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Synopsis Of

Effects of Incorporating ZnO Nanowires on the Moisture Absorption and Mechanical Properties of Composites

A Thesis

To be submitted by

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1 Abstract

Polymer composites are widely used in many applications due to their high specific stiffness and strength properties. However, designing of polymer composites with high durability is still a challenge particularly in moisture environments. It has been well established that the moisture absorption takes place through the matrix and it then accumulates in the matrix and fiber/matrix interface. This results in the loss of mechanical properties of composites. Researchers have used several techniques like matrix modification, fiber functionalization and fiber modification using carbon nanotubes (CNT) to reduce the moisture intake and/or to improve the fiber/matrix interface bonding. Fiber modification using ZnO nanowires (ZnO NW) is also a potential technique to reduce the moisture absorption as well as interface strengthening in composites. However, the effects of ZnO NW incorporation on the moisture absorption of composites have not been reported in the literature. *For the first time, this study explores how the incorporation of ZnO NW in the interface affects the moisture absorption and the resultant mechanical properties of glass and carbon composites.* Prediction of moisture absorption dynamics is also critical in the design of composites. Researchers have used various analytical models based on Fickian and non-Fickian diffusion to characterize the moisture absorption in polymer composites. Among the several models, one-dimensional hindered diffusion model (1D HDM) was found to be very effective and has been widely used to relate the moisture absorption parameters with the inherent microstructure of composites. However, relation between the moisture absorption parameters and the mechanical behaviour of composites has not been studied. *For the first time, this work used 1D HDM for the extraction of moisture absorption parameters and explored its relation with the mechanical behaviour of composites.*

ZnO NW were coated onto glass and carbon fabrics to modify the fiber/matrix interface in the composites. The bare (uncoated) and coated fabrics were used in the fabrication of composites. Four different types of composites - glass fiber/epoxy, ZnO NW incorporated glass fiber/epoxy, carbon fiber/epoxy and ZnO NW incorporated carbon fiber/epoxy were investigated in this research. Moisture absorption of composites were investigated using experiments, analytical and numerical studies. Mechanical performance of composites were investigated using longitudinal tension, short beam shear, mode-1 fracture toughness tests. While the moisture absorption was found to decrease the interlaminar shear strength (ILSS) of glass composite, it was found to decrease the ILSS, tensile properties, and fracture toughness of carbon composites. The incorporation of ZnO NW was found to decrease the moisture absorption in both glass and carbon composites, increase the tensile modulus of dry and wet glass composites by 17%, and prevent the delamination failure of wet carbon composites in tensile tests. Also, ZnO NW incorporation was found to increase the fracture toughness of all composites with a maximum of 141% improvement for dry carbon composite. Importantly, ZnO NW incorporation was believed to increase the stiffness and prevent bending failure of DCB arm in wet carbon composites.

The experimental results showed the moisture absorption to degrade the interface in carbon fiber/epoxy composite to a relatively larger extent. Analytical results showed the

hindrance coefficient (ratio of bound to unbound moisture) of composites was found to increase proportionately with the increase in the volume of interfacial regions. Only in carbon/epoxy composite, it did not increase proportionately due to the relatively larger degradation of interface. This mutually related well with mechanical test responses wherein carbon/epoxy exhibited anomalous failure modes due to relatively larger degradation of interface. Numerical simulations of moisture absorption in composites using time-varying boundary conditions matched very well with experimental as well as 1D HDM results. This validated the characteristic diffusion coefficient (D_z) of composites that were calculated using 1D HDM.

Further studies like contact angle measurements, Fourier Transform Infrared Spectroscopy analysis and tensile testing of post-cured wet carbon composites were carried out to verify its larger interface degradation. The studies showed possibility of relatively incompatible sizing/surface treatments in carbon fibers. This could impacted the curing and moisture absorption and thereby resulted in larger interface degradation in wet carbon composites. However, incorporation of ZnO NW provided interfacial strengthening and reduced the interface degradation in wet carbon composites. The uniqueness of this research includes demonstrating the benefits of ZnO NW to reduce the moisture absorption and the moisture-induced degradation in composites and demonstrating the relation between the moisture absorption parameters and the mechanical behaviour of composites. The research presented potential ways of using ZnO NW to tailor the moisture absorption and resultant mechanical properties of composites.

2 Objectives

The objectives of the research are:

1. To reduce the moisture absorption and improve the mechanical properties of glass/epoxy and carbon/epoxy composites through ZnO NW incorporation.
2. To investigate the interfacial moisture storage and study the relation between moisture absorption parameters and mechanical behaviour of composites.
3. To describe the moisture absorption behaviour of composites and validate the characteristic diffusion coefficient through numerical modeling.
4. To investigate any abnormal mechanical behaviour of composites due to moisture absorption.

