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FLUORESCENCE SPECTROSCOPIC ANALYSIS OF BIODEGRADED PRESSURE-SENSITIVE LABELS MADE FROM AGRO-INDUSTRIAL AND POST-CONSUMER WASTE

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Abstract: *Today, more than ever, sustainability is at its highest peak of daily interest for all business sectors, especially involving label and packaging industries. Usage of paper products made from alternative fiber sources is a very important topic that directly supports circular economy in everyday life. Although paper products should be recycled or re-used as secondary source of raw - material, a vast volume of products end their life at landfill, especially still in our region, causing excessive accumulation in the environment. For the purpose of this research, fluorescence intensity was measured on three different biodegraded pressure sensitive label material samples (PSL), made from agro-industrial and post-consumer waste. PSL materials utilized in this research are widely used for labelling various products, for example, wine, luxury products, food etc. and are compiled of 3 parts: facestock, adhesive and liner. PSL materials are enriched with optical brighteners to give the final product the desired optical properties. Fluorescence spectroscopy is a direct measure of optical brightener concentration within the substrate. Biodegradation was performed by usage of soil burial test under aerobic conditions. Laboratory soil burial experiments were conducted at room temperature (25±2°C) by placing the unprinted label paper substrates; facestock and adhesive (delaminated from the liner) horizontally in field soils in 2L laboratory glass containers, orientated adhesive down. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. Substrates were buried for a period of 2, 4, 7, 10 and 13 days. Sample's fluorescence intensity was measured before and after incubation in the soil containers. The samples were dug out after designated time, rinsed with distilled water to remove soil particles from the surface, air dried and measured. Fluorescence intensity was measured by using Ocean Optics USB2000+ spectrometer using a 30 mm wide integrating sphere under (8:di) measuring geometry with the addition of LSM Series LED light source at 365 nm. LED light source is operated via a smart controller during the measurement. A constant current of 0.140 A was kept stable in order to maintain a constant excitation light source with the aim to excite fluorescence whitening agents within the samples. As previously research shows the presence of optical brighteners in composition of fibre based PSL, fluorescence spectroscopy of biodegraded samples indicates decomposition of optical brighteners.*

Key words: pressure sensitive labels; fluorescence spectroscopy, sustainable self-adhesive labelling materials, biodegradation

1. INTRODUCTION

In everyday life sustainability is, particularly by the wide public, narrowed down solely into its environmental dimension. Well known fact is that in the paper industry, the main raw material for paper production is wooden fibres, either virgin or recycled. Due to rising demand of paper industry raw material in general (including paper – cellulose-based product that are not directly related to graphic printing industry), we witness an obvious trend towards sustainable fibre sourcing and sustainable and controlled forestry, especially lately as European countries ban various plastic packaging and promote methods of reducing usage of plastic (Labels&Labeling, 2021).
If the example of citrus crush paper is considered, which is produced in Italy, we can see that a large proportion of the 600,000 tons of bio-waste from juice production in the form of citrus mesh in the country is used for its production. Some ratio of the citrus mash is used to produce essential oils, biofuels, and candied fruit, but a large share is still accessible for paper production and thus saved from landfill. The process remains the same as for other kinds of paper, but less energy is used and no additional chemicals. In the production of these paper types 20% drop in CO_2 emission is achieved in comparison to standard label papers.

