*American Journal of Advanced Research*, 2021, 5–2
December. 2021, pages 01-06
doi: 10.5281/zenodo.5807844
http://www.ibii-us.org/Journals/AJAR/
ISBN 2572-8849 (Online), 2572-8830 (Print)

# Effect of Architecture on Silk/Resin Wettability for Silk Reinforced Composites

Lauren D. Cotten, Ava L. Robson and Youssef K. Hamidi*

Mechanical Engineering Program, College of Science and Engineering, University of Houston-Clear Lake, 2700 Bay Area Blvd., Houston, Texas 77058, USA

*Email: Hamidi@UHCL.edu

Received on June 06, 2021; revised on November 18, 2021; published on December 28, 2021

## Abstract

In the last few decades, fiber reinforced composites have been established as the materials of choice for lightweight applications in a large spectrum of applications ranging from aerospace, defense, and marine industries to automotive products and consumer goods. With the growing shift to sustainable resources, natural fibers, especially plant fibers, received increased interest throughout the years. Among these natural fibers, silks stand out with low stiffness and a high failure strain, unlike conventional fibers such as carbon or glass. Although gaining traction as a natural alternative reinforcement, silk still has little to no commercial uses despite its higher performance. Besides its higher mechanical properties and lightweight, silk exhibits other attractive properties such as improved flame retardancy and biodegradability.

To take advantage of these features, proper fiber/matrix adhesion must be achieved. Such silk/matrix bonding can be inferred from the silk/resin affinity during composite manufacturing. In this study, the affinity/wettability of several silk/resin systems were analyzed via static contact angles using *imageJ* software to determine candidates for silk reinforced composite laminates with better adhesion. To this end, a combination of four silk fibers and three resin systems were investigated. The investigated silk fibers were Ahimsa, Charmeuse, Habotai, and Tussah; and the resins included a vinyl ester (Hydrex) and two epoxies (INF114 and INR). For Tussah fibers, initial contact angles were consistently one of the lowest. However, these fibers exhibited a higher contact angle over time compared to the other silk fibers studied. Conversely, Ahimsa silk fibers showed the highest initial contact angle, then quickly dropped to complete wetting. Habotai fibers dropped towards complete wetting quickly, however, consistently slowed considerably shortly after. Charmeuse fibers performed similarly to Ahimsa fibers with Hydrex, however was considerably slower to wetting with the other resins. Among the investigated resins, Hydrex showed the best affinity to silk fibers with the majority of the lowest initial contact angles and the fastest to complete wetting. INF114 consistently receded at a slower, albeit steady, rate until reaching complete wetting apart from Tussah. INR showed the highest initial contact angles and never reached complete wetting after an hour for two of the four silks investigated. Therefore, the best silk/resin affinity was observed for the Ahimsa and Charmeuse silk fibers and the Hydrex vinyl ester resin. In future work, silk composites with these constituents would be investigated.

*Keywords: Natural-Fiber Composite, Contact Angle, Silk, Wettability, Fiber Architecture*

## 1 Introduction

Advanced composite materials are often sought after for their lightweight and outstanding combinations of strength and stiffness (Hamidi et al., 2005; Inamdar et al., 2018; King et al., 2014; Zweben, 1981). Natural fiber reinforced composites have gained interest in the commercial sector due to their biodegradability as awareness of impacts on the environment become stronger (Ramli et al. 2018). Thus far, this shift to green materials can largely be seen in the automotive industry as cellulose fibers replace glass and carbon fibers (Holbery and Houston, 2006). Many natural fibers offer enhanced mechanical properties, lower cost, and lower processing temperatures over synthetic fibers (Pickering et al., 2016; Wumba et al., 2003). Wong et al. (2010) study of short bamboo fibers at various fiber volume fractions showed an improvement in yield strength over neat resin for nearly only the 10mm length and only a slight improvement in the modulus of elasticity at the same length. However, bamboo shows higher variation in geometric uniformity of diameter among brittle fibers and determined a decreasing trend in average strength with an increasing mean diameter (Wang et al., 2015). Plant fibers are often treated with Sodium Hydroxide (NaOH) solution to remove the cementing materials lignin and hemicellulose which in turn improves the interfacial affinity when manufacturing composites. Mohd Izwan et al. (2020) evaluated tensile, thermal, and morphological properties of variously treated sugar palm fibers with

NaOH and benzoylation. Fibers only treated with NaOH increased tensile strength but only partially removed the lignin and hemicellulose. Those additionally treated with benzoyl also increased in tensile strength however also showed degradation in thermal stability. Pereira et al. (2017) manufactured epoxy matrix composites reinforced with continuously aligned jute fibers and found an increase in the absorbed impact energy with increasing fiber volume fraction. A 30% fiber volume fraction resulted in an absorbed impact energy of 214 J/m. This value higher than some other composites such as coir/resin or curaua/resin systems, however substantially lower than similarly manufactured banana/resin composites found by Assis et al. (2014).

