

This is the peer reviewed version of the following article:

Statistical evaluation of the degradation mechanism of bio-based materials for sustainable food-packaging / Faro, E.L., Barbi, S., Barbieri, F., Corradi, S., Fava, P., Montorsi, M.. - In: MATERIALS TODAY COMMUNICATIONS. - ISSN 2352-4928. - (2026), pp. 116189-116189. [10.1016/j.mtcomm.2026.116189]

Terms of use:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

09/10/2026 12:32

(Article begins on next page)



Statistical evaluation of the degradation mechanism of bio-based materials for sustainable food-packaging

Emanuela Lo Faro^{a, b}, Silvia Barbi^{c, *}, Francesco Barbieri^c, Sara Corradi^c, Patrizia Fava^{a, b}, Monia Montorsi^{c, d}

^a Department of Life Sciences, University of Modena and Reggio Emilia, via Amendola 2, Reggio Emilia, 42122, Italy

^b Interdepartmental Centre BIOGEST-SITEIA, University of Modena and Reggio Emilia, Piazzale Europa 1a, Reggio Emilia, 42124, Italy

^c Department of Sciences and Methods for Engineering, University of Modena and Reggio Emilia, via Amendola 2, Reggio Emilia, 42122, Italy

^d Interdepartmental Research Center for Industrial Research and Technology Transfer in the field of Integrated Technologies for Sustainable Research, Efficient Energy Conversion, Energy Efficiency of Buildings, Lighting and Home Automation (EN&TECH), University of Modena and Reggio Emilia, Piazzale Europa 1a, Reggio Emilia, 42124, Italy

ARTICLE INFO

Keywords:

PCL
Coatings
DoE
Paper
Composting

ABSTRACT

In packaging materials design, enhanced barrier coating materials typically correlate with slower microbial breakdown; This can lead to a decline in the overall performance of biobased packaging materials by inhibiting their ability to be biodegraded or composted at the end of their life cycle. Thereafter, material design must integrate biodegradation testing into performance evaluation. In this context, the aim of this research is to evaluate, through a statistical approach, the rate of soil degradation of different environmentally friendly paper-based packaging materials and the factors that influence it. Experimentally, 4 types of biobased coatings composed of PCL, cutin, glycerol, starch and agar, were applied on paper and their properties were assessed before and after burial in soil for 14 and 28 days. In detail, weight variation, chemical structure, morphology and mechanical properties were assessed. The results demonstrated that the type of soil rather than the type of coating led to the clearest detriments of the mechanical properties (p -value < 0.005), reaching the complete degradation in a universal soil ($pH = 6.5$) in 20 days. ESEM analyses confirmed the general degradation of coatings in universal soil, while degradation in acidic soil ($pH = 4.5$) resulted in total removal of starch coating, while PCL and cutin/glycerol coating showed almost no morphological degradation. The degradation trend is potentially related to the microbiological activity plausibly favored by the pH environment of the universal soil.

1. Introduction

Paper is a well-known sustainable alternative to plastic in the food packaging sector, as it is biodegradable and leaves no long-term polluting residues, contributing to a significantly lower environmental impact [1]. Nevertheless, packaging materials must ensure the safe transport, distribution, and handling of products, protecting them from impact and compression. These materials must also provide good protection against moisture, oxygen, and light, thereby reducing chemical and biological deterioration. In addition, it is essential that food packaging materials are inert, meaning they do not release harmful compounds that could alter the sensory characteristics of food or pose a health risk. In this context, despite its many benefits, paper also has disadvantages: its low resistance to water and moisture makes it unsuitable for many products

that require waterproofing, and the same applies to grease resistance. In addition, the production of paper packaging can lead to considerable environmental challenges due to the variety of waste streams generated by industry [2]. To mitigate these impacts, eco-friendly biomaterials, also known as biopolymers, are increasingly being promoted in the papermaking process. Research is therefore focusing on sustainable alternatives with improved properties and lower environmental impact than the cellulosic products currently available on the market.

Bio-based polymers can be evaluated as suitable alternatives to polymeric coatings available on the market to protect paper, thereby overcoming their poor environmental safety and potential risks to human health. In recent years, the development of fully biodegradable coatings and formulations has gained a pivotal role in materials science, driven by the urgent need to replace fossil-based plastics with eco-friendly al-

* Corresponding author.

E-mail address: silvia.barbi@unimore.it (S. Barbi).

ternatives. For instance, current research has successfully leveraged the biodegradability of cellulose derivatives, such as ethyl cellulose, to develop functional coatings that ensure a low environmental footprint and rapid breakdown at the end of their life cycle [3]. Concurrently, significant advancements have been focused on evaluating the biodegradation performance and functional properties of water-soluble matrices like polyvinyl alcohol, which are increasingly adopted to design environmentally friendly protective films [4]. Furthermore, substantial progress has been made in blending biodegradable polyesters with natural polymers like starch to engineer advanced composite films for sustainable active packaging applications, emphasizing how functional additives interact with the degradable matrix [5]. This widespread focus on green formulations highlights the critical importance of systematically evaluating how these biopolymer mixtures degrade under real environmental conditions.

Among them a strong focus must be given to the biodegradable ones, such as PLA, starch, cellulose, cutin and agar, either alone or in multi-layer combinations [6–11]. The degradation of polymers and biopolymers generally refers to a series of complex phenomena that lead to the total breakdown of materials, resulting in the fragmentation of macromolecules into low molecular weight fragments. This phenomenon leads to changes such as the appearance, disappearance, and transformation of chemical groups, as well as changes in physical properties or performance, such as loss of mechanical properties, brightness, discoloration. If chemical and organic substances in the environment are key players, this process is defined as biodegradation [12]. The biodegradation products consist of (i) biogas such as CO_2 and CH_4 and (ii) liquid or solid compounds such as water, biomass, or minerals [9]. Biodegradation mechanisms are not easy to define in detail as each polymer or biopolymer follows a different degradation path, which depends on several intrinsic and extrinsic factors [13]. Examples of intrinsic factors are the polymer's chemical structure, morphology, molecular weight, hydrophilicity or hydrophobicity behavior, surface characteristics, melting temperature, elastic modulus. Regarding extrinsic conditions, we can list temperature, pH, oxygen level, nutrients, humidity, and UV exposure [6,14–16].

Due to the high number of variables, it is challenging to define predictive models to estimate the biodegradation path of a material in terms of time and products, thereafter biodegradation tests must be considered. Among them, the burial test is one of the least expensive and reproduces natural environmental conditions. In this test, the material is buried in a selected soil and controlled environment for a defined period, and any variation in the material properties (e.g., weight, morphology, chemical structure and mechanical) over this period should be monitored [17].

Recent studies have increasingly utilized the soil burial test to assess the environmental degradability of biopolymers specifically developed for food packaging and paper-based packaging substrates, offering realistic simulations of material breakdown in terrestrial ecosystems. For example, starch–nanocellulose films incorporating bioactive extracts showed significant biodegradation under soil burial conditions, with marked weight loss and morphological changes relevant for biodegradable food wraps, demonstrating their potential as sustainable packaging alternatives to conventional plastics [18]. Ternary biocomposites composed of poly(butylene adipate-co-terephthalate) (PBAT), thermoplastic starch, and cellulose exhibited measurable soil burial degradation, highlighting the influence of blend composition on mass loss and surface deterioration, which is crucial for film packaging performance [19]. Long-term in-field burial tests of starch/PBAT mulch films revealed progressive deterioration over extended periods, underlining how polymeric blends degrade differently in real soil environments, with implications for biodegradable packaging disposal and microplastic formation [20]. The role of soil burial tests has also been documented in evaluations of cellulose films, showing complete microbial assimilation within weeks to months, underscoring the importance of natural soil conditions in degrading paper-like materials used in packaging [21]. Soil burial investigations of Mater-Bi/PCL bio-blends showed that while the inclu-

sion of PCL reduced the overall degradation rate compared to pure starch phases, these blends still exhibited moderate mass loss and surface changes over twelve weeks, relevant for packaging film life-cycle assessments. In the same study temperature was found to be strongly correlated with the rate of PCL degradation under controlled conditions, suggesting a significant role for microbial activity, which is indeed influenced by temperature [19]. Methodological reviews additionally emphasize that soil burial assessments provide critical insights into the actual degradation kinetics and mechanisms of composite biopolymer films intended for food packaging applications, despite variations caused by soil microbiota and environmental factors [22]. Nevertheless, considering the high variability of environmental conditions and material mixtures, the literature does not provide a reliable comparison among different paper-based packaging materials that would allow predictive assessment of material behavior.

In the present paper, as a first novelty compared with the consolidated literature, a statistical approach to the experimental burial test of environmentally friendly coatings for packaging paper was applied to obtain statistical models with predictive power and to overcome the drawbacks of burial tests regarding poor standardization and reproducibility. Secondly, five different materials specifically designed for food packaging were compared: (i) Uncoated paper; (ii) Paper coated with a mixture of starch, agar, and glycerol; (iii) Paper coated with PCL; (iv) Paper with a mixture of PCL and cutin; (v) Paper coated with a mixture of PCL, cutin, and glycerol. Thirdly, each material was buried in two types of soil (universal and acid) for a period of four weeks to evaluate how external factors, namely the burial environment, influence the speed and effectiveness of the induced biodegradation mechanism in terms of weight loss and changes in material structure. Finally, optical spectroscopy was evaluated as a possible non-destructive and low cost method to assess material decomposition.

2. Materials and methods

2.1. Materials

The samples were produced using Advantage MG White High Gloss paper (Serchio Distribuzione, Rome, Italy) as a substrate. This material consists of long-fiber white sulfate cellulose, with a grammage of 35 g/m^2 and a thickness of $48 \mu\text{m}$. See Table 1 for further technical specifications.

Polycaprolactone (PCL, Sigma Aldrich, Taufkirchen, Germany), was employed as the main component of the coatings. It has an average molecular weight of $80,000 \text{ g/mol}$, a melt flow index between 2.01 and 4.03 g/10 min (160°C , 5 kg), and a water content of $< 0.5\%$. Cutin, supplied by TomaPaint (Canneto sull'Oglio, MN, Italy), is a waxy material ranging in color from reddish to dark brown. Glycerol (Sigma Aldrich), used as a plasticizer and fluidizer, is a colorless liquid with a density of 1.26 g/cm^3 and a molecular weight of 92.09 g/mol . Ethyl acetate (Sigma Aldrich), used as a solvent, has a purity of $> 99.5\%$, high volatility, and a molecular weight of 88.11 g/mol . Finally, potato starch was purchased from a local market, while agar powder was purchased from Sigma Aldrich.

For the burial test two types of soils were considered: (i) the universal soil (GEOTEC S.r.l., Bolzano), having a pH of 6.5, certified according to the UNI EN 12580 standard [23]. Its physical properties include by an apparent dry density of 150 kg/m^3 and a total porosity of 92% v/v. In terms of composition, it consists mainly in descending order of volume of acid peat and simple uncomposted vegetable soil improver; (ii) the acid soil (GEOTEC S.r.l., Bolzano), which has a pH of 4.6, also certified according to UNI EN 12580 [23]. Its physical properties include an apparent dry density of 110 kg/m^3 and a total porosity of 93% v/v. Its main components are acidic peat and pumice.

