

DEVELOPMENT AND PROGRESSION OF DAMAGE IN FLAX FIBRE REINFORCED COMPOSITES UNDER CYCLIC HYGROSCOPIC LOADING

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Abstract

In the present study, the degradation of unidirectional flax fibre composites induced by cyclic hygroscopic loading was investigated. Epoxy and polypropylene (PP) were used as matrix systems and the fibre volume fraction was approximately 35%. The composites were cycled 10 times between the oven-dry state (80°C, <1.2% RH) and the saturated state (80°C, 80% RH). During the cycles, diffusion coefficients and equilibrium moisture contents (EMC) of the composites were monitored. Every other cycle the internal damage of the samples was inspected using micro computed tomography (μ -CT) and the transverse flexural composite properties were evaluated using destructive mechanical testing.

The EMC of composite specimens remained constant from cycle to cycle, excluding the occurrence of capillary condensation. Diffusion coefficients increase with increasing cycle number, most likely due to the development of damage in the composite. This damage development was confirmed using μ -CT to visualize the microstructure of the composite wherein voids were detected.

1. Introduction

Flax fibres can absorb moisture from the environment due to the hygroscopic nature of their constituent polymers. A higher moisture content in flax fibres is associated with a decrease in stiffness of the fibres and a dimensional change of the fibres due to swelling [1], [2].

The latter will generate significant hygroscopic stresses when the fibres are embedded in a polymer matrix which inevitably leads to the formation of damage over time. Although several publications investigated the effect of wetting and drying on the composite properties, moisturization of the composites is usually performed by using liquid water to reduce cycling times. This can lead to leaching of certain components in the fibres and generally does not represent the effective in-service behaviour of a flax fibre composite. Moreover, the internal microstructural damage and its progression has not been visualized to this date [3]–[7].

When microscopic defects develop, the diffusion rate accelerates due to increased accessibility of the composite to moisture [8]. In turn, increased diffusion coefficients decrease the time necessary to reach saturation in the material. Under cyclic humidity conditions this could lead to faster degradation of the composites.

Finally, the EMC can increase significantly in subsequent wetting cycles. This phenomenon is associated by the lower vapor pressure of water in capillaries such as micro voids, a process known as capillary condensation [8].

This paper aims to examine the effects of moisture absorption in unidirectional flax fibre composites by exposing them to an environment with a predetermined relative humidity, avoiding interaction of the material with liquid water. The damage which develops in several wetting and drying cycles is linked to the diffusion coefficients and EMC of the composite materials. The extent of damage was quantitatively assessed by analysing the void content of the composite in oven dry state and its impact on the mechanical properties was evaluated by transverse flexural tests.

2. Materials & Methods

2.1 Fibres & matrix systems

Unidirectional hackled flax fibre tape (Flaxtape 200, Lineo NV) with an areal density of 200 g/m² was used to produce the composites.

A bisphenol A epoxy resin (Epikote 828LVEL) was mixed with 1,2 diaminocyclohexane to produce the epoxy matrix for part of the composite specimens.

Polypropylene (PP) films (Propex GmbH) with a thickness of 20 µm were used as matrix material for the remainder of the specimens.

2.2 Composite production

Prior to any form of impregnation flax fibres were dried in an oven at 60°C for 24 hours.

Flax fibre - epoxy unidirectional composites were produced with vacuum assisted resin infusion. The fibre volume fraction was set to 35% and the specimen thickness to 2 mm. After production the average volume fraction of the composites was 36 ± 2%. All other dimensions are in accordance with ASTM D7264/D7264M prescribing the dimensions to be used for unidirectional composite test specimens in flexion. Curing of the resin was performed under vacuum at 70°C for 1 hour supplemented by a post-cure step at 150°C for 1 hour.

Unidirectional flax fibres were impregnated with PP by stacking flax fibre layers with PP films followed by compression molding at 170°C and 20 bar for 10 minutes whereafter the plates were cooled to room temperature. The fibre volume fraction was set to 35% and the specimen thickness to 2 mm. Specimen dimensions are again in accordance with ASTM 3039/3039 M and ASTM D7264/D7264M.

