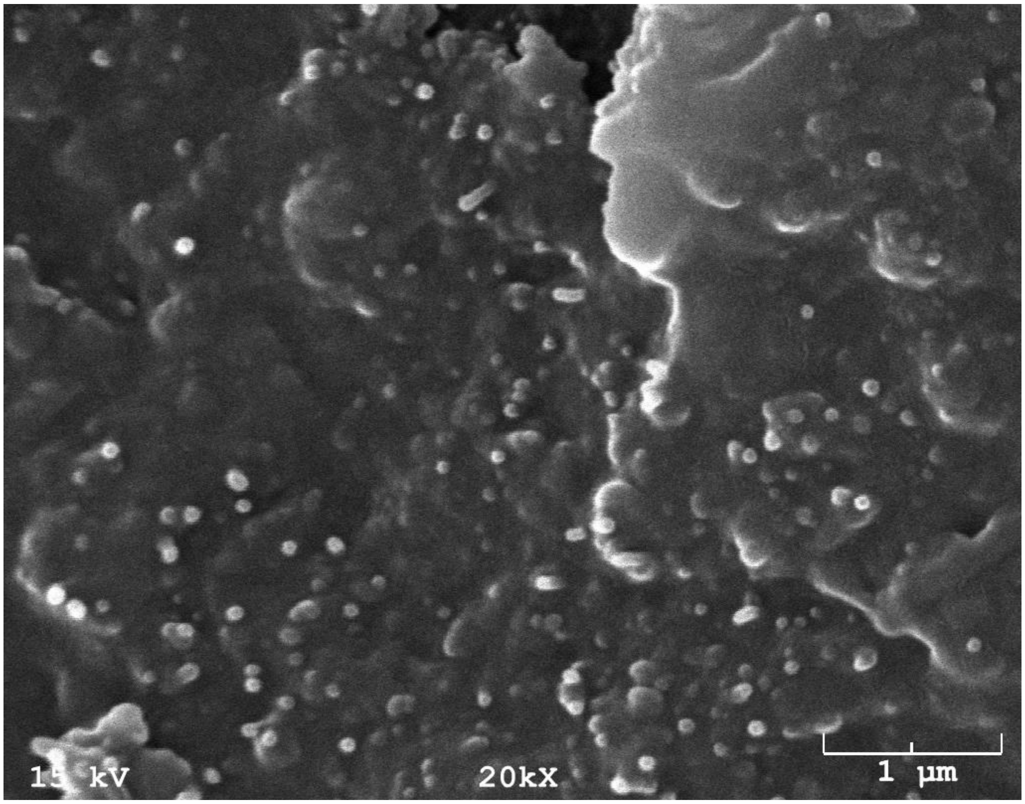

Figure 34: SEM image for dry 2.0% nanotube content sample magnification 20,000x zoomed in from Figure 33

From the comparison of the images between the moisture absorption samples and the dry samples it can be seen that the fracture planes are reduced when moisture equilibrium has been reached from the samples. The dry samples showed less of a random, shattered fracture pattern, and instead followed a more uniformly followed fracture pattern similarly to the samples with 1.5% nanotube content. The similarities between the dry and 1.5% nanotube content samples suggests that the samples did not reach as high of an equilibrium as other samples, which could be expected to be seen from the moisture parameter recovery.

3.2. MOISTURE ABSORPTION EXPERIMENTAL DATA

Moisture absorption experimental data has been collected over seven to eleven months, depending on the unique nanotube content samples. The neat samples have been immersed in moisture for eleven months, while the 3.0% nanotube content samples have been immersed for, the least amount of time, seven months. Each category of specific planar size, thickness and nanotube content has eight samples producing raw data for that category. The eight different samples were averaged for that category to reduce the experimental uncertainty. The averages for each category were displayed in different plots where one of the two properties (planar size and thickness) does not vary while the second property changes. Each of the resultant six graphs has three separate curves that were run through a numerical code to recover the moisture absorption parameters and validate the experimental data.

3.3. MOISTURE PARAMETER RECOVERY AND VALIDATION

The moisture parameter recovery was done by using the approximate numerical solution for the hindered diffusion model described by Equations 6 and 7. The moisture absorption parameter recovery must first validate the experimental data used. The validation process uses two different curves to recover the moisture absorption parameters. Following the recovery of moisture absorption parameters, the third curve, which will only have different dimensions, can be validated by fitting those moisture absorption parameters to that particular sample size. The resultant projection for the moisture uptake curve should closely resemble the third curve. This same process should be done to validate the other two curves, resulting in data that can be treated as having the same moisture absorption parameters.

3.3.1. VALIDATION OF NEAT EPOXY SAMPLES

Figure 35 displays the experimental results of the neat epoxy samples of 1.5mm thickness with all three of the planar sizes (i.e., 0.75inx 0.75in, 1.0inx 0.75in and 1.25inx 1.25in). In this figure, there are noticeable differences between the three planar sizes during the initial moisture uptake. The different planar sizes are shown as three separate colors; the 0.75inx 0.75in samples data points are displayed as blue rectangles; the 1.0inx 0.75in samples data points are shown as green rectangles; the final planar size,1.25inx 1.25in, are displayed as red rectangles. Moisture content is displayed along the vertical axis where the values are represented by percentage, and the horizontal axis shows the square root time for each particular data point. The figure shows differences in the initial uptake with the larger two planar sizes quickly converging to a similar trend, while the smallest planar size remains at higher moisture content than the other two. The smallest planar size showing higher moisture equilibrium could partly be explained by the small mass of the particular samples, where a change of 0.0001 grams could result in a 0.02% change in moisture content level.

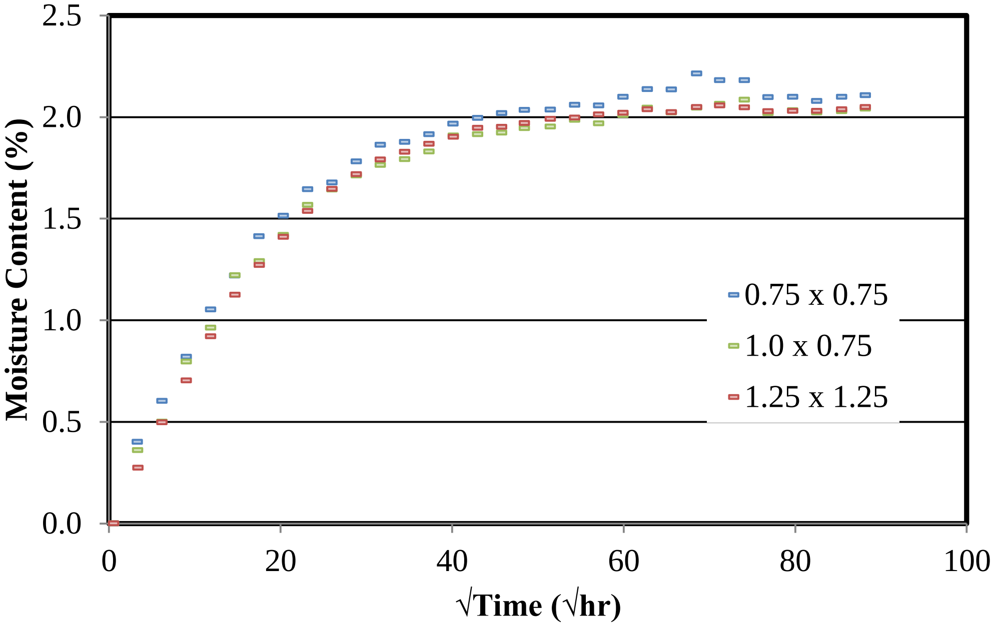

Figure 35: Experimental data for neat epoxy with a constant thickness of 1.5mm showing the three different planar sizes

From Figure 35 the different moisture data will be entered into the numerical solution code to produce the moisture parameters for this case. The code will be run for two of the curves to recover moisture parameters. These moisture parameters will then be used to validate the third curve. Each of the curves will be validated using the other two curves resultant moisture parameters. The initial guesses for the code to run will have the same diffusion coefficients for each of the dimensions because the coefficients should be equal to each other being in an isotropic material such as neat epoxy.

Table 2 displays the initial guesses for each of the moisture parameters besides the moisture equilibrium, which changes depending on the experimental data inputted into the system. As Figure 35 shows all three of the planar size’s experimental data run closely together to allow for an easier observation, the validation results are shown on three separate graphs.

Table 2: Initial guesses for recovery of moisture parameters through numerical solution

	D_z (mm2/hr)	D_x (mm2/hr)	Dy (mm2/hr)	β (hr^{-1})	γ (hr^{-1})
Initial Guess	0.002	0.002	0.002	0.001	0.0005

The first moisture parameter validation was done using the 1.5mm thickness and 0.75inx 0.75in planar size neat epoxy samples as shown in Figure 36. The recovered data points were found by finding the moisture absorption parameters using the 1.5mm thickness, 1.00inx 0.75in samples and the 1.5mm thickness, 1.25inx 1.25in samples, in combination. The plot is shown without the data points but instead with a representative line as a way to make the plot less cluttered and more clearly comparable. In this figure, the experimental data collected is displayed as a blue line, while the validating line produced by the recovered moisture parameters is displayed as a red line. The figure shows the moisture equilibrium level, along with the initial uptake, produce similar results for both the experimental data along with the theoretical data from the recovered parameters. The experimental data shows fluctuation from square root twenty hours until the end of recovery resulting in noticeable differences in data.

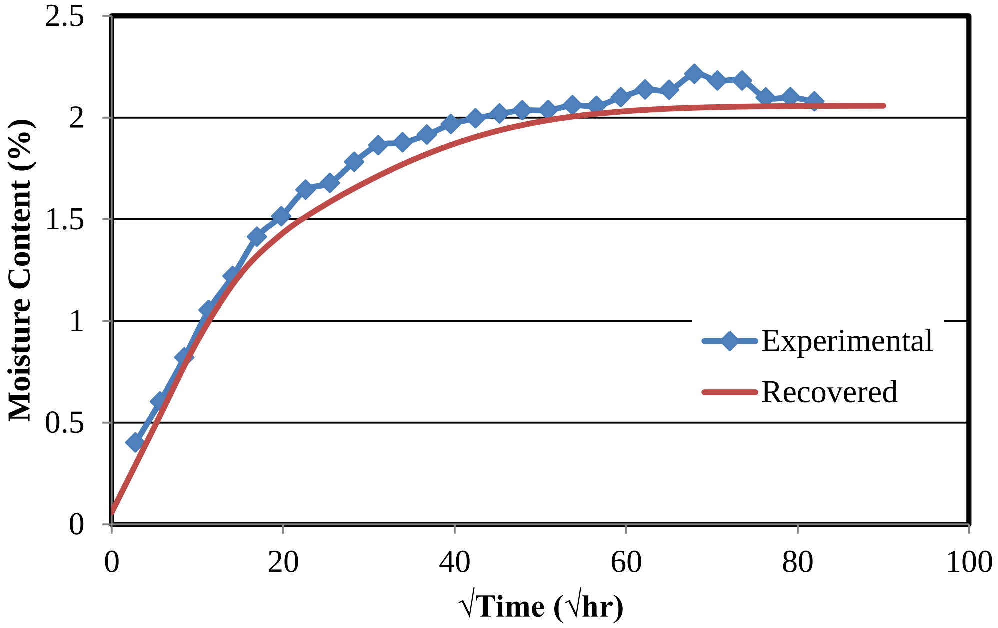

Figure 36: Validation of neat epoxy samples with 1.5mm thickness and 0.75in x 0.75in planar size

Similarly to Figure 36, Figure 37 shows the validation of the 1.5mm thickness neat epoxy samples, but for the planar size of 1.00in x 0.75in. The recovered data points were found by finding the moisture absorption parameters using the 1.5mm thickness, 0.75in x 0.75in planar size samples and the 1.5mm thickness, 1.25in x 1.25in planar size samples. In Figure 37, the experimental data is displayed as a solid blue line without showing locations of major data points to reduce the clutter of the graph. The projected data based on the recovered moisture absorption parameters is shown as a solid red line. The experimental data shows small fluctuations throughout the moisture uptake, but not as significantly as the smaller planar size samples displayed in Figure 36. The comparison between the two data plots shows close similarity during moisture uptake and as the uptake continues the recovered data follows the experimental data accurately ending with higher moisture equilibrium, but with the fluctuation that occurs the experimental data could once again trend upward to match the projected curve.

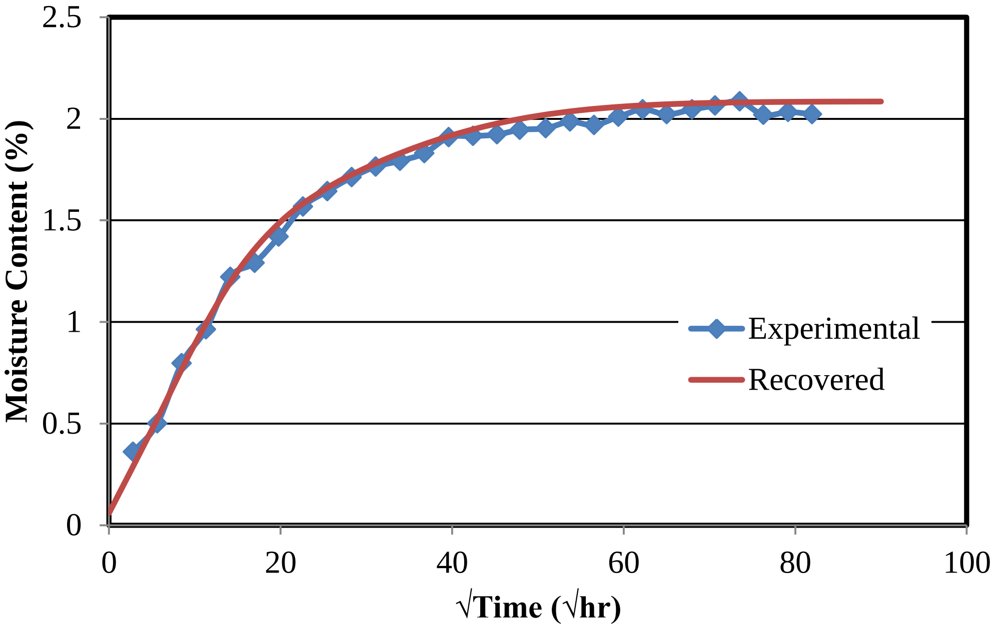

Figure 37: Validation of neat epoxy samples with 1.5mm thickness and 1.00in x 0.75in planar size

Figure 38 shows the validation of the 1.5mm thickness neat epoxy samples, but for the planar size of 1.25in x 1.25in instead. The recovered data points in this case were found by taking the moisture absorption parameters from the 1.5mm thickness, 0.75in x 0.75in planar size samples and the 1.5mm thickness, 1.00in x 0.75in planar size samples. In Figure 37 the experimental data is displayed as a solid blue line without showing locations of major data points to reduce the clutter of the graph. The projected data, based on the recovered moisture absorption parameters, is shown as a solid red line. The experimental data shows similar trends but lesser amounts of fluctuation to Figure 37, the decrease in fluctuations between each of the figures can be explained by the sample sizes getting larger and minimizing the error from mass change. Mass change having less effect on the moisture content level allows the samples to have a more stable growth rate as the figures display. The validation for this size shows strong correlation between both of the data sets throughout the entire moisture uptake with the experimental data slightly separating from the model predictions.

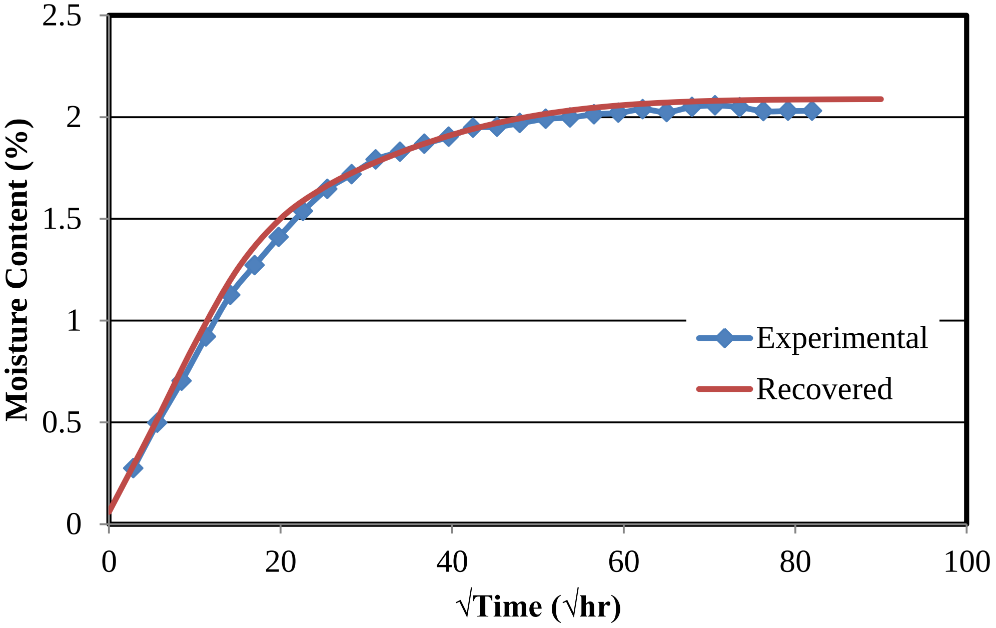

Figure 38: Validation of neat epoxy samples with 1.5mm thickness and 1.25in x 1.25in planar size

Each of these three previous figures displays that using two of the curves to find the moisture absorption parameters will accurately project the moisture uptake of the third curve. Being able to accurately project the moisture uptake of different planar sizes shows that regardless of the changes in the planar size, there will not be different moisture absorption parameters at 1.5mm thickness, as expected. This same procedure has been run for the three different thicknesses with similar results. All of these experimental data plots then go through the same numerical method procedure, but for running all three curves on the plot instead. Running all three of the curves at once is used to find a best fit using all data available once the data is validated. Once all this data is compiled there will be an overall comparison for neat epoxy samples and how the thickness of the samples affects the moisture absorption parameters.

Table 3 shows the results of running the changing planar size calculations when all three curves were used to recover the moisture absorption parameters. The table shows a small but unexpected variance in the different parameters depending on the thickness of the samples. The diffusion parameters between the three thicknesses are not exactly the same but are still closely related in all of the results. The experimental data results in thicknesses that show slight differences, but with nothing that would suggest that changing the thickness will make specific changes to the moisture absorption parameters.

Table 3: Recovered moisture absorption parameters comparison for changing thicknesses in neat epoxy samples

Thickness (mm)	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**M∞ (%)**
1.5	$1.29x10^{-3}$	$2.80x10^{-3}$	$8.74x10^{-4}$	$3.65x10^{-4}$	2.09
1.7	$1.14x10^{-3}$	$2.40x10^{-3}$	$8.19x10^{-4}$	$2.77x10^{-4}$	1.94
2.0	$1.48x10^{-3}$	$2.04x10^{-3}$	$7.05x10^{-4}$	$2.92x10^{-4}$	1.99

For the same epoxy samples all of the validation techniques were used to develop the comparison between each of the planar size. Table 4 displays the comparison of the moisture parameters based on the planar size. These values were found by taking the three different thickness curves for each planar size and treating them as having the same moisture parameters outputting accurate values. Table 4 shows that regardless of the planar size for neat epoxy samples the diffusion through the thickness has a constant value, but the planar diffusivity has been affected more showing differences in each of the values.

Table 4: Recovered moisture absorption parameters comparison for changing planar size in neat epoxy samples

Planar Size	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**$M\infty$ (%)**
0.75in x 0.75in	$1.063\text{x}10^{-3}$	$1.38\text{x}10^{-3}$	$5.87\text{x}10^{-4}$	$1.47\text{x}10^{-4}$	2.04
1.00in x 0.75in	$9.62\text{x}10^{-4}$	$2.25\text{x}10^{-3}$	$5.45\text{x}10^{-4}$	$1.26\text{x}10^{-4}$	1.98
1.25in x 1.25in	$1.012\text{x}10^{-3}$	$1.85\text{x}10^{-3}$	$1.06\text{x}10^{-3}$	$3.37\text{x}10^{-4}$	1.98

The highest planar diffusion coefficient comes from the 1.0in x 0.75in planar size samples, which also has the lowest thickness diffusion coefficient by a small margin. Both the beta and gamma terms are similar in the smaller planar sizes, but the largest planar size shows significant differences in both of the terms from the other two. The 1.25in x 1.25in planar size samples have the larger values in both beta and gamma cases meaning the probability for these bound, or unbound, molecules to become unbound, or bound, is highest when the planar size is larger. With the beta and gamma terms being greater for the higher planar size this would suggest more moisture uptake during the later parts of the moisture absorption process than the smaller samples. The moisture equilibrium levels for each of the planar sizes are comparable with the two larger planar sizes having the same moisture equilibrium value, as expected, with the smallest planar size sample trending about 3% higher than the others. Although each of the moisture equilibrium values are expected to be the same value for a neat epoxy sample the 3% difference shown could partially be explained by the small mass that shows larger fluctuation with the same 0.0001 gram mass gains.

