THE PERFORMANCE OF FLAX REINFORCED COMPOSITES FOR WIRELESS AND SPORT APPLICATIONS: NATURAL ADDITIVES AND SANDWICH CONCEPTS

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Abstract:

In this study, flax reinforced composites are studied for their long-term performance in terms of electromagnetic signal attenuation and mechanical performance. The use of flax fibres and rosin are studied for applications of natural fibre reinforced composites with antimicrobial features. The thermoplastic matrix used is polylactic acid (PLA) and the thermoset matrix used is a partly biobased epoxy. Laminates are prepared for accelerated algae growth (AG) studies (42 days, Klebsormidium flaccidum) and rain-ultraviolet (340 nm, rain, 18 days) ageing conditioning. The signal attenuation at the range of ultra-high frequencies (2.5 GHz) is measured using the split-disk dielectric resonator (SPDR) method. The results indicate that the flax reinforcement is the main source of degradation whether attenuation or mechanical performance is considered.

Keywords: flax; pine rosin; soil burial; algae; signal attenuation

1. Introduction

1.1 Natural components in advanced fibrous composites

Natural fibre reinforced composites (NFRC) are applied in ever wider application areas. Therefore, the functionalities, e.g., attenuation to electromagnetic signals in wireless applications [1,2] along with bonding characteristics in sandwich concepts are important. For this, the design and processing methods require in-depth studies. Especially the long-term mechanical durability combined with functional performance are not known well. Moreover, the use of polymer composites often requires additives to be used. The reason for using additives can be to improve fire resistance or dimensional stability as well as to minimize microbial and ultraviolet (UV) degradation within long-term environmental conditions. For NFRC, these targets are ever more important. Especially moisture can be detrimental to NFRC where the reinforcement is typically hydrophilic and fibre treatments should modify the compatibility with moisture and wetting by polymeric resins [3]. Moisture can result in changes in the ligno-cellulosic structure of natural fibres in composites [4]. It is important to note that there are fungal species inside fibres, e.g., flax – inherent because of the dew-retting process, and these fungi can affect the degradation of flax in composite materials [5].

NFRCs are preferred materials for lightweight structural components where vibration-damping behaviour is of importance [6]. Currently, these components are typical in the industry sectors of infrastructure construction, transportation, and sports gear [7, 8]. In general, NFRCs are seen as ecological alternatives to traditional carbon and glass fibre reinforced composites. To reach truly environmentally friendly but operational efficient products, it is essential to research the long-term durability of NFRCs further.

1.2 Rosins

Pine rosin (RO) is a product of the forest industry and its application to composites, instead of toxic rivals, can prove to be especially advantageous. Rosin is a complex mixture of numerous compounds, and its exact composition depends on the annual variation and plant. It is mainly an amorphous system of rosin acids, lipophilic compounds and phenol extracts. The rosins from conifer trees (e.g., *Pinus pinaster* and *P. sylvestris*) are probably the most typical ingredients studied for antimicrobial applications. The antimicrobial effects of RO are well-known over several fields and products. For medical applications, rosin has been applied in the forms of polymer-blended fibres [9], nano-fibres [10], food packaging films [11] and various tissue applications of medicine [12]. RO has been reported to be a relatively efficient antimicrobial against viruses and bacteria strains, such as *Escherichia coli*, *Streptococcus pneumoniae* and *Salmonella enterica* [13]. In addition, unlike many of the synthetic counterparts, RO can give long-term and weather-resistant effects against human health-endangering bacteria [14] and also resistance against fungi [15]. Animals and insects use rosin in various ways; ants use rosin in their nests, and it has been found to improve the health of the nest [16] – rosin could perhaps be used to adjust fungal-bacterial degradation of natural fibres in human-made structures.