Crush paper includes by-products from citrus fruits, coconut, cocoa, grapes, cherries, lavender, corn, olives, coffee, kiwi fruits, hazelnuts, and almonds. These natural raw materials are saved from landfill and used to make these distinctive and vivid papers.
Also, there is a tendency of using renewable non-tree biomass like seaweed and algae for paper production. The possibility of upcycling, meaning using discarded materials in such a way as to create a product of higher quality or value than the origin is also increasingly present. For example, discarded leather residue from the manufacturing process can be used to replace almost 25% of wood pulp in the paper production process. It is noteworthy that all of these papers are recyclable and biodegradable.
All pressure sensitive materials, also known as self-adhesive materials, comprise of three functional parts: facestock, adhesive and liner. The importance of pressure-sensitive label industry is proven by its constant business and consumption growth. As various market researchers show, the global self-adhesive labels market size is projected to grow from USD 47.9 billion in 2021 to USD 62.3 billion by 2026, at a CAGR of 5.4% from 2021 to 2026. With the increasing demand for convenience and quality food products, people are opting for packaged food products, where the product information and other product details need to be clearly presented to the consumer (Research and Markets, 2022).
One of the ways of making fibre based labels facestock whiter is by bleaching the pulp and incorporating fluorescence whitening agents (FWAs) in the paper pulp during it's production (Pauler, 2012). Role of the FWAs is to absorb excitation light in the UV part of the spectrum because that energy is needed for excitation from ground state. Molecules remain briefly in the excited state and emit energy at higher wavelengths during emission. Since part of the energy is consumed or converted into another form, the emitted energy is lower and is reflected in the spectrum as a shift (Brand & Johnson, 2008; Itaqaki, 2000).
It is convenient to measure fluorescence using integrating sphere (Shaw & Li, 2008; Zwinkels, 2010; Zwinkels et al., 2014). Fluorescence spectroscopy measures power of the radiation absorbed by the molecule. Biodegradation by burial testing is a way of examining the decomposition ability of organic substrates with the help of microorganisms and different abiotic components (Vukoje et al., 2017). Possibility of composting paper and it's forms is previously studied by various authors (Alvarez et al., 2009; Tomšič et al., 2007; Venelampi et al., 2003). FWAs as a paper component can be decompose by prolonged exposure to microorganisms in the soil. The decrease in FWA concentration can be confirmed with the drop in fluorescence intensity of the sample under study.

2. MATERIALS AND METHODS

2.1 Characteristics of the pressure-sensitive labels made from agro-industrial and post-consumer waste used in the study

Avery Dennison is a world leading producer of PSLs from agro-industrial and post-consumer waste. Natural by-products of citrus fruits, grapes, cherries, lavender, corn, barley, olives, coffee, kiwi fruits, hazelnuts and almonds are micronized and then combined with virgin tree and recycled fibers together with other necessary additives to produce Crush paper. In this research thee PSLs from the Crush series, citrus fruits, grapes, and barley, were selected. After the production of citrus juice there is 60 % leftover in the form of citrus mash. Depectinized mash is further micronized and reused for the production of Crush Citrus facestock paper (Avery Dennison Corporation, 2021).

Table 1: Properties of the used PSLs given by the manufacturer (Avery Dennison Corporation, 2021)

Sample name	Fasson ® rCRUSH CITRUS FSC S2030-BG45WH FSC	Fasson ® rCRUSH BARLEY FSC S2030-BG45WH FSC	Fasson ® rCRUSH GRAPE FSC S2047N-BG45WH IMP FSC
Designation	C	B	G
Basis weight ISO 536/g·m² (facestock)	100	90	90
Basis weight ISO 536/g·m² (liner)	70	70	70
Caliper ISO 534/ µm (facestock)	130	110	114
Caliper ISO 534/ µm (liner)	61	61	61

Similar production is for barley based facestock. Following the use of malted barley in brewing and whiskey production the by-product of the fermentation process (exhausted barley malt) is micronized and reused for the production of Crush Barley facestock (Avery Dennison Corporation, 2021). Similarly, the residue from the grape pressing process (marc) after the distillation process is dried further micronized. The resulting flour is then mixed with water and natural fibres to produce a unique ecological paper: Crush Grape (Avery Dennison Corporation, 2021).
Favini's sustainable Crush paper is paired with an Avery Dennison adhesive to match the application. Adhesives are chosen to maintain the integrity of the facestock, including the tactility, visual aesthetic, and printability, while ensuring the finished pressure-sensitive label can withstand the demands of production, use, and recyclability.

2.2 Soil burial test under aerobic conditions

Biodegradation was performed by usage of soil burial test under aerobic conditions. Laboratory soil burial experiments were conducted at room temperature (25±2) °C by placing the unprinted label paper substrates size 30 x 30 mm (Vukoje et al., 2017). Facestock and adhesive (delaminated from the liner) were placed horizontally in field soils in 2L laboratory glass containers, orientated adhesive down. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. Substrates were buried for a period of 2, 4, 7, 10 and 13 days. Sample's fluorescence intensity was measured before and after incubation in the soil containers. The samples were dug out after designated time, rinsed with distilled water to remove soil particles from the surface, air dried and measured.