2.3 Hygroscopic loading

Immediately after production the composite samples were transferred to an oven at 80°C where the relative humidity (RH) of the air was not controlled. However, since the air entering the oven has an approximate RH of 50% at 20°C, the RH in the oven was reduced to less than 1.2%. The samples remained here until the loading cycles began.

Hygroscopic loading was achieved by placing the samples in a climatic chamber (Weiss WKL 64) at 80°C and 80% RH. The mass of the samples was measured initially in the oven dry state and subsequently at regular intervals after hygroscopic loading had started. Once saturated, the samples underwent the reverse process and were dried again in the oven following the scheme in figure 1. After

the drying was completed, one cycle was finished. This process was repeated for a total number of 10 cycles.

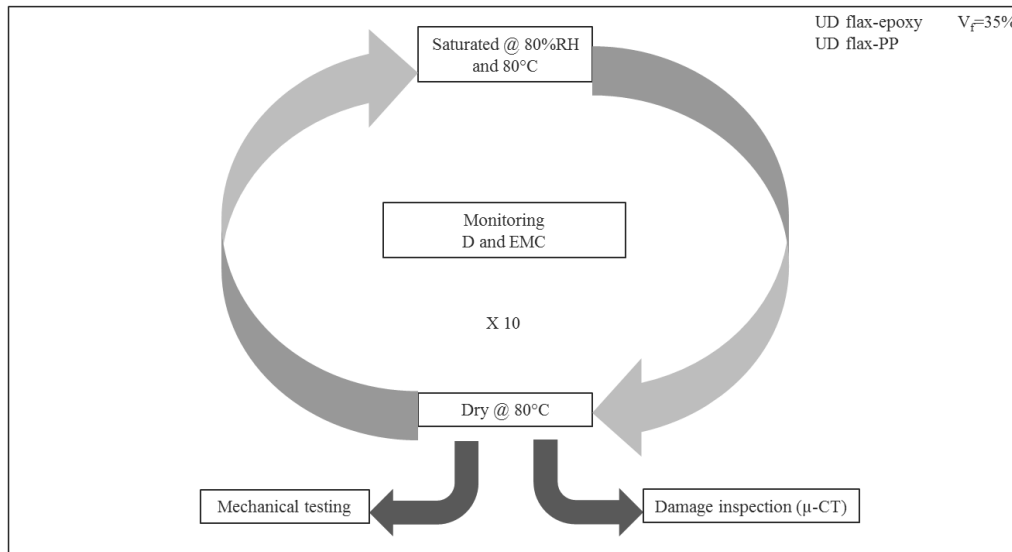


Figure 1: Scheme of the hygroscopic cycle, repeated ten times. The diffusion coefficient and EMC were monitored at regular intervals during each cycle. Damage inspection and mechanical testing was performed every other cycle.

2.3.1 Calculation of the moisture content

The moisture content at time t , M_t , is calculated using equation 1, where W_t is the mass of the sample at time t and W_i is the oven dry mass of the sample before hygroscopic loading.

$$M_t = \frac{W_t - W_i}{W_i} \quad (1)$$

A sample is considered to be saturated when the change in moisture content after at least 1 hour is less than 0.01%.

2.3.2 Calculation of the diffusion coefficient

In most hygroscopic loading cases, flax fibre composites exhibit Fickian diffusion behavior [4], [9], [10]. For a transversely isotropic specimen with sealed edges the moisture concentration, c , obeys equation 2. Herein, D_z is the through-the-thickness diffusion coefficient of the composite.

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \quad (2)$$

However, edge sealing is particularly difficult for composites where the fibres themselves provide significant pathways for moisture entering the material. Hence, unsealed specimens were chosen and equation 2 expands to equation 3 assuming transverse isotropy, where D_x represents the diffusion coefficient in the fibre direction.

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_z \left(\frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (3)$$

It has been established that in this case the apparent “global” diffusion coefficient, D , can be determined from equation 4 [11]. Here, h is the sample thickness.

$$M_t = \frac{4EMC}{h} \sqrt{\frac{t}{\pi}} \sqrt{D} \quad (4)$$

This global diffusion coefficient is related to the directional diffusion coefficients by equation 5 [11]. Here, w is the dimension of the sample in the direction perpendicular and in the plane of the fibres and l is the sample dimension in the direction of the fibres.

$$D = D_z \left(1 + \frac{h}{w} + \frac{h}{l} \sqrt{\frac{D_x}{D_z}} \right)^2 \quad (5)$$

By choosing two samples for which at least one of the sample dimensions is different, the directional diffusion coefficients are both determined.