2. Experimentation

2.1 Laminate preparation

The raw materials of this work included components for 1) thermosetting and 2) thermoplastic matrix composite laminates. The reinforcing fibres were flax fibres in the form of fabric (2×2 twill) (200 g/m^2, Biotex). Flax-reinforced composite laminates were prepared by using ≈30% biobased epoxy (Super Sap, Entropy Resins) and vacuum-assisted resin infusion. In details, Super Sap CLR (with CLS hardener) and Super Sap INH, to adjust the viscosity, were used for infusion processing. The laminates were made with a stacking sequence of [0/45]SE. The reinforcement was dehydrated before infusion carefully (80 °C, 1 hour, following 100 °C for 1 hour). The mould had a glass surface and a vacuum bag (Δp = 0.5 bar) was applied over it. The cured laminates were post-cured (80 °C, 2 hours).

Rosin was blended with poly lactic acid (PLA) (2003D, Ingeo, Nature Works) at 200 °C with gum rosin (pine gum rosin, acid value of 167 mg KOH/g, Forchem) by using a twin-screw extruder (TSE 25E, Brabender). For the mixing, the crashed RO-particulates were simultaneously mixed with PLA granulate (≈5% mass/mass rosin). A hot press was used to prepare actual laminates. PLA without and with rosin was used (granulated after extrusion). A metal frame was used to confine PLA (and RO) during pressing at an exact volume. Flax-reinforced PLA laminates were pressed by stacking (pre-pressed) PLA and flax layers (lay-up [0/45]SE) and pressing (180 °C, 100 bar, 5±1 minutes for single layer, 8±0.1 minutes for final layer stack). When RO-blended PLA

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was sued, press temperature was lowered to 160 °C. The flax was dehydrated before the compression moulding (90 °C, 2 hours).

2.2 Soil burial

In this work, applied soil burial conditioning was applied by using a commercial garden composter (220eco, Biolan). For observing the conditions during the burial, the compost was instrumented with two outside measurement points (recording temperature and relative humidity) and two internal sensors (temperature). The compost was built into four sections by using stainless steel (AISI 304) mesh. These sections divided the volume into mechanically separated zones but allowed essentially free flow of moisture and heat. Also, the sectioning allowed to keep rosin-containing samples separated (i.e., no bare specimens below that would be contaminated by possible rosin secretion downwards) but still conditioning by the same microbial medium and conditions. The soil medium was a mixture of low-nutrition commercial garden peat (Biolan) (nitrogen 15 mg/l, phosphorus 100 mg/l, potassium 500 mg/l) and forest humus, leaves, small branches (200/50 (volume/volume) ratio). In addition, 4.8 % (volume/volume) of moisture was applied in steps (water temperature ≈37 °C). The microbial process was boosted by using commercial compost activators mixed within the medium (Multikraft Produktions und Handels) and in water (Neko). It should be noted that rather mild microbial process (and temperature) was targeted to simulate typical household composting process. During the burial, a temperature change of $\Delta T \approx 10$ °C (maximum temperature 16 °C) was recorded.

2.3 Rain and ultraviolet irradiation conditioning

The harsh effects of ultraviolet (UV) irradiation and sequentially applied water (rain) were studied for the NFRC specimens by using a UV-rain chamber Xe-3 (Q-SUN). The applied test sequence of two steps used for cycling are given in Table 1. The total conditioning time was 432 hours (18 days, 2-hour cycles) (see standard ISO 4892-2-2013 for additional information). The size of each laminate piece was 60 mm × 60 mm (nominal thickness 2.6 mm). After the UV-rain conditioning, the dehydrated specimens were transported in plastic bags for attenuation measurements (see Section 2.6).

Table 1: Steps of rain-UV irradiation condition for cyclic environmental conditioning for 18 days

Phase	UV irradiation (340 nm)	Duration	Chamber condition
1	0.39 W/m^2, black panel temperature 63 °C	108 minutes	(≈38 °C, ≈50% RH)
2	(No UV)	12 minutes	Dark, water spray

2.4 Algae growth cabinet

The effects of rosin in the laminates were studied on accelerated algae growth (AG). AG studies covered in total 42 days, using *Klebsormidium flaccidum*, at 90% RH, 25 °C. A small amount of algae was dosed on the laminated specimens, which were then placed inside a specialized conditioning cabinet. The specimens were kept aligned (20°) during the conditioning. Nutrient solution was sprayed on the specimens for 7 seconds at a time (0,3 l/minute) every 3 hours. Carbon dioxide was purged into the cabinet for 5 seconds (8 l/minute) every (1) hour. The redgreen light was applied for 12 hours in 24-hour cycles. After the algae growth studies, the specimens were transported in plastic storage bags for measurements (see Section 2.6).

