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Interface modification and the influence on damage development of flax fibre – Epoxy composites when subjected to hygroscopic cycling

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ABSTRACT

The moisture sensitivity of natural fibre composites limits their use in structural applications. Degradation of the fibre–matrix interface is likely to occur when the material is subjected to variable moisture conditions. This study investigates the damage development in unidirectional flax fibre reinforced epoxy composites during hygroscopic cycling. It is expected that the insertion of a silicone interphase increases interfacial toughness and therefore postpones or avoids interface degradation. Various silicones and a silane coupling agent were used in an attempt to enhance the long-term behavior of the composite. Hygroscopic cycling was performed by varying the relative humidity between approximately 25 and 80% at 80 °C. When examining the flax-epoxy reference composite, regression analysis showed a significant decline of the transverse strength during six consecutive wet-dry cycles. The degradation of the mechanical properties is attributed to fibre–matrix debonding and to cohesive failure in the fibre bundles. Both damage mechanisms are visualized in a unique three-dimensional model. Contrary to the hypothesis, the insertion of a silicone interphase led to an accelerated decrease of the transverse strength. Computed tomography analysis confirmed the weakening of the fibre–matrix interphase. Although the damage development was altered, the composites having a thin silicone interphase did not show a significant decrease in longitudinal stiffness and strength. This result is promising as it suggests that stress transfer is not significantly hindered.

1. Introduction

Bio-based materials are considered a valuable asset to facilitate the transition to a sustainable and circular economy. Following this trend, natural fibre reinforcements have been gaining importance in the composites sector. Although plant fibres, such as flax, hemp, jute and sisal, are already well established in certain industries, including the automotive sector, their use is mainly limited to non-structural applications [1,2]. A key aspect that hinders further implementation of natural fibre composites is their poor long-term durability when subjected to variable moisture conditions. The origin of this negative characteristic can be found in the natural tendency of the fibres to absorb moisture. When the composite is subjected to a more humid environment or a drier environment, the fibres will respectively swell and shrink. Consecutive wet-dry cycles lead to compressive and tensile stresses in the surrounding matrix which eventually causes the interface to degrade. The mechanical properties, water diffusion rate and equilibrium moisture content of the composite are significantly affected. Immersion in liquid water is the most common method to study the influence of hygroscopic loading. Fibre-matrix debonding, splitting of the fibre bundle, matrix cracking and leaching of water-soluble constituents are the main damage mechanisms reported in the literature [3–7]. Transverse tensile or bending tests on unidirectional (UD) composites are common methods to evaluate the quality of the interface. Equal forces are asserted to matrix, interface and fibres, and failure will occur in the weakest link. Because the interface is the limiting factor in most cases, degradation of the fibre–matrix interface due to hygroscopic stresses will lead to a decrease in transverse stiffness and strength. In literature, the general strategy to enhance the durability of natural fibre composites is to lower the equilibrium moisture content of the fibre using chemical bulk treatments. However, to the authors' knowledge, there is no

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treatment reported which completely prevents the absorption of moisture [8]. In addition, bulk treatments tend to lower the mechanical properties of the fibre [9]. Therefore, a novel route is proposed which shifts the focus to the improvement of the toughness of the interface.