2.3 Visual evaluation

Visual evaluation process can be used as a first indicator of degradation process, when visible changes of the surface structure, for example: defragmentation, change in colour and/or formation etc. can be seen. However, these changes without usage of other quantifying methods do not prove the existence of degradation process in terms of microbial activity (Shah et al., 2008; Vukoje et al., 2017). Photos of paper samples were taken from the containers in sampling times in order to visually evaluate the facestock degradation over time. Samples were visually observed in lighting booth X-rite Judge II for the purpose of evaluation of structural, colour and surface change of the tested facestock and the presence of optical brighteners, as well as their performance after soil burial test under aerobic conditions. Two types of illuminants, D50 and UV, were used for the observation of the samples. The Canon EOS D450 camera with 50 mm, 1/30 s at f5.6, ISO 400 (Japan) was used for the imaging of the samples.

2.4 Fluorescence spectroscopy

Fluorescence spectroscopy measurements were done using USB 2000+ spectrometer (Ocean Optics), 30 mm integrating sphere with (8:di) geometry, and 365 nm LED light source (Ocean Insight-LSM Series). Stability of the excitation light was obtained using smart controller. Fluorescence intensity data were processed with OcenView software and the results will be presented in the spectral range between 350 and 600 nm. The method proved to be reliable in our previous research (Vukoje et al., 2021).

3. RESULTS

3.1. Visual evaluation

Figure 1 shows the images used for visual evaluation of PSL facestocks before and after soil burial test. All samples show differences in colour and structure change, especially after 13 days of biodegradation, which proves the presence of significant degradation process. PSL samples based on barley and citrus residue show similar biodegradation result after 13 days of aerobic exposure, while grape based PSL (facestock and adhesive) dissolve almost completely.
Regarding the images obtained under UV light, it is evident that grape based PSL facestock has the highest ratio of FWA which disintegrates proportionately and symmetrically during exposure to the burial testing. Citrus based PSL shows the lowest concentration of FWA based on the visual evaluation.