2.5 Interlaminar shear strength testing

This work focused on testing laminates under flexural loading using the three-point bending condition (short-beam three-point bending according to ASTM D 2344) to determine interlaminar shear strength (ILSS). The specimens' planar size was 8 mm × 20 mm (nominal thickness 2.6 mm). The target was to emphasize the shearing component of load and to aim at interlaminar failure. A universal testing machine was used to generate the load (electrical 5967, Instron). The ILSS testing was applied for specimens in the reference condition (ambient conditions) and after the soil burial condition. For epoxy (matrix), a support pin span of 9 mm was used. For PLA, a support pin span of 11 mm was used (per recommendations in the standard procedure). A constant displacement rate of 1.0 mm/minute was used for testing.

2.6 Signal attenuation measurements

Signal attenuation at frequencies typical of various 5G applications [1,2] was studied for the different composites before and after AG. Here, the method of split-disk dielectric resonator (SPDR) was used. The SPDR here was used at 2.45 GHz signal generator (QWED) with a Microwave Frequency Q-Meter (QWED). The sample size was 60 mm × 60 mm (thickness 2.5-3.0 mm). The measurements were made at a constant signal frequency of 2.45 GHz for all specimens and sample-specific thickness was measured to determine attenuation (permittivity, loss factor). Measurements were made in ambient room conditions (21 °C, 50% RH).

3. Results and analysis

3.1 ILSS performance of flax reinforced composites after soil burial

The ILSS determined for the reference specimens and after the soil burial (SB) conditions are given in Table 2. Before SB, the composites without rosin have a similar level of ILSS. The composites with RO blended into PLA have 44.5% lower ILSS compared to the reference that might be due to the lower mechanical properties of RO itself. After SB, the loss in the ILSS value of FX-PLA (-10%) is more pronounced compared to the FX-EPX (-3%). The ILSS value of FX-PLA is relatively stable after a period of soil burial which is promising for the long-term performance of composites. The loss in ILSS values for both composite systems after SB can be due to the intrinsic porosity of flax fibres (e.g., lumen) acting as a channel for moisture diffusion and microbial degradation [17]. The drastic decrease (-58%) in the ILSS value of the FX-PLA-RO after the SB period could be due to the porous morphology of specimens.

Table 2: Flexural behaviour in terms of ILSS for flax reinforced composites before and after SB

Series	ILSS before SB (ref)	ILSS after SB (14 days)	Δ ILSS
FX-EPX	18.6 MPa	18.0 MPa	-3.3 %
FX-PLA	18.4 MPa	16.6 MPa	-10.1 %
FX-PLA-RO	10.2 MPa	4.2 MPa	-58.3 %

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3.2 Growth of algae on specimen surfaces

The algae coverage after the AG period of 42 days on the specimen surfaces was essentially similar for the different laminates. It should be noted that surface roughness can affect the algae observed on the surfaces for this type of test arrangement. However, the algae observed on the non-reinforced PLA-RO (smooth surfaces) was similar compared to the reinforced laminates.

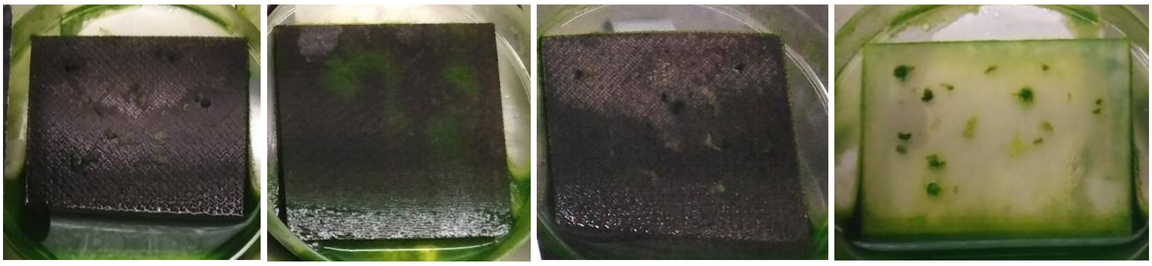


Figure 1. Photographs of laminates applied to AG studies (left to right): series FX-EPX, FX-PLA, FX-PLA-RO, PLA-RO)