In this study UD flax fibre reinforced epoxy composites were produced and their long term behaviour was evaluated. It was decided to vary the environmental moisture content instead of immersing in liquid water as it is a more realistic loading case for many applications. In addition, this loading case avoids damage related to wash out fibre components. The main objective of this research is to examine whether the insertion of an elastomeric silicone between fibre and matrix enhances the durability of flax-epoxy composites by mitigating the stresses resulting from the differences in hygroscopic expansion. Good adhesion of this third phase to both fibre and matrix is necessary to retain the toughening effect in consecutive wet and dry cycles. Silicone elastomers based on a polydimethylsiloxane (PDMS)-like backbone and an alkoxysilane crosslinker were evaluated in this research. The polycondensation chemistry of silicone allows the hydroxyl functionalities of flax fibre to be incorporated in the silicone lattice [10,11]. Therefore, good adhesion with the fibre is expected in all the proposed formulations. To promote adhesion with the epoxy matrix, amino-functionalized alkoxysilanes were used in one formulation. Although improvement of the long-term behaviour due to the insertion of the silicone interphase is expected, the overall performance of the composite might be impaired, especially when the fibres are fully encapsulated by silicone. A first adverse impact on the composite performance might be a decrease of the transverse properties before hygroscopic cycling because the mechanical properties of silicones are relatively low. Secondly, the longitudinal properties might be comprised due to the low shear stiffness which has an effect on the stress transfer from the matrix to the reinforcing fibres. Composites produced with untreated and 3-aminopropyltriethoxysilane (APS) treated flax fibre were used as a reference. The latter was selected because this treatment is known to improve interfacial strength and stiffness in contrast to the insertion of a soft silicone interphase [12]. The damage development during wet-dry cycles was evaluated based on three-point bending tests and X-ray computed tomography. In this exploratory study, interfacial toughness in the different systems was not quantified.

2. Materials and methods

2.1. Materials

Unidirectional (UD) flax tape with an aerial weight of 200 g/m^2 was provided by Lineo NV (Belgium). Epikote 828 LVEL epoxy with a 1,2-diaminocyclohexane (Dytek DCH-99) hardener from Hexion was selected as matrix. Three phase composites were produced by the insertion of a thin silicone layer. Two commercial silicones, Evonik Tegopac bond 160 and Wacker Elastosil E43, and one self-selected formulation were evaluated. The latter was based on polydimethylsiloxane (PDMS) with a molecular weight of 2000 g/mol and (3-aminopropyl)triethoxysilane (APS), both supplied by Sigma Aldrich (Belgium). The molar ratio of this mixture was 1:2.

2.2. Composite production

In this research UD composite plates with a fibre volume fraction (Vf) of approximately 35% and a thickness of 2 mm were produced. Vacuum assisted resin infusion was the production method of choice. Impregnation with epoxy resin was performed at 45 °C, followed by curing at 70 °C for 1 h and postcuring at 150 °C for 1 h. The composites having a modified interphase were produced in three steps. The silicone layer or APS coupling agent was applied on the fibres by means of a dip coating process and then cured before embedding the coated fibres in the epoxy matrix. The pretreatment of the fibres, namely the application of the layer and curing of the coating, is described below.

2.2.1. Pretreatment of the fibres

To promote chemical coupling with the hydroxyl functionalities of the fibres, the silicone coating was cured at high temperatures in a humid environment and contact with water was avoided in the initial stages of the process. All silicone coatings were applied according to the same protocol. Firstly, the UD tapes were dried for at least 48 h at 60 °C to assure the oven dry state. After this, the fibres were immersed for 10 min in a 0.5–3 wt% (wt%) solution of silicone in toluene. Contamination of the solution with water was avoided to prevent early condensation of the silicone which can already occur at room temperature [10]. Every 5 UD tapes, the solution was renewed to limit the potential change in concentration. After evaporation of the solvent in an oven at 60 °C, the silicone was cured for 10 h at 110 °C and an approximate humidity of 20%. The humidity was controlled by a saturated magnesium chloride (MgCl) solution which will be discussed in section 2.3. Good adhesion between the silicone layer and the fibre is likely since the curing reaction was initiated above 100 °C, at which chemical bonding with the fibre can take place [13]. The remaining functionalities in the cured silicone layer influence the adhesion with the matrix. The thickness of the silicone layer is linearly dependent on the silicone concentration in the dipping liquid [14]. The exact thickness is unknown. The coupling agent, APS, was applied according to a similar protocol which only differs by the type of solvent, in this case, ethanol.