Relative to other natural fibers, silk possesses lower density, higher impact strength, higher tensile strength, and a higher elongation at break (Cheung et al., 2009; Hamidi et al., 2018.2; Hamidi et al., 2019; Ranakoti et al., 2019). Silk is also known for being the only continuous natural fiber as well as the only to exist as a filament (Shah et al., 2014). Some silk fibers are even reported to exhibit a higher toughness than that of Kevlar (Liu and Zhang, 2014; Hakimi et al., 2006). Shah et al. (2014) determined that silk's fine structure resulted in less required compaction pressure over flax and hemp to achieve the same fiber volume fraction. Additionally, that silk's compatibility was similar if not higher than some E-glass fabrics. This translates as potential improved transfer of energy (or load) between the resin matrix and fiber reinforcement in silk reinforced composites (SFRCs). This improvement also depends on the affinity at the silk/resin interface as composite performance is known to depend on the bond quality at the fiber/matrix interface (Barraza et al., 2002, Barraza et al., 2017). Yuan et al. (2010) reported uniaxially-aligned *bombyx mori* silk fiber reinforced composites degummed and treated with solution of LiBr and impregnated into a regenerated silk fibroin matrix exhibited only small degradations in the silk's original properties. Yang et al. (2017) Impact toughness of silk/epoxy composite at ambient and sub ambient temperatures at 30% and 60% volume fraction. At ambient temperature composites were found to have 3x more flexural strength and 10x larger breaking energy and showed an increase in specific modulus, specific strength, as well as ductility when reduced to sub ambient temperatures of -150$^{o}$C.

Though silk offers outstanding benefits, it has yet to find its place in commercial applications to take advantage of its potential, more specifically, in weight bearing applications. While scientific research is growing regarding silk composites, it is still limited. Resin is naturally hydrophobic while silk is hydrophilic. This causes insufficient interfacial bonding or affinity when manufacturing silk fiber reinforced composites (Hamidi and Altan, 2017, Hamidi and Altan, 2018.1). However, adding a surface treat ment such as methanol (MeOH) has been shown to reduce silk/resin affinity and increase complete wetting time by as much as 48% (Menjivar et al., 2020). Cost and annual production constraints are also considerations that could be compensated for by the benefits a SFRC could provide over traditional composites.

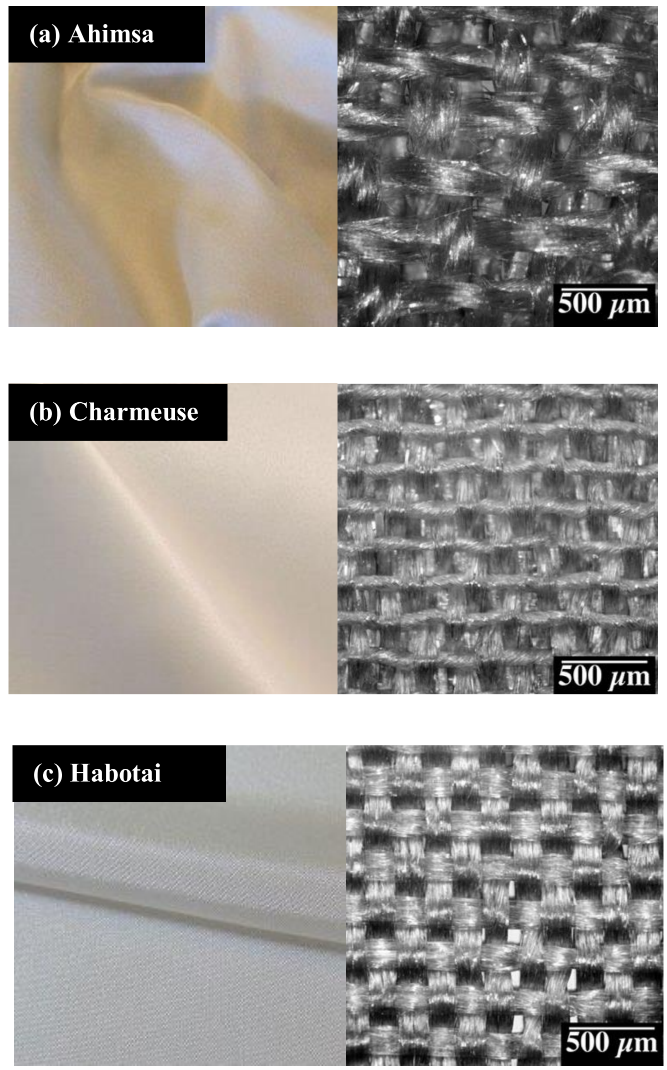
In manufactured silk fabrics, there are three main weave structures: satin, plain, and twill. Within these structures, fibers can be manufactured into various weights or thicknesses. Both weave structure and fiber weight make up the architecture of silk fabric and have been shown to vary in mechanical properties (Kim, 2002). These variations could in turn affect the quality of silk/resin wetting and the adhesion at the silk/matrix interface. To take advantage of silks inherent physical and mechanical properties as a constituent material in advance composites, the relationship architecture has with interfacial adhesion must investigated to identify potential silk/resin systems suitable for manufacturing SFRCs. In this study, the effects of silk architecture on Silk/Resin Wettability are investigated for silk reinforced composites using different resin systems and different fiber architectures.

