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Effects of Silk Humidity Exposure on Silk/Resin Affinity for Silk Reinforced Composites

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Abstract

Thanks to its comparable specific mechanical properties to glass fibers, silk is a natural fiber that can be used as an eco-friendly alternative to synthetic reinforcing fibers in composite materials. Compared to natural fibers, especially plant fibers, silk enjoys higher mechanical performances, lower density, and higher elongation even at low temperatures, silk also exhibits other attractive qualities like flame resistance and being naturally continuous. However, silk is known to be prone to moisture absorption from surrounding humid environments. Moisture absorption may alter the silk/resin dynamics during composite manufacturing, and later lead to premature degradation in the composite thermomechanical properties. This study investigates the effect of humidity on silk/resin wettability using two different resins (one epoxy and one vinyl ester) and three different silk architectures. Silk fibers are first exposed to different relative humidity environments. Subsequently, the affinity of the conditioned silk to a set of resins is assessed through measurements of silk/resin contact angle over time. Different silk/resin systems were observed to have contrasting responses to humidity exposure. While some silk/resin systems, such as Ahimsa/epoxy, did not show any change after humidity exposure. Other combinations showed tremendous susceptibility of silk/resin affinity to prior exposure of silk to humidity. For instance, although starting at virtually the same initial hydrophobic contact angle of ~123 degrees, Habotai silk/epoxy samples had contrasting wetting times. While the dried Habotai silk reached full wetting after around 5 minutes, the silk samples exposed to humidity took around 1 hour to reach full impregnation. These findings demonstrate the importance of humidity exposure control in silk reinforced composites.

Keywords: Natural-Fiber Composites, Contact Angle, Silk, Wettability, Humidity.

1 Introduction

In recent years, a sustained shift occurred towards natural fiber composites to attain better sustainability (Pickering, et all, 2015; Parbrin, et al., 2019). Natural fiber composites have several advantages, including but not limited to, low density, high specific strength and stiffness, low hazard manufacturing processes, and production requires little energy (Pickering, et al., 2015; Parbrin, et al., 2019). Plant fibers have been more commonly used recently, and they include flax, hemp, jute, sisal, among others (Sood and Dwivedi, 2017). While these plant fibers have been getting more attention, they do not possess the advantageous properties of silk. Not only is silk the only natural fiber that is continuous, but it also has lower density, higher impact strength, and better flame resistance compared to their plant counterparts (Hamidi, et al., 2018). While silk fibers have lower stiffness, their flexural and tensile strength is comparable to that of plant fibers, and have better interfacial properties, impact strength, and strength performance (Shah, et al., 2014). Further, studies have shown that some silk fibers have better specific mechanical properties than that of Nylon, Kevlar, and even higher specific tensile strength than steel (Hardy and Scheibel, 2010).

Compared to the most commonly-used fiber reinforcement, E-glass, Sil exhibits improved specific properties (Hamidi, et al., 2018.2; Hamidi, et al., 2019; Shah, et al., 2014). Silk/epoxy laminates have even been reported to show specific properties comparable to glass/epoxy composites despite a lack of silk/resin affinity that induced silk composites with excessive void contents and low fiber/matrix bonding (Hamidi, et al., 2017; Hamidi, et al., 2018.1). These findings suggest that with an appropriate silk/resin affinity, silk reinforced laminates would surpass their glass reinforced counterparts.

While silk has so much potential, it is also known to be prone to moisture absorption. In a study conducted on Bombyx mori silk, researchers observed that the silk absorbed as much as 23% moisture uptake when exposed to 75% relative humidity (Agarwal, et al., 1998). This is significant since moisture affects the mechanical performance of silk fibers, and would therefore affect the yielded behavior of silk reinforced composite laminates. For instance, moisture has been reported to reduce both the flexural strength and flexural modulus of elasticity by 25% and 20%, respectively (Hamidi, et al., 2018). While high moisture sensitivity is one of the drawbacks for using silk, it should be noted that the more commonly used plant fibers are also prone to moisture sensitivity (Shah, et al., 2014). In addition, moisture in the silk would potentially affect the dynamics between the resin and the fibers. These attractions, or affinity, is known to affect the fiber impregnation during composite manufacturing and later the strength of fiber/matrix bond within the fabricated composite laminate (Barraza et al., 2002, Barraza et al., 2017). An inadequate fiber/resin affinity would also result in increased void occurrence and reduced mechanical properties (Hamidi and Altan, 2018, Hamidi and Altan, 2018).