2.3. Hygroscopic conditioning

The composites were subjected to hygroscopic cycling by alternately conditioning in wet and dry environments at a constant temperature of 80 °C. The experiments were performed at elevated temperatures to speed up the ageing and water diffusion process. For the damage development analysis with μCT, the oven dry state was selected as the dry condition to minimize the volume change resulting from the evaporation of moisture during scanning. The "dry" condition for the mechanical test specimen corresponds to relative humidity (RH) of 25% which is a more realistic "dry" state. In both protocols, the wet condition corresponds to RH 78%. The RH was controlled in airtight containers, using saturated magnesium chloride (MgCl) and potassium chloride (KCl) solutions which reach respectively 25 and 78% at 80 °C [15]. The condition in the containers was verified in a previous study [16]. The first absorption and desorption curves were recorded based on the weight increase to assure saturation at the predefined condition. All hygroscopic cycling experiments started after conditioning in the dry state. One cycle accounts for both absorption and desorption. Before mechanical testing, the samples were conditioned for at least 3 weeks at 20 °C, RH 54% by making use of a saturated magnesium nitrate ($Mg(NO_3)_2$) solution [15].

2.4. Three-point bending test

The mechanical analysis was performed based on three-point bending tests. The transverse properties were determined after hygrothermal ageing cycles 0,1,2,3 and 6. This study focusses on the evolution of the transverse strength as it is most influenced by the potential degradation of the interface. All samples were conditioned before testing as described in section 2.3. All tests were

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performed according to the ASTM D 7264 standard on an Instron 5567 equipped with a 1 kN load cell. The testing speed, span-to-thickness ratio and specimen thickness were respectively 1 mm/min, 32:1 and 2 mm. Due to the non-linear stress strain behaviour of flax fibre, the longitudinal modulus was calculated between 0 and 0.1% strain as proposed by Bensadoun et al. [17]. The longitudinal composite properties were normalized to a Vf of 35% to improve comparability. The rule of mixtures, Eqs (1) and (2), was used for the normalization of the composite stiffness (E) and strength (σ). E_f and E_m correspond to respectively the fibre and matrix modulus, σ_f and $\sigma_m^{'}$ to respectively the fibre and matrix tensile stress (at the fibre failure strain) and V_f and V_m are the fibre and matrix volume fraction. E_c and σ_c stand for respectively the measured composite bending stiffness and composite maximal bending stress.

$$E_c = V_f E_f + V_m E_m \quad (1)$$

$$\sigma_c = V_f \sigma_f + V_m \sigma_m^{'} \quad (2)$$

2.4.1. Statistics

A two-sided *t*-test was performed to quantify the statistical difference between two group means. The difference is called significant at the alpha = 0.05 level. The population variances were supposed to be equal. The statistical significance of the variation in transverse strength during hygroscopic cycling was evaluated based on linear regression analysis. A one-sided hypothesis test was performed to check whether the slope of the regression line is greater or equal to zero, the null hypothesis, versus the one-sided alternative. The decrease of the transverse properties over the different wet-dry cycles is called significant if the p-value <0.05. The measured property at cycle "x" was assumed to be normally distributed and variances are equal at each hygroscopic ageing cycle. The error bars in the graphs correspond to the 95% confidence interval which was composed using the standard deviation and the Student t distribution corresponding to the sample size.

2.5. X-ray computed tomography

X-ray computed tomography was adopted to analyse the internal damage of the composites after hygroscopic cycling. The absorbance of the X-rays correlates to the density of the material in a certain volume of the examined specimen. Since flax fibre, epoxy matrix and voids all have a different density, the internal composition and structure can be revealed. A void was defined as an internal cavity filled with air or other gasses where there is no material present. The scans were performed on a Phoenix Nanotom S 180 kV μCT system from General Electric equipped with a Molybdenum target. The X-ray tube voltage and current were set to respectively 53 kV and 265 μA. The obtained voxel size was 1.25 × 1.25 × 1.25 μm. The Phoenix datos|x reconstruction software was used to assign a grey value to each volume element, or voxel, and to reconstruct a three dimensional model of the composite. The non-destructive nature of the method allows imaging of the same sample before and after each hygroscopic cycle. The ageing protocol was described in section 2.3. For each composite sample, the exact same volume of interest of approximately 1.35 mm^3 was extracted from the core of the specimen and used for analysis. An incision was used as reference point. Matlab (R2016a) was used to separate the voids from fibre and matrix based on their grey value. The method was described earlier by depuydt et al. [16] and adopts a dual threshold hysteresis function. The extracted binary images were used to calculate the void content. Quantitative analysis was performed on two specimens for each composite type. The evolution of voids during hygroscopic cycling was linked to the development of damage and visualized with Avizo (v9.5).

