Properties of Woven Natural Fiber-Reinforced Biocomposites

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ABSTRACT: Woven natural fiber-reinforced composites were fabricated using four different flax fabrics and two biobased epoxy resin matrices. The reinforced composites were prepared using resin infusion technique and fiber volume fractions of between 28–35% were achieved using this method. The fiber matrix interaction and the failure mechanism in the composite were observed using scanning electron microscopy. The flexural strength and modulus on the warp and weft directions were characterized and it was found that based on yarn count and yarn thickness change in the flexural strength was observed. Dynamic water absorption and thickness swelling were observed for a certain period of time and depended on pore volume and fiber volume fractions. Among the fabric architecture, on the weft direction satin weave with low fiber volume fraction has achieved the highest flexural strength and modulus of 220 MPa and 11.7 GPa respectively.

KEYWORDS: Biobased composites, natural fiber, mechanical properties, resin infusion technique

1 INTRODUCTION

The utilization of natural fibers as reinforcement in structural composites has currently been increased due to their light weight, excellent damping properties, as well as their potential environmental benefits [1, 2]. The resin matrices which are commonly used for preparing natural fiber-reinforced composites are from fossil fuel-derived resources. Currently the use of renewable resources as chemical feedstock for synthesizing polymeric resins has attracted considerable attention due to limited fossil fuel resources and huge fluctuation in oil prices, sustainable development, and consumer demand for more eco-friendly products. Therefore, the use of natural fibers as reinforcement in the composites in combination with biobased resins would considerably increase the renewable content of the final material, with the additional advantage of nontoxicity and biodegradability for some of them.

Thermosetting resins are mainly used as matrices for preparing biobased composites, and the most commonly used techniques to prepare the composites have been compression molding, liquid molding and hand-layup. The renewable resources like plant oils, polysaccharides, proteins and lignins are interesting raw materials which can substitute partially, and to some extent totally, the fossil fuel-derived polymers in the biobased thermoset resin. Synthesis of liquid molding resin derived from plant oils was patented by Wool *et al.* [3]. The resins described in the patent resemble the unsaturated polyester, vinyl ester, and epoxy resins which are used as polymer matrix material in high performance natural fiber-reinforced composites. Similarly, several studies have dealt with the preparation and properties of biobased thermoset resins from various renewable resources [4, 5].

In composites, the natural fiber reinforcement can be of different forms (long, short, woven or nonwoven) and among them woven natural fiber reinforcement has an advantage since it allows for precise placement and simple processing, which could improve the mechanical properties of the composite. There are only very few reports on composites with woven fabric and biobased thermoplastic/thermoset resin. Adekunle *et al.* [6] investigated the impact and flexural properties of flax fabrics and Lyocell fiber oriented composite made using biobased thermoset. It was found that plain and dobby weave architecture can give better reinforcing effects and the flexural properties could also be improved with an increase in outer ply thickness. Baghaei *et al.* [7] characterized the polylactic acid (PLA)-based biocomposites made from

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woven polylactic acid/hemp-Lyocell hybrid yarn fabrics. The composites made from satin weave Lyocell/PLA gave the best mechanical properties. In addition, combining hemp with Lyocell in a PLA matrix improves the mechanical properties of the composites. Zhu *et al.* [8] investigated the structural performance of flax-reinforced composites from tannin resin and bioepoxy system. The investigation suggested that fabric arrangement could be properly tailored to balance the tensile and impact properties of the flax-reinforced composites. Khot *et al.* [9] investigated the mechanical properties of the flax fiber reinforcement with biobased thermoset resin. It was reported that the flax composites had tensile and flexural strengths in the ranges of 20–30 and 45–65 MPa, respectively.

In the current investigation, four different woven flax fabrics along with two different biobased resins were used to prepare the composites. The composites were fabricated by using the vacuum infusion process, and the benefit of using this process is that it has better fiber-to-resin ratio than the vacuum bagging technique. During resin infusion, the product has to be filled completely, and for this knowledge about the permeability behavior of the textile preform is more important, which is directly related to the rate of impregnation and filling time. Hence the flow behavior of the resin during the impregnation was also investigated. Finally, the mechanical properties and the water absorption behavior of the composites were also investigated in this work.

2 MATERIALS AND METHODS

2.1 Materials

The woven flax fabrics (Weave Nr. 1-3, Table 1) were manufactured at Leinenweberei Vieböck GmbH, Austria, using specially designed low-twist and standard flax yarns. Low-twist flax yarns (68 Tex) were purchased from Safilin, France, and standard flax yarns (105 and 67 Tex) were purchased from Vieböck.

Weave Nr. 4, designated as hopsack in the text, was purchased from Composites Evolution Ltd., Chesterfield, United Kingdom. The cylindrical yarns are manufactured from aligned fibers held together by a polyester yarn going in a spiral manner along the flax yarn [10]. The linear density of the above flax yarns is 250 Tex. The photographed and microscopic images of the fabric types are shown in Figures 1–4. Two different commercial biobased resin matrices were used for manufacturing biocomposite. The first resin, Greenpoxy 56, containing 56% "green" carbon and its hardener GP 505 was purchased from Sicomin, France. Densities of resin and hardener were

Table 1 Types and properties of flax fabrics used for fabricating biocomposites.