This study uses the change of silk/resin contact angles over time to investigate silk/resin affinity. Contact angle measurements are commonly used to evaluate the nature of a solid surface and its potential to create a high strength adhesive fiber/matrix bond (Menjivar et al., 2020; Extrand, 2004). Fiber/resin contact angles can be used as an excellent indicator of whether the resin will wet the dry fibers. In practice, contact angles lower than 90° are considered hydrophilic, and the fibers are expected to be impregnated by the resin as shown in Figure 1. Conversely, contact angles higher than 90° are the considered hydrophobic, indicating a low affinity between the resin and the fibers, yielding challenging wetting behavior (Marmur, 2017).

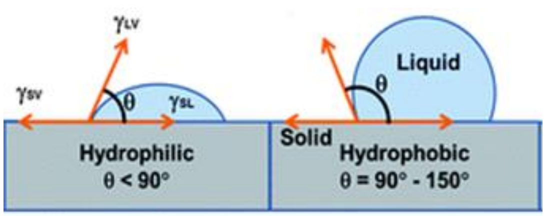

Fig. 1. Hydrophobic and hydrophilic behaviors of solid/liquid systems assessed by contact angles.

Using the contact angle as an indicator for silk/resin wettability during composite laminate manufacturing, this study investigates the effects of moisture content on silk/resin affinity using different controlled humidity conditions and different resins and different silk fiber architectures with the intent to identify optimal silk/resin conditions to be used in further studies to manufacture composites laminates reinforced with eco-friendlier silk fibers.

2 Materials and methods

2.1 Materials

This experiment was conducted using three different silk types and two different resins. shown in Tables 1 and 2. The first resin was an epoxy, INF 114, while the second, Hydrex, was a vinyl ester. Both resins were purchased from Fiberglass Supply, USA; and have manufacturer-reported viscosities ranging from 500~1500 cP as shown in Table 1.

The three silks used were mulberry silks ahimsa, charmeuse and habotai. These silks were purchased from Aurora Silk, Inc., Portland, OR, USA. Properties for the resin were reported by manufacturers. These investigated silk fabrics exhibit diverse characteristics as presented in Table 2 and. For instance, Ahimsa is a spun (noncontinuous) filament fiber woven into a satin weave; Charmeuse is a reeled (continuous) filament fiber woven into a satin weave, and Habotai is a reeled filament fiber woven into a plain weave. These contrasting microstructures can be observed as shown in microscopic images shown in Figure 2.

Table 1. Description of the resin systems studied.

Resin	Polymer Type	Manufacturer	Viscosity [in cP]
INF 114	Epoxy	PRO-SET	1433
Hydrex 100	Vinyl ester	Hydrex	525

Figure 2. Sample microscopic images of silk architecture at 50X magnification for: (a) Ahimsa silk, (b) Charmeuse silk, and (c) Habotai silk.

