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Short Communication

Effect of Silk Treatment on Silk/Resin Wettability

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Abstract

Silk is being pursued as viable alternative reinforcement to widely used glass fibers, especially for environmentally cautious industries. Although silk is known to exhibit comparable specific mechanical properties to glass fibers, only scarce commercial applications employ silk composite laminates. Foiling associated fabrication-induced defects would significantly improve silk composites' performances, and thus widen their industrial applications. One such defect is weak silk/matrix bond induced by poor fiber/resin wettability. In this study, silk treatment effects on silk/resin wettability is investigated through contact angle measurements for different resin/silk systems with different treatments. The silk/resin affinity is used to evaluate the reinforcement/matrix bonding potential, which in turn determines the mechanical properties of the silk reinforced composites. Two silk surface treatments are explored: epichlorohydrin (ECH), methanol (MeOH), in addition to a baseline with no coating. Furthermore, three resins are investigated including a vinylester and two epoxies. Treating the silk fibers with MeOH consistently yielded an improved silk/resin affinity for all resins investigated. For instance, the complete impregnation of MeOH silk by one epoxy resin is observed to be 48% shorter compared to baseline plain silk, from 882 to 461 seconds. Furthermore, among investigated resins, the vinylester resin displayed the best silk/resin affinity for all treatments, exhibiting initial contact angles of 45.7°, 56.1°, and 51.7° for silk fibers with no sizing, ECH sizing, and MeOH sizing, respectively. Total impregnation times followed a similar trend with 21, 15, and 12 seconds, respectively. The superior affinity obtained with vinylester resin and MeOH treatment indicates the potential for an improved silk/resin bond, yielding enhanced mechanical performance for silk composites.

Keywords: Natural-Fiber Composites, Contact angle; Silk; Natural Fiber; Fiber Sizing.

1 Introduction

Due to their light weight and higher mechanical properties compared to traditional materials, advanced composites have become prevalent key industries, including aerospace, automotive, and energy (Hamidi and Altan, 2018; Hamidi et al., 2005). In order to achieve a desired performance, these load-bearing composites are usually made from carefully selected constituent materials usually including reinforcing fibers, and a polymeric matrix. More recently, environmental concerns have led to an increased interest in biodegradable and natural based alternatives (Shah et al., 2014).

Silk is a potential ideal candidate for continuous reinforcement in advanced composites as it exhibits one of the highest mechanical performances compared to other natural fibers (Chen et al, 2018; Hamidi et al., 2018a; Hsia et al., 2011; Shah et al., 2014; Wu et al., 2019; Yang et al., 2017; You et al., 2018). For instance, Bombyx mori silk is reported to exhibit a tensile strength of 600 MPa with 18% elongation and 150 MJ/m^3 energy to break (Hsia et al., 2011), which yield specific properties comparable or better than commonly used E-glass fibers. Furthermore, silk composites are reported to perform particularly better than those reinforced with other natural fibers. Shah et al., for example, reported that flax composites performed better than silk laminates (Shah et al., 2014). The authors observed silk composite to have an ultimate tensile strength of 109-113 MPa, while flax composites only performed between 63-89 MPa at comparable fiber content.

A few studies investigated silk composites performance and reported specific mechanical performances comparable to glass composites despite lack of fiber treatment and higher defect occurrence (Chen et al, 2018; Hamidi et al., 2018a; Hamidi et al., 2018b). Woven silk/epoxy laminates fabricated by vacuum resin assisted transfer molding (VARTM) were reported to exhibit comparable specific flexural strength and stiffness to glass/epoxy composites (Hamidi et al., 2018a; Hamidi et al., 2018b). The authors also reported a weak silk/epoxy bond that limited the fiber/matrix load transfer, thus lowering the final composite's performance. This bond can generally be improved by applying a treatment to the fibers, commonly referred to as sizing.

The effects of fiber treatment, also referred to as sizing, on conventional composites are well established. In addition, sizing has been reported to be particularly effective in improving the mechanical properties of natural fiber reinforced composites (Mittal, 2017; Ovlaque et al., 2020; Shah et al., 2014; Shehu et al., 2016; Singh et al., 2017; Sinha and Rout, 2009).

