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Natural weathering of composites developed from cellulose waste and post-consumer paper

Intemperismo natural de compósitos desenvolvidos com o uso de amido termoplástico com resíduo de celulose e papel pós-consumo

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ABSTRACT

The development of materials that are highly degradable at the end of their life cycle helps reduce the volume of solid waste disposed of in landfills. This study aimed to produce composites from cellulose and paper residues as reinforcing fibers and from thermoplastic starch (TPS) as a matrix to analyze the effect of exposure to natural weathering in the environments of two Universities, one in Brazil (Universidade Feevale) and the other in Finland (HAMK). During the test period, the season in Brazil was summer, with high temperatures and solar radiation; in Finland, the season was winter, with negative temperatures, high air humidity, and snowfall. The materials were prepared using the tape-casting method and characterized by Dynamic Mechanical Analysis (DMA) and Thermogravimetric Analysis (TGA), having been subjected to the weather for 0, 28, and 42 days at Universidade Feevale and HAMK. At the end of each period, they were characterized by Scanning Electron Microscopy (SEM) and photographs. The results showed that the thermal stability of the composites was better compared to TPS and cellulose, and superior mechanical properties were shown in the cellulose-based composite. Thus, heterogeneous mixtures emerged from the addition of fibers to the polymer matrix. After the environmental exposure, the visualization of the micrographs and photographs indicated that the samples exposed in the two environments were brittle, shrunken, yellowed, and cracked. It was also verified that the samples exposed at Universidade Feevale suffered greater environmental degradation, and the incorporation of fibers in the composites delayed this effect at the two study sites.

Keywords: environmental degradation; solid waste; tape-casting; thermoplastic starch.

RESUMO

O desenvolvimento de materiais facilmente degradáveis ao fim da vida útil auxilia na redução do volume de resíduos sólidos dispostos nos aterros sanitários. Este estudo teve como objetivo produzir compósitos com o uso de resíduos de celulose e papel como fibras de reforço e amido termoplástico (TPS) como matriz, de modo a analisar o efeito da exposição ao intemperismo natural em ambientes distintos de duas universidades no Brasil (Universidade Feevale) e na Finlândia (Häme University of Applied Sciences — HAMK). No período de realização do ensaio, a estação no Brasil era verão, com elevadas temperaturas e radiação solar; já na Finlândia a estação era inverno, com temperaturas negativas, elevada umidade do ar e incidência de neve. Os materiais foram elaborados por meio do método *tape-casting* e caracterizados por análise dinâmico-mecânica (DMA) e análise termogravimétrica (TGA), tendo sido submetidos às intempéries por 0, 28 e 42 dias na Universidade Feevale e na HAMK e, ao fim de cada período, foram caracterizados por microscopia eletrônica de varredura (MEV) e fotografias. Os resultados mostraram que a estabilidade térmica dos compósitos foi melhor em comparação a seus componentes individuais, e propriedades mecânicas superiores foram apresentadas pelo compósito à base de celulose. Assim, misturas heterogêneas surgiram com a adição de fibras à matriz polimérica. Após a exposição ambiental, a visualização das micrografias e fotografias revelou que as amostras expostas nos dois ambientes ficaram quebradiças, encolhidas, amareladas e apresentaram fissuras. Verificou-se, também, que as amostras expostas na Universidade Feevale sofreram maior degradação ambiental, e a incorporação das fibras nos compósitos retardou esse efeito nos dois pontos de estudo.

Palavras-chave: degradação ambiental; resíduos sólidos; *tape-casting*; amido termoplástico.

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Introduction

Recently, the rise in agricultural production resulted in increased generation of associated waste (Santos et al., 2021). Even before this situation, environmental concerns have been increasing over the last decade, which, in turn, generates discussion in the national and international Communities (Brasil, 2022). To prevent environmental impacts from waste, it is necessary to perform an integrated approach and adopt an effective system that includes all stages of waste management, from its origin to its final destination (Mersoni and Reichert, 2017). In this way, integrated solid waste management aims to achieve sustainability on the premises of environmental protection, economic development, and health promotion (Olivo et al., 2021).

In Brazil, based on the national solid waste policy (Política Nacional de Resíduos Sólidos, Law No. 12.305/2010), objectives were established that define integrated and environmentally-adequate management of solid waste in the country: non-generation, reduction, reuse, recycling, solid waste treatment, final waste disposal, clean technologies to minimize environmental impact, and sustainable standards for the production and consumption of services and goods, among others. Furthermore, this law considers that waste segregation and reverse logistics are important instruments for the implementation of shared responsibility for the product life cycle (Brasil, 2010).

Regarding the pulp and paper industry specifically, a statistics report from the Brazilian Pulp and Paper Association (Bracelpa, 2013) shows that in 2011 11,324 tons of short fiber bleached pulp and 2,745 tons of printing and writing paper were produced in Brazil. In the last three decades, intensive campaigns have sought to promote paper recycling, which could reduce pollution, promote the conservation of landfill spaces, and contribute to tree preservation, which is justified due to the generation of positive externalities, such as direct amenities, soil conservation, and carbon sequestration (Tatouchoup, 2016). In this way, data from the Brazilian Association of Public Cleaning and Special Waste Companies (ABRELPE, 2021) show that the total volume of recovered paper in 2021 was 190,822 tons (47,6%), with the potential to reduce 22,827 tons of equivalent CO_2 (13.1%) due to recovered paper.

In addition, many countries show an increase in paper recovery rate, an index that estimates collected scrap composition compared to apparent paper consumption, as in Canada, for example, which shows a rise from 11 (1990) to 24% (2012) (Tatouchoup, 2016; ANAP, 2021). In Brazil, data from 2019 shows that the printing and writing paper recovery rate was 35% of the total production (ANAP, 2021).

Considering the paper waste generated and the increased recovery rate in several countries, it is understood that it is possible to add value to waste from the resulting scrap of the production process of bleached pulp, as well from post-consumer office paper to develop an innovative material based on these resources that comes from forest fibers and is easily degraded in natural environments due to their short life cycle. In pratice, the reuse of pulp and paper waste as raw materials for the production of new inputs is associated with the circular economy concept, which proposes a deep transformation that reduces the impact of human activities on the environment (Machado et al., 2020).

Fiber waste can be used to prepare biodegradable composites, allied to the implementation of improvements in solid waste management, which is essential to reduce volumes that otherwise would be disposed of (Rivera et al., 2016). To improve the mechanical properties of thermoplastic starch (TPS) films, plant fibers (lignocellulosic fibers, cellulose, bark), which have low cost and high availability, are added to act as ecological reinforcement in composite materials when mixed with TPS matrix (Koohestani et al., 2018; Kumar et al., 2018; Chueangchayaphan et al., 2019). In general, formulation, production, and fiber/matrix compatibility are factors that affect the damping properties and microstructure of composites (Xie et al., 2018).

Starch is one of the most studied and promising agricultural resources for the production of biodegradable polymers as a matrix for application in biodegradable composites (Rosa et al., 2009; Liu et al., 2020). Adding a plasticizer to starch, such as glycerol, sorbitol, and propylene glycol, for example, is critical because starch has a decomposition temperature that is below its melting point. High temperatures and shear during processing disruptures starch granules and result in a flexible and continuous polymer matrix. The choice of the plasticizer, in turn, changes properties, and plasticizer use is a rule when starch is considered to be the polymeric matrix (Dai et al., 2009; Volpe et al., 2018). In this way, TPS is the denomination associated with the processable plasticized starch that is obtained (Kahvand and Fasihi, 2020).