Table 1

Materials main properties (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

Properties		Methods		UCP	SA	PCL	PCLCU	PCLCUGLY
Basis Weight	g/m ²	ISO 536		35	56.7 ± 1.5	45.2 ± 2.15	47.30 ± 3.60	51.1 ± 3.14
Tensile Strength	kN/m	ISO 1924-3	MD	3.5	1.94 ± 0.11	5.51 ± 0.60	0.48 ± 0.02	0.45 ± 0.03
			CD	1.5	0.83 ± 0.12	3.14 ± 0.12	0.22 ± 0.03	0.22 ± 0.03
Tear Strength	mN	ISO 1974	MD	280	/	/	/	/
			CD	420	/	/	/	/
Burst Strength	kPa	ISO 2758		165	/	/	/	/
Air Resistance (Gurley)	s	ISO 5636-5		28	/	/	/	/
Cobb-60"MG Side	g/m ²	ISO 535		21	/	/	/	/
Gloss	%	TAPPI 480 om-99		26	/	/	/	/
Brightness	%	ISO 2470		82	/	/	/	/
Opacity	%	ISO 2471		55	/	/	/	/
Thickness	µm	ISO 534		48	151 ± 24	54 ± 3	58 ± 2	60 ± 3
Fat Resistance (Kit 12)				/	4.33 ± 0.6	12	12	12

For Uncoated paper (UCP) the data are taken from the supplier technical datasheet (MD: Machine direction; CD: Cross direction).

2.2. Specimens manufacturing

For the coating phase, sheets of paper (210 × 297 mm) with the properties listed in Table 1 were coated using an Automatic Film Applicator Compact AB3650 (TQC Sheen). This technique uses stainless steel bars with spiral grooves to ensure a uniform coating thickness over the entire surface of the sample; in this work, bars with a nominal thickness of 100 µm were used. The application was carried out at a speed of 20 mm/s, distributing 7 mL of film-forming solution on each sheet, deposited with an automatic pipette before spreading. A total of four coatings were prepared to cover the paper with different formulations as listed in Table 2: PCL, starch, agar, and glycerol (SA), PCL (PCL), PCL and cutin (PCLCU), and PCL, cutin, and glycerol (PCLCUGLY).

The coating solutions were obtained by dissolving 10 g of polycaprolactone in 100 mL of ethyl acetate at 80 °C in a water bath under continuous magnetic stirring, using a reflux condenser to minimize solvent loss. This procedure yielded the PCL base solution. Depending on the target formulation, cutin and glycerol were subsequently incorporated into the PCL solution. Cutin was added at a PCL: cutin weight ratio of 1:0.6 to

produce the PCLCU samples, while glycerol was added at a PCL:glycerol weight ratio of 1:0.05 to obtain the PCLCUGLY samples. The mixtures were stirred for 40 min to ensure complete dispersion of all components within the ethyl acetate.

Instead, for the starch and agar based coating, the coating solution was prepared by combining an organic phase and an aqueous phase. The organic phase was obtained by solubilizing 10% w/v PCL in ethyl acetate under magnetic stirring and heating at 80 °C until complete dissolution of the polymer, and glycerol was added at 1% w/w PCL. At the same time, the aqueous phase was prepared by dispersing starch (10% w/v) and agar (1.5% w/v) in distilled water, keeping the mixture under stirring and heating until complete gelatinization and solubilization of the components. Subsequently, the two phases were combined by adding 2% w/v total solution of surfactant Tween80, necessary to promote emulsification between ethyl acetate and water, thus obtaining a homogeneous suspension suitable for coating application.

2.3. Burial soil test

The burial test was conducted according to an adapted protocol based on the ISO 846 (Method C) guidelines for soil burial testing by embedding specimens in soils for a period of 28 days under controlled and consistent conditions [24]. Pots measuring 600 × 190 × 100 mm (L × W × H) were filled with 2900 g of soil and 1 L of demineralized water. Paper samples were cut into strips of 200 × 25 mm to allow partial burial. Following the methodology described by Ahmed et al. [25], each strip was folded in half and buried to 50% of its length, leaving the remaining half exposed to air (Fig. 1). This approach enabled the recovery and analysis of samples at multiple time points, with the exposed portion of each strip marked with unique codes to identify the corresponding sample type. For each coating type, three replicates were prepared, including uncoated control samples (UCP). After embedding all specimens, the pots were sealed with cling film to maintain a consistent soil

Table 2

Coatings formulation. (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

Samples	PCL %*	Starch %**	Agar %**	Cutin %***	Glycerol %***	Tween80%****
UCP	0	0	0	0	0	0
SA	10	10	1.5	0	1	2
PCL	10	0	0	0	0	0
PCLCU	10	0	0	60	0	0
PCLCUGLY	10	0	0	60	5	0

*(w/v ethyl acetate); ***(w/v water); ***(w/w PCL dry weight); ****(w/v total solution).

**Fig. 1.** Burial soil test.

moisture level. Environmental conditions within the pots were continuously monitored using a data logger (Elitech Technology Inc., model RC-51H), which recorded temperature and relative humidity in real time with accuracies of $\pm 0.5^\circ\text{C}$ and $\pm 3\%$, respectively. This ensured precise control of the microenvironment to which the paper samples were exposed throughout the burial period. Finally, the pots were placed in an isolated chamber to minimize external influences and maintain stable experimental conditions.

2.4. Experimental plan

Burial soil tests were performed considering two types of soil and five different coated paper samples, including the uncoated sample. Also, time was considered as the degradation was observed for a total period of 28 days and property measurements were performed every 14 days. These 3 variables (Time, Soil and Material) were considered with their range or levels (Table 3) to build up the experimental plan based on a fractional multi-level factorial design for a total of 20 RUN as listed in Table 5. The Design Expert 13 code (Statease, USA) was employed to set up the experimental plan and to analyze the data. The values considered for each RUN and shown in Table 5 are the average of three replicates of the same RUN. The following properties were measured as responses after 14 and 28 days of burial: weight loss (WL), Young modulus (E), tensile strength (σ), elongation at break (ϵ) and reflectance at three different wavelengths that correspond to the instrument's boundary range and its mid-point.

2.5. Characterization

2.5.1. Weight loss

Each week, three samples of each material were extracted from each pot. The samples were then carefully cleaned with a brush and dried in an oven at 80°C overnight. Once dry, the samples were weighed using an analytical balance and reburied. The procedure was repeated weekly for the entire duration of the experiment, which lasted four weeks. This methodology allowed observation of a progressive reduction in the weight of the individual strips of material throughout the experiment. The following formula (1) was used to calculate the percentage weight loss of the samples:

$$\text{Weight loss \%} = ((\text{initial weight} - \text{final weight}) / \text{initial weight}) \times 100 \quad (1)$$

where initial weight is the dry weight of the sample before the biodegradability test, while final weight is the dry weight of the sample after the test.

2.5.2. Mechanical properties

The tensile strength, elongation and Young's modulus of the paper samples were determined using a Zwick/Roell Z1.0 dynamometer (Ulm, Germany) in accordance with ASTM D882 [26]. The test specimens were rectangular in shape, measuring 200×50 mm, and were conditioned at controlled temperature and humidity (25°C and $45\%\text{RH}$), as required by the reference standard, before the measurements were taken. The test was conducted using a constant crosshead speed tensile testing machine equipped with grips capable of ensuring uniform clamping and preventing slippage or premature damage to the sample near the grip-

ping areas. The experimental parameters adopted were as follows: Initial Grip Separation: 125 mm; Rate of Grip Separation: 12.5 mm/min; Initial Strain Rate: 0.1 mm/mm-min. The collected data were processed by the TESTEXPERT®II (V3.31) software (Zwick/Roell, Ulm, Germany). All the samples were analyzed before the burial soil test and then after 14 and 28 days the burial soil test.

2.5.3. Structural properties

To assess any chemical variation due to degradation, an FTIR spectrophotometer (Vertex 70 Bruker) equipped with a Mid-Band MCT detector operating in the $8000\text{--}600\text{ cm}^{-1}$ wavelength range and employing a Golden-Gate ATR sample holder (Heated-Diamond top plate) was used. All measurements were performed twice on each sample, taking care to analyze the coated side for all samples except, of course, UCP.

An environmental scanning electron microscope (Quanta-20 Fei Company – Oxford Instruments) was used. Micrographs were taken at 25 kV and magnifications from $100\times$ to $2000\times$ with backscattered electrons.

2.5.4. Optical reflectance

Samples were scanned with a NeoSpectra scanner, which operates within the NIR range of $1350\text{--}2500$ nm. The scanner uses a single indium gallium arsenide photodetector, and a halogen lamp as the light source. The NeoSpectra measures the spectrum of reflected light in a limited area of the material, namely a circle with a 6 mm diameter and a spectral resolution of 8 or 16 cm^{-1} . A calibrated Spectralon panel (Labsphere) with $> 99\%$ reflectance is used as white reference. The integration time for each spectrum was set at 2 s. Each scan produces interferograms that NeoSpectra Collect, the software of the instrument, converts into NIR spectra in the $1350\text{--}2500$ nm domain through FFT (fast Fourier transform). Savitzky–Golay (SG) filtering is used for spectral processing, specifically to remove noise and smooth the spectra. The relative Reflectance was assessed considering the starting material, with the formula:

$$R_r = ((R_{28\text{ days or }14\text{ days}} - R_{0\text{ days}}) / R_{0\text{ days}}) * 100 \quad (2)$$

where R_r is the relative reflectance of the material, $R_{28\text{ days}}$ and $R_{14\text{ days}}$ are the measured reflectance's after 28 or 14 days of burial, and $R_{0\text{ days}}$ is the measured reflectance of the undegraded material.

2.6. ANOVA

ANOVA (Analysis of Variance) allows the evaluation of which factors and interactions significantly influence the responses. ANOVA decomposes the total variability of the experimental data into contributions from the model and from random error [27]. In this work, a p-value (probability that all the variability comes from a random source) of less than 0.05 indicates that the corresponding factor has a statistically significant effect on the response. ANOVA also supports model validation by quantifying how well the fitted model explains the experimental data. In this sense, the R^2 (coefficient of determination) measures the proportion of the total variability in the response that is explained by the model, while the adjusted R^2 (adj R^2) expresses the same information corrected for the number of experimental points used to build each model. The predictive R^2 (pred R^2) indicates the capability of a model to explain response variability when applied to a new set of samples. An R^2 or an adj R^2 value close to 1 indicates a strong explanatory power of the experimental model. In the same way a pred R^2 close to 1 suggests a good predictive power of the model and the possibility of employing the mathematical model to generate forecasts [27].

When multiple responses are involved, as in the case of this research, optimization becomes more complex and the desirability function is used to convert each response into a dimensionless scale ranging from 0 (completely undesirable) to 1 (fully desirable) [27]. Individual desirabilities are then combined into an overall desirability index employing the goal and importance of each response as weights, also taking in ac-

Table 3

Input variables (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

Input variables	Type	Range or Levels
Soil	Categoric	2 (U = universal soil, A = acid soil)
Material	Categoric	5 (UCP, SA, PCL, PCLCU, PCLUGLY)
Time	Numeric	14–28 days

Table 4
Responses and desiderability function criteria.

Response	Acronym	Goal	Importance
Weight loss (%)	WL	to maximize	5
Young's Modulus (MPa)	E	to minimize	2
Tensile strength (MPa)	σ	to minimize	2
Elongation at break (%)	ε	to minimize	2
Reflectance at 2500 nm (%)	R2500	to maximize	1
Reflectance at 2000 nm (%)	R2000	to maximize	1
Reflectance at 1500 nm (%)	R1500	to maximize	1

count the result of the ANOVA of each single factor (Table 4). In fact, models with a lacking data fitting are associated with the lowest importance (1) [27]. These criteria have been applied also in the Goal and Importance stated in Table 4, therefore highest importance has been attributed to the most significant model, calculated from the ANOVA, and vice versa.