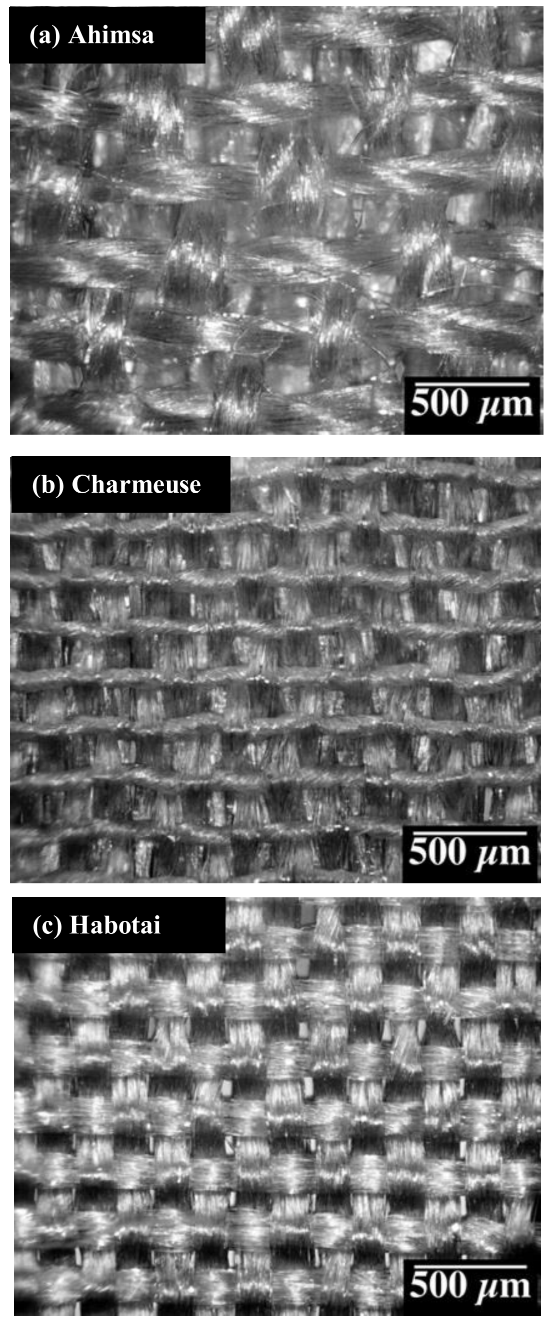

Table 2. Types and characteristics of investigated fibers.

Silk Designation	Silk Type	Source	Weave	Filament	Weight (oz/yd)

Ahimsa	Cultivated	India	Satin	Spun	3
Charmeuse	Cultivated	China	Satin	Reeled	1
Habotai	Cultivated	China	Plain	Reeled	2

Data obtained from Aurora Silk, Inc. website

2.2 Methods

2.2.1 Fiber preparation

Three samples of each silk were cut into strips. Each specimen was approximately 50mm by 200mm in size. During cutting and placement each specimen was handled by the edges to avoid contaminating the surface with any oils. Silk fibers were exposed to varying levels of relative humidity, 0%, 50%, and ambient humidity in the open lab environment, seen in Table 2, which were defined as the three sample sets.

2.2.2 Drying sample

To dry silk fibers, the silks were placed within a vacuum oven (Thermo Scientific) for 72 hours at 45°C to ensure that all humidity that the silks had absorbed would be removed. Silk samples were weighed before and after they were placed within the vacuum oven to monitor the humidity level. The silk samples were then suspended between lab stands and a video was taken to measure the silk/
resin affinity.

2.2.3 Conditioned samples at 50% relative humidity

After drying each silk sample of each architecture and weighing them, samples were placed within a humidity chamber (Fisher Scientific) set at 50% relative humidity for 72 at ambient air temperature. The weight was measured once the samples had been conditioned to measure the amount of moisture the samples had attained. The samples were then carefully hung between the lab stands to record the silk/resin affinity.

2.2.4 Conditioned samples at ambient humidity

Silk samples of each architecture type were removed from the vacuum oven and placed in ambient humidity for 72 hours. The weights of the fibers were then taken to measure the amount of moisture that they absorbed. Once this was done the silks were carefully hung between the lab stands to measure the affinity between silk and resin.

2.2.5 Silk/resin contact angle measurement

A pipette was used to place one drop of resin onto the surface of the suspended fiber. This process was video recorded in real-time; total time defined as the time of the resins initial contact with the fabric surface until reaching complete wettability or a 60-minute maximum, whichever occurred first.

2.2.6 Image Analysis

For each silk/resin system, chronological change of static contact angles was analyzed using *imageJ* software with a contact angle plug in. At least eleven still frame images were obtained and analyzed from the unedited video over the total time. Samples of such images are depicted in for illustration in Figure 3 hereafter. The contact angle plug in was selected after opening each image in *ImageJ*. Data points were placed on the lower corners first with five additional points placed around the drop. Manual points procedure was selected from the menu bar.

3 Results and discussion

After measuring the contact angle of the different silk/resin combinations investigated, the contact angles were analyzed over time. All silk/resin systems exhibited an initial contact angle higher than 90°, suggesting a hydrophobic initial affinity between all resins and all fibers, and thus a difficult wettability during composite manufacturing.

However, the contact angle was observed to change with time with varying slopes for the studied silk/resin systems. A detailed investigation into the effect of silk architecture on the silk/resin affinity was conducted in a different study (Cotten et al., 2021)

3.1 Absorbed moisture by silk fibers after humidity conditioning

As shown in Table 2, all dried silk samples all have a moisture content of 0%. That is expected by design of the drying experiments. Once the different silk samples are exposed to an environment with 50% relative humidity for 72 hours, they absorb between 4 and 5% of moisture. Ahimsa is observed to absorb, in average, a 5.1% mass intake of humidity. Charmeuse and Habotai, on the other hand, show a slightly lower mass intake with 4.2 and 4.7%, respectively.

