Biodegradable PCBs with PLA/flax substrate: FTIR and SEM analysis of soil degradation

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Abstract— Recently, polylactic acid and flax-textile-based, reinforced, flame retarded composite was introduced, which is promising in terms of PCB applications as a substitute for the dielectric. This paper extends our knowledge with analytical investigations on the substrates, specifically degradation in natural environments. After preparing bare laminate samples and assembled, one-sided demonstrational circuits with traditional surface mounting technology, the boards were introduced to natural composting in a composting bin with outdoor ambiance and FR4-based reference samples. The boards were kept in the soil for 43 weeks. In selected time points, the samples were subjected to the following analytical investigations: Fourier-transform infrared spectroscopy (FTIR) to reveal the composition of the surface structure before and during degradation; scanning electron microscopy (SEM) to analyze the topography and the structure before and during degradation. As FTIR showed, PLA is still dominant on the surface of the boards after 37 weeks of degradation. The analysis also revealed that after ~40 weeks of soil degradation, the cellulose (from the reinforcement textile) was exposed to the surface. The SEM analysis showed cracks and minor degradation of the PLA on the surface of the boards during the weeks, revealing contaminations and microbiological remains. sEM also showed that PLA is heavily present on the reference surface and the degraded samples. Microbe specimens were also investigated on the degradable samples, while the reference boards contained no similar findings.

Keywords—sustainable electronics, green electronics, biodegradable PCB, PLA and Flax composite, FTIR, SEM, degradation

I. Introduction

A possible path to obtaining sustainability in electronics is to change the material set with environmentally friendly alternatives, enabling reduced load on the environment. Bio-based, degradable [1] composites in packaging and printed circuit board technologies (PCB) are in the emerging phase.

Currently, traditional materials in the electronics industry meet the short-term needs of consumers and different industry sectors. Providing a competitive alternative is difficult, and the upscaling of such technologies is still a question.

New materials, as sustainable alternatives, face many challenges in achieving proper reliability. [1] Over time, a substrate of sufficient quality could be present on the market as an alternative, where the applicability is not significantly inferior to non-environmentally friendly options. A carrier with plannable degradation would be a partial solution to the rapidly growing e-waste crisis. If there is an alternative that is not significantly more expensive and similarly efficient, it could be incorporated into the green goals of many companies, their innovation efforts, or their progress toward sustainability in general.

Less than 20% of e-waste is now recycled and reused or reused, with the remainder being disposed of in landfills or remanufactured [2]. One of the largest categories of e-waste is printed circuit board (PCB) waste. Research is starting to get more comprehensive on the topic; now, separate review articles are discussing the different aspects of cellulose-acetate (CA), polylactic acid (PLA), silk proteins, gelatin, flax fiber, polyvinyl alcohol, or even mycelium-based substrates. [3, 4] An interesting example from the recent literature involves mycelium skin for a sustainable, flexible substrate for electronics; the material is thermally stable up to 200°C and decomposes after two weeks under suitable soil conditions [5]. Recently, an LED-based demonstrational circuit was fabricated from a composite of PLA and cotton fibers with silver ink-based conductors; this PCB is compostable and loses 5% of its weight in 6 months while in soil [6]. However, more traditional approaches can also be found in the literature. Recently, a Shellac-paper-based composite was introduced for PCB application [7]. As a starting material, paper is applicable for flexible electronics [8]. Wood and veneer have also been investigated as possible alternatives for rigid printed boards [9].

Recently, we introduced a PLA/flax-based composite [1], successfully used as a rigid, sustainable substitute for FR4. The boards are composed of flax-textile, PLA powder, and foil, are flame-retarded, and at the moment, two-sided PCBs are achievable; assembly is possible with surface mount technology. The substrate is 1.6 mm thick; the copper is standard 1 oz. Subtractive technology forms the circuit pattern, and traditional surface mounting technology (SMT) steps are applied to form the assembly with pick and place and reflow. The board is compatible with all standard apparatus in the technologies mentioned above. In this paper, our motivation was further to explore [1] the degradability of different samples. The degradation study focuses on soil-based decomposing [10, 11]. While PLA (and thus our sample) is classically only degradable in controlled degrading environments [12], it is essential to see how the boards perform in soil-based environments.