3. Results

3.1. ANOVA and DoE modeling

A preliminary observation of Table 5 shows that different trends can be detected between samples buried in the two soils. Weight loss (WL) is clearly higher in universal soil at the end of the test (28 days), reaching 100% for all samples, while WL for samples buried in acidic soil remains in the 18–66% range. A similar difference emerges at 14 days as WL in universal soil ranges between 60% and 73%, but it does not exceed 55% in acidic soil. The mechanical property values suggest that both soils promote rapid degradation of all materials, as many samples degraded to the point where no measurement was possible. This is true for all samples buried in universal soil and also true for those buried in acidic soil, suggesting that some materials degrade more slowly under acidic conditions. It should be noted that, to confirm the validity of the approximation which treats mechanical property values as zero when they are not measured—an ANOVA analysis was conducted in parallel without including mechanical properties, confirming the results presented below in terms of the desiderability function and the optimal degradation point. In fact, this approximation was taken into account in the desiderability table (Table 4) by assigning a low importance to the mechanical properties. Obviously, there is a strict connection between sample degradation in terms of mechanical properties loss and increased WL, as when a ma-

terial is almost completely dissolved in soil, no mechanical property can be evaluated further. Similarly, when evaluating the mechanical properties, it becomes clear that this trend is greatly pronounced, since in universal soil—which has a pH close to basic it is not even possible to assign a value to the mechanical properties because the samples are completely dissolved in the soil. Regarding relative reflectance, values at 14 days appear higher for samples buried in universal soil with respect to acid soil, while the opposite trend is observed after 28 days. However, the number of input variables and their levels suggest the likely presence of synergistic or competitive effects that cannot be identified without proper statistical analysis. In addition, the hypothesized main trends need formal validation through statistical analysis.

Table 6 provides a first assessment of the role of the input variables, declared in Table 3 and described in paragraph 2.4, and their interactions on the responses through ANOVA. All models are significant, as the associated p-values are consistently below 0.05. The “significant inputs” column highlights *Soil* and *Days*, as well as their interaction, as the inputs with the highest frequency of significance across all responses. In addition, *Soil* is the only significant input for the models concerning mechanical properties, while the variable *Materials* and its interaction with *Soil* are significant only for WL. R^2 and Adj R^2 are particularly high for WL (0.97) and relatively low (0.31) for relative reflectance at 1500 nm (RL1500), while the other responses show values slightly higher than 0.50. Table 6 shows that pred R^2 has a trend like adj R^2 , although with lower values. This means that, except for WL (pred R^2 = 0.93) the other models can explain the variability within this experimental set but have limited predictive power.

All the significant models can be represented graphically through the interaction plots (from Figs. 2–4) and in 3d contour plots (From Fig. S5–S9) to assess not only each variability trend but also quantitatively their variation within specific confidence intervals (dashed lines in the interaction plots). The interaction plots provide a clear visual representation of how the effect of one factor on the response depends on the level of another factor. When the lines in the interaction plot are approximately parallel, this indicates that there is little or no interaction between the factors (Fig. 2b–e and Fig. 3). Conversely, non-parallel or crossing lines suggest the presence of a significant interaction effect (Fig. 2a and Fig. 4). In such cases, the influence of one factor cannot be interpreted independently of the other. The magnitude of the interaction can be qualitatively assessed by the distance and slope differences between the lines. Strong deviations from parallelism indicate that the combined effect of the factors is relevant to the response. These visual

Table 5
Complete experimental plan (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

Run	Input Variables			Responses						
	A:Days	B:Soil	C:Materials	WL (%)	σ (MPa)	ε (%)	E (MPa)	R2500 (%)	R2000 (%)	R1500 (%)
1	28	A	PCLCUGLY	26	0.49	1.3	50.11	54.98	31.1	12.36
2	28	U	UCP	100	0	0	0	11.11	-2.39	-0.07
3	14	A	SA	15	1.12	0.91	60	-0.49	-3.15	-3.56
4	28	U	PCLCUGLY	100	0	0	0	29.71	5.1	1.29
5	14	A	PCL	12	0.51	1.24	100	-9.92	-7.35	-5.01
6	14	U	PCL	60	0	0	0	21.23	7.85	3.53
7	14	A	UCP	55	0	0	0	14.19	6.21	2.58
8	14	U	SA	68	0	0	0	20.1	4.02	0.37
9	28	U	PCL	100	0	0	0	27.08	6.54	2.52
10	14	U	PCLCUGLY	60	0	0	0	28.92	9.86	3.98
11	28	A	PCL	18	1.15	1.46	70.06	50.31	28.14	13.63
12	14	U	UCP	73	0	0	0	22.99	9.93	5.99
13	28	A	UCP	66	0	0	0	15.78	3.47	-1.4
14	14	A	PCLCUGLY	11	1.16	0.87	132	19.35	10.97	4.62
15	28	U	SA	100	0	0	0	30.37	4.61	-0.23
16	14	A	PCLCU	15	0.145	1.6	50.3	5.53	0.7	-2.38
17	14	U	PCLCU	65	0	0	0	32.89	13.72	6.43
18	28	A	SA	45	0.65	2.1	58	43.39	20.59	5.96
19	28	U	PCLCU	100	0	0	0	41.28	14.36	8.8
20	28	A	PCLCU	24	0	0	0	62.29	31.4	11.99

Table 6
ANOVA (see Table 4 for acronyms description).

Response	Significant inputs	p-value	R ²	Adj R ²	Pred R ²
WL	Days, Soil, Materials, Days-Soil, Soil-Materials	< 0.0001	0.98	0.97	0.93
σ	Soil	0.0002	0.54	0.51	0.43
ϵ	Soil	0.0002	0.54	0.51	0.43
E	Soil	0.0002	0.54	0.51	0.43
R2500	Days, Soil, Days-Soil	0.0012	0.62	0.55	0.41
R2000	Days, Soil, Days-Soil	0.0027	0.58	0.50	0.34
R1500	Days, Soil, Days-Soil	0.0290	0.42	0.31	0.10

observations are consistent with the ANOVA results, where significant interaction terms are associated with low p-values. Regarding the different coating formulations, it is remarkable that only WL is affected and that samples using SA, PCLCU and PCLCUGLY show the lowest WL values (always in acid soil) as shown in Fig. 2. This result suggests a favorable mechanism for soil degradation of these coating materials.

Analyzing the relative reflectance values at 2500, 2000, and 1500 nm, it is possible to observe distinct patterns depending on the Soil and Days (Fig. 4). Although it is not possible to identify the specific material degrading within a soil, as Materials is not significant for these responses, it is evident that all materials buried in universal soil exhibit stable relative reflectance throughout the entire test period, whereas samples in acidic soil show an increasing trend. Considering the results of the previous responses (WL and mechanical properties) this suggests that higher relative reflectance corresponds to a greater degree of degradation when materials are buried in acid soil. Thereafter, it can be concluded that optical spectroscopy could capture the degradation trend only for acid soil. In addition, R2000 (Fig. 4b) allows clear discrimination between the two soil types, as samples degraded in acid soil display higher relative reflectance, also considering the standard error of the trend (dashed lines), compared to those degraded in universal soil.

As described in paragraph 2.6 the desirability function was calculated and results are shown in Fig. 5, with the aim of comparing the behavior of uncoated paper (Fig. 5a) and coated paper samples (Fig. 5b). In this context, it should be reiterated that Table 4 was generated in part based on the results of the ANOVA; therefore, models with low statistical significance (R1500, R2000 and R2500) were taken into account but given little weight. As shown in Fig. 5, the coating application enhances the difference in sample behavior between universal and acid soil, as the universal soil strongly increases desirability and, consequently, degradation. These results suggest that the universal soil acts as a better environment for the degradation of coating as well. Conversely, desirable time appear to be influenced only slightly the coating application, and the possible highest desirability could be reached after 20 days for universal soil and after 22 days for acid soil for any coated sample, considering the results of the calculated model.

3.2. ESEM analysis

The ESEM analysis shows the quality of the coatings obtained for the different samples before (Fig. 6a) and after (Fig. 6b and Fig. 6c) the degradation test. Regarding the samples before the test, all coated samples exhibit a clear difference from UCP, which shows the typical porous structure composed of paper fibers. Among the coated samples, PCLCUGLY has the most uniform coating with no detectable defects. This confirms the positive role of glycerol in improving coating performance, as the use of cutin without glycerol results in some defects related to coating thickness (PCLCU) [28]. Similar defects are observed in PCL, although paper fibers are always coated. The only sample that shows

partially uncoated fibers is SA, indicating that, despite the addition of agar to the mixture, the starch-based coating still presents defects, as previously reported by Lo Faro et al. [29].

Figs. 6b and 6c show the surface of the samples 28 days after burial in universal and acidic soil, respectively. Since the samples buried in universal soil exhibited complete degradation, the images were taken from the portions that remained immediately above the soil, right at the beginning of the degraded sample area. Nevertheless, observing the part located near the degraded sample area still allows some considerations regarding the degradation process. First, the two soils affect the coatings differently. Samples buried in universal soil (Fig. 6b) show coatings characterized by several cracks and detachments in multiple areas, with the only exception of PCLCUGLY, whose coating is almost intact but presents distributed superficial cavities. This result is consistent with the fact that the starting coating structure of PCLCUGLY is the most homogeneous and, as a consequence, less affected by degradation, as defects in the starting material structure may also influence the mechanism of degradation. Acidic soil (Fig. 6c) leads to more varied results, as PCLCU coating shows some cracks, whereas PCLCUGLY and PCL show no apparent signs of coating degradation. In PCL, it is possible to distinguish the structure of the paper fibers under the coating, similarly to the corresponding sample in Fig. 6a. SA, instead, shows complete degradation of the coating, resulting in a surface similar to UCP, made only of damaged paper fibers. These results are also consistent with the fact that the most homogeneous coating (PCLCUGLY) leads to the least degraded materials, and conversely. In addition, it is worth noting that no paper fibers are detectable in the universal soil samples (Fig. 6b) under the detached coatings. Finally, some structures detected during the ESEM analysis (Fig. S1) suggest the presence of fungi and bacteria on the degraded materials, suggesting that biodegradation was at least partially carried out by such organisms.

3.3. FTIR analysis

Fig. 7 shows representative spectra of the undegraded materials. Since there are no significant differences among the coated materials, a representative spectrum for the average coated sample is reported in the figure, only the SA spectrum is reported here. In fact, each FTIR spectrum reflects mainly the PCL one, as it is the main component of each formulation [30,31]. However, clear differences are observed between the spectra of the coated materials and UCP. UCP is the only material that exhibits a broad peak with a maximum in the 3329–3291 cm⁻¹ range, attributed to water molecules directly linked through hydrogen bonds to the OH groups of cellulose and hemicellulose, and a low-intensity peak at 2899 cm⁻¹ corresponding to C–H bond vibrations. In addition, the broad peak at 1027 cm⁻¹ originates from C–OH bond vibrations, while deformation of the C–H bond generates the peak at 660 cm⁻¹ [32].

The undegraded coated sample (Fig. 7) exhibits several peaks that are not present in UCP, such as those at 2943 and 2865 cm⁻¹, generated respectively by the asymmetric and symmetric stretching of CH₂ groups. The peaks around 1471, 1366, and 731 cm⁻¹ are also produced by CH₂, specifically from deformation modes. The strong peak at 1721 cm⁻¹ corresponds to stretching of the C=O in ester or carbonyl groups. The peaks at 1163 and 1107 cm⁻¹ are attributable to symmetric and asymmetric stretching of C–O–C bonds. The peaks around 1419 and 961 cm⁻¹ originate from deformation of O–H in carboxyl groups, while the peaks at 1046 and 1240 cm⁻¹ are associated with stretching of C–O–C and O–H bonds in polysaccharides [33–35].