3. Results and conclusions

3.1. Mechanical properties

The mechanical properties before and during hygroscopic cycling were evaluated based on three-point bending tests. The longitudinal properties, normalized to a Vf of 35%, are shown in Fig. 1. Results show that the longitudinal properties are not significantly affected after treatment with the silane coupling agent. In contrast with literature where improvements of stiffness and strength up to 40% are reported. It is suggested that the fibre fineness and cleanliness of the examined reinforcement is high [6,12]. Neither the addition of amine bonding sites on the fibre surface, nor the extraction of the waxes and other impurities aided by the solvent, lead to a significant enhancement of the interface. The longitudinal properties of the composites produced with fibres coated in a 3 wt% solution were reduced. The p-values for the difference in stiffness and strength compared with the flax-epoxy reference correspond to respectively 0.009 and 0.006 for PDMS/APS, and 0.020 and 0.025 for Evonik Tegopac Bond 160. Considering the rapid absorption of environmental moisture of flax fibres, it is difficult to accurately determine the silicone pickup of the dry fibres on a weight basis. Therefore, the concentration of the dipping solution is mentioned. Based on the work of Pavlidou et al. [14], it is supposed that for the same polymer, the coating thickness is linearly dependent with the concentration of the polymer in the dipping liquid. It is concluded that the longitudinal properties are not significantly affected when *the c*oncentration in the dipping liquid, and thus the coating thickness, is low. This might suggest that the stress transfer from matrix to fibre is not significantly hindered with the insertion of a thin interphase, which is a crucial characteristic for fibre reinforced composites. Although the concentration of the silicone in the dipping solution was set at discrete values, the weight pickup can differ due to variation of the physical and chemical properties of the elastomeric interphase. In addition, the mechanical properties and adhesion to fibre and matrix of each of the silicones was not quantified. Therefore, the systems are not in detail compared amongst each other.

Transverse three-point bending tests were performed as a method to quantify the damage development when subjected to variable environmental moisture. The evolution of the transverse strength for the examined composites is given in Fig. 2. Regression analysis revealed a significant decline over the six hygroscopic ageing cycles for the reference composite. The absolute reduction is comparable with a recent study regarding the durability in moist environments [18]. In general, immersion studies show a more dramatic damage evolution [3,7]. The former might indicate that leaching of water-soluble fibre constituents has a large impact on the damage development in natural fibre composites. This discrepancy also stresses the importance of the selection of an ageing protocol which is in agreement with the intended application. Results show a slight increase in transverse strength after treatment with the amino functionalized silane, APS. Flax epoxy systems intrinsically have a strong interface and further optimization is confined by the strength of the middle lamella of the fibre bundles [19,20]. In addition, the damage progress was not significantly altered as the decline in transverse strength is similar. The transverse strength of the composites having a silicone interphase dropped dramatically before or in an early stage of the hygroscopic cycling process. This might indicate that fibre matrix debonding is

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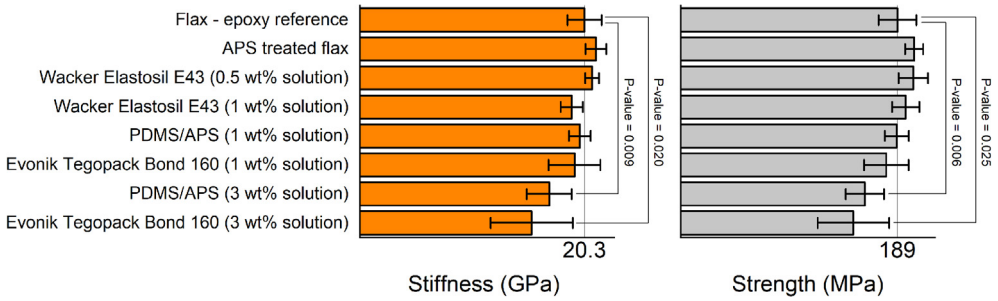