3 Existing Gaps Which Were Bridged

The research gaps that were addressed are:

1. Fiber modification technique refers to the coating of fibers with nanomaterials and then using the coated fibers in the composite structures. In the literature, coating of fibers with carbon nanotubes (CNT) has been widely explored to reduce the moisture absorption as well as to increase the fiber/matrix interface strength [Garcia

et al. (2008*a*,*b*); Godara *et al.* (2010); Rubio-González *et al.* (2020)]. Coating of fibers with ZnO nanowires (ZnO NW) has been explored to improve the fiber/matrix interface strength [Ehlert *et al.* (2013); Swaminathan *et al.* (2018)]. However, coating of fibers with ZnO NW to synergistically reduce the moisture absorption and improve the interface strength in composites has not been explored. ***For the first time, this research explores how the incorporation of ZnO NW in the interface synergistically affects the moisture absorption and the mechanical properties of composites.***

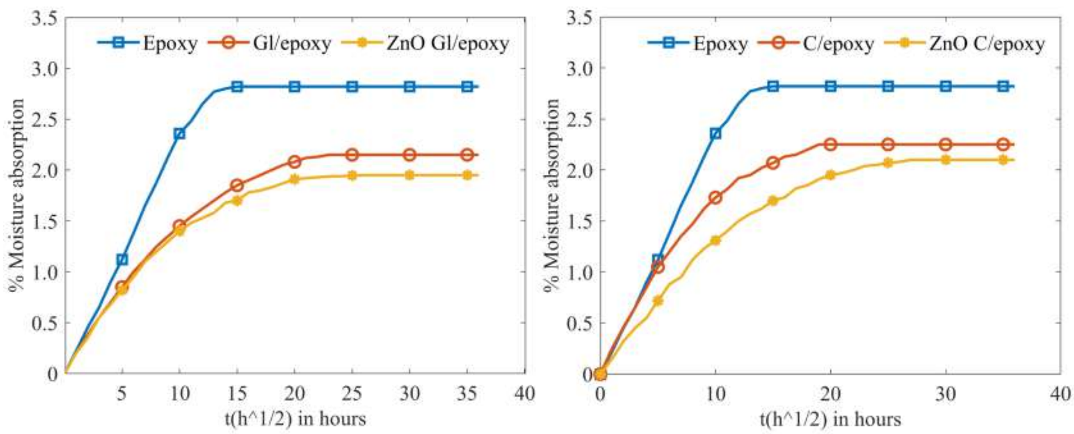
2. As moisture absorption in polymer composites decreases the mechanical performance, understanding of moisture absorption dynamics and mutually relating it to the microstructure and mechanical performance of composites is very critical. Various analytical models based on Fickian and non-Fickian diffusion have been used to characterize the moisture absorption parameters in polymer composites. Among the several models, one-dimensional hindered diffusion model (1D HDM) has been widely used to derive the moisture absorption parameters [Carter and Kibler (1978); Santos *et al.* (2019); Guloglu and Altan (2020a); Guloglu *et al.* (2020b)]. The derived moisture absorption parameters have also been mutually related with the microstructure of the composites. However, the mutual relation between the derived parameters and the mechanical performance of the composites has not been reported in the literature. ***This research uses 1D HDM to extract the moisture absorption parameters, and for the first time, it explores the mutual relationship between the extracted parameters and the mechanical performance of composites.***

4 Most Important Contributions

4.1 Reducing moisture absorption and increasing interface strength

For the first time, this research explored using ZnO NW for synergistic reduction in moisture absorption and improvement in fiber/matrix interface strength of polymer composites. The results showed that incorporation of ZnO NW reduced the moisture absorption and significantly increased the fiber/matrix interface strength. The important results to highlight these contributions are summarized below.

Figure 1 shows the moisture absorption behaviour of epoxy resin and composites. As it can be observed, incorporation of ZnO NW reduced the moisture absorption in glass and carbon composites. Also, incorporation of ZnO NW was found to have profound impact on the mechanical behaviour of composites. Figure 2 shows the failure modes of glass composites under tension test, wherein all the samples were found to fail by conventional fiber fracture followed by grip-to-grip longitudinal splitting. Figure 3 shows the failure modes of glass composites under fracture toughness test, wherein all the samples failed by pure delamination. Figure 4 shows the failure modes of carbon composites under tension test. It can be observed that all the samples, except the wet carbon composite, failed by conventional fiber fracture followed by grip-to-grip longitudinal splitting. Wet carbon composite sample alone failed by delamination and this indicated fiber/matrix interface degradation due to moisture absorption. However, it can be noted that incorporation of ZnO NW prevented the delamination failure under tension tests. Figure 5 shows the failure modes of carbon composites under fracture toughness test. It can be observed that all the samples, except the wet carbon composites, failed by pure delamination. Wet carbon composites samples alone failed by bending arm failure and this indicated fiber/matrix interface degradation due to moisture absorption. However, it can be noted that incorporation of ZnO NW prevented the bending arm failure under fracture toughness tests. Table 1 shows the average initiation fracture toughness of glass and carbon composites. The value in the paranthesis indicates the standard deviation. It can be observed that incorporation of ZnO NW significantly increase the fracture toughness of glass composite (by 40%) and carbon composite (by 140%) in dry condition. This was attributed to mechanical interlocking and good interface bonding provided by ZnO NW. The results showed that ZnO NW provided synergistic benefits of reducing the moisture absorption and increasing the fiber/matrix interface strength of polymer composites.