Degradation of the materials causes some changes in the FTIR, but no specific differences were found between spectra of samples degraded in universal and acidic soil, suggesting that the same mechanism supports the biocoatings degradation independently from the soil, but with different kinetics. Due to this homogeneity, only spectra degraded in acidic soil are shown in Fig. 7, but the other spectra are reported in the Supplementary data as Fig. S3 and Fig. S4. These spectral modifications provide a qualitative understanding of the chemical mechanisms driv-

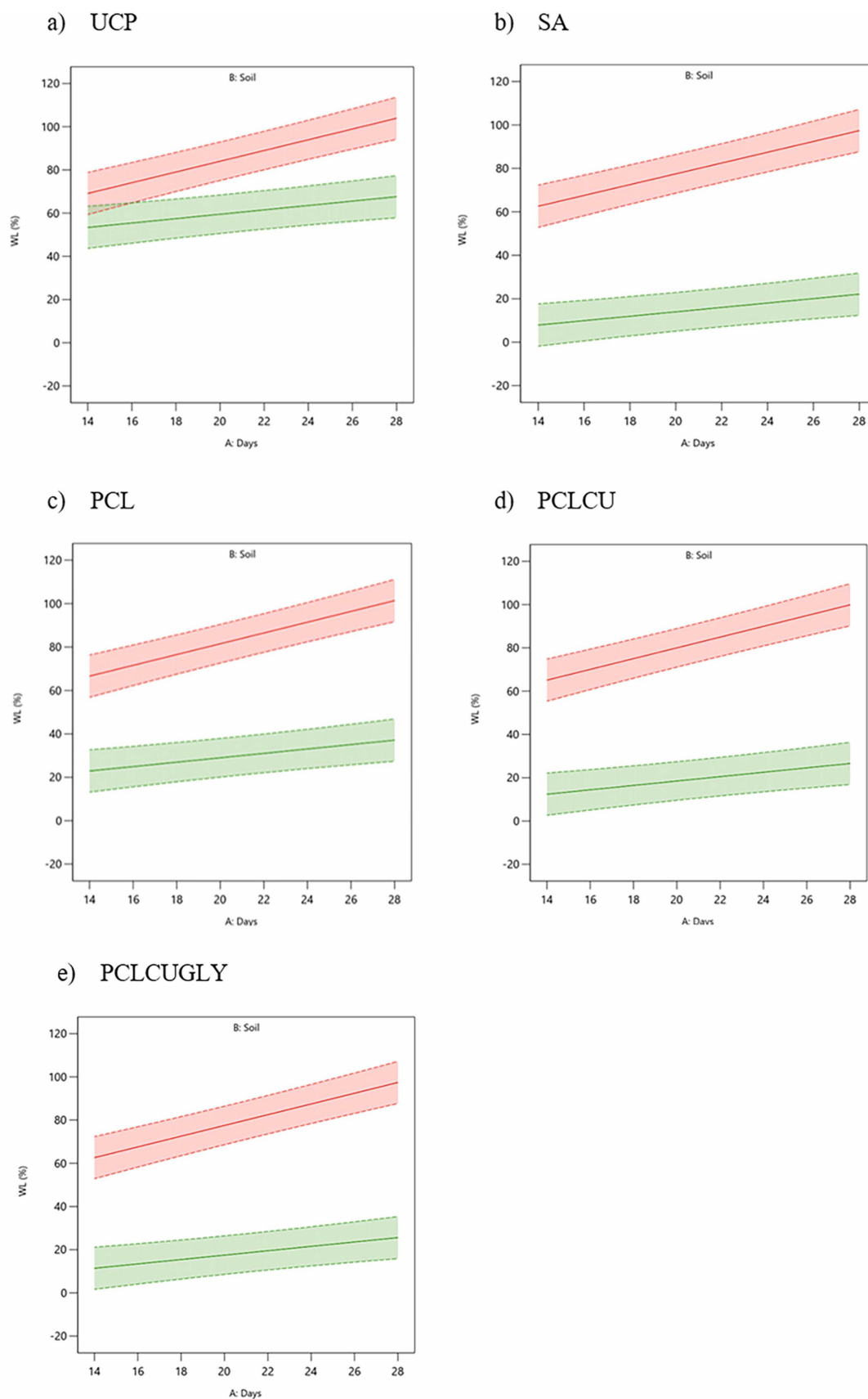


Fig. 2. Interaction plot for the response WL, where RED indicates the result for Universal soil and GREEN indicates the Acid soil a) UCP b) SA c) PCL d) PCLCU e) PCLCUGLY.

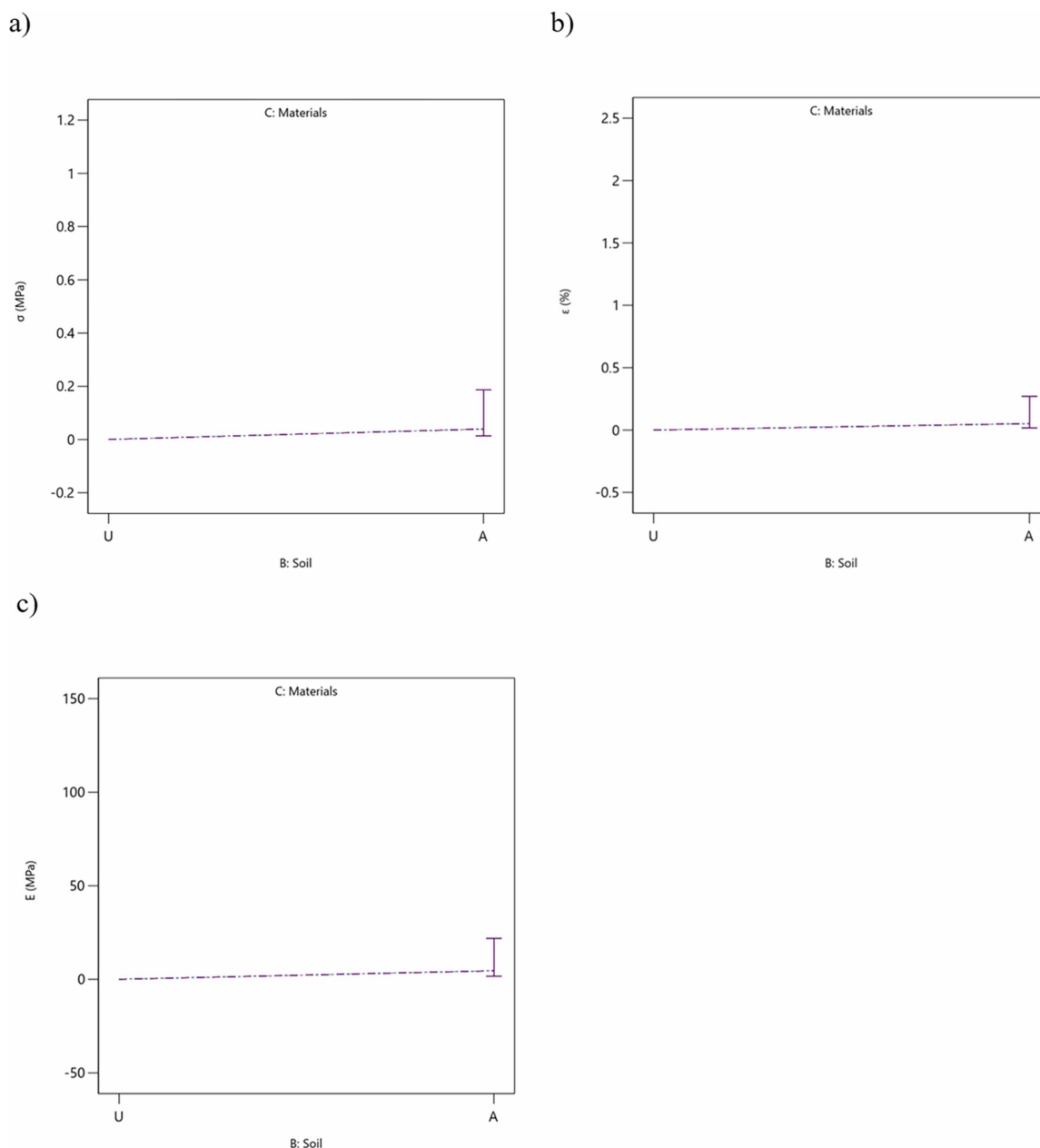


Fig. 3. Interaction plot for the responses of the mechanical properties: a) σ b) ϵ c) E.

ing the degradation process, focused primarily on the cellulose core. In the UCP spectrum, the peak at 2899 cm^{-1} disappears and is replaced by two peaks at 2922 and 2854 cm^{-1} , both originating from CH_2 groups. This shift directly reflects the enzymatic hydrolysis of crystalline cellulose by soil microorganisms [36]; the first peak is often associated with asymmetric stretching of $-\text{CH}_2$ groups due to an increase in less ordered cellulose regions (amorphous cellulose) and low-molecular-weight fragments resulting from chain scission [36]. The second peak is due to symmetric stretching of $-\text{CH}_2$ as chains gain conformational freedom, driven by hydrogen bonding disruption and oxidation that introduces new polar groups nearby.

A second variation in the UCP spectrum is the appearance of peaks at 1639 cm^{-1} and $1547\text{--}1551\text{ cm}^{-1}$. The former is attributed to changes of the H–O–H bond angle, while the origin of the latter can be attributed to Amide II vibration, associated with microbial proteins and enzymatic residues. While these bands inevitably include contributions from the organic matter and microbial biomass absorbed from the surrounding soil matrix, their appearance represents a direct chemical

footprint of suggesting biological colonization during paper biodegradation [37–39]. All degraded coated materials show a new broad peak at $3276\text{--}3282\text{ cm}^{-1}$, attributed to water bound to the material. The peak at $1547\text{--}1551\text{ cm}^{-1}$ can be attributed to Amide II vibration as for UCP. Finally, the peak in the $1627\text{--}1638\text{ cm}^{-1}$ range originates from stretching of $\text{C}\equiv\text{C}$ double bonds and is linked to the presence of phenolic acids, commonly associated to the presence of fungi or humic substances [34], in accordance with what was suggested in by the ESEM analysis in paragraph 3.2. Therefore, rather than a standalone quantitative tool for material mass loss, which was independently assessed via weight loss measurements, FTIR here serves as a powerful qualitative indicator of the polymer-microbe-soil surface interactions [40].