Fabric name	Weave type	Linear mass density of fiber yarn		Yarn count	Areal weight
Weave Nr.1	Plain	Warp	105 Tex	13 yarns/cm	245 g/m^2
		Weft	68 Tex	13 yarns/cm	
Weave Nr.2	Plain	Warp	68 Tex	13 yarns/cm	245 g/m^2
		Weft	105 Tex	13 yarns/cm	
Weave Nr.3	Satin	Warp	67 Tex	13 yarns/cm	205 g/m^2
		Weft	68 Tex	17 yarns/cm	
Weave Nr.4 (Hopsack)	Plain (4x4)	Warp	250 Tex	7 yarns/cm	500 g/m^2
		Weft	250 Tex	7 yarns/cm	

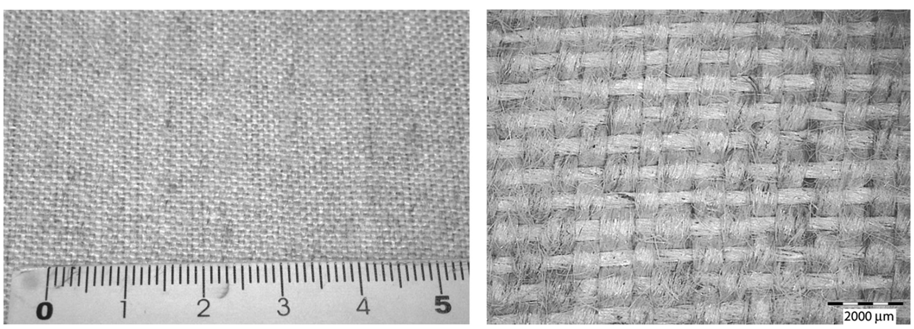

Figure 1 Flax fabric Weave Nr.1 (Plain Weave) and its microscopic view.

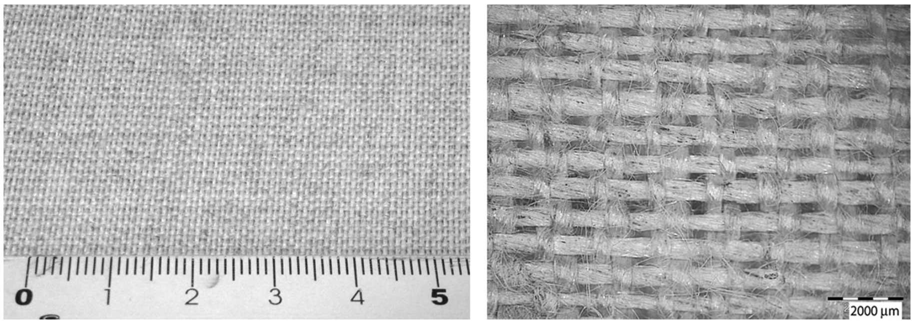

Figure 2 Flax fabric Weave Nr.2 (Plain Weave) and its microscopic view.

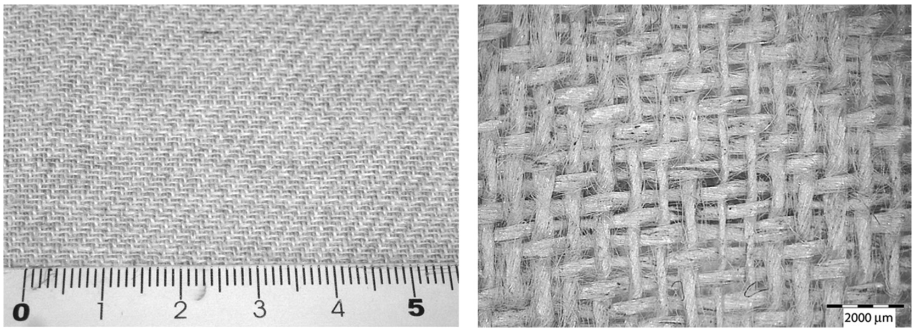

Figure 3 Flax fabric Weave Nr.3 (Satin Weave) and its microscopic view.

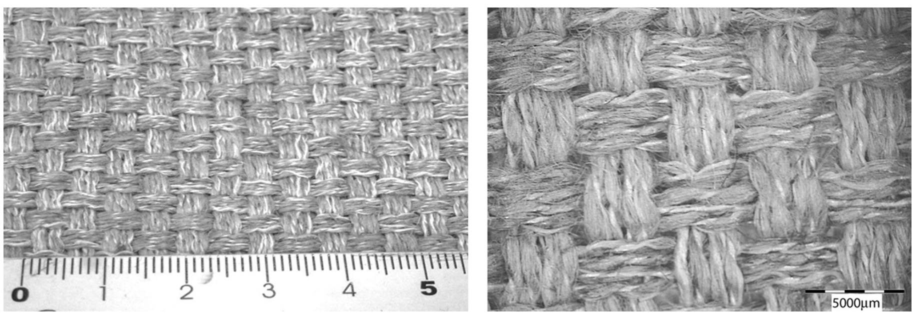

Figure 4 Hopsack flax fabric (Plain Weave) from Composites Evolution and its microscopic view.