(a) Glass/epoxy (b) Carbon/epoxy

Figure 1: Moisture absorption behavior of epoxy resin and composites

Figure 2: Failure modes of glass composites under tension test

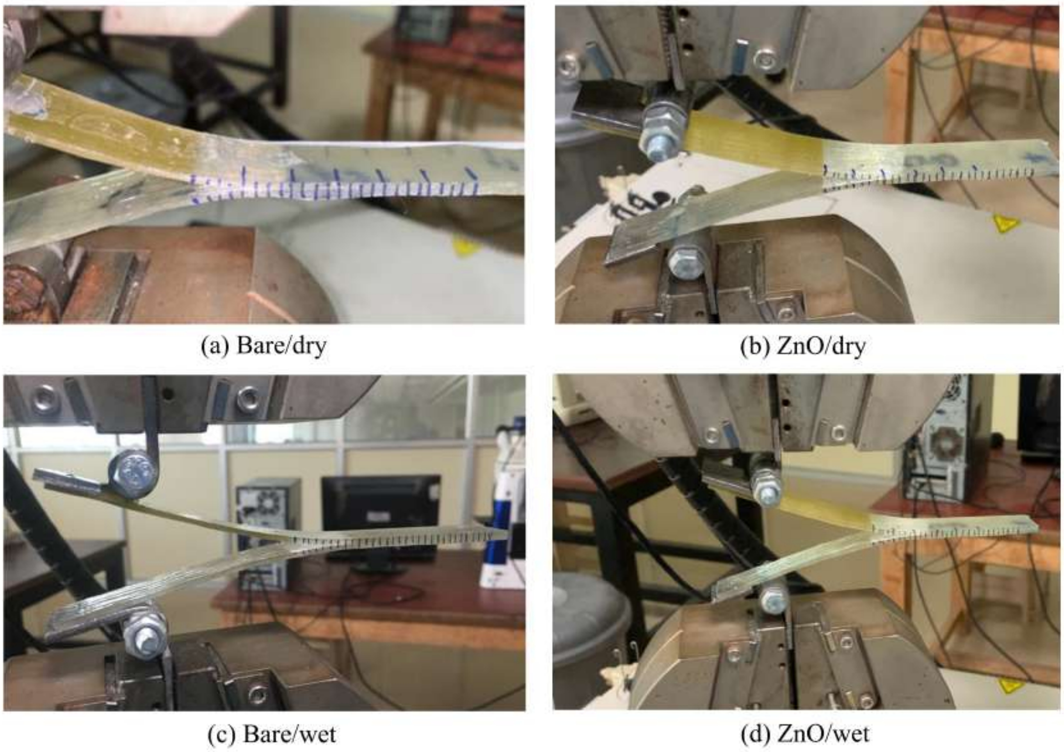


Figure 3: Glass composites during crack propagation stage under fracture toughness test

Figure 4: Failure modes of carbon composites under tension test

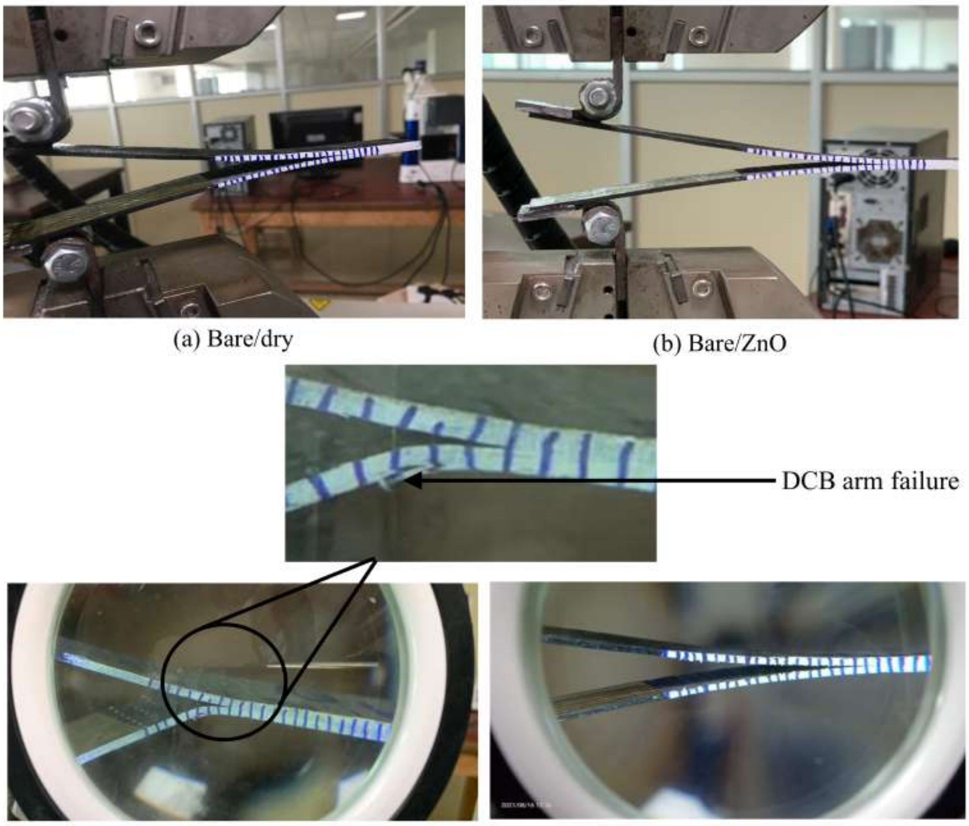


Figure 5: Carbon composite during crack propagation stage under fracture toughness test

