Composites Part C: Open Access 6 (2021) 100198

Contents lists available at ScienceDirect

Composites Part C: Open Access

journal homepage: www.sciencedirect.com/journal/composites-part-c-open-access

Accelerated ageing of surface modified flax fiber reinforced composites

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ARTICLE INFO

Keywords:
Flax fibers
Epoxy coating
Silane treatment
Polyamide
Climate chamber
Biocomposites

ABSTRACT

The overall aim of this study is to evaluate application-oriented potential of biocomposites made of surface-modified flax fibers for use in engineering thermoplastics. The scope of the study includes analysis of the effect of a partially bio-based epoxy-coating, a silane treatment and a combined epoxy-coating / silane treatment of the flax fibers on the mechanical behavior of biocomposites after thermo-oxidative aging. The treated flax fabrics were subjected to tensile tests as well as scanning electron microscopy (SEM) to compare their mechanical behavior and fracture surface. The natural fiber reinforced biocomposites were manufactured through film-stacking of the treated fabrics and polyamide 6 (PA6) using hot-pressing. The durability of the biocomposites after climate-change tests was confirmed via tensile and bending testing. The results show beneficial mechanical behavior of treated fabrics and corresponding biocomposites, but also negative affected durability of treated composites after climate-change tests. Treatment of the fabrics with subsequent accelerated aging leads to a similar low level of tensile and bending moduli.

1. Introduction

In many applications, polymers substitute metals or ceramics due to economic reasons, like costs and beneficial properties as for example their lightweight and mechanical strength. However, in the recent years, there has been a growing demand for sustainable materials in packaging as well as in the technical fields, like in automotive industries. [1] Since Europe aims at becoming the first climate-neutral continent in 2050, many research topics focus on strategies for bio-based substitutes of plastics and filler components to reduce their CO_2 footprint. [2,3] Scientific attempts take place by using high amounts of bio-based materials for manufacture of bioplastics and natural fibers as suitable filler components in fiber-reinforced composites for structural applications. [4,5] Lightweight construction as a central idea for a reduced emission of greenhouse gas for transport sector plays an important role in innovative technologies. [6,7] Therefore, natural fibers in their naturally grown structure possessing high damping properties, strain, beneficial recycling options and a high availability offer a promising solution for use in composite materials. [8,9]

Natural fibers consist of cellulose, hemicellulose, lignin, pectin, other plant-associated substances like waxes and moisture. Depending on the sort and part of the plant as well as the growing conditions, the chemical composition of these fibers varies. [10,11] According to the later use, natural fibers can serve as a reinforcing material for short or endless fiber-reinforced composites. One of the main drawbacks of natural fibers is their comparably low temperature stability. [12] For short-term duration, it is up to 200 °C, for long-term duration at temperatures above 100 °C decomposition and discoloration take place. [13] Due to this, until now it is difficult to introduce natural fibers in engineering thermoplastics with melting temperatures >200 °C. There are different approaches to overcome the problem of low thermal stability of these fibers. A common way is to introduce natural fiber textiles into a thermosetting resin with low curing temperature instead of thermoplastic matrix or use standard thermoplastics with lower melting points like polyethylene or polypropylene. A use of engineering thermoplastics would broaden the field of possible applications of biocomposites due to improved mechanical performance, higher durability and enhanced thermal and chemical stability. In literature, there are only few reported studies directly aiming on improvement of the thermal stability of natural fibers, such as use of a flexible thermoset coating and subsequent introduction in a polyamide as a feasibility study with only one layer natural fibers [14]. Most of the reported research studies focus on mechanical improvement, while thermal characterization is considered as a minor matter. [14–16]

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https://doi.org/10.1016/j.jcomc.2021.100198
Received 23 June 2021; Received in revised form 30 September 2021; Accepted 22 October 2021
Available online 24 October 2021

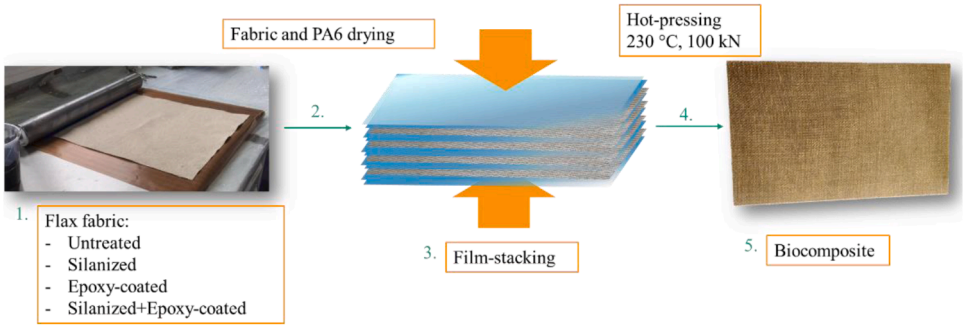

Fig. 1. Schematic depiction of the manufacturing process of the biocomposites.

Accelerated aging is a method to define long-term duration of materials in a reduced time frame. Artificial climate aging aims on an outdoor climate simulation including UV-light. Light-induced aging is adjustable via UV-lamp accelerated aging chambers, sometimes equipped with a spray system for additional humidity. Regarding components for application in automotive section, time lapsed testing in a climate chamber is a valuable instrument to analyze durability towards high and low temperatures as well as humidity. Thermo-oxidative aging simulates long-term exposure of composite materials to analyze thermal degradation behavior. [17] Delamination effects may occur for biocomposites at ambient climate conditions as well. [18] In this study, the focus lies on the weathering by a climate chamber with cyclic test of temperature and humidity, examining possible delamination due to changing environmental conditions.

Previous studies have proven the feasibility of spray-coating natural fibers while remaining flexible for incorporation into polyamide 6 (PA6) matrix. The biocomposites show superior mechanical and slightly enhanced thermal properties compared with uncoated fabric-reinforced composites. Additionally, thermogravimetric analysis (TGA) measurement was conducted and discussed, while an epoxy-coating has shown a slight increase in thermal stability. [19] A follow-up study focused on isothermal property comparison of epoxy-coated flax fabrics and uncoated fabrics introduced into PA6 under thermo-oxidative aging. The results show higher tensile properties and a considerably improved resistance towards thermo-oxidative atmosphere compared with uncoated flax-composites. [20]

The presented research work ties up these studies and continues by using combined fiber-treatments like silanization and partially biobased epoxy resin coating as well as additional climate-change tests and isothermal hot-pressing tests to examine further thermal influence on treated and untreated natural fibers and their corresponding biocomposites.