Fig. 1. Longitudinal composite properties normalized to Vf = 35% before hygroscopic cycling. Weight fraction refers to the concentration of the silicone in the dipping liquid. Error bars correspond to the 95% confidence interval. Reference line corresponds to the average properties of the flax-epoxy composite. P-value is shown when the group mean was significantly different, P-value < 0.05, compared with the group mean of the flax-epoxy reference composite. The statistical indicator was obtained by performing a two-sided student-*t* test, assuming equal population variances.

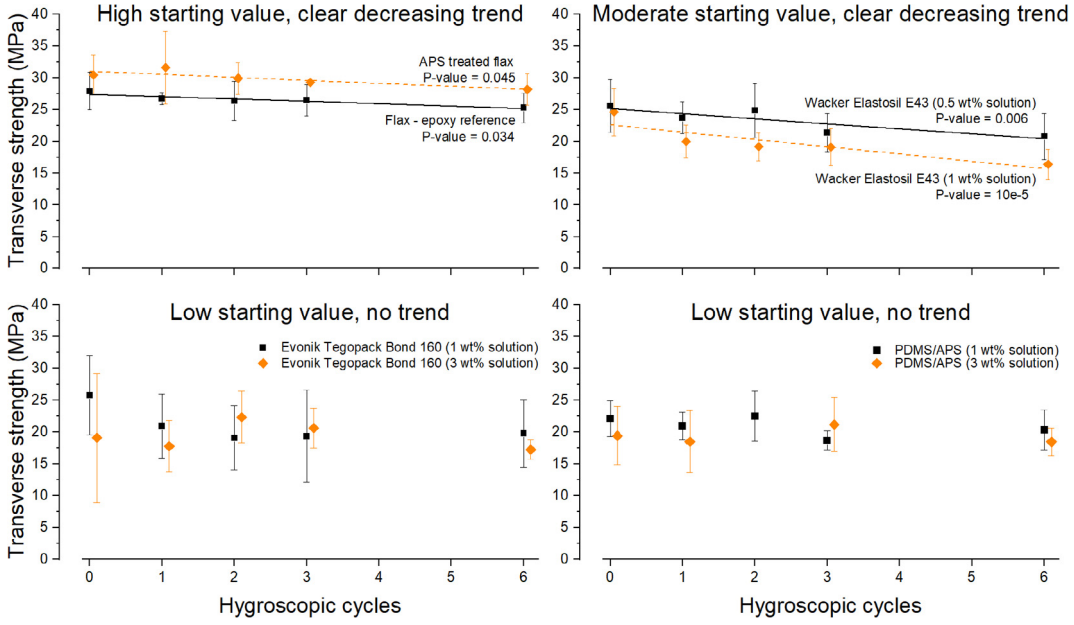

Fig. 2. Evolution of the transverse composite strength during hygroscopic cycling. Weight fraction corresponds to the concentration of the silicone in the dipping liquid. Cycle X corresponds to the number of hygroscopic ageing cycles. Cycle 0 is before hygroscopic cycling. Cycle 1 is after conditioning at 80% RH and subsequent drying at 25% RH. P-value obtained from regression analysis. Error bars correspond to the 95% confidence interval.

initiated with the insertion of a silicone interphase. The toughness and high strain to failure of the silicone could not be exploited as a consequence.