II. Experimental

A. *Sample preparations*

The PLA/flax laminates contain flax textiles with PLA layers in between, and is also treated with biocompatible flame-retardants. The thickness of the boards was configured to form traditional 1,55 mm substrates. The structure is finalized with the lamination of standard 1 oz copper layers used on the top side of PCB technology. Our samples were prepared according to the following parameters.

We started from ~200x300 mm sheets. One sheet was prepared without copper; the other was laminated with copper. The non-laminated group of the boards was cut into 10x20 mm pieces, and the laminated group of boards was treated with traditional subtractive PCB processing [13] to obtain a simple one-sided printed circuit design (with a blinker functionality) in the exact dimensions. The boards were subjected to heat transfer in an IR-based reflow oven to simulate the assembly conditions. The alloy was chosen as a low-temperature solder (SnBiAg) at a 138°C melting point. The maximum of the heating profile was set to 170°C. The samples were subjected to 43 weeks of degradation in natural soil. A few pieces were left out on the laboratory ambiance.

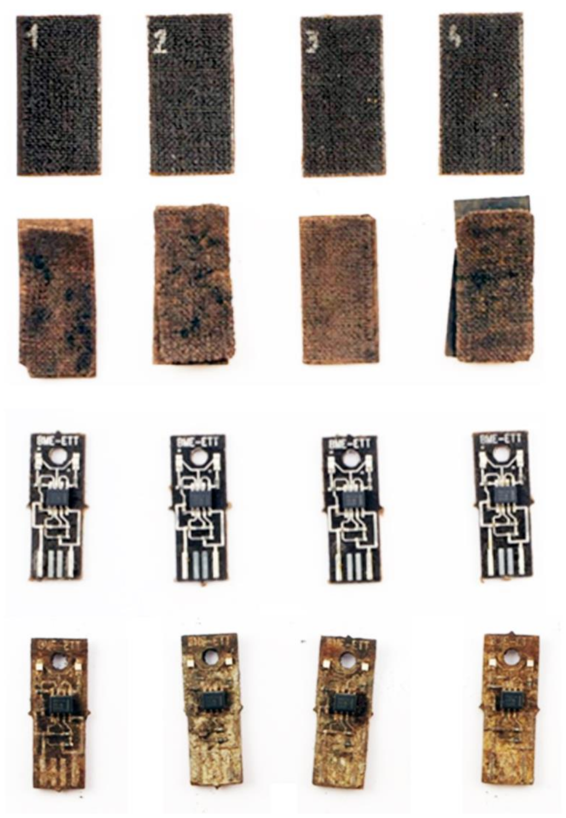

Fig. 1. From top to bottom: bare PLA/Flax dielectric substrate at the starting point of the experiments; the same after degradation of 43 weeks (with delaminating layers); PLA/Flax-based assembled blinker circuits; the same after 43 weeks of degradation.

The degradation tests started during 2023 summer. In this paper, we focus on the 29th-43th weeks, as we found changes and notable results during the springtime (February-May), as the weather became warmer during continental springtime. A composting bin (Fig. 2) was placed in one of the outside areas between campus buildings (47°28'36.0"N 19°03'24.2"E), where the 32 samples were buried for soil decomposition. The bin was filled with approximately 0.5 meters of natural soil, and on top of the samples, a layer of additional fresh, filtered soil (~0.15 m) was added.

Figure 1 presents samples of our investigations. The results will follow those obtained from the view of a bare dielectric without copper, a one-sided blinker circuit, and will refer to the FR4 samples. The one-sided blinker has different surfaces on the sides, as the processed side was laminated with copper and subtracted to form traces. This side is less rough than the bare side. We must note, that the copper ions formed during soil degradation is expected to have effect on the process. The pieces were dried, cleaned, and brushed before measurements.