Table 1: Fracture toughness of composites

	Bare/dry (G_{IC}) kJ/m^2	ZnO/dry (G_{IC}) kJ/m^2	Bare/wet (G_{IC}) kJ/m^2	ZnO/wet (G_{IC}) kJ/m^2
Glass	0.11 (0.02)	0.19 (0.04)	0.16 (0.02)	0.23 (0.03)
Carbon	0.22 (0.03)	0.53 (0.13)	-	0.28 (0.01)

4.2 Relationship between moisture absorption parameters and mechanical behaviour

The research used the one-dimensional hindered diffusion model (1D HDM) to extract the moisture absorption parameters, and for the first time it explored the relationship between the extracted parameters and the mechanical performance of composites. The results showed a mutual relation between the hindrance coefficient and the failure behaviour of composites. The important results to highlight these contributions are summarized below.

1D HDM was used to describe the moisture absorption behaviour and extract the moisture absorption parameters [Carter and Kibler (1978); Guloglu and Altan (2020a); Guloglu *et al.* (2020b)]. As per this model, the total moisture concentration is expressed as the sum of unbound (mobile, free to diffuse) moisture concentration *n(z, t)* and bound (immobile, not free to diffuse) moisture concentration *N(z, t)*. The 1D moisture absorption is then defined by the Eqs. (1) and (2) as given below [Carter and Kibler (1978)].

$$D\frac{\partial^2 n}{\partial z^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \tag{1}$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \tag{2}$$

where, *n* is the number density of unbound water molecules, *N* is the number density of bound water molecules, γ is the probability that an unbound (mobile) water molecule becomes bound (immobile) and β is the probability that a bound (immobile) water molecule becomes unbound (mobile). At the saturation, the ratio of bound water molecules to unbound water molecules can be described by a non-dimensional hindrance coefficient μ as:

$$\mu = \frac{N_\infty}{n_\infty} = \frac{\gamma}{\beta} \tag{3}$$

where, n_∞ is the maximum unbound moisture content and N_∞ is maximum bound moisture content at the saturation. For a plate of thickness *h* that is under 1D moisture absorption, the bound *N(z,t)* and unbound moisture concentration *n(z,t)* is given by the Eqs. (4) and (5), respectively.

$$N(z,t) = \frac{\gamma}{\beta}n_\infty \left\{ 1 - \frac{4}{\pi}\sum_{i=1}^{\infty(odd)} (-1)^{\frac{i-1}{2}} \frac{r_i^+ \exp\left(-r_i^- t\right) - r_i^- \exp\left(-r_i^+ t\right)}{i\left(r_i^+ - r_i^-\right)} \cos\left(\frac{\pi i z}{2\delta}\right) \right\} \tag{4}$$

$$n(z,t) = n_\infty \left\{ \begin{array}{l} 1 - \frac{4}{\pi}\sum_{i=1}^{\infty(odd)} (-1)^{\frac{i-1}{2}} \frac{r_i^+ \exp\left(-r_i^- t\right) - r_i^- \exp\left(-r_i^+ t\right)}{i\left(r_i^+ - r_i^-\right)} \cos\left(\frac{\pi i z}{2\delta}\right) + \\ \frac{4}{\pi\beta}\sum_{i=1}^{\infty(odd)} (-1)^{\frac{i-1}{2}} \left(r_i^+ r_i^-\right) \frac{\exp\left(-r_i^- t\right) - \exp\left(-r_i^+ t\right)}{i\left(r_i^+ - r_i^-\right)} \cos\left(\frac{\pi i z}{2\delta}\right) \end{array} \right\} \tag{5}$$

where,

$$r_i^\pm = \frac{1}{2}\left\{ \left(Ki^2 + \gamma + \beta\right) \pm \sqrt{(Ki^2 + \gamma + \beta) - 4K\beta i^2} \right\}$$

$$K = \frac{\pi^2 D_z}{h^2}$$

where, *K* is the characteristic diffusion constant and D_z is the characteristic diffusion coefficient of unbound water molecules in the composite. By integrating the sum of unbound and bound moisture concentration through the plate thickness, the total weight gains of absorbed moisture with respect to time *M(t)* is given by the Eq. (6).