Concerning the degradation processes of biodegradable composites, the most known forms are biodegradation and degradation by weathering. Within the scope of sustainable development, new materials are designed to have greater biodegradability properties, since biodegradation occurs in three stages (biodeterioration, biofragmentation, and assimilation), without neglecting abiotic factors (Lucas et al., 2008).

Environmental exposure is another way of investigating the photochemical resistance of polymers, with several environmental factors being considered, such as ultraviolet radiation, visible light, temperature, humidity, and weather since such factors affect the chemical structure of the polymer to cause degradation. It is noteworthy that the intensity of these elements in the natural environment significantly changes according to the year season, time of the day, and place of exposure, making natural exposures unique and often unreproducible (Fechine et al., 2006). Observations such as color change, formation of cracks and pores, surface roughness, and defragmentation are possible modifications to be seen in samples of materials subjected to weathering (Tomacheski et al., 2018). In general, both forms of degradation decrease the performance of cellulose fibers-reinforced composites, inducing changes in physical and mechanical properties (Dungani et al., 2019). Table 1 shows some of the current research regarding the evaluation of natural weathering effects on different materials.

Table 1 – State-of-the-art research on materials exposed to natural weathering.

Authors	Objectives	Conclusions
Fuentes-Talavera et al. (2015)	Evaluate the natural weathering of nine formulations of polypropylene composites with three proportions and sizes of pine wood particles, analyzing the change in clarity, surface morphology, and impact resistance to identify which formulations perform better in outdoor products.	The photodegradation of the wood particles resulted in the modification of the clarity of the polypropylene-wood composites, considering a higher proportion and smaller particle size. The increase from 40 to 50% wood in the formulations was proportional to the increase of microcracks and the greater effect of weathering on the composites, which had a lower loss of weathering impact resistance compared to pure polypropylene.
Pereira et al. (2017)	Analyze the calorimetric properties of OSB panels after exposure to natural and artificial weathering to establish a preliminary correlation of the effect caused on the physical and mechanical properties of the panels.	The effect of exposure to natural weathering was more aggressive, which resulted in significant degradation of the surface, evidenced by high variation in coloration and reduction in the modulus of rupture.
Lima et al. (2020)	Evaluate the changes in the properties of polypropylene/bamboo fiber (PP/BF) composite and the influence of the use of coupling agent (CA) after natural aging for one year.	All composites exposed to weathering showed a reduction in their properties, but the use of CA promoted greater stability in the mechanical, physical, and thermal properties; and the results for the use of CA of natural origin were similar to the ones for synthetic origin. Thus, it was concluded that the use of citric acid as CA can promote greater interaction between the fibers and the polymer.
Moreno et al. (2022)	Study the behavior of unsorted wood of Eucalyptus globulus when exposed to natural weathering for one year in the city of La Plata (Argentina). We sought to evaluate the color change and some effects, relating to wood moisture and climate variables.	There were significant changes in the surface appearance of Eucalyptus globulus wood, especially from the initial stages up to 150 days of the study period. The wood showed grayish color, higher level of cracking, stains, and rotting. The colorimeter parameters were negatively affected by monthly average temperature and dew temperature, while they were not significantly influenced by solar radiation and precipitation. The presence of cracks was correlated with moisture content, but there was no correlation with color parameters. The incidence of deterioration evaluated by the presence of chromogenic or xylophagous fungi was very low (6%), depending on the moisture content.

It is crucial to understand the degradation behavior of new polymers in a wide variety of conditions, coming from formulations with different additives. Changes in specific properties need to be identified, as well their causes in function of the variation of the accumulated environmental parameters that accelerate changes in the material's characteristics. Polymer estimated lifetime submitted to different environments is essential to material applications (Laycock et al., 2017).

Based on the above-mentioned factors, this study aimed to investigate the natural weathering of reuse of cellulose and office paper waste as reinforcement fibers in the composition of TPS biodegradable composites placed in two different sites, one in Brazil (Universidade Feevale) and the other in Finland (HAMK — *Häme University of Applied Sciences*).

The experiment

composite materials were prepared from commercially available corn starch, glycerin, cellulose waste, office paper waste, and deionized water. Cellulose and office paper waste were crushed before use.

Corn starch was dried at 90°C while cellulose waste and office paper waste were dried at 60°C. All drying procedures were performed in a circulating air oven and kept in desiccators. Reference TPS was produced from 14 g of starch (70%) with 6 g of glycerin (30%) dissolved in 370 mL of deionized water. The two composites in the study, also produced from dissolution in 370 mL of deionized water, were from 9.8 g of starch, 4.2 g of glycerin (70% polymeric matrix), and 6 g of fibers (30% fiber). The one made from cellulose waste was named TPS/CW30 and the one from office paper waste TPS/PW30. Table 2 indicates the composition of the samples produced for this study.

All solutions were prepared with starch and glycerin dissolution in a 70°C thermostatic bath (Fisatom 572S model) for 15 minutes under mechanical stirring at 50 rpm (Fisatom, 715 model). Composite samples were produced from cellulose and paper waste was added at the final five minutes of the mixture. In this research, we used a temperature of 70°C for the production of TPS films, following several studies that used similar parameters, such as those by Famá et al. (2006), Bertuzzi et al. (2007), Osés et al. (2009), and Moraes et al. (2013).

Film samples were cast from spreading solutions over Teflon® plates with a spatula, based on a tape-casting method (Moraes et al., 2013). Water evaporation was conducted over 48 h, successfully forming TPS films and their composites. Figure 1 schematically shows the preparation method of composites from cellulose waste (TPS/CW30) and from paper waste (TPS/PW30).

Film samples from TPS and its composites were then evaluated concerning degradation by natural weathering according to Switzerland standards (ISO, 2009a; 2009b). Two sites were chosen to perform the degradation evaluation, one in Brazil (Universidade Feevale) and another one in Finland (*Häme University of Applied Sciences* HAMK). Films placed over a 45° angled panel were exposed to natural weathering for six weeks (42 days). Two samples of each film were taken from Universidade Feevale and HAMK panels after four weeks (28 days) and two additional samples of each film were taken after six weeks (42 days).

The criterion for determining the maximum time to perform the natural weathering test was estimated based on the formulation of the composites produced in this study, which contain 70% of TPS as a polymer matrix. Since synthetic polymers require longer weather exposure to study the effect of environmental degradation on these materials, when it comes to biodegradable polymers, this time becomes considerably shorter. Rodrigues et al. (2006) produced blends with low-density polyethylene and up to 2% mango starch, which were subjected to natural degradation. The authors concluded that the starch content, as well as the exposure time, correlated with the formation of voids in the polymer matrix. Thus, the degradation of starch improves the fragmentation of blends in short weathering times, considering that the degradation was initiated between 30 and 60 days of exposure to weather. In this research, in contrast, as the materials are mostly composed of TPS, removing the samples after four and six weeks is considered satisfactory.

Figure 2 shows samples on the panels placed to perform the natural weathering test at Universidade Feevale, at the geographic coordinates of 29°40'10.2"S 51°07'15.4"W.

Table 2 – Compositions of the samples produced in this work.