3.2. Damage analysis based on X-ray computed tomography

X-ray computed tomography was performed to understand, quantify and visualize the damage evolution during hygroscopic cycling. For each sample, the same volume was tracked during hygroscopic cycling to monitor the damage evolution. The results cannot be directly compared with the decline in transverse strength since the ageing protocol is different, as discussed in section 2.3. In Fig. 3, a pair of three-dimensional reconstructions of a flax-epoxy sample is shown. The voids which comprise fibre lumen and damage are shown in blue. The focus was put on three regions of interest to visualize the two most important damage mechanisms namely fibre–matrix debonding and fibre splitting. Before ageing, mainly cylindrical features appear which correspond to the naturally present lumen of the elementary flax fibres. Multiple fibre lumens are clustered as a flax fibre bundle consists of several elementary fibres [21]. After one wet-dry cycle, significant damage emerged which propagated in fibre direction. Fibre-matrix debonding occurred at the edges of the fibre bundles which is most likely a result of the tensile and shear stresses accumulating at the interface during desorption [22]. Moreover, cracks propagating across the fibre bundle are shown. An explanation of this behaviour can be found in the multi-phase structure of flax fibres where the elementary fibres are bound together with pectins. Cracking or splitting of the fibre bundles is a result of failure of the internal interfaces. The former is inherently linked with a strong fibre–matrix interface as it allows the build-up of the critical stress inside the fibre bundle [20]. Matrix cracks, which are often reported in literature and attributed to the swelling of the fibres, were not observed. A feature should span at least three voxels to be distinguished from noise. Therefore, matrix cracking might have occurred but remained under the detection limit. Nevertheless, fibre–matrix debonding and splitting of the fibre bundle are the predominant damage mechanism suggesting that the majority of the damage occurs during desorption. When comparing this observation with the evolution of transverse stress in section 3.1, it is unlikely that significant damage shown after one hygroscopic cycle had little effect on the transverse strength. This discrepancy might

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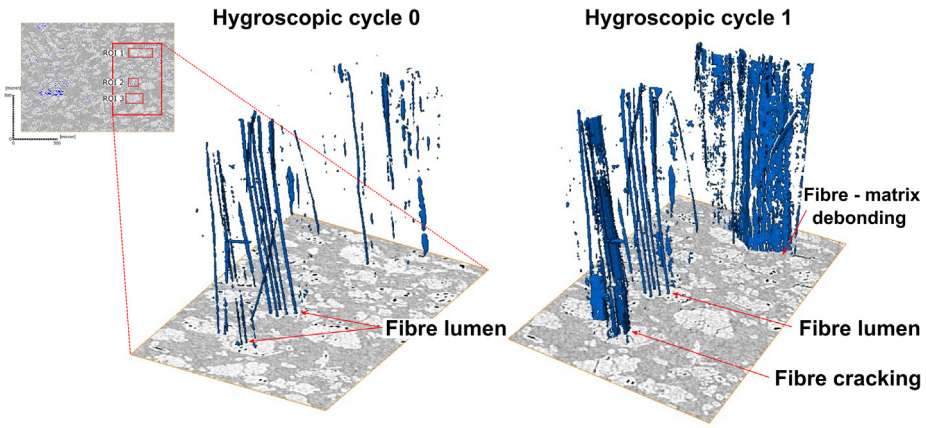

Fig. 3. Three dimensional reconstruction of the voids inside a flax fibre reinforced epoxy sample obtained with X-ray computed tomography. Cycle X corresponds to the number of hygroscopic ageing cycles. Cycle 0 is before hygroscopic cycling. Cycle 1 is after conditioning at 80% RH and subsequent drying to the oven dry state. Three regions of interest (ROI) are shown. Fibre bundles, matrix and voids are shown in respectively light grey, dark grey and blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