B. Analytical tools

Fourier-transform infrared spectroscopy (FTIR, Bruker Tensor, Opus 6.5.) was used to reveal the composition of the structure in between degradation steps. Scanning electron microscopy (SEM, FEI

Inspect S50) and SEM-Energy Dispersive Spectroscopy (EDX) were used to analyze the topography and the structure before and after degradation.

III. Results

A. FTIR results

Figure 2 shows an example measurement of 3 points of a basic dielectric sample after 29 weeks of degradation. The results are very similar, but there are slight changes, which could point to the presence of local contaminations of the soil. Therefore, we have to note that the measurements will have slight changes even along the surfaces of one sample.

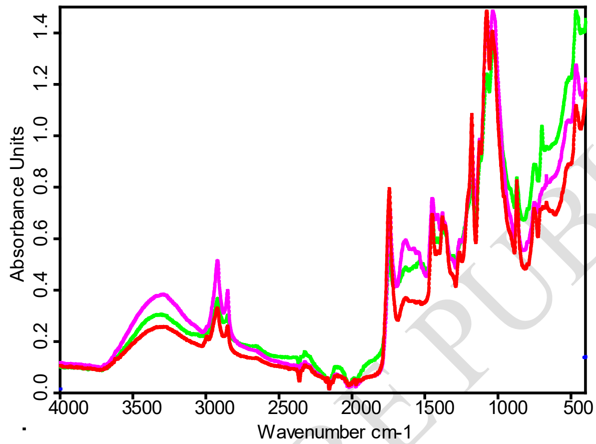

Fig. 2. FTIR spectra of three different measurement points of the bare dielectric substrate (29th week)

Figure 3 presents the degradation of the bare dielectric for two months. Between the 29 and 37 weeks (Feb-Apr.), no significant changes were observed.

At this point, we had to compare the obtained spectra with the database information of PLA (filament), which, as Figure 4 shows, were practically identical. At this point, we suggested that PLA is still dominant on the surface, meaning that the degradation did not reach the cellulose-based fibers. However, more interesting findings were inspected after this point. At this stage of the research, the assembled circuits and the bare laminates presented similar results.

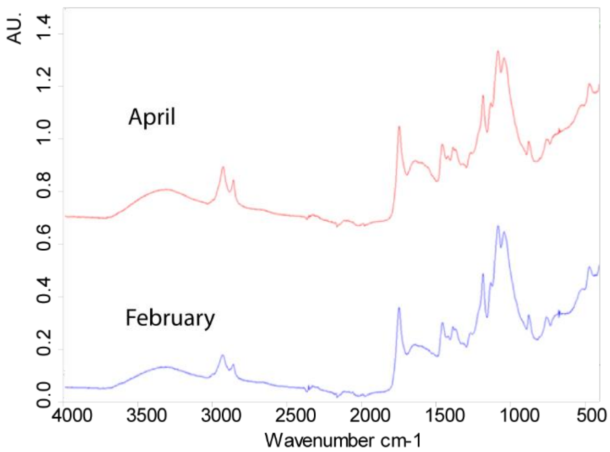

Fig. 3. Spectrum is the same between two months of degradation (29th-37th weeks).

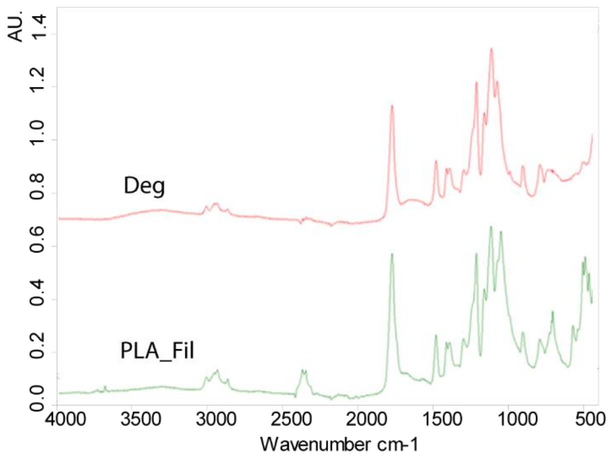

Fig. 4. The spectrum reveals that the board (Deg) and the database plot of a PLA filament (PLA_Fil) are very similar, meaning that PLA is dominant at the surface. (37th week)