## 2 Materials and Methods

### 2.1 Materials

#### 2.1.1 Fibers

Four types of silk were investigated in this study purchased from Aurora Silk, Inc., Portland, OR, USA. Mulberry silk is produced by the *bombyx mori* mulberry silkworm. Of this type, 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. Tussah is produced by the *antheraea pernyi* Chinese oak silk moth. Each of the investigated silk fabrics exhibits distinct characteristics as presented in Table 1 and shown in Figure 1.



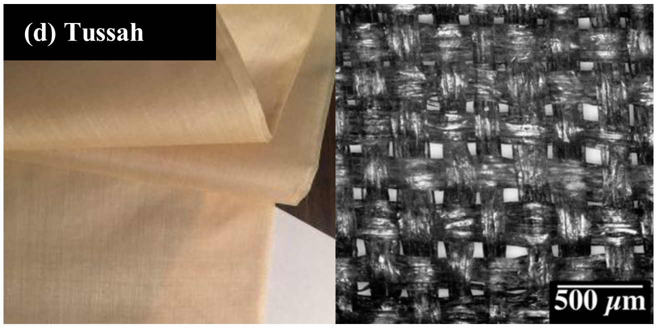



**Figure 1. Silk fabric and corresponding macro- and micro-architectures: (a) Ahimsa silk, (b) Charmeause silk, (c) Habotai silk, and (d) Tussah silk architectures.** Left: macroscopic silk fabric images. Right: microscopic images of silk architecture at 50X magnification.

**Table 1.** Fiber Types investigated.

| Silk Designation | Silk Type | Source | Weave | Filament | Weight (oz/yd) | Momme (mm) |
|---|---|---|---|---|---|---|
| Ahimsa | Cultivated | India | Satin | Spun | 3 | 36 |
| Charmeuse | Cultivated | China | Satin | Reeled | 1 | 12 |
| Habotai | Cultivated | China | Plain | Reeled | 2 | 10 |
| Tussah | Wild | India | - | Hand Reeled | 1.7 | 20 |

Data obtained from Aurora Silk, Inc. website.

#### 2.1.2 Resins

Three resins were investigated: two epoxy resins and one vinyl ester resin. Epoxy resin INF114 is manufactured by PRO-SET, USA. Epoxy resin is made by Super Sap; and the vinyl ester resin, Hydrex, is made by Hydrex, USA. All three resins were purchased from Fiberglass Supply, USA; and have manufacturer-reported viscosities ranging from 520~2200 cP as shown in Table 2.

**Table 2.** Resin types and properties at 22$^{o}$C

| Resin | Resin Type | Viscosity (cP) |
|---|---|---|
| INF 114 | Epoxy | 1433 |
| INR | Epoxy | 2200 |
| Hydrex | Vinyl Ester | 525 |

#### 2.1.3 Equipment

Silk fabric was suspended in order to avoid interaction between the resin and any supporting material. for the sake of consistency, each silk strip was subjected to identical loads during contact angle measurements. Equipment used to suspend silk specimens, as pictured in Figure 1, included lab stands, binder clips, 20g weights, contrasting back drop and steel bar stock.

