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Polycaprolactone/cutin blends for the improvement of moisture barrier and grease resistance of paper for food use

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ABSTRACT

The increasing demand for sustainable food packaging has driven interest in biodegradable coatings to enhance the functional properties of paper-based materials, whose poor moisture barrier and grease resistance limit direct application in food packaging. This study investigates the potential of polycaprolactone (PCL)/cutin blend-based coatings at improving the functional properties of paper intended for food packaging applications. Two different PCL:cutin ratios (1:0.6 and 1:1) were applied on paper, with and without glycerol, as single and double-layer using the bar coating technique. The coated samples were evaluated for water vapor transmission rate (WVTR), grease resistance, contact angle, mechanical strength and seal strength. The findings indicate that the coatings significantly enhanced the moisture barrier, achieving a reduction of about 90 % of the WVTR with a double-layer coating made with PCL:cutin ratio of 1:0.6 (405 ± 12 g·day^{-1}·m^{-2}), compared to uncoated paper (4348 ± 69 g·day^{-1}·m^{-2}). Grease resistance tests confirmed that all coated samples exhibited maximum oil repellency, maintaining effectiveness even after mechanical folding. These results highlight the functionality of cutin, a naturally derived biopolymer, in enhancing PCL-based coatings as an effective and eco-friendly alternative for food packaging. The optimal formulation (PCL:cutin 1:0.6, double-layer coating) ensures moisture and grease resistance, good mechanical properties, making it a promising sustainable solution for the packaging industry.

1. Introduction

The environment is being adversely affected by the continuing rise in pollution, which is impairing the Earth's regenerative capabilities.

Consequently, there is a growing inclination among consumers to adopt conscientious and sustainable consumption habits. In fact, consumers are increasingly expressing a desire for packaging that generates less waste, utilizes reusable materials, recyclable or compostable once consumed (Otto et al., 2021).

Until now, consumers have generally held a negative perception of food packaging, primarily due to factors such as the use of petrochemical resources and the generation of waste that pollutes the oceans (Bauer et al., 2023). As a result, consumers are increasingly open to new packaging innovations that utilize renewable resources, biodegradable plastics, and offer improved recycling possibilities. Packaging, particularly in the realm of food packaging, has to be designed and conceptualized with recycling and recovery in mind, either through complete or partial processes, benefiting the environment and conserving materials and energy. The end of life has become a recurring theme and always more often packaging sustainability is a reason for choice of a food product (Hull et al., 2022).

As a consequence, there is a notable consumer perception favoring paper and cardboard for food packaging, as they are viewed as more environmentally friendly (Otto et al., 2021). Furthermore, the interest on the use paper as packaging material is growing, because it offers two elements crucial for the current environmental context: functionality and compostability. Nevertheless, paper's physical properties are not always optimal, particularly its resistance to moisture and grease. Therefore, the scientific community is increasingly focused on improving the physical characteristics of paper and cardboard and enhancing their functionality, as antimicrobial and antioxidant properties, to enable wider application in the field of food packaging (Lo Faro et al., 2024; He et al., 2021; Kunam et al., 2024; Zhu et al., 2023).

Among biodegradable polymers one of the most promising is poly (ε-caprolactone) (PCL), which is widely utilized in the formulation of coatings, including those for paper. PCL can be used alone (Lo Faro et al.,

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2021; Cigula et al., 2020) or in blends combined with other polymers (Lo Faro et al., 2023; Sundar et al., 2020; Sachan et al., 2023). PCL is a flexible, biodegradable aliphatic polyester synthesized from petroleum sources. It is notable for its low glass transition temperature (Tg) of −60 °C and a melting temperature (Tm) that ranges between 55 and 70 °C. PCL is produced through the ring-opening polymerization of ε-caprolactone (ε-CL), a process that facilitates the formation of long polymer chains.