2.4 Damage inspection

A Phoenix Nanotom 180 was used to collect x-ray images of specimens after every other cycle in the dry state, starting from the initial material immediately after production. All scans were performed using a molybdenum target. The x-ray tube acceleration voltage was set to 53 kV and the current level to 265 μ A creating a spot size of 0.84 μ m on the detector (2400 pixels x 2400 pixels). After reconstruction the resulting voxel size was 1.4 μ m³.

2.5 Mechanical testing

2.5.2 Flexural tests

Flexural tests were performed following ASTM D7264/D7264 M every other cycle. The crosshead displacement rate was set to 1 mm/min. An Instron 5567 was equipped with a load cell of 1 kN and the crosshead displacement rate was set to 1 mm/min. All tests were done on oven dry specimens with a span length of 64 mm with a total sample length of 80 mm.

3. Results & Discussion

3.1 EMC

The EMC of the composite specimens is shown in figure 2. The flax-epoxy samples absorb more moisture as the epoxy matrix itself can absorb 1.3% of moisture. Although the values tend to fluctuate here, there is no statistical evidence to conclude the EMC values rise or fall throughout the cycles ($p=0.25$ for flax-epoxy and $p=0.15$ for flax-PP). Phenomena such as capillary condensation which would

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indicate the presence of liquid water therefore do not occur. Fluctuations in EMC can occur when the samples are given insufficient time to fully saturate. This could indicate that the criterium to decide when a sample was fully saturated was not entirely adequate in this case.

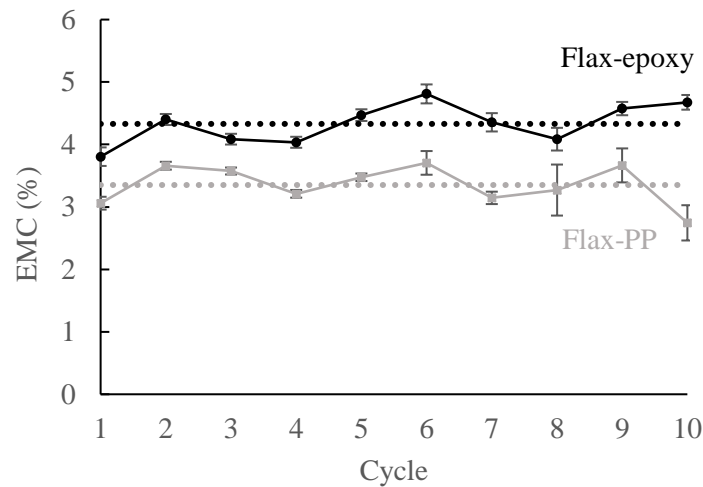


Figure 2: EMC of the composites throughout the cycles (in saturated condition). Dotted lines indicate the average EMC value throughout the cycles.

3.2 Damage development

3.2.1 Damage visualization

Figure 3 visualizes the developed internal damage in the flax-epoxy and flax-PP samples after 10 cycles compared to the reference state immediately after production. The epoxy composite shows evidence of fibre-matrix debonding. This either means that the generated hygroscopic stresses must have exceeded the interfacial strength or that microscopic cracks, that formed during cycling, have lead to stress concentrations which could initiate fibre-matrix debonding. For the PP composite, fibre matrix debonding is also present which is to be expected due to the very weak interface between the hydrophobic PP and hydrophilic flax fibres.

In addition, the flax-epoxy composite also suffers from fibre-fibre debonding which is the effective transverse splitting of the technical flax fibre. The elementary flax fibres in a technical fibre are glued together by a relatively weak interphase. When tensile and shear stresses are generated within such a fibre the interphase fails and this leads to internal decohesion. For this phenomenon to occur the fibre-matrix interface must be strong enough to develop a critical stress state in the fibre itself. This is the reason why flax-epoxy composites suffer from this effect and flax-PP composites do not.