2. Materials and methods

2.1. Materials

The used flax fabrics for reinforcement are twill 1/3 fabrics, woven with a double rapier weaving machine of Van de Wiele at the HOFZET. Flax yarns of 200 tex were woven to a fabric with areal weight of 437 g/m^2 according to the procedure described in previous paper. [21] Polyamide 6 (PA6) film with a thickness of 0.1 mm was purchased from jura-plast GmbH. As a thermosetting resin system for coating, a partially bio-based epoxy resin Greenpoxy SR 56 (bisphenol A-based) and an isophorone diamine-based hardener SR 8822 supplied by Sicomin were combined with a reactive thinner EPD BD by R&G Faserverbundwerkstoffe GmbH. The reactive thinner (RT) can be mixed up to 10 wt% with the resin system without significant reduction of mechanical properties according to the manufacturer. For silane treatment, 3-aminopropyltriethoxysilane (APTES) from ACROS Organics was used as received with no further purification. APTES was chosen as a suitable and extensively investigated silane coupling agent, especially for natural fibers and an epoxy matrix. [22]

2.2. Treatment of the weaved textiles and composite manufacture

Four different samples were manufactured for each biocomposite. The fabrics and biocomposites were named after the following sample code (see Table 1):

2.2.1. Modification of textiles

Silanization of the fabrics was performed with a 2% solution of APTES in ethanol for 2 h with subsequent washing of excess in distilled water for three times. The textiles were dried at 80 °C for at least 2 h in a circulating air oven.

For the tensile tests of the fabrics, textiles were cut into strips of 5 cm x 30 cm. Similarly, for the manufacture of biocomposites, textiles were cut into pieces of 30 cm x 35 cm. Epoxy coating of the flax fabrics or silanized flax fabrics was done with a mixture of resin and hardener in a ratio of 100 : 31 with addition of 10% reactive thinner. 10% were chosen for the maximum possible dilution due to increased application. The resin system was applied onto the flax surface and impregnated by a roll (17 kg) at both sides. The samples were weighted to ensure a similar resin to fabric ratio. The epoxy loading of each fabric was 40–43 wt%.

2.2.2. Manufacture of biocomposites

The manufacturing process is depicted in Fig. 1 and mainly consists of five steps: At first (1.), the fabrics get prepared and afterwards dried (2.) to prevent moisture uptake. Then, the fabrics and PA6-sheets get film-stacked (3.) for the hot-pressing process (4.) to manufacture the biocomposite (5.). The total amount of bio-content in the biocomposite of a F-EP-PA6 is approximately around 54 wt%, according to resin manufacturer specification. [23]

Each composite consists of four layers of flax fabrics and ten layers of PA6 (Fig. 1) to reach the required thickness of 4 mm for bending and tensile tests. For pre-drying the PA6 sheets, untreated and silanized fabrics were stored in an air-circulation oven at 80 °C over night. Epoxy-coated fabrics were dried in a desiccator at room temperature over night to prevent further curing of the resin system at elevated temperatures. The size of the fabrics and PA 6 sheets was 30 cm x 35 cm.

Before processing the pre-dried fabrics (F) and PA6 (/) sheets were alternating stacked (//F//F//F//F//) and placed at 80 °C in an oven for 15 min to avoid moisture uptake. Afterwards, they were hot-pressed at 230 °C with 100 kN and cooled down to 80 °C under pressure using a RUCKS KV 322 hot-press. The all in all hot-press process including the cool down took 15 ± 2 min. Ensuring a successful compression moulding process, previously an optimization process of hot-press parameters took place with subsequent computer tomography and mechanical analyses as described elsewhere. [24]

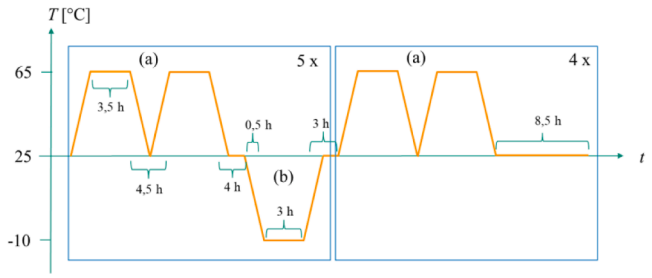

Fig. 2. Schematic depiction of the heating and cooling cycles in the climate chamber. (a) stands for a heating period of 25 °C to 65 °C while (b) means a cooling cycle from 25 °C to −10 °C.

2.3. Climate-chamber tests

In an Espec Thermotec ARS 1100 climate chamber the samples were hung and conditioned after DIN EN 60,068–2–38:2009 with cycles from −10 to +65 °C at 93% relative humidity (Fig. 2). The total time of the fabrics and biocomposites in the chamber was 10 days, including a conditioning step of 24 h at 55 °C and a humidity of 18% r. H. The temperature (T)/ relative humidity (RH) cyclic test is an alternation of the conditions (a), which is $T = 25$ to 65 °C and RH = 93% and (b), which is $T = 25$ to −10 °C and RH = 25%. Each plateau at 65 °C is kept for 3.5 h, while the ramps to reach 65 °C and 25 °C are set on 2 h. 25 °C is held for 30 min in phase (a). Between phase (a) and (b) there is a ramp of 2 h to reach 25 °C, a plateau for 2 h and a ramp of 30 min to reach −10 °C, which is held for 3 h. The cycle of heating and cooling is running for 5 times. The following heating cycles after the program of heating and cooling ran 5 times is analogue to that with a plateau of 25 °C for 8.5 h. This cycle is running in total 4 times. 15 samples for each fabric and 20 samples for each biocomposite were tested.