PCL exhibits relatively high hydrophobicity and a degree of crystallinity between 45 % and 60 %. While these structural characteristics generally reduce the accessibility of polymer chains to microorganisms — since biodegradation predominantly occurs in the amorphous regions — PCL is still considered a biodegradable polymer due to the enzymatic activity of lipases and other microorganisms (Goldberg, 1995; Mohamed & Yusoh, 2016; Auras et al., 2022; Detyothin et al., 2010). The combination of flexibility, biodegradability, and favorable thermal properties makes PCL an attractive material for various applications, particularly in areas such as packaging, biomedical devices and coatings.

Due to its biodegradability, PCL is increasingly being explored as an eco-friendly alternative to traditional petroleum-based plastics, especially in applications where sustainable materials are desired. Its ability to degrade in natural environments makes it suitable for use in coatings, where it can provide functional benefits while minimizing environmental impact (Fayyazbakhsh et al., 2025).

Another promising biodegradable polymer of natural origin is cutin. Cutin is a biopolymer found in the cell walls of higher plants, primarily composed of long-chain fatty acids (C16 and C18) that are esterified to form a complex three-dimensional structure. This unique chemical composition endows cutin with several desirable properties, including excellent film-forming capabilities, high hydrophobicity, and superior resistance to water vapor and other environmental factors (Simões et al., 2023; Hood et al., 2021). The film-forming ability of cutin could allow it to create effective barriers on paper substrates, enhancing their performance in packaging applications (Manrich et al., 2017). This is particularly important for food packaging, where moisture and gas permeability can significantly impact the shelf life and quality of the packaged products (Mengozzi et al., 2025). By incorporating cutin into coatings for food packaging, it could be possible to improve the barrier properties of paper. Additionally, cutin's natural origin and biodegradability make it an attractive alternative to conventional synthetic coatings, which often have environmental drawbacks. As consumers and industries increasingly prioritize sustainability, cutin-based coatings can provide a viable solution that aligns with eco-friendly packaging initiatives (Benítez et al., 2020).

Specifically, cutin can be extracted from by-products such as tomato seeds and peels, as described by Cifarelli et al. (2016). This approach is motivated by the fact that a small processing plant manages to generate about 2000–2500 kg of by-products from every 110,000 kg of fresh tomato; equal to 1.8–2.3 % of production in the form of peels and seeds. Furthermore, considering that tomatoes ranked as the most produced vegetable with 186 million tonnes processed globally in 2022 (lFAO, 2023), it is evident that there is a significant annual availability of by-products of tomato processing that can be exploited for cutin extraction.

The main goal of this study is to enhance the performance of paper for direct food contact by coating it with biodegradable polymers, enabling biodegradable packaging solutions. In this context, we prioritize biodegradability over bio-renewability, as the persistence of non-degradable materials represents a major environmental issue. PCL, although fossil-based, was selected for its biodegradability, processability, and mechanical properties, offering a balanced approach to sustainability that considers both material origin and end-of-life management.

Various coating solutions were prepared by solubilizing polycaprolactone (PCL) at a concentration of 10 % w/v in ethyl acetate and mixing it with different ratio of polymer:cutin (a ratio of polymer:cutin of 1:0.6 and 1:1), with or without the addition of glycerol. Glycerol was optionally included in the formulations to investigate its potential role in enhancing the penetration of the coating into the pores of the paper. Coated paper samples were evaluated for several properties, including thickness, grammage, WVTR, contact angles with water and oil, grease resistance (using Kit 12), and mechanical properties.