Table 2. Percent moisture content absorbed moisture by each silk type after different humidity conditioning.

Silk Type \ Conditioning	Drying [0% RH]	72 Hours at 50% RH	72 Hours Ambient Humidity
Ahimsa	0%	5.1%	4.7%
Charmeuse	0%	4.2%	3.9%
Habotai	0%	4.7%	3.5%

When exposed to ambient environment, or room humidity, the silk fibers absorb a slightly lower, but comparable, moisture content. After 72 hours in the lab, Ahimsa samples absorbed in average a 4.7% moisture content, which is about 8% than at 50% RH. A similar trend is observed for Charmeuse and Habotai silks, with moisture uptakes of 3.9 and 3.5%, respectively. These findings, although similar, would help assess the effect of slight changes in silk moisture content on the silk/resin affinity.

3.2 Silk humidity exposure effects on silk/vinyl ester affinity

In this section, the effect of different humidity conditioning schemes on the contact angle between the vinyl ester resin and the three silk types is investigated.

For the Ahimsa silk, and as depicted in Figure 3, the three levels of moisture content do not seem to induce a significant change in silk/resin affinity. At t= 0s, the three conditioning schemes yield similar contact angles. The dried sample showed an initial contact angle of 125 degrees. The 50% and ambient humidity samples registered initial contact angles of 118 and 127 degrees, respectively.

In addition, both humidified samples reached complete wetting slightly faster (~18%) than the dried Ahimsa fibers. Both moisture containing Ahimsa samples reached full wetting (a contact angle of 0) at 93 seconds; while the dried silk sample took 110 seconds to be fully impregnated by the vinyl ester drop. Therefore, humidity exposure is not observed to induce noticeable change in the silk/vinyl ester affinity for the Ahimsa architecture.

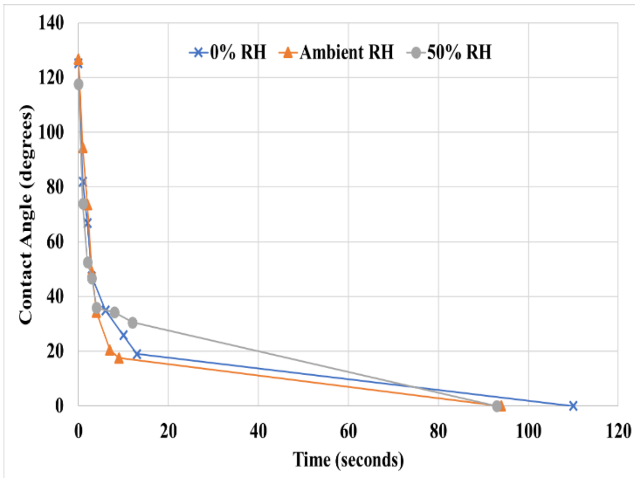

Fig. 3. Effect of humidity exposure on the silk/resin affinity for the Ahimsa/vinyl ester system.

Change with time of the contact angle of the Charmeuse silk/vinyl ester is depicted in Figure 4 for different humidity conditioning schemes. Starting with virtually the same initial contact angle (120~125 degrees), the Charmeuse silk samples show different behaviors after being exposed to humidity.

As Figure 4 depicts, dried Charmeuse samples take 174 seconds to reach complete wetting. Once the silk absorbs around 4.2% moisture under 50% RH, this time is dramatically reduced by 55% to reach 79 seconds. A similar trend is observed for ambient humidity. At 3.9% moisture content, the time to reach complete wetting for Charmeuse silk is reduced to 99%. The observed trend suggests a faster wetting, or improved silk/resin affinity, at higher moisture contents.

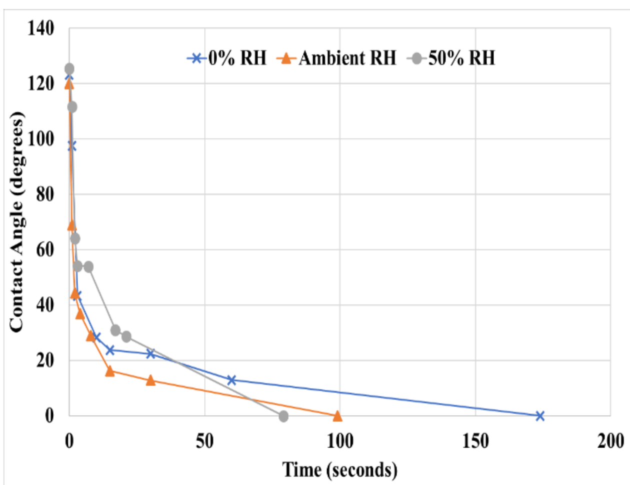

Fig. 4. Effect of humidity exposure on the silk/resin affinity for the Charmeuse/vinyl ester system.