For instance, Singh et al. (2017) reported improvement on tensile and flexural properties for treated jute, sisal, and banana fibers via NaOH treatment. In a recent review of surface treatment on natural fibers including included jute/PLA, Ramie/PLA, non-woven hemp/PLA, and Coir/PBS, Silane was reported to yield the highest increase in tensile strength (Mittal, 2017). Shehu et al. (2016), on the other hand, utilized an alkali treatment on guineacorn husk particulate bio-composites and reported an increase in flexural strength and modulus regardless of filler content. Other researchers reported improvements in degradation temperature (Sinha and Rout, 2009), interlaminar shear strength and fracture toughness (Ovlaque et al., 2020), flexural properties (Ranjan and Goswami, 2019; Webo et al., 2018; Webo et al., 2020; Giri et al., 2018), and compressive and tensile strength and stiffness (Webo et al., 2018; Webo et al., 2020). For example, Wilson et.al reported improvements in: (i) tensile strength from 52 to 62 MPa (Webo et al., 2020), (i) tensile modulus from 2.9 to 4.2 GPa (Webo et al., 2020), and (iii) compressive strength from 65 to 106 MPa (Webo et al., 2018). Giri et al. (2018) also reported increases in tensile and flexural properties with the use of potassium permanganate as a fiber treatment. Izwan et.al (2020) applied a surface treatment to sugar palm fibers that increased tensile strength for all treated samples reaching a tensile strength of 174 MPa. Another research group achieved a 37% increase in interfacial shear stress treating bamboo fibers (Fuentes et al. 2019). The fiber treatment consisted of applying UV light to fiber surface and resulted in a decrease of the fiber/resin contact angle when comparing untreated to treated samples.

Applying a surface treatment affects the chemical composition of the fiber surface improving fiber wettability. Higher wettability results in an improved fiber/matrix bond, and thus a better load transfer between the matrix and the fibers yielding increased mechanical performance (Hamidi et al., 2018a; Hamidi et al., 2018b; Marmur et al., 2017; Shah et al., 2014). In this study, silk/resin wettability is investigated through contact angle measurements for three resin systems and three treatments of woven silk fabric.

2 Materials and Methods

The silk used in this study is satin ahimsa purchased from Aurora Silk, Inc., Portland, OR, USA. It was produced from degummed cultivated *Bombyx mori* mulberry silk. The silk was cut into a total of nine 1” x 2” samples. Three resins and three treatments were used in this study. The application of the resins onto the silk was done by using a pipette. Information regarding the resins involved as well as what they will be referred to as moving forward are shown in Table 1 along with treatment designation.

Table 1. Resin and Sample Treatment Designations

Resin name	Resin Type	Resin Designation	Treatment (Sizing) Designation
INF 114 (PRO-SET)	Epoxy	PRO-SET	Plain Silk
INR (SUPER SAP)	Epoxy	INR Epoxy	Epichlorohydrin (ECH)
Hydrex (Hydrex)	Vinylester	Hydrex	Methanol (MeOH)

The epichlorohydrin (ECH) treatment (A.k.a. sizing) was achieved through a three-step process. First, a woven silk preform sample is incubated in 100 ml of 5% epichlorohydrin/ 95% MeOH for 2 hours with stirring at room temperature in a beaker. Second, the reactant was then drained, and the silk square is washed three times with MeOH (100ml of MeOH/ each wash). Then, the silk preform is finally dried for 1 hour at room temperature under a hood. The methanol treatment (MeOH), on the other hand, involved two steps identical to the last two steps of ECH treatment. An other benchmark was performed using E-glass fiber preform with a standard industrial sizing.

Contact angles were captured through filming the shape of a drop of resin on the silk fiber over time. To this end, the contact angle (θ) change with time was filmed between the initial value (θ_i) at drop until its complete absorption into the silk sample ($\theta_f = 0°$). The measurement and analysis of the contact angle was conducted using the image analysis software tool *ImageJ*. Using its Contact angle plugin, the contact angle is commonly measured by identifying the solid-liquid interface from images obtained at different times, such as the one depicted in Fig. 1.