1.152 and 0.99 g/cm^3, respectively. The second resin, Supersap, containing 17% renewable content was purchased from Entropy Resins, Spain. The epoxy resin Super Sap CLR was used along with the INF curing agent. Densities of resin and hardener were 1.17 and 0.95 g/cm^3, respectively.

2.2 Methods

The biocomposites were fabricated using vacuum infusion process. In the manufacturing process, flax reinforcement is laid into the mold without any resin and enclosed by the stack of bagging material. The stack sequences were as follows: peel ply, perforated film, infusion mesh and the bagging film. The vacuum was applied before resin infusion, and once all the air has been removed, the liquid epoxy resin mixed with curing agent is introduced into the reinforcement through a flexible hose and distributed with the help of a polypropylene spiral hose. Under vacuum pressure, resin infuses through the reinforcement and the supply of resin is cut off once the resin completely fills the mold. The samples were cured at room temperature for the duration of 16–18 h and then post cured at 100 °C for the duration of 6 h. The curing conditions were chosen as prescribed by the supplier.

The three-point bending tests (flexural strength and modulus) were carried out for the biocomposites

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on a Frank 81565 testing machine (Zwick GmbH & Co. KG, Ulm, Germany). For the water absorption and thickness swelling test, the specimens were immersed in deionized water for a certain period of time. Afterwards, samples were taken out and the surface water was wiped off using blotting paper. The change in weight and thickness were measured with respect to immersion time and it was performed until a constant weight gain was achieved. The percentage of water absorption (W_{WA}) and thickness swelling (T_{TS}) of the specimens was determined using the following equations.

$$W_{WA} = \frac{W_e - W_0}{W_0} \times 100$$

where W_0 is the weight of specimen before immersion and W_e is the weight of the specimen after a certain duration of time.

$$T_{TS} = \frac{T_e - T_0}{T_0} \times 100$$

where T_0 is the thickness of the specimen before immersion and T_e is the weight of the specimen after a certain duration of time.

The fiber, matrix and pore volume fractions of the composites were calculated using the following formulae, assuming that on a macroscopic scale, composite material can be divided into three volumetric components; fiber, matrix and porosity. The total volume of the composite is the summation of three individual volumes.

$$v_c = v_f + v_m + v_p$$

where v is volume and the subscripts c, f, m and p denote composite, fiber, matrix and porosity, respectively. Mass of the composites is the addition of both fiber and matrix.

$$m_c \equiv m_f + m_m$$

where m is mass and the subscripts c, f and m denote composite, fiber and matrix, respectively. The fiber volume (v_f) is calculated using the formula described below

$$v_f = \frac{m_f}{\rho_f} \equiv \frac{n * m'_f * A_c}{\rho_f}$$

$$v_m = \frac{m_m}{\rho_m}$$

where n is the number of plies, m'_f is the areal weight of the plies, A_c is the surface area of the rectangular composite, ρ_f and ρ_m are the densities of the fiber and matrix respectively. The literature value was considered for the density of the fiber (1.5 g cm^{-3}). The pore volume v_p is calculated using the following formula:

$$v_p = \left(v_c - v_f\right) - \frac{m_c - m_f}{\rho_m}$$

where m_c is the weight of the composite.
From the calculated pore (v_p) and fiber (v_f) volumes, the volume fractions (φ) of the pore, fiber and matrix were determined using the formula:

$$\varphi_p = \frac{v_p}{v_c} = \frac{v_p}{A_c * t_c}$$

$$\varphi_f = \frac{v_f}{v_c} = \frac{v_f}{A_c * t_c}$$

$$\varphi_m = 1 - \varphi_f - \varphi_p$$

where t_c is thickness of the composite.

The fiber/matrix interaction and failure mechanism in the biocomposite cross section were studied using scanning electron microscopy (SEM). The specimens were sputtered with a thin layer of conducting material and analyzed using a Hitachi TM-3000 SEM at 5kV accelerating voltage.

3 RESULTS AND DISCUSSION

The properties of the biobased biocomposites fabricated using woven flax fabrics are shown in Table 2. The areal weight of the hopsack fabric is higher than other fabrics, hence only 2 plies were required for manufacturing biocomposites. The thickness of the biocomposites was between 1.75–1.9 mm and densities were in the range of 1.25 ± 0.03 g/cm^3. The calculated fiber volume fraction for the biocomposites containing Weave Nr. 1, 2 and hopsack flax fabrics were around 35% but the biocomposites with Weave Nr. 3 (satin weave) fabrics had only 29% fiber volume fraction. When the weave architectures are compared, satins have longer floats, fewer intersections, and a more open construction. Hence, they have achieved lower fiber content. As per Shah and Clifford [11], at low fiber content, due to low yarn permeability but high overall permeability, the yarn is not properly impregnated and thus intra-yarn voids may form which are relatively low.

3.1 Impregnation Behavior

The most significant influence on the permeability was given by the fiber volume fraction, the porosity and the compact behavior. The permeability (k) was based

Table 2 Properties of the biocomposites fabricated using biobased matrix resin.