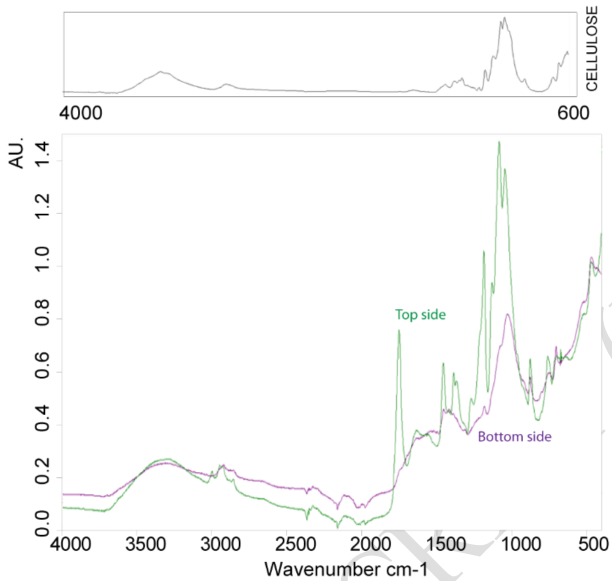

Fig. 5. Top and bottom side of assembled PCB at 43th week.

Figure 5 presents the most interesting finding. At around 43th week (May), we found that the spectrum of the bottom side of the assembled sample showed significant difference between the top side and compared to previous results It was found that while on the top side, the PLA-based peaks were still dominant (see Figures 4-5), on the bottom side, the PLA-based peaks seemed to lowered, and the remaining spectrum was very similar to the database information regarding cellulose, which represents the appearance of flax-textile.

B. Results of SEM, microbiological aspects

Figure 6 shows an interesting phenomenon. The samples at 37th week (April) started to show presence of microorganisms. On the figure, both fungi and bacteria are present, which is further apparent from the latter Figure 7. It has to be noted, that the PLA layer covering the flax-fibres is also heavily cracked, although intense chipping is not present.

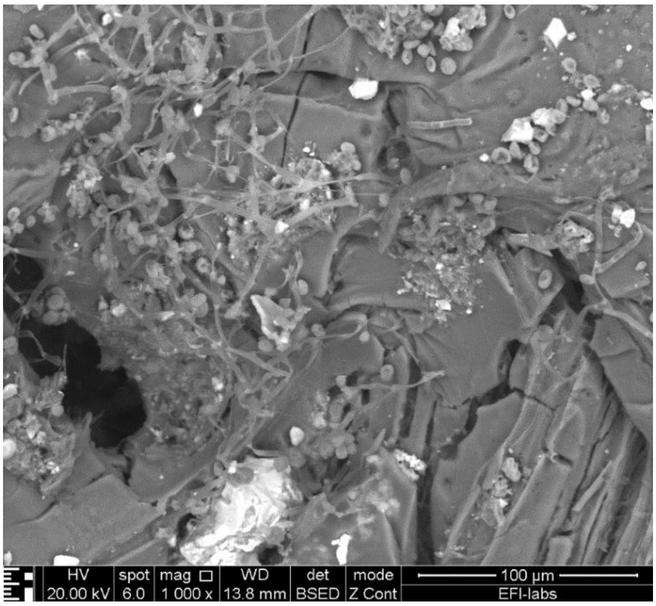

Fig. 6. Cracked PLA surface and various microbiological lifeforms on bare dielectric after 37 weeks.