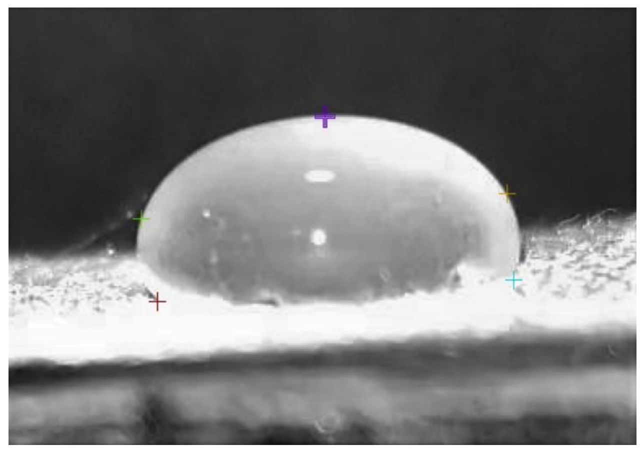

Fig. 1. Sample image of a resin drop on silk preform used to measure silk/resin contact angle via *ImageJ* software.

3 Results and Discussion

The affinity of the solid/liquid system is typically classified based on the measured initial contact angle values (θ). A silk/resin relationship is considered parahygrophobic for θ > 90°, where the resin “likes: the silk and tends to diffuse into its surface. On the other hand, a θ < 90° indicates a parahygrophilic relationship and the resin would not wet the silk (Marmur et al., 2017). Examples of phobic and philic relationships are presented in Figures 2(a) and 2(b), respectively.

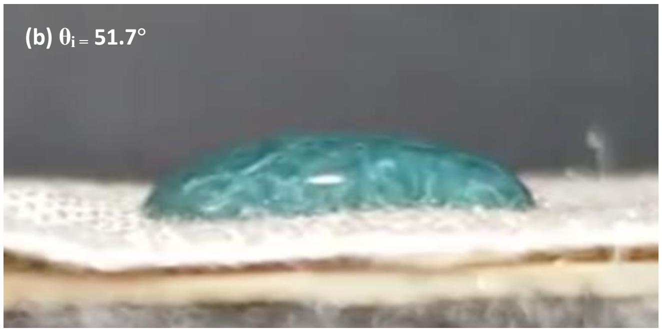

Fig. 2. Sample Image of A Silk/Resin Relationship: (a) a Phobic Relationship Between INR Epoxy and MoOH Silk, And (B) A Philic Relationship between Hydrex Vinylester and MeOH Silk.

3.1 Effect of Silk Treatment on Its Wettability

Silk fiber treatment can be critical in defining the composite performance since a higher silk/resin affinity would yield improved impregnation during composite manufacturing, which in turn would result in a stronger silk/matrix bond and reduced defects such as voids and dry spots (Hamidi and Altan, 2017).

Plain silk is used as a benchmark in order to assess the effects of the ECH and MeOH treatments on the silk/resin wettability. Once both treatments were applied to the silk samples an observation of the InfraRed (IR) spectra was conducted. It was determined that the treatments applied to the samples had no difference in IR spectra (525- 4000 cm^{-1}) between the untreated silk, silk incubated in MeOH, and silk incubated in ECH/MeOH mixture.

Although IR analysis did not show any difference in the three sizing spectra, different silk/resin contact angles were investigated for all fiber/resins systems studied. The measured initial contact angle values of all investigated fiber/resin systems are presented in Table 2. The first observation is that θ_i values comparable between glass and silk fibers, and between the different fiber treatments (Plain, ECH, and MeOH), as the contact angles varied within a 2 to 5% interval.

Furthermore, ECH treatment was observed to consistently render the silk fiber slightly more parahygrophobic, as the initial contact value is consistently higher than its plain counterpart for each resin.

Table 2. Measured Initial Contact Angle (θ_i) of Silk/Rein Systems Investigated, and Glass/Resin Baselines.

Sizing / **Resin**	PRO-SET	INR Epoxy	Hydrex
E-glass	143.4°	142.1	47.2°
Plain Silk	137.6°	138.0	45.7°
ECH Silk	145.0°	140.4	56.1°
MeOH Silk	142.2°	133.0	51.7°

MeOH treatment, on the other hand, consistently induced a higher affinity to all three resins compared to the ECH sizing, indicating an improved wettability and potentially a silk composite with higher performance. However, mixed results were observed when comparing MeOH-sized to plain silk fibers. While increases of respectively 3.3 and 13.1% were observed after the MeOH treatment for PRO-SET and Hydrex resins, a 3.6% drop in θ_i was seen for the INR epoxy. This slight difference in the effect of the treatment on the contact angle at t = 0 s can be attributed to variability in the hydroxy groups present in each epoxy.