$$M(t) = M_m \left\{ \begin{array}{c} 1 - \frac{8}{\pi^2} \sum_{i=1}^{\infty(\text{ odd })} \frac{r_i^+ \exp\left(-r_i^- t\right) - r_i^- \exp\left(-r_i^+ t\right)}{i^2\left(r_i^+ - r_i^-\right)} + \\ \frac{8}{\pi^2}\left(K \frac{\beta}{\beta+\gamma}\right) \sum_{i=1}^{\infty(\text{ odd })} \frac{\exp\left(-r_i^- t\right) - \exp\left(-r_i^+ t\right)}{\left(r_i^+ - r_i^-\right)} \end{array} \right\} \tag{6}$$

Assuming 2β and 2γ to be very less compared to characteristic diffusion constant *K*, a useful approximate solution for estimating the total moisture absorption behavior is given by the Eq. (7).

$$M(t) = M_m \left\{ \begin{array}{c} \frac{\beta}{\beta+\gamma} e^{-\gamma t}\left(1 - \frac{8}{\pi^2} \sum_{i=1}^{\infty(\text{ odd })} \frac{1}{i^2} e^{-\left(\frac{\pi t D_z i^2}{h^2}\right)}\right) + \\ \frac{\beta}{\beta+\gamma}\left(e^{-\beta t} - e^{-\gamma t}\right) + \left(1 - e^{-\beta t}\right) \end{array} \right\} \tag{7}$$

When the exposure time for moisture absorption is large enough, the following approximate solution given by the Eq. (8) can be used for estimating the total moisture absorption behavior.

$$M(t) = M_m \left\{ \left(1 - \frac{\gamma}{\gamma+\beta}\right) \exp(-\beta t) \right\}, \quad 2\gamma, 2\beta \ll K, t \gg 1/_K \tag{8}$$

If the unbound β and bound γ parameters are known, the 1D HDM characteristic diffusion constant *K* can be estimated from the approximate solution given in the Eq. (9).

$$M(t) = \frac{4}{\pi^{\frac{3}{2}}}\left(\frac{\beta}{\beta+\gamma}\right) M_m \sqrt{Kt}, \quad 2\gamma, 2\beta \ll K, \quad t < \frac{0.7}{K} \tag{9}$$

Further, if the unbound β and bound γ parameters are known, the maximum unbound moisture content n_∞ corresponding to the pseudo-saturation level can be estimated from the Eq.(10).

$$n_\infty = \frac{\beta}{\beta+\gamma} M_m \tag{10}$$

For 1D HDM, four absorption parameters namely: M_m — the maximum moisture content at saturation, γ - the probability that an unbound molecule becomes bound, β - the probability that a bound molecule becomes unbound, and D_z — the 1D HDM characteristic diffusion coefficient are needed to completely describe the moisture absorption behaviors. The procedure used for the determination of these parameters from the experimental moisture absorption data is described herein. The maximum moisture content M_m was determined from the experimental gravimeteric data. The Eq. (8) was rewritten in the form of straight line equation as in the Eq. (11) and a straight line graph was generated. The slope of the straight line was taken as β -the probability that a bound molecule becomes unbound. The intercept of the straight line was taken as $\ln\left(\frac{\gamma}{\beta+\gamma}\right)$. Using this relation the γ -the probability that an unbound molecule becomes bound was calculated.

$$\ln\left(1-\frac{M(t)}{M_m}\right)=\ln\left(\frac{\gamma}{\beta+\gamma}\right)-\beta t \tag{11}$$

When the unbound β and bound γ parameters were known, the Eq. (9) was used to determine the 1D HDM characteristic diffusion constant *K*. Then, the 1D HDM characteristic diffusion coefficient was calculated as $D_Z = Kh^2/\pi^2$. The maximum unbound moisture content n_∞ and the maximum bound moisture content N_∞ was determined using the Eqs. (10) and (3), respectively. Finally, the recovered parameters were used to determine the bound *N(z,t)*, unbound *n(z,t)* and total *M(t)* moisture absorption behaviors using the Eqs. (4), (5) and (6), respectively.

In this research, the four moisture absorption parameters (M_m, β, γ, D_z) - were extracted for various composites based on the above described procedure. Then, the bound *N(z,t)*, unbound *n(z,t)* and the total *M(t)* moisture absorption behaviour for various composites were determined. The results are listed in Table 2. It can be inferred that the presence of interfacial regions in the composites enabled the storage of bound moisture and increased the hindrance coefficient (ratio of bound to unbound moisture) proportionately with the increase in the volume fraction of fibers / ZnO NW. However, in carbon fiber/epoxy composite, the hindrance coefficient did not increase proportionately with the increase in the volume fraction of fibers. This was due to the relatively larger degradation of interface in the carbon fiber/epoxy composite which allowed conversion of some bound moisture to unbound moisture. These findings mutually related well with the mechanical responses, wherein carbon fiber/epoxy composite was found to exhibit anomalous failure modes due to the relatively larger degradation of interface.