4. Discussion

Weight loss is one of the most frequently used methods for evaluating the biodegradation of polymers due to its simplicity and immediacy in quantifying the changes undergone by a material over time using a

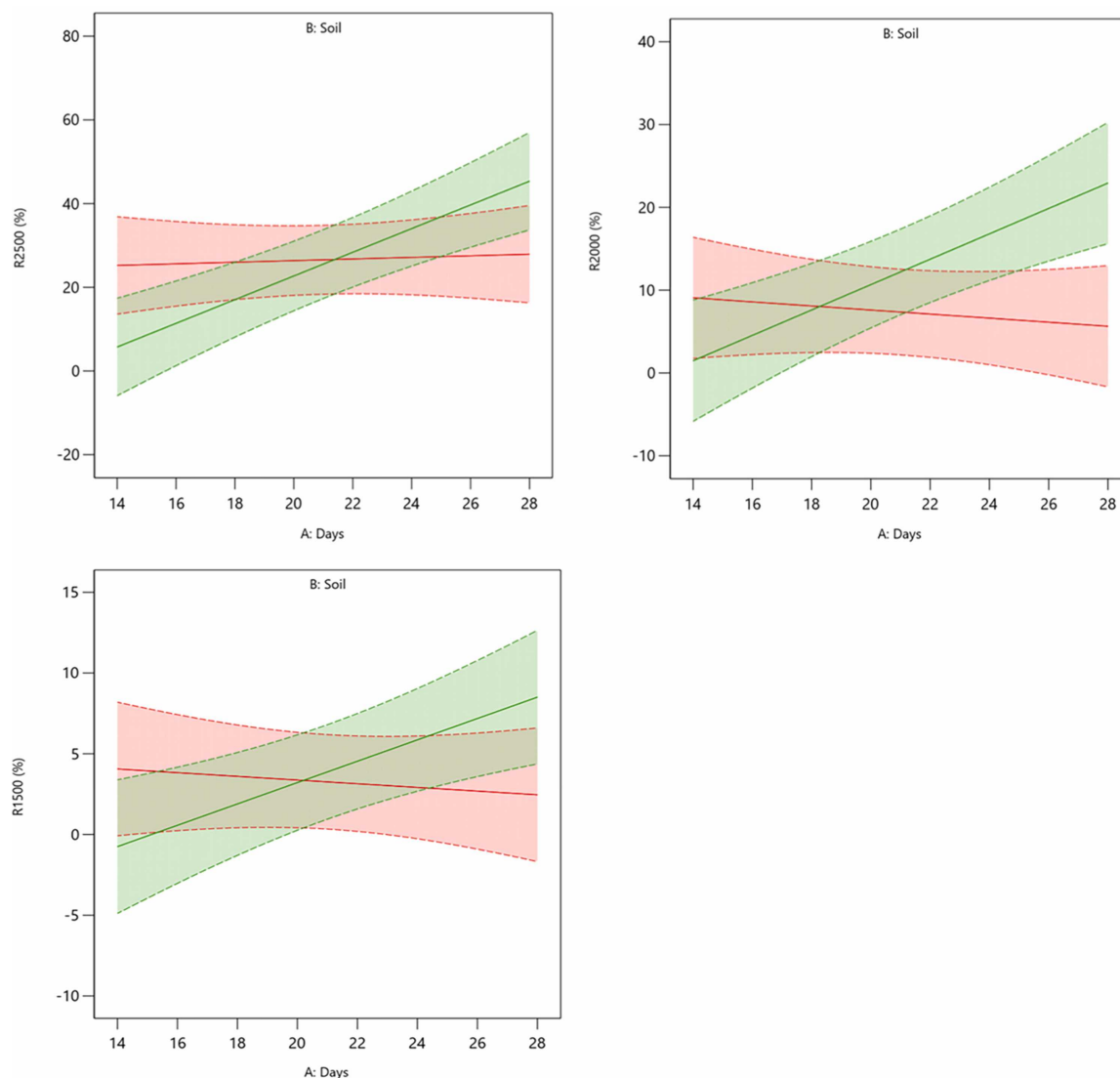


Fig. 4. Interaction plot for the responses of the spectroscopy measurement where RED indicates the result for Universal soil and GREEN indicates the Acid soil: a) R2500 b) R2000 c) R1500.

simple analytical balance. This technique has the advantage of being applicable both in the field and in the laboratory, but there is no guarantee that all fragments (especially those not visible to the naked eye) will be included in the analysis because they may be lost during the sample cleaning process. Since weight loss measurements are difficult to extrapolate, it is preferable to supplement this approach with other analytical methods, such as respirometry or FTIR methods. The weight loss of the polymer alone does not guarantee its absorption by microorganisms, as demonstrated, for example, by respirometry analysis. It is therefore important to perform multiple verification methods on the same sample to obtain a more complete picture of its biodegradation [15].

In Fig. 8, the percentage weight loss of the uncoated control paper samples (UCP) and those coated with the different formulations is shown. The analysis of weight variation over time highlights how both soil type and coating composition strongly influence the degradation kinetics of the coated paper samples. As illustrated in Fig. 8, UCP is the most susceptible material in both soils, as expected since no coating is applied. In universal soil UCP and the other samples showed rapid degradation that was complete (100%) within approximately twenty days, consistent with the calculated 41 desirability function, whereas in acidic soil the process resulted in a weight loss for UCP equal to 71% after 28 days. These results align with recent literature demonstrating that

pH is a critical factor influencing microbial community stability and the efficiency of lignocellulose degradation, with soil acidification known to strongly hinder the decomposition process [41]. Interestingly, despite the initial protective barrier expected from the coatings, the simultaneous 100% weight loss achieved by both UCP and coated formulations within 20 days suggests an aggressive microbial attack in universal soil. In such optimal environments, microorganisms rapidly induce microfissures and pores in the coating layer; once this barrier is breached, the highly hydrophilic underlying cellulose fibers become exposed, leading to an accelerated, autocatalytic degradation process that equals the kinetics of the uncoated control [42].

ESEM analysis highlights these dynamics, since the structure of UCP sample buried in acidic soil (Fig. 6c) clearly shows the paper fibers with limited damage compared with the undegraded material (Fig. 6a), while the sample buried in universal soil shows no recognizable structure of any fiber (Fig. 6b). This confirms the inhibitory effect of low-pH environments on microbial activity [43,44], a phenomenon well-documented in previous studies where unfavorable acidic conditions were shown to reduce or inhibit the activity of degrading microorganisms, ultimately slowing down the degradation of cellulosic materials [45].

The polymeric coatings exhibited a clear barrier effect. PCL showed the highest resistance under both conditions, particularly in acidic soil,

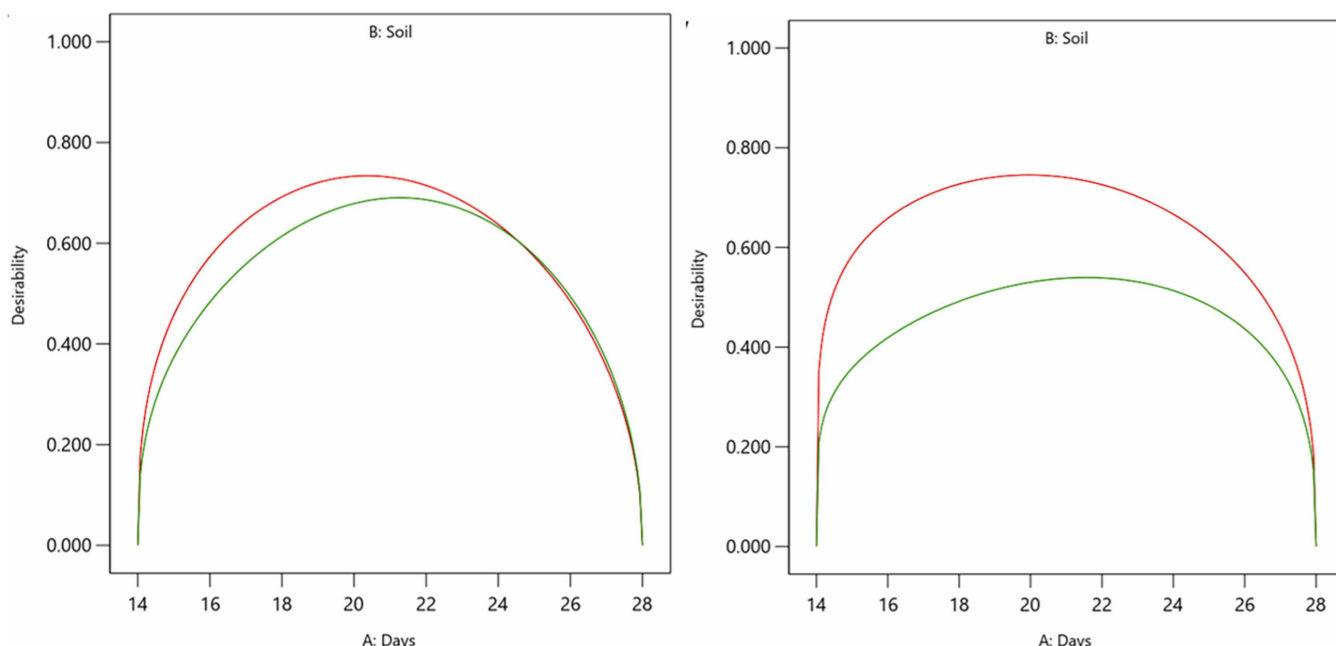


Fig. 5. Desiderability function for Uncoated (a) and Coated sample (average on all the investigated materials) (b); RED indicates the Universal soil and GREEN the acid soil.

where final weight loss was equal to 27% at the end of the test. This observation is consistent with studies reporting the limited hydrolyzability of PCL at extreme pH values and its preferential degradation under neutral or slightly alkaline conditions [46,47]. This is also confirmed by ESEM images, which show that PCL coating is virtually undegraded in the acidic environment (Fig. 6c), but exhibits some defects and cracks after burial in universal soil (Fig. 6b).

In PCLCU, the incorporation of cutin alone into PCL slightly increased susceptibility compared with PCL in acidic soil (WL = 33%, Fig. 8), also leading to the formation of cracks in the coating (Fig. 6c). This likely happened because cutin, although hydrophobic, contains ester linkages that are susceptible to microbial enzymatic attack [48]. Conversely, the addition of glycerol (PCLCUGLY) reduced degradation compared with PCLCU, despite glycerol plasticizing effect, which increases coating permeability. ESEM analysis confirms different dynamics between PCLCU and PCLCUGLY in the two soils. In fact, PCLCU shows a partially intact coating both in universal and acidic soils (Figs. 6b, 6c), while in universal soil PCLCUGLY shows a degraded coating characterized by circular structures maybe due to biological activity (Fig. 6b). On the opposite side, PCLCUGLY samples show almost no defects after 28 days in acidic soil (Fig. 6c). These observations suggest that cutin may promote greater microbial susceptibility. Moreover, both in acidic and universal soils PCLCUGLY samples show weight loss greater than PCL and lower than PCLCU, as shown in Fig. 8. This again suggests that addition of cutin enhances the coating degradation, while addition of glycerol hinders it. The accelerating effect of cutin can be attributed to its structural nature as a plant biopolymer. Its incorporation disrupts the semi-crystalline network of PCL, providing a more amorphous and accessible target for soil-dwelling microorganisms that secrete specialized esterases and cutinases, which are highly efficient in co-degrading PCL matrices [49].

Particularly noteworthy is the weight loss dynamic of SA samples (Fig. 8), which exhibited pronounced degradation in both soil types: complete disappearance within twenty days in universal soil, and significantly lower resistance in acidic soil compared to PCL-only samples (PCL). This trend reflects the well-known susceptibility of starch and other natural polysaccharides to enzymatic and microbial degradation [50,51], indicating that the incorporation of hydrophilic components into coatings accelerates biodeterioration processes even under less favorable conditions. This result is also confirmed by FTIR analysis de-

scribed in paragraph 3.3 and by morphological analysis that shows complete degradation in universal soil (Fig. 6b) and high degradation in acidic soil (Fig. 6c) for PCL samples. Furthermore, also the microscope analysis confirms this mechanism, as the observation through electron microscopy (Fig. S1) detected different structures in several degraded samples that we believe could be reasonably identified as fungal sack-shaped and citriform spores, and bacteria [52–54]. In addition, also color change moving to a yellowish color with green-dark random spots after degradation could indicate the presence of microbial activity (Fig. 9 and Fig. S2).

From a biodegradation standpoint, the "optimal" performance of the developed coatings cannot be defined by a single static parameter, but rather emerges from a precise synergy between the material's chemical formulation and the specific environmental conditions of disposal. Overall, the results clearly demonstrate that the optimal conditions for accelerating degradation kinetics are met in nutrient-rich, neutral soil, which provides the ideal environment to maximize microbial metabolic activity. Conversely, environmental acidity acts as a significant limiting factor, restricting microbial proliferation and consequently decelerating the bio-assimilation process, in strong agreement with the findings of Pandey et al. [55].