Although the θ_i value can indicate such relationships, the wettability of a silk sample can also be inferred by the change of the contact angle over time. In other words, a better wettability of the silk by the resin is expected for lower duration of time to reach θ_f. Therefore, the total duration, t_t, between the drop and the complete wetting of the fibers need to be analyzed in order to fully evaluate the effect of sizing on silk/resin affinity. Figure 3 depicts how the contact angle changes over time for the Hydrex vinylester resin. Although similar trends were observed for all three resin systems, the lower initial value makes the analysis easier to illustrate for the Hydrex resin.

The silk treatment is observed to extensively affect the total time to complete impregnation, t_t. Although starting at relatively close values of contact angle, it takes the hydrex resin respectively 21, 15, and 21 seconds to reach a contact angle of 0 for the plain, ECH, and MeOH treatments, respectively. Figure 3 also shows a somewhat equivalent drop during the first 5-8 seconds in the contact angle for all three treatments. The major take home observation here is that both ECH and MeOH treatments improve the overall silk/resin affinity compared to the plain silk. This is worth mentioning since it is counter-intuitive when considering the initial contact angle. A similar trend is observed for the other two resin systems investigated as shown in Table 3.

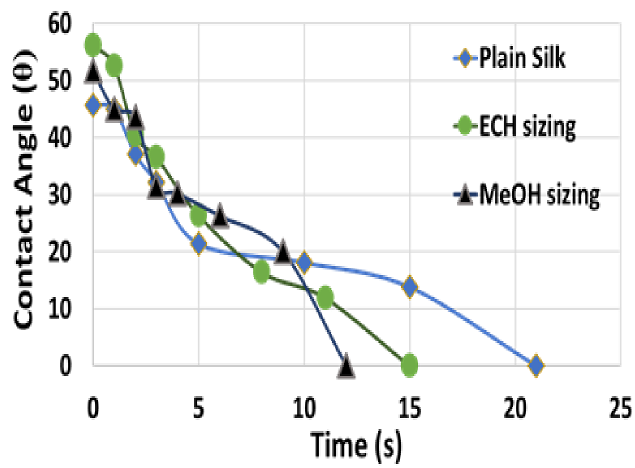

Fig. 3. Effect of Silk Treatment on the Contact Angle Change over Time for Hydrex Vinylester resin.

Table 2. Measured total time to complete impregnation (t_t) where the Contact Angle reaches zero ($\theta_f = 0$) for Silk/Rein Systems Investigated.

Sizing / **Resin**	PRO-SET (seconds)	INR Epoxy (seconds)	Hydrex (seconds)
E-glass	70	-	-
Plain Silk	180	882	21
ECH Silk	150	840	15

MeOH Silk	120	461	12

In contrast with the parahygrophilic Hydrex vinylester resin, both epoxy resins showed typical parahygrophobic behavior, with total times to complete wetting reaching 882 and 180 s for INR epoxy and PRO-SET resins. These times of almost 15 and 3 folds of t_t measured for glass fibers, and are extremely lengthy compared to usual times expected for composite manufacturing processes, which strongly suggests a poor wetting, which in turn is responsible for the poor fiber/matrix bond that hinders the mechanical performance of the silk/epoxy composite.

Furthermore, MeOH treatments is consistently yielding an improved silk/resin affinity compared to both plain and ECH silk for both phobic epoxy resins, with reduction in total time to complete impregnation ranging from 20-33% for PRO-SET epoxy to 45-48% for INR epoxy. This is comparable the 20-13% reduction in t_t observed for the Hydrex vinylester resin after the application of ECH and MeOH silk treatments.

These findings stress the importance of analyzing the contact angle temporal variation when investigating fiber/resin wettability, instead of basing the affinity measurement solely on the initial contact angle.