Table 2: Moisture absorption parameters of resin and composites

Material	V_f (%)	1D HDM D_z ($\times 10^{-3}\, mm^2/hr$)	β ($10^{-3}/hr$)	γ ($10^{-3}/hr$)	M_m (%)	μ
Epoxy resin	-	2.80	N/A	N/A	2.82	0.00
Gl/epoxy	37	21.2	7.3	21.2	2.15	2.90
ZnO Gl/epoxy	36	36.0	8.7	31.4	1.95	3.61
C/epoxy	48	20.2	9.5	22.6	2.25	2.38
ZnO C/epoxy	46	24.3	6.2	24.0	2.10	3.87

To validate the characteristic diffusion coefficient (D_z) of composites that were calculated using 1D HDM, numerical simulations were performed. To account for the non-Fickian diffusion in composites, the numerical simulations were performed using the model (as shown in Figure 6) with time-varying boundary conditions. This model was created as a plain rectangular plate without separate definition of resin and fiber regions. The model was taken as a representative of the composite plate as a whole. Linear quadrilateral (DC2D4) element was used in this model. The diffusion coefficient of unbound water molecules as obtained from 1D HDM was used as an input diffusion coefficient D_z in the numerical simulations. The change in mass concentration with time as obtained from moisture absorption experiments was used as the boundary conditions. An in-built function in Abaqus software was used to define the change in mass concentration with time as the boundary condition along one extremity of the symmetric region. Figure 7 shows the comparison of moisture absorption from experiments, analytical and numerical analysis. It can be observed that the results from the numerical modeling matched very well with the results from experiments and analytical modeling. This validated the characteristic diffusion coefficient (D_z) that was calculated using 1D HDM.

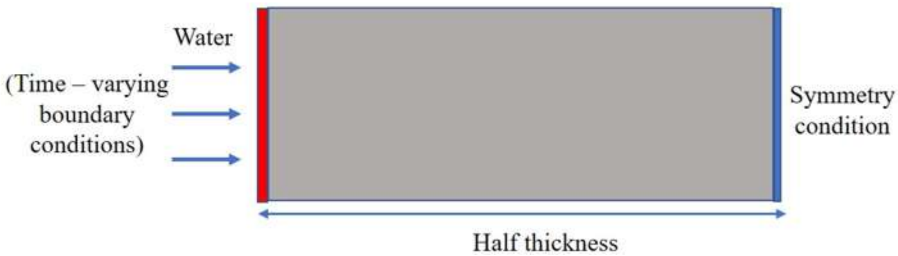


Figure 6: Model used for numerical simulation of moisture absorption

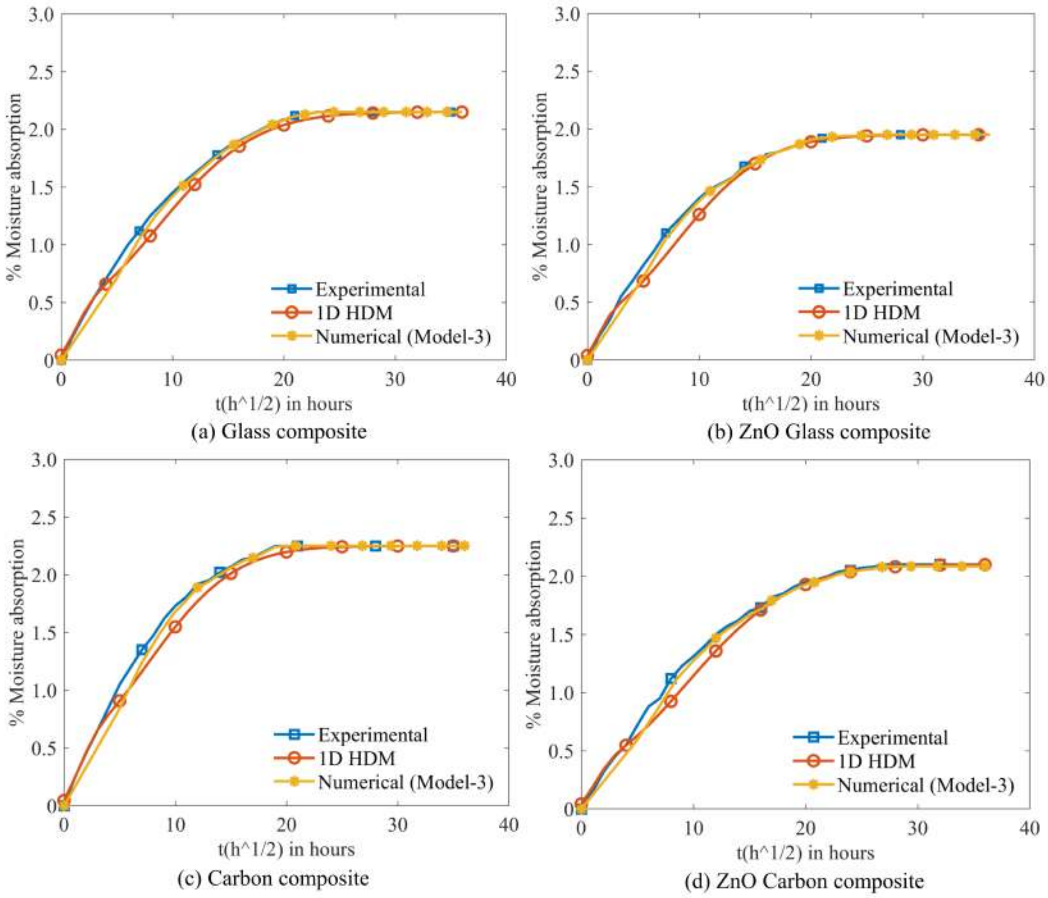


Figure 7: Comparison of moisture absorption from experiments, analytical and numerical analysis