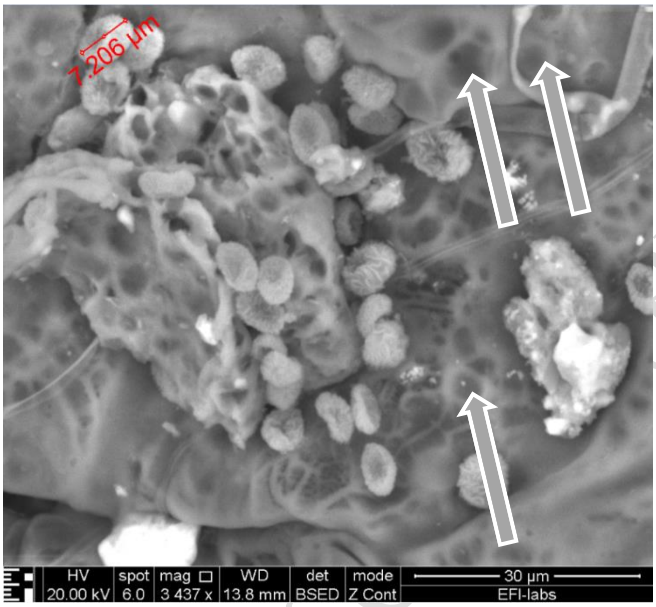

Fig. 7. Spherical/donut forms (7.2 µm diameter, as noted by marking) of microorganisms investigated on the top of the bare dielectric sample. It must be noted that the surface PLA layer suffers deformation (as shown by arrows) due to the SEM analysis.

The differences between the 37th and 43th week (April and May) must be noted. The first SEM analysis destroyed the microbiological lifeforms due to the vacuum and the scanning electron beam. After a month, the old bacteria and fungi remains were found to be in stacked ball-like formations next to the soil debris parts. Figure 8 shows these remains.

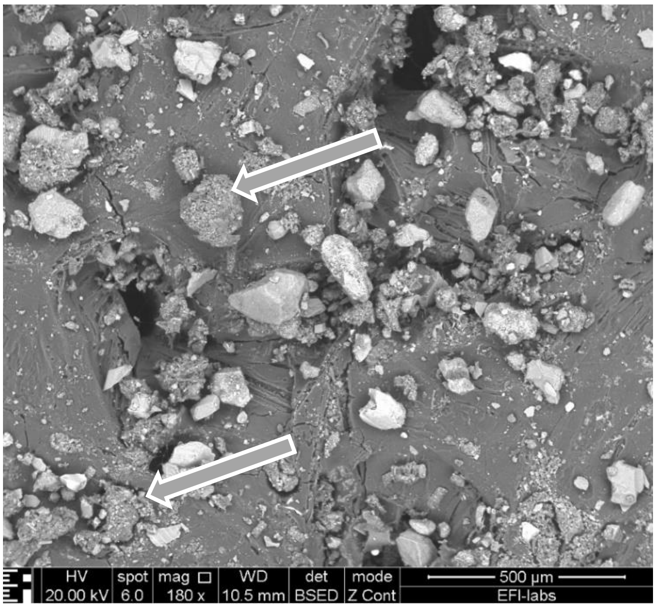

Fig. 8. Ball-like formations of previously scanned, now dead microorganism remains (43th week, dielectric sample)

As for the same samples (unprocessed dielectric), we found that new mycelium lines formed. This is shown in Figure 9.

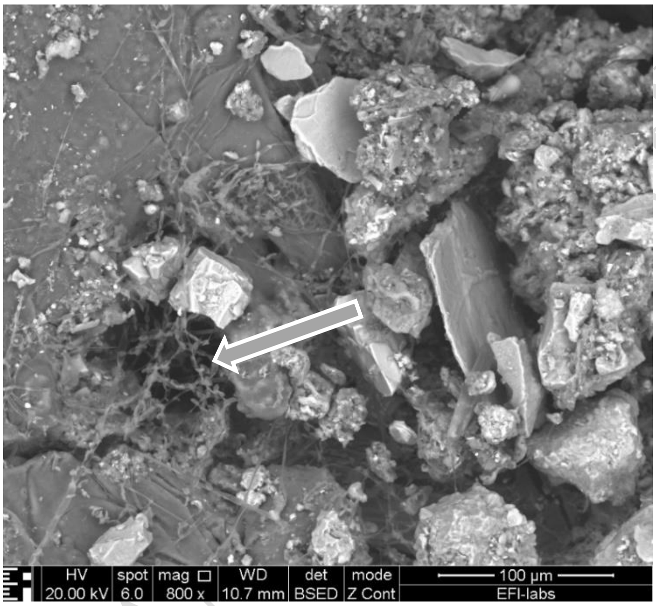

Fig. 9. Newly detected mycelia (43th week, dielectric samples)