3.2 Effect of Resin on Silk Wettability

In addition to silk fiber treatment, the selection of a suitable resin with an appropriate wettability to the silk fibers used may prove critical in determening the composite performance. Like silk sizing, a finding a resin with higher affinity with the silk fibers would improve fiber impregnation during composite manufacturing, in turn improving the silk/matrix bond and reducing process-induced defects (Hamidi et al., 2018a; Hamidi et al., 2018b).

The initial contact values of 142.2, 133.0, and 51.7°, and the total times of 461, 120, and 12 seconds were already presented in Tables 2 and 3, respectively. The focus of this section is to analyze the effect of resins on the silk/resin affinity. Figure 4 compares the wetting behavior of the three resin systems when impregnating MeOH-sized silk fibers. The affinity between each of the resins and the MeOH-treated silk fibers can show how the silk wettability changes over time through the resin/silk contact angle θ(t). It is worth noting that similar trends were observed for both the plain silk and the ECH-treated silk.

The Hydrex resin is observed to consistently exhibit lower contact angle with the silk fibers, indicating a higher affinity and suggesting a higher fiber/matrix bond compared to both epoxies investigated. Furthermore, the contact angle between the silk fibers and INR epoxy presented an exponential drop in the first 20-40 seconds, but lingered for extended durations to reach complete wetting, as depicted on Fig. 4. A similar trend, although 4 to 5-fold faster, was observed for the silk/PRO-SET system.

These findings reinforce the importance of including the fiber/resin system affinity during the design stage of any composite material.

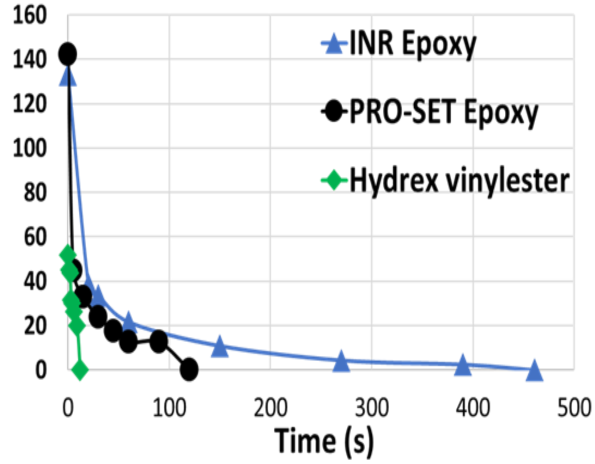

Fig. 4. Effect of Resin on the Contact Angle Change over Time for the three resin systems investigated: INR Epoxy, PRO-SET Epoxy and Hydrex Vinylester.

4 Conclusions

Thanks to its high specific mechanical properties, comparable to those of commonly used glass fibers, silk can be a viable alternative reinforcement to glass, especially industries seeking environmentally friendly products. However, silk enjoys limited commercial applications as a composite reinforcement, in part due to a week silk/matrix bond that reduce load transfer and diminish mechanical performance.

In this study, silk treatment effects on silk/resin wettability were investigated through for three different resins (two epoxies and a vinylester) and three different silk treatments (epichlorohydrin (ECH), methanol (MeOH), and plain for baseline benchmarking). Contact angle measurements, both initial and over time were used to evaluate silk/resin affinity. The silk/resin affinity can be a strong indicator of the expected silk/matrix bond, which conditions the mechanical performance of the silk composites.

Treating the silk fibers with MeOH consistently yielded an improved silk/resin affinity for all resins investigated. For instance, the wetting of MeOH silk by one epoxy resin is observed to reduce the total time to complete wetting by as much as 48% compared to baseline plain silk, from 882 to 461 seconds.

Furthermore, among investigated resins, the vinylester resin was observed to exhibit the best silk/resin affinity for all treatments, with initial contact angles of 45.7°, 56.1°, and 51.7° for plain silk fibers, ECH sizing, and MeOH sizing, respectively. The total impregnation times followed a similar trend with 21, 15, and 12 seconds, respectively.

The higher affinity observed between MeOH-treated silk fibers and the vinylester resin and treatment indicates the potential for an improved silk/resin bond, yielding enhanced mechanical performance for silk composites.

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Conflict of Interest: none declared.

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