Component / Sample code	Thermoplastic starch (TPS) (%)	Cellulose waste (%)	Paper waste (%)
TPS	100	0	0
TPS/CW30	70	30	0
TPS/PW30	70	0	30

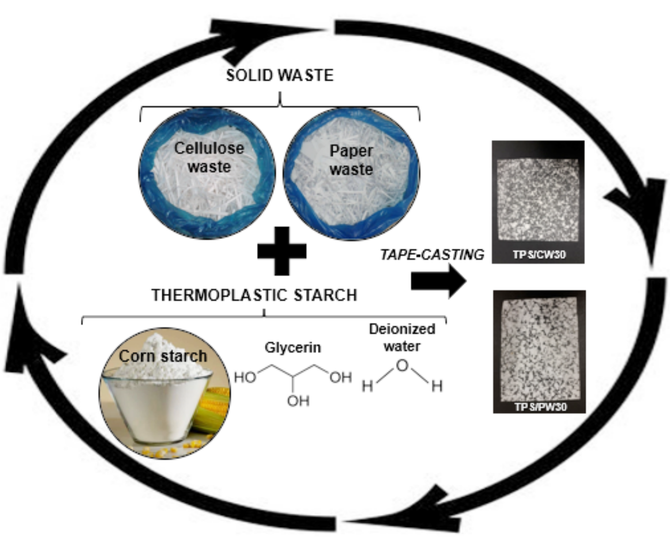


Figure 1 – Obtaining samples of TPS/CW30 and TPS/PW30.

Figure 3 shows samples on the panels placed to perform the natural weathering test at *Häme University of Applied Sciences* (HAMK), at the geographic coordinates of 60°58'35,9"N 24°28'34,8"W.

Table 3 shows the weather conditions at both sites where the natural weathering test was performed.

In Brazil, the current season during the period of study was summer, the average wind speed was 4 km/h and the amount of rain was about 165 mm (data measured at Universidade Feevale by Wireless Vantage Pro 2 apparatus from Davis Instruments). In Finland, the current season was winter, the average solar irradiation was 667 W/m, the average precipitation was 0.86 mm, and the accumulated snow reached 15 cm (data from Hämeenlinna station of the Finnish Meteorological Institute).

Thermogravimetric analysis was used to measure mass changes in the samples in a Perkin Elmer STA 6000 from 25 up to 1,000°C, at a heating rate of 20°C/min under 20 mL/min nitrogen atmosphere.

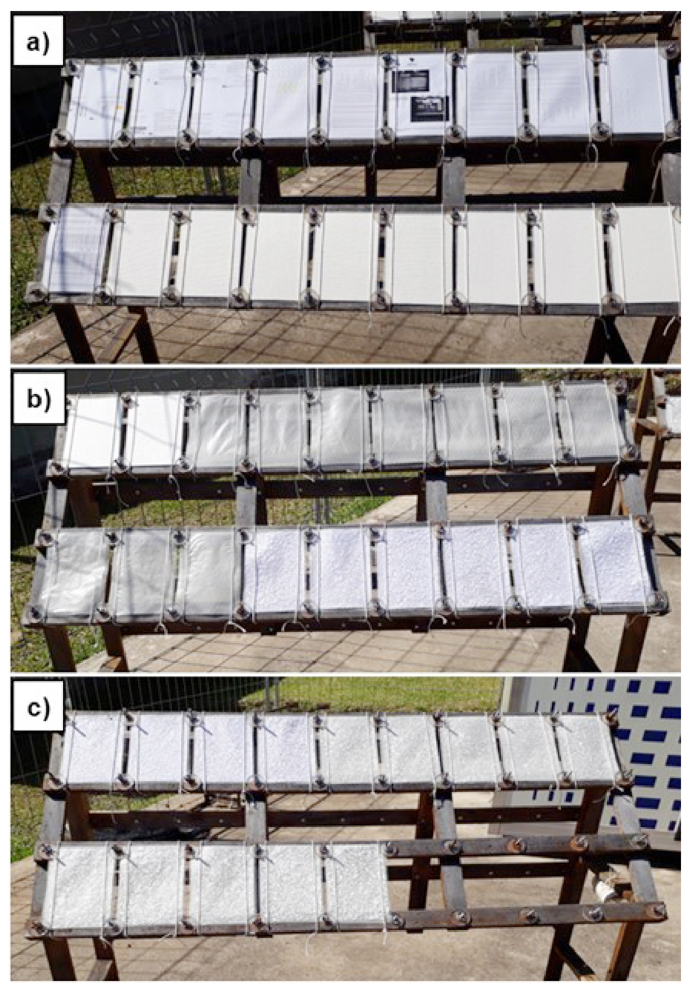
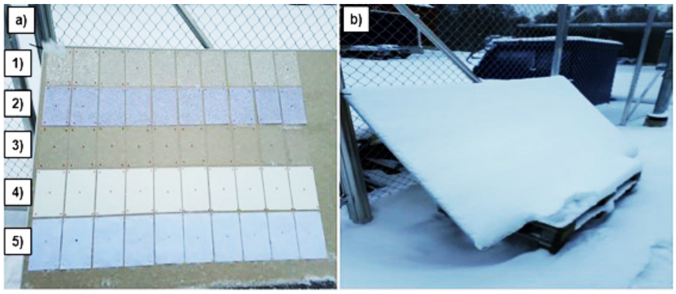


Figure 2 – Outdoor stations at Universidade Feevale with samples of (A) Paper and cellulose; (B) Cellulose, TPS, and TPS/PW30; (C) TPS/PW30 and TPS/CW30.



1: TPS/CW30; 2: TPS/PW30; 3: TPS; 4: cellulose waste; 5: paper waste.
Figure 3 – Outdoor station in HAMK with a two-point view: (A) Outdoor station image on the first day of environmental exposure; (B) Outdoor station after 42 days of environmental exposure.

Table 3 – Weather conditions at Universidade Feevale (Novo Hamburgo, Brazil) and HAMK (Hämeenlinna, Finland) during the period of exposure to inclement weather.

Place	Minimum temperature (°C)	Maximum temperature (°C)	Minimum relative humidity (%)	Maximum relative humidity (%)
Novo Hamburgo	30	31	65	73
Hämeenlinna	-11	-4	75	96

Tensile strength was measured in a Mettler Toledo, DMA 1 STAR System, operating in film tension mode at a tension rate of 0,1 N/min from 0 to 10 Nat constant temperature of 20°C.

Morphology was obtained from gold sputtering samples in a JSM-6510LV JEOL scanning electron microscope operating at 5 kV voltage, applying 500x and 1,000x magnifications. Photographic images from a Samsung Galaxy J5 Prime mobile phone were used to verify the color, transparency, roughness, and shine of the samples. Comparisons were made based on the photographic images of the samples before and after 28 and 42 days of natural weathering.

Results and Discussion

The thermal stability of the reference TPS and its composites, without weathering, are shown in Figure 4.

The degradation temperature and mass loss of each sample are shown in Table 4.

Data from Figure 4 and Table 3 show that TPS presents three steps of thermal degradation, being the first of about 10% in the range of 27-103°C associated with water evaporation; the second step of about 8% in the range of 103-234°C associated with plasticizer degradation. These two thermal events are related to low-molecular-weight components (Genovese et al., 2018; Volpe et al., 2018; Fazeli et al., 2019). Glycerin degradation temperature was reported as about 198°C thus being present in the second step (Corradini et al., 2009). The third step of thermal degradation was in the 234-304 C range, corresponding to a greater intensity in sample degradation, with about 68% of mass loss in the TPS and associated with starch degradation (Genovese et al., 2018; Ghanbari et al., 2018a; Zain et al., 2018).

