EFFECT OF MOISTURE ON ELECTRICAL RESISTIVITY OF CNT REINFORCED EPOXY NANOCOMPOSITES

Sima Navabizadeh, Suong V. Hoa and Iosif Daniel Rosca

Concordia Center for Composites
Department of Mechanical and Industrial Engineering
Concordia University
Center for Research in Polymers and Composites in Quebec (CREPEC)
Montreal, Quebec, Canada
hoasuon@alcor.concordia.ca
Web Page: http://concom.encs.concordia.ca

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Abstract
Adding carbon nanotubes into epoxies has been shown to enhance the electrical conductivity of the epoxy. This can be used for many applications such as improving the paintability of the epoxy composites, health monitoring for epoxy composite structures, enhancing the electro magnetic shielding (EMI) of the polymer etc. However, when the modified polymer is exposed to moist environment over some length of time, water diffuses into the epoxy and modifies the properties of the material. The presence of water in the epoxy can modify the electrical behavior of the material, and this can affect the use of electrical conductivity as a way to monitor its integrity. This paper presents an investigation on the effect of moisture on the electrical resistivity of epoxy containing carbon nanotubes. First, effect of different type of nanotubes, and different concentrations of nanotubes on the rate of diffusion as well as the maximum amount of water absorbed were examined. Subsequently, the change in thickness of the samples as a result of the absorption of water was examined. The change in electrical resistivity in the samples as they absorb water was measured.

1. Introduction

Epoxy composites are light-weight materials offering superior properties such as high strength and stiffness and good chemical resistance. They have a wide range of applications in engineering structures such as automobiles and aircrafts. The addition of carbon nanotubes as multifunctional materials to epoxies , further expands their applicability. Carbon nanotubes (CNTs) are nanoscale particles with large aspect ratios (length to diameter), and provide exceptional electrical and thermal conductivity, along with reinforcing the mechanical performance of epoxies. Epoxy composites reinforced with carbon nanotubes, depending on the structure and the content of CNT, can attain a high level of electrical conductivity, and have the potential to be used in electronics industries, as well as sensors for structural health monitoring techniques [1, 2]. However, one drawback in utilizing these materials is that, due to their hydrophilic characteristics, epoxies tend to absorb water in humid environment. The transport of water into the material alters the functionality of carbon nanotubes and affects the inherent and acquired properties of epoxies. That is to say, the electrical properties of the nanocomposite will be subject to change.

There have been significant amount of work on the absorption of water into epoxy composites [3,4]. However, there has been a few work on the effect of water absorption on the electrical properties of epoxy containing CNTs. From the only publication found in the literature [5], the authors made CNT

reinforced epoxy plates with 0.3, 0.5, and 1 wt.% contents of CNT, immersed them in water, and measured their in-situ electrical resistance at different time intervals through the length of the material. For all CNT concentrations, they observed that the electrical resistance initially increased and reached a peak, and then monotonically decreased until the end of immersion. The drops in electrical resistance were more pronounced for samples with less CNT concentrations. They did not provide any information on the dimensions of the samples, and no explanation of the mechanism of electrical resistivity decrease was offered.

2. Experimental:

The Epoxy resin used was EPON™ Resin 862 or Diglycidyl Ether of Bisphenol F supplied by Momentive, USA.

Multi-walled carbon nanotubes were provided from two different suppliers. The first two experiments were conducted using Baytubes® C150P MWCNT purchased from Bayer, Germany. The fabricated samples exhibited very high resistivity values, and noticeable standard deviations were obtained for five samples with the same CNT content. Therefore, to acquire higher conductivity and precision in the electrical resistivity of the samples and to narrow the variability of the values, this CNT was later replaced by Industrial Grade MWCNT supplied by NanoLab Inc., USA. The physical and electrical characteristics of both carbon nanotubes are summarized in Table 1. As can be seen from the table, the aspect ratio of the NLIG carbon nanotube is more than five times bigger than that of C150P, which results in an improved agglomeration of nanotubes, more convenient formation of conductive paths, and finally, lower percolation threshold [1].

Table 1: Comparison of dimensional and percolation properties of Baytubes® C150P and NanoLab Industrial Grade (NLIG) MWCNTs [1].