Video was captured with an iPhone12 held into place with a clamp. A level was used to level the bar stock as well as the clamp holding the iPhone12.

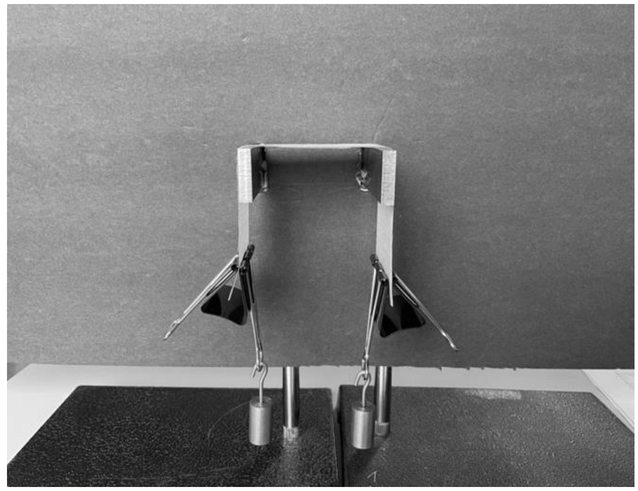


**Fig. 2. Silk suspension apparatus.**

## 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.

#### 2.2.2 Experimental Method

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.

#### 2.2.3 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

## 3.1 Silk effect on silk/resin affinity

Although Ahimsa exhibited consistently higher initial contact angles as shown in Table 3, it also reached complete wetting consistently the fastest compared to all systems. As Figure 2 depicts, Ahimsa/Hydrex system was the fastest to reach full wetting at 94 seconds (1:34 minutes), followed by Ahimsa/INF114 system at 275 seconds (4:35 minutes).

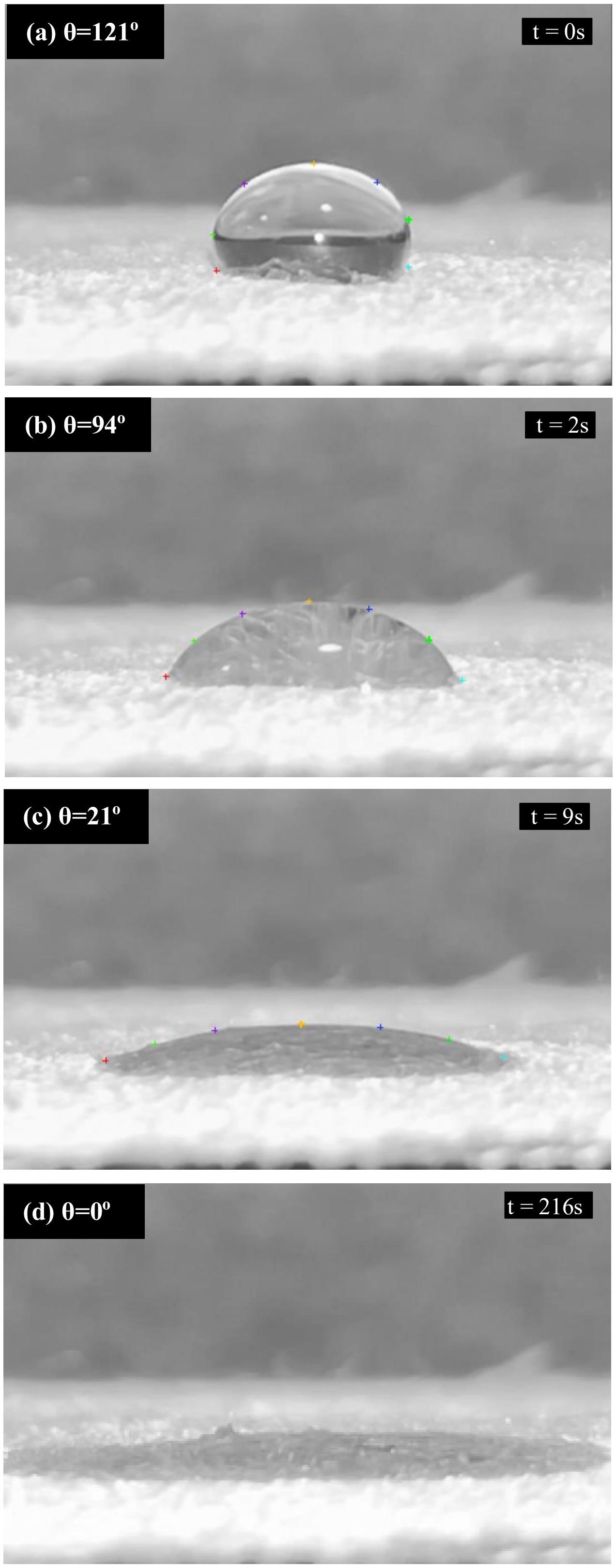



**Fig. 3. Sample contact angle analysis**. Measurement of the change at the solid-liquid interface from initial contact to complete wetting with *imageJ* software.