From Table 3, it is possible to see that the composites show the same thermal events verified for TPS. Therefore, the first step is related to sample dehydration, and, remarkably, the composites show this step at about 80°C (7% mass loss), which is a lower temperature than TPS and a higher temperature than fiber waste. Such behavior could be related to the drying procedure of fiber waste (Gómez et al., 2007). Related to the second step, decomposition temperatures were 216 and 223°C, corresponding to 12 and 16% of mass loss for TPS/CW30 and TPS/PW30, respectively. In this step, TPS and paper plasticizers were decomposed, which was not observed in the cellulose waste. The step of higher mass loss, verified in all samples, indicates the maximum processing temperature, being attributed to starch and cellulose depolymerization (Ghanbari et al., 2018a; Fazeli et al., 2019).

The experimental results from this study indicated that the maximum degradation temperatures were 360°C (cellulose waste), 352°C (paper waste), 304°C (TPS), 323°C (TPS/CW30), and 322°C (TPS/PW30). From these data, it is possible to see that the composites have a degradation temperature in the intermediate range of their constituents, being lower than fiber waste and higher than TPS matrix, which in turn indicates an improvement in the thermal stability of the composites due to new hydrogen bonds of natural polymers in the samples. Similarly, the introduction of fibers has been shown to improve the thermal stability of materials (Behera et al., 2018; Fazeli et al., 2019).

The mechanical properties of the samples before weathering are shown in Figure 5.

From Figure 5, it is possible to note that TPS shows higher deformation and lower tensile strength among the studied samples. Cellulose shows lower deformation and higher tensile strength, which emphasizes its potential as a reinforcing material. Likewise, paper waste showed a decrease in deformation; however, its tensile strength was similar to TPS. Individual mechanical performance of materials is essential for analyzing the performance of composites. Thus, TPS/PW30 showed lower elongation and tensile strength compared to TPS. In the case of TPS/CW30, the introduction of cellulose fibers increased tensile strength when compared to TPS. Such behavior indicated that a synergistic interaction between fibers and matrix results in composites being capable of withstanding higher mechanical loads than their constituents (Ghanbari et al., 2018b).

The SEM images of TPS samples before and after natural weathering exposure at Universidade Feevale and HAMK for 28 and 42 days are shown in Figure 6. TPS before weathering shows partial rupture of starch granules due to processing, resulting in a uniform plasticized film containing swollen particles. The starch/solvent ratio directly affects the gelation process, taking into account moisture absorption, granules swelling, and crystallinity reduction (Zhong et al., 2009).

Comparing TPS films before and after natural weathering, it is possible to see the presence of spread particles over the polymeric matrix, which could indicate the presence of particulate materials, being at a higher amount in the exposed surfaces at Universidade Feevale.

For the environmental management of a city, knowledge of air quality is very important, since the sources of pollutants can be fixed or mobile. Fixed sources are given by polluting activities such as industries and businesses, while mobile sources come from vehicles on city roads, which have the potential to harm the environment and people's health (Krüger et al., 2021). In the two exposure sites of this research, both at Universidade Feevale and HAMK, the panels were fixed in isolated areas, but with buildings and intense vehicular traffic around them, which may have contributed to negatively affecting the air quality in both cases, a fact that corroborates the deposition of particulate matter in the samples.

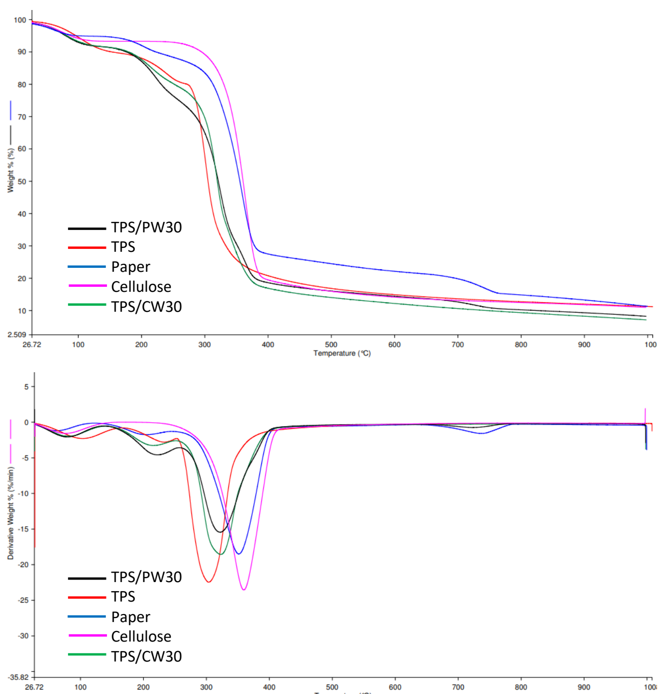


Figure 4 – TPS/PW30, TPS, Paper, Cellulose, and TPS/CW30 (A) TG and (B) DTG (no weathering).

Regarding air pollution in Finland, it is estimated to be linked to one of the main environmental health risks in the country. Researchers quantified the impacts of ozone (O_3) and carbon dioxide (NO_3) particles in the year 2015 to analyze the related uncertainties using a high spatial resolution chemical transport model for the exposures, and they were fitted to the observed concentrations. Air pollution was found to cause a burden of 34,800 disability-adjusted life years, given that for the disease burden, fine particles were the main contributor (74%), also according to previous works of the literature. The attributable burden was denominated by mortality, resulting in 32,900 years of life lost (95%). The impacts were distinct among the population age groups, considering that the burden was higher for the adult population over 30 years (98%) due to the dominant role of mortality impacts (Lehtomäki et al., 2018).

In addition, little information exists on ambient fine particulate matter (PM2.5) concentrations in residential areas where wood burning is done for recreational purposes and secondary heating. Researchers collected outdoor PM2.5 samples in one central location and in domestic outdoor locations from a panel of 29 residents in a suburb of Kuopio, Finland. They identified that wood combustion significantly affects air quality also in areas where it is not the primary heating source. In epidemiological panel studies, central site measurements may not sufficiently capture the daily variation in PM2.5 exposure from local wood combustion (Yli-Tuomi et al., 2015).

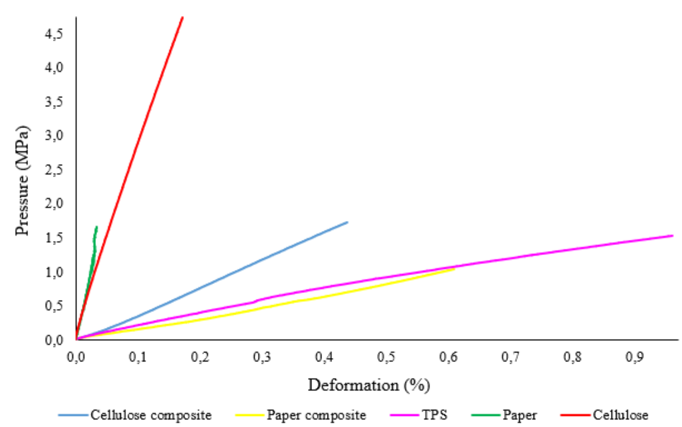


Figure 5 – Stress x deformation curves of TPS/CW30, TPS/PW30, TPS, paper, and cellulose (no weathering).

Table 4 – Temperature ranges and mass loss in the composites and their constituents.

Sample	1st T (°C)	1st ML (%)	2nd T (°C)	2nd ML (%)	3rd T (°C)	3rd ML (%)	4th T (°C)	4th ML (%)
Cellulose	76	6	-	-	360	80	-	-
Paper	62	4	205	6	352	62	737	6
TPS	103	10	234	8	304	68	-	-
TPS/CW30	82	7	216	12	323	70	-	-
TPS/PW30	81	7	223	16	322	59	724	4

T: temperature; ML: mass loss up to a given degradation temperature.