	Length (μm)	Diameter (nm)	Aspect Ratio	Percolation Threshold p_c (wt.%)	Intrinsic Conductivity σ_0 (S/m)
C150P	0.61	11.61	52.7	0.1883	3981.2
NLIG	3.34	11.54	289.4	0.0117	23075.3

Three concentrations of MWCNT (0.3 %wt, 0.5%wt, and 1%wt), were considered for the epoxy system. Since the percolation threshold of the C150P was nearly 0.2 wt.%, the minimum CNT content was chosen to be 0.3 wt.%, in order to obtain stable electrical conductivity. The CNTs were mixed in the epoxy by three-roll milling using the laboratory scale three-roll mill EXAKT 80E, from EXAKT Technologies Inc., Germany.

For each of the CNT contents, i.e. 0, 0.3, 0.5, and 1 wt.%, five panels with thicknesses of approximately 1.5 mm were obtained. The thickness of the panels was deliberately made small to omit the edge effects, and to be able to use a two-dimensional method for measuring the electrical resistivity. Panels were cut, using an electrical rotating saw, into square plates of 45x45 mm. Figure 1 shows the final cut and trimmed plate, ready to be dried, and then immersed in the water bath.
In order to get the initial weight and electrical resistance data, the prepared plates needed to obtain full dryness. They were placed in an oven at 110 °C for more than 24 hours, and they were weighed every four hours until a constant minimum weight was obtained. They were then kept in a desiccator cabinet before immersing into water, and their dry-condition weight, thickness, and electrical resistivity were
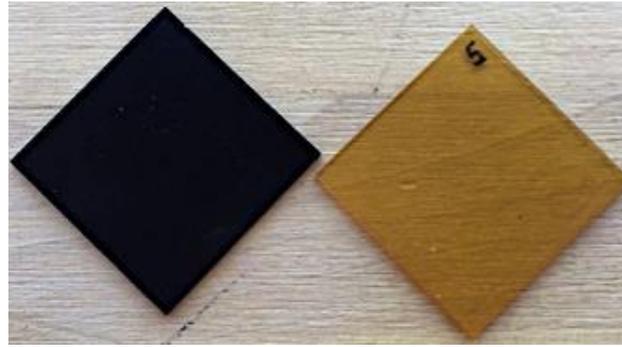
Figure 1: CNT reinforced (left) and neat (right) prepared plates for water immersion procedure

measured and recorded. A constant temperature water bath equipped with a sealing lid was used. It was filled with distilled water, and the lid was always kept closed to avoid the entrance of impurities and contaminants into the water. The constant temperature was set to room temperature (25 °C) for the first experiment, and 40 °C for all other experiments.

Water Uptake and Diffusivity

The absorption of water at each time interval was calculated by measuring the weight of the plates (*m*), and using Eq. 1. The average of water uptake of five samples with the same MWCNT concentration was obtained as well. The water uptake values were plotted against the square root of time as a means to observe the flow of water absorption. Diffusivity values were also calculated using Eq. 2.

$$W_t (\%) = \frac{m_t - m_0}{m_0} \times 100 \qquad (1)$$

$$D = \frac{\pi}{16} \left(\frac{a}{W_\infty / W_0} \right)^2 K^2 \qquad (2)$$

where D is the diffusion coefficient, W_∞ and W_0 are weight gains at saturation and dry conditions, respectively, a is the thickness of the plate, and K is the slope of the linear region of the plot of W_t versus the square root of time.

Thickness

A caliper was installed on a fixed stand to minimize the operating errors. Nine points were marked on the surface of each plate, and the thickness of each point was measured and recorded at all time intervals. The thicknesses of the plates were defined by the average of these constant nine points for electrical resistivity calculations.

Electrical Resistivity

Van Der Pauw method, a commonly used technique for measuring the electrical resistivity of plate-shaped conductive materials, was used. Current source Keithly 6220 DC, and nanovoltmeter Keithly 218A were utilized. The setup, as shown in Figure 2, contains four probes that connect to the four corners of the plate with minimum contacts. Current is passed through one edge, points 1 and 2, and the voltage is measured at the parallel edge, points 3 and 4. The probes are then shifted 90 degrees, and with the same current passing through the adjacent edge, the second voltage is measured. The process continues until four voltages are achieved, and having the current and thickness, and using the Van Der Pauw equations as shown below, electrical resistivity is calculated (Eqs. 3-6) [6].
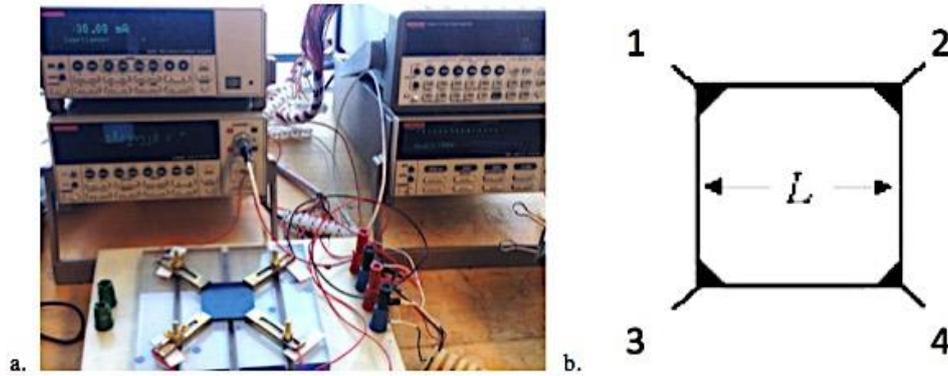
Figure 2: a) Resistivity measurement assembly, and b) schematic of a plate and four probes .