In parallel, the tactical choice of the coating components allows for the fine-tuning of these optimal properties based on the target application. The use of a hydrophobic synthetic matrix like PCL, or the inclusion of specific hydrophilic plasticizers, shifts the system toward extended material persistence and prolonged structural stability. On the other hand, the incorporation of natural biopolymers (such as starch, agar, or cutin) breaks this persistence, accelerating the loss of structural integrity of the paper core. Therefore, the "optimal coating property" is inherently tunable: a blend rich in natural components performs optimally for rapid end-of-life disintegration in neutral soils, whereas a higher synthetic-to-natural ratio ensures optimal performance when extended shelf-life or stability in acidic environments is required.

Regarding the mechanical tests performed on the samples before burial and after 14 and 28 days of soil exposure, it was not possible to carry out tensile tests on the samples buried in universal soil. Their degradation had already reached a very high level after just two weeks, making the tests unfeasible. Therefore, only the results obtained from the different types of paper subjected to the soil burial test in acidic soil

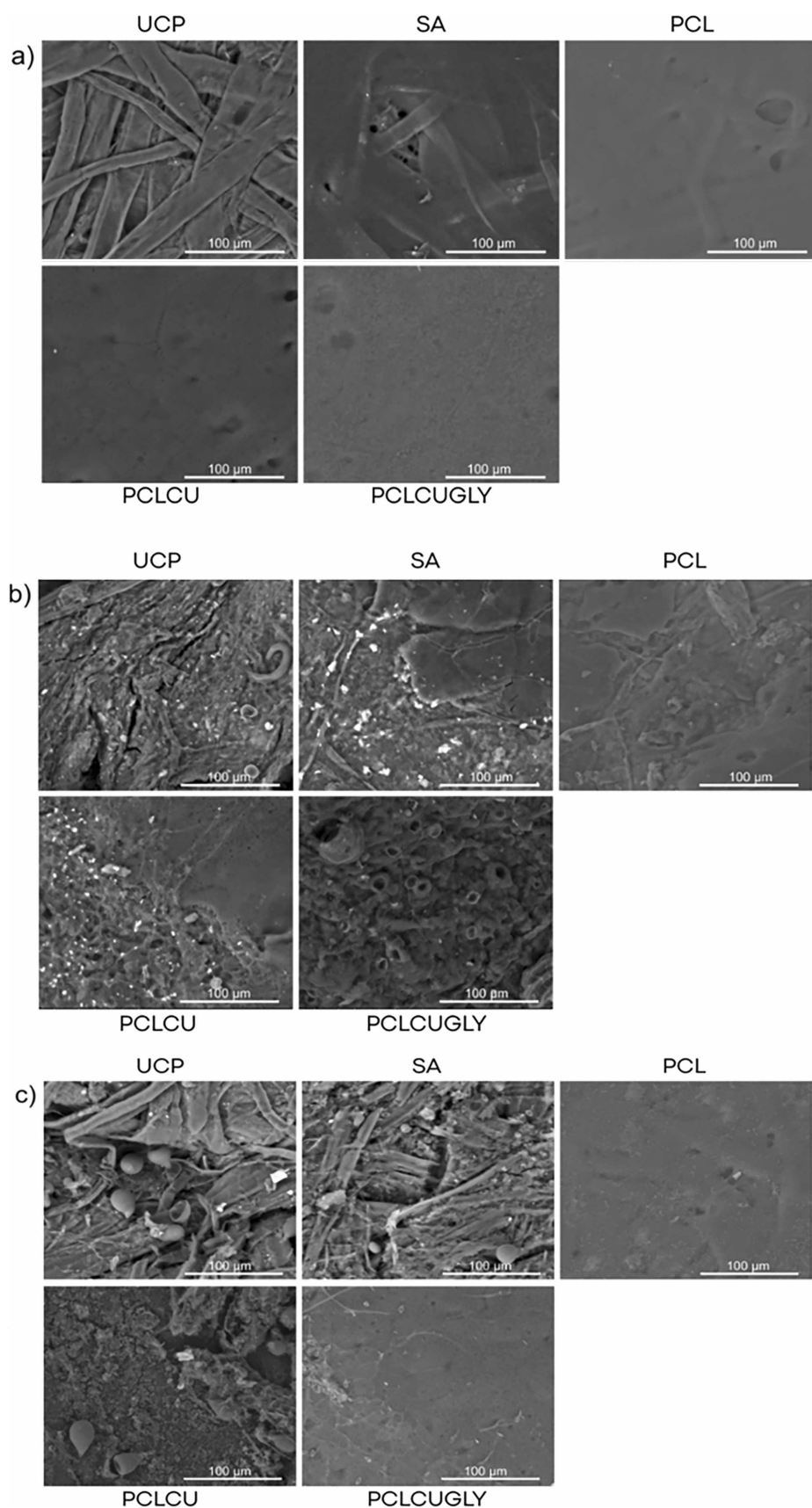


Fig. 6. ESEM images of the uncoated and coated paper samples a) not degraded, b) after 28 days of burial test in universal soil and c) after 28 days of burial test in acidic soil.

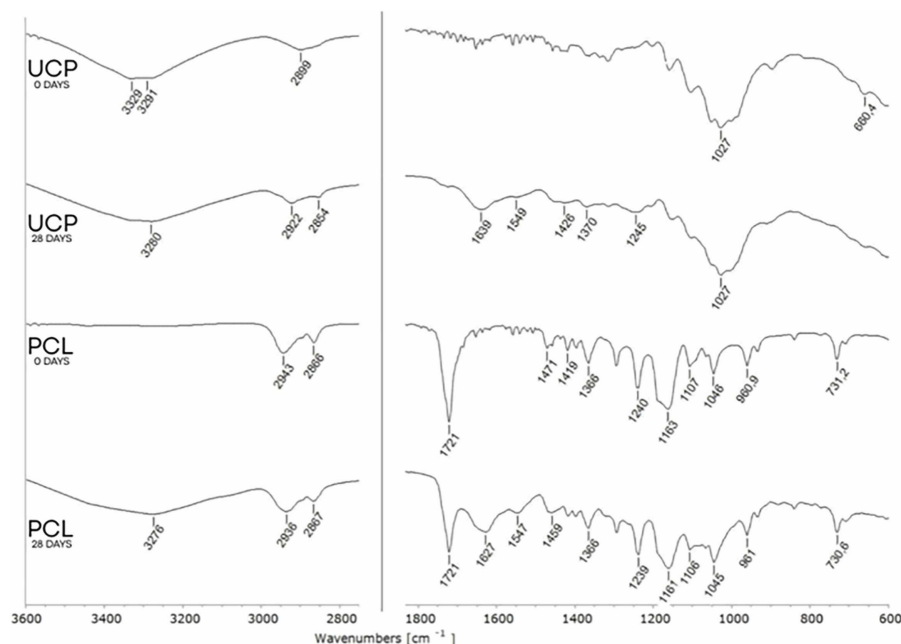


Fig. 7. Selected FTIR spectra of uncoated and coated samples before and at the end of the degradation test.

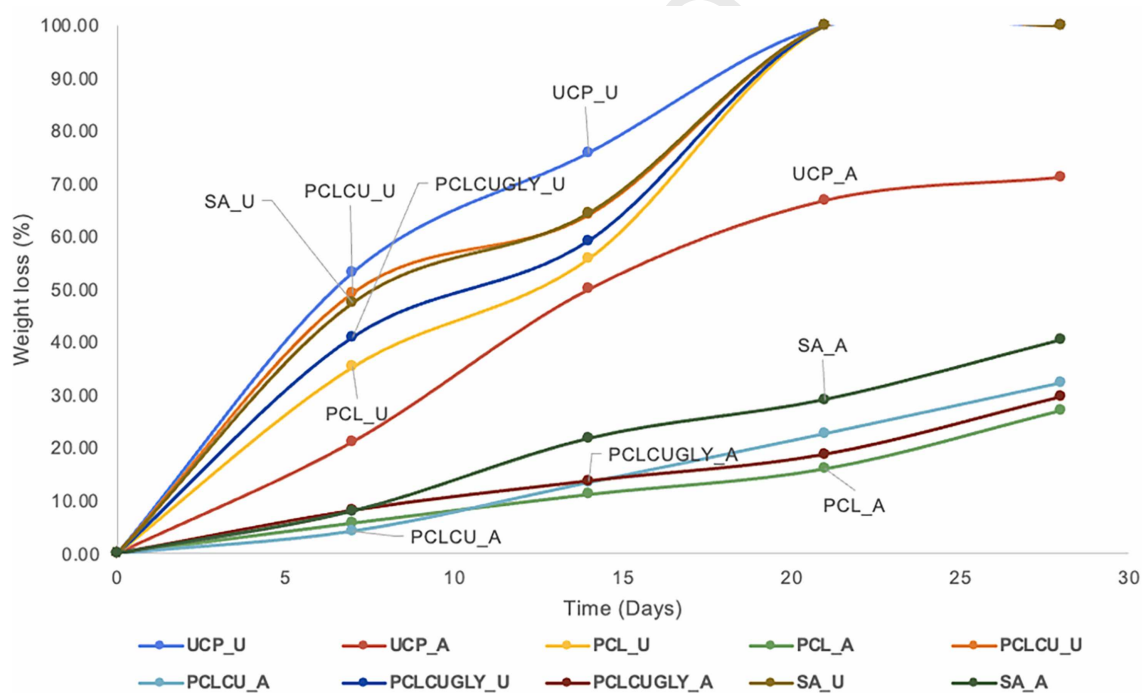


Fig. 8. Weight loss (%) of samples during the 28 days of the burial test in universal (U) and acidic (A) soils (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

will be analyzed below.

The tensile strength analysis (Table 7) revealed significant differences among the tested samples. At T0, the uncoated paper (UCP) exhibited the highest tensile strength (72.22 ± 4.95 MPa), whereas paper coated with PCL (PCL) retained relatively high values (63.90 ± 2.61 MPa). Samples containing cutin (PCLCU and PCLCUGLY) displayed intermediate tensile strength (47.53 ± 4.46 and 50.57 ± 2.09 MPa, respectively), while the SA samples, coated with the PCL/agar/starch mixture, showed the lowest values (31.11 ± 0.27 MPa). Conversely, elongation at break at T0 was highest for the SA samples, with an approximate 25% increase compared to UCP. PCL-coated

samples also exceeded the elongation of UCP, whereas samples containing cutin (PCLCU and PCLCUGLY) exhibited slightly lower elongation values. Regarding the Young's modulus, uncoated paper (UCP) demonstrated the expected high stiffness and low deformability, with values of 9353 ± 337 MPa. Coating with PCL led to a decrease in stiffness, which was further accentuated in samples incorporating cutin (PCLCU and PCLCUGLY). The chemical nature of cutin, composed primarily of lipid esters [56], has been shown to induce heterogeneous microstructures with discontinuities in the polymer network [55,56], resulting in reduced tensile strength and Young's modulus, along with increased flexibility of the coating. The lowest modulus values were



Fig. 9. Qualitative comparison between the samples after 28 days of burial in the two soil types.

Table 7

Mechanical properties measured on samples undegraded (T0) and buried in acidic soil for 14 days (T14) and for 28 days (T28). Samples buried in universal soil were too degraded to allow measurement of any mechanical property. (UCP: Uncoated Paper, SA: Starch-Agar, PCL: Polycaprolactone, CU: Cutin, GLY: Glycerol).