Next, Figure 7 presents the images obtained by SEM of the pulp and paper samples without environmental exposure and with exposure after 28 and 42 days at Universidade Feevale and HAMK. Pulp and paper waste has a complex morphology, which is characterized by an interwoven network of non-uniform diameters containing voids. Moreover, the system itself is not homogeneous (De Spirito et al., 2008). The same morphological pattern is shown in the images of unprocessed pulp and paper fibers, which show an average diameter of approximately 12 µm.

Regarding the pulp and paper morphologies after natural weathering, it is estimated that fiber degradation occurred due to environmental conditions, and this result became clearer when analyzing the morphologies of the materials that were exposed. In highlight, after 28 days of pulp weathering at Universidade Feevale, one can notice the presence of rounded structures on the fibers, which may correspond to microorganisms, structures that were not found in the micrographs obtained before the test (pulp and paper not exposed to weathering) and in the micrographs of pulp and paper after environmental exposure at HAMK. As cellulose is degraded mainly by effective contact with water and other external agents (De Spirito et al., 2008), the porosity of the cellulosic material increases, and it is likely that the pores of the samples in this study were saturated with water.

Paper sheets also contain small and large pores alternating at random (Teodonio et al., 2016). The degradation of paper, in turn, occurs due to the synergistic action of environmental factors and internal variables (such as metallic impurities and fatty acids). These events, on a nanometer scale, entail further hydrolysis of glucose bonds and oxidation of cellulose chains. In general, the effect of aging on pulp and paper fibers can be seen in the reduction of the degree of polymerization, making the optical and mechanical properties inferior. The resulting products of this process are phenolics by the degradation of lignin, cellulose oligomers, aliphatic organic acids, volatile organic compounds, and simple sugars (Zervos, 2010; Castro et al., 2011).

Figure 8 presents the SEM images of the TPS/CW30 and TPS/PW30 samples without environmental exposure and with exposure after 28 and 42 days at Universidade Feevale and HAMK.

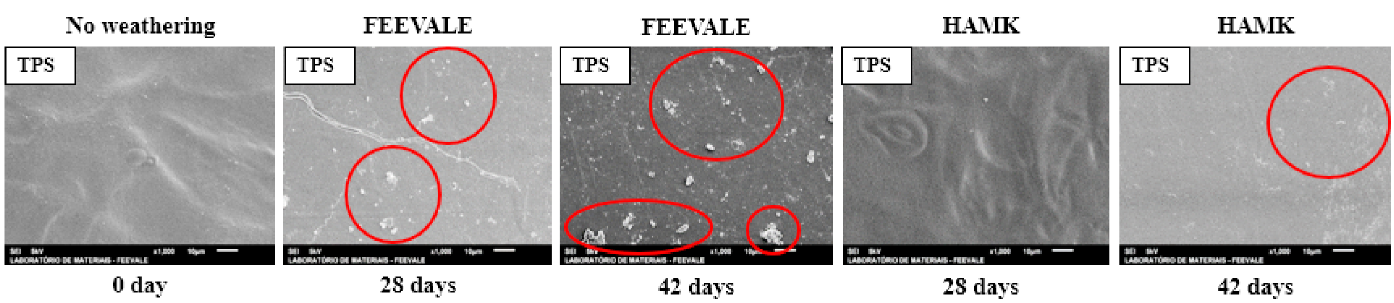


Figure 6 – Micrographs (1000x) of TPS before and after the weathering period at Universidade Feevale and HAMK.

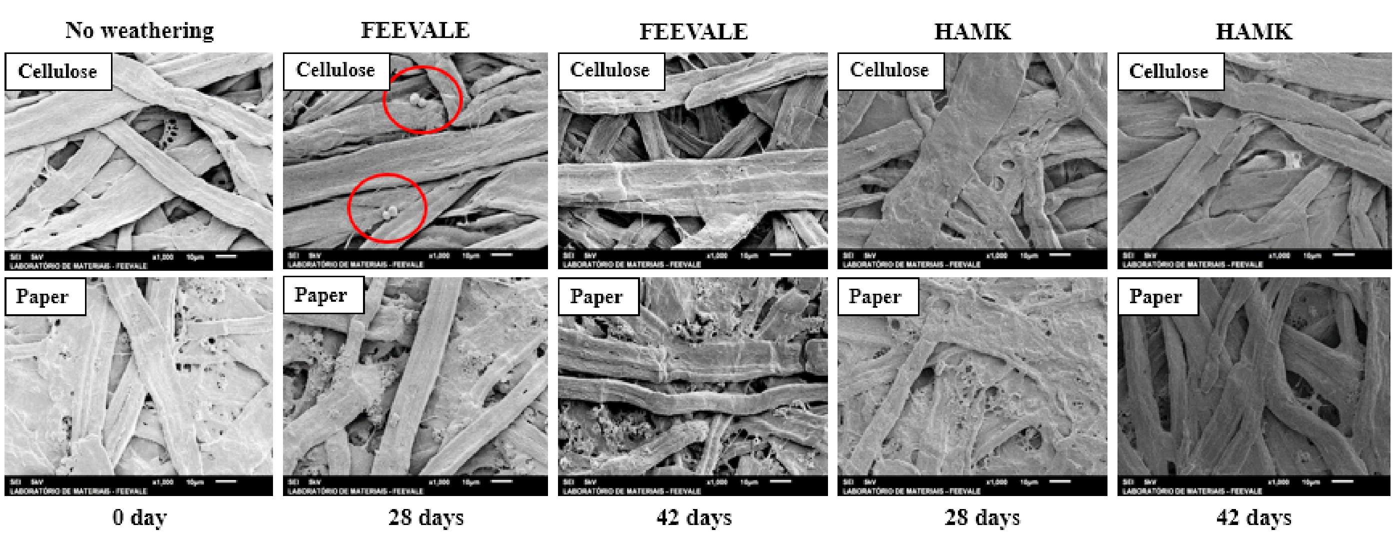


Figure 7 – Micrographs (1000x) of cellulose and paper before and after the weathering period at Universidade Feevale and HAMK.

The surfaces of the composites without the application of the natural weathering test are characteristic of materials that have been in contact with the environment during drying. The pulp and paper fibers are randomly distributed over the entire length of the TPS matrix. Such characteristics indicate that the fiber/matrix interfacial adhesion was adequate, although it resulted in a heterogeneous mixture, because the miscibility was affected by the formation of irregular fiber particles. Thus, the agglomeration of the fibers interfered with the microstructure of the composite films, preventing their homogeneous and regular distribution (Fahrngruber et al., 2019).

Furthermore, it is considered that when compared to composites produced with cellulose waste, composites with paper waste may have limited application due to the printed ink and additives from the printing industry. Therefore, further studies are needed to investigate which techniques are effective for removing impressions or ink discoloration, such as abrasion or chemical procedures (Counsell and Allwood, 2006).

The analysis of the morphologies of TPS/CW30 and TPS/PW30 after weathering, similarly to its components, also indicated the appearance of particulate material, cracks, and voids in the fibers found in the polymer matrix, especially in the samples submitted at Universidade Feevale, as highlighted in the images of 28 and 42 days of exposure to weathering. Regarding the HAMK samples after the weathering period, no significant changes were seen in the micrographs compared to the images without performing the test. For the samples exposed at the two sites in this study, analogous to what Varsavas and Kaynak (2017) reported, it is believed that the cellulosic fibers of the composites produced in this research have begun to lose adhesion to the TPS.