It is interesting to see that on the "assembled side," there are no microbes to be presented. This could be because the copper layer enables copper ion release, which is considered to be antimicrobial [14]. However, deeper cracks could also be located at the top side of the assembled board, where different microbes colonies could be visualized. The SEM photos are shown in Figures 10 and 11 (smaller and larger magnification).

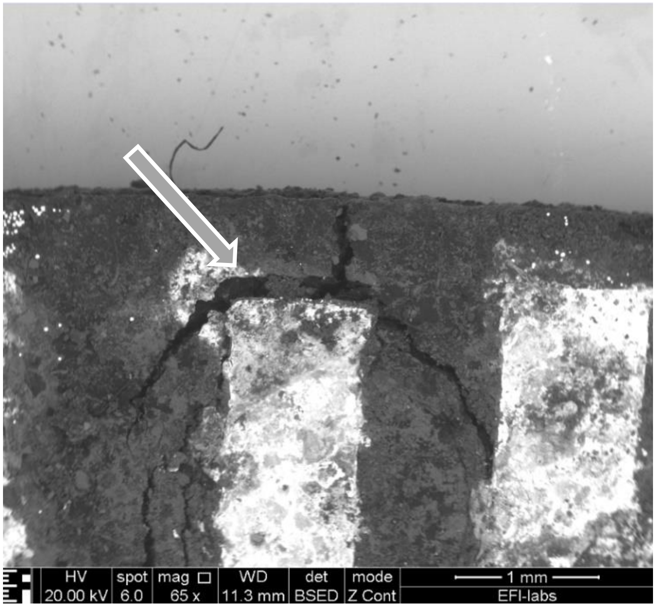

Fig. 10. Cracks from the top side of the degraded and assembled boards at 43th week. The surface is devoid of microbes, the inside of the cracks are not.

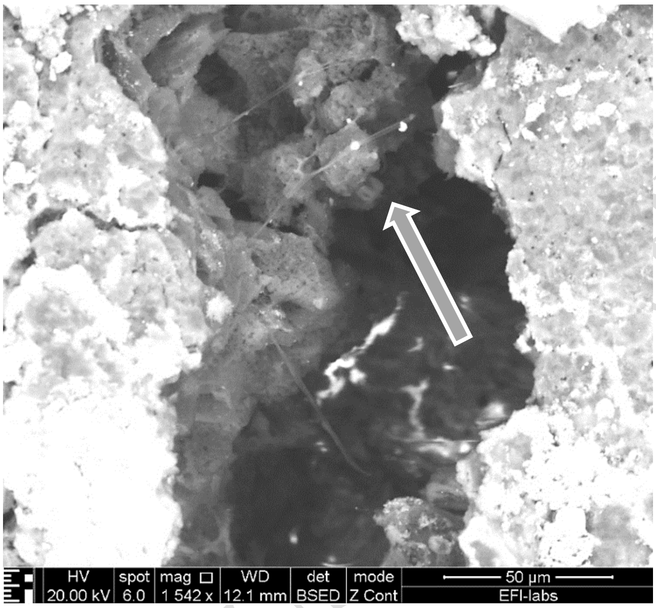

Fig. 11. Microbiological colonies in the depth of the crack.