2.4. Hot-press tests

For defining the isothermal duration for the hot-press process of a single fabric layer, fabrics of the size of 5 cm x 30 cm were placed in a hot-press at 230 °C. They were pressed at 50 kN to ensure a heat conduction for 30 s, 60 s, 180 s, 300 s and 600 s. The duration time is chosen analogue to the compression moulding, which is 60 s hot pressing with cool down to 80 °C and a cooling rate of approximately 3–5 K/min. The biocomposites last up to 10 min in a high temperature environment. Therefore, a range of 30 s 600 s was chosen. The pressed fabrics were subsequently subjected to tensile testing as described below to compare their mechanical behavior and investigate a possible influence of the surface modifications.

2.5. Mechanical testing

Prior to mechanical testing, all samples were conditioned for 88 h at standard conditions of 23 °C and a relative humidity of 50%.

2.5.1. Fabrics

Fabrics, including the single layers of the hot-press tests, were tested via Zwick Roell Z020 at standard conditions of 23 °C and 50% relative humidity according to DIN EN ISO 13,934–1 in standard warp direction. Tests revealed mechanical properties of force / breaking tension and the tensile strength of the samples.

2.5.2. Biocomposites

The manufactured biocomposite specimens were prepared using a diamond saw. Tensile tests according to ISO 527–4 and four-point bending tests according to DIN EN ISO 14,125 were conducted via Zwick Roell Z100 TEW at standard conditions (23 °C, 50% relative humidity). The samples were tested using a 100 kN load cell and a speed of 2 mm/min.

2.6. Scanning electron microscopy and energy-dispersive X-Ray spectroscopy analysis

The mechanically tested samples were prepared for scanning electron microscopy (SEM) imaging (Zeiss EVO 60 EP) via sputter-coating. The surface of the climate conditioned textiles and the fracture surfaces of the biocomposites were scanned at an accelerated voltage of 5–10 kV under high vacuum atmosphere. Energy dispersive X-ray spectroscopy (EDS) analysis was performed at different positions of the silane-coated samples to investigate the distribution of silane-molecules.

2.7. Color measurement

Surface treatment commonly leads to change i.e. darkening of the natural fiber color. This change may play an important role for industrial use. However, currently, a quantitative determination of the natural fiber's color after treatment is hardly mentioned in the literature, thus inhibiting the transfer of the research finding in industrial use. In this study, the color measurement of the textile samples was conducted using Spectrophotometer UltraScan VIS (FMS Jansen GmbH & Co. KG HunterLab) to define heat-induced coloration. Specimens of the size of 5 × 10 cm were measured at two different locations. The average L*a*b*

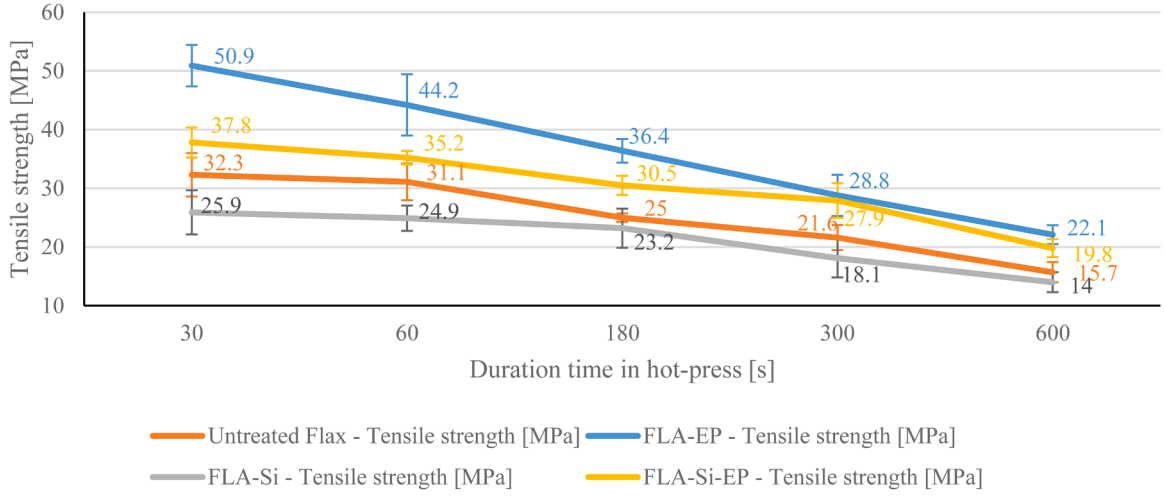

Fig. 3. Results of tensile tests of the hot-pressed single fabric layers.

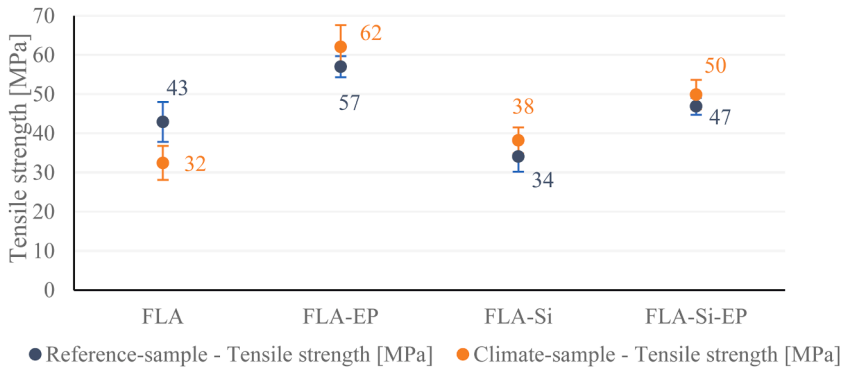

Fig. 4. Results of tensile tests: non-weathered single fabric layers (blue) in comparison with weathered samples in climate chamber (orange).

values of the two measurements represent the results reported in this paper.