The maximum time to reach complete wetting was in combination with INR resin at 862 seconds (14:22 minutes).

**Table 3.** Measured initial contact angles, $\theta_i$, of each silk/resin system.

| Silk | INR | INF114 | Hydrex |
|---|---|---|---|
| Ahimsa | 134° | 141° | 121° |
| Charmeuse | 127° | 107° | 114° |
| Habotai | 130° | 130° | 113° |
| Tussah | 104° | 122° | 108° |

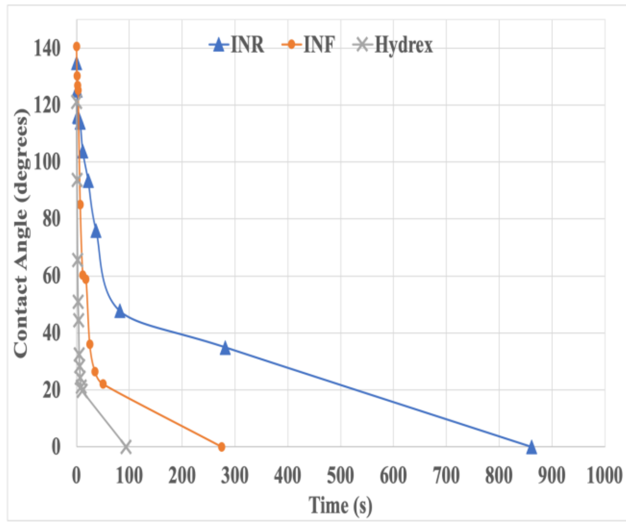



**Fig. 4. Effect of resin on the silk/resin affinity for the Ahimsa silk.**

On the other hand, charmeuse/Hydrex system wetted the quickest in 96 seconds (1:36 minutes) as seen in Figure 3. Charmeuse/INR and Charmeuse/INF114 systems were less impressive with total times of 2023 seconds (33:43 minutes) and 1225 seconds (20:25 minutes), respectively.

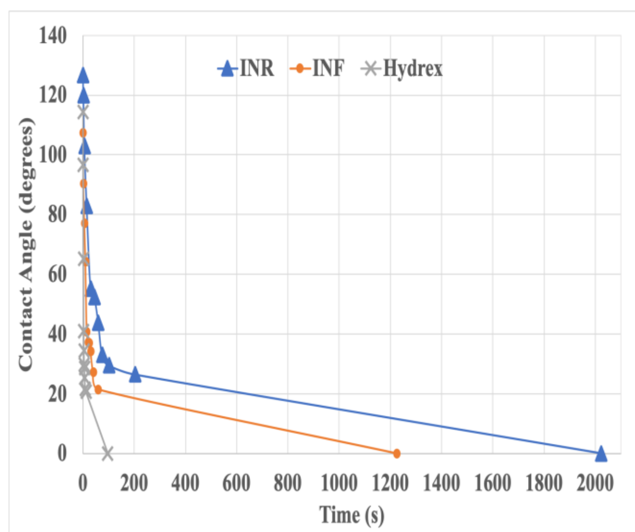



**Fig. 5. Effect of resin on the silk/resin affinity for the Charmeuse silk.**

Conversely, habotai/INR system, depicted in Figure 4, stagnated during wetting at 1992 seconds (33:12 minutes). Habotai/INF114 and Habotai/Hydrex systems showed a significant improvement with total times of 960 seconds (16:00 minutes) and 137 seconds (2:17 minutes), respectively.