Further investigations were carried out to verify the relatively larger interface degradation in wet carbon composites. Contact angle measurements showed relatively less wettability of carbon fibers with epoxy and this could be attributed to incompatible sizing/surface treatments in carbon fibers. This also resulted in relatively more weakening of O-H bond in wet carbon composites under FTIR studies. Also, post-cured wet carbon composites did not undergo delamination and failed by conventional longitudinal failure under tensile tests. From these studies, it was deduced that the sizing could have impacted the curing and thereby the moisture absorption which resulted in relatively larger interface degradation in wet carbon composites. However, incorporation of ZnO NW provided interfacial strengthening and reduced the interface degradation in wet carbon composites. This research showed the benefits of ZnO NW to reduce the moisture absorption and moisture-induced degradation in composites. The research presented potential ways of using ZnO NW to tailor the moisture absorption and resultant mechanical properties of composites.

5 Conclusions

This research investigated the effects of ZnO NW incorporation on the moisture absorption and mechanical behaviour of composites. Unidirectional glass and carbon fabrics were coated with ZnO NW using a low-temperature hydrothermal process. The average length of ZnO NW in glass and carbon fabrics was 1.2 and 0.8 μm, respectively. The average diameter of ZnO NW in glass and carbon fabrics was 200 and 100 nm, respectively. The morphology studies showed uniform and precipitate-free deposition of ZnO NW on glass and carbon fabrics. The bare (uncoated) and coated fabrics were used to fabricate glass/epoxy and carbon/epoxy composites using vacuum assisted resin transfer moulding (VARTM) process. Moisture absorption, longitudinal tension, short beam shear, and mode-1 fracture toughness tests were conducted. Analytical modeling using one-dimensional hindered diffusion model (1D HDM) was performed to describe the moisture absorption and to extract the moisture absorption parameters. Numerical modeling was performed to describe the moisture absorption and to validate the characteristic diffusion coefficients that were calculated by 1D HDM.

The composites displayed varying degrees of hindered non-Fickian moisture absorption behavior due to the presence of fibers, ZnO NW and their interfaces. Composites with ZnO NW were found to display more pronounced hindered diffusion than their bare counterparts due to the presence of additional ZnO NW and interfaces. In glass composites, moisture absorption was found to reduce the ILSS by $\sim$29%. In carbon composites, it was found to reduce the tensile strength by $\sim$9%, tensile modulus by $\sim$13%, ILSS by $\sim$12% and fracture toughness (% not quantified). Importantly, moisture absorption was found to impact the fiber/matrix interface to a greater extent in carbon composite than in glass composite. As a result, wet carbon composites failed by delamination in tension tests and by bending of DCB arm in fracture tests.

In glass composite, ZnO NW incorporation was found to reduce the moisture absorption. It increased the tensile modulus of dry and wet glass composites by $\sim$17%, and decreased the ILSS of dry and wet glass composites by $\sim$32% and $\sim$39%, respectively. This decrease in the ILSS was attributed to the brittle nature of ZnO NW coated glass fabrics which sensitively affected the ILSS. ZnO NW incorporation increased the initiation fracture toughness of dry and wet glass composites by 73% and 44%, respectively. It also increased the propagation fracture toughness of dry glass composite by 28%. In carbon composite also, ZnO NW incorporation was found to reduce the moisture absorption. It increased the ILSS of dry and wet carbon composites by $\sim$13% and $\sim$17%, respectively. It also increased the initiation and propagation fracture toughness of dry carbon composites by 141% and 73%, respectively. Importantly, it was found to reduce the extent of fiber/matrix interface degradation in wet carbon composite. As a result, it prevented the delamination failure of wet carbon composites in tension tests and DCB arm bending failure of wet carbon composites in fracture tests. The increments in the fracture toughness of ZnO NW incorporated glass composites and the increments in the ILSS as well as the fracture toughness of ZnO NW incorporated carbon composites were attributed to the mechanical interlocking and good interface bonding provided by ZnO NW. The fracture surface of all ZnO NW incorporated composites displayed significant surface roughness, fiber pull-outs and cohesive failure indicative of high fracture toughness due to mechanical interlocking and good interface bonding provided by ZnO NW.

For all the composites, the prediction of moisture absorption behavior using one-dimensional hindered diffusion model (1D HDM) matched very well with the experimental results. The presence of interfacial regions in the composites enabled the storage of bound moisture and increased the hindrance coefficient (ratio of bound to unbound moisture) proportionately with the increase in the volume fraction of fibers/ZnO NW. However, in carbon composite, the hindrance coefficient did not increase proportionately with the increase in the volume fraction of fibers. This was due to the relatively larger degradation of interface in the carbon composite which allowed conversion of some bound moisture to unbound moisture. These findings mutually related well with the mechanical responses, wherein wet carbon composite was found to exhibit anomalous failure modes due to the relatively larger degradation of interface.