Biocomposite	Number of Plies	Biocomposite thickness t [mm]	Biocomposite density ρ [g/cm³]	Fiber volume fraction V_f[12] (Standard Deviation) [%]	Pore volume fraction V_p[12] (Standard Deviation) [%]
Weave Nr.1 -GP56/GP505	4	1.80	1.28	34.7 (0.9)	7.1 (1.2)
Weave Nr.1 -Supersap/INF	4	1.75	1.25	35.8 (0.6)	8.4 (1.2)
Weave Nr.2 -GP56/GP505	4	1.80	1.28	34.7 (0.4)	7.2 (1.0)
Weave Nr.2 -Supersap/INF	4	1.80	1.26	34.3 (0.7)	8.6 (1.1)
Weave Nr.3 -GP56/GP505	4	1.80	1.26	28.7 (0.5)	6.6 (1.1)
Weave Nr.3 -Supersap/INF	4	1.80	1.22	29.3 (0.3)	6.5 (1.5)
HOP -GP56/GP505	2	1.90	1.27	34.7 (0.4)	8.0 (1.3)
HOP -Supersap/INF	2	1.90	1.24	32.7 (0.6)	10.4 (1.4)

on Darcy's law, and it was monitored on major (k1) and minor axes (k2) for the Hopsack and Weave 1 flax fabric. The k1 and k2 values were more or less the same for both the fabrics at the fiber volume fraction of 32%. The measured permeability values for the Hopsack and Weave 1 fabrics are 1.003×10^{-10} m² and 2.378×10^{-10} m² respectively. The hopsack fabric has a thicker yarn compared to other weave patterns, which caused a relatively high pore volume fraction. According to Shah and Clifford [11], if the yarn and overall permeability are similar but the capillary flow in the yarn dominates, inter-yarn voids are formed during processing. If the permeability of the fabric is high then it is quite easy to impregnate and less time is needed to fill the mold. To evaluate the differences in the permeability between two fabrics, the Weave 1 and hopsack fabrics were draped on three-dimensional hemispherical parts and impregnated with Greenpoxy 56 using the resin infusion technique. The shape of the flow front and the part filling time were determined for the Weave 1 and hopsack fabrics. The total filling time for the Weave 1 and Hopsack is 17:20 and 13:00 min respectively. Actually, it was observed that for the hopsack fabric the capillary flow inside the fiber yarns is higher than Weave 1 and the evolution of the resin front through these two fibers at various time intervals is shown in Figure 5.

For all the composites, the flow front velocity during infusion is not linear; for instance, almost half of the hemispherical mold was wetted by the resin for the hopsack fabric at only 25% of the total filling time. At 13 min of impregnation time, the hopsack was completely wetted with the resin, whereas Weave 1 has achieved only 75% of its filling time. As a result, hopsack fabric had a better permeability and its weave structure has a governing effect on the filling time and the flow front. Nevertheless, the flow front can result in the formation of voids and dry-spots within the fabric preforms. A complex dual-scale flow of resin in fibrous preform was observed for the hopsack fabric (Figure 5), which can cause voids in the biocomposite.

3.2 Mechanical Performance and Fracture Behavior

The flexural strength (Figure 6) and modulus (Figure 7) of the biobased matrices were compared with the strength of the biocomposites and it showed that both values were significantly increased by the natural fiber reinforcement. In between these two biobased resins, the flexural strength of the Super Sap resin (125 MPa) was higher than Greenpoxy (102 MPa).

Some differences in the flexural strengths of the composites were observed on the fabrics warp and weft direction, which is primarily due to the variation in yarn count, yarn thickness and twist angle. For the Weave 2 and 3, the flexural strengths on the weft direction are higher than in warp direction. The warp yarns are prestressed during the weaving itself, hence they achieved lower flexural strength. A significant rise

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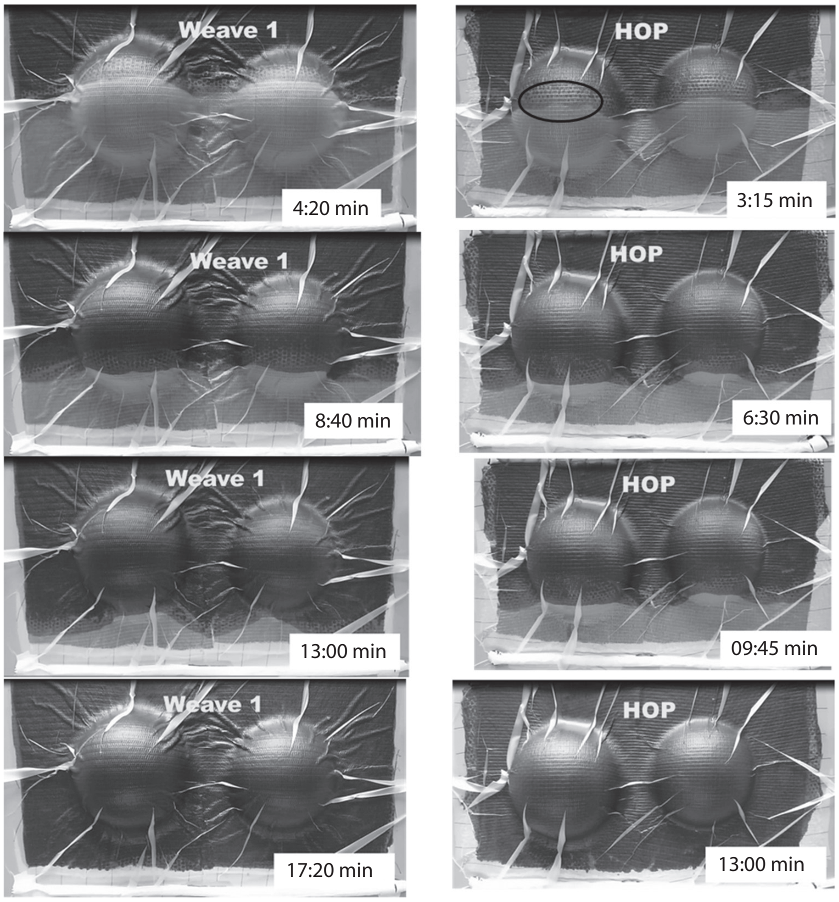