3.3 Determined signal attenuation after AG and rain-UV conditioning

The measurement results of attenuation are shown for specimens after the algae growth conditioning (AG) and rain-UV conditioning in Table 3 and Table 4, respectively.

Table 3: Measured permittivity and loss factor before and after algae conditioning.

Series, condition	Permittivity	Δ (vs. ref.)	Loss factor	Δ (vs. ref.)
FX-EPX, ref	3.10	-	0.0871	-
FX-PLA, ref	3.02	-	0.0364	-
PLA-RO, ref	2.73	-	0.0052	-
FX-PLA-RO, ref	2.98	-	0.0351	-
FX-EPX, wet	n/a	n/a	n/a	n/a
FX-PLA, wet	n/a	n/a	n/a	n/a
PLA-RO, wet	6.20	+127%	0.0933	+1707%
FX-PLA-RO, wet	n/a	n/a	n/a	n/a
FX-EPX, dried	3.23	+4%	0.1188	+36%
FX-PLA, dried	3.12	+3%	0.0485	+33%
PLA-RO, dried	2.77	+1%	0.0061	+18%
FX-PLA-RO, dried	3.08	+4%	0.0540	+54%

In Table 3, it can be seen that the addition of the flax reinforcement led to an increase of the value of permittivity and loss factor. These parameters of attenuation were lowest for the non-reinforced PLA-RO series – similarly before AG (reference state) as well as after AG (and dehydration) (i.e., dried specimens). The results indicate that algae growth and possible ageing effects permanently affected the loss factor but not the measured permittivity.

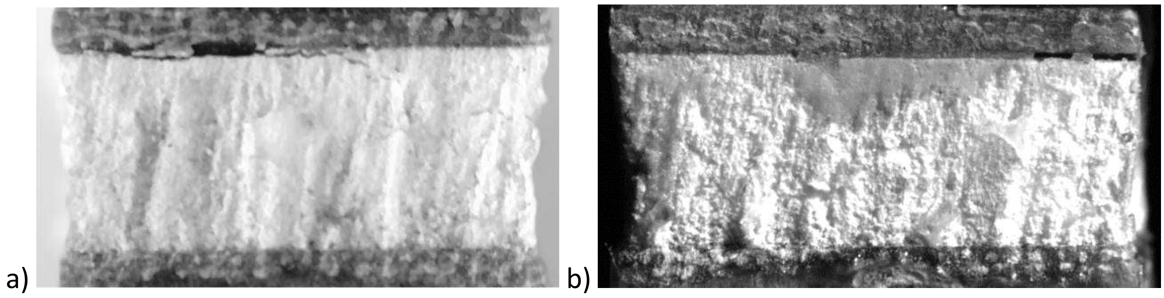
The attenuation measurements after the rain-UV conditioning of 432 hours (18 days) are shown in Table 4. Based on the results, it can be seen that the changes (for the dehydrated specimens) are similar to those after the algae growth and conditioning when it comes to the determined level or permittivity. Interestingly, the changes in the loss factor are relatively small except the results for the flax-reinforced rosin-PLA (series FX-PLA-RO), which gained multitudes of more attenuation-affecting ageing during the conditioning (+ ×10). A similar trend among the tested series related to the algae growth and conditioning was seen (+ ×2) in Table 3. Interestingly, the increase in loss factor for the non-reinforced PLA-RO series was low. It seems that the combination of rosin and flax results in electro-mechanical changes due to conditioning by algae or moisture and UV.