3.3.2. VALIDATION OF 1% NANOTUBE CONTENT SAMPLES

Neat epoxy samples showed they can validate the different sizes of samples by using the moisture parameters given by the two other curves. This was able to show that regardless of the planar size or thickness of the sample, using the obtained moisture parameters can project the moisture uptake curves of any different dimension of neat epoxy samples. The same study will be done on the samples with nanotube reinforcement to see if the addition of nanotubes will affect the consistency between the data for a specific nanotube content level.

In the neat epoxy samples section, the plot and validation were done having a constant thickness and changing the planar size, but the same process was done by using constant planar sizes with changing the thicknesses within the recovery process. Figure 39 displays the experimental data from the particular sample description of having 1.0% nanotube content and 1.25in x 1.25in planar size with the three different thicknesses displayed as separate curves. The experimental data points in this figure are displayed as 1.5mm, 1.7mm and 2.0mm in squares of colors blue, orange and red, respectively. As should be expected from experimental data with changing thicknesses the thickest sample has the slowest moisture uptake while the thinnest samples has the quickest initial moisture uptake. The moisture uptake shows different rates, but the moisture equilibrium of the 1.7mm and 2.0mm samples are the same based on the respective curves ending on top of each other. The 1.5mm thickness samples should, theoretically, have the same moisture equilibrium level on the graph as well, but has a slightly higher level at this point. Although the samples have been immersed for ten months the slight difference could be accounted for over a longer period of time as the data does overlap previously.

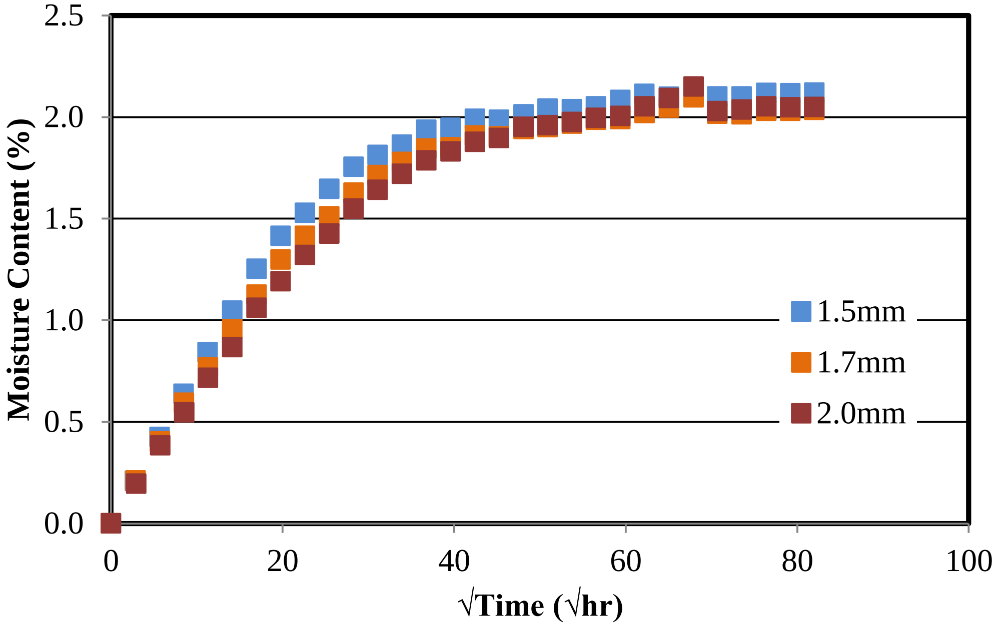

Figure 39: Experimental data of 1.0% nanotube content 1.25in x 1.25in planar size samples with changing thickness

Although the moisture absorption properties are potentially different for a case where nanotubes are involved in the fabrication, the same initial guesses will be made for the numerical solution to keep the recovery process as uniform for all tests as possible. The addition of nanotubes could potentially affect the validation process by having less consistency which would show a larger difference in the experimental curve and the recovered curve from the numerical solution.

Figure 40 displays the validation curve for the 1.0% nanotube content samples of planar size 1.25in x 1.25in with a 1.5mm thickness. The horizontal axis in this figure shows the square root time of the overall moisture uptake curve. For this particular sample size, nanotube content and thickness the samples have been immersed in a room temperature moisture bath for 10 months giving the samples enough time to reach a steady representation of moisture equilibrium. Both the experimental and the recovered moisture curve, the blue and red lines respectively, closely follow the same initial moisture uptake showing the diffusion coefficients recovered closely relate to those of the experimental data. The experimental data and the moisture absorption properties that were recovered overlap towards the end of the moisture uptake showing an accurate representation of the moisture equilibrium of the experimental data.

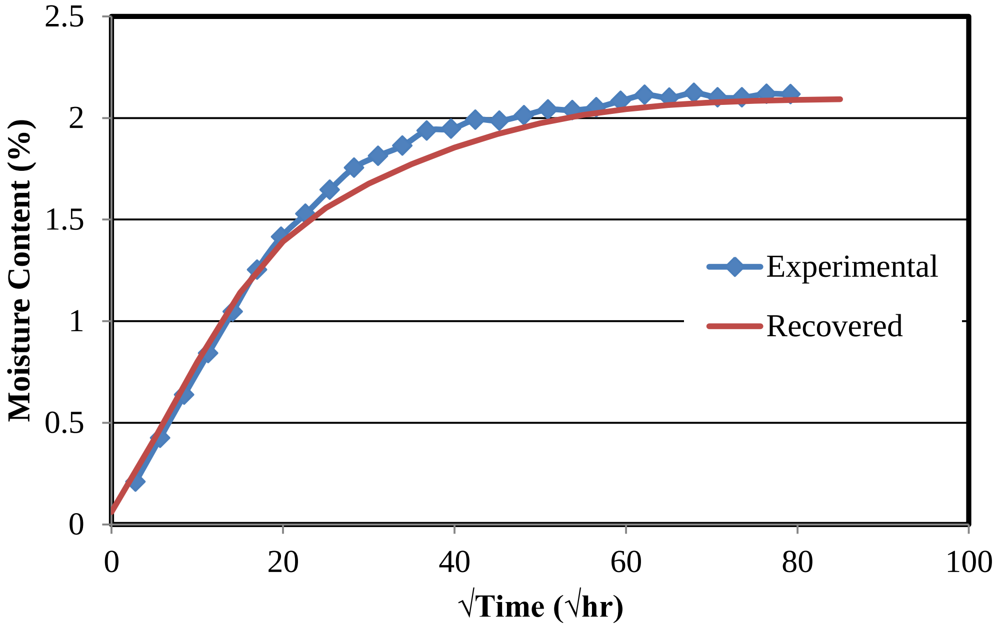

Figure 40: Validation of 1.0% nanotube content 1.25in x 1.25in planar size samples with a 1.5mm thickness

While both the diffusivity and the moisture equilibrium show correlation the differences in data occur in the transition, where the recovered data assumes the data will follow a slower uptake to get to the moisture equilibrium. Based on the initial figure for the three curves it can be seen they are closely related throughout the process with the largest variance in the experimental data also taking place at that particular location. With the experimental data showing the largest variance in the transitional area it would make sense that based on the curves for 1.7mm thickness and 2.0mm thickness the recovered data would assume the curve for the 1.5mm thickness to be more closely related to the two, resulting in the gap in that particular area.

Figure 41 shows the comparison and validation of the samples with 1.0% nanotube content, 1.25in x 1.25in planar size and a thickness of 1.7mm based on the curves of the samples with the same properties but with differing thicknesses of 1.5mm and 2.0mm and the experimental data for the particular properties. The approximate solution for the moisture absorption parameters results in the assumption that the moisture uptake relies on the diffusivity while the moisture uptake towards the end relies on the beta and gamma terms. In Figure 41 it can be seen that throughout the initial uptake to square root forty hours the validation from the recovered parameters matches closely with the experimental data. Towards the end of the moisture uptake the recovered parameters show that the curve should continue an upward trajectory while the experimental data suggests the moisture equilibrium level is lower. Based on Figure 39 the influence of the curves on the moisture absorption properties can show why the moisture equilibrium is trending higher for the recovered case to the experimental data in Figure 41. When projecting the new curve using the recovered parameters first there is a best fit parameters for the initial two curves that are assumed to have the same moisture parameters as the new curve. The problem with this case is the 1.5mm curve has a moisture equilibrium level trending slightly higher, along with there being a jump in the 2.0mm curve, skewing the moisture equilibrium slightly, resulting in a moisture equilibrium prediction being 0.1% higher than the experimental data is displaying.

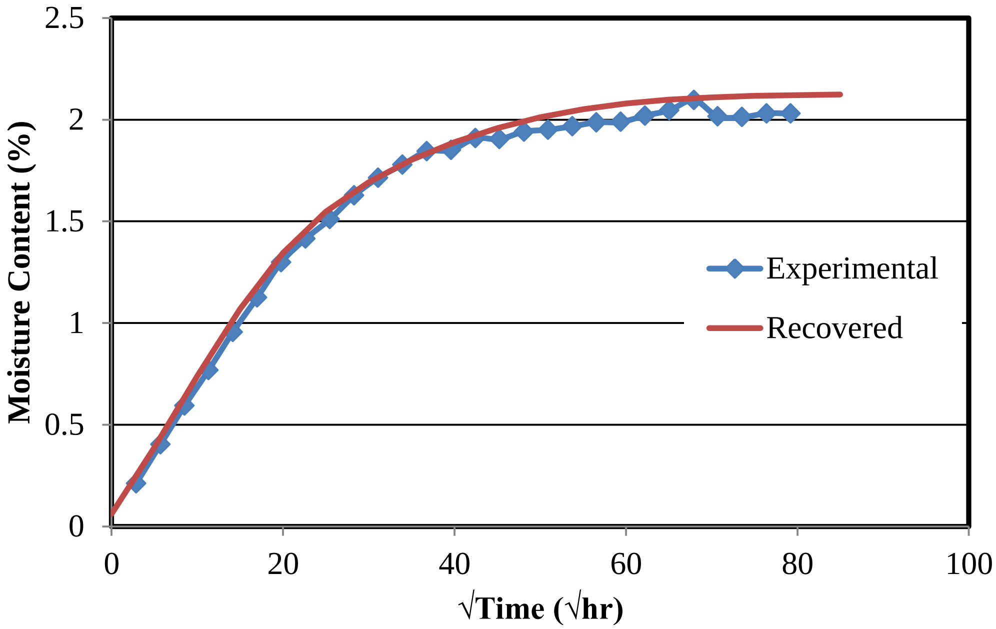

Figure 41: Validation of 1.0% nanotube content 1.25in x 1.25in planar size samples with a 1.7mm thickness

The 1.7mm thickness experimental curve has a similar jump and drop as the 2.0mm thickness where the curve reaches the moisture equilibrium for the recovered data showing the jump that occurred may be projected to occur again or a continuous small increase in uptake until it potentially does reach the projected curve.

The final curve that needs to be validated and compared to the recovered moisture parameters is the 2.0mm thickness with those same properties as the previous curves (i.e., 1.0% nanotube content and 1.25in x 1.25in planar size). Within this figure, there are two different curves displayed, one being the experimental data for the samples of the specifications and the projected curve of the moisture absorption properties that were recovered using the 1.5mm thickness and 1.7mm thickness experimental data with the 1.0% nanotube content and 1.25in x 1.25in planar size. Based on the two curves it can be seen that the recovered moisture parameters project a curve closely related to the experimental data. During the initial moisture uptake the two curves are constantly overlapping showing the diffusion coefficient is accurately representing this portion of the data.

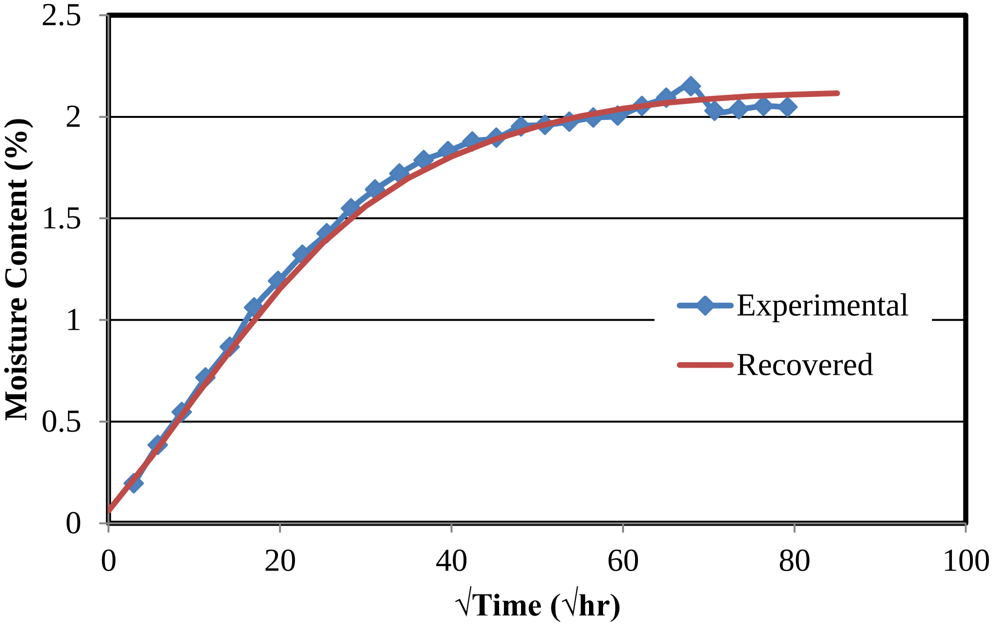

Figure 42: Validation of 1.0% nanotube content 1.25in x 1.25in planar size samples with a 2.0mm thickness

The recovered data continues to closely follow the experimental data until the experimental data has an unexpected spike where the recovered data then splits the difference of the peak resulting in showing the moisture equilibrium higher than the final points of the experimental data. Accounting for the jump in the experimental data the samples may still have the potential to have an upward trend from its current point giving the moisture equilibrium projected by the recovered parameters an accurate representation of where the experimental data for this thickness could be. Figure 42 shows a strong similarity with the two different curves implying the validation for the 2.0mm thickness experimental curve based on the 1.5mm and 1.7mm thickness curves was successful.

As the previous figures showed the validation of the third curves for the specific case of the 1.25in x 1.25in planar size samples the same tests were done with the other two planar sizes along with all the thicknesses. Following the validation tests the three curves were all evaluated at once to find the moisture absorption parameters for the average of the three curves. Table 5 displays the results of the three curve evaluation for the 1.0% nanotube content samples with three different planar sizes. Unlike with the neat epoxy, the 1.0% nanotube content samples do not have exactly the same thickness and planar diffusion showing a slight drop in the thickness diffusion and a jump in the planar diffusion. The case for the 1.0% nanotube content samples the planar diffusion is greater than the diffusion through the thickness suggesting that with the planar diffusion is more affected by the addition of nanotubes than the thickness diffusivity.

Table 5: Recovered moisture absorption parameters comparison with changing planar size for 1.0% nanotube content samples

Planar Size	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**$M\infty$ (%)**
0.75in x 0.75in	$9.32\text{x}10^{-4}$	$2.75\text{x}10^{-3}$	$9.75\text{x}10^{-4}$	$3.36\text{x}10^{-4}$	2.12
1.00in x 0.75in	$7.93\text{x}10^{-4}$	$2.80\text{x}10^{-3}$	$9.20\text{x}10^{-4}$	$2.00\text{x}10^{-4}$	2.05
1.25in x 1.25in	$9.97\text{x}10^{-4}$	$4.21\text{x}10^{-3}$	$9.88\text{x}10^{-4}$	$4.15\text{x}10^{-4}$	2.08

The probability for a bound molecule to become unbound shows similar values for each of the different planar sizes, but some differences are shown with the probability for an unbound molecule to become bound. The moisture equilibrium is nearly the same for each of the planar sizes with a difference of 0.07% moisture content at the most. The diffusion through the thickness of the 1.00in x 0.75in planar size samples show a lower value than the two other planar sizes, but a similar planar diffusion to the smaller 0.75in x 0.75in planar size sample.

Table 6 summarizes the recovered moisture absorption properties for the 1.0% nanotube content samples at different thicknesses. These parameters were recovered by using all three of the planar size experimental curves at once for each individual thickness. For the case of 1.0% nanotube content samples with changing thickness all of the moisture absorption parameters are close in value showing that regardless of thickness the moisture absorption parameters are unchanged. The diffusion coefficients show similarities to those values in Table 5 as well, which would suggest that regardless of thickness or planar size the moisture absorption properties go unchanged making moisture absorption projection of different sizes possible by assuming the same parameters as any other size. The table displays the 1.5mm thickness having higher moisture equilibrium by a maximum of 0.05%, but still higher than between the other two thicknesses of 2.08% and 2.06% for 1.7mm and 2.0mm thickness, respectively.

Table 6: Recovered moisture absorption parameters comparison with changing thickness for 1.0% nanotube content samples

Thickness (mm)	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**M∞ (%)**
1.5	$8.76x10^{-4}$	$2.80x10^{-3}$	$9.54x10^{-4}$	$3.57x10^{-4}$	2.13
1.7	$1.21x10^{-3}$	$2.68x10^{-3}$	$9.10x10^{-4}$	$4.50x10^{-4}$	2.08
2	$1.34x10^{-3}$	$2.92x10^{-3}$	$1.06x10^{-3}$	$5.04x10^{-4}$	2.06

For the 1.0% nanotube content samples, the different curves in the experimental data were able to be verified based on other experimental data. Unlike the neat epoxy, there is a larger variance in the diffusion coefficient depending on what direction the moisture is diffusing through the sample. With the addition of nanotube reinforcement into the samples the planar diffusion was more greatly affected than the thickness diffusion. A situation like this could occur because the edge area is much smaller than the planar area making the nanotubes cover more of the area.

3.3.3. VALIDATION OF 3% NANOTUBE CONTENT SAMPLES

To see the affect the nanotube content has on the validation of the different curves, or the potential differences in moisture absorption parameters, the largest nanotube content would have the largest fluctuation. The 3% nanotube content samples were the highest nanotube content samples made in this experiment making the validation of curves important to look at for these samples. Along with looking at the highest nanotube content level the smallest planar size will also be shown to show the potential largest differences in experimental curve and recovered moisture parameters projected curve.

The experimental data shows three separate curves for samples with 3.0% nanotube content and 0.75in x 0.75in planar sizes which are different thicknesses of 1.5mm, 1.7mm and 2.0mm. In a figure containing three different thicknesses the moisture uptake would be slowest for the thickest samples because the moisture properties should not be changed. Figure 43 shows that with the thickness change the initial moisture uptake will be as projected with the 2.0mm thickness samples having the slowest uptake and the 1.5mm thickness samples having the quickest initial uptake. Different initial moisture uptake will happen, but the differing thicknesses should still reach the same moisture equilibrium where all three of the curves will overlap at some point. Figure 43 shows that both the 1.7mm and 2.0mm samples do overlap and end with similar moisture equilibrium points, but the 1.5mm thickness samples have a small overlap and end at a higher moisture equilibrium level. The experimental data suggests that when validating the curves of this figure the 1.5mm thickness samples will most likely trend higher than its recovered parameters and could result in projecting a higher curve for the thicker samples.

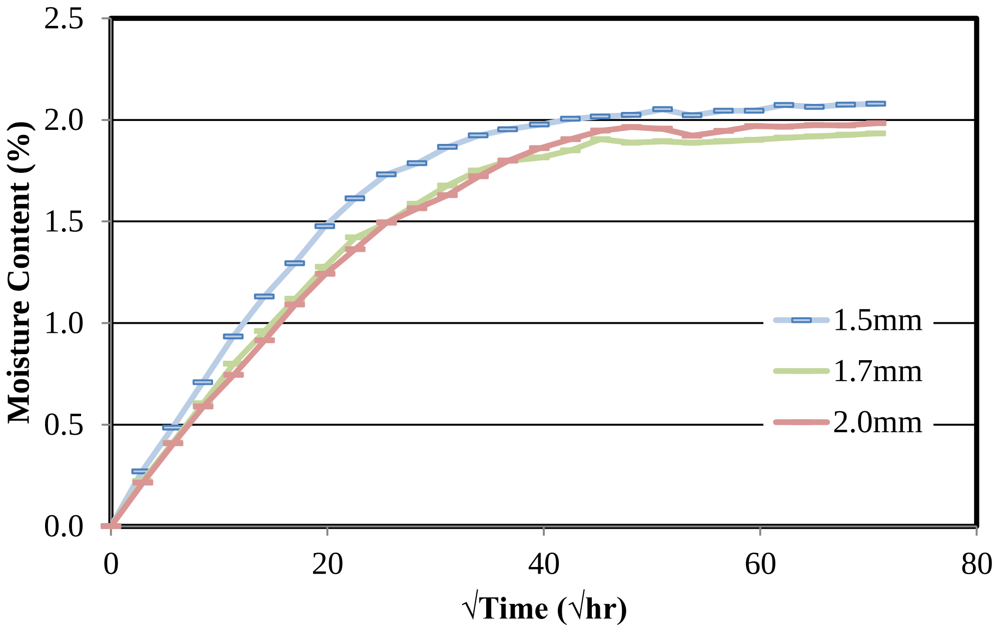

Figure 43: Experimental data for 3.0% nanotube content samples with planar size 0.75in x 0.75in and changing thickness

From looking at Figure 43, it was projected that the curve from the recovered parameters would end with lower moisture equilibrium than the experimental data of the 1.5mm thickness samples. Figure 44 displays the validation for the 3.0% nanotube content samples with planar size of 0.75in x 0.75in and a thickness of 1.5mm. The 1.5mm thickness experimental curve ends with higher moisture equilibrium than the projected curve from the recovered moisture parameters. The higher nanotube content level for the smallest possible planar size and thinnest sample could have affected the moisture uptake the most in a situation like this resulting in the higher moisture equilibrium value. Although the moisture equilibrium value ended up being projected lower than the experimental results show, the initial moisture uptake shows strong correlation between the two curves. With the initial uptake having similar values for both of the curves the diffusivity should be estimated correctly because the initial uptake is most heavily affected by the diffusion coefficients.