Figure 5 The flow front at 25%, 50%, 75%, and 100% of the filling time for the Weave 1 and Hopsack fabrics.

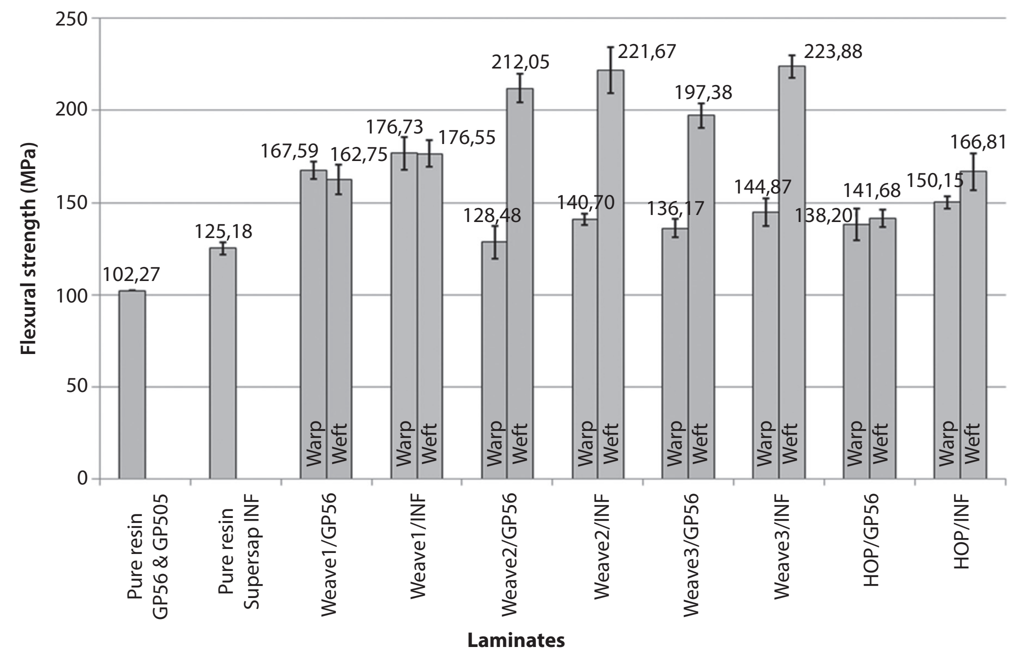

Figure 6 Flexural strengths of the biocomposites prepared using biobased resins.

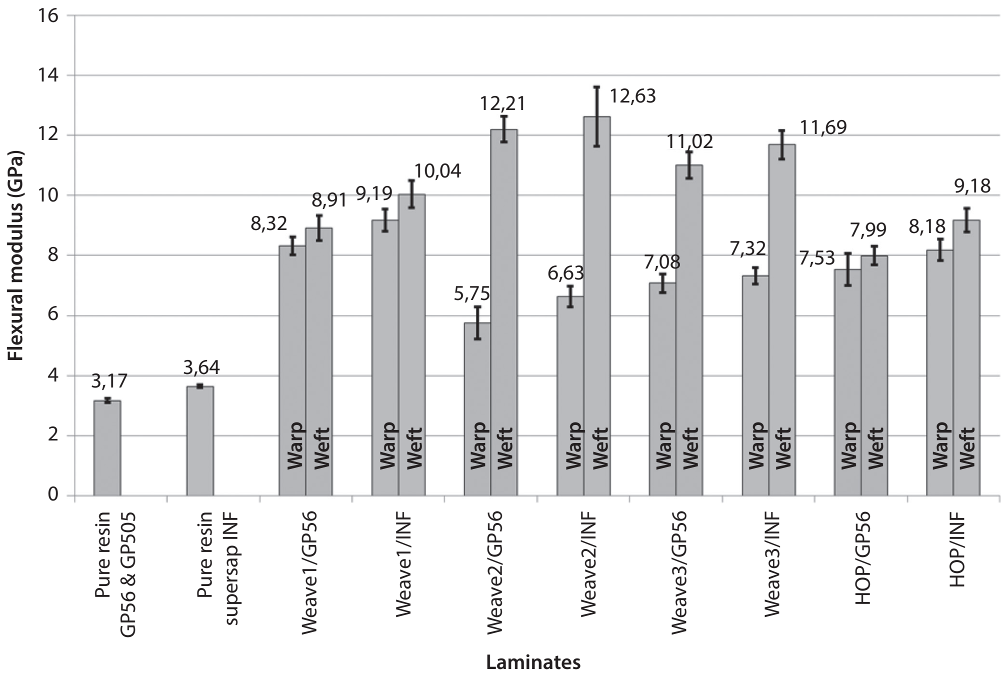

Figure 7 Flexural modulus of the biocomposites prepared using biobased resins.