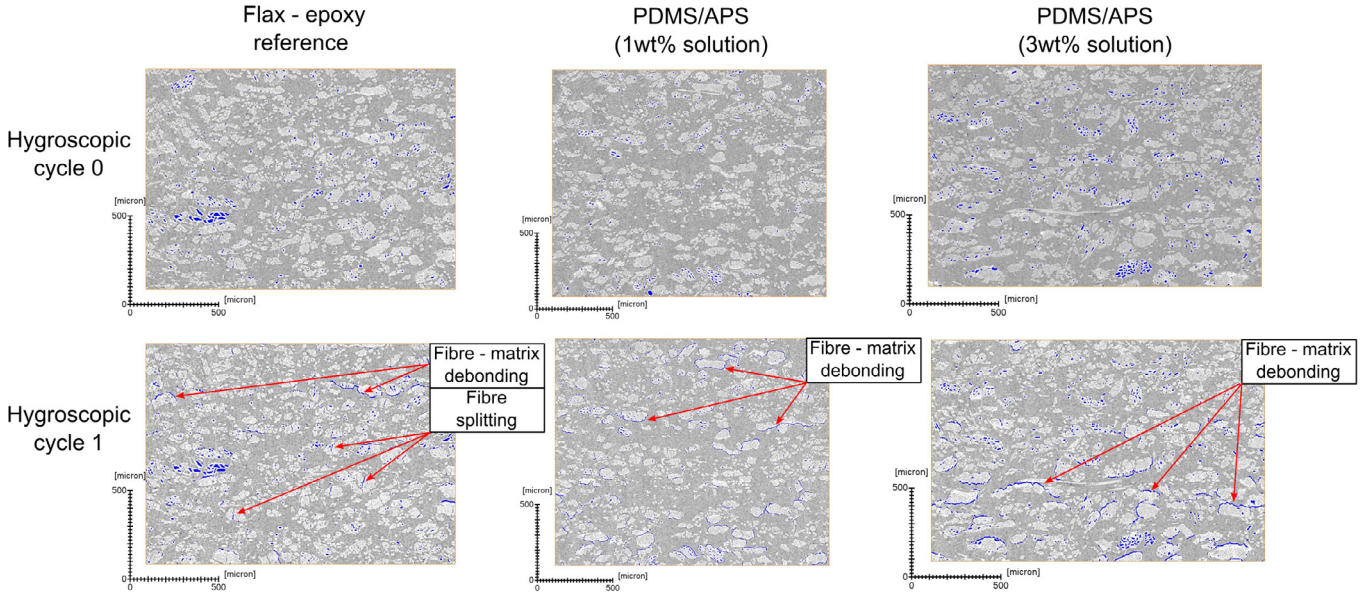

Fig. 4. Cross sections of the flax-epoxy composites with and without silicone interphase during hygroscopic cycling, obtained with X-ray computed tomography. Weight fraction corresponds to the concentration of the silicone in the dipping liquid. Cycle X corresponds to the number of hygroscopic ageing cycles. Cycle 0 is before hygroscopic cycling. Cycle 1 is after conditioning at 80% RH and subsequent drying to the oven dry state. Fibre bundles, matrix and voids are shown in respectively light grey, dark grey and blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

indicate that the additional hygroscopic load resulting from desorption to the oven dry state, compared to desorption to 25% RH, strengthens the damage progress.

The damage evolution for the composites having a PDMS/APS interphase was also monitored because adhesion with the matrix was most likely to be high in this system. In Fig. 4, cross sections of the different composites at two points in time are shown. The insertion of the silicone interphase did not seem to have had a large influence on the impregnation or the quality of the composites after production (cycle 0). No clear difference in fibre individualisation and no traceable damage was observed in neither of the composites. In Table 1, quantitative data is shown of the increase in voids during the hygroscopic ageing. It was supposed that the initial void fraction corresponds to the fibre lumen and did not change during the wet-dry cycles. The increase in voids was attributed to the development of damage. Because the absolute value is low, the calculated increase is prone to error which could be a result of small variations in image quality, segmentation and examined volume. Therefore, these values are only an indication. Results show a consistent increase of the void fraction. Overall, the damage development in composites having a silicone interphase proceeded faster which is in line with the evolution in transverse properties as discussed in section 3.1. Both the quantitative and visual analysis indicate that there was no clear influence of the concentration of the silicone in the dipping liquid. Fibre matrix debonding seems to be the only damage mechanism for the composites having a PDMS/APS interphase, as shown in Fig. 4. The absence of fibre splitting indicates that the strength of the fibre–matrix interphase is weakened. The silicone interphase did not allow stresses to be accumulated in the fibre bundle and failed before the critical stress of the middle lamellae could be reached. Good adhesion between the silicone interphase and the fibre is likely because the porous fibres are thoroughly wetted with the diluted silicone solution, and the reaction conditions permit

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Table 1
Quantitative analysis of the void content based on X-ray computed tomography images. Weight fraction refers to the concentration of the silicone in the dipping liquid. Two samples are tested for each composite type. Cycle X correspond to the number of hygroscopic ageing cycles. Cycle 0 is before hygroscopic cycling. Cycle 1 is after conditioning at 80% RH and subsequent drying to the oven dry state.