$$R_{12,34} = \frac{V_4 - V_3}{I_{12}} \tag{3}$$

where $R_{12,34}$ is the electrical resistance obtained, with current passing through points 1 and 2, and voltage measured through points 3 and 4.

$$R_{vertical} = \frac{R_{12,34} + R_{34,12}}{2} \tag{4}$$

$$R_{horizontal} = \frac{R_{23,41} + R_{41,23}}{2} \tag{5}$$

$R_{vertical}$ and $R_{horizontal}$ are the averages calculated for the vertical and horizontal edges, respectively. The electrical resistivity ρ is obtained using equation (6):

$$\exp\left(-\frac{\pi t}{\rho} R_{horizontal}\right) + \exp\left(-\frac{\pi t}{\rho} R_{vertical}\right) = 1 \tag{6}$$

where t is the thickness of the plate and ρ is the resistivity.

3. Results:

Figure 3 shows the water uptake of C150P MWCNT reinforced nanocomposite plates immersed in room temperature water. It can be seen from the curve that the water uptake follows a linear upward trend until approximately 1.5% weight gain, and gradually falls into a nonlinear increase, as plates get closer to reaching their saturation. This course of movement is in accordance with Fick's first law of diffusion. It can also be seen that all epoxy plates reached their saturation at around 2%.

Furthermore, the curve shows that CNT content does not have an influence on the level of saturation of epoxy nanocomposites, and regardless of the crowd of carbon nanotubes, the epoxy will reach its water saturation at around 2%. However, there is a difference in the rate of water uptake before saturation depending on the amount of nanotube in the plate, which is shown more clearly in Figure 4. According to this figure, the highest rate of water uptake goes to plates with 0.5 wt.% MWCNT, and the lowest rate is for plates with 1 wt.% MWCNT. The plates with 0.3 wt.% or the smallest content of MWCNT, have a rate of water uptake more than that of 1 wt.% and less than 0.5 wt.%. This phenomenon can be explained by
considering two hypotheses. On one hand, carbon nanotubes have hydroxyl groups on their surface, and attract water molecules due to the tendency to form hydrogen bonds. Therefore, they encourage water molecules to enter the samples at a higher rate, and the more the MWCNT content in the batch, the faster water is absorbed inside the sample. On the other hand, MWCNTs can act as barriers and limit the movement of water molecules into the plates. When there is a higher crowd of nanotubes, the distance between the nanotubes is less, and the barrier effect becomes more pronounced. Water molecules cannot move around easily, and hence the diffusion rate is decreased.
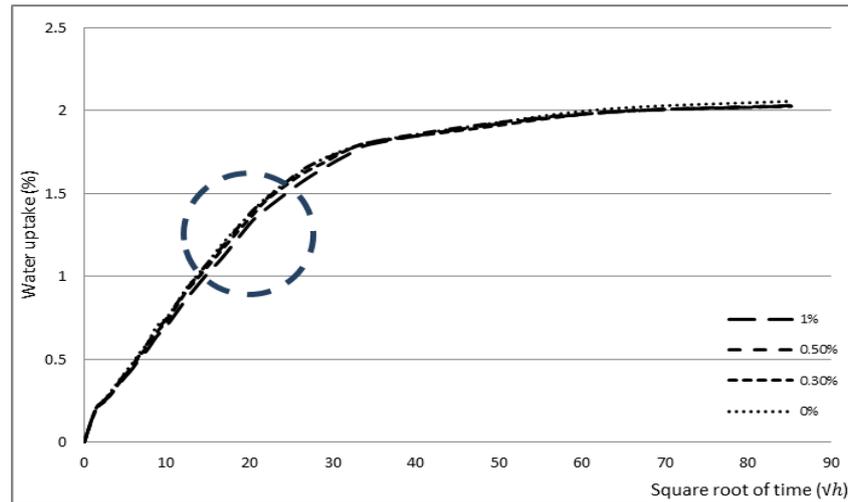
Figure 3. Average water uptake of plates with 0, 0.3, 0.5, and 1 wt.% C150P MWCNT immersed in room temperature water (the dotted circle is magnified in Figure 4).
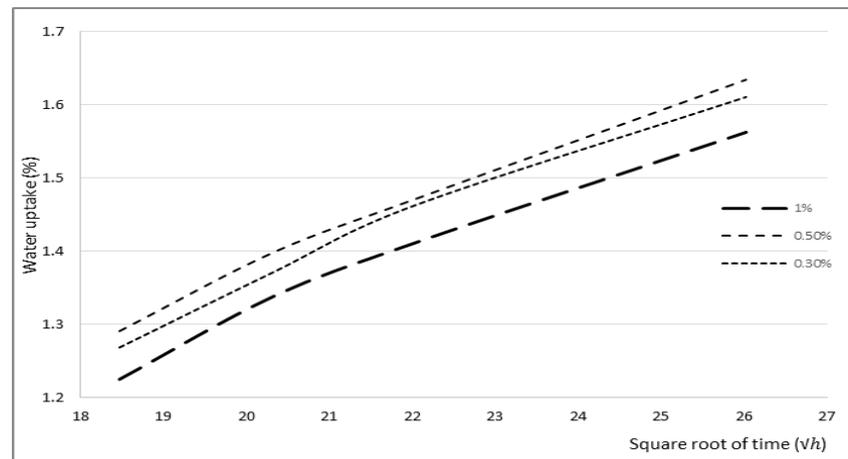