2. Materials and methods

2.1. Materials

In this work, a calendered bleached paper (Advantage MG White High Gloss, Mondi Group, Addlestone, UK) was used, kindly supplied by C.C.M. Coop. Cartai Modenese Soc. Coop. (Modena, Italy); in Table 1 its technical data are shown. PCL was purchased from Sigma Aldrich (Taufkirchen, Germany), with an average MW of 80,000 g/mol, a water content < 0.5 % and a melt flow index (160 °C/5 kg) of 2.01–4.03. Ethyl acetate (Ethyl acetate - ACS reagent, purity > 99.5 %, Mw: 88.11 g/mol) and glycerol (1,2,3- Propanetriol, Glycerin, purity > 99.5 %, Mw: 92.09 g/mol) were purchased from Sigma Aldrich (Taufkirchen, Germany). The cutin was supplied by the company TOMAPAINT s.r.l. (Parma, Italy) and is provided with food-grade certification, according to European (Regulation EU 10/2011 and subsequent updates and modifications) and American (FDA Title 21 CFR, Cap 1, Subpart B and C) legislation. It consists of a high-purity resin, primarily composed of 10,16-dihydroxyhexadecanoic acid, obtained from tomato via extraction and retaining a partially depolymerized structure of the natural biopolymer.

2.2. Preparation coating solutions and film samples

The coating solutions were prepared following the method described in our previous works (Lo Faro et al., 2021; Lo Faro et al., 2023) with slight modifications. PCL (10 g/100 mL) and variable amounts of glycerol were dissolved in ethyl acetate, after which cutin was dispersed according to the specific formulation to be prepared (see Table 2). A refrigerated system was employed for solvent recovery to maintain a constant solution volume. The coating solutions, 7 mL each layer, were spread onto the base paper samples (210 × 300 mm) via bar coating by means of a Compact AB3650 (TQC Sheen) automatic film applicator, working under a fume hood. All paper sheets were coated using a bar with a nominal coating thickness of 100 μm and an application speed of 50 mm/s. Afterwards the coated paper samples were dried under a fume hood for about 30 min in order to remove the solvent and then dried at 80 °C for 1 h; the process was repeated in the case of samples with a double layer of coating. The samples were kept for 24 h at room temperature before testing.

By varying the proportions of the solution components and the number of layers of coatings applied to the base paper, nine different samples were produced (Table 2)

Table 1
Technical data sheet of uncoated paper.

Properties		Methods		
Basis Weight	g/m^2	ISO 536		35
Tensile Stregth	kN/m	ISO 1924-3	MD	3.5
			CD	1.5
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

Table 2
Experimental paper samples as resulting from the application of different PCL-based coatings.

Sample Code	PCL			Number of layers
	%w/v	PCL:glycerol ratio	PCL:cutin ratio	
UCP	/	/	/	/
PCL	10	/	/	1
PCL6s	10	/	1:0.6	1
PCL6d	10	/	1:0.6	2
PCLG6s	10	1:0.05	1:0.6	1
PCLG6d	10	1:0.05	1:0.6	2
PCL1s	10	/	1:1	1
PCL1d	10	/	1:1	2
PCLG1s	10	1:0.05	1:1	1
PCLG1d	10	1:0.05	1:1	2

Similarly, the PCL, PCL6, PCLG6, PCL1, and PCLG1 solutions were used to obtain standalone films via the solvent casting technique. For each formulation, 10 mL of solution was poured into a 170 mm diameter Petri dish and left to evaporate overnight at room temperature to promote solvent removal and facilitate subsequent film peeling.

2.3. Methods

2.3.1. Grammage and thickness

Grammage was determined by weighing with an analytical balance (accuracy 0.0001 g) specimens (1 cm^2) randomly cut from three sheets of each sample of both uncoated and coated paper. The results are expressed in g/m^2 as the mean value of 10 replicates. Thickness was measured, using a digital micrometer (Syntek, New York, NY, USA) with a sensitivity of 0.001 mm. Three measurements were taken on both sides and at the center of 10 rectangular specimens (150 × 25 mm), cut from three sheets of uncoated and coated paper. A total of 30 measurements were performed, from which the mean and standard deviation values were calculated. Both measurements were carried out under controlled conditions at 25 °C and 45 % RH.