3. Results and discussion

3.1. Tensile strength of fabrics

The tensile properties of untreated as well as treated flax fabrics serve as a reference for the hot-pressed biocomposites consisting of four layers of textiles. Previously conducted single-fiber tensile tests published elsewhere of flax and epoxy-coated flax show high standard deviations [24]. Single-tensile fiber tests are not sufficiently suitable for epoxy-coated fibers, since flax exhibits a higher tensile strength in comparison with epoxy-coated flax regarding the fineness. [24] To determine the hot pressing behavior, single layer of untreated and treated flax fabrics were placed, as previously described, in a hot-press for a different duration time and compared to each other regarding their mechanical properties. The results of the tensile tests of the fabrics are shown in Fig. 3.

The results show for all of the samples a decrease in tensile strength during hot-pressing for 30 s to 600 s at a temperature of 230 °C. The loss of mechanical strength for the untreated flax is 51% while for the silanized fabric the decrease is 46%. The initial part of the curve progression for the silanized fabric is slightly flatter than the curves of the untreated and epoxy-coated samples. Nevertheless, silanized fabrics have a lower starting value than the untreated flax and the epoxy-coated fabric. As reported by Barczewski et al. [25]., the fabrics probably become more brittle after the silanization and therefore show lower tensile strength. Puglia et al. [26] showed a reduction in tensile strength after silanization as well, but pointed out a beneficial behavior in thermal properties. Tensile strength of FLA-EP decreases between 30 s and 600 s by 57%, while silanized and epoxy-coated FLA-Si-EP decreases by 48%. However, the tensile strength of FLA-EP at 30 s is 57% higher than the tensile strength of the untreated flax. After 600 s FLA-EP is still 40% higher than untreated flax.

The cyclic climate tests in the climate chamber include a low temperature of −10 °C and a moderate temperature of 65 °C. In this test setup, the textiles hang in a high moisture atmosphere leading to a potential fiber damage due to water uptake and expansion at temperatures below 0 °C. The results of the tensile tests are shown in Fig. 4.

As expected, the tensile strength of the untreated fabric decreases after 10 days of alternating climate. The other three samples show very narrow results of tensile strength before and after the cyclic climate test, whereas the climate samples have slightly higher values in comparison with their unconditioned references. A silanization of the flax fabrics leads to generally lower tensile strengths compared to untreated fabrics. This effect is reported by Barczewski et al. [25] as well and may originate from an embrittlement due to silanization. The epoxy resin covers the

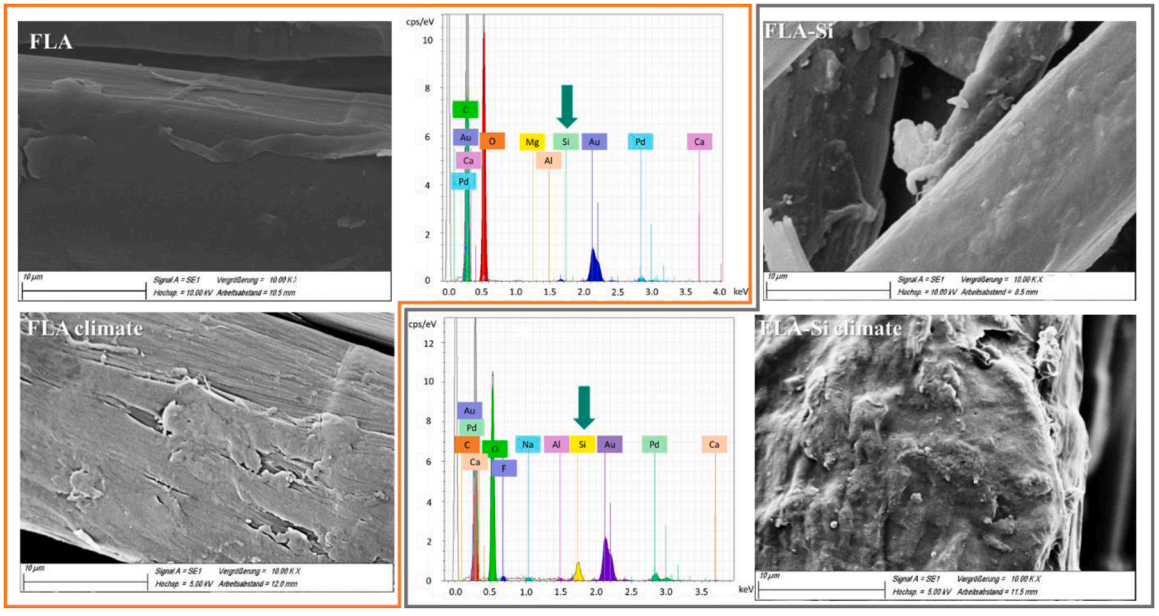

Fig. 5. SEM-images of untreated flax (FLA) and silanized flax (FLA-Si) before and after climate-change-test. EDS-measurement results of the fiber surface of FLA and FLA-Si for verification of silane-treatment.

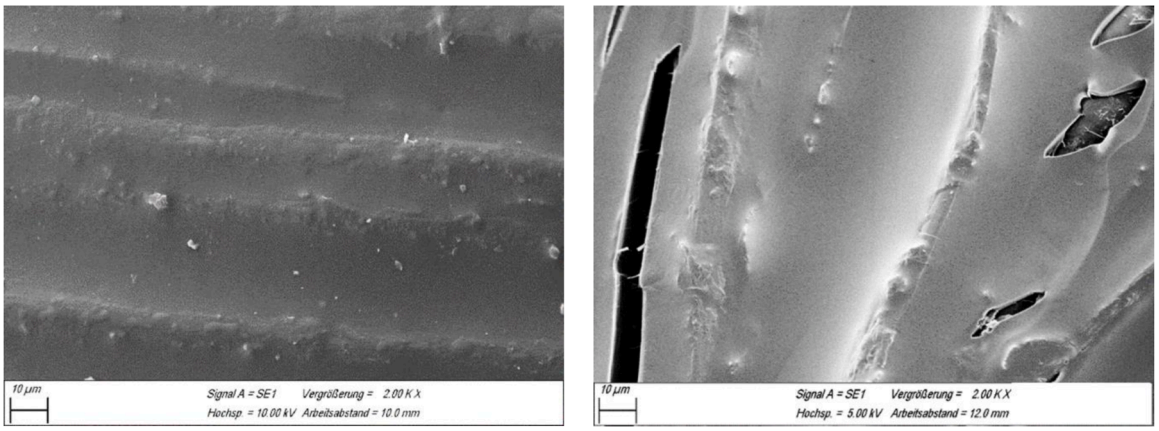

Fig. 6. Comparison of FLA-EP (left) and FLA-EP after climate chamber (right).