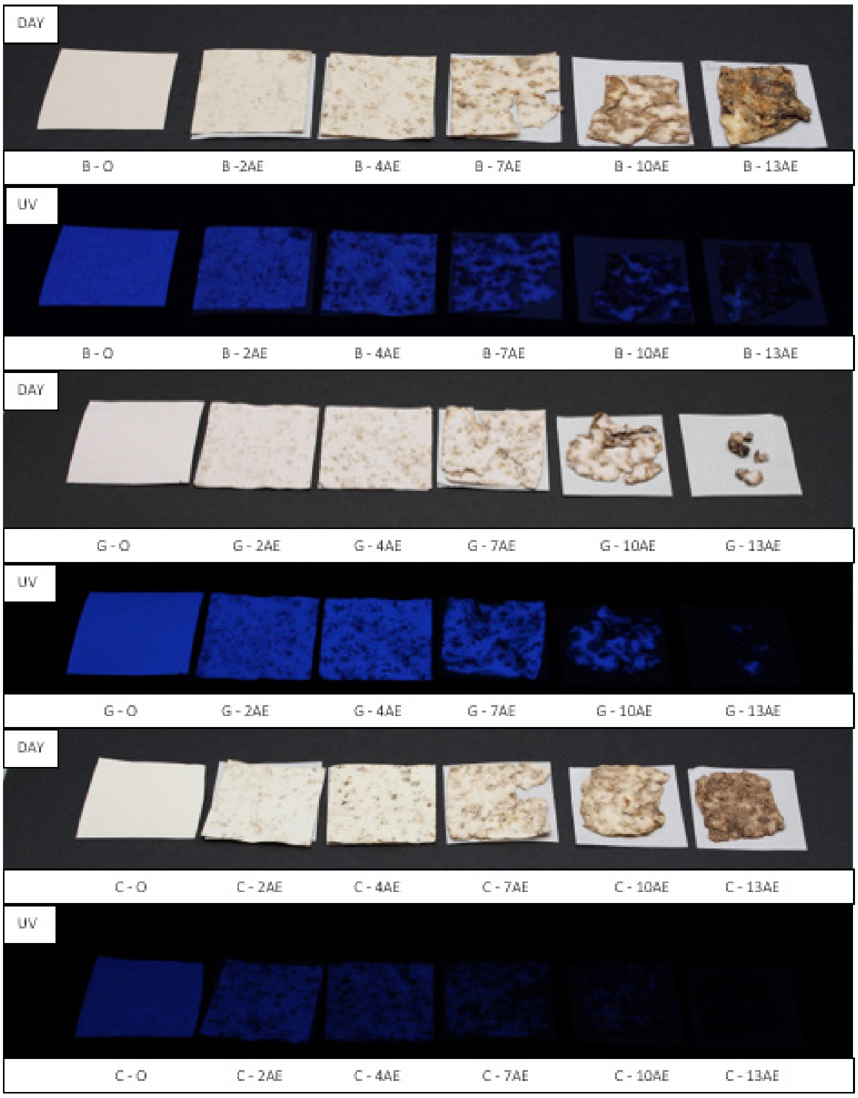

Figure 1: Visual evaluation of fibre based pressure sensitive facestock under illuminant D50 (DAY) and illuminant UV (UV); original before and after 2, 4, 7, 10, 13 days of soil burial test

3.2. Fluorescence spectroscopy

Fluorescent whitening agents used in paper industry are active in the area from 390 to 600 nm, while they absorb light in the UV part of the spectrum (Mercer, 1990; Shakespeare & Shakespeare, 2009). Fluorescence intensity in the excitation area can give significant information regarding the activity of FWAs, namely inactive FWAs reflect high amount of incident light. Excitation fluorescence intensity is much higher than the emission fluorescence intensity due to numerous interactions of light with the different types of PSL facestock constituents. Processed fluorescence intensity spectra of all samples before and after burial test in the period of 2, 4, 7, 10 and 13 days is showed in Figures 1-3. Fluorescence intensity emission spectra of all PSL facestocks made from agro-industrial and post-consumer waste correspond to the emission of the OBAs in the blue part of the spectrum with two characteristic peaks at 441 nm and 478 nm for all PSL facestocks and additionally peak at 414 nm for citrus and barley based PSL facestock (Coppel, 2010; Coppel, 2013; Pauler, 2012; Vukoje et al., 2021). Amount of FWAs in the any paper, including PSL facestock is proportional to the area of fluorescence intensity summed over all wavelengths in the visible part of the spectrum (Zwinkels et al., 2014). From the look of the emission fluorescence intensity diagram, more precisely the area under the curve, of all original samples it is obvious that different PSL facestocks have different ratios of fluorescence whitening agents which highly influences the proportion of absorbed light at excitation wavelength. Thus, fluorescence intensity of grape based PSL facestock (Figure 2) shows the highest absorption level at 365 nm, while for citrus (Figure 1) and barley (Figure 3) based PSL facestock this value is three, i.e. 3.5 times lower.

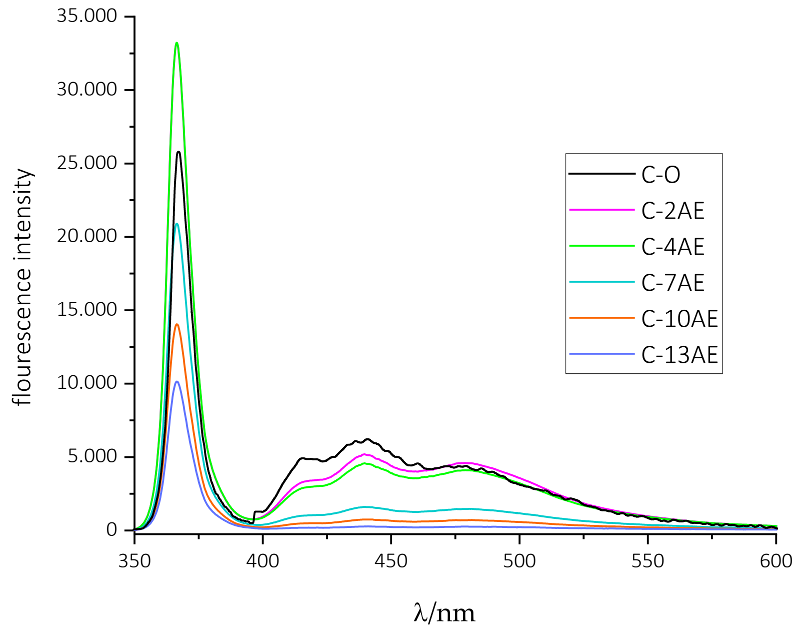

Figure 2: Fluorescence intensity spectra of original citrus fibre based PSL samples and citrus fibre based PSL samples after 2, 4, 7, 10, 13 days of soil burial test

After two days of burial there are no major differences in the mentioned values. After 4 days of burial test the absorption values decrease for citrus and grape based PSL facestocks, while the absorption for barley slightly increases.