2.3.2. SEM analysis

The section and surface morphology of the paper samples was examined using scanning electron microscopy (SEM) with a Nova NanoSEM 450 (FEI, Hillsboro, OR, USA) equipped with a Low Voltage Detector (LVD). The analysis was conducted follow the method described by Lo Faro et al. (2021) under low vacuum conditions (80 kPa) and an accelerating voltage of 10 kV. High-resolution images were obtained at various magnifications (500 ×, and 1000 ×) and tilts (0° to 40°), facilitating the observation of both cross-sectional and surface features of the samples.

2.3.3. Contact Angle Determination with Water and Castor Oil

Contact angle (CA) measurements were conducted using an OCA 15EC contact angle meter, with data analysis performed via OCA 20 software (Dataphysics), according to the sessile drop method. For each sample type of coated paper samples, 10 × 100 mm paper strips were fixed on the sample holder; CA values were obtained by depositing 3 μL of water or 7 μL of castor oil onto the surface of the samples. For each sample, ten replicates were performed, and the average CA was calculated. The water or castor oil CA was recorded immediately after the drop deposition.

2.3.4. Grease resistance determination

The grease resistance was tested by using the standard method T 559 pm-02 (or "Kit 12" test) (TAPPI, 2002), a widely recognized procedure for evaluating the performance of paper coatings (Gietl et al., 2009; Jiang et al., 2014; Ham-Pichavant et al., 2005). In this test, twelve different grease solutions were employed, with surface tensions ranging from 0.038 mN/m (the least aggressive solution, pure castor oil) to 0.022 mN/m (the most aggressive solution, a mixture of toluene and heptane in a 55/45 ratio). A material is classified as resistant to grease penetration if it achieves a kit number of 8 or higher (Adibi et al., 2023).

Solutions with higher numbers are more aggressive, having lower surface energies (i.e., Solution 1 is the less aggressive, while Solution 12 is the most aggressive). A drop of each solution of the kit test was gently dropped onto the surface of each sample and quickly removed with a clean absorbent cloth after 15 s. The tested area was examined and evaluated, giving a specific value to each sample corresponding to the number of the kit test solution that shows the first signs of degradation.

The Kit 12 test was repeated after subjecting the samples to folding to evaluate the integrity of the coating under mechanical stress and to determine whether the folding compromised the resistance to fat and oil. Samples of dimensions 10 × 10 cm were prepared, which were folded onto themselves twice: once in the horizontal direction and once in the vertical direction. After reopening the samples, the evaluation along the folds was conducted using Kit 12.

2.3.5. Water Vapor Transmission Rate (WVTR) and Water Vapor Permeability (WVP)

The WVTR measurement of the different samples was performed in triplicate according to the ASTM E96/E96M-24a (2024) standard method with slight modification (Lo Faro et al., 2021). Ten grams of silica gel were put inside a 25 mL glass vials to achieve a 0 % internal relative humidity (RH). The samples were glued on the top of the vials, with the coated part inwards to prevent water vapor tangential diffusion, and they were placed in a climate chamber (CH 150—CLIMATEST Climatic Chamber, ARGO LAB, Giorgio Bormac, Carpi (MO)) set at 38 °C (+/− 1 °C) and with 90 % RH. The vials were weighed 2 times a day for the 5 days of storage. The WVTR value ($g \cdot day^{-1} \cdot m^{-2}$) was calculated using the following formula:

$$WVTR = [\Delta W/(\Delta t \times A)] \times 24 \quad (1)$$

where "ΔW/Δt" represents the weight gain as a function of time ($g \cdot h^{-1}$), obtained as the slope of the linear regression of the mass gain versus time, and "A" corresponds to the exposed surface of the film (7.85×10^{-5} m^2).

The water vapor permeability (WVP; $g \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot Pa^{-1}$) of the film samples was calculated using the following equation:

$$WVP = [WVTR \times L] / \Delta P \quad (2)$$

where:

- WVTR is the Water Vapor Transmission Rate ($g \cdot day^{-1} \cdot m^{-2}$),
- L is the film thickness, (mm)
- ΔP is the water vapor partial pressure difference across the film (Pa).