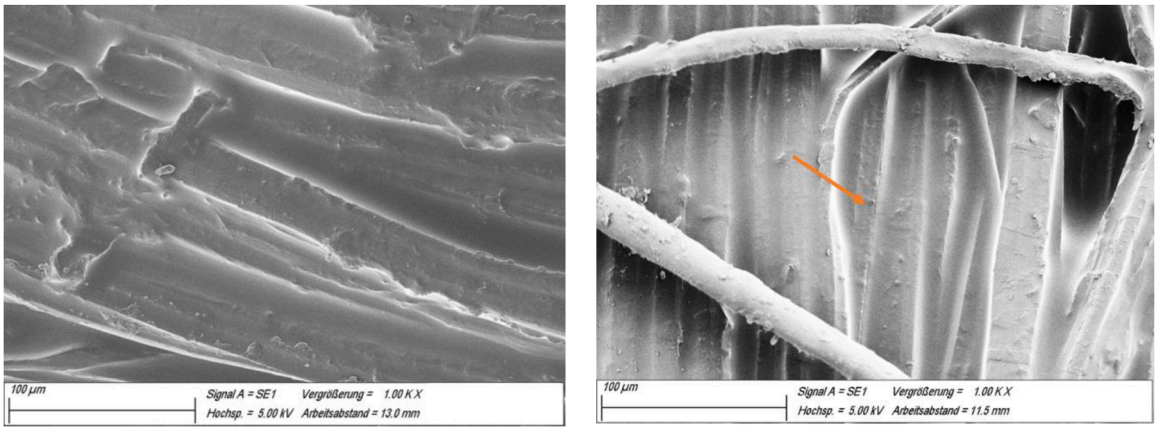

Fig. 7. Comparison of FLA-Si-EP (left) and FLA-Si-EP after climate chamber (right).

fibers and increases the cohesion of the woven structure in both directions of warp and weft. Therefore, the textiles reach slightly higher tensile strength. While testing, untreated fabrics defibrillate whereas coated fabrics have an abrupt breaking point.

3.2. SEM-imaging and EDS-measurements of the textiles

To compare different treatments of the textiles, SEM images and EDS-measurements were conducted. The EDS measurement of textiles was additionally used to ensure that the silanization occurred. The EDS-spectrum shows a successful silanization due to a measurable amount of Si in comparison with untreated flax (Fig. 5). The SEM-image of untreated flax reveals its topology. Compared with flax after the climate-chamber test, a significant difference in fiber damage is observed. Silanized flax shows a smooth layer at the surface. An EDS-measurement proves the successful silane treatment.

Fabrics with an epoxy coating show after the climate chamber test cracks in their surface compared with epoxy coating of untreated fabrics (Fig. 6 and Fig. 7). Weathering of the coated samples leads to humidity uptake and as a result, cracks and delamination between fiber and epoxy arise.

3.3. Color measurements of textiles

The results of the color measurement of the treated textiles are represented in Fig. 8. The principal results show quantitatively that flax treated with epoxy is more than twice as darker as the untreated FLA-Si. The measurement according to the CIE Lab color system provides a quantitative information about the lightness (L*) and four colors represented by a* and b* axes. [27] The value of L* varies between 0 (black) and 100 (white). The axis a* varies from -a (green) to $+a$ (red) and b* from -b (blue) to $+b$ (yellow). Minimum and maximum values of -127 and $+127$ are commonly used for a* and b*. The obtained L*, a*, b* values obtained for reference fabrics are comparable with those reported in literature [28] for various natural fibers. At the same time, slight deviations are possible due to different measuring devices and natural character of the material types. The darkness increases by increase of the treatment time. Compared with the reference sample, the untreated textile treated for 600 s is by approx. 36% darker. Similarly, increase of the treatment time leads towards yellow ($+b$*) and red colors ($+a$*) of the specimen. The flax fabric treated with silane shows similar behavior as in the case of FLA, especially regarding L* and b* values. The main step towards yellow ($+b$*) takes place after the first 30 s. Afterwards, this effect is stepwise increased with the increase of the treatment time. In the case of epoxy-coated flax, the lightness of the initial specimen (0 s) is approx. 40% lower than that of FLA or FLA-Si. Similarly, as by FLA or FLA-Si, the L* decreases with increase of the treatment time. Consequently, after 600 s of treatment, the L* for FLA-EP is approx. 18, while for FLA and FLA-EP, it is 45 and 42, respectively.

The color measurement of the fabrics treated with epoxy and silane shows similar tendency regarding the change of the lightness. However, in the case of the individual values, the L* lies between that of the FLA-EP and FLA-Si specimens treated for the same time period. For example, while the lightness after 60 s is 56 for FLA-Si and 30 for FLA-Si, it is 43 for FLA-Si-EP. Similarly, after 600 s, the L* is 18 for FLA-EP and for 42 FLA-Si, but 30 for FLA-Si-EP. This observation leads to assumption that