		Tensile Strength			Elongation at the Break			Young's Modulus		
		MPa			%			MPa		
		T0	T14	T28	T0	T14	T28	T0	T14	T28
UCP	average	72.22	/	/	1.41	/	/	9354	/	/
	ds	4.95	/	/	0.10	/	/	337	/	/
PCL	average	63.90	0.73	1.17	1.58	1.42	1.48	7375	102	71
	ds	2.61	0.31	0.22	0.06	0.25	0.15	241	68	2
PCLCU	average	47.53	1.25	/	1.28	1.74	/	6721	56	/
	ds	4.46	0.49	/	0.07	0.35	/	51	18	/
PCLCUGLY	average	50.57	1.42	0.52	1.32	1.20	1.43	6848	90	52
	ds	2.09	0.36	0.43	0.14	0.46	0.21	99	11	20
SA	average	31.11	0.86	0.69	1.88	1.60	1.98	3004	64	57
	ds	0.27	0.37	0.09	0.03	0.90	0.62	314	5	20

observed in SA samples coated with the PCL/agar/starch mixture, in which the polysaccharides were dissolved in water. The presence of water likely contributed to the decrease in Young's modulus, as numerous studies have demonstrated that water absorption in cellulosic substrates facilitates lubrication of cellulose–cellulose interactions and weakens hydrogen bonding, thereby reducing the overall rigidity of the paper [57–60].

A different trend was observed for tensile strength in samples measured at T14 and T28 (14 and 28 days post-burial). Values decreased sharply, often falling below 1 MPa regardless of sample type or time, indicating progressive structural degradation of all coated paper samples. A similar drastic decline was observed in Young's modulus, with values in many cases dropping well below 100 MPa. In contrast, elongation at break remained largely unaffected over the same period.

The degradation results obtained for the biocoated paper highlight the importance of accurately quantifying degradation variables such as degradation rate, half-life, and environmental sensitivity. These parameters provide essential information on how long the coating can maintain its barrier and mechanical functions during use while ensuring efficient degradation at the end of its life cycle. Accurate degradation modeling reduces uncertainty and minimizes the need for over-engineering, which can otherwise increase material consumption by 10–20% [61].

Reliable degradation data also support optimized packaging design and waste management. Even modest reductions in material usage can have substantial economic and environmental benefits; for example, an 8% reduction in packaging weight has been estimated to eliminate approximately 1.6 million tons of material annually and generate savings exceeding USD 3 billion [62].

Furthermore, realistic degradation data improve life cycle assessment accuracy and end-of-life management strategies, with composting

scenarios potentially avoiding up to 5.6 million tons of CO₂-equivalent emissions per year compared with landfill disposal [63]. Therefore, the degradation behavior observed for the biocoating not only demonstrates its biodegradability but also provides quantitative evidence supporting more sustainable and cost-effective paper-based packaging systems. 5. Conclusion

In this study on the biodegradation of biopolymer-coated paper, the factors influencing the rate of decomposition were analyzed. The results show that degradation is mainly dependent on the exposure environment and conditions. It was found that universal soil, having a neutral pH, probably promotes microbial activity, leading to rapid and complete degradation of the material in about twenty days. In contrast, acidic soil significantly slows down the process, keeping degradation below 70% even after almost a month. The type of coating biopolymer was also found to influence the overall degradation rate. Among the materials tested, PCL and glycerol offered the greatest resistance to degradation. Conversely, the addition of cutin reduced overall resistance, accelerating the loss of structural integrity in the paper. Mechanical tensile tests and FTIR analysis confirm these results revealing a significant decline in properties in all samples exposed to acidic soil, except for elongation at break in samples with PCL, while samples in neutral pH soil decomposed before testing could be performed. NIR optical reflectance, tested as a potential low-cost degradation-tracking tool, should be considered as merely and limited preliminary observation, as only acidic-soil degradation appears to correlate meaningfully with NIR reflectance. Future developments arising from this study may involve research into new polymers that integrate the advantages of the materials characterized here, tailored tests useful to determine color alterations in coated materials, as well as specific analyses aimed at assessing microbial activity and identifying the fungi or bacteria that develop on paper samples.

CRediT authorship contribution statement

Emanuela Lo Faro: Formal analysis, Conceptualization. **Silvia Barbi:** Writing – original draft, Software. **Francesco Barbieri:** Investigation, Data curation. **Sara Corradi:** Investigation. **Patrizia Fava:** Writing – review & editing, Supervision. **Monia Montorsi:** Supervision, Funding acquisition.

Funding

This work was supported by the Ecosystem for Sustainable Transition in Emilia- Romagna, project funded by European Union under the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5—NextGenerationEU, Call for tender n. 3277 dated 30/12/2021, Award no.: 0001052 dated 23/06/2022”.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.mtcomm.2026.116189](https://doi.org/10.1016/j.mtcomm.2026.116189).

Data availability

All the data are reported in the submitted paper.

References

- [1] European Commission, Commission Staff Working Document: Measuring progress towards a circular economy - a monitoring framework, SWD(2023) 306 final, Brussels, 2023. Available on EUR-Lex: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52023DC0306>.
- [2] M.J. Ahmed, J. Ashfaq, Z. Sohail, I.A. Channa, A. Sánchez-Ferrer, S.N. Ali, A.D. Chandio, Lignocellulosic bioplastics in sustainable packaging – recent developments in materials design and processing: a comprehensive review, *Sustain. Mater. Technol.* 41 (2024) e01077, <https://doi.org/10.1016/j.susmat.2024.e01077>.
- [3] B. Zdanikowski, J. Szalapak, A. Kądziała, T. Cigula, M. Vukoje, S. Lepak-Kuc, M. Jakubowska, Z. Żolek-Tryznowska, Development of environmentally friendly flexible electronics based on ethyl cellulose – silver microflakes composite, *Mater. Des.* 260 (2025) 114981, <https://doi.org/10.1016/j.matdes.2025.114981>.
- [4] E. Lo Faro, K. Park, K. Sadeghi, P. Fava, J. Seo, Antimicrobial coating films: development by adding zinc–melamine complex to polyvinyl alcohol and antimicrobial performance, *Prog. Org. Coat.* 198 (2025) 108420, <https://doi.org/10.1016/j.porgcoat.2024.108420>.
- [5] B. Shin, A.K. Singh, N. Bumbudsanpharoke, S. Ko, Biodegradable polyester–starch composite films functionalized with phenolic compounds: advances, challenges, and prospects for sustainable active packaging, *Polymers* 18 (2026) 1437, <https://doi.org/10.3390/polym18121437>.
- [6] S. Nizamuddin, A.J. Baloch, C. Chen, M. Arif, N.M. Mubarak, Bio-based plastics, biodegradable plastics, and compostable plastics: biodegradation mechanism, biodegradability standards and environmental stratagem, *Int. Biodeterior.* Biodegrad. 195 (2024) 105887, <https://doi.org/10.1016/j.ibiod.2024.105887>.
- [7] N. Jannatiha, T.J. Gutiérrez, Recycling and revalorization of PLA and PHA-based food packaging waste: a review, *Sustain. Mater. Technol.* 44 (2025) e01364, <https://doi.org/10.1016/j.susmat.2025.e01364>.
- [8] D. Poddar, K. Pandey, S.-J. Kim, H.M. Yoo, Development of electrosprayed assisted shellac-MOF particle coated paper for food packaging and its environmental impacts, *Sustain. Mater. Technol.* 42 (2024) e01192, <https://doi.org/10.1016/j.susmat.2024.e01192>.
- [9] H. Eslami, T.H. Mekonnen, Flexible and green multilayer paper coating for barrier enhancement of paper packaging, *Sustain. Mater. Technol.* 37 (2023) e00694, <https://doi.org/10.1016/j.susmat.2023.e00694>.
- [10] Y. Zhang, H. Luo, Y. Li, Z. Li, Y. Wen, Z. Wang, B. Fan, Q. Li, Y. Li, Antimicrobial keratin-based sustainable food packaging films reinforced with citric acid-modified cellulose nanocrystals, *Sustain. Mater. Technol.* 42 (2024) e01133, <https://doi.org/10.1016/j.susmat.2024.e01133>.
- [11] Y. Zhou, R. Zhang, Y. Hu, X. Liang, Z. Feng, W. Li, L. Yang, Z. Long, A superhydrophobic, self-healing, and recyclable cellulose paper based on a dynamically cross-linked interface for packaging applications in high-humidity environments, *Sustain. Mater. Technol.* 45 (2025) e01629, <https://doi.org/10.1016/j.susmat.2025.e01629>.
- [12] S. Jiang, Y. Liang, S. Shi, C. Wu, Z. Shi, Improving predictions and understanding of primary and ultimate biodegradation rates with machine learning models, *Sci. Total Environ.* 904 (2023) 166623, <https://doi.org/10.1016/j.scitotenv.2023.166623>.
- [13] N.T. Dintcheva, Overview of polymers and biopolymers degradation and stabilization towards sustainability and materials circularity, *Polymer* 306 (2024) 127136, <https://doi.org/10.1016/j.polymer.2024.127136>.
- [14] V. Suresh, R. Shams, K.K. Dash, A.M. Shaikh, K. Béla, Comprehensive review on enzymatic polymer degradation: a sustainable solution for plastics, *J. Agric. Food Res.* 20 (2025) 101788, <https://doi.org/10.1016/j.jafr.2025.101788>.
- [15] S. Baidurah, Methods of analyses for biodegradable polymers: a review, *Polymers* 14 (2022) 4928, <https://doi.org/10.3390/polym14224928>.
- [16] G.I. Edo, W. Ndudi, A.B.M. Ali, E. Yousif, A.N. Jikah, E.F. Isoje, U.A. Igbuku, A.N. Mafe, R.A. Opiti, C.J. Madueke, A.E.A. Essagah, D.S. Ahmed, H. Umar, Biopolymers: an inclusive review, *Hybrid Adv.* 9 (2025) 100418, <https://doi.org/10.1016/j.hybadv.2025.100418>.
- [17] D. Briassoulis, A. Mistriotis, N. Mortier, M. Tosin, A horizontal test method for biodegradation in soil of bio-based and conventional plastics and lubricants, *J. Clean. Prod.* 242 (2020) 118392, <https://doi.org/10.1016/j.jclepro.2019.118392>.
- [18] E. Malekzadeh, A. Tatari, M. Dehghani Firouzabadi, Effects of biodegradation of starch-nanocellulose films incorporated with black tea extract on soil quality, *Sci. Rep.* 14 (2024) 16841, <https://doi.org/10.1038/s41598-024-69841-2>.
- [19] A. Hejna, M. Barczewski, P. Kosmela, O. Mysiuikiewicz, M.R. Saeb, Soil burial degradation of chemically compatibilized poly(butylene adipate-co-terephthalate)/thermoplastic starch/poly(ϵ -caprolactone)/cellulose biocomposites, *Int. J. Biol. Macromol.* 282 (2024) 136801, <https://doi.org/10.1016/j.ijbiomac.2024.136801>.
- [20] F. Convertino, S.C. Carroccio, M.C. Cocca, S. Dattilo, A.C. Dell'Acqua, L. Gargiulo, L. Nizzetto, P.M. Riccobene, E. Schettini, G. Vox, D. Zannini, P. Cerruti, The fate of post-use biodegradable PBAT-based mulch films buried in agricultural soil, *Sci. Total Environ.* 948 (2024) 174697, <https://doi.org/10.1016/j.scitotenv.2024.174697>.
- [21] S.S. Rumi, S. Liyanage, N. Abidi, Soil burial-induced degradation of cellulose films in a moisture-controlled environment, *Sci. Rep.* 14 (2024) 6921, <https://doi.org/10.1038/s41598-024-57436-w>.
- [22] A. Dirpan, A.F. Ainani, M. Djalal, A review on biopolymer-based biodegradable film for food packaging: Trends over the last decade and future research, *Polymers* 15 (2023) 2781, <https://doi.org/10.3390/polym15132781>.
- [23] UNI EN 12580:2023, Soil Improvers and Growing Media – Determination of a Quantity, Ente Nazionale Italiano di Unificazione (UNI), Milan, Italy, 2023.
- [24] ISO 846, Plastics — Evaluation of the Action of Microorganisms, International Organization for Standardization, 2019.
- [25] S. Ahmed, A.M. Hall, S.F. Ahmed, Comparative biodegradability assessment of different types of paper, *J. Nat. Sci. Res.* 8 (2018) 9–20.
- [26] ASTM D882-18, Standard Test Method for Tensile Properties of Thin Plastic Sheeting, ASTM International, West Conshohocken, PA, USA, 2018.
- [27] D.C. Montgomery, *Design and Analysis of Experiments*, 10th ed., John Wiley & Sons Inc., Hoboken, NJ, USA, 2021.
- [28] J.A. Heredia-Guerrero, A. Heredia, E. Domínguez, R. Cingolani, I.S. Bayer, A. Athanassiou, J.J. Benítez, Cutin from agro-waste as a raw material for the production of bioplastics, *J. Exp. Bot.* 68 (2017) 5401–5410, <https://doi.org/10.1093/jxb/erx272>.
- [29] E. Lo Faro, A. Bonofiglio, S. Barbi, M. Montorsi, P. Fava, Polycaprolactone/starch/agar coatings for food-packaging paper: statistical correlation of the formulations' effect on diffusion, grease resistance, and mechanical properties, *Polymers* 15 (2023) 3921, <https://doi.org/10.3390/polym15193921>.
- [30] K. Phillipson, J.N. Hay, M.J. Jenkins, Thermal analysis FTIR spectroscopy of poly(ϵ -caprolactone), *Thermochim. Acta* 595 (2014) 74–82, <https://doi.org/10.1016/j.tca.2014.08.027>.
- [31] T. Elzein, M. Nasser-Eddine, C. Delaite, S. Bistac, P. Dumas, FTIR study of polycaprolactone chain organization at interfaces, *J. Colloid Interface Sci.* 273 (2004) 381–387, <https://doi.org/10.1016/j.jcis.2004.02.001>.
- [32] R. Pavithra, S. Gunasekaran, E. Sailatha, S. Kamatchi, Investigations on paper making raw materials and determination of paper quality by FTIR-UATR and UV-Vis DRS spectroscopy, *Int. J. Curr. Res. Acad. Rev.* 3 (2015) 42–59.
- [33] S. Salehpour, M.A. Dubé, Reaction monitoring of glycerol step-growth polymerization using ATR-FTIR spectroscopy, *Macromol. React. Eng.* 6 (2011) 85–92, <https://doi.org/10.1002/mren.201100071>.
- [34] A. Cifarelli, I. Cigognini, L. Bolzoni, A. Montanari, Cutin isolated from tomato processing by-products: extraction methods and characterization, in: *Proceedings of the 4th International Conference on Sustainable Solid Waste Management*, Cyprus, 2016.
- [35] C. Pozo, S. Rodríguez-Llamazares, R. Bouza, L. Barral, J. Castaño, N. Müller, I. Restrepo, Study of the structural order of native starch granules using combined FTIR and XRD analysis, *J. Polym. Res.* 25 (2018) 1651, <https://doi.org/10.1007/s10965-018-1651-y>.
- [36] E. Malekzadeh, A. Tatari, M. Dehghani Firouzabadi, Effects of biodegradation of starch-nanocellulose films incorporated with black tea extract on soil quality, *Sci. Rep.* 14 (2024) 18817, <https://doi.org/10.1038/s41598-024-69841-2>.
- [37] A.C.S. Talari, M.A.G. Martinez, Z. Movasaghi, S. Rehman, I.U. Rehman, Advances in Fourier transform infrared (FTIR) spectroscopy of biological tissues, *Appl. Spectrosc. Rev.* 52 (2016) 456–506, <https://doi.org/10.1080/05704928.2016.1230863>.
- [38] S. Chatterley, P. Laity, C. Holland, T. Weidner, S. Woutersen, G. Giubertoni, Broadband multidimensional spectroscopy identifies the Amide II vibrations in silkworm films, *Molecules* 27 (2022) 6275, <https://doi.org/10.3390/molecules27196275>.
- [39] A.A. Shah, F. Hasan, A. Hameed, S. Ahmed, Biological degradation of plastics: a comprehensive review, *Biotechnol. Adv.* 26 (2008) 246–265, <https://doi.org/10.1016/j.biotechadv.2007.12.005>.
- [40] S. Kliem, M. Kreutzbruck, C. Bonten, Review on the biological degradation of polymers in various environments, *Materials* 13 (2020) 4586, <https://doi.org/10.3390/ma13204586>.
- [41] Y. Wang, Y. Chen, X. Gao, Q. Wang, M. Cui, D. Zhang, P. Guo, Unveiling the driving role of pH on community stability and function during lignocellulose degradation in paddy soil, *Front. Microbiol.* 15 (2024) 1338842, <https://doi.org/10.3389/fmicb.2024.1338842>.
- [42] W. Sridach, K.T. Hodgson, M.M. Nazhad, Biodegradation of paperboards, *BioResources* 2 (2007) 179–192.
- [43] B. Zhao, Y. Wang, L. Li, L. Ma, Y. Deng, Z. Xu, Adjusting pH of the secondary composting materials to further enhance the lignocellulose degradation and promote the humification process, *Sustainability* 15 (2023) 9032, <https://doi.org/10.3390/su1519032>.
- [44] M. Tuomela, Biodegradation of lignin in a compost environment: a review, *Bioresour. Technol.* 72 (2000) 169–183, [https://doi.org/10.1016/S0960-8524\(99\)00104-2](https://doi.org/10.1016/S0960-8524(99)00104-2).
- [45] R.W. Chia, J.-Y. Lee, H. Kim, J. Jang, Microplastic pollution in soil and groundwater: a review, *Environ. Chem. Lett.* 19 (2021) 4211–4224, <https://doi.org/10.1007/s10311-021-01297-6>.