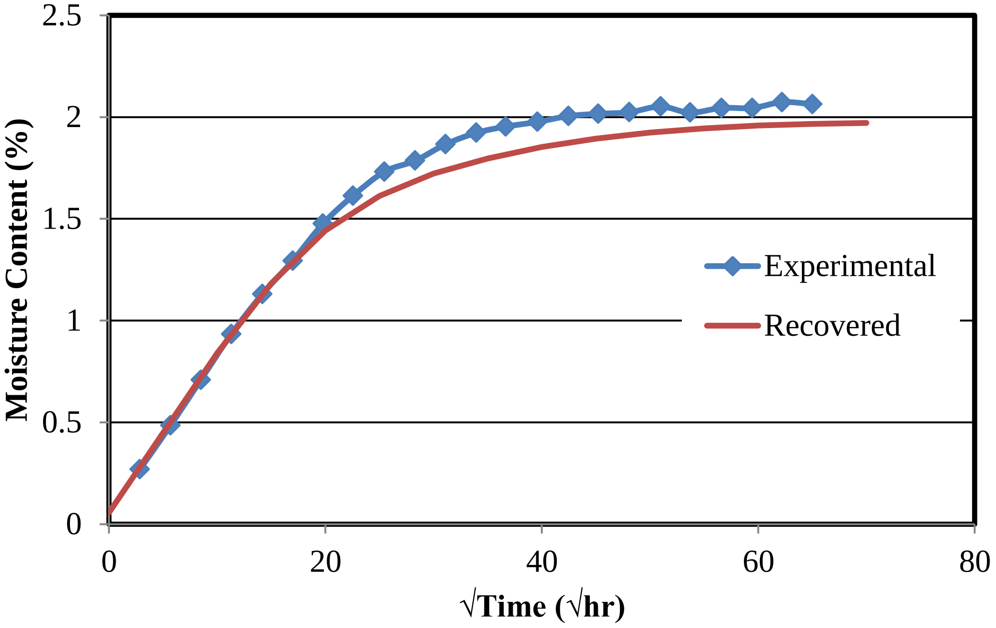

Figure 44: Validation of 3.0% nanotube content 0.75in x 0.75in planar size samples with a 1.5mm thickness

The 1.5mm thickness samples trends higher in moisture equilibrium compared to the other two thicknesses in Figure 43, the projected curve from the moisture absorption properties recovered by the 1.5mm thickness and the 2.0mm thickness could result in a high projection for the 1.7mm thickness validation. Figure 45 shows the validation for the 1.7mm thickness samples with 3.0% nanotube content and a planar size of 0.75in x 0.75in. As expected, from the high moisture uptake of the 1.5mm thickness samples, the projected curve from the recovered moisture absorption parameters results in a higher moisture uptake than the 1.7mm thickness curve. The projected curve throughout the entirety of moisture uptake trends more quickly toward moisture equilibrium along with having higher moisture equilibrium. The experimental data and the projected curve do overlap at one point, but instead of the projected curve leveling off at that point, as the experimental data does, the projected curve continues to grow. This particular data set has been immersed in moisture for the least amount of time; the figure shows the experimental data still increasing towards the end of the plot, which could result in the recovered parameters projecting the experimental data, will continue to grow.

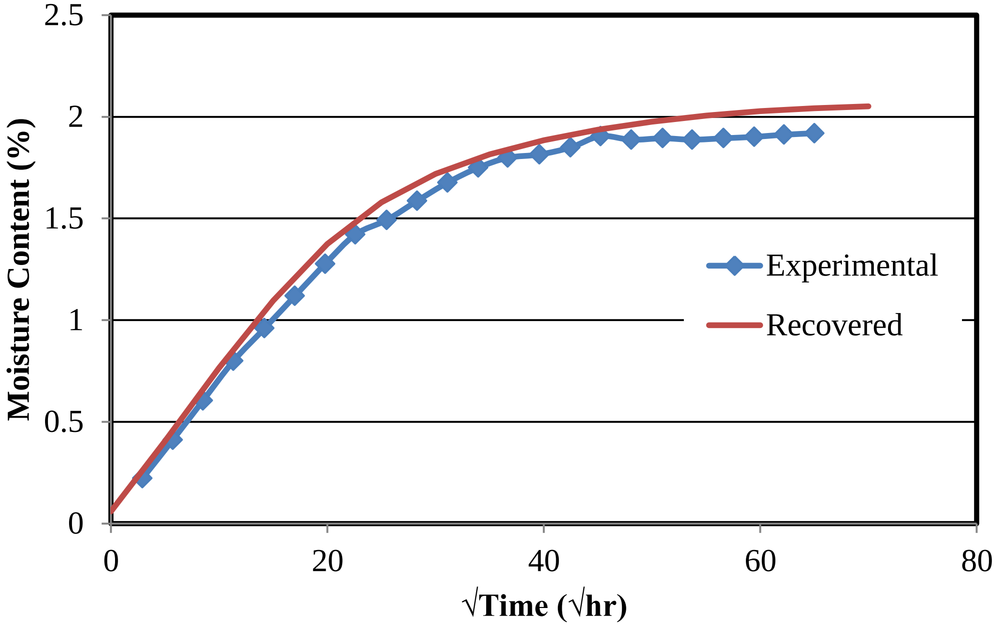

Figure 45: Validation of 3.0% nanotube content 0.75in x 0.75in planar size samples with a 1.7mm thickness

The first two validations of the 3.0% nanotube content samples the recovered parameters produced curves that had similarities, but did not fully follow the experimental data. Figure 46 shows the validation of the 3.0% nanotube content samples with a planar size of 0.75in x 0.75in and a thickness of 2.0mm. With the 2.0mm thickness the data should be more consistent with less fluctuation because the change in mass will affect the moisture content to a lesser extent. The curves shown on Figure 46 are experimental data along with the projected curve for the moisture absorption parameters recovered by the 1.5mm and 1.7mm thickness samples with the same other properties. The previous validation curves for this section have been unsuccessful for different moisture properties, but these two curves show close similarity throughout the entirety of moisture uptake. Many different experimental curves have shown a jump in the curve where the projected curve from the recovered properties will typically become offset to the experimental curve. In this case the jump and drop in the data did not result in as big of an offset in the two curves because the experimental curve increased in moisture absorption again after it had dropped instead of staying constant from where the drop was.

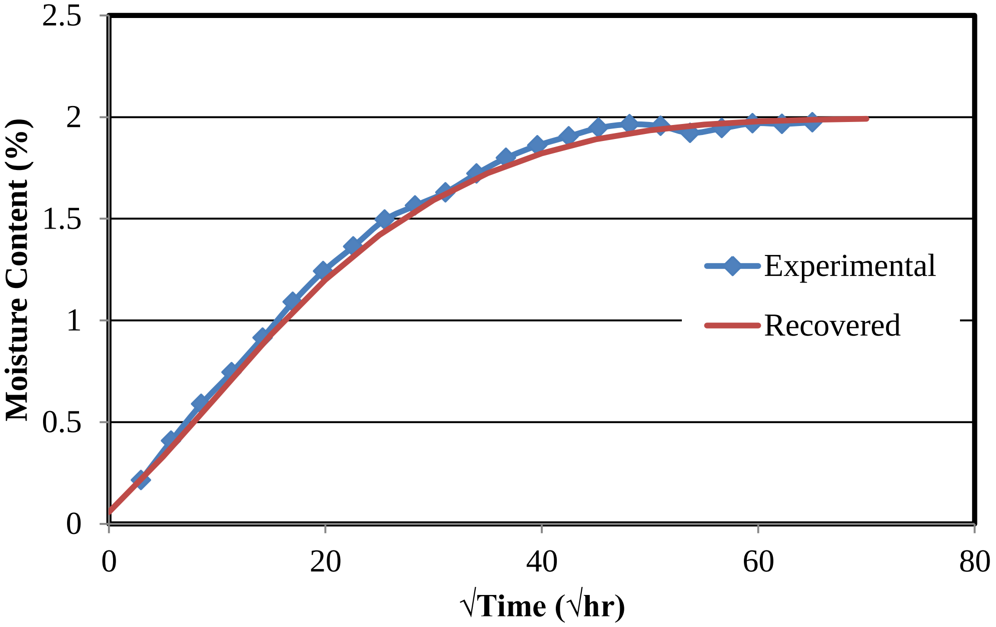

Figure 46: Validation of 3.0% nanotube content 0.75in x 0.75in planar size samples with a 2.0mm thickness

For the 3.0% nanotube content samples the effect of changing planar size is shown in Table 7. The variance in the data has led back to the neat epoxy samples where both of the diffusion coefficients are similar in value. The diffusion coefficients are comparable for all three planar sizes, suggesting the planar size for these larger nanotube content samples is not changing the moisture absorption. Although all three of the diffusion coefficients are comparable, the values for the smallest planar size are the lowest and the values for the 1.00in x 0.75in planar size are the highest through the thickness, but much smaller for the planar diffusivity. Even with the planar diffusion coefficient being much lower than the other two, the amount of available area to go through is much smaller means the overall affect that value plays on the moisture uptake is not as significant resulting in still a comparable moisture equilibrium value with the 1.25in x 1.25in planar size samples. The moisture equilibrium values are similar for two of the cases with a drop off for the smallest case of about 0.1% moisture content. The lowered moisture equilibrium for the smallest planar size could be explained by the length of the nanotubes affecting diffusion more significantly than it does for the larger planar sizes, along with the change in mass affecting moisture content level more significantly.

Table 7: Recovered moisture absorption parameters for 3.0% nanotube content samples with changing planar size

Planar Size	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**M∞ (%)**
0.75in x 0.75in	1.22×10^{-3}	1.35×10^{-3}	1.54×10^{-3}	6.65×10^{-4}	1.99
1.00in x 0.75in	1.62×10^{-3}	2.25×10^{-4}	1.41×10^{-3}	8.00×10^{-4}	2.08
1.25in x 1.25in	1.48×10^{-3}	1.52×10^{-3}	1.51×10^{-3}	9.08×10^{-4}	2.12

The changing planar size did not show significant differences between data, but the changing thickness does. Table 8 shows the moisture absorption parameters for 3.0% nanotube content samples with changing thickness recovered by using the three experimental data curves of different planar sizes for each thickness and considering their moisture absorption properties to be the same, as they should be. Through this process the results show a variety of values for both diffusion coefficients along with the moisture equilibrium values. These samples have been immersed for 7 months and, from the curves, the experimental data still shows some fluctuation that could be resulting in the wide range of moisture absorption properties that could become more consistent if the experimental data stabilizes more.

Table 8: Recovered moisture absorption parameters for 3.0% nanotube content samples with changing thickness

Thickness (mm)	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**M∞ (%)**
1.5	$6.21\text{x}10^{-4}$	$2.44\text{x}10^{-3}$	$2.99\text{x}10^{-4}$	$4.87\text{x}10^{-5}$	2.21
1.7	$1.09\text{x}10^{-3}$	$1.55\text{x}10^{-4}$	$9.99\text{x}10^{-4}$	$3.23\text{x}10^{-4}$	2.05
2	$7.04\text{x}10^{-4}$	$4.77\text{x}10^{-3}$	$3.12\text{x}10^{-3}$	$4.15\text{x}10^{-4}$	1.95

The additional time would mainly affect the beta, gamma and moisture equilibrium terms because the diffusion coefficients do not affect the later moisture uptake much and the initial moisture uptake has already passed. The diffusion coefficients show considerable differences between the planar and thickness diffusivity. The thickness diffusivity still shows closer relation to the neat epoxy samples than the planar diffusivity does, suggesting the addition of nanotubes affect the planar diffusivity more significantly than the diffusion coefficient through the thickness.

3.4. MOISTURE ABSORPTION PARAMETERS COMPARISON

After the validation of the data had taken place the next step would be to compare how the nanotube weight content affected each of the moisture absorption properties for the different categories of samples. The different categories are distinguished as either a specific planar size or a specific thickness of samples. These categories were 0.75in x 0.75in planar size samples, 1.00in x 0.75in planar size samples, 1.25in x 1.25in planar size samples, 1.5mm thickness samples, 1.7mm thickness samples and 2.0mm thickness samples. For each of these six categories there are five different moisture absorption properties that are being compared, which are thickness diffusivity, planar diffusivity, probability for a bound molecule to become unbound, probability for an unbound molecule to become bound and moisture equilibrium. Each of these properties has the potential to have different relationships with the addition of nanotubes. The relationship between the increase in nanotube contents and the moisture absorption properties should be shown to be the same, or close to the same, for each of the different sizing categories because it has been previously established that the planar size and thickness has little to no effect on the moisture absorption properties.

3.4.1. SAMPLES WITH PLANAR SIZE OF 0.75in x 0.75in

The first set of recovered moisture parameters looked at will be from the 0.75in x 0.75in planar size samples. These samples are the smallest planar size samples so the edge effects will be the greatest for this particular planar size, making it the most three-dimensional.

The diffusion coefficient through the thickness has been shown in Figure 47 for all samples of planar size 0.75in x 0.75in comparing the value between each of the nanotube weight content values. The nanotube weight content values for each of the points are 0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0% and 3.0%. From this figure it can be seen that there is a changing diffusion coefficient depending on the nanotube weight content. It can be seen that from the neat epoxy samples to the 0.5% nanotube content samples there is a constant decrease in the diffusion coefficient having a peak at this particular percentage. The relationship of 0.5% nanotube content samples to the 1.5% nanotube content samples there is an increase in diffusion coefficient showing a peak at

1.5% nanotube content. Following the diffusion coefficient value at 1.5% nanotube content the diffusion coefficient shows less of a change with a slight drop for 2.0% nanotube content and another slight increase for the 3.0% nanotube content level. This figure suggests that nanotube content for 0.75in x 0.75in planar size samples there is a decrease in thickness diffusion coefficient until 0.5% nanotube content, and then it will start to negatively affect the thickness diffusion coefficient with the increase of nanotube content level.

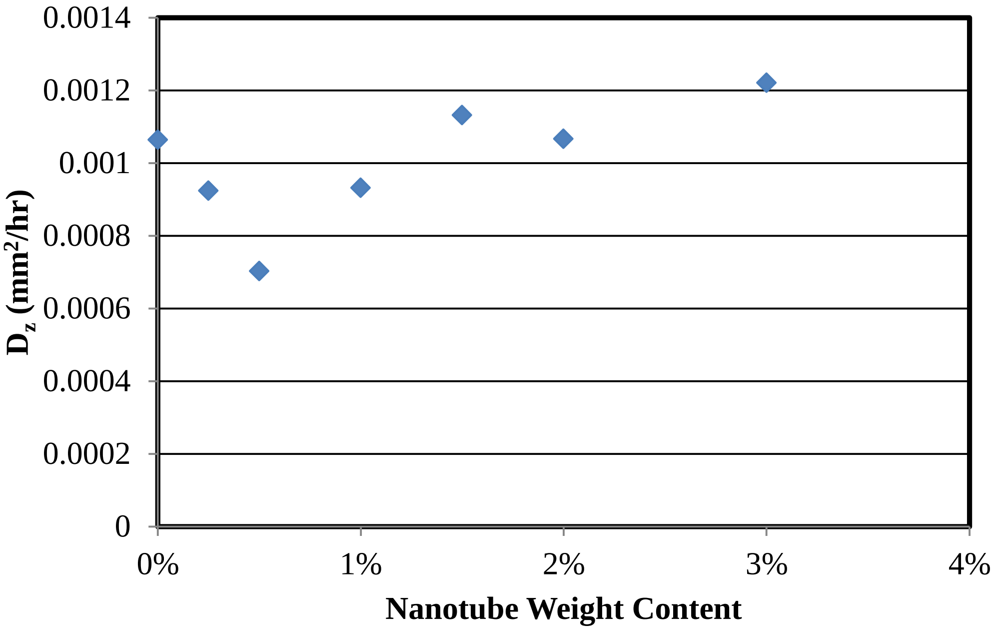

Figure 47: Comparison between thickness diffusivity for 0.75in x 0.75in planar size samples based on nanotube weight content

Looking at the relationship between the nanotube weight content and the thickness diffusivity the relationship showed that at 0.5% nanotube weight content the thickness diffusivity shows the largest decrease. Figure 48 looks at the comparison between nanotube weight content and planar diffusivity for samples of planar size 0.75in x 0.75in. Figure 48 shows an opposite relationship from the thickness diffusivity for the planar diffusivity. There is an increase in planar diffusivity until 0.5% nanotube weight content where there is a peak and the planar diffusivity begins to decrease again. The largest decrease in planar diffusivity occurs at 2.0% nanotube weight content with a close similarity to the 1.5% nanotube weight content. Along with having an opposite relationship as the thickness diffusivity the range of values is much larger as well with the y-axis scale going from 0.0005 to 0.004 unlike the thickness diffusivity where the scale goes from 0.0002 to 0.0014. The larger range of diffusivity values suggests that with the addition of nanotubes the planar diffusivity is more greatly affected than the thickness diffusivity.

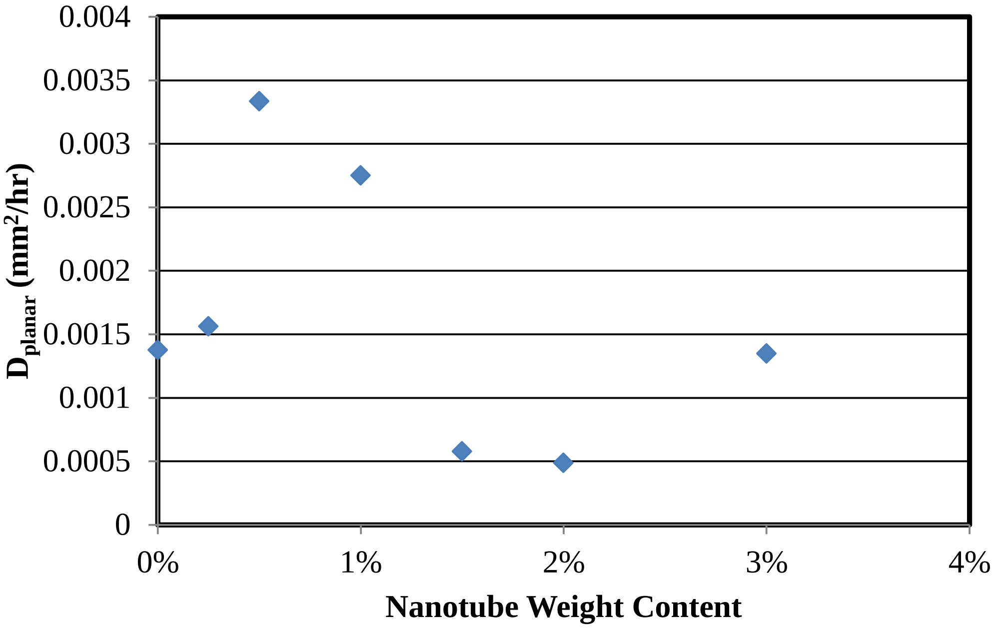

Figure 48: Comparison between planar diffusivity for 0.75in x 0.75in planar size samples based on nanotube weight content

The probability for a bound molecule to become unbound will affect the moisture uptake during the later portion. Having a larger probability suggests the moisture equilibrium will take longer to be reached because the samples moisture content will be constantly changing during later portions of the moisture uptake. This principle can be displayed by having a moisture curve where instead of fully leveling off the curve continues to slowly increase. Figure 49 shows the relationship between the nanotube content and the probability for a bound molecule to become unbound, β. The relationship between the two properties overall shows that with the increase in nanotube content there is an increase in β. While the general trend is for an increase in β with an increase in nanotube content there are two outliers to this rule: initially the β term decreases for the 0.25% nanotube weight content as well as the 1.5% nanotube weight content having a spike in the relationship with the highest β term. The spike for the 1.5% nanotube weight content could be related to how the different nanotube weight contents blended while during the fabrication process, producing less dispersed nanotubes within the sample.

Similarly to the probability for a bound molecule to become unbound, the probability for an unbound molecule to become bound follows a similar trend. As shown in Figure 50 there is once again an initial drop to the 0.25% nanotube weight content sample value. With the small initial drop there is again a step and steady incline until the highest nanotube weight content, 3.0%.