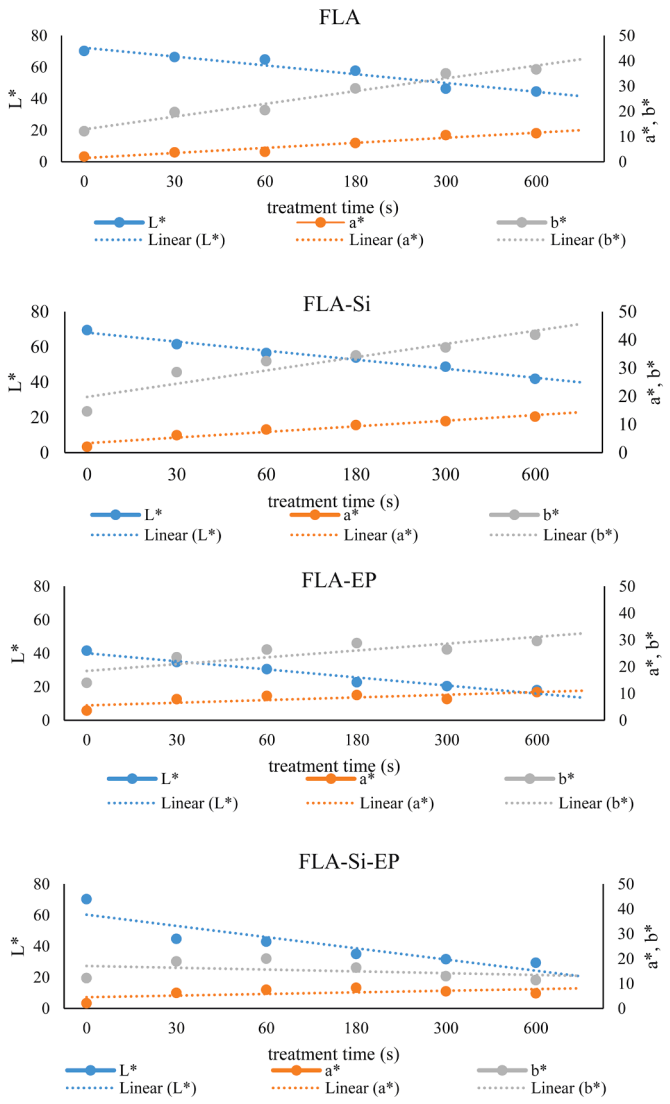

Fig. 8. L*, a* and b* values obtained during color measurement of the untreated fabrics (FLA), treated with silane (FLA-Si), epoxy resin (FLA-EP) and silane/epoxy resin (FLA-Si-EP).

the silanization of the flax fabrics acts as a barrier cover for epoxy resin, thus, reducing its penetration into the fabric and yarn structure and inhibiting the darkening of the fibers. At the same time, the a* and b* colors show a completely different behavior than the L*. Particularly, the values who an increase up to 60 s and a decrease afterwards. Since there are no published studies on quantitative investigation of color change of the natural fiber textiles after surface treatment, currently, it is not possible to compare accurately the results with the literature. However, due to importance of the color specifications for commercial applications, this topic should be investigated in a separate study.

3.4. Tensile and bending properties of biocomposites

In this part, the results of the mechanical tests of the biocomposites are presented. The fiber-orientation of the fabrics in the biocomposites is for each sample in standard warp direction. Tensile tests (Fig. 9) ($n = 10$) as well as four-point bending tests ($n = 12$) in the direction of warp, which is the longitudinal axis of the sample, were conducted as described.

The tensile moduli of untreated composites show comparably higher values. It is noticeable that epoxy coated flax in PA6 has the highest tensile modulus while silanized with and without epoxy coated flax in the composite contrarily shows the lowest. This observation was also reported by Barczewski et al. [25] with silanized fabrics incorporated in epoxy matrix, giving reason, that the silanization could possibly affect the fiber structure. Before the climate test, the composites of F-PA6 followed by F-EP-PA6, have the highest tensile strengths, silanized samples are remarkably lower. This is probably due to enhanced brittleness of silane-coating promoting a delamination process of the PA matrix and the treated fabrics. In the case of F-EP-PA6 silane treatment did not take place. Mechanical interactions as well as possible chemical reaction of PA6 and epoxy-system are a conceivable reason for elevated mechanical properties before climate test. [29]

Samples, which were hung in the climate chamber show very similar tensile moduli around 3.5 GPa. Epoxy coating in this case leads to a smaller standard deviation. The reference sample F-PA6, F-Si-PA6 and F-Si-EP-PA6 have slightly higher strength than at the beginning, whereas epoxy coated F-EP-PA6 in contrast to this loses tensile strength. A possible reason for the loss in mechanical properties of the treated fabrics is an introduction of humidity from climate chamber with subsequent delamination due expansion of the water while negative temperatures in the cooling cycle.

Bending tests of the samples with incorporated fabrics in the direction of longitudinal axis (warp) verify the results of the tensile tests concerning the moduli and strengths of the untreated composites (Fig. 10). Their tendencies are very similar to the tensile test results. After the climate chamber test, the bending moduli of F-EP-PA6, F-Si-PA6 and F-Si-EP-PA6 sink to a lower level of 2.2–2.6 GPa, whereas the reference sample possess a bending modulus of 3.6 GPa.

Regarding the tensile and bending moduli, all of the tested samples show a significant decrease of their properties after climate stress (see Table 2). Irrespective of the initial values, F-PA6 and F-Si-PA6 have a

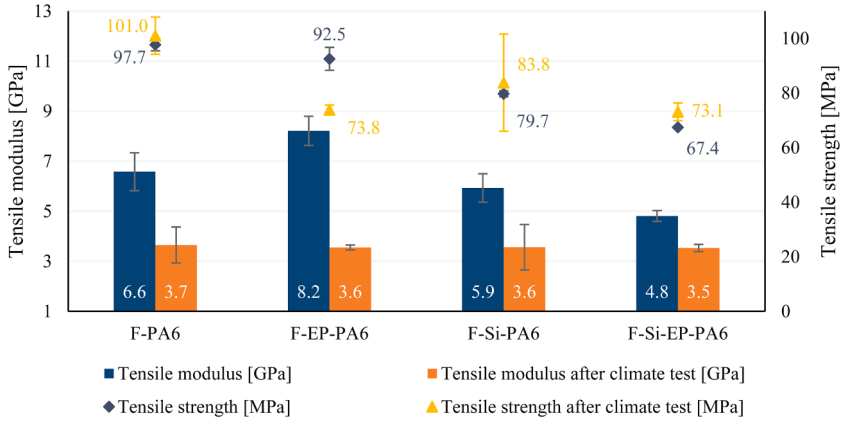

Fig. 9. Tensile tests of the flax composites (blue) and flax composites after the climate chamber test (orange) in standard warp direction.