In general, micro-cracks that form on the surface can turn into macro-cracks as a result of erosion, and surface roughness tends to increase with weathering time (Tolvaj et al., 2013; Mohebby and Saei, 2015). In addition, thickness plays an important role regarding roughness and crack formation in samples, as thinners samples deform more easily (Arpaci et al., 2021). After viewing the micrographs, it is suggested that the abiotic degradation of the composites also started at the interface between the TPS matrix and the pulp and paper fibers, since the incorporation of the fibers slowed down the deterioration of the TPS/CW30 and TPS/PW30 composite samples in the two natural environments of this study.

Figure 9 presents the photographs of the TPS samples after 0, 28, and 42 days of exposure to weathering, at Universidade Feevale and HAMK. In general, the macroscopic visualization of the samples after environmental exposure was similar in both study environments. It was noticed that the films containing starch lost flexibility and became extremely brittle and twisted. This behavior is associated with retrogradation, an undesirable and frequent phenomenon in starches, which is an aging process in which the unstructured starch molecules during plasticization are slowly positioned into helical arrangements or new V-type conformations, so as to give rise to more brittle materials due to increased crystallinity (Area et al., 2019). And during long-term storage of TPS films, water absorption occurs (Bootklad and Kaewtatip, 2013). The total shrinkage generated by retrogradation and relaxation can be more than 10%, varying with processing technology, and can last for a few weeks. Therefore, photographs are an excellent macroscopic technique to examine the retrogradation of TPS films, as they point out the textural and mechanical changes (Matignon and Tecante, 2017).

Figure 10 shows the photographs of the pulp and paper samples after 0, 28, and 42 days of natural exposure at Universidade Feevale and HAMK. According to Arpaci et al. (2021), the initial color of wood after natural weathering is also influenced by other external agents, such as biotic factors (molds) and dirt. Photodegradation of cellulose is mainly caused by water and ultraviolet radiation, which causes the chemical decomposition of its chains and, consequently, discoloration and decay (Dungani et al., 2019). In general, a reduction in water absorption implies an increase in the dimensional stability (Trinh et al., 2012) of the material.

The paper samples after exposure to weathering underwent irreversible changes during the period, similarly to the cellulose samples.

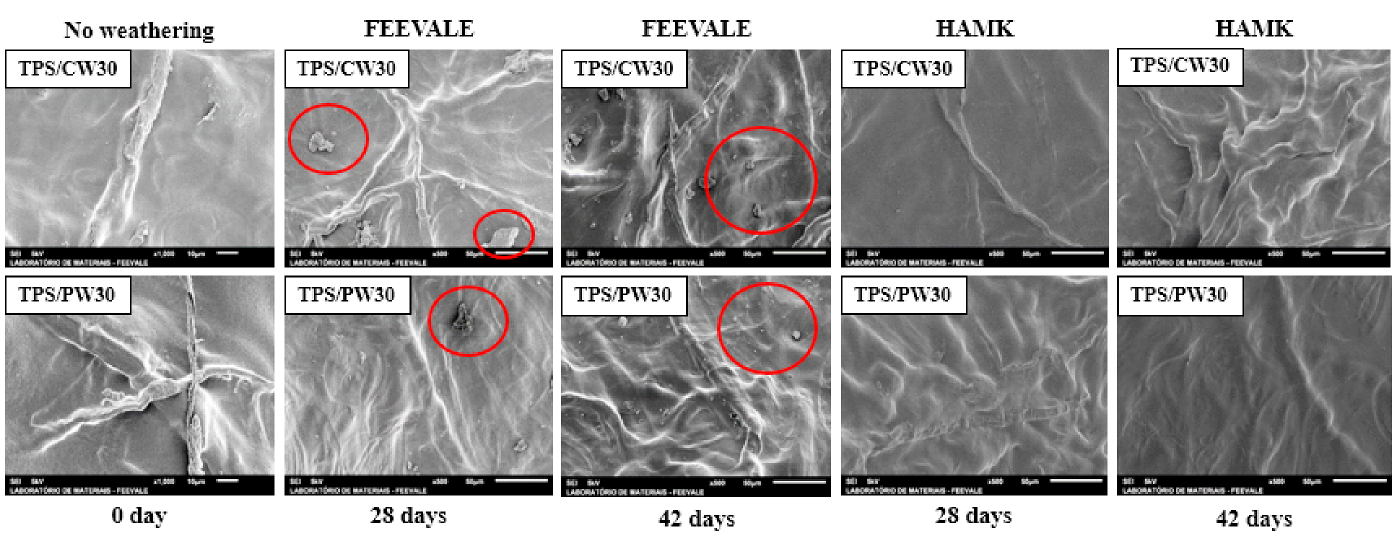


Figure 8 – Micrographs (500x and 1,000x) of TPS/CW30 and TPS/PW30 before and after the weathering period at Universidade Feevale and HAMK.

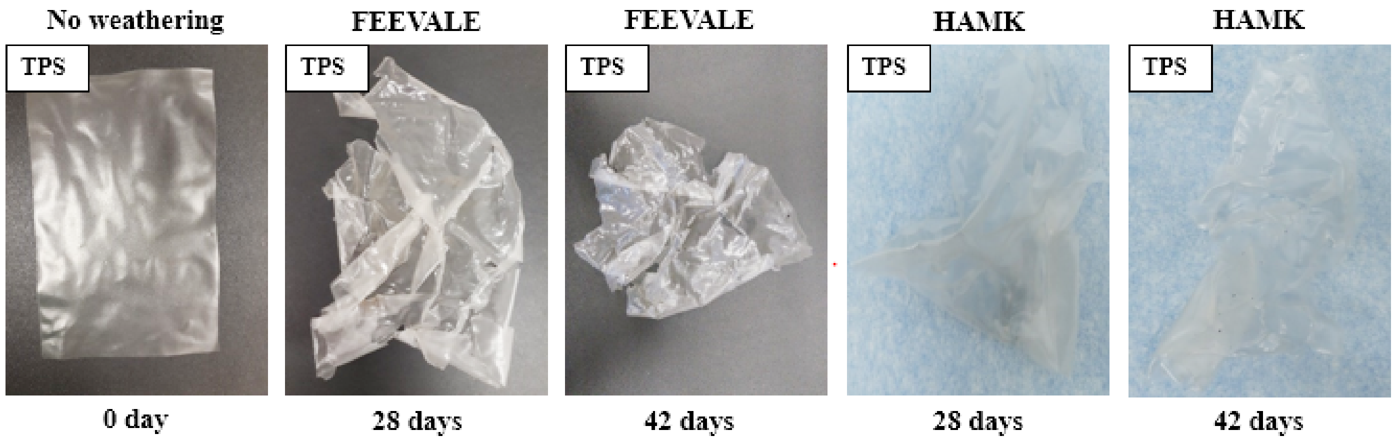


Figure 9 – Photographs of TPS before and after the weathering period at Universidade Feevale and HAMK.