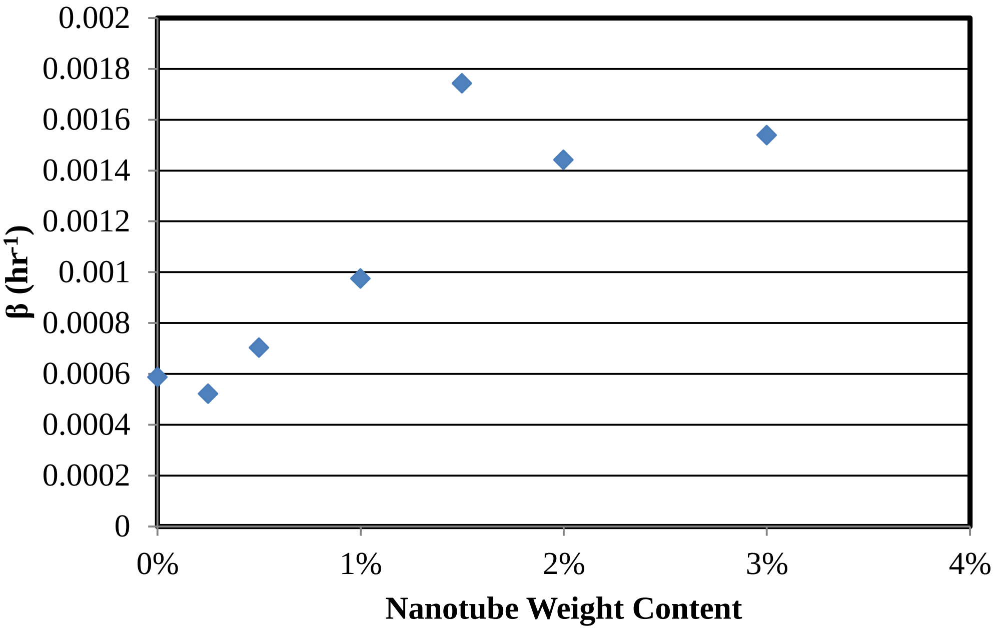

Figure 49: Comparison of the probability for a bound molecule to become unbound for 0.75in x 0.75in planar size samples based on nanotube weight content

Once again, the 1.5% nanotube weight content proves to be an outlier with a sudden jump in what was previously a fairly linear relationship starting at 0.25% nanotube weight content until 3.0% nanotube weight content. In comparison to the beta terms the gamma terms are commonly lower, but tend to follow the same general trend. Based on Figure 50 the relationship between nanotube weight content and γ for the 0.75in x 0.75in planar size samples would be there is a minimum γ value for the case of 0.25% nanotube content, but from that point on there is an almost linear relationship between the increase of γ and increase of nanotube weight content.

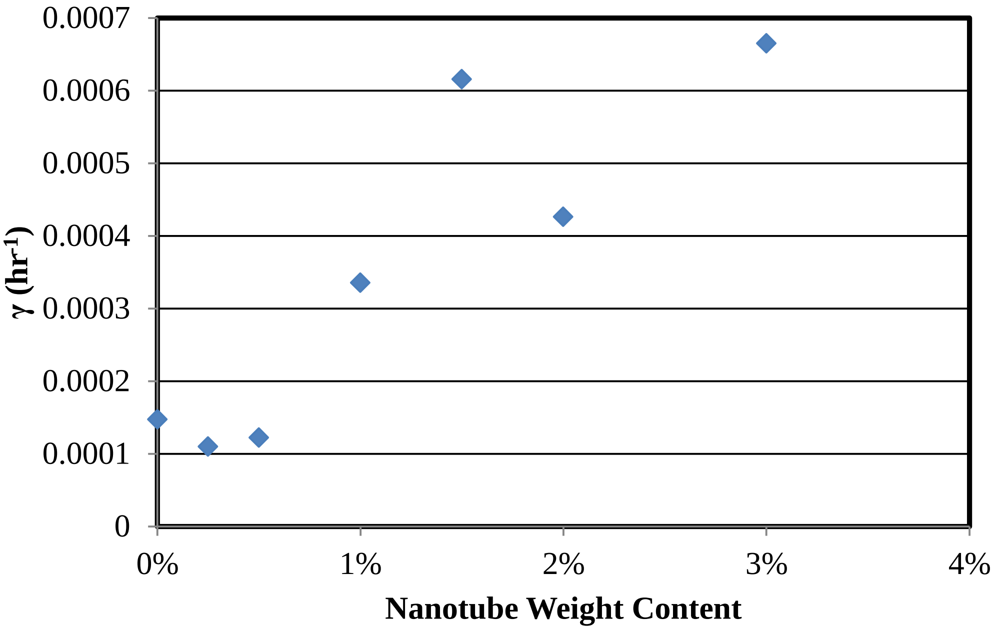

Figure 50: Comparison of the probability for an unbound molecule to become bound for 0.75in x 0.75in planar size samples based on nanotube weight content

The final moisture absorption property to be looked at for this planar size of sample would be the moisture equilibrium level, the point that the samples can no longer take in any more moisture. Many of the other moisture absorption parameters showed a general trend and not randomly switching one way or the other for increasing and decreasing. Figure 51 shows the comparison between the nanotube weight content and the moisture equilibrium with moisture equilibrium values from about 2% to 2.17%. From the figure, if the 1.5% and 3.0% nanotube weight content are disregarded, the moisture equilibrium follows a similar trend as the γ and β figures before it. There is an initial drop in moisture equilibrium for the 0.25% nanotube weight content followed by an increase until the 2.0% nanotube weight content. The 1.5% nanotube weight content along with the 3.0% nanotube weight content show the lowest values, but do not follow the trend for the rest of the nanotube weight contents. Based on Figure 51 the relationship shows that once the nanotube weight content reaches 2.0% the moisture equilibrium starts to decrease again, but with only one nanotube weight content following that point it cannot be seen if it is part of a trend or if the 3.0% nanotube content shows similar outlier traits as the 1.5% nanotube content samples.

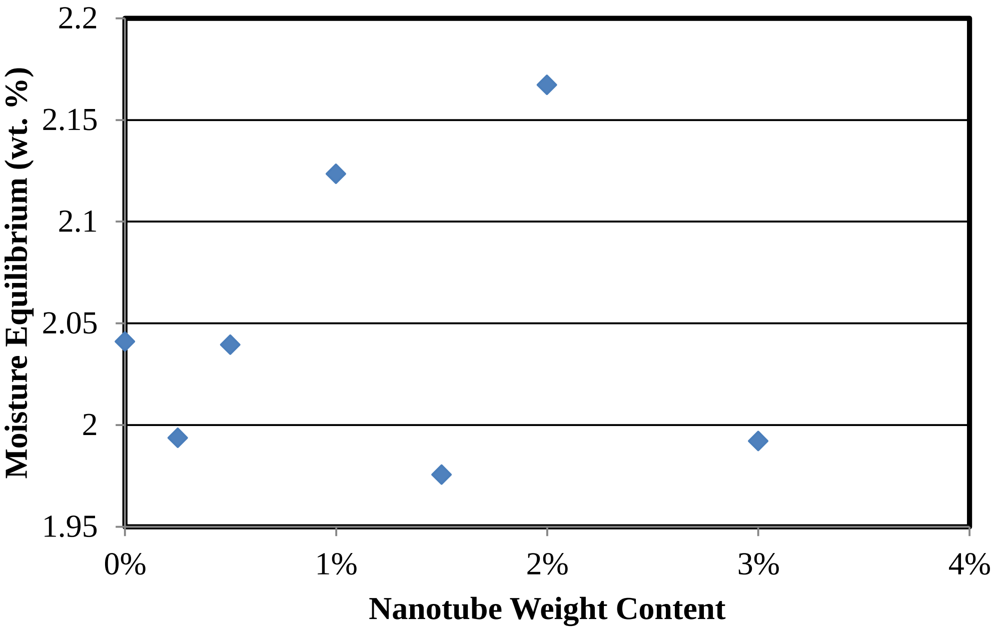

Figure 51: Comparison between moisture equilibrium for 0.75in x 0.75in planar size samples based on nanotube weight content

Table 9 shows a numerical summary of the previous graphs that had been shown. The values are all shown graphical in the previous five figures the exact numbers can be found in the table. It shows more clearly the differences in the two different diffusivities and how the addition of nanotubes does or does not affect them differently. The table shows that for the neat samples the two diffusivities are nearly the same, which would be expected because the samples are made of a single material all the way through without fibers, so the material should have the same diffusivity in every direction. As more nanotubes are added the gap between the two diffusivities increases until the highest nanotube content where they match up similarly once again.

Table 9: Summary of moisture absorption parameters for 0.75in x 0.75in planar size samples with changing nanotube content

NT Content	D_z (mm^2/hr)	D_{planar} (mm^2/hr)	β (hr^{-1})	γ (hr^{-1})	M∞ (%)
0%	1.06×10^{-3}	1.38×10^{-3}	5.87×10^{-4}	1.47×10^{-4}	2.04
0.25%	9.24×10^{-4}	1.56×10^{-3}	5.21×10^{-4}	1.10×10^{-4}	1.99
0.50%	7.03×10^{-4}	3.34×10^{-3}	7.02×10^{-4}	1.22×10^{-4}	2.04
1.00%	9.32×10^{-4}	2.75×10^{-3}	9.75×10^{-4}	3.36×10^{-4}	2.12
1.50%	1.13×10^{-3}	5.78×10^{-4}	1.74×10^{-3}	6.16×10^{-4}	1.98
2.00%	1.07×10^{-3}	4.85×10^{-4}	1.44×10^{-3}	4.26×10^{-4}	2.17
3.00%	1.22×10^{-3}	1.35×10^{-3}	1.54×10^{-3}	6.65×10^{-4}	1.99

The table also shows that the trends shown in the figures overall are still pretty close in value and there was not a particular nanotube content that resulted in significantly different moisture absorption properties. The table makes it clear that the moisture equilibrium of five out of the seven nanotube contents are within 0.06% of each other, which came down to potentially 0.0004 grams difference. Although the values are shown to be close the overall trend of that data with increasing nanotube content shows there are consistent changes with the addition of nanotubes.

3.4.2. SAMPLES WITH PLANAR SIZE OF 1.00in x 0.75in

The next planar size samples to be looked at are the 1.00in x 0.75in samples. Previously based on the validation and comparison of the figures for the smaller planar sizes, the same trend as the 0.75in x 0.75in planar size should be followed. Along with the trend of the data the numbers should be comparable to all the other planar size samples because it was established that planar size and thickness result in the same or little change in, moisture absorption properties.

Figure 52 shows the comparison between the thickness diffusivity and the nanotube weight content based on the samples with planar size 1.00in x 0.75in. This figure should follow a similar pattern to Figure 47 based on the knowledge that planar size does not affect the moisture absorption properties. Figure 52 shows the trend for the thickness diffusivity to be an initial decrease until 0.5% nanotube weight content where it peaks at a lowest point, and then starts an upwards trajectory that continues until the highest nanotube weight content 3.0%. From this figure the optimal amount of nanotubes to decrease thickness diffusivity would be 0.5% by weight. The same statement could have been made for the plot in Figure 47 reinforcing the trend.

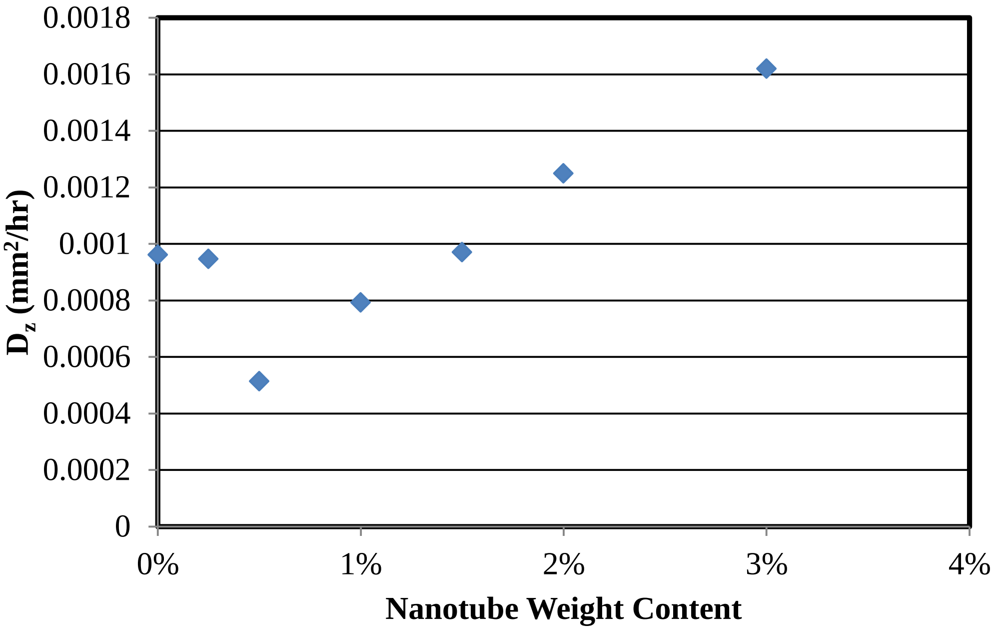

Figure 52: Comparison between thickness diffusivity for 1.00in x 0.75in planar size samples based on nanotube weight content

Planar diffusivity based on nanotube weight content for samples of planar size 1.00in x 0.75in can be seen in Figure 53. This figure shows that there is an initial drop in planar diffusivity between neat epoxy and 0.25% nanotube content. Following this point there is a steep rise in planar diffusivity with 0.5% nanotube content which has the highest planar diffusivity between all the nanotube content levels. Once the 0.5% nanotube content hump has been passed the rest of the data points show the natural trend of increasing nanotube content results in decreasing planar diffusivity, this shows the opposite effect of nanotube content on planar diffusivity than it does on thickness diffusivity. As the nanotube content increases the amount of moisture that can diffuse through the edges will decrease after the initial 0.5% nanotube content.

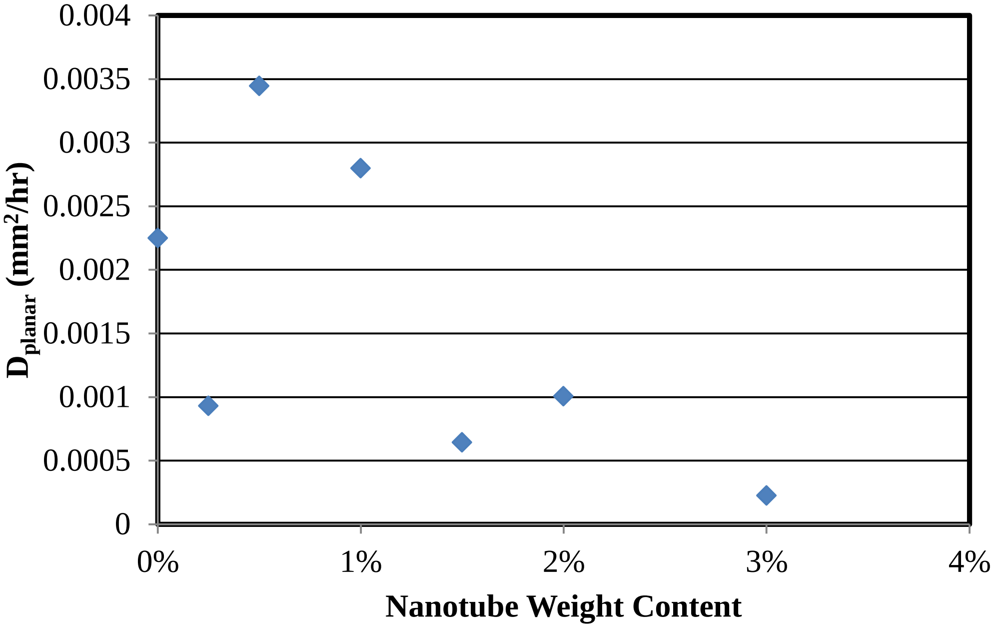

Figure 53: Comparison between planar diffusivity for 1.00in x 0.75in planar size samples based on nanotube weight content

Based on the planar size 1.00in x 0.75in the moisture absorption property β, probability for a bound molecule to become unbound, and the nanotube weight content are compared. Previously this moisture absorption property has shown an increase with increasing nanotube weight content, except for the initial slight drop at 0.25% nanotube weight content. Figure 54 shows similarities to the previous graphical representation for the smaller planar size, but the 0.25% nanotube content does not show a drop but instead an equal β term to the neat epoxy samples. The 1.5% nanotube content samples, once again, show a large sudden increase that does not seem to fit within the trend developed by the rest of the plot points. Including the 1.5% nanotube weight content samples that particular size shows the highest β value, but by disregarding that weight content for the trend to fit more smoothly shows that as the nanotube weight content increases, after the 0.25% nanotube content samples, the probability for the bound molecules to become unbound also increases.

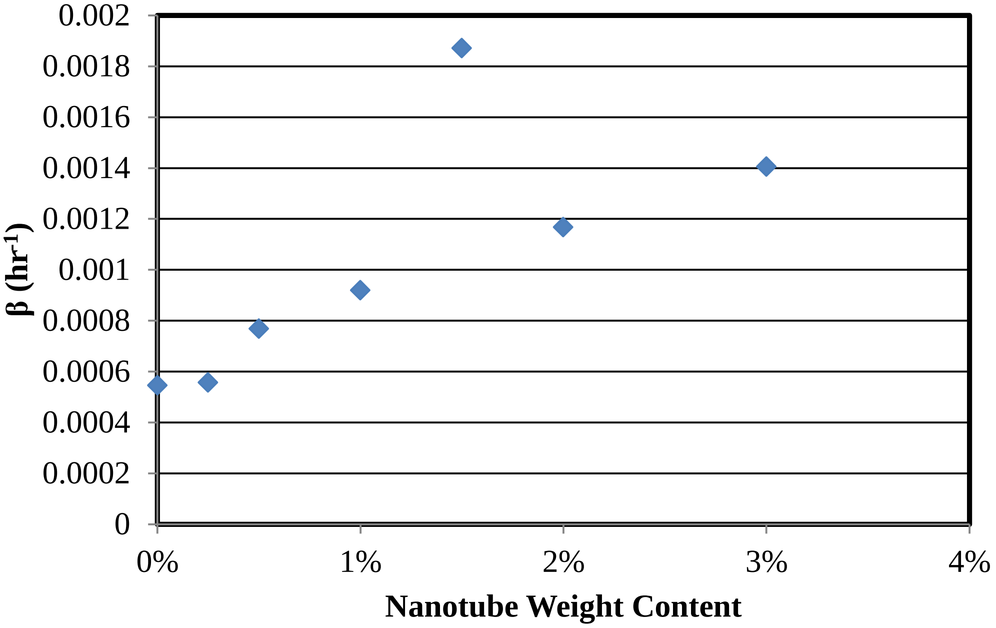

Figure 54: Comparison of the probability for a bound molecule to become unbound for 1.00in x 0.75in planar size samples based on nanotube weight content

The probability for an unbound molecule to become bound will typically follow the same trend as the probability for a bound molecule to become unbound. For the planar size of 1.00in x 0.75in the trend shown by the probability for a bound molecule to become unbound was to have an initial decrease followed by a constant increase with increasing nanotube weight content. Figure 55 shows that the γ values do, in fact, follow the same trend as the β values. The figure shows an initial decrease in γ with increasing nanotube weight content—until 0.5% nanotube weight content—followed by a linear increase relationship between γ and nanotube content, besides the 1.5% nanotube content outlier that has been present in many of the relationships. Figure 55 shows a similar trend as Figure 50, the relationship between the same terms for the 0.75in x 0.75in planar size samples, further reinforcing the statement that planar size does not affect the moisture absorption properties.

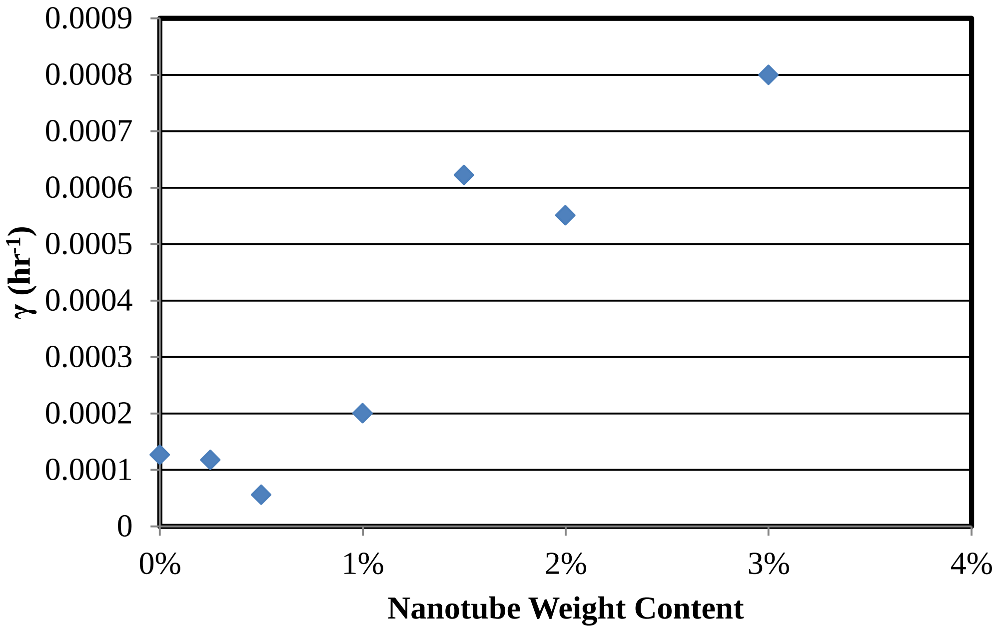

Figure 55: Comparison of the probability for an unbound molecule to become bound for 1.00in x 0.75in planar size samples based on nanotube weight content

Previously the trend for the relationship between moisture absorption and nanotube weight content has been an initial decrease in moisture equilibrium followed by an increasing moisture equilibrium with increasing nanotube weight content until 2.0% nanotube content was reached, but 1.5% nanotube content interrupts the trend, as it has for all of the other moisture absorption properties. Figure 56 shows that the trend for moisture equilibrium and nanotube content relationship holds true for the 1.00in x 0.75in planar size. The addition of nanotubes shows beneficial effects for the moisture absorption reduction in only the 0.25% nanotube content samples and the 1.5% nanotube content samples. The fabrication of the 1.5% nanotube content samples produced less dispersed nanotubes than other nanotube content levels, resulting in a lower moisture equilibrium level. The 0.25% nanotube content, on the other hand, has showed more consistency with trends from moisture properties and nanotube content relationships, and not appearing as an outlier.