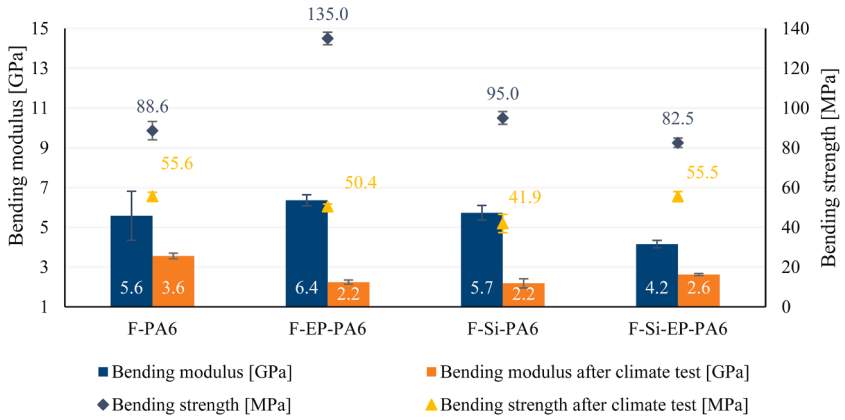

Fig. 10. Results of the bending tests of flax composites (blue) and flax composites after climate chamber test (orange) in standard warp direction.

lower loss of their bending modulus after the climate chamber tests in comparison with F-EP-PA6 and F-Si-PA6. The loss of tensile moduli is similar, while F-Si-PA6 shows a decrease comparable to F-PA6. The highest gap between before and after the climate chamber test is registered for the F-EP-PA6.

Referring to the reference sample F-PA6 with untreated flax fabrics as incorporation, a comparison of bending and tensile moduli of the modified composites are presented in Table 3. Except of F-Si-EP-PA6, all of the samples with coated fabrics show higher bending and tensile moduli compared with F-PA6. The highest difference is registered for the tensile modulus of epoxy coated flax in PA6. After the climate chamber test, the bending properties are decreasing significantly up to −40%. The tensile properties are decreasing as well, but only up to −3.3%.

Climate chamber tests introduce humidity to the natural fibers, leading to expansion at the lower temperatures and subsequent damages of fibers and fiber-matrix adhesion. The climate cycles up to moderate 65 °C affect the moisture uptake only little. In comparison with the tensile tests of the single fabrics, there are remarkable differences. Tensile tests of the single fabric layers show after the climate stress slightly elevated mechanical properties for coated samples, whereas biocomposites are affected by the climate test. This leads to the assumption, that the infiltration of humidity followed by negative temperatures destroys fiber matrix adhesion resulting in lower mechanical properties. Compared with long-term thermal duration at isothermal conditions (23 °C and 110 °C) as in previous studies described by Shamsuyeva et al. [20], moisture uptake in the presented climate chamber seems to have a significant higher impact towards mechanical stability than the previously conducted aging at 110 °C. Bazan et al. [30] describe an introduction of flax fibers into bio-polyethylene as a reinforcement increasing stiffness and lowering brittleness. After accelerated aging at elevated temperatures in an autoclave and a relative humidity of 100%, water absorption and thermal degradation were higher than unfilled bio-polyethylene samples.

All in all, one of the main findings of this study is, that the treatments of silanization, epoxy-coating and the combination of both methods lead to a decreased long-term behavior. All tested methods seem to damage the fiber structure and/or lower the fiber-matrix interactions after conducting an accelerated aging test. In literature, chemical treatments such as silanization, alkali treatment and isocyanate treatments are commonly used to strengthen the fiber-matrix adhesion of biocomposites, e.g. by mechanical interaction due to a rougher fiber surface. [31] Davies et al. [32] reported a decrease in mechanical strength of single fiber tensile tests of flax fibers by increasing relative humidity.

The deterioration of the composites in this study seems to be affected by the treatments and a subsequent accelerated aging.

3.5. *SEM-imaging of biocomposites*

Cross-sections of the randomly selected samples after bending testing were analyzed via SEM-imaging visualizing their breaking properties. The loss of bending properties for all of the samples lies at >30%. In the case of F-PA6, the cross-section shows fiber-pullout after the climate chamber tests at a magnification of 50 (Fig. 11) which represent the deterioration of the interfacial quality due to the climate stress.

The SEM-images of the other samples with coated fabrics are presented in Fig. 12. Silanized flax in PA6 has a smooth surface whereas the surface of the corresponding sample after climate chamber test seems to be more brittle. In the case of epoxy coated samples, the surface near to the fracture tends to lose thermoset coating. Silanized flax with and without epoxy coating in PA6 shows even under standard conditions

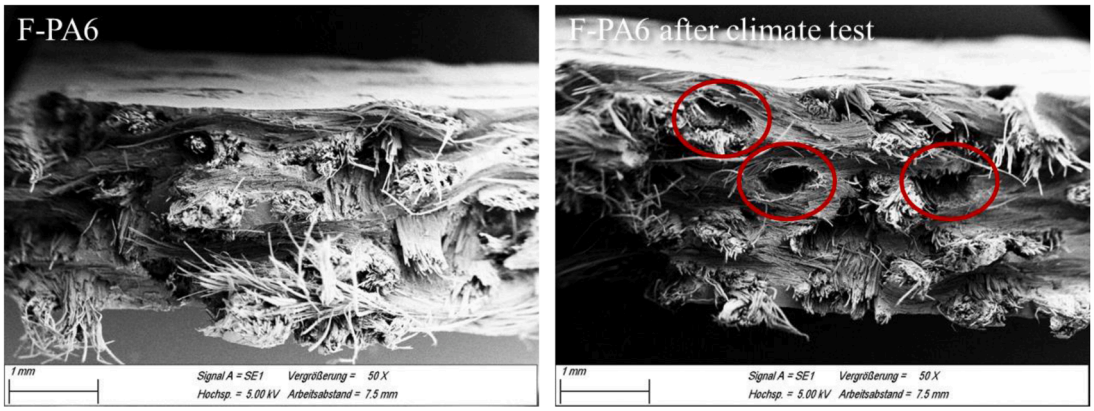

Fig. 11. SEM-image of F-PA6 (left) and F-PA6 after climate chamber test (right) with marked fiber pull-outs (circle).