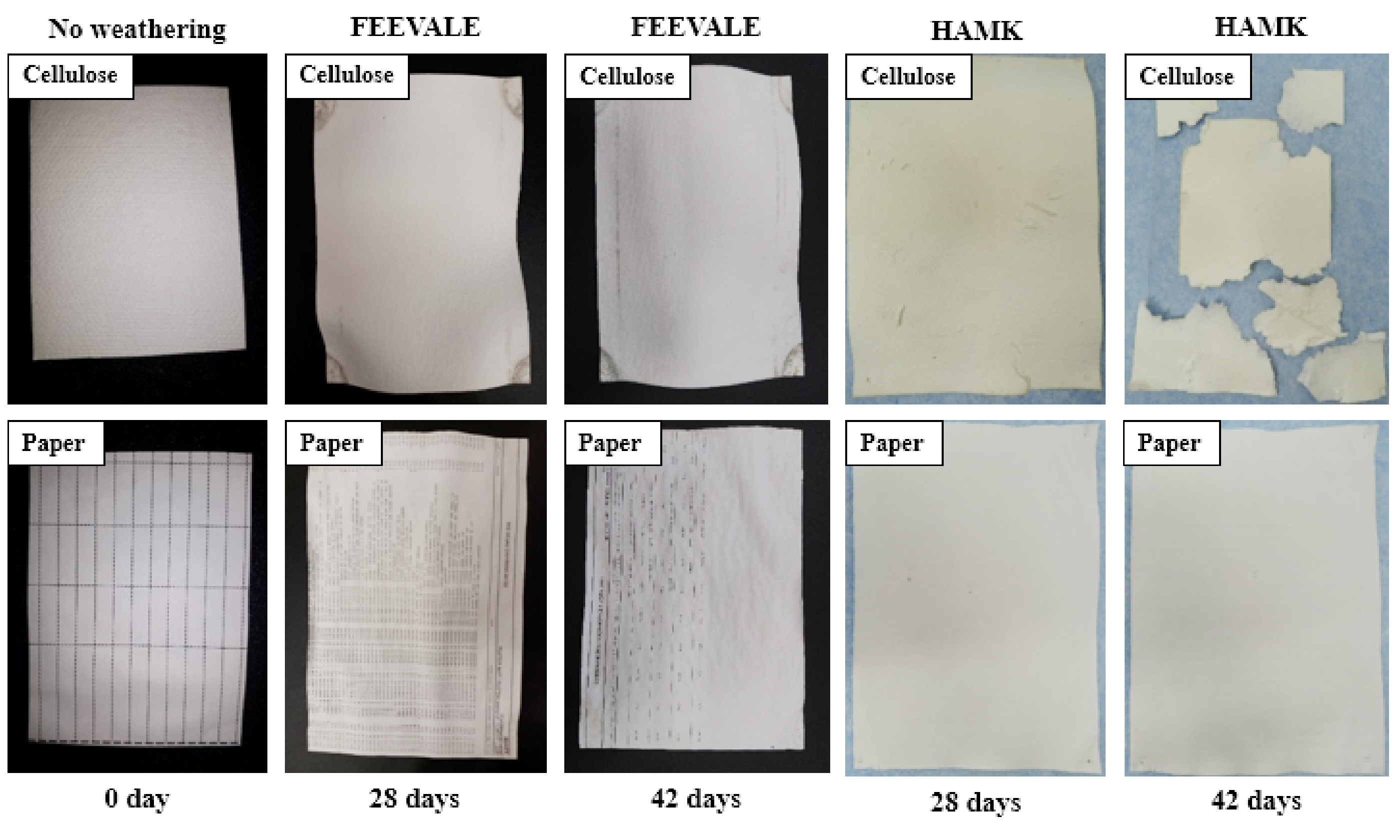


Figure 10 – Photographs of cellulose and paper before and after the weathering period at Universidade Feevale and HAMK.

In addition, the color of the material is an indication of quality, since solar radiation modifies the appearance. The yellowing of wood is a consequence of the loss of water-solubilized lignin, which may result in the formation of chromophores (Fabiyi et al., 2008). In agreement with this fact, the color change of the fibers in this study is justified after the weathering period, even though in the production of pulp there is a step designed to remove the lignin, a minimal amount remaining may already be enough to cause yellowing in the pulp and paper.

Liu et al. (2017) also identified that wood exposed to natural conditions is initially degraded by the loss of lignin, which causes the color change of its surface and, over time, the darkening is due to the migration of extractives and the existence of micro-cracks on its surface. Zupanc et al. (2018) stated that the water performance of most materials deteriorates with weathering, having identified that weathering has considerable influence on the water performance of wood and the greatest deterioration is given for thermally modified wood. Thus, the authors highlighted the importance of optimizing methods that can predict the moisture behavior of wood in external applications.

A factor highlighted in this research is that the climatic conditions were extreme at the two points studied during the sample submission interval. While in Novo Hamburgo the season at the time was the summer, typical of the subtropical climate of southern Brazil, with high temperatures (between 30 and 31 °C), high relative humidity (between 65 and 73%), and rain on isolated days, in the city of Hämeenlinna the recorded temperatures were considerably lower (between -11 and -4°C) and the relative humidity was higher (between 75 and 96%). At HAMK there was snow during almost the entire period, which caused flakes to cover the entire surface of the samples, which may have facilitated the natural degradation effect, and the incidence of solar radiation was lower. Thus, it is believed that at Feevale, due to the higher incidence of solar rays, the yellowing effect on the samples was greater.

According to SBD-RS (2018), summer solar radiation in Brazil is more harmful in the state of Rio Grande do Sul (RS) compared to the northeastern states, due to seasonality. The RS is still hit by airwaves containing little ozone from Antarctica, which makes ultraviolet rays more dangerous. In the city of Hämeenlinna (Finland), on the other hand, Weather Spark (2018) reports that the intense winter is characterized by being long, icy, with cloudy skies, very little sunshine due to snow precipitation, and high wind intensity.

One study investigated interannual variability and climate change over time in a reindeer herding region (RMA) in northern Finland. The herders' knowledge of weather measurements over the past 30 years was assessed by means of a questionnaire, as well as the impacts on grazing during the four seasons. Given the analysis of indices such as temperature, precipitation, and snow relevant to grazing activity, climate changes were found to be consistent with previous studies, as the greatest number of changes were identified in the winter period. The researchers concluded that a holistic understanding of future change adaptation and climate change impacts requires simultaneous analyses of data from different sources, more co-planned governance solutions, and co-defined research with local practitioners, as the study approach can leverage dialogue between these practitioners, researchers, and policymakers (Rasmus et al., 2020).

Next, Figure 11 presents the photographs of the TPS/CW30 and TPS/PW30 samples after 0, 28, and 42 days of environmental exposure at Universidade Feevale and HAMK.

Regarding the results that can be analyzed from the photographs of the TPS/CW30 and TPS/PW30 composites, it can be noticed that the images demonstrated effects analogous to those of their compositions, with a tendency to retrogradation due to the predominance of TPS. Thus, considering the two selected points of this study, it can be seen that in a short term the TPS suffered a greater environmental impact when analyzing the changes in the characteristics of the samples of all materials exposed to weathering.

It is also noteworthy that the inclination of the samples is also a factor that intensifies degradation, because in tropical regions, i.e., with more intense solar radiation, exposure facing horizontally suffers greater environmental degradation and, consequently, has more harmful effects compared to vertical exposure (90° angle of the ground). Still, horizontal positioning leads to greater proliferation of microorganisms because the surfaces remain wetter for longer (ISO, 2009a), especially in the case of materials that are naturally subject to the action of microorganisms, such as TPS and composites containing TPS. Therefore, regarding the positioning aspect of the samples, it is understood that the 45° angle was adequate and the impact was observed in both research sites, as it is suggested that in Brazil the high temperatures provided an ideal environment for the proliferation of microorganisms on the samples, while in Finland snow deposition and high humidity may have also contributed. The observation of the photographs of the composites shows that the effect that the weathering caused on both sets of samples, both at Universidade Feevale and HAMK, in general, were quite similar. In this sense, it cannot be said that there were relevant differences in view of this macroscopic visualization.