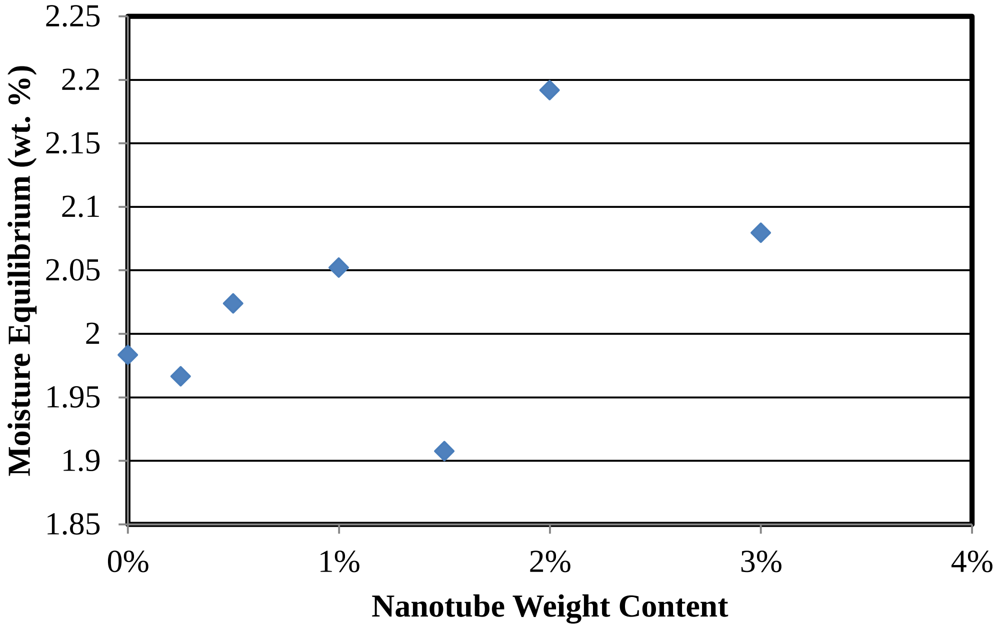

Figure 56: Comparison between moisture equilibrium for 1.00in x 0.75in planar size samples based on nanotube weight content

Table 10 displays the numerical values found for each of the different moisture absorption properties for the 1.00in x 0.75in planar size samples. The values for the thickness diffusivity are similar for four out of the seven nanotube contents, but still have a 68% difference between the highest and lowest values, 3.00% and 0.50% nanotube content, respectively. For this planar size the relationship between the diffusion coefficients in thickness and planar size appears for the 0.25% and 2.00% nanotube content samples.

Table 10: Summary of moisture absorption parameters for 1.00in x 0.75in planar size samples with changing nanotube content

NT Content	D_z (mm^2/hr)	D_{planar} (mm^2/hr)	β (hr^{-1})	γ (hr^{-1})	M∞ (%)
0%	9.62×10^{-4}	2.25×10^{-3}	5.45×10^{-4}	1.26×10^{-4}	1.98
0.25%	9.46×10^{-4}	9.29×10^{-4}	5.56×10^{-4}	1.17×10^{-4}	1.97
0.50%	5.14×10^{-4}	3.45×10^{-3}	7.68×10^{-4}	5.59×10^{-5}	2.02
1.00%	7.93×10^{-4}	2.80×10^{-3}	9.20×10^{-4}	2.00×10^{-4}	2.05
1.50%	9.70×10^{-4}	6.43×10^{-4}	1.87×10^{-3}	6.22×10^{-4}	1.91
2.00%	1.25×10^{-3}	1.01×10^{-3}	1.17×10^{-3}	5.51×10^{-4}	2.19
3.00%	1.62×10^{-3}	2.25×10^{-4}	1.41×10^{-3}	8.00×10^{-4}	2.08

Once again the moisture equilibrium values have a peak at 2.00% nanotube content samples with a value of 2.19%, noticeably higher than the rest of the nanotube content samples that typically stay relatively close to each other right around 2.0% moisture content. Similarly to the previous planar size, the β values are shown to consistently be higher values than the γ values, meaning the bound molecules are more likely to become unbound than the unbound molecules are to become bound. The numerical values of the trends that were seen when plotting each of the moisture properties against the nanotube weight content represent the percentage differences between the property values.

3.4.3. SAMPLES WITH PLANAR SIZE OF 1.25in x 1.25in

The final planar size from the experiment was the largest planar size, 1.25in x 1.25in. This planar size showed the most consistency within its data because the larger size is more forgiving about small mass changes. Showing the most consistency would suggest that the trends from the previous two planar sizes should be similar, but with a more stabilized trend with less fluctuation.

The relationship between thickness diffusivity and nanotube weight content for samples with planar size 1.25in x 1.25in can be seen in Figure 57. Commonly, the relationship between these two properties has been an initial decrease in thickness diffusivity followed by a constant increase with increasing nanotube weight content. Figure 57 shows some differences from the previous planar size comparison of the same moisture property. There is not initial drop in this case; instead the first two samples have an initial rise that does not seem to fit well within the trend, followed by the rest of the nanotube weight contents. After the initial jump the 1.0% nanotube content takes its similar path of being similar to the neat epoxy sample, and from this point there is a gradual increase in thickness diffusivity as there is an increase in nanotube weight content. The nanotube content levels from 1.0% to 3.0% follows the same trend as the planar sizes previously shown, reinforcing the idea that from 1.0% nanotube content on there is a relationship of increasing diffusivity with increasing nanotube content.

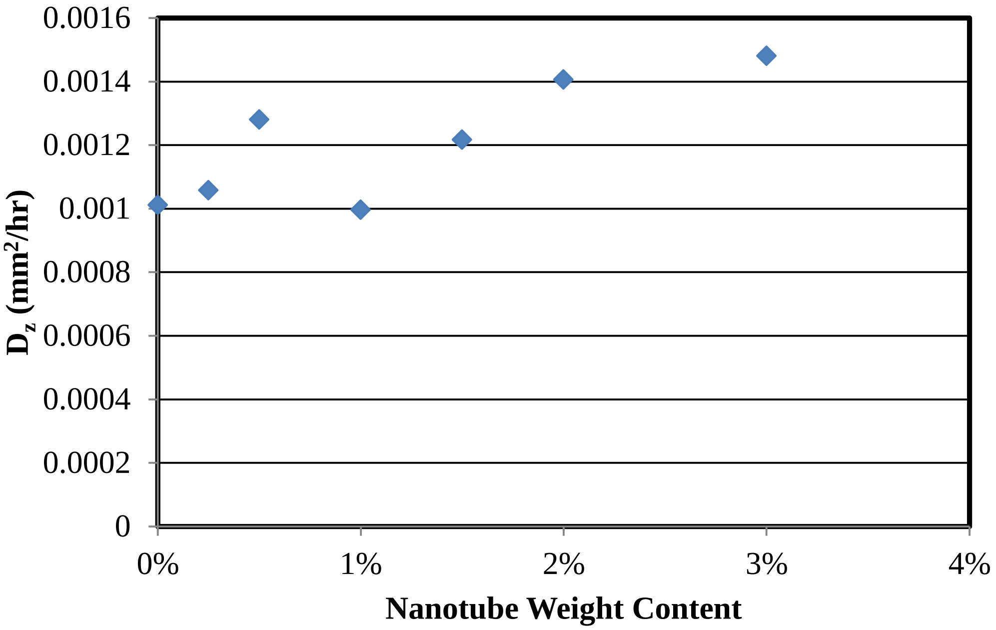

Figure 57: Comparison between thickness diffusivity for 1.25in x 1.25in planar size samples based on nanotube weight content

Figure 58 shows the relationship between the planar diffusivity and the nanotube weight content. Previously, the relationship has been shown as nanotube weight content increases there in an increase in planar diffusivity until 0.5% nanotube content followed by a decrease in planar diffusivity. Figure 58 shows, in general, the same trend, but with 1.0% nanotube content being the peak of increasing planar diffusivity. Previously the 1.0% nanotube content sample would make a similar jump from the 0.5% nanotube content sample, but in the decreasing direction instead of the increasing direction. The thickness diffusivity showed the first two samples acting differently, but in this case the increase in planar diffusivity value from neat to 0.5% nanotube content stays constant to previous examples reinforcing that the 1.0% nanotube sample shows the differing trend in this case. As expected from the larger planar size samples the consistency from the experimental data has shown an overall closer grouping.

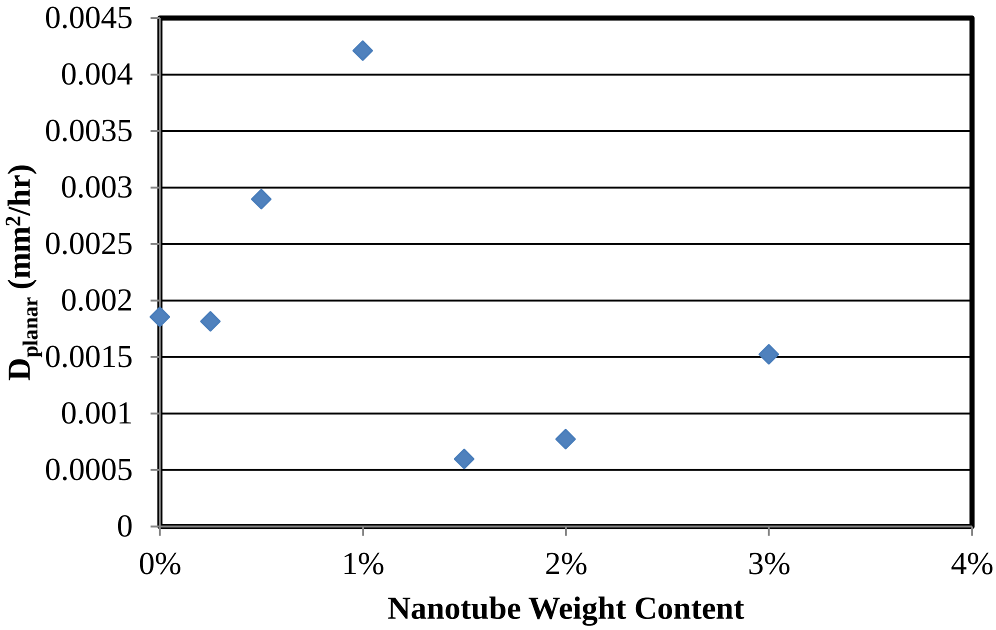

Figure 58: Comparison between planar diffusivity for 1.25in x 1.25in planar size samples based on nanotube weight content

The probability for a bound molecule to become unbound, β, always shows an increase with the nanotube weight content increasing. Typically, in this term, the 1.5% nanotube content sample will take a drastic jump in comparison to the rest of the β values. The larger planar size does not result in as drastic of a change in trend with the 1.5% nanotube content sample, which was expected based on the idea that the fluctuation should not be as drastic. Similarly to the previous moisture absorption property the 1.0% nanotube content shows differences from other planar sizes, instead of having an increase from the 0.5% nanotube content samples, the 1.0% nanotube content samples decrease back to the level of the neat epoxy. Although the data appears to be more grouped than in previous cases, the typical drastic increase in β from the 1.5% nanotube content skews the data, but the rest of the values show similar increases to previous planar sizes.

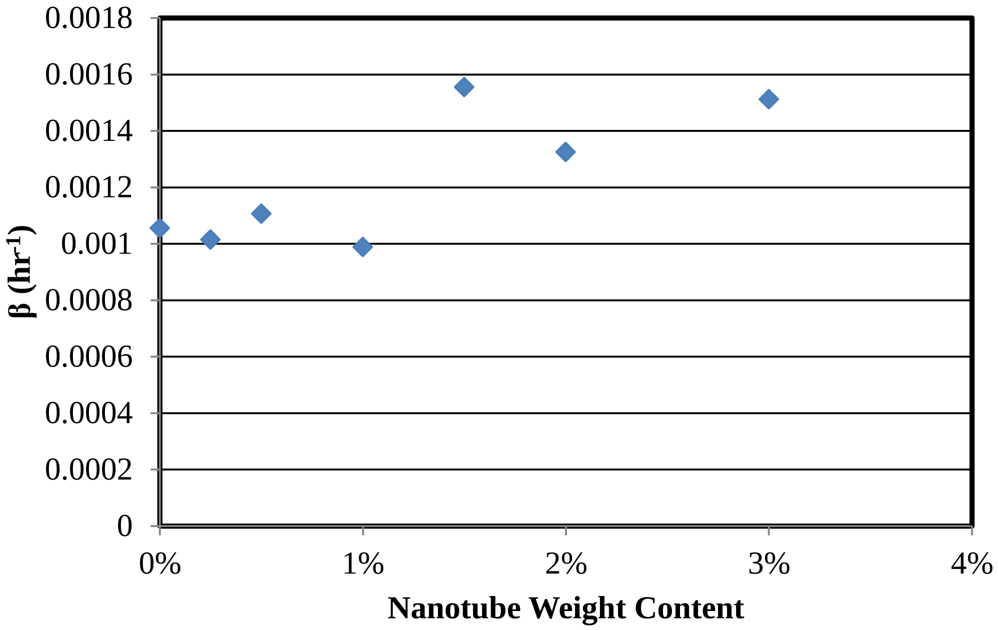

Figure 59: Comparison of the probability for a bound molecule to become unbound for 1.25in x 1.25in planar size samples based on nanotube weight content

For the previous two planar sizes the γ term, probability for an unbound molecule to become bound, has shown an initial small decrease followed by a constant increase for increasing nanotube weight content. Figure 60 shows the relationship between γ and nanotube weight content. The general trend for this relationship for the 1.25in x 1.25in planar size samples shows a constant increase with increasing nanotube weight content. Typically the 0.5% nanotube content samples have shown a decrease in γ instead of the increase that was shown in Figure 60. The unexpected behavior for this planar size has been for the 0.5% and 1.0% nanotube content samples. All of the sample with similar thicknesses and nanotube contents come from the same main laminate so an explanation for a situation where trends are different would be the samples did not have a homogeneous nanotube dispersion and instead potential clusters of nanotubes are present. The 1.5% nanotube content samples also show a less drastic jump from the trend as was shown in the β value as well.

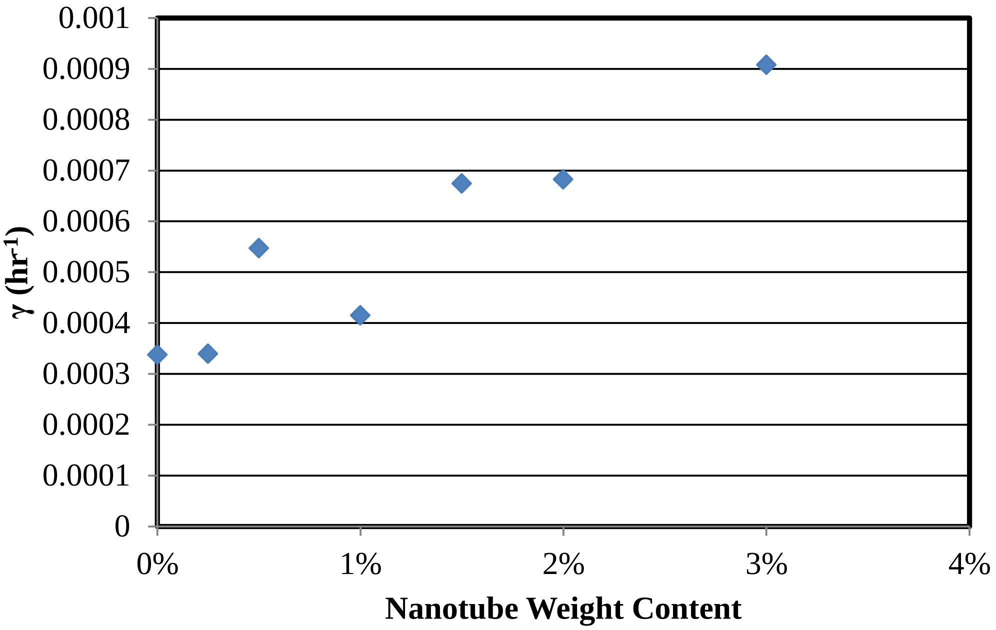

Figure 60: Comparison of the probability for an unbound molecule to become bound for 1.25in x 1.25in planar size samples based on nanotube weight content

Moisture equilibrium's relationship with the nanotube weight content has general been an initial dip followed by a parabolic relationship with a consistent drop in moisture equilibrium value from the 1.5% nanotube content samples. From the previous moisture absorption properties relationships with nanotube weight content at 1.25in x 1.25in planar size, the expected drop from the 1.5% nanotube content sample should be less drastic, but still present. Figure 61 shows the relationship between moisture equilibrium and nanotube weight content for samples with a planar size 1.25in x 1.25in. The lowest moisture absorption value coming from the 0.25% nanotube content samples consistently has been shown for all planar sizes, typically along with the 1.5% nanotube content samples, but for this case that drastic drop in moisture equilibrium from the 1.5% nanotube content samples was more moderate, as expected. The drop off for the 3.0% nanotube content sample was seen in all of the planar sizes, but with that being the only nanotube content percentage following 2.0% it cannot be seen if the moisture equilibrium would continue this decreasing tendency or if the moisture equilibrium would begin to increase again.

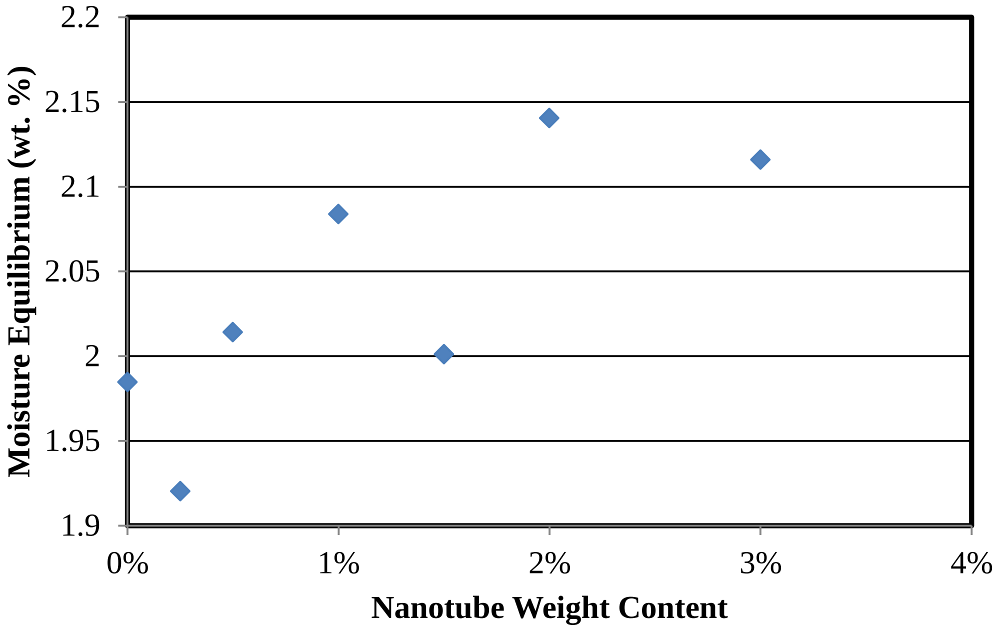

Figure 61: Comparison between moisture equilibrium for 1.25in x 1.25in planar size samples based on nanotube weight content

Numerically the planar and thickness diffusivities are more similar to the 0.75in x 0.75in planar size case when the neat and 3.0% nanotube content samples show closer values to each other again, which should be more accurate because neat epoxy specifically should have the same value for both because it is neat epoxy with no impedance within the samples. The 3.0% nanotube content samples showing the similar values for both diffusivities shows that the dispersion from earlier was relatively homogeneous in the samples.