It is highly likely that once the fibre-fibre debond reaches the fibre-matrix interface, fibre-matrix debonding is initiated by the induced stress concentration at that location.

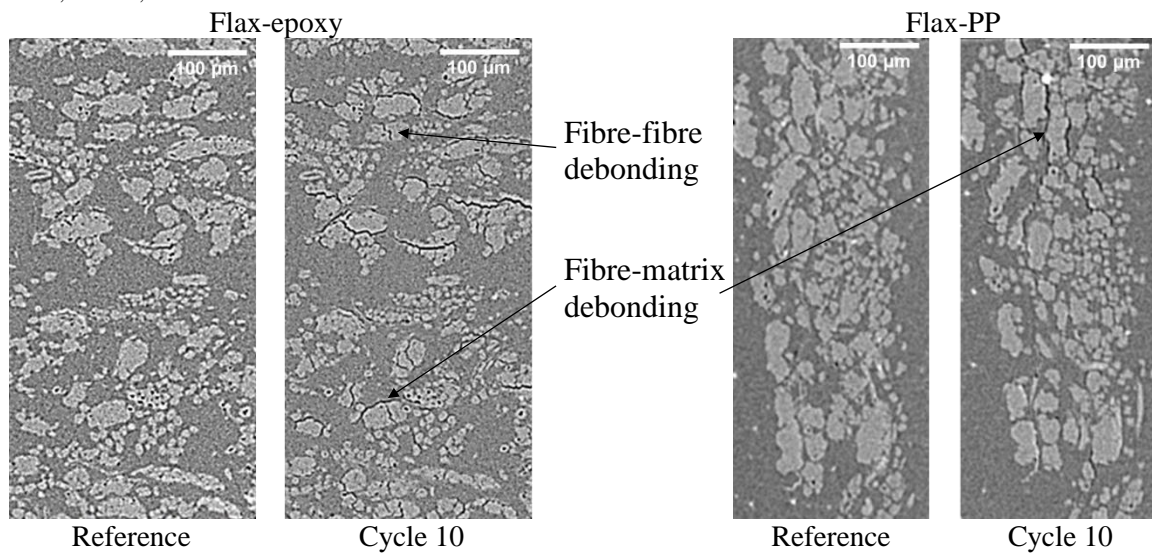


Figure 3: μ -CT damage visualization of two composite specimens with different polymer matrix. After 10 cycles both fibre-fibre debonding and fibre-matrix debonding has developed in the epoxy composite. In contrast, the flax-PP sample only shows fibre-matrix debonding.

3.2.1 Void content & impact on the diffusion coefficient

Void content of the composites increases with increasing cycle number, representing the extent of fibre-fibre and/or fibre-matrix debonding. Overall, the void content increases faster for flax-PP which is due to the weak fibre matrix interface which can be seen in figure 4a.