in the flexural values was observed for the Weave 2 and 3 on the weft direction, which is due to the use of thin yarns on the warp direction. Also, for the hopsack fabric, a slight increase in flexural strength was observed and the reason is that more yarns were used in the weft (11 yarns) direction than in warp (7 yarns) direction. The flexural modulus of the pure resin and composites were also determined and are shown in Figure 7. The composite with Weave 3 fabric have achieved higher modulus than Weave 1. Both fabrics include the same type of yarn, but this difference in modulus can be explained by a higher count of yarns in the weft direction for the Weave 3 (17 yarns) than Weave 1 (13 yarns). The Weave 3 flax fabric, which has satin weave architecture, achieved around 11 GPa flexural modulus even at low fiber content. The maximum stiffness was achieved on the weft direction while using Weave 2 fabrics.

The microstructure of the biocomposites was analyzed using scanning electron microscopy. The micrographs of the fractured surface are shown in Figure 8. The biocomposites with the Weave Nr. 1 and Weave Nr. 2 reinforcements had free long fibers on the surface and few voids on the matrix region. In addition, some fiber borders were cracked very close to the matrix, which reveals a good adherence at the interfaces. In the yarn bundle, the gaps were reduced and densely packed structures were observed in the composites (Figure 8a and 8b).

This implies a good compatibility between the matrix and fiber. The biocomposites with the Weave Nr. 3 flax fabrics (Figure 8c) had yarn breakage and micropores in and around the fiber bundles. The matrix resin had enveloped the fiber bundles but the yarn still remains not completely impregnated, as is observed from the uncompressed fiber bundle. The biocomposite with hopsack fabric (Figure 8d) showed fiber breakage and fiber pullout, the breakage remaining the dominant factor. The voids in between the fiber yarns or yarn bundles were observed and correspond to the calculated free pore volume fraction. As a whole, the fiber matrix interaction was good enough for all the weave types. But different levels of voids were observed in the composites based on fiber architecture and yarn thickness.

3.3 Water Absorption and Thickness Swelling

The dynamic water absorption and thickness swelling values for the pure resin and composites are shown in Figures 9 and 10. The Greenpoxy resin absorbs more water than the Super Sap resin but both had water absorption values less than 2%. The rate of water-uptake for all the biocomposites was high up to 264 h (11 days) and after 11 days water uptake starts to achieve saturation for some biocomposites. The composite constituted of Weave 3 fabric with Super

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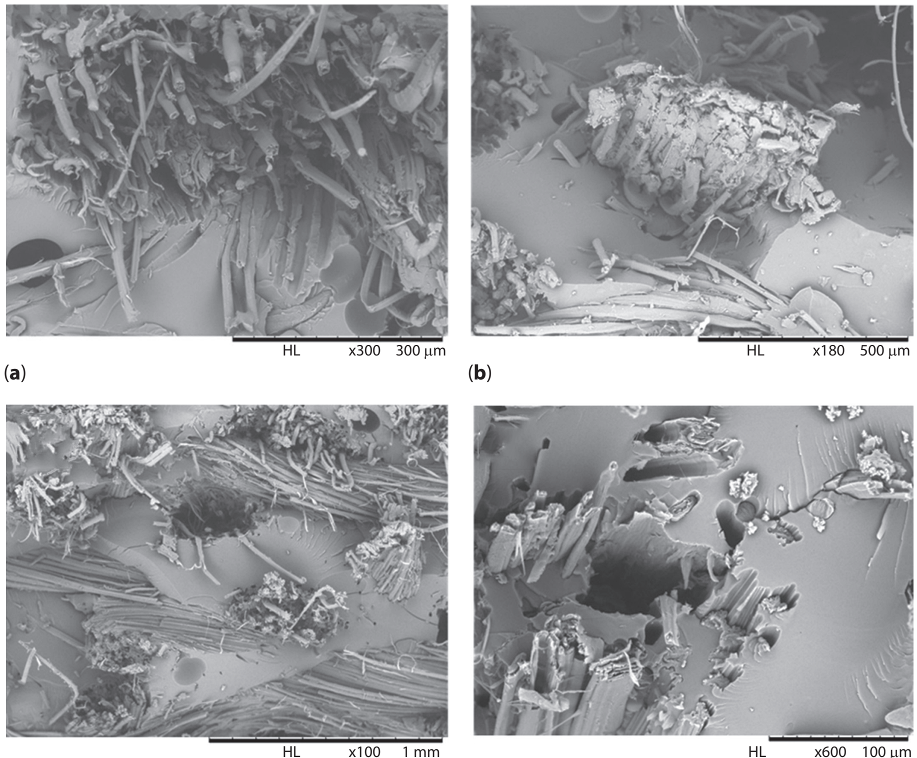

Figure 8 SEM micrographs of fractured surfaces of biocomposites reinforced with Weave Nr.1 (**a**), Weave Nr. 2 (**b**), Weave Nr. 3 (**c**), and hopsack fabric (**d**). Note that different levels of magnification were chosen in order to represent the structural peculiarities of each weave type.