Table 11: Summary of moisture absorption parameters for 1.25in x 1.25in planar size samples with changing nanotube content

NT Content	D_z (mm^2/hr)	D_{planar} (mm^2/hr)	β (hr^{-1})	γ (hr^{-1})	M∞ (%)
0%	$1.01x10^{-3}$	$1.85x10^{-3}$	$1.06x10^{-3}$	$3.37x10^{-4}$	1.98
0.25%	$1.06x10^{-3}$	$1.81x10^{-3}$	$1.01x10^{-3}$	$3.40x10^{-4}$	1.92
0.50%	$1.28x10^{-3}$	$2.89x10^{-3}$	$1.11x10^{-3}$	$5.47x10^{-4}$	2.01
1.00%	$9.97x10^{-4}$	$4.21x10^{-3}$	$9.88x10^{-4}$	$4.15x10^{-4}$	2.08
1.50%	$1.22x10^{-3}$	$5.97x10^{-4}$	$1.55x10^{-3}$	$6.74x10^{-4}$	2.00
2.00%	$1.41x10^{-3}$	$7.71x10^{-4}$	$1.32x10^{-3}$	$6.82x10^{-4}$	2.14
3.00%	$1.48x10^{-3}$	$1.52x10^{-3}$	$1.51x10^{-3}$	$9.08x10^{-4}$	2.12

As has been common for all planar sizes the moisture equilibrium values for more of the nanotube contents fall around 2.0%, while the higher moisture equilibrium values are close to the 2.15% mark, specifically 2.14% and 2.12% in this case. The β and γ values continue to show a common relationship between the two of them where the β value has higher values. 1.25in x 1.25in planar size moisture absorption properties reinforces that the planar size does not have an effect on the moisture absorption properties and showed trends that follow the same general trend as the 0.75in x 0.75in and 1.00in x 0.75in planar size samples.

3.4.4. SAMPLES WITH THICKNESS OF 1.5mm

Based on the earlier look at neat epoxy samples and how planar size and thickness affected those samples, regardless of planar size or thickness the neat epoxy showed similar moisture absorption properties. After looking at the results for planar sizes and how nanotube weight content affected the moisture absorption properties at each of those sizes the thicknesses have been individually looked at as well. When nanotubes were added to the samples they showed a more noticeable change to the properties with changing thickness than they did for changing planar size, which could result in differences in results for the two different sections.

Figure 62 displays the thickness diffusivity relationship with the nanotube weight content for all samples with a thickness of 1.5mm. The points along the plot are placed at the different nanotube weight contents of 0%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0% and 3.0%. As the nanotube weight content increases there is an initial decrease in thickness diffusivity until 0.5% nanotube content, followed by an increase to the 1.0% nanotube content samples, ending with a final gradual decrease in thickness diffusivity until the 3.0% nanotube weight content where the diffusivity reaches the lowest point. The planar size samples consistently had an initial drop in diffusivity followed by a constant increase showing the difference for the 1.5mm thickness samples. The decrease in thickness diffusivity for a 1.5mm thickness sample as the nanotube weight content increases shows a situation where the nanotubes are constantly working as a blockade slowing the moisture diffusion.

Figure 63 displays the relationship between the planar diffusivity and the nanotube weight content for samples that are 1.5mm thick. Throughout the study of different planar size samples it had been shown that the planar diffusivity would initially increase with increasing weight content and then constantly decreases from a certain point on.

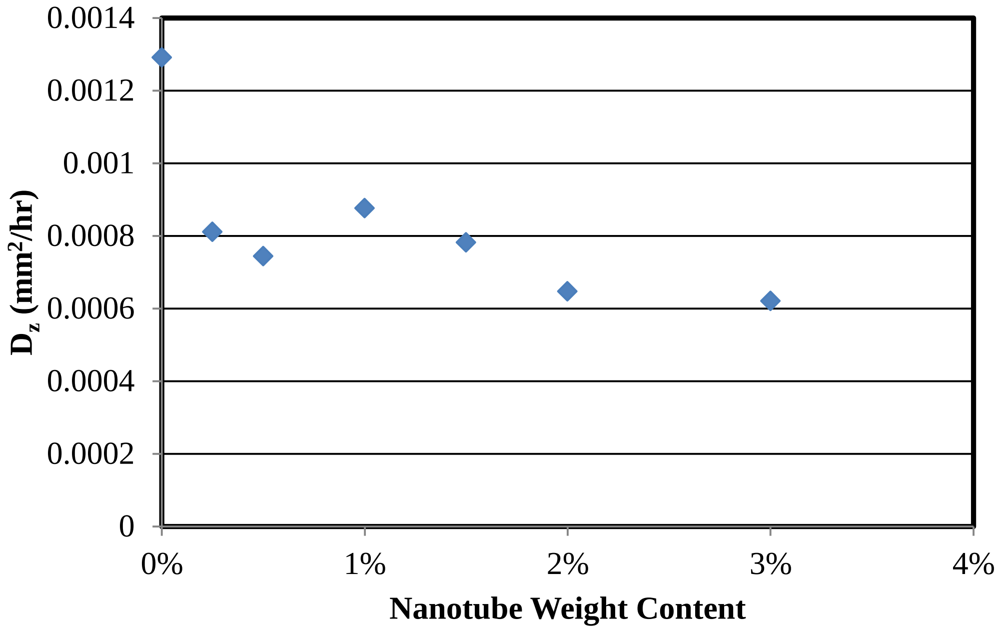

Figure 62: Comparison between thickness diffusivity for 1.5mm thickness samples based on nanotube weight content

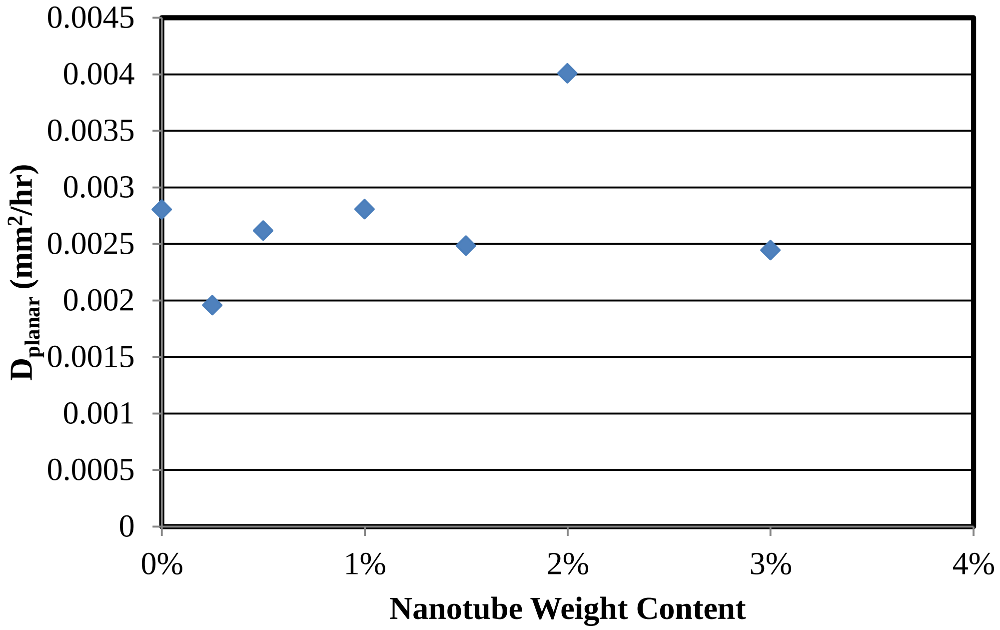

Figure 63: Comparison between planar diffusivity for 1.5mm thickness samples based on nanotube weight content

Figure 63 shows a more consistent trend for planar diffusivity depending on nanotube weight content where the planar diffusivity stays relatively equal to the neat epoxy for all nanotube contents besides 0.25% and 2.0%, which decreases and increases planar diffusivity, respectfully. Based on Figure 63 the addition of nanotubes into an epoxy laminate of 1.5mm thickness there will be no change to the planar diffusivity.

The probability for a bound molecule to become unbound is one of the properties that affect the long term moisture uptake along with the probability for an unbound molecule to become bound. The smaller the value the more likely the molecules are to stay bound and keep stable moisture equilibrium. Figure 64 shows the relationship with this property and the nanotube weight content for all samples that have a thickness of 1.5mm. As the figure shows the initial movement of the β value decreases with the nanotubes added, but quickly returns to about the neat epoxy’s value. After the β value returned to a similar value at 0.5% nanotube weight content the plot shows a constant decrease until 3.0% nanotube weight content. The addition of nanotubes for samples with thickness 1.5mm the addition of nanotubes will result in a decrease in the probability for bound molecules to become unbound.

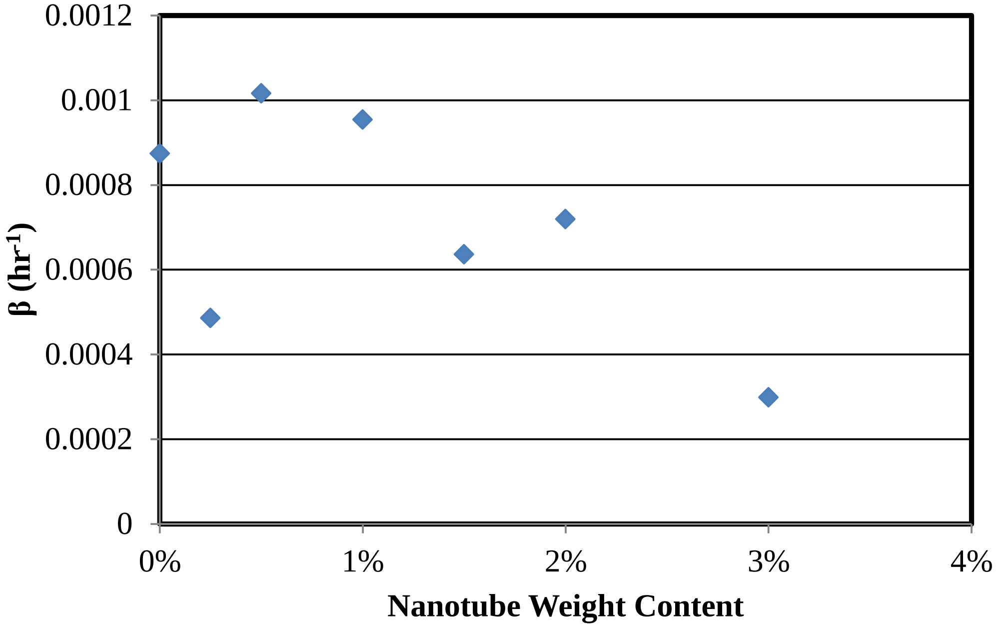

Figure 64: Comparison of the probability for a bound molecule to become unbound for 1.5mm thickness samples based on nanotube weight content

The probability for an unbound molecule to become bound trends similarly to the probability for a bound molecule to become unbound, which should result in a sharp decrease for 0.25% nanotube content, an increase back to slightly greater than the neat epoxy for the 0.5% nanotube content samples followed by a constant decrease in probability for an unbound molecule to become bound. By looking at Figure 65 that trend described has been shown with a less significant increase from 0.25% to 0.5% nanotube content. The values for γ shown on the y-axis are just over twice as small as those values for β. For both of the cases the second lowest probability came from the 0.25% nanotube content samples. The difference between the neat epoxy and the 0.25% nanotube content moisture absorption properties are typically similar to each other because of the small amount of additional nanotubes.

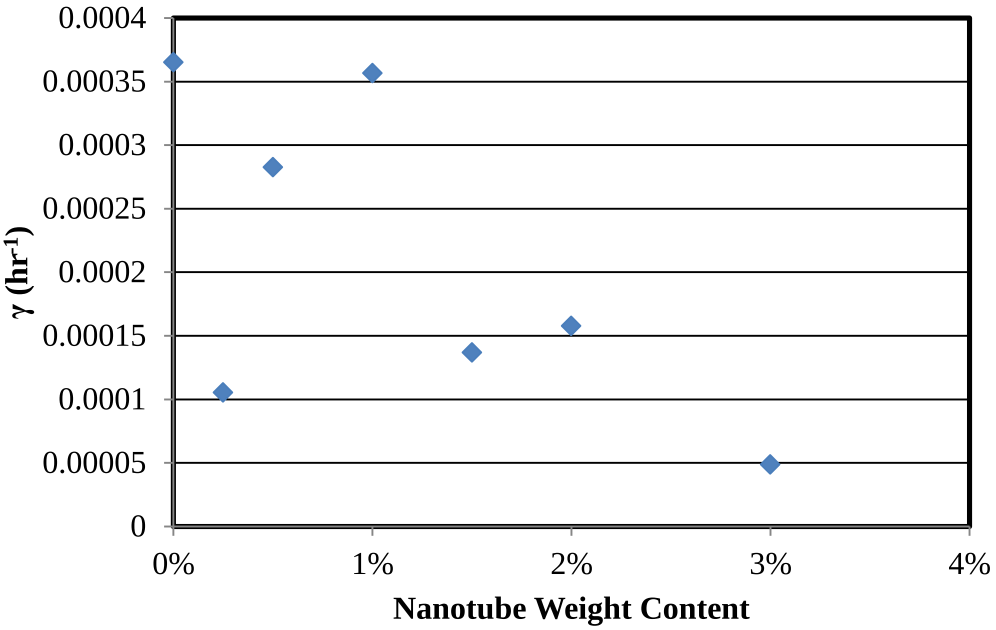

Figure 65: Comparison of the probability for an unbound molecule to become bound for 1.5mm thickness samples based on nanotube weight content

Previous moisture absorption properties have all shown that as the nanotube content increases the moisture equilibrium will increase until 2.0% nanotube content where it will reach a maximum then have a decrease for the 3.0% nanotube content. Figure 66 shows the relationship between moisture equilibrium and nanotube weight content for samples with 1.5mm thickness. Shown in this figure the moisture equilibrium values start much higher than previous comparisons. As the nanotube weight content increases the moisture equilibrium increases, but once again the maximum moisture equilibrium value is found at 2.0% nanotube weight content. The result of the moisture equilibrium study shows that many of the moisture equilibrium values are still within 0.04% of each other, but with a significant increase for the 2.0% and 3.0% nanotube weight content samples. Between all the different categories that are studied the 1.5mm thickness samples have shown the highest moisture equilibrium values.

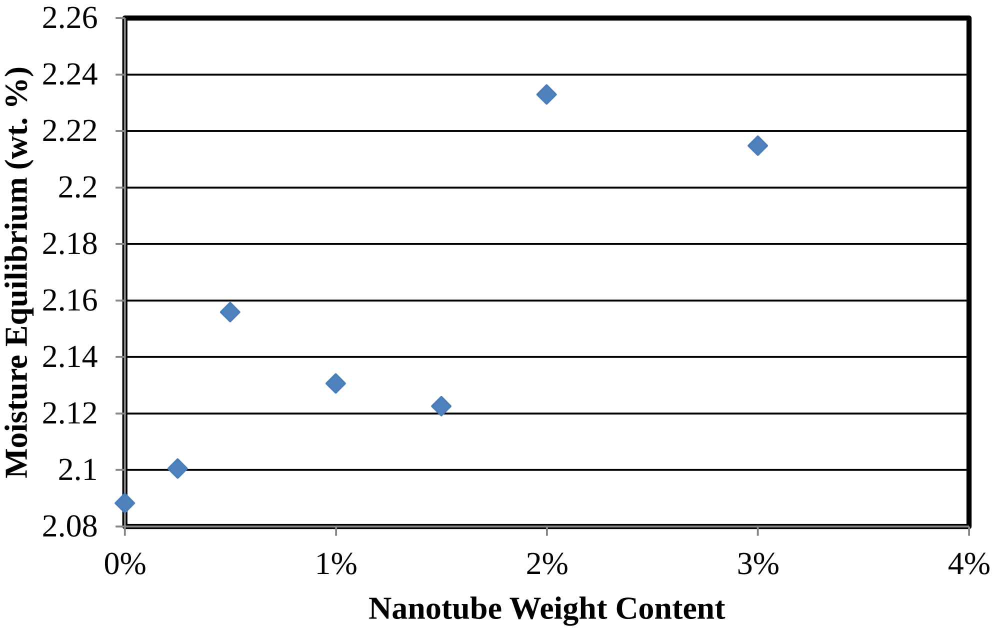

Figure 66: Comparison between moisture equilibrium for 1.5mm thickness samples based on nanotube weight content

The summary of all the numerical values for samples of thickness 1.5mm for the moisture absorption properties can be seen in Table 12. The range of values does not show the typical neat epoxy correlation where both types of diffusivity have close to the same value. Between the different nanotube contents the neat and 0.25% samples do show the closest similarities between planar and thickness diffusivity, which shows that with increased addition of nanotubes the potential for uneven diffusivity increases as well. The planar diffusivity stays more consistent than the thickness diffusivity in this case suggesting the addition of nanotubes affect the diffusivity more through the thickness than it does in the planar direction for samples that have a thickness of 1.5mm. Throughout all of the studies it has been shown that the relationship between β and γ has consistently shown that the β values are always larger numbers than the γ values.

Table 12: Summary of moisture absorption parameters for 1.5mm thickness samples with changing nanotube content

NT Content	**D_z (mm^2/hr)**	**D_{planar} (mm^2/hr)**	**β (hr^{-1})**	**γ (hr^{-1})**	**$M\infty$ (%)**
0%	$1.29x10^{-3}$	$2.80x10^{-3}$	$8.74x10^{-4}$	$3.65x10^{-4}$	2.09
0.25%	$8.11x10^{-4}$	$1.95x10^{-3}$	$4.86x10^{-4}$	$1.05x10^{-4}$	2.10
0.50%	$7.44x10^{-4}$	$2.62x10^{-3}$	$1.02x10^{-3}$	$2.83x10^{-4}$	2.16
1.00%	$8.76x10^{-4}$	$2.80x10^{-3}$	$9.54x10^{-4}$	$3.57x10^{-4}$	2.13
1.50%	$7.82x10^{-4}$	$2.48x10^{-3}$	$6.36x10^{-4}$	$1.37x10^{-4}$	2.12
2.00%	$6.47x10^{-4}$	$4.01x10^{-3}$	$7.19x10^{-4}$	$1.58x10^{-4}$	2.23
3.00%	$6.21x10^{-4}$	$2.44x10^{-3}$	$2.99x10^{-4}$	$4.87x10^{-5}$	2.21

The moisture equilibrium values vary by a maximum of 0.14% showing similar total differences to the moisture equilibriums found by planar size. While the variance in the moisture equilibrium continues to be similar the values for the moisture equilibrium start higher at 2.08% instead of previously around 1.98%. The addition of nanotubes into samples that have 1.5mm thickness reduces all moisture absorption properties except for the moisture equilibrium. This could be explained by the addition of nanotubes reduces the dispersion of nanotubes, which slows the overall diffusivity, but allows for more moisture to stay within the sample.

3.4.5. SAMPLES WITH THICKNESS OF 1.7mm

As the thickness of a sample increases it was shown previous that this would change the moisture properties more significantly than the changing of the planar size. Based on that information it would be assumed that the 1.7mm thickness samples may not follow the trends of the 1.5mm thickness samples as well as each of the different planar size samples showed moisture absorption property trends. Overall trends of increasing and decreasing may stay the same, but the range of values could be different.

Figure 67 shows the relationship between the thickness diffusivity and the nanotube weight content for samples of thickness 1.7mm. From the figure it can be seen that the thickness diffusivity stays relatively consistent throughout the addition of increasingly more nanotubes. Based on the small changes the relationship could be stated that initially there is a decrease in thickness diffusivity until samples of nanotube content 0.5%. An increase in thickness diffusivity can be seen between 0.5% and 1.0% nanotube content, and values over 1.0% show a slight decrease. All of the data for these thickness diffusivities is shown to be within 0.0003 mm^2/hr. Although many other thickness diffusivity plots showed a standard trend for the relationship, because of how close all of these are in diffusivity the trend seems to be that no affect has been made on the thickness diffusivity by the addition of nanotubes.

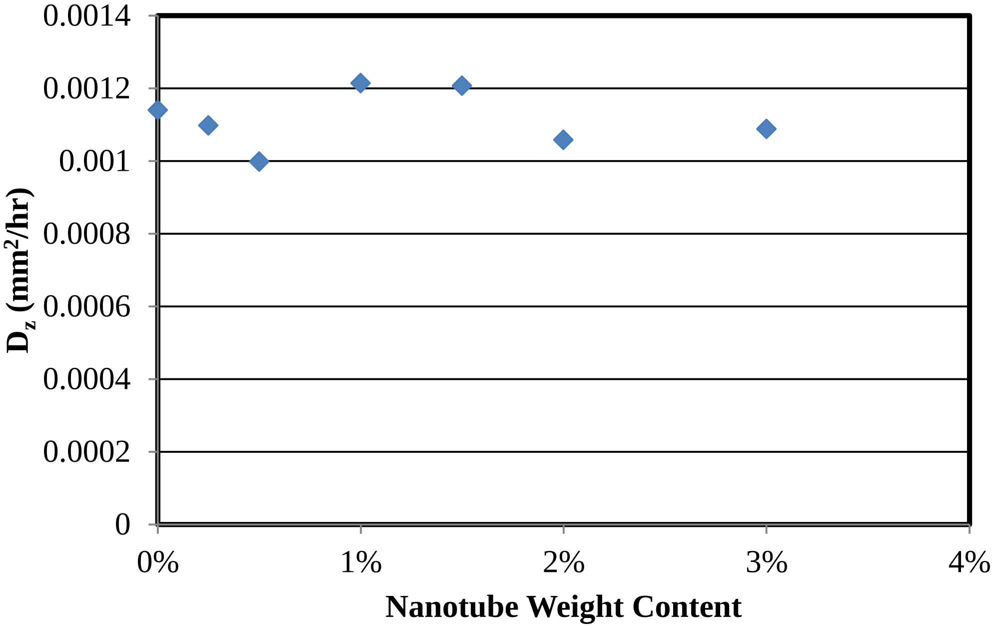

Figure 67: Comparison between thickness diffusivity for 1.7mm thickness samples based on nanotube weight content

Figure 68 shows the relationship between the planar diffusivity and the nanotube weight content for samples with thickness of 1.7mm. The planar diffusivity, unlike the thickness diffusivity, does show changes depending on the amount of nanotubes within the sample. From the neat epoxy samples to the 3.0% nanotube content samples there is a general trend of decreasing planar thickness with the increasing nanotube weight content. There are two nanotube weight content samples that do not follow the same trend as the rest of the values where there is a sudden increase in planar diffusivity, this happens at 1% and 2% nanotube content. The neat epoxy sample shows the second highest planar diffusivity to the 1.0% nanotube content.