2.3.6. Mechanical properties

The mechanical properties of coated paper samples were determined by a dynamometer equipped with a 0.5 kN load cell (Zwick/Roell, Ulm, Germany).

The tensile strength measurements of paper samples were determined according to ASTM D882 (2018). For each sample, 20 specimens (dimensions of 150 × 25 mm) were taken: 10 in the machine direction (MD) and 10 in the cross-direction (CD). The dynamometer settings were: initial strain 0.1 mm/mm, initial grip separation 125 mm, and speed of grip separation 12.5 mm/min. The collected data were processed by the TESTEXPERT®II (V3.31) software (Zwick/Roell, Ulm, Germany). The following mechanical properties have been measured: Young's modulus (E—MPa), tensile strength (σ—MPa), and elongation at tensile strength (ε—%).

Measurements of the seal strength (N/25 mm) of paper samples were determined according to ASTM F88/F88M-09 (2009). For each sample, 10 samples were taken: each sample consisted of two paper sheet (dimensions of 150 × 25 mm) which were heat sealed at 150 °C for 10 s

using impulse sealer. The heat-sealed samples were cooled at room temperature. Each tail of the specimen was secured in opposing grips and the seal remains unsupported while the test was being conducted. The initial grip distance of the sample at the dynamometer machine was 50 mm during the test and the speed was set at 200 mm/min.

2.3.7. Statistical analysis

The data are presented as the mean values of ten replicates (± standard deviations). To evaluate the effects among the samples, an analysis of variance (ANOVA) was performed on values from each test and a multivariate analysis of variance (MANOVA) was performed on the values obtained from samples coated with formulations containing cutin. The MANOVA aimed to assess how the samples differed in relation to the tested characteristics and to determine the impact of the three considered variables: cutin percentage, the presence or absence of glycerol, and the number of coating layers. Consequently, samples that did not meet these three conditions were excluded from the dataset used for the variance analysis. When significant effects were observed ($p \leq 0.05$), Tukey's post-hoc test was used for pairwise comparisons. The homoskedasticity and normal distribution of the data were verified before statistical analysis, that, were performed using Statistica® version 8.0 (StatSoft Inc., Tulsa, OK, USA).

3. Results and discussion

3.1. Grammage and thickness

Grammage and thickness data of the experimental samples and the base paper are represented in Figs. 1 and 2, respectively. As can be inferred, these two values increase if a coating (double or single) layer is deposited on the surface of the reference paper.

Analyzing the sample weights (Fig. 1) obtained through a double-layer coating, no significant differences were observed between PCLG1d and PCL1d compared to respective PCLG6d and PCL6d. This suggests that the amount of cutin has a negligible effect on sample grammage. Furthermore, the results of Tukey's HSD test following ANOVA confirm the absence of a statistically significant difference among the samples.

Similarly, in the samples obtained with a single layer of coating, regardless of the amount of cutin and the presence or absence of glycerol, all samples (PCL6s, PCLG6s, PCL1s, PCLG1s) exhibited similar weight values, highlighting that neither the level of cutin not the presence of glycerol affected grammage, as even evident from statistical analysis.

Regarding thickness (Fig. 2), the samples PCLG6d and PCL6d unexpectedly exhibited greater thickness compared to their homologous samples with a higher amount of cutin (PCLG1d and PCL1d), as also confirmed by the Tukey's HSD test from ANOVA. This phenomenon may arise from several factors, particularly the possibility that the higher percentage of cutin in the solutions PCLG1d and PCL1d facilitated the penetration of the solution into the natural pores of the paper, created by the irregular arrangement of cellulose fibers.