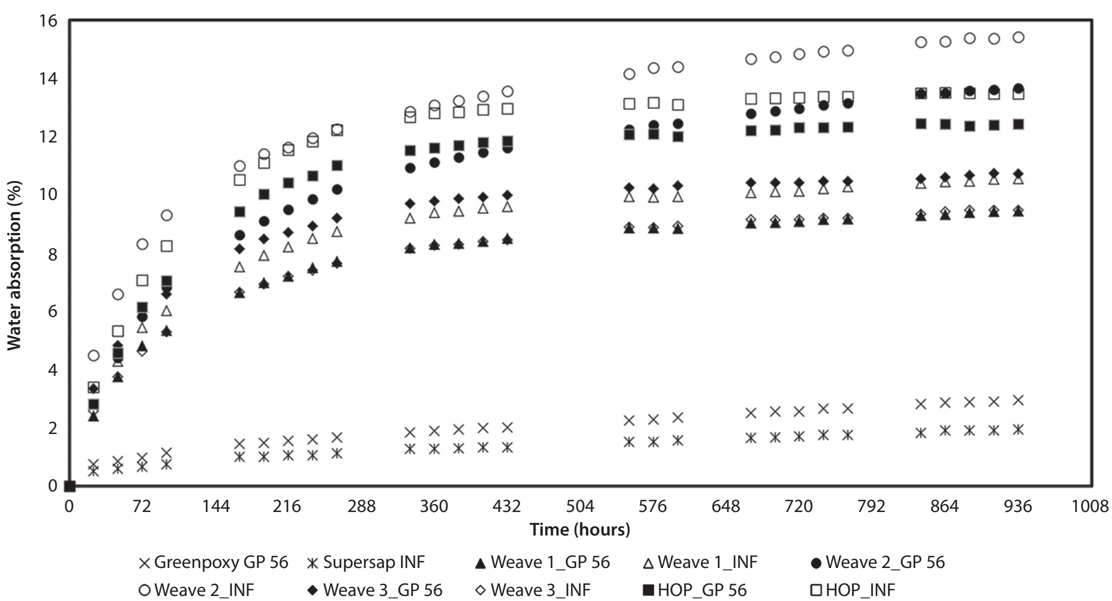

Figure 9 Water absorption behavior of the biocomposites prepared using biobased resins.

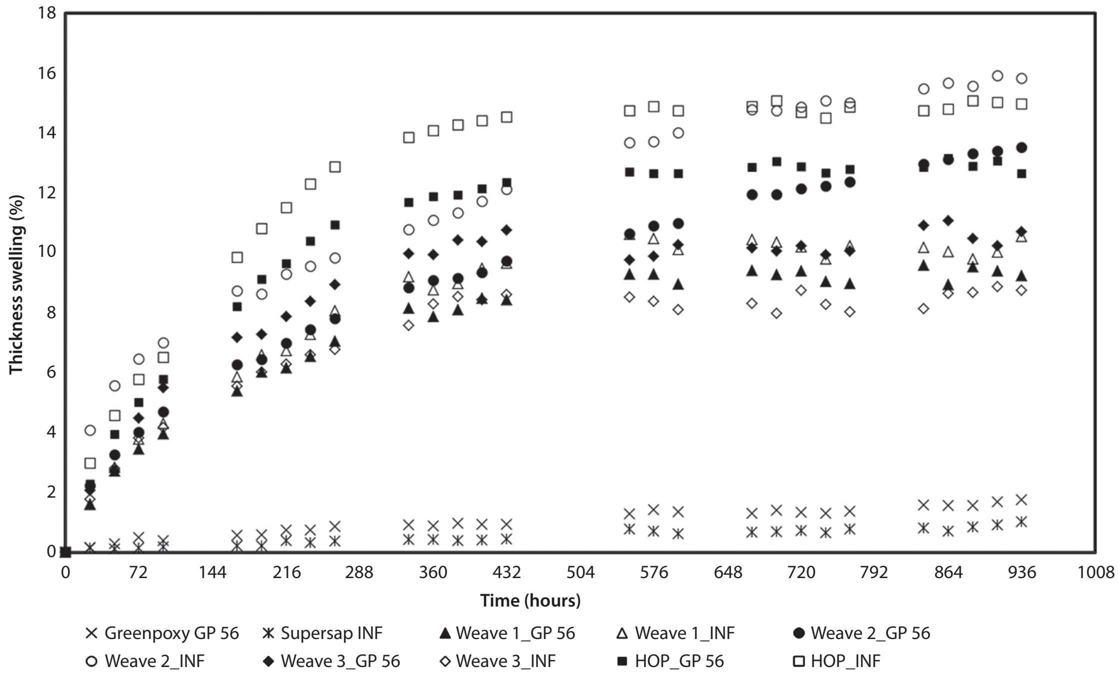

Figure 10 Thickness swelling behavior of the biocomposites prepared using biobased resins.

Sap (INF) resin had the lowest fiber volume fraction (Table 2) and also showed the lowest water absorption value. The fiber bundles were masked with the matrix resin and it prevented the water uptake. The highest level of water absorption was observed for the biocomposites having Weave 2 fabrics with Super Sap matrix with a pore volume fraction of 8.6%. Similarly, hopsack fabric along with Super Sap resin had the second highest level of water absorption with a pore volume fraction of 10.4%. These different results in water absorption values highlight the correlation between the pore volume fraction and the water penetration into the biocomposite. The water molecules, which are small enough to pass through the micropores, are likely to cause the swelling of the fibers, and cause a relatively high water uptake. The water absorption values were also found to be influenced by the fiber loading.