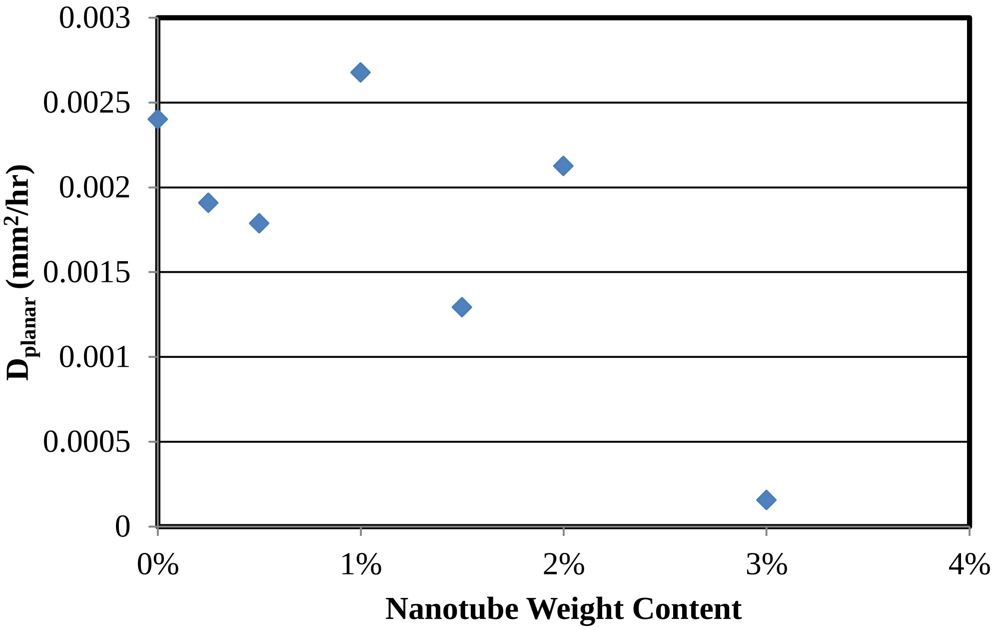

Figure 68: Comparison between planar diffusivity for 1.7mm thickness samples based on nanotube weight content

For the 1.5mm thickness samples the probability for a bound molecule to become unbound showed a decreasing trend with the increasing nanotube weight content. The same moisture absorption property and nanotube weight content were shown for the 1.7mm thickness in Figure 69. Unlike the 1.5mm samples, the 1.7mm thick samples show increases and decreases in the values. Initially β decreases with increasing nanotubes until 0.5% nanotube content, but then starts to increase until 1.5%

nanotube content where it then gradually decreases again until the 3.0% nanotube content samples. Increases and decreases in β show the amount of nanotubes within the samples continuously affect the probability for a bound molecule to become unbound, almost always increasing from neat epoxy. Many of the other studies have shown either an increase or a decrease overall, while the 1.7mm thickness samples show regardless of nanotube content the probability of a bound molecule to become unbound there could be an increase or a decrease.

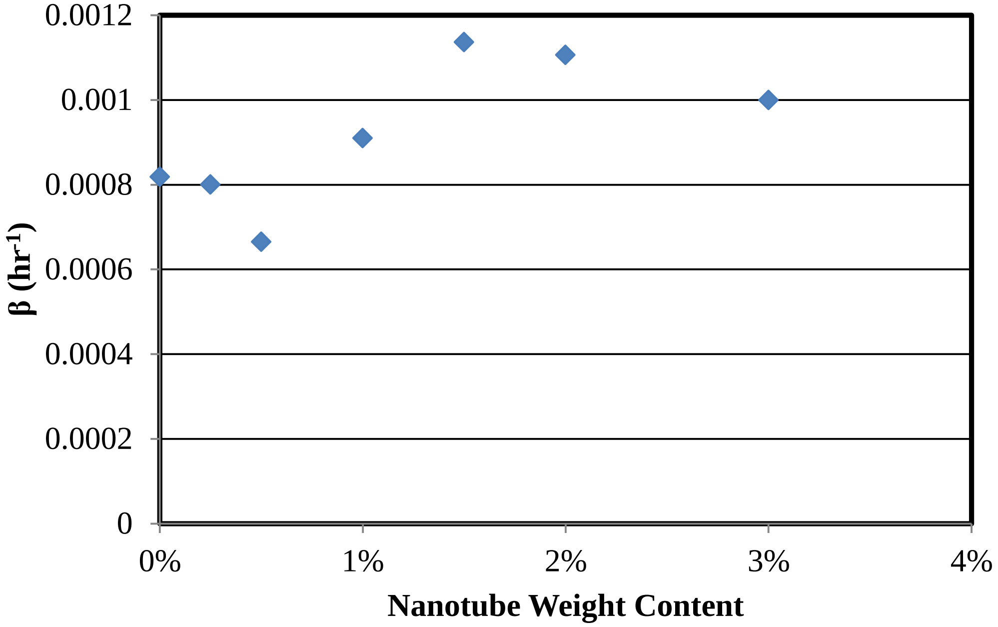

Figure 69: Comparison of the probability for a bound molecule to become unbound for 1.7mm thickness samples based on nanotube weight content

Commonly, it has been seen the probability for a bound molecule to become unbound, and the probability for an unbound molecule to become bound show relatively the same relationship with the nanotube weight content. Figure 70 shows the relationship between γ and the nanotube weight content. As expected the relationship shown in Figure 70 follows similar patterns to the relationship between Figure 69. The probability for an unbound molecule to become bound shows more closely related values than for the bound molecules to become unbound. As the γ values decrease the moisture absorption becomes closer to Fickian diffusion behavior, so the increase in the value makes sense with increasing nanotube content where the early values have relatively low impedance.

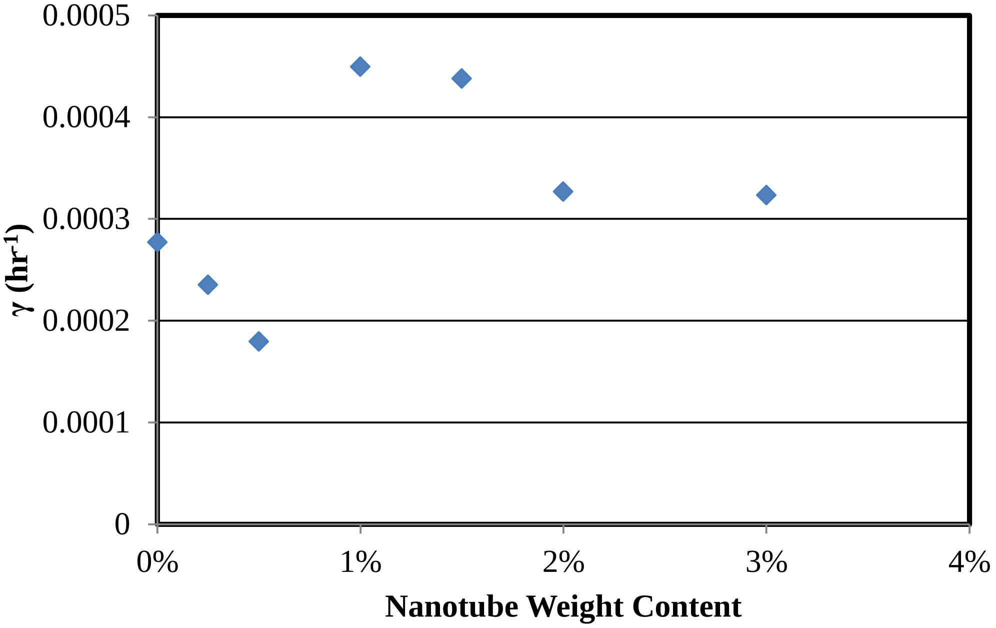

Figure 70: Comparison of the probability for an unbound molecule to become bound for 1.7mm thickness samples based on nanotube weight content

The moisture equilibrium values typically have fallen within approximately 0.15% of each other, regardless of nanotube content. For the samples with 1.7mm thickness the moisture equilibrium relationship with nanotube weight content has been displayed in Figure 71. The moisture equilibrium values have a general trend of increasing with the increasing nanotube weight content, which seems to be void related because the nanotubes should not be retaining moisture and are taking up space that would, in other cases, have moisture in that area. Nanotube content samples of 0.25% typically have shown a decrease in moisture equilibrium before the increasing trend with increasing nanotubes.

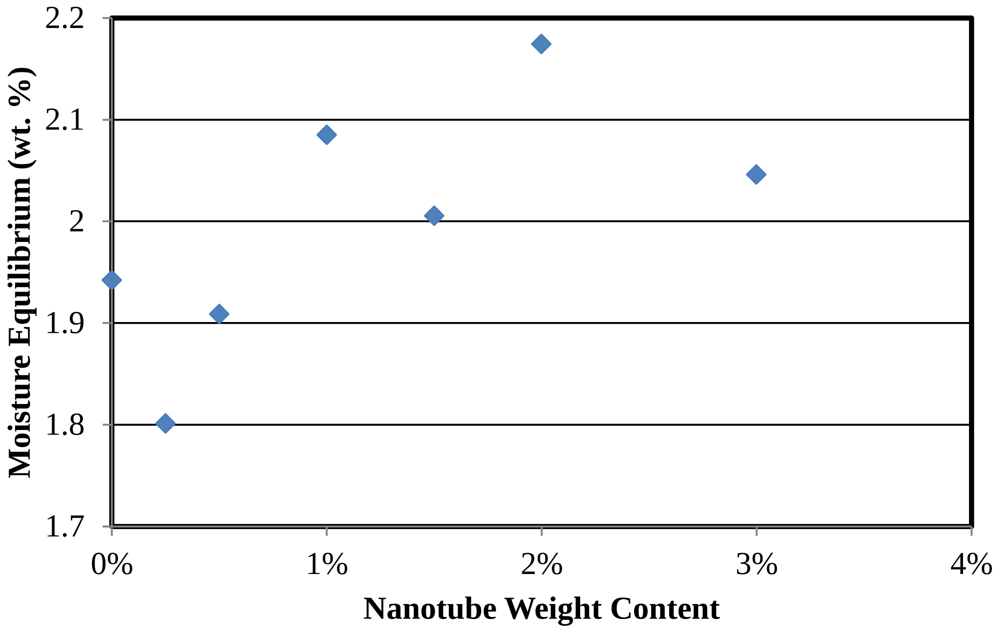

Figure 71: Comparison between moisture equilibrium for 1.7mm thickness samples based on nanotube weight content

A small percentage of nanotubes resulted in more homogeneously dispersed nanotubes. The samples for the 1.5% nanotube content and the 3.0% nanotube content have consistently shown that lower moisture equilibrium levels than the percentages are them. With only the 3.0% nanotube content level following the 2.0% nanotube content level the trend seen cannot be determined if the moisture equilibrium will continue to fall or if the 3.0% nanotube content moisture equilibrium level shows the same drop and rise as the 1.5% nanotube content moisture equilibrium.

The summary of the moisture absorption properties found for the 1.7mm thickness samples can be seen in Table 13. From the table the first noticeable change from previous tables would be the larger range in moisture equilibrium. Previously, moisture equilibrium shows a range of values separate by approximately 0.15%, but in the case of 1.7mm thickness samples the moisture equilibrium shows a range from 1.80% to 2.17%.

Table 13: Summary of moisture absorption parameters for 1.7mm thickness samples with changing nanotube content

NT Content	D_z (mm^2/hr)	D_{planar} (mm^2/hr)	β (hr^{-1})	γ (hr^{-1})	M_∞ (%)
0%	1.14×10^{-3}	2.40×10^{-3}	8.19×10^{-4}	2.77×10^{-4}	1.94
0.25%	1.10×10^{-3}	1.91×10^{-3}	8.00×10^{-4}	2.35×10^{-4}	1.80
0.50%	9.98×10^{-4}	1.79×10^{-3}	6.65×10^{-4}	1.79×10^{-4}	1.91
1.00%	1.21×10^{-3}	2.68×10^{-3}	9.10×10^{-4}	4.50×10^{-4}	2.08
1.50%	1.21×10^{-3}	1.29×10^{-3}	1.14×10^{-3}	4.38×10^{-4}	2.01
2.00%	1.06×10^{-3}	2.13×10^{-3}	1.11×10^{-3}	3.27×10^{-4}	2.17
3.00%	1.09×10^{-3}	1.55×10^{-3}	9.99×10^{-4}	3.23×10^{-4}	2.05

The 2.17% moisture content has been common with all of the different thicknesses and planar sizes, but the lower end of the moisture equilibrium typically shows to be around 2.0%. The 0.25% nanotube content samples are significantly lower than the rest of the moisture equilibriums separated by itself by 0.11% moisture content. The 1.7mm thickness samples also show the strongest correlation between the thickness and planar diffusivities throughout the different nanotube content levels. The diffusivities both showed the most consistent levels individually, as well, seemingly being unaffected by the addition of nanotubes.

3.4.6. SAMPLES WITH THICKNESS OF 2.0mm

The thickest of the samples made were the 2.0mm thickness samples. The 2.0mm thickness samples would have the most significant edge effects taking place, because the edges are closer to the planar dimensions in size. The 1.5mm and 1.7mm thickness samples showed many differences in the moisture absorption properties resulting in an expectation that the 2.0mm thickness samples would have differences from both of the previous two thicknesses.

The relationship between the thickness diffusivity and the nanotube weight content has changed between the two previous thicknesses of samples, where the 1.5mm thickness samples showed a decrease in the thickness diffusivity as the nanotube weight content increased, the 1.7mm thickness samples showed essentially no change in the diffusivity value. Figure 72 shows the comparison of the thickness diffusivity depending on the nanotube weight content for samples of 2.0mm thickness. These samples follow how the 1.5mm thickness samples trended, with a general decrease in diffusivity as the nanotube content increases.

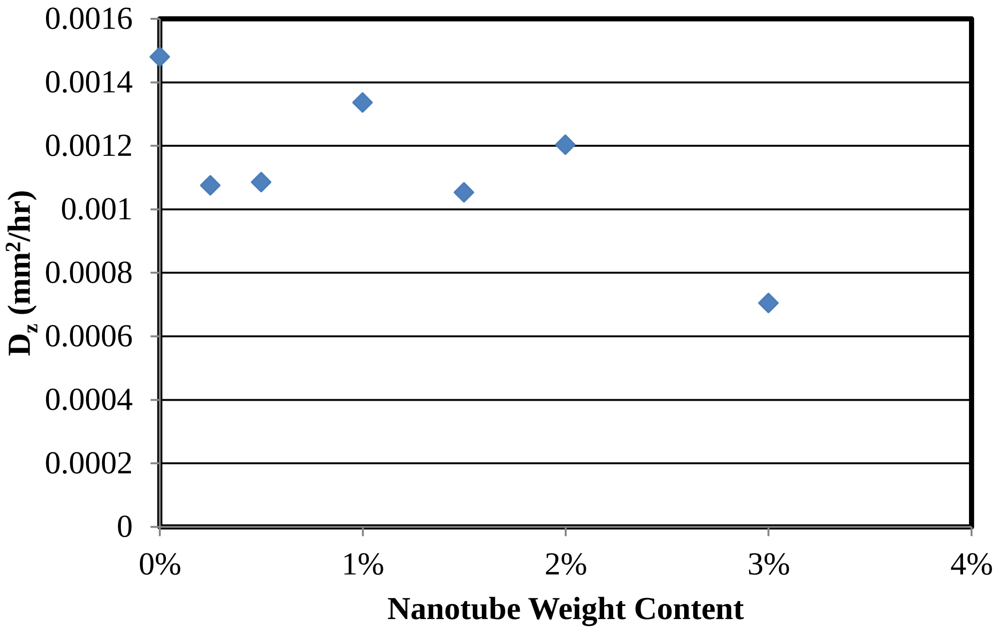

Figure 72: Comparison between thickness diffusivity for 2.0mm thickness samples based on nanotube weight content

The plot shows a combination between the two because after the initial decrease in diffusivity with the addition of 0.25% nanotubes the rest of the values stay relatively consistent until the large decrease in diffusivity for the 3.0% nanotube content samples. The significant change in the moisture absorption properties for the 3.0% nanotube content samples has not been seen throughout the rest of the studies. These samples being the thickest along with the 3.0% nanotube content samples having the shortest amount of time being immersed, these traits could affect the moisture absorption properties that are recovered because the experimental data has not been stabilized for as long of a time.

The planar diffusivity relationship with nanotube weight content for samples of 2.0mm thickness can be seen in Figure 73. The relationship between these two properties shows that with the increase in nanotube weight content the planar diffusivity changes around 0.001mm^2/hr which relates more closely to the 1.5mm thickness samples making the 1.7mm thickness samples seem to be the size that are acting differently than the other two. Similarly to the thickness diffusivity plot the planar diffusivity shows the 3.0% nanotube content samples making a distinct jump in value to the other nanotube content samples.

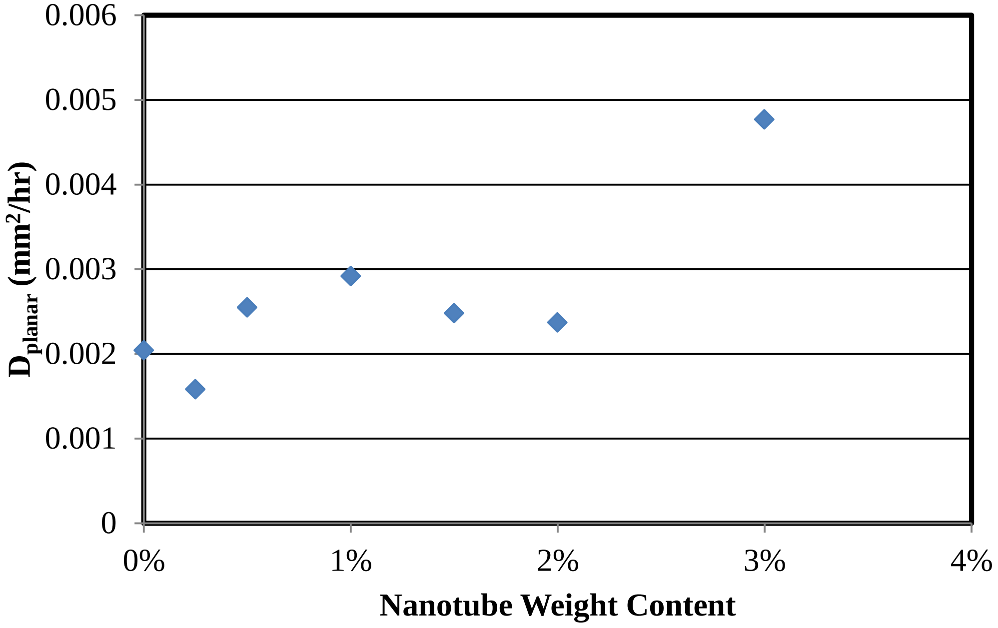

Figure 73: Comparison between planar diffusivity for 2.0mm thickness samples based on nanotube weight content

The 3.0% nanotube content samples showing such a large difference for moisture absorption property reinforces that the experimental data for these samples could have possibly not had the time to stabilize as well as the other samples, skewing the moisture absorption properties that were recovered.

The probability for a bound molecule to become unbound relationship with nanotube weight content for samples with thickness 2.0mm has been shown in Figure 74. For the case of samples with thickness of 2.0mm the β that was recovered stays constant from the neat epoxy through the 2.0% nanotube content. The theme throughout the 3.0% nanotube content samples has been the drastic change in some way between the moisture absorption property values for that compared to the rest of the samples. For the β value the 3.0% nanotube content shows a drastic increase representing that the molecules are more likely to change from being bound to unbound.