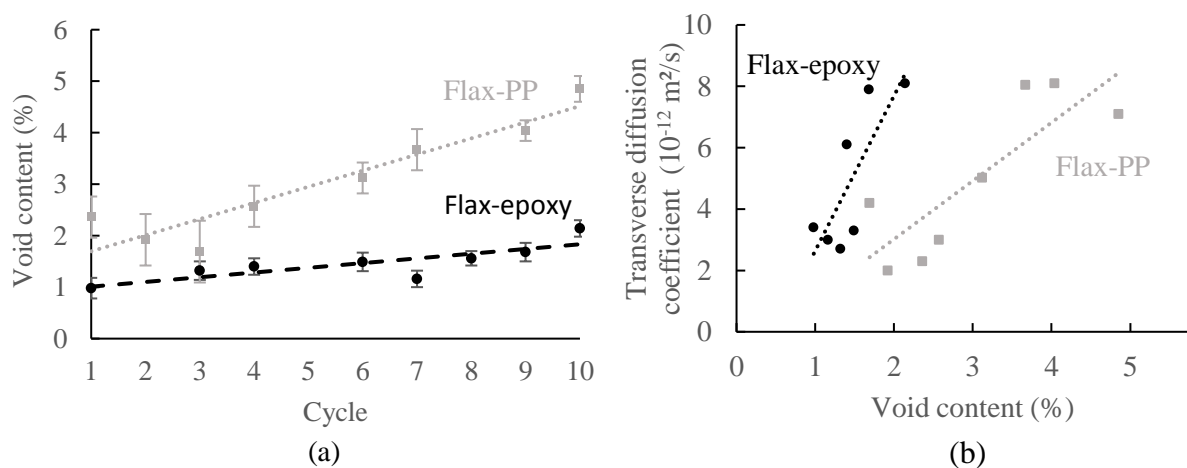


Figure 4: (a) Increase of void content with increasing cycle number for the composites. (b) Impact of void content on the transverse diffusion coefficient.

The increasing void content has a direct impact on the transverse diffusion coefficient of the composite, shown in figure 4b. Diffusivity in gasses is several orders of magnitude larger than the diffusion in solids. When debonding occurs the created void in the material acts as a diffusion accelerator around that location as moisture can move much more freely in this confined space increasing the total diffusivity of the material.

Although the void content in flax-PP composite is higher than for flax-epoxy, the transverse diffusion coefficient of the flax-PP composite remains lower due to the hydrophobicity of the PP.

3.3 Mechanical properties

Damage development has a significant effect on the mechanical properties of the composites especially in the transverse direction. In figure 5a and b, a decrease in stiffness and strength can be seen for PP composites already after the first cycle. The weak interface in this composite is thus degraded immediately by the hygroscopic load.

Flax-epoxy composites show greater resistance to these hygroscopic stresses. Stiffness and strength decline gradually over the cycles. After 5 cycles, both stiffness and strength remain constant indicating that a critical amount of damage has been accumulated. Further debonding does not lead to a further decrease in mechanical properties. Comparing the values after cycle 9 with the virgin material the decrease in stiffness reaches approximately 45% for both composites whereas strength values are reduced by 16% and 55% for flax-PP and flax-epoxy, respectively. The smaller decrease in flexural strength for flax-PP can be attributed to the intrinsically lower adhesion between fibre and matrix in the virgin material. In contrast to flax-epoxy composites, no covalent bonding between fibre and matrix can occur in flax-PP.