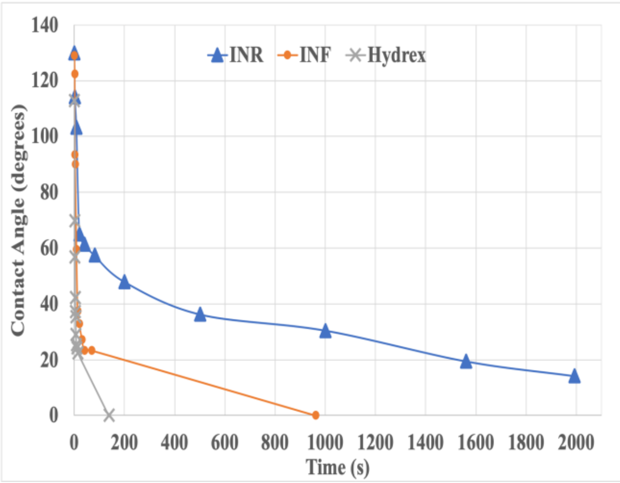



**Fig. 6. Effect of resin on the silk/resin affinity for the Habotai silk.**

Finally, tussah systems, shown in Figure 5, stagnated with resin left on the surface. All systems were filmed over a complete interval of 60 minutes and appeared to reach a contact angle it would not reduce past; 39° for INR, 41° for INF114, and 34° for Hydrex. It is possible that the resin was still dropping at a rate unable to be seen or captured in the allotted time frame with the available resolution.

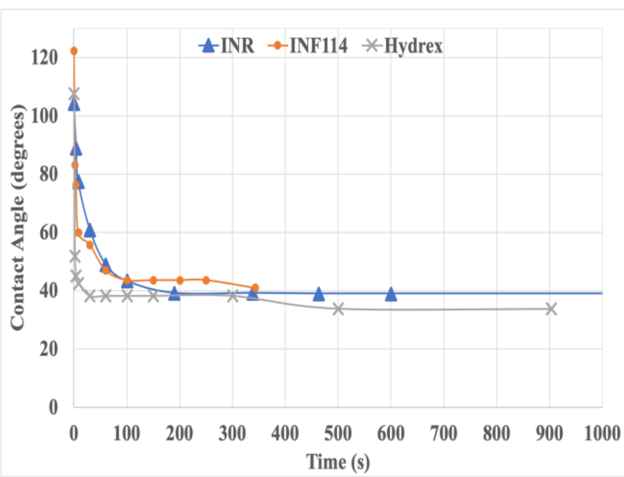
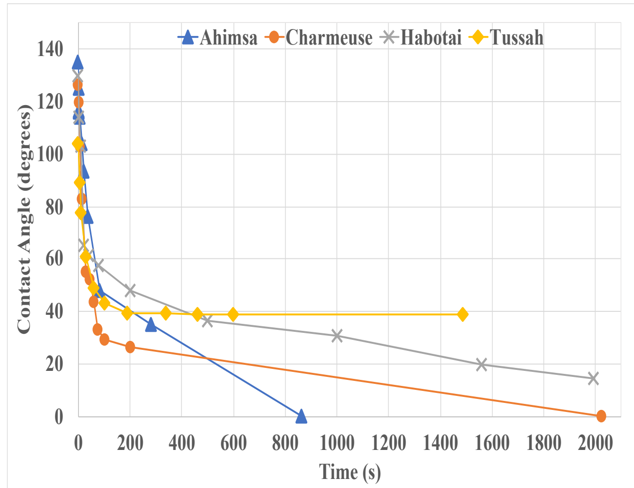



**Fig. 7. Effect of resin on the silk/resin affinity for the Tussah silk.**

### 3.2 Resin effect on silk/resin affinity

INR epoxy stagnated on two of the systems, Habotai and Tussah, as depicted in Figure 6. Ahimsa/Hydrex system completely wetted the quickest in 862 seconds (14:22 minutes) and Charmeuse/INR system wetted the slowest in 2023 seconds (33:43 minutes).

**Fig. 8. Effect of silk architecture on the silk/resin affinity for INR Epoxy**.

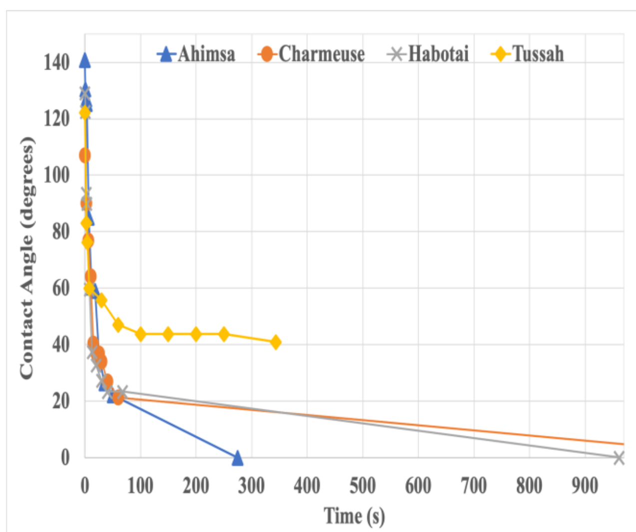



In Figure 7, Tussah/INF114 system stagnated on the surface at 343 second (5:43 minutes). Charmeuse/INF114 system reached complete wetting the slowest at 1225 seconds (20:25 minutes). Ahimsa/INF114 and Habotai/INF114 systems were completely wetted in shorter amounts of time at 275 (4:33 minutes) and 960 (16:00 minutes) seconds, respectively.