Habotai silk, on the other hand, shows a mixed result as depicted in Figure 5. All three Habotai silk samples start with a similar silk/vinyl ester affinity, showing initial contact angles of 124 degrees for the dried sample, 110 degrees for the 50% RH conditioning, and 115 degrees after ambient conditioning.

However, the dried sample does not reach complete impregnation faster nor slower. In fact, it takes 127 seconds for the dried sample to be fully wet. Meanwhile, the 50% RH conditioned sample at 4.7% moisture content requires only 93 seconds to be fully impregnated. In contrast, the sample conditioned at ambient humidity at only 3.5% moisture content requires a record 733 seconds to reach full impregnation. These findings are conflicting, and require further investigation.

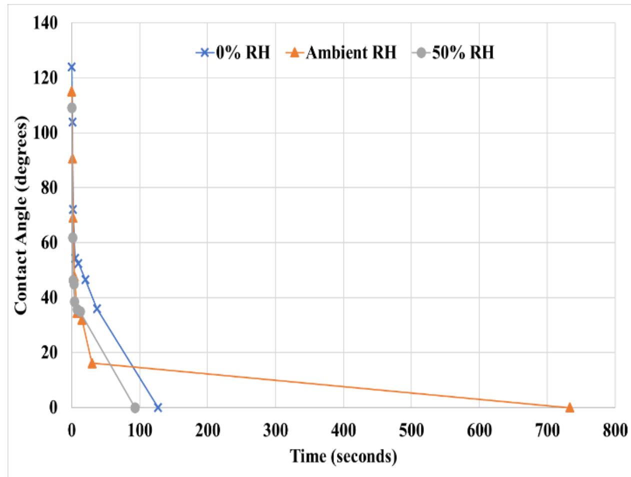

Fig. 5. Effect of humidity exposure on the silk/resin affinity for the Habotai/vinyl ester system.

3.3 Silk humidity exposure effects on silk/epoxy affinity

Similarly to the vinyl ester resin, the effect of absorbed moisture on the silk/epoxy affinity is investigated. Change with time of the contact angle of the Ahimsa silk/epoxy is depicted in Figure 6 for different humidity exposures.

Regardless of the prior exposure to humidity, the initial contact angle between the epoxy resin and the Ahimsa fibers was observed to be hydrophobic in the range of 124~134 degrees. The slight 7% variation did not seem to follow any pattern.

Reaching complete wetting, on the other hand, showed a clear pattern. While the dried Ahimsa silk fibers reached full impregnation after 440 seconds, absorbing around 5.1% moisture (50%RH) was observed to increase that time to 633 seconds. A moisture content of 4.7% after ambient humidity conditioning changed the necessary time for full wetting to 339 seconds. These findings for Ahimsa silk suggest the existence of an optimal moisture content for which the wetting time is the shortest.

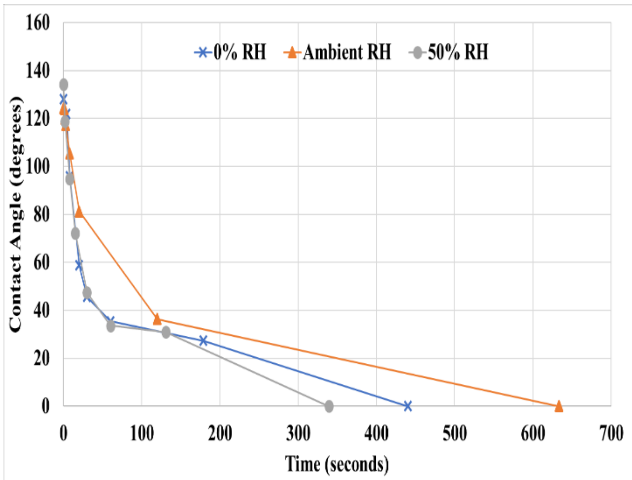

Fig. 6. Effect of humidity exposure on the silk/resin affinity for the Ahimsa/epoxy system.