Furthermore, on the recycling potential of post-consumer plastic packaging waste in Finland, a survey identified that in the year 2014 between 86,000 and 117,000 tons of plastic waste from packaging was generated, which is equivalent to 18 kg / person / year. The authors concluded that the applicability of plastic waste for a given product must be assessed individually, as quality requirements are often product-specific. Also, to properly estimate the recycling potential, one must take into account the quality and quantity of the plastic waste to ensure the sustainability of this value chain. In the planning phase, the economic and environmental impacts of the required processes need to be assessed to generate benefits for society and operators (Dahlbo et al., 2018).

Already in Finland's agricultural sector, an estimated 12,000 tons of plastic waste is generated per year, with more than half consisting of baled packaging films. In Finland, only 10% of plastic film waste is recycled, while 70% goes to landfills. Relying on the fact that recycling plastic materials is key to achieving a circular economy, a survey assessed the economic and environmental implications of bale packaging collection and recycling in the Finnish context. It was concluded that the system scenario that collects waste once a year offers 27% more savings and presents 36% less global warming potential compared to the system that collects waste twice a year.

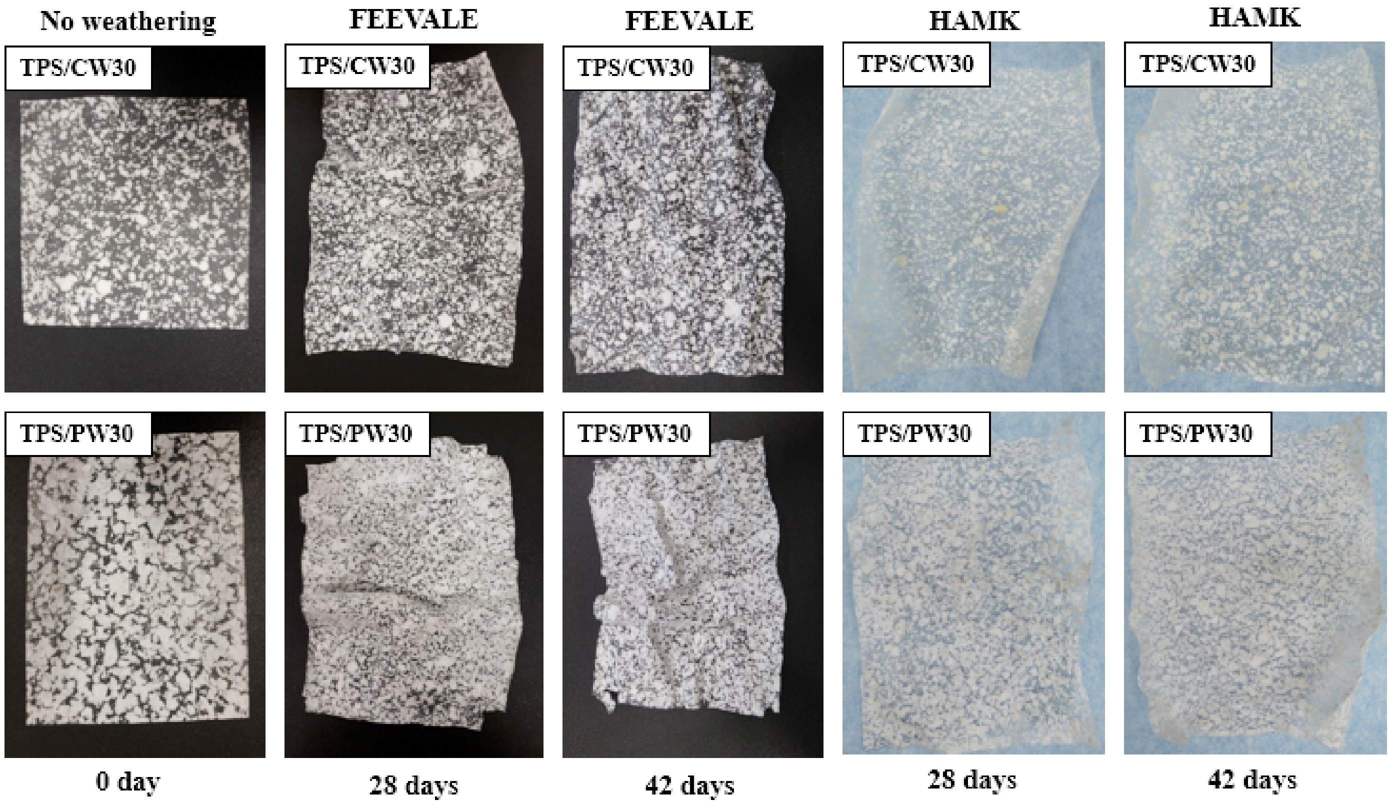


Figure 11 – Photographs of TPS/CW30 and TPS/PW30 before and after the weathering period at Universidade Feevale and HAMK.

Thus, it was shown that recycling the bale wrapper can provide environmental and economic savings and is an important pillar for prioritization by decision-makers (Mayanti and Helo, 2022).

Conclusion

Based on this study, it can be concluded that the introduction of cellulose and paper fibers to the TPS matrix results in heterogeneous materials; moreover, composites reinforced with cellulose waste are more promising for future packaging applications, as they have better mechanical performance and thermal stability when compared to pure TPS and pure cellulose. Additionally, it was found that the composite samples started the retrogradation process after the environmental exposure period at both sites, and showed brittleness, cracking, and yellowing due to their components. However, when comparing the weathering exposure sites, it is possible to conclude that the most aggressive natural environment to the samples was the one at Universidade Feevale; a fact that is due especially to the drastic difference in climatic conditions, solar radiation, and relative humidity compared to HAMK. The samples that suffered the greatest impact from environmental degradation were those made of TPS, and the incorporation of fibers in the TPS/CW30 and TPS/PW30 formulations delayed a little the effect of environmental variables, reasonably increasing the durability of these materials. Considering that there are very few studies that address the environmental exposure of materials made with natural polymers, these results refer to an important advance in science regarding the submission of materials in the environment.

Finally, it is understood that it is possible to substitute materials made from synthetic polymers with those produced in this research, but it is suggested that their application includes products with short durability, since films containing TPS, cellulose waste, and post-consumer paper degrade rapidly when exposed to weathering, also due to the process of retrogradation of the TPS matrix. Thus, it is concluded that the production of biodegradable composites is a viable alternative to add value to the waste from pulp to minimize direct disposal in landfills, aiming to achieve sustainable development according to the objectives of Law No. 12.305/2010

Contribution of authors:

GOMES, N. F.: Conceptualization; Data curation; Formal Analysis; Writing – Original Draft; Writing — Review & Editing. RODRIGUES, T. F.: Data curation; Writing — Original Draft; Writing — Review & Editing. SANTOS, K.L.: Data curation; Writing — Original Draft. CELSO, F.: Supervision; Methodology; Writing — Original Draft; Writing — Review & Editing. VUORIO, T.: Resources; Methodology; Writing — Original Draft. JAHNO, V.D.: Conceptualization; Resources; Supervision; Methodology; Writing — Original Draft; Writing — Review & Editing.

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