- [46] M.A. Woodruff, D.W. Hutmacher, The return of a forgotten polymer—polycaprolactone in the 21st century, *Prog. Polym. Sci.* 35 (2010) 1217–1256, <https://doi.org/10.1016/j.progpolymsci.2010.04.002>.
- [47] M. Karamanlioglu, R. Preziosi, G.D. Robson, Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): a review, *Polym. Degrad. Stab.* 137 (2017) 122–130, <https://doi.org/10.1016/j.polymdegradstab.2017.01.009>.
- [48] S. Singha, V. Gowda, M.S. Hedenqvist, Plant cuticle-inspired polyesters as promising green and sustainable polymer materials, *ACS Appl. Polym. Mater.* 3 (2021) 4088–4100, <https://doi.org/10.1021/acscapm.1c00585>.
- [49] A. Sánchez-Reyes, M.Á. Martín-Lara, G. Blázquez, M. Calero, Biodegradation of poly(ϵ -caprolactone): microorganisms, enzymes, and mechanisms, *Int. J. Mol. Sci.* 26 (2025) 5826, <https://doi.org/10.3390/ijms26125826>.
- [50] E. Chiellini, A. Corti, S. D'Antone, R. Solaro, Biodegradation of poly (vinyl alcohol) based materials, *Prog. Polym. Sci.* 28 (2003) 963–1014, [https://doi.org/10.1016/s0079-6700\(02\)00149-1](https://doi.org/10.1016/s0079-6700(02)00149-1).
- [51] M. Avella, J.J. De Vlieger, M.E. Errico, S. Fischer, P. Vacca, M.G. Volpe, Biodegradable starch/clay nanocomposite films for food packaging applications, *Food Chem.* 93 (2005) 467–474, <https://doi.org/10.1016/j.foodchem.2004.10.024>.
- [52] J. Porras-Saavedra, E. Palacios-González, T. Tovar-Benítez, H. Contreras-Lavida, E.P. Houbbron, M. Canul-Chan, Development, soil biodegradation, and kinetics evaluation of starch-based bioplastic from *Sechium edule* and *Phaseolus vulgaris*, *Waste Biomass Valoriz.* 16 (2025) 1353–1367, <https://doi.org/10.1007/s12649-024-02734-7>.
- [53] J. Augustine, J. Abraham, Fungal biodegradation of amlodipine and lisinopril by *Penicillium citrinum*: towards a sustainable approach to pharmaceutical wastewater treatment, *Curr. Microbiol.* 82 (2025) 348, <https://doi.org/10.1007/s00284-025-04330-x>.
- [54] W. Shang, H. Xin, X. Hou, L. Wu, L. Wu, Multifunctional SERS substrate for simultaneous detection of multiple contaminants and photothermal removal of pathogenic bacteria, *ACS Appl. Mater. Interfaces* 16 (2024) 51679–51689, <https://doi.org/10.1021/acscami.4c10473>.
- [55] K. Pandey, D. Poddar, H. Yoo, pH-responsive cellulose nano fiber entrapped thyme oil composite coated paper for active paper packaging, *Sustain. Mater. Technol.* 46 (2025) e01723, <https://doi.org/10.1016/j.susmat.2025.e01723>.
- [56] G.C. Arya, S. Sarkar, E. Manasheroova, A. Aharoni, H. Cohen, The plant cuticle: an ancient guardian barrier set against long-standing rivals, *Front. Plant Sci.* 12 (2021) 663165, <https://doi.org/10.3389/fpls.2021.663165>.
- [57] S. Acosta, A. Jiménez, M. Cháfer, C. González-Martínez, A. Chiralt, Physical properties and stability of starch-gelatin based films as affected by the addition of esters of fatty acids, *Food Hydrocoll.* 49 (2015) 135–143, <https://doi.org/10.1016/j.foodhyd.2015.03.015>.
- [58] S. Mukherjee, A. Sengupta, S. Preetam, T. Das, T. Bhattacharya, N. Thorat, Effects of fatty acid esters on mechanical, thermal, microbial, and moisture barrier properties of carboxymethyl cellulose-based edible films, *Carbohydr. Polym. Technol. Appl.* 7 (2024) 100505, <https://doi.org/10.1016/j.carpta.2024.100505>.
- [59] B. Lin, J. Auernhammer, J.-L. Schäfer, R.W. Stark, T. Meckel, M. Biesalski, B.-X. Xu, Humidity influence on mechanics of paper materials: joint numerical and experimental study on fiber and fiber network scale, *Cellulose* 29 (2022) 1129–1148, <https://doi.org/10.1007/s10570-021-04355-y>.
- [60] C. Helbrecht, F. Schmitt, T. Meckel, M. Biesalski, B.J.M. Etzold, S. Schabel, Mechanical properties of paper saturated with a hydrophobic ionic liquid, *BioResources* 18 (2023) 2842–2856.
- [61] T. Garbowski, Evaluating safety factors in corrugated packaging for extreme environmental conditions, *Packag. Rev.* 1 (2024) 6–15, <https://doi.org/10.15199/42.2023.4.1>.
- [62] E.D. Georgakoudis, G.G. Pechlivanidou, N.S. Tipi, Sustainable packaging design: packaging optimization and material reduction for environmental protection and economic benefits to industry and society, *Appl. Sci.* 15 (2025) 8289, <https://doi.org/10.3390/app15158289>.
- [63] Biorepack & Sustainable Development Foundation, Environmental and Economic Impact Assessment of Compostable Plastics Recycling in Europe, Institutional Report, Rome, 2024. Available online: <https://www.biorepack.org>.