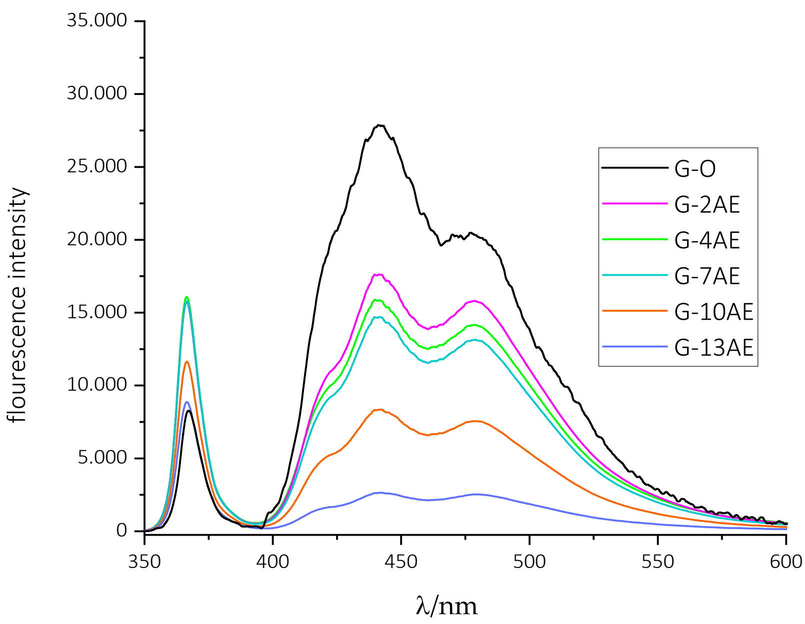

Figure 3: Fluorescence intensity spectra of original grape fibre based PSL samples and grape fibre based PSL samples after 2, 4, 7, 10, 13 days of soil burial test

Seven days burial test stands out as a turning point where all three PSL facestocks show the increase in absorption at 365 nm wavelength, which follows same regularity for next two intervals, 10 days, and thirteen days. After 13 days of aerobic degradation all samples have similar absorption values at the excitation wavelength.

Emission part of the spectrum, 400-600 nm, can explain the behaviour of the incident light. Fluorescence intensity spectra of citrus based PSL facestock decreases in the are between 400 and 450 nm, while the peek at 471 nm remains unchanged after first two intervals of burial test. Significant decrease in the emission intensity spectrum can be seen after seven days of burial tests, which is manifested by the loss of characteristic bands and the general disappearance of the emission spectrum (Figure 1). This behaviour corresponds to the absorption result in the emission part of the spectrum Namely, burial test, cause decomposition of florescence whitening agents within the PSL facestock among ardor components. Decomposition of FWAs causes less active material for absorbing UV light. After seven days of decomposition most of the FWAs were decomposed making room for other PSL facestock ingredients to absorb UV light.