Considering that cutin is primarily composed of fatty acids, as highlighted by Cifarelli et al. (2016), and considering that the literature (Vieira et al., 2014; Mehta et al., 2014; Jadhav et al., 2024) indicates that fatty acids can effectively reduce the viscosity of synthetic polymer solutions, behaving similarly to plasticizers, it can be hypothesized that an increase of the cutin percentage in solution could reduce its viscosity, thus promoting penetration into the pores of the paper, resulting in a lower presence of cutin on the surface. Supporting this, images obtained via scanning electron microscopy (SEM), presented in Fig. 3, illustrate that samples with ratio polymer:cutin of 1:0.6 had a higher thickness compared to those with ratio polymer:cutin of 1:1.

Finally, the analysis of samples coated with a single-layer demonstrated that the inclusion of glycerol in the coating solutions did not have a significant impact on thickness, as confirmed by the MANOVA (Table 4).

3.2. SEM analysis

The cross-section morphology of the uncoated and coated paper samples, analyzed via scanning electron microscopy (SEM), is illustrated in Fig. 3. The uncoated paper sample exhibited a characteristic open and porous network structure with a non-uniform surface texture. In contrast, the typical cellulose fiber network and pores were not visible in the coated samples. This observation indicates that the coating was uniformly distributed across all samples, effectively covering the paper fibers and sealing the surface pores, albeit with some variations among the different samples.

The use of glycerol did not facilitate the penetration of the coating into the paper structure: indeed, scanning electron microscopy (SEM) images show no visual differences between the samples coated with and without glycerol in the formulation. This observation is reinforced by the absence of statistically significant differences in the thicknesses of samples with and without glycerol in the coating. Cutin acts as a more effective fluidizing agent compared to glycerol. Due to its higher

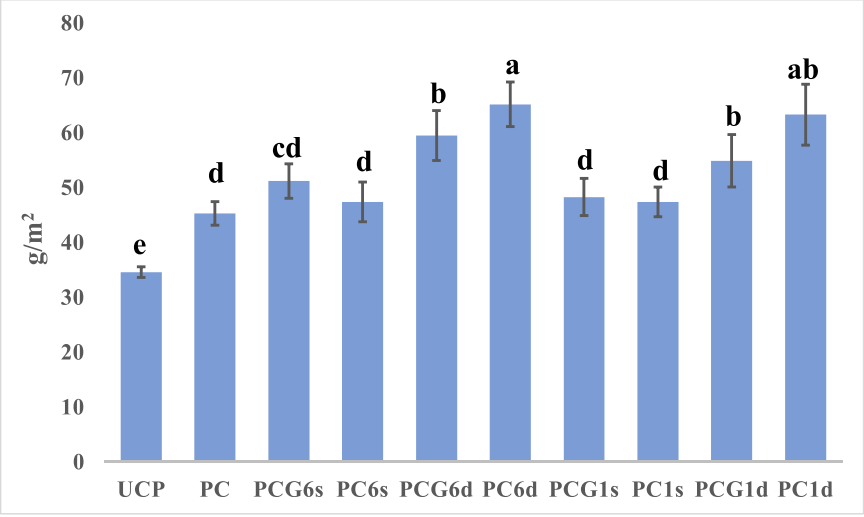

Fig. 1. Mean values with standard deviation of grammage of uncoated (UCP) and coated samples. Results of Tukey's HD test from ANOVA are reported as lowercase letters (a > b > c, etc.). Different letters identify significantly different samples.