Figure 4: Average water uptake of plates with 0.3, 0.5, and 1 wt.% CNT at room temperature (magnified section taken from figure 3).

Using the two mentioned hypotheses, one can conclude that for the case of 0.5 wt.% MWCNT, there is a higher number of CNTs in the material compared to 0.3 wt.%, and this leads to a stronger attraction of water molecules inside the samples before saturation. On the other hand, the crowd of carbon nanotubes in 1 wt.% samples is twice as high as the 0.5 wt.%. Therefore, the barrier effect becomes more significant and dominates the movement of water molecules resulting in a slower water uptake inside the samples. Diffusivity values were obtained using the linear section of the curve of water uptake, and Eqs. 2, and are shown in Table 1.

Table 1 Diffusivity values for plates with neat epoxy and three CNT concentrations

CNT concentration (wt%)	Diffusivity (mm^2/sec)
1	1.280×10^{-7}
0.5	1.305×10^{-7}
0.3	1.285×10^{-7}
0	1.253×10^{-7}
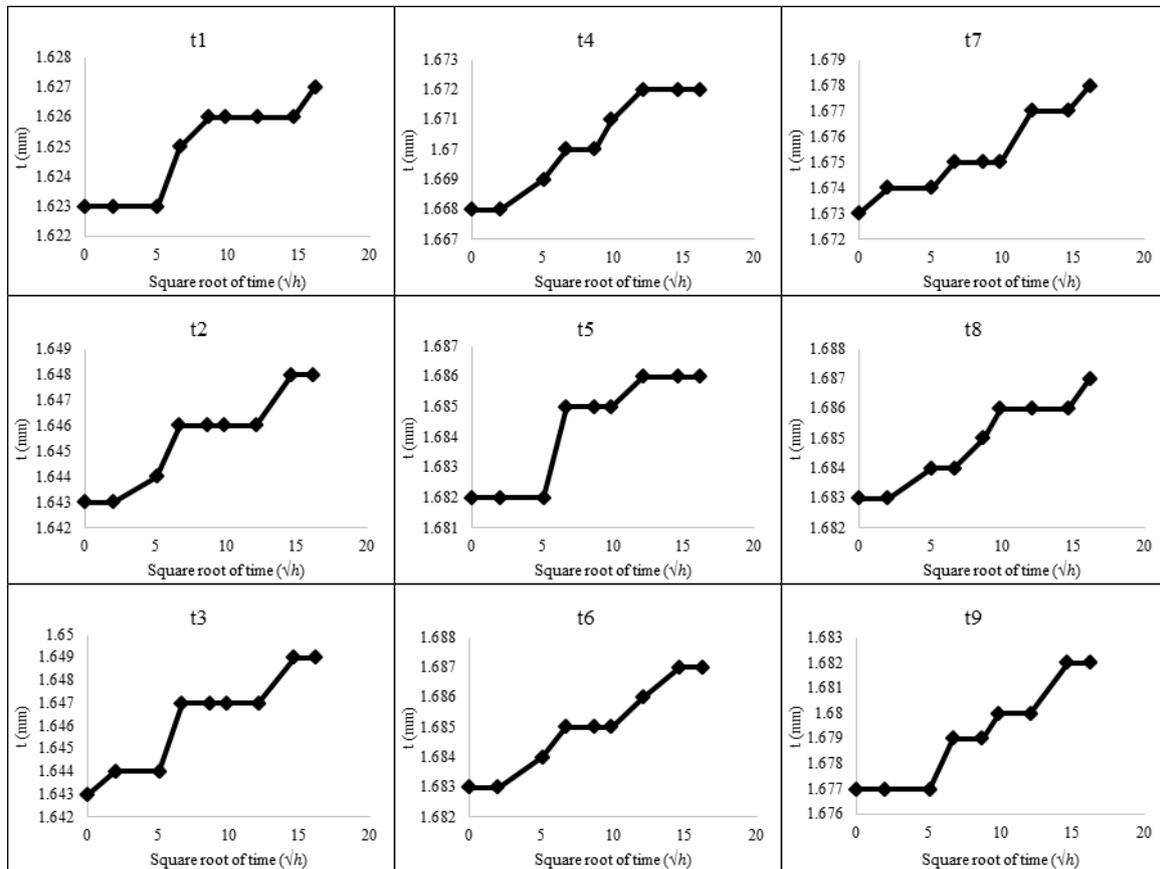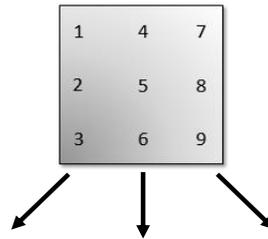
Figure 5: Thickness of nine designated points on epoxy plate 1 (of 5) containing 0.5 wt.% IG MWCNT.

Thickness change:

The thicknesses at nine points designated on the surface of each plate were measured and recorded. Figure 5 shows thickness change of each point throughout the immersion procedure for plates containing 0.3, 0.5, and 1 wt.% IG and C150P MWCNT. As can be seen from the figure, the thickness starts growing after a few hours of immersion, which indicates that water diffuses inside the material and plasticizes the polymer chains resulting in the swelling of plates. It has been shown in the literature that, whether epoxy is exposed to a humid environment or immersed in water, it absorbs water, and the interaction between water and epoxy molecules follows two different mechanisms [7]. One mechanism supports the concept of free water, which fills up the free spaces inside the composite without forming any bonds. In the case of an epoxy containing CNT, this type of water accomplishes the same goal. It fills up the free spaces between the epoxy chains and carbon nanotubes, and does not react with the functional groups inside the material. Therefore, it shows no contribution to the changes in the dimensions of the plates. The second mechanism is ruled by so called bound water, which forms hydrogen bonds with the hydroxyl functional groups of epoxies or N-H functional groups of amines. Bound water type I breaks Van der Waals forces between polymer chains and acts as a plasticizer. It