Hydrex/Tussah system also stagnated at 900 seconds (15:00 minutes). Relatively quicker times, as depicted in Figure 8, are shown for the other three systems. Habotai/Tussah and Charmeuse/Tussah systems were completely wetted in 137 seconds (2:17 minutes) and 96 seconds (1:36 minutes), respectively. Ahimsa/Tussah system was the quickest to complete wetting at time of just over 90 seconds (1:30 minutes).

As these results show, silk architecture is observed to have a substantial impact on the affinity of the silk/resin interface. The best affinity is exhibited the Ahimsa/Hydrex system, closely followed by the Charmeuse/Hydrex system. It is worth noting that initial contact angle is not an effective indicator of affinity as Ahimsa consistently produced the highest initial contact angles and was the quickest to drop to complete wetting for all resins.

**Fig. 9. Effect of silk architecture on the silk/resin affinity for INF114 Epoxy.**



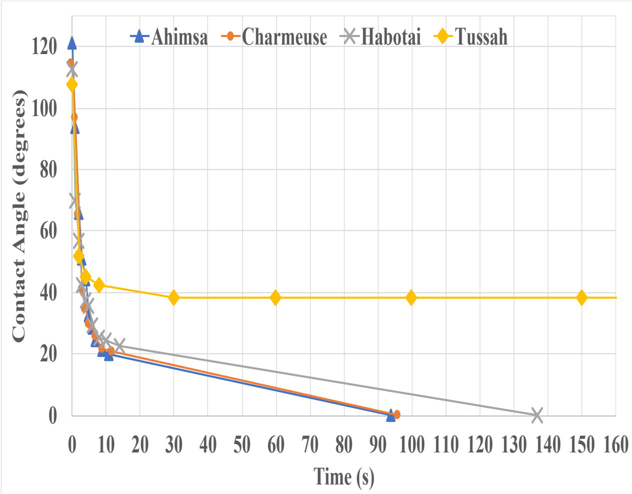



**Fig. 10. Effect of silk architecture on the silk/resin affinity for Hydrex vinyl**.

## 3 Conclusion

Various silk architectures were investigated to determine their effects on wettability of several silk/resin systems. The aim of this study was to identify silk/resin systems with higher affinity so that composites manufactured of these materials completely utilize silk's superior mechanical and physical propertied. Static contact angles were obtained for each silk/resin system over time and qualitatively compared. In doing so, it was found that Hydrex consistently dropped to complete wetting in the shortest amount of time for all resins. It was concluded that Ahimsa/Hydrex and Charmeuse/Hydrex systems exhibited the highest affinity by producing the shortest complete-wetting durations. In the future, it would be of interest to manufacture silk fiber composite laminates using these candidates for improved mechanical properties.

## Acknowledgements

The authors would like to acknowledge the support provided by the grant Engaged Learning to Promote STEM Graduation (ELPSG), funded by HSI program of NSF.

## Funding

This work has been supported by the Faculty Research and Support Fund at the University of Houston-Clear Lake.

*Conflict of Interest:* none declared.

## References

Barraza et al. (2002). Elastomeric sizings for glass fibers and their role in fiber wetting and adhesion in resin transfer molded composites. *Composite Interfaces*, **9**(6): 477-508. doi: 10.1163/15685540260494083

Barraza et al. (2017), Performance of Glass Woven Fabric Composites with Admicellar-Coated Thin Elastomeric Interphase. *Composites Interfaces*, **24**(2): 125-148, 2017. doi:10.1080/09276440.2016.1193345

Cheung, H.Y. *et al.* (2009). Study on the Mechanical Properties of Different Silkworm Silk Fibers. *Journal of Composite Materials,* 43(22), 2521–2531. doi:10.1177/0021998309345347

Gosline, J. M. *et al.* (1999). The Mechanical Design of Spider Silks: From Fibronin Sequence to Mechnical Function. *The Journal of Experimental Biology*. 202, 3295-3303.