Numerical simulations of moisture absorption behavior in composites using Fickian model were found to follow the rule of mixture. That is, the maximum moisture absorption and diffusion rate decreased proportionately with the increase in the volume fraction of fibers. However, due to the effects of interfacial moisture storage, the maximum moisture content and diffusion rate in composites were found to be significantly higher under experimental tests. Numerical simulations of moisture absorption behavior in composites using time-varying boundary conditions were found to match very well with the experimental as well as 1D HDM results. This validated the diffusion coefficients of mobile water molecules in composites that were calculated using 1D HDM.

Further investigations were carried out to verify the relatively larger interface degradation in wet carbon composites. Contact angle measurements showed relatively less wettability of carbon fibers with epoxy and this could be attributed to incompatible sizing/surface treatments in carbon fibers. This also resulted in relatively more weakening of O-H bond in wet carbon composites under FTIR studies. Also, post-cured wet carbon composites did not undergo delamination and failed by conventional longitudinal failure under tensile tests. From these studies, it was deduced that the sizing could have impacted the curing and thereby the moisture absorption which resulted in relatively larger interface degradation in wet carbon composites. However, incorporation of ZnO NW provided interfacial strengthening and reduced the interface degradation in wet carbon composites.

This research showed the benefits of ZnO NW to reduce the moisture absorption and moisture-induced degradation in composites. The research presented potential ways of using ZnO NW to tailor the moisture absorption and resultant mechanical properties of composites.

6 Organization of the Thesis

The proposed outline of the thesis is as follows:

1. Chapter 1: Introduction
   This chapter provides the background and motivation, research gap and uniqueness of the research, objectives of the research, and scope of the research.

2. Chapter 2: Literature Review
   This chapter provides a general literature review to describe the background of this research work. First, the mechanisms of moisture absorption in polymers and composites are discussed. Then, the effects of the moisture absorption on the mechanical properties of composites are reviewed. Following this the state-of-the-art techniques for reducing the moisture absorption and/or improving the mechanical properties of polymer composites are reviewed. Finally, the chapter is concluded with a review on analytical modeling and numerical modelling approaches for characterizing the moisture absorption in polymer composites.

3. Chapter 3: Experiments
   This chapter provides details on the fabrication, characterization and testing of composites. First, the type of fabrics, resin system and the chemicals used for ZnO NW synthesis are described. Following this, synthesis of ZnO NW using a low-temperature hydrothermal method is described. Then, vacuum assisted resin transfer molding (VARTM) procedure used for the fabrication of various composites is described in detail. To evaluate the performance, the composite samples were subjected to various characterization and testing like moisture absorption, tension, short beam shear, mode-1 interlaminar fracture toughness, contact angle measurement and Fourier Transform Infrared Spectroscopy (FTIR) analysis. The details of these techniques are described in the final section of this chapter.

4. Chapter 4: Analytical and Numerical Modeling
   This chapter provides details on the procedure for analytical and numerical modeling of moisture absorption in composites. Analytical modeling was carried out to characterize the moisture absorption and to extract the moisture absorption parameters. First, based on Fickian model, a detailed procedure to characterize the moisture

absorption in epoxy resin is described. Then, based on one-dimensional hindered diffusion model (1D HDM), a detailed procedure to characterize the moisture absorption in composites is described. Following this, the procedure for the numerical modeling of moisture absorption in epoxy and composites is described in the final section of this chapter.

5. Chapter 5: Results and Discussion
   This chapter provides details on the moisture absorption behaviour of resin and composites and the effects of moisture absorption on the mechanical properties of composites. Also, this chapter provides details on the effects of ZnO NW incorporation on the moisture absorption and mechanical properties of composites. First, the morphology and structure of ZnO NW are described. Then, moisture absorption, tensile, short beam shear, and fracture toughness properties of all the composites are described in that order. Herein, the mechanical properties of dry as well as the moisture absorbed composites are discussed. Following this, analytical and numerical modeling of moisture absorption are discussed. Finally, studies like contact angle measurement, FTIR analysis and tensile testing of post-cured wet carbon composite are described to verify its extensive fiber/matrix interface degradation.

6. Chapter 6: Conclusions
   This chapter provides the conclusions of the research and some recommended future works.

7 List of Publications

1. Kannan M, Swaminathan G, and Venkat N (2022). Effects of incorporating ZnO nanowires on the moisture absorption and mechanical properties of composites *Polymer Composites,* 43(6), 3992-4006, Impact factor : 5.2, doi:https://doi.org/10.1002/pc.26673

2. Kannan M, and Swaminathan G (2023). Investigations on interfacial moisture storage and its relation to the mechanical behavior in polymer composites *Polymer Composites,* 44(3), 1562-1574, Impact factor : 5.2, doi:https://doi.org/10.1002/pc.27188

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1. **Carter, H. G.** and **K. G. Kibler** (1978). Langmuir-type model for anomalous moisture diffusion in composite resins. *Journal of composite materials*, **12**(2), 118–131.

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