increases the movement of polymer chains and eases the swelling of the material, and therefore, a change in the dimensions of the plates is detected.

Electrical Resistivity

The electrical resistivity values at dry condition at each time interval were recorded for all the plates containing multi-walled carbon nanotubes. The range of resistivity for each MWCNT concentration of the C150P MWCNT reinforced plates in the dry condition is shown in Table 2.

Table 2: Resistivity values for plates with three C150P MWCNT concentrations.

| CNT Content (wt.%)	Resistivity ρ (Ω.cm)
1	210-250
0.5	990-1500
0.3	6500-19000

It is easily noticeable that, as the content of CNT in the nanocomposites increases, the electrical conductivity improves, or better say, the electrical resistivity decreases. For the plates with 0.3 wt.% MWCNT there is a considerably wide range of resistivity among the five plates (6500-19000). This could be due to their CNT content being close to the percolation threshold of the carbon nanotube, which is 0.188 wt.%. It can also be said that, carbon nanotubes due to their high polarity, have a tendency to attract each other and entangle. There is always a certain amount of MWCNT agglomerations randomly dispersed inside a batch of material, and this amount is considerably low for the case of 0.3 wt.% MWCNT. Since the five plates were made from the same batch, this random dispersion caused some plates to have more numbers of entanglements than others, which led to a difference in conductivity from one plate to another. The change in electrical resistivity as a function of immersion time at room temperature is shown in figure 6. The electrical resistivity of all samples was found to have an upward trend. In other words, water absorption caused the electrical resistivity of CNT-reinforced epoxy nanocomposites to increase. One possible explanation for this behavior is the absorption of the water plasticizes the epoxy material and cause swelling. This swelling moves the carbon nanotubes apart from each other. This can cause reduction in the number of contacts between the nanotubes. This in turn can cause the increase in electrical resistivity.