Charmeuse silk/epoxy results are depicted in Figure 7, and show a different pattern. In fact, the moisture content does not seem to affect the Charmeuse/epoxy affinity. First, all initial contact angles were within 7% of each other, and showed hydrophobic behavior (121~138 degrees range). The times required to reach full wetting for all three conditionings were also extreme, in the range of 1300~1600 seconds (~30 minutes). Again, no clear trend with respect to moisture content was observed.

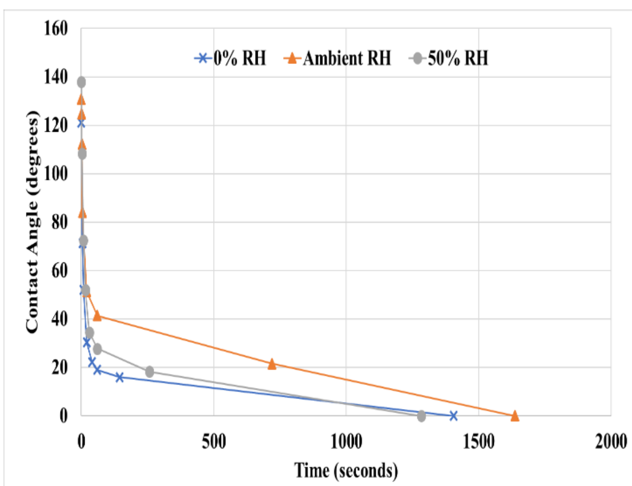

Fig. 7. Effect of humidity exposure on the silk/resin affinity for the Charmeuse/ epoxy system.

The Habotai silk/epoxy showed the widest effect of moisture content on silk/epoxy affinity as depicted in Figure 8. Although starting at the same hydrophobic initial contact angle (~123 degrees), the dried silk sample reached full impregnation after only 317 seconds (~5 minutes). The two humidified samples at 3.5and 4.7 % moisture content required both 3600 second (1 hour) to reach full wetting. This 12-fold increase in the wetting time show the enormous susceptibility of silk/epoxy affinity to moisture.

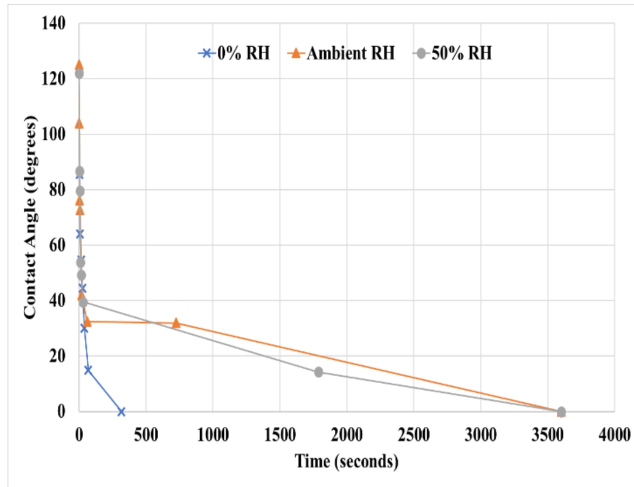

Fig. 8. Effect of humidity exposure on the silk/resin affinity for the Habotai/ epoxy system.

All these findings demonstrate the wild effects that silk moisture, and silk humidity exposure prior to composite manufacturing, can have on silk/resin affinity.

4 Conclusion

Increased interest in natural fibers as eco-friendly alternatives to synthetic reinforcing fibers is growing in composite materials. Silk is a candidate with huge potential since it enjoys higher mechanical performances, lower density, However, silk is known to be prone to moisture absorption from surrounding humid environments during and prior to composite manufacturing. In this study, we investigated the effect of humidity on silk/resin wettability using three different silk architectures. Silk fibers were exposed to different relative humidity environments; and the conditioned silk affinity to an epoxy and a vinyl ester resin was assessed through silk/resin contact angle measurements. Silk/resin systems showed opposing responses to humidity exposure. While Ahimsa/epoxy system, for instance, did not show any change after humidity exposure. Other silk/resin systems showed extreme susceptibility to prior exposure of silk to humidity. For example, Habotai silk/epoxy affinity was observed to change dramatically after exposure to humidity. While the dried Habotai silk reached full wetting after around 5 minutes, the silk samples exposed to humidity took around 1 hour to reach full impregnation. These findings demonstrate the importance of humidity exposure control in silk reinforced composites.

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Conflict of Interest: none declared.

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