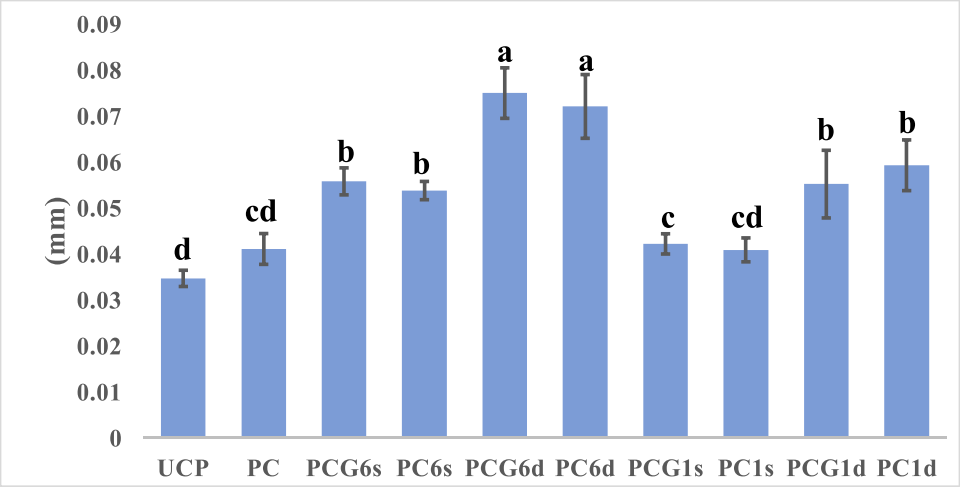

Fig. 2. Mean values with standard deviation of thickness of uncoated and coated samples. Results of Tukey's HD from ANOVA test is reported as lowercase letters ("a" > "b" > "c", etc). Different letters identify significantly different samples.

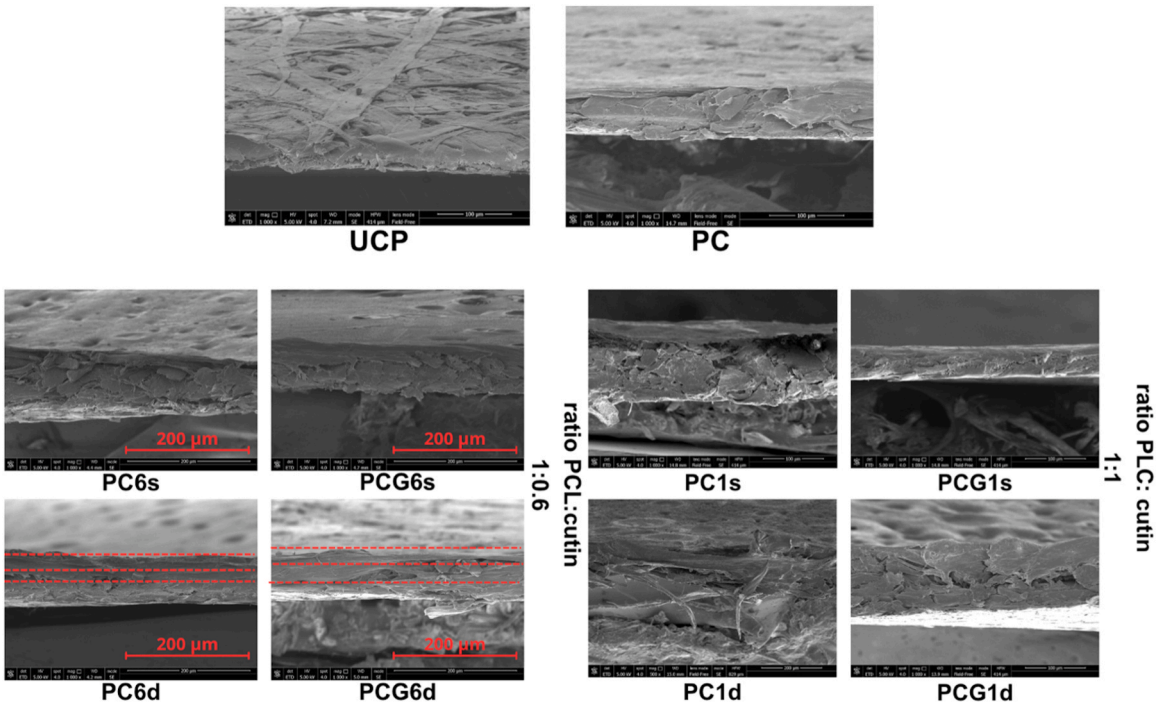

Fig. 3. SEM micrographs of cross section of uncoated and coated samples.

concentration (polymer:cutin ratio of 1:0.6 and 1:1), cutin facilitates the penetration of the coatings into the pores of the paper, rendering the effect of glycerol negligible in comparison.