Table 4: Measured permittivity and loss after rain-UV conditioning of 18 days.

Series, condition	Permittivity	Δ (vs. ref. in Table 3)	Loss factor	Δ (vs. ref. in Table 3)
FX-EPX, 18 days	3.01	-3%	0.0838	-4%
FX-PLA, 18 days	3.06	-1%	0.0340	+9%
PLA-RO, 18 days	2.70	-1%	0.0054	+7%
FX-PLA-RO, 18 days	2.95	+1%	0.0485	+38%

3.3 Bonding of NFRC laminates to form sandwich panels

Pre-manufactured NFRC laminates can be combined with different core materials to form sandwich panels – these are used to enhance structural properties without increasing weight too much. A practical way of joining laminate skins to core materials also depends on the matrix type in use (see Fig. 2). The pre-manufactured (cured) FX-EPX laminates (with thermoset epoxy resin) need to be joined by using the adhesive bonding method. In this process, the thickness of the panel is controlled with side supports (or alternatively a mould) and a vacuum line can be used to remove trapped air (voids) from the adhesive layer. When using thermoplastic-matrices in skins, i.e., FX-PLA laminates, the laminates were heated in an oven up to a temperature exceeding the softening point (of the matrix) but to stay away from the decomposition temperature of flax (around 200 °C). Following the bonding phase, the panel is next placed in a cooled mould to let the panel cool down evenly and to prevent significant deformation due to residual stresses.



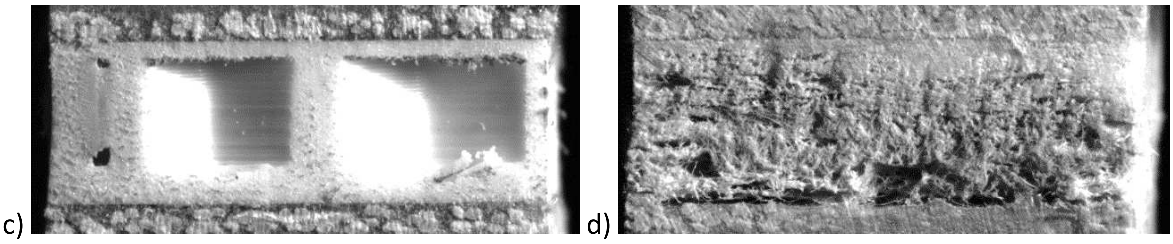


Figure 2. Bonding concepts of NFRCs: a) NFRC bonded to expanded polystyrene (EPS) foam by adhesive bonding under vacuum; b) NFRC to expanded polystyrene (EPS) foam by infusing dry flax fibers directly to core; c) NFRC bonded to PLA 3D-printed honeycomb core by hot-pressing; d) NFRC bonded to foamed cellulose [18] by adhesive bonding under vacuum.

4. Conclusions

This work aimed to study the effects of pine rosin in flax fibre reinforced composites when ageing effects due to soil burial, algae growth and rain-UV are considered. Changes in ultra-high frequency signal attenuation and mechanical performance were determined and reported. The combination of rosin and flax results in changes in composites that requires further research. The laminates in this study included thermosetting (epoxy) matrix composites and thermoplastic (PLA) matrix composites. The results in the study indicated the following outcomes:

- ILSS, measured after 14 days of soil burial and subsequent dehydration before testing, showed significant decrease in flax composites where rosin was blended with PLA.
- Algae (*Klebsormidium flaccidum*) growth was essentially similar on the surfaces of flax reinforced laminates and non-reinforced rosin-blended PLA.
- Signal attenuation after the study of algae growth and subsequent dehydration before testing showed that the algae accumulation and possible ageing of the composites in moist conditions permanently increased the loss factor but no permittivity. Before dehydration, right after algae growth studies, the attenuation was successfully measured only for the non-reinforced rosin-blended PLA.
- Signal attenuation after cyclic rain-UV conditioning over 18 days and subsequent dehydration before testing indicated that the ageing by combined UV irradiation and rain results in permanent increase in loss factor but not in permittivity.

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