Type of composite	Void content (%)			Increase (%)
	Cycle 0	Cycle 1	Cycle 3	Cycle 0 → 1
Flax – epoxy reference	0.63	0.75	0.78	19
	0.53	0.62	0.66	17
PDMS/APS (1 wt% solution)	0.45	0.64	/	42
	0.44	0.58	/	32
PDMS/APS (3 wt% solution)	0.72	1.03	/	43
	0.71	0.87	/	23

chemical coupling as described in section 2.2.1. Therefore, insufficient adhesion with the matrix is proposed as a possible explanation. The difference in polarity between the hydrophobic silicone and a rather polar epoxy matrix, and the lack of mechanical interlocking on the possibly smooth silicone layer might further substantiate this reasoning [23]. Contrary to the results, good adhesion between the PDMS/APS interphase and the matrix was expected because of the presence of amino functionalities which could, similarly to the APS treatment, form chemical bonds with the epoxy matrix. However, adhesion is not solely dependent on the ability to form chemical bonds. The unknown and potentially low bulk properties of the silicone formulation might also be a possible explanation for the underperformance of the silicone formulations. Detailed future analysis of the fracture surface with scanning electron microscopy might point out if adhesive or cohesive failure of the interphase occurred.

3.3. Conclusions and outlook

UD flax fibre reinforced epoxy composites showed a significant decline in transverse strength when subjected to hygroscopic cycling between 25% and 80% RH. The obtained results were less dramatic as previously reported for immersion tests. It is concluded that the hygroscopic loading protocol should be carefully selected in function of the intended application. Computed tomography analysis indicated that fibre–matrix debonding and the failure of the internal interfaces of the fibre bundles are the predominant damage mechanisms resulting from hygroscopic stresses.

Although fibre treatment with APS led to a slight improvement of the composite properties, regression analysis on the decline of transverse strength did not show a significant difference with the flax-epoxy reference. It is concluded that the damage development was not significantly altered after treatment with the silane coupling agent.

Various silicone interphases were investigated as they might mitigate the hygroscopic stresses and improve the toughness of the interface. Contrarily to the hypothesis, all composites having an elastomeric silicone interphase showed a significant drop in transverse strength before or in an early stage of hygroscopic cycling. Computed tomography revealed that the interface was weakened, concluded from the absence of cracks inside the fibre bundle. Insufficient adhesion between the silicone interphase and the epoxy matrix due to the difference in polarity and the lack of mechanical interlocking is proposed as a possible explanation. Chemical coupling between the epoxy resin and the available amino functionalities in one of the examined silicones was apparently insufficient to prevent debonding. Alternatively, the limited strength properties of the silicones might provide an explanation for the observed debonding at or in the interphase. Analysis of the longitudinal properties indicated that that stress transfer, which is a critical property of fibre reinforced composites, was not significantly hindered with the insertion of a thin elastomeric interphase, which is a positive finding.

Further research is required to evaluate the potential benefits of interfacial toughening on the long term behaviour of natural fibre composites subjected to moisture. In this context, the authors are investigating alternative elastomeric interphases which have superior mechanical properties, particularly increased strength while the high elongation to failure is retained. Adhesive failure between the epoxy matrix and the elastomeric layer is counteracted by enhancing the physical interactions.

CRediT authorship contribution statement

Gilles Koolen: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Jeroen Soete:** Software, Validation, Formal analysis, Visualization. **Aart W. van Vuure:** Validation, Resources, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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