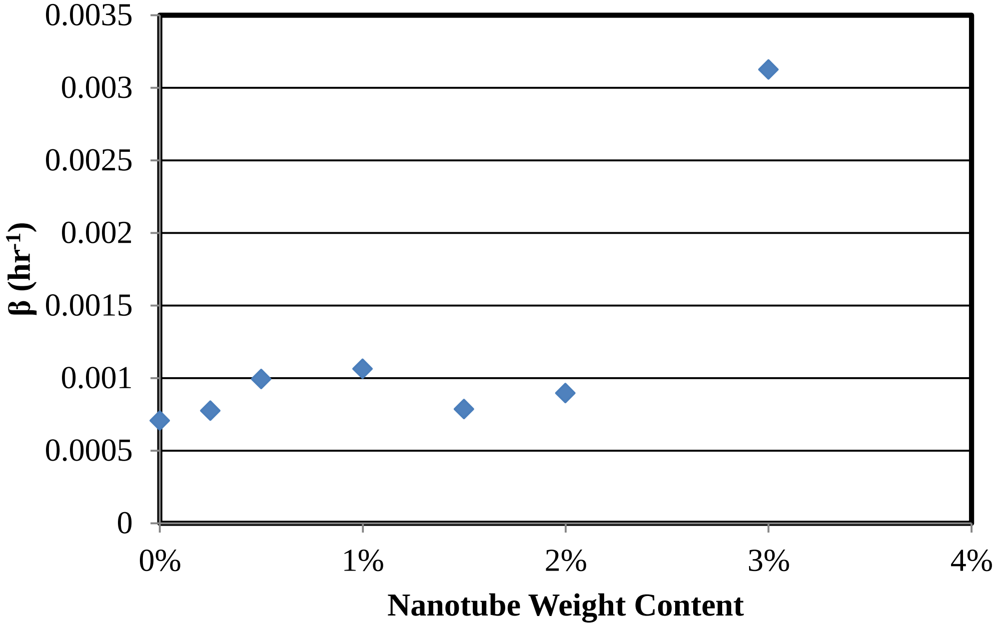

Figure 74: Comparison of the probability for a bound molecule to become unbound for 2.0mm thickness samples based on nanotube weight content

The presence of nanotubes increasing the β value would be the assumed based on factors such as the moisture equilibrium consistently increasing with the increasing nanotubes because the β term affects the long term moisture uptake instead of the initial moisture uptake.

The probability for an unbound molecule to become bound typically will have the same relationship with the nanotube weight content as the probability for a bound molecule to become unbound. Figure 74, when ignoring the 3.0% jump in β the relationship shown in Figure 75 follows a similar trend. Figure 75 shows the relationship between the probability for an unbound molecule to become bound and nanotube weight content for samples with thickness 2.0mm.

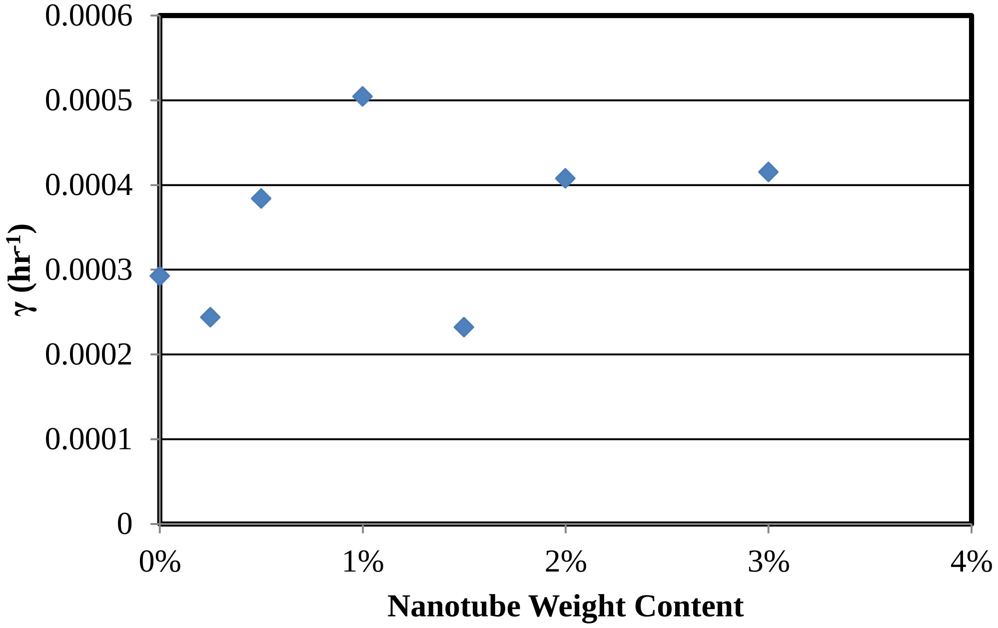

Figure 75: Comparison of the probability for an unbound molecule to become bound for 2.0mm thickness samples based on nanotube weight content

The relationship shows an initial increase until the 1.0% nanotube content samples followed by a decrease that levels off for the 2.0% and 3.0% samples at a higher value than the neat epoxy. The increase in γ has been shown throughout most sample categories resulting in more potential change in moisture uptake within the later stages, and showing the moisture uptake to be less Fickian.

Moisture equilibrium has shown the propensity to increase with the increasing nanotube weight content showing that nanotubes increase the available area for the moisture to fill in a sample. The multiple nanotube weight content samples show a similar trend besides the 1.5% and 3.0% nanotube content samples. The moisture equilibrium relationship with the nanotube weight content has been shown in Figure 76 for samples that are 2.0mm thickness.

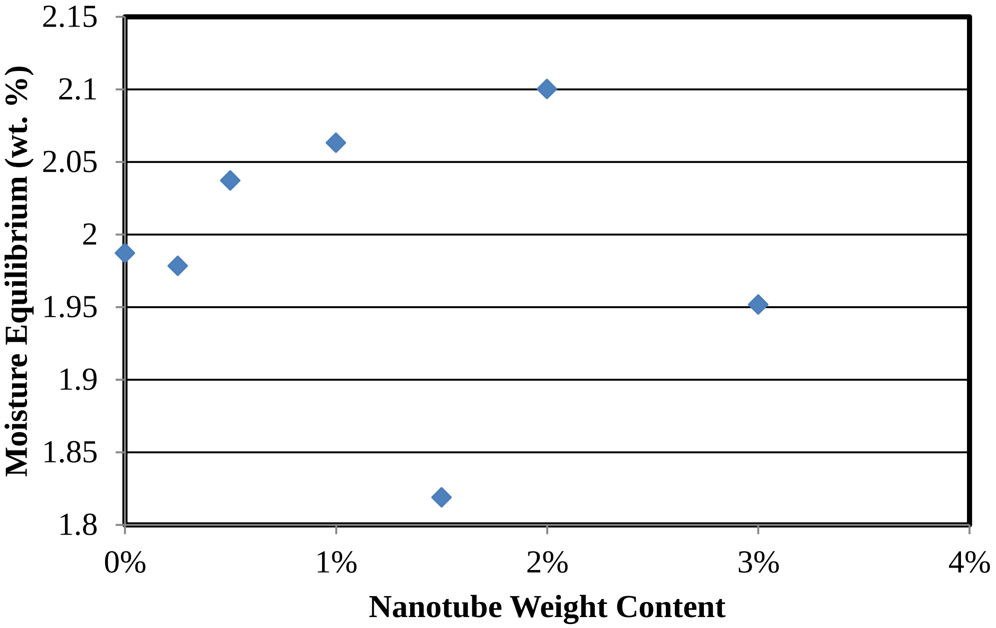

Figure 76: Comparison between moisture equilibrium for 2.0mm thickness samples based on nanotube weight content

The 1.5% nanotube content samples have consistently shown a decrease in moisture equilibrium compared to the rest of the samples based concluding that the 1.5% nanotube samples microstructure should be different than the other samples. The 3.0% nanotube content samples moisture equilibrium values along with the β and γ trending randomly compared to the other samples has been explained by the shorter experimental time where the samples were not able to fully stabilize for the moisture equilibrium value.

Table 14 shows the summary of moisture absorption parameters for samples with a 2.0mm thickness along with changing nanotubes. From the table it can be seen that the values for the thickness diffusivity are much closer than the trend from the figure shows.

Table 14: Summary of moisture absorption parameters for 2.0mm thickness samples with changing nanotube content

NT Content	D_z (mm^2/hr)	D_{planar} (mm^2/hr)	β (hr^{-1})	γ (hr^{-1})	M_∞ (%)
0%	1.48×10^{-3}	2.04×10^{-3}	7.05×10^{-4}	2.92×10^{-4}	1.99
0.25%	1.08×10^{-3}	1.58×10^{-3}	7.73×10^{-4}	2.44×10^{-4}	1.98
0.50%	1.08×10^{-3}	2.55×10^{-3}	9.91×10^{-4}	3.84×10^{-4}	2.04
1.00%	1.34×10^{-3}	2.92×10^{-3}	1.06×10^{-3}	5.04×10^{-4}	2.06
1.50%	1.05×10^{-3}	2.48×10^{-3}	7.85×10^{-4}	2.32×10^{-4}	1.83
2.00%	1.20×10^{-3}	2.37×10^{-3}	8.94×10^{-4}	4.08×10^{-4}	2.10
3.00%	7.04×10^{-4}	4.77×10^{-3}	3.12×10^{-3}	4.15×10^{-4}	1.95

All but the 3.0% nanotube content samples show a close similarity in numerical value to the neat epoxy. The planar diffusivity shows similar values to the thickness diffusivity but partially higher. The planar diffusivity should show similar if not equal values to the thickness diffusivity at the neat epoxy samples. Although the planar diffusivity samples are constantly higher than the thickness diffusivity, the range of values follows the same trend as the thickness diffusivity showing the two diffusivities are changing as a pair and not alone. Moisture equilibrium shows a similarly large range of values to the 1.7mm thickness samples where the lower end of the moisture equilibrium shows a value of 1.83%, which had commonly been around 2.0% for the lower end of moisture equilibrium.

CHAPTER 4: CONCLUSION

The addition of nanotubes as a reinforcement for epoxy laminates did have an effect on the moisture absorption properties. The addition of nanotubes did not have a distinctly positive or negative effect on the moisture absorption properties depending on the nanotube content within the samples. The addition of nanotube content, regardless of the size of the sample, resulted in an overall increase in the moisture equilibrium from the neat epoxy. The addition of nanotube did not necessarily have a continuous rise in the moisture equilibrium as the nanotube content increased, but with the presence of nanotubes the moisture equilibrium level was increased. The maximum moisture equilibrium reaches a maximum value with the 2.0% and 3.0% nanotube content samples where there was a noticeable jump in the values from the other nanotube content samples. The probability for a bound molecule to become unbound and the probability for an unbound molecule to become bound showed a direct relationship with the increasing nanotube content. The increasing probabilities with increasing nanotube content were expected because with the addition of more nanotubes, the sample becomes more nonuniform resulting in a higher chance for the water molecules exhibit a higher level of non-Fickian behavior. The increased probabilities affect the moisture uptake more during the later stages of moisture uptake instead of the early stages, which are more dependent on the diffusivity values from the samples.

The diffusion coefficients affect the rate that moisture can diffuse into the material. The diffusion coefficients control the early Fickian portion of the moisture uptake, the linear growth at the start of immersion in water. The planar and the thickness diffusivities had different relationships when changing the nanotube content.

For the planar diffusivity, the general relationship with the nanotube content was an initial increase in the planar diffusivity at small nanotube content levels followed by an overall decrease with increasing nanotube content above 1.0% by weight. The thickness diffusivity, on the other hand, showed a general trend of the opposite relationship where nanotube content increases and there was an initial decrease in thickness diffusivity followed by a consistent increase. The thickness diffusivity had a smaller range of changing values from the planar diffusivity with the addition of nanotubes, suggesting the nanotube addition affects the edge effects more than the planar effects.

The relationship between the different moisture absorption properties and the nanotube content at higher nanotube levels could have been affected by the nanotube dispersion. The nanotube weight contents of 0.25% and 0.5% displayed the best dispersion among the samples with the 1.5% and 3.0% nanotube content samples displaying the worst dispersion of nanotubes. In general, the addition of nanotubes negatively affected the nanotube dispersion within the sample. The nanotube dispersion has the potential to skew the recovered moisture absorption parameter data because having samples with heavily concentrated nanotube clusters no longer acts as that specific nanotube weight content.

References

[1] Alessi, S., D. Conduruta, G. Pitarresi, C. Dispenza, and G. Spadaro. "Accelerated Ageing Due to Moisture Absorption of Thermally Cured Epoxy Resin/polyethersulphone Blends. Thermal, Mechanical and Morphological Behaviour." Polymer Degradation and Stability 96 (2011): 642-48.

[2] Wong, T. C., and L. J. Broutman. "Moisture Diffusion in Epoxy Resins Part I. Non-Fickian Sorption Processes." *Polymer Engineering and Science* 25.9 (1985): 521-28.

[3] Lin, Y.c., and X. Chen. "Moisture Sorption–desorption–resorption Characteristics and Its Effect on the Mechanical Behavior of the Epoxy System." *Polymer* 46.25 (2005): 11994-2003.

[4] Chen, X, S. Zhao, and L. Zhai. "Moisture Absorption and Diffusion Characterization of Molding Compound." *Journal of Electronic Packaging* 127.4 (2005): 460.

[5] Radha, J.c., and C. Ranganathaiah. "Effect of Hygrothermal Aging on the Diffusion of Seawater in Epoxy/glass Composites Studied by Positron Lifetime Spectroscopy." *Polymer Composites* 29.2 (2008): 149-55.

[6] Zheng, Q., and R.j. Morgan. "Synergistic Thermal-Moisture Damage Mechanisms of Epoxies and Their Carbon Fiber Composites." *Journal of Composite Materials* 27.15 (1993): 1465-478.

[7] Popineau, S., C. Rondeau-Mouro, C, Sulpice-Gaillet, and M. E.r. Shanahan. "Free/bound Water Absorption in an Epoxy Adhesive." *Polymer* 46.24 (2005): 10733-0740.

[8] Zhou, J., and J. P. Lucas. "Hygrothermal Effects of Epoxy Resin. Part I: The Nature of Water in Epoxy." *Polymer* 40.20 (1999): 5505-512.

[9] Zhou, J., and J. P. Lucas. "Hygrothermal Effects of Epoxy Resin. Part II: Variations of Glass Transition Temperature." *Polymer* 40.20 (1999): 5513-522.

[10] El-Sa'ad, L., M. I. Darby, and B. Yates. "Moisture Absorption by Epoxy Resins: The Reverse Thermal Effect." *Journal of Materials Science* 25 (1990): 3577-582.

[11] Barkoula, N. M., A. Paipetis, T. Matikas, A. Vavouliotis, P. Karapappas, and V. Kostopoulos. "Environmental Degradation of Carbon Nanotube-modified Composite Laminates: A Study of Electrical Resistivity." *Mechanics of Composite Materials* 45.1 (2009): 21-32.

[12] Wang, B., X. Zhou, J. Yin, and L Wang. "Investigation on Some Matrix-dominated Properties of Hybrid Multiscale Composites Based on Carbon Fiber/carbon Nanotube Modified Epoxy." *Journal of Applied Polymer Science* 128.2 (2013): 990-96.

[13] Zulfli, N. M., A. A. Bakar, and W. Chow. "Mechanical and Water Absorption Behaviors of Carbon Nanotube Reinforced Epoxy/glass Fiber Laminates." *Journal of Reinforced Plastics and Composites* 32.22 (2013): 1715-721.

[14] Guadagno, L., L. Vertuccio, A. Sorrentino, M. Raimondo, C. Naddeo, V. Vittoria, G. Iannuzzo, E. Calvi, and S. Russo. "Mechanical and Barrier Properties of Epoxy Resin Filled with Multi-walled Carbon Nanotubes." *Carbon* 47.10 (2009): 2419-430.

[15] Chen, Z., D. Pierre, H. He, S. Tan, C. Pham-Huy, H. Hong, and J. Huang. "Adsorption Behavior of Epirubicin Hydrochloride on Carboxylated Carbon Nanotubes." *International Journal of Pharmaceutics* 405.1-2 (2011): 153-61.

[16] Li, K., C. Zhang, Z. Du, H. Li, and W. Zou. "Preparation of Humidity-responsive Antistatic Carbon Nanotube/PEI Nanocomposites." *Synthetic Metals* 162.23 (2012): 2010-015.

[17] Jeon, H., J. Park, and M. Shon. "Corrosion Protection by Epoxy Coating Containing Multi-walled Carbon Nanotubes." *Journal of Industrial and Engineering Chemistry* 19.3 (2013): 849-53

[18] Lee, J. H., K. Y. Rhee, and J. H. Lee. "Effects of Moisture Absorption and Surface Modification Using 3-aminopropyltriethoxysilane on the Tensile and Fracture Characteristics of MWCNT/epoxy Nanocomposites." *Applied Surface Science* 256 (2010): 7658-667.

[19] Gojny, F. H., J. Nastalczyk, Z. Roslaniec, and K. Schulte. "Surface Modified Multi-walled Carbon Nanotubes in CNT/epoxy-composites." *Chemical Physics Letters* 370.5-6 (2003): 820-24.

[20] Ciecierska, E., A. Boczkowska, K. J. Kurzydlowski, I. D. Rosca, and S. V. Hoa. "The Effect of Carbon Nanotubes on Epoxy Matrix Nanocomposites."*Journal of Thermal Analysis and Calorimetry* 111 (2013): 1019-024.

[21] Agnihotri, P., S. Basu, and K.k. Kar. "Effect of Carbon Nanotube Length and Density on the Properties of Carbon Nanotube-coated Carbon Fiber/polyester Composites." *Carbon* 49.9 (2011): 3098-106.

[22] Wang, Y., C. Zhang, Z. Du, H. Li, and W. Zou. "Synthesis of Silver Nanoparticles Decorated MWCNTs and Their Application in Antistatic Polyetherimide Matrix Nanocomposite." *Synthetic Metals* 182 (2013): 49-55.

[23] Chen, W., L. Duan, L. Wang, and D. Zhu. "Adsorption of Hydroxyl-and Amino-Substituted Aromatics to Carbon Nanotubes."*Environmental Science & Technology* 42.18 (2008): 6862-868.

[24] Konidari, M. V., D. N. Soulas, K. G. Papadokostaki, and M. Sanopoulou. "Study of the Effect of Modified and Pristine Carbon Nanotubes on the Properties of Poly(vinyl Alcohol) Nanocomposite Films." *Journal of Applied Polymer Science* (2012).

[25] Kuznetsova, A., D. B. Mawhinney, V. Naumenko, J. T. Yates, J. Liu, and R.e. Smalley. "Enhancement of Adsorption inside of Single-walled Nanotubes: Opening the Entry Ports." *Chemical Physics Letters*321.3-4 (2000): 292-96.

[26] Li, D., H. Cui, Q. Fan, Y. Duan, Z. Yuan, L. Ye, and J. Liu. “Study into the Application of Single-Wall Carbon Nanotubes in Isotropic Conductive Adhesives.” *International Conference on Electronic Packaging Technology and High Density Packaging*. (2011): 430-35.

[27] Abacha, N., M. Kubouchi, T. Sakai, and K. Tsuda. "Diffusion Behavior of Water and Sulfuric Acid in Epoxy/organoclay Nanocomposites." *Journal of Applied Polymer Science* 112.2 (2009): 1021-1029.

[28] Alamri, H., and I. M. Low. "Effect of Water Absorption on the Mechanical Properties of Nanoclay Filled Recycled Cellulose Fibre Reinforced Epoxy Hybrid Nanocomposites." *Composites: Part A* 44 (2013): 23-31.

[29] Al-Qadhi, M., N. Merah, Z. M. Gasem, N. Abu-Dheir, and B. J. Abdul Aleem. "Effect of Water and Crude Oil on Mechanical and Thermal Properties of Epoxy-ClayNanocomposites." *Polymer Composites* 96 (2013).

[30] Glaskova, T., and A. Aniskevich. "Moisture Absorption by Epoxy/montmorillonite Nanocomposite." *Composites Science and Technology* 69 (2009): 2711-715.

[31] Kumar, A., and S. Roy. "Modeling of Anomalous Moisture Diffusion in Nanographene Reinforced Thermoset Polymers." *Composite Structures* 122 (2015): 1-7.

[32] Voo, R., M. Mariatti, and L. C. Sim. "Thermal Properties and Moisture Absorption of Nanofillers-filled Epoxy Composite Thin Film for Electronic Application." *Polymers for Advanced Technologies* 23.12 (2012): 1620-627.

[33] Soheilmoghaddam, M., M. Uzir Wahit, S. Mahmoudian, and N. Abdul Hanid. "Regenerated Cellulose/halloysite Nanotube Nanocomposite Films Prepared with an Ionic Liquid." *Materials Chemistry and Physics* 141.2-3 (2013): 936-43.

[34] Grace, L.r., and M.c. Altan. "Characterization of Anisotropic Moisture Absorption in Polymeric Composites Using Hindered Diffusion Model."*Composites Part A: Applied Science and Manufacturing* 43.8 (2012): 1187-196.

[35] Grace, L.r., and M.c. Altan. "Three-dimensional Anisotropic Moisture Absorption in Quartz-reinforced Bismaleimide Laminates."*Polymer Engineering & Science* 54.1 (2013): 137-46.

[36] Grace, L.r., and M.c. Altan. "Non-fickian Three-dimensional Hindered Moisture Absorption in Polymeric Composites: Model Development and Validation." *Polymer Composites* 34.7 (2013): 1144-157.