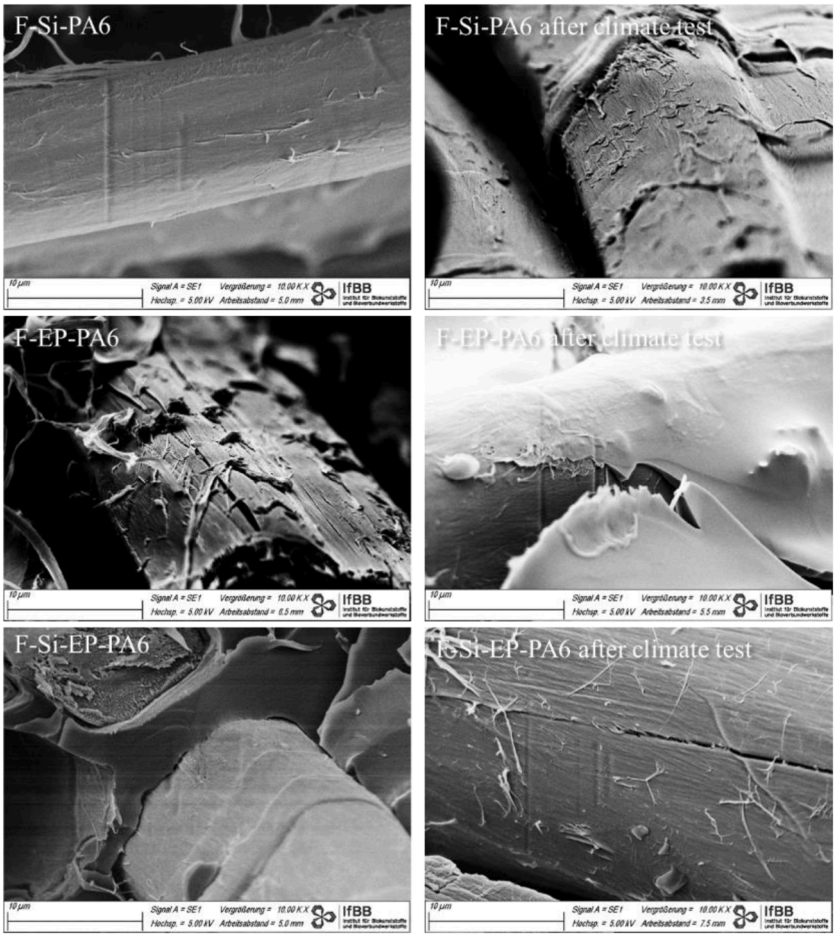

Fig. 12. SEM-image of the composites with modified textiles (left) and the corresponding samples after climate chamber test (right).

partially a weaker fiber matrix adhesion leading to lower mechanical properties. After the climate test fiber damages appear at the surface, supporting the results of mechanical testing before and after climate test. The climate test reduces the tensile and bending moduli to a very similar low level, induced by a decreased fiber-matrix-adhesion.

4. Conclusions

Accelerated aging of the fabrics and the biocomposites was conducted via climate-change tests from −10 °C up to +65 °C for 10 days. Subsequent mechanical testing revealed, that the level of bending and tensile moduli before and after the climate-change tests show considerable decrease for the biocomposites while the treated single layer fabrics slightly increase. Infiltration of humidity with following negative temperatures seem to have an influence on the fiber matrix adhesion for the coated and uncoated fabrics as well. However, the single fabrics show increased tensile properties due to embrittlement of applied coatings after climate change tests. Epoxy treated fabrics additionally have a much higher mechanical potential and a higher starting value for isothermal hot-pressing tests. The decomposition of flax and treated flax samples was reported by color measurements and starts immediately in slight discoloration after 30 s of isothermal hot-pressing at 230 °C, revealing a deterioration of the natural fibers. Nevertheless, this study shows a potential way to enhance mechanical behavior of flax fabrics and corresponding biocomposites resulting in higher bending and tensile strength as well as reduced standard deviations. Further work as for example different methods to block hydroxyl groups of the natural fibers like acetylation, benzoylation, etc. is required to reduce sensitivity of natural fibers towards humidity. Long term stability of natural fiber reinforced composites in different environments is one of competitions to overcome for development of ecofriendly materials.

Table 1

Table 1
Sample code of the manufactured textiles and biocomposites.

Code	Sample
Fabrics	
FLA	Untreated flax fabric
FLA-EP	Epoxy / RT-coated flax fabric
FLA-Si	Silanized flax fabric
FLA-Si-EP	Silanized and epoxy/RT-coated flax fabric
Biocomposites	
F-PA6	Untreated flax fabric in PA6
F-EP-PA6	Epoxy / RT-coated flax fabric in PA6
F-Si-PA6	Silanized flax fabric in PA6
F-Si-EP-PA6	Silanized and epoxy / RT-coated flax fabric in PA6

Table 2
Percental loss of mechanical properties [%] before and after a climate chamber test.

	Loss of bending modulus [%]	Loss of tensile modulus [%]
F-PA6	34,59	45,36
F-EP-PA6	64,78	56,76
F-Si-PA6	61,95	39,97
F-Si-EP-PA6	36,87	26,61

Table 3
Percentage comparison of the results of the modified composites (silanization and epoxy coating) with unmodified reference sample F-PA6 (100%) before and after the climate chamber test.

	Comparison of modified composites with F-PA6 before climate chamber test		Comparison of modified composites with F-PA6 after climate chamber test	
	Bending modulus	Tensile modulus	Bending modulus	Tensile modulus
F-PA6	100	100	100	100
F-EP-PA6	+13,98	+47,13	−38,63	−2,74
F-Si-PA6	+2,69	+6,27	−40,27	−2,47
F-Si-EP-PA6	−25,63	−13,80	−28,22	−3,29

Declaration of Competing Interest

None

Funding

This research was partially funded by the German Federal Ministry of Education and Research, grant number 031B0502 within the scope of the project “DeFiCoat” and partially from own resources.

Acknowledgments

The authors would like to thank Jana Winkelmann and Ricardo Wege for manufacturing the weaved fabrics for this study.

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