The thickness swelling is a nonreversible process which results from the release of residual compressive stress after water absorption. The thickness swelling for the pure resin is considerably lower because it contains no hydrophilic fibers, which are likely to catch and retain water to a larger extent. On the other hand, in biocomposites with hopsack fabric and Super Sap resin, up to 16% thickness swelling was observed with a pore volume fraction of around 10.4%. Water penetrates into the pores, which are mainly concentrated around the natural fiber reinforcement, making them swell. As a consequence, the whole material is irreversibly deformed due to these internal mechanical forces of swelling, resulting in a gain in volume along the thickness direction which eventually reduces the packing density. At the initial stage of up to 264 h (11 days) a steep increase in thickness swelling was observed but after 288 h (12 days) a huge variation in the thickness swelling was observed. Again the pore volume and fiber loading has a huge influence on the thickness swelling behavior of the biocomposites.

4 CONCLUSION

This article investigated the mechanical properties of the woven flax fiber-reinforced composites with biobased epoxy matrix resin. The long-term water absorption and thickness swelling behavior of the composites were also investigated. In terms of resin wetting, the in-plane permeability of the Hopsack fabric is higher than the Weave 1 type, and from this it was found that capillary flow in the fiber yarn is dominated in the hopsack fabric. But Hopsack achieved high pore volume fraction due to the complex dual flow of resin. The composites having plain weave and satin weave fabrics on the weft directions have achieved the highest flexural strength (around 220 MPa). Comparing the two biobased epoxy resins, the Super Sap achieved the best flexural strengths

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when used alone as well as in composites. The dynamic water absorption was relatively high for the hopsack fabric, as it appears to be in correlation with the pore volume fraction. The results of this work provide evidence that biobased composites with woven fabric reinforcements and biobased resins are suitable for structural application.

REFERENCES

1. H. Cheung, M. Ho, K. Lau, F. Cardona, and D. Hui, Natural fiber composites. *Compos. Part B-Eng.* **40**, 655–663 (2009).
2. A.K. Mohanty, M. Misra, and G. Hinrichsen, Biofibres, biodegradable polymers and biocomposites: An overview. *Macromol. Mater. Eng.* **276**, 1–24 (2000).
3. R. Wool, S. Küsefoglu, G. Palmese, S. Khot, and R. Zhao, High modulus polymers and composites from plant oils. US Patent 6121398, assigned to University of Delaware, Newark (2000).
4. J.M. Raquez, M. Deléglise, M.F. Lacrampe, and P. Krawczak, Thermosetting (bio)materials derived from renewable resources: A critical review. *Prog. Polym. Sci.* **35**, 487–509 (2010).
5. A. Dotan, Biobased thermosets, in *Handbook of Thermoset Plastics*, Hanna Dodiuk and Sydney Goodman (Eds.), pp. 577–622, William Andrew Publishing, San Diego, CA 92101, USA (2013).
6. K. Adekunle, S.W. Cho, C. Patzelt, T. Blomfeldt, and M. Skrifvars, Impact and flexural properties of flax fabrics and Lyocell fibre-reinforced bio-based thermoset. *J. Reinf. Plast. Compos.* **30**, 685–697 (2011).
7. B. Baghaei, M. Skrifvars, and L. Berglin, Manufacture and characterization of thermoplastic composites made from PLA/hemp co-wrapped hybrid yarn prepregs. *Compo. Part A: Appl. S.* **50**, 93–101 (2013).
8. J. Zhu, A. Sauget, E. Nassiopoulos, A. Pizzi, C. Avril, J. Njuguna, and H. Abyhankar, Structural performances of flax reinforced composites from tannin resin and bio-epoxy. *Transport Research Arena Conference*, Paris (2014).
9. S.N. Khot, J.J. Lascala, E. Can, S.S. Morye, S.I. Williams, G.R. Palmese, S.H. Kusefoglu, and R.P. Wool, Development and application of triglyceride-based polymers and composites. *J Appl. Polym. Sci.* **82**, 703–723 (2001).
10. P. Ouagne and D. Soulat, Complex shape forming of flax fabrics: Analysis of the solutions to prevent defects, in *Green Biorenewable Biocomposites: From Knowledge to Industrial Applications*, V.J. Thakur and M.R. Kessler (Eds.), pp. 241–272, CRC Press (2015).
11. D.U. Shah and M.J. Clifford, Compaction, permeability and flow simulation for liquid composite moulding of natural fibre composites, in *Manufacturing of Natural Fibre Reinforced Polymer Composites*, M.S. Salit, M. Jawaid, N.B. Yusoff, and M.E. Hoque (Eds.), chap. 4, pp. 65–99, Springer Publishing, Cham, Switzerland (2015).
12. B. Madsen and H. Lilholt, Physical and mechanical properties of unidirectional plant fibre composites—An evaluation of the influence of porosity. *Comp. Sci. Tech.* **63**, 1265–1272 (2003).