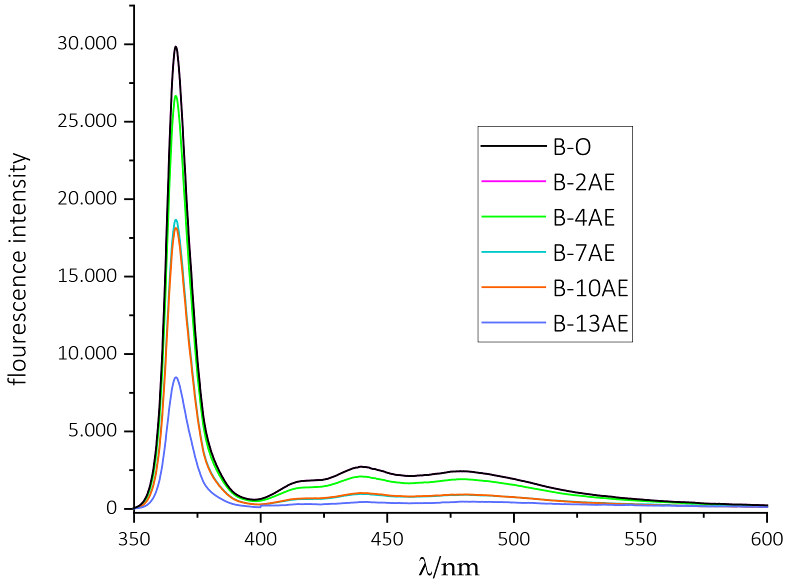

Figure 4: Fluorescence intensity spectra of original barley fibre based PSL samples and barley fibre based PSL samples after 2, 4, 7, 10, 13 days of soil burial test

Grape based PSL facestock has the highest level of FWAs (Figure 2). First three cycles of burial test reduced the fluorescence intensity in the emission part of the spectrum, but the characteristic peaks remained at the same place (Figure 2). Significant change can be seen after ten days of aerobic degradation where the overall spectrum dropped to 30% of its initial value. Likewise, broadening of peaks at 441 nm and 491 nm is observed. Last burial test interval, thirteen days resulted in significant decomposition of FWAs which is confirmed by the flattening of the spectrum, i.e. further expansion of the characteristic bands. Again, fluorescence intensity spectra in the emission part of the spectrum correspond to the excitation part values. With the more pronounced decomposition of FWAs in PSL facestock absorption of the UV light decreases. After that, due to the further decomposition of the FWAs and the papers surface structure, the incident UV light is significantly scattered and absorbed in the interior of the paper.

For barley we can say that it has the lowest level of FWA according to the appearance of the fluorescence intensity spectrum in the visible part of the EM (Figure 3). With exposure of samples to aerobic degradation the fluorescence intensity spectrum tends towards zero. In order for FWAs to be effective they have to be combined with non-lignin pulp since lignin is known for it's high absorbance in the UV part of the spectrum, same as FWA (Pauler, 2012). It was found that grape fibres residue from wine making processes contains as high as 30 % cellulose, 21 % hemicellulose and 17 % lignin (Amedola et al., 2012; Prozil et al., 2012). At the same time, citrus fibres collected from juice production contains significantly lower ratios of cellulose (16 %) and hemicellulose (10 %) (Lundberg et al., 2014). Barely fibres resulting from whiskey production and brewing beer contain 17% cellulose and 28% lignin (Mussatto et al., 2006). Due to this, and from the fluorescence spectroscopy measurement, it can be concluded that most of the lignin from the grape marc after the distillation process is chemically removed to enable FWAs.

4. CONCLUSION

High growth of self-adhesive labels market is mainly a result of increase rapid urbanization, demand for pharmaceutical supplies, increasing consumer awareness, and growth of the e-commerce industry (Research and Markets, 2022).
When using alternative fibre sources, the paper making process in its core remains the same, as for other kinds of paper, but less energy is used and no additional chemicals. In the production of papers utilized in this research, manufacturers state that 20% drop in CO_2 emission is achieved in comparison to standard label papers.
Sustainable fibre-based products have their usage status proven and justified by everyday greater demand, increasing consumption and constant product development.
In this research, the rate of decomposition of FWAs in three types of pressure sensitive labels made from agro-industrial and post-consumer waste (grape march, citrus juice residue and exhausted barley malt) by means of burial testing were examined. Samples were buried for periods of 2, 4, 7, 10 and 13 days. The presence of FWAs in the substrate was tracked by means of fluorescence spectroscopy. Critical point, regarding the FWA activity is 7 days, at which point there was a major drop in fluorescence intensity for all samples. After thirteen days of exposure to aerobic soil testing, FWAs are completely decomposed. Further research will evaluate the decomposition rate of other substrate characteristics by means of weight loss, FT-IR spectroscopy, scanning electron microscopy and so on.
Also, subsequent research will be dedicated to biodegradation processes of alternative fibre labels applied on various types of cardboard, both in unprinted and printed versions, simulating real market usage and today less appropriate, but unfortunately realistic products' end of life, especially in our region.

5. LITERATURE

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