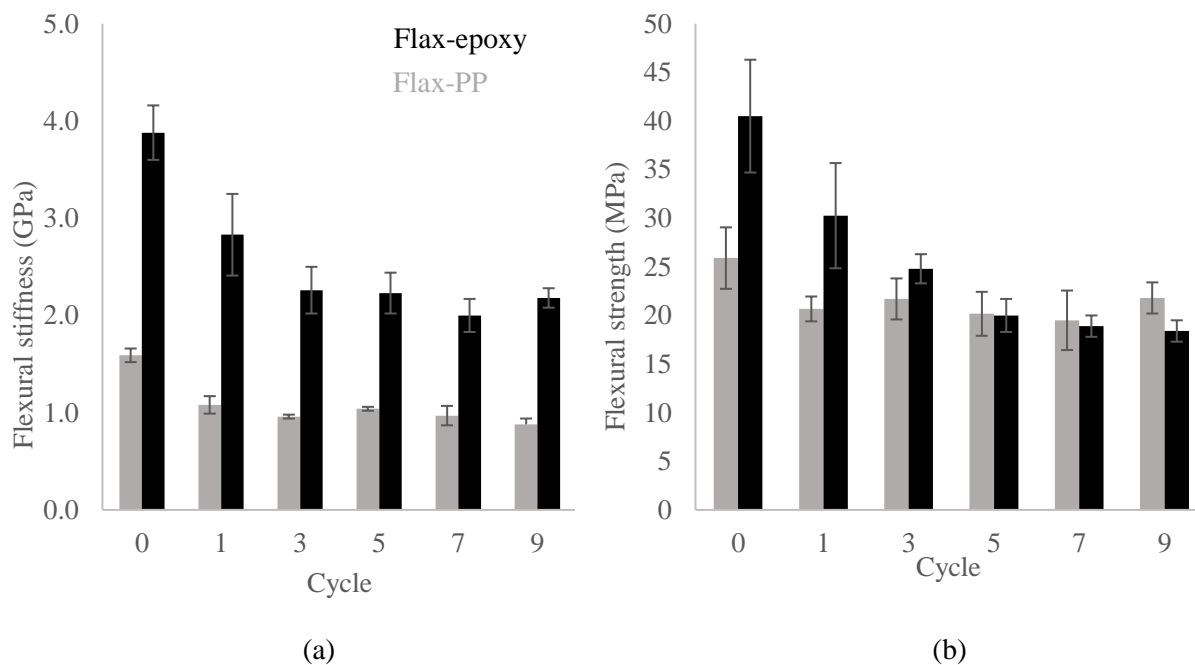


Figure 5: (a) Transverse flexural stiffness and (b) transverse flexural strength of the composites with increasing cycle number. (cycle 0 = reference oven-dry state)

4. Conclusions

Unidirectional flax fibre composites were hygroscopically loaded in cycles without the presence of liquid water. The development of damage, EMC, diffusion coefficients and transverse flexural properties were monitored for both thermoset (epoxy) and thermoplastic (PP) composites.

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EMC measurements confirm that liquid water was not formed during the cycling of the samples. μ -CT images of the cycled samples show that fibre-matrix debonding is a dominant mechanism in the damage development. For flax-epoxy composites, the higher interfacial adhesion between epoxy and flax fibres also lead to fibre-fibre debonding.

As the extent of damage, represented by the void content in the material, rises, the transverse diffusion coefficient of the composites increases.

Finally, the formation of damage leads to a significant decrease in mechanical properties. After merely 5 cycles the transverse flexural strength of epoxy composites decreased with 40% compared to the value measured immediately after production.

References

- [1] D. Scida, M. Assarar, C. Poilâne, and R. Ayad, "Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite," *Compos. Part B Eng.*, vol. 48, pp. 51–58, May 2013.
- [2] A. le Duigou, J. Merotte, A. Bourmaud, P. Davies, K. Belhouli, and C. Baley, "Hygroscopic expansion: A key point to describe natural fibre/polymer matrix interface bond strength," *Compos. Sci. Technol.*, vol. 151, pp. 228–233, Oct. 2017.
- [3] R. H. Newman, "Auto-accelerative water damage in an epoxy composite reinforced with plain-weave flax fabric," *Compos. Part A Appl. Sci. Manuf.*, vol. 40, no. 10, pp. 1615–1620, Oct. 2009.
- [4] M. Assarar, D. Scida, a. El Mahi, C. Poilâne, and R. Ayad, "Influence of water ageing on mechanical properties and damage events of two reinforced composite materials: Flax-fibres and glass-fibres," *Mater. Des.*, vol. 32, no. 2, pp. 788–795, Feb. 2011.
- [5] A. Le Duigou, P. Davies, and C. Baley, "Seawater ageing of flax/poly(lactic acid) biocomposites," *Polym. Degrad. Stab.*, vol. 94, no. 7, pp. 1151–1162, 2009.
- [6] A. Le Duigou, A. Bourmaud, P. Davies, and C. Baley, "Long term immersion in natural seawater of Flax/PLA biocomposite," *Ocean Eng.*, pp. 1–9, Sep. 2014.
- [7] A. Le Duigou, P. Davies, and C. Baley, "Exploring durability of interfaces in flax fibre/epoxy micro-composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 48, pp. 121–128, May 2013.
- [8] J. C. Halpin, "The Role of the Matrix in Fibrous Composite Structures," in *The Role of the Polymeric Matrix in the Processing and Structural Properties Composite Materials*, Boston, MA: Springer US, 1983, pp. 3–17.
- [9] M. Berges *et al.*, "Influence of moisture uptake on the static, cyclic and dynamic behaviour of unidirectional flax fibre-reinforced epoxy laminates," *Compos. Part A Appl. Sci. Manuf.*, vol. 88, pp. 165–177, Sep. 2016.
- [10] J. Summerscales, N. Dissanayake, A. Virk, and W. Hall, "A review of bast fibres and their composites. Part 2 – Composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 41, no. 10, pp. 1336–1344, Oct. 2010.
- [11] C.-H. Shen and G. S. Springer, "Moisture Absorption and Desorption of Composite Materials," *J. Compos. Mater.*, vol. 10, pp. 2–20, 1976.