Heim, M. *et al.* (2009). Spider Silk: From Soluble Protein to Extraordinary Fiber. *Angewandte Chemie International Edition,* 48(20), 3584–3596. doi:10.1002/anie.200803341

Hsia,Y. *et al.* (2011). Spider Silk Composites and Applications. *Metal, Ceramic and Polymeric Composites for Various Uses.* 303–324. doi: 10.5772/22894.

Hamidi, Y. K. et al. (2005) Polymer composites. In Encyclopedia of Chemical Processing; Lee, S., Ed.; Decker Publisher: New York, NY, USA, 2005; pp. 2313–2322. ISBN 978-0-8247-5563-8.

Hamidi, Y. K. and Altan, M.C. (2017) Process induced defects in liquid molding processes of composites.Int. Polym. Proc.32.527–544.

Hamidi, Y. K. and Altan, M. C. (2018) Process-induced defects in resin transfer molded composites. In Comprehensive Composite Materials II, Vol. 2; Beaumont, P.W.R., Zweben, C.H., Eds.; Elsevier: Amsterdam, The Netherlands, pp. 95–106.

Hamidi, Y.K. et al. (2018) Silk as a Natural Reinforcement: Processing and Properties of Silk/Epoxy Composite Laminates. Materials. **11**: 2135. 10.3390/ma11112135.

Hamidi, Y. K. et al. (2019) Manufacturing Silk/Epoxy Composite Laminates: Challenges and Opportunities. *AIP Conference Proceedings* **2065**, 030025. 10.1063/1.5088283

Hakimi, O. *et al.* (2007). Spider and mulberry silkworm silks as compatible biomaterials. *Composites Part B: Engineering*, **38**(3), 324–337. doi: 10.1016/j.compositesb.2006.06.012

Inamdar, A. et al. (2018). Thermoplastic-Toughened High-Temperature Cyanate Esters and Their Application in Advanced Composites. *Industrial & Engineering Chemistry Research*, 57(13), 4479–4504. doi:10.1021/acs.iecr.7b05202

Jariwala, H., & Jain, P. (2019). A review on mechanical behavior of natural fiber reinforced polymer composites and its applications. *Journal of Reinforced Plastics and Composites*, 073168441982852. doi:10.1177/0731684419828524

King, J. A. et al. (2014). Mechanical properties of graphene nanoplatelet/epoxy composites. *Journal of Composite Materials,* **49**(6), 659–668. doi:10.1177/0021998314522674

Kim, C., Cho, G., & Na, Y. (2002). Effects of Basic Weave Differences in Silk Fabric and Yarn Type Variations in Satin Weave on Sound Parameters. *Textile Research Journal*, **72**(6), 555–560. doi:10.1177/004051750207200616

Menjivar S., Cotten L., Hamidi Y.K. (2020). Effect of Silk Treatment on Silk/Resin Wettability. *American Journal of Advanced Research*, **4**(2), 7-11. 10.5281/zenodo.4105415

Ranakoti, L., Gupta, M. K., & Rakesh, P. K. (2019). Silk and Silk-Based Composites: Opportunities and Challenges. *Materials Horizons: From Nature to Nanomaterials*, 91–106. doi:10.1007/978-981-13-6019-0_7

Shah, D.U. *et al.* (2014) Can silk become an effective reinforcing fibre? A property comparison with flax and glass reinforced composites. *Composites Science and Technology*. **101**, 173–183. //doi.org/10.1016/j.compscitech.2014.07.015

Shah, D.U. *et al.* (2014). Opportunities for silk textiles in reinforced biocomposites: Studying through-thickness compaction behaviour. *Composites: Part A*. **62**, 1–10. doi: 10.1016/j.compositesa.2014.03.008

Shao, Z., and Vollrath, F. (2002). Surprising strength of silkworm silk. *Nature*. 418(6899), 741–741. doi:10.1038/418741a

Wambua, P., Ivens, J., & Verpoest, I. (2003). *Natural fibres: can they replace glass in fibre reinforced plastics? Composites Science and Technology*, ***63****(9), 1259–1264*. doi:10.1016/s0266-3538(03)00096-4

Yang, K. *et al.* (2017). Enhancing the Mechanical Toughness of Epoxy-Resin Composites Using Natural Silk Reinforcements. *Scientific Reports*. **7**(1). doi:10.1038/s41598-017-11919-1

Zweben, C. (1981). Advanced composites for aerospace applications. *Composites*, **12**(4), 235–240. doi:10.1016/0010-4361(81)90011-2