4. Conclusion:

The absorption of water into epoxy containing CNT is shown to have increase in the thickness of the samples. It also cause increase in the electrical resistivity of the composite material.

Acknowledgments
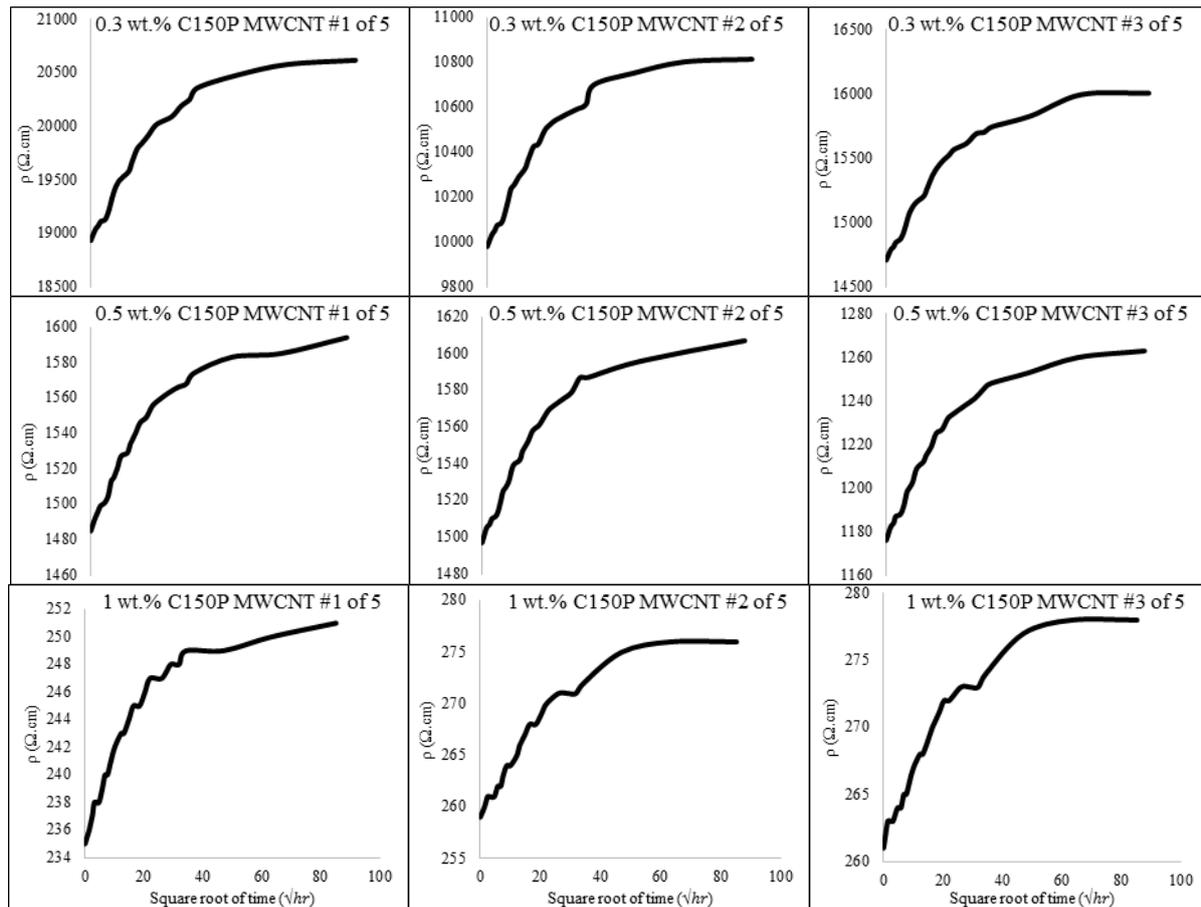
Figure 6: Resistivity of nanocomposite plates reinforced with 0.3, 0.5, and 1 wt.% C150P MWCNT immersed in room temperature water.

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