Figure 12 presents an optically observable example, where white "filaments" were observable on the back of the natural dielectric samples. The filaments were observed in SEM as well. The next figure (Fig. 13) reveals the form of them. It was found that the white lines are practically remains of fungi structures. The EDX analysis showed ~32 wt% Carbon and ~15 wt% Calcium content at a specific measurement point on the structure According to Bindschedler et al. (2016), the formations are biomineralized calcite ($CaCO_3$), formed by fungi along mycelium, which is suggested by the structure's geometry. The formations are similar to the presented fungal hyphae coated with calcium oxalate crystals in the paper [15]. Further microbiological analysis is needed to reveal the specific microbes along the surfaces.

It must be noted that no degradation, no microbes, or changes were observed on the control FR4 samples. It also has to be noted that around the 43rd week, the natural samples started to fall apart layer-by-layer.

Fig. 12. White filaments found with optical microscopy on bare dielectric samples. 43th week.

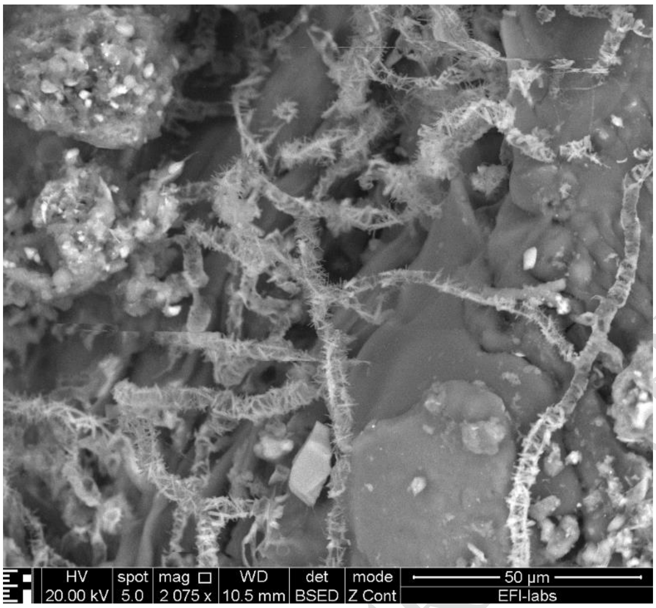

Fig. 13. White filaments found with optical microscopy on bare dielectric samples. 43th week.

IV. Conclusions

To sum up the soil degradation of PLA/flax composite printed circuit board substrates, the most important findings are concluded in this chapter based on the measurement methods.

A. *Conclusion of the results*

The FTIR analysis showed that the spectrum obtained from various measurement points along the surfaces (both sides) of both unprocessed dielectric substrates and processed and populated PCBs was dominated by the PLA, which was concluded with a comparison of PLA spectrum. It was found that minor differences could be found around measurement points, but overall, the spectra are similar and comparable. No significant change was found during the 29th and 37th weeks, but after 43 weeks, cellulose started to appear and PLA started to disappear in the spectrum, showing local degradation of the PLA. Copper may provide an antimicrobial effect on the circuit side of the boards.

During our soil degradation studies, various microbes were observed on the dielectric samples when springtime and warmer weather came. The microbes were repopulating the PCB from measurement to measurement (as SEM analysis destroyed them). Around the 43rd week, optically observable mycelia-based ($CaCO_3$) filaments were found, further increasing the presence of various microbes on the surfaces of the degradable substrates. This shows that our material is susceptible to the settlement of microbes. We could not find microbes on the top side of the assembled PCBs. In the cracks from the top sides, they were observable.

B. *Future paths*

The work will be extended with industrial decomposing apparatus and process, where the degradation will be compared with the natural decomposition in soil-based compost.

The microbe samples have to be investigated (DNA-analysis) to have a connection between their presence and the decomposition of the PLA in the given environment.

C. *Sustainability analysis*

The work connects to Sustainability Development Goals (SDG) SDG9 and SDG12 directly, as the material set is a part of an innovative approach to ease environmental load of electronics, both from the aspect of mass manufacturing, industrial substitution of harmful constituents, thus the aspect of material set and the final consumer behaviour.

Acknowledgment *(Heading 5)*

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