Indeed, the variation in the quantity of cutin used plays a crucial role in the penetration of the coating into the paper samples. It is evident that the presence of the coating layers is more pronounced in the samples containing a polymer:cutin ratio of 1:0.6. This is also reflected in the thickness measurements; as shown in Fig. 2, the samples with a polymer: cutin ratio of 1:0.6 exhibit greater thickness compared to the same samples formulated with a ratio polymer:cutin of 1:1.

Furthermore, the presence of the double coating layers is clearly visible in the PCL6d and PCLG6d samples, as indicated by the arrows in Fig. 3. In both cases, the presence of the two distinct coating layers is evident, and this could have a positive impact on the paper diffusion or transmission of gases and water vapor.

3.3. Water vapor transmission rate (WVTR) and water vapor permeability (WVP)

The standalone films of pure PCL and its blend with cutin and glycerol were realized in order to investigate the intrinsic properties of the individual materials, particularly concerning their water vapor barrier, under controlled conditions.

Fig. 4 shows the WVP values of PCL film and films obtained blending PCL, cutin and glycerol. The reference PCL film and the PCLG06 sample (containing cutin at a 1:0.6 PCL:cutin ratio and glycerol) displayed the lowest WVP values, with no statistically significant difference between them. The addition of glycerol alone (PCL06) led to a slight, non-significant increase in WVP, while films containing higher amounts of cutin (PCLG1 and PCL1, 1:1 PCL:cutin ratio) exhibited significantly higher WVP values. These results suggest that moderate amounts of

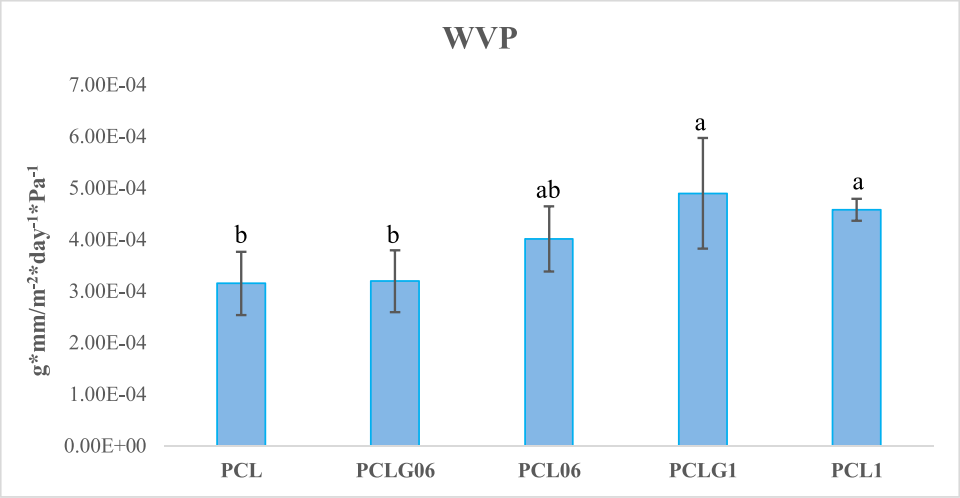

Fig. 4. WVP ($g \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot Pa^{-1}$) value of film samples. Results of the ANOVA of all samples reported as p-values. ns = $p > 0.05$; * = $p \leq 0.05$; ** = $p \leq 0.01$; *** = $p \leq 0.001$. Results of Tukey's HSD test is reported as lowercase letters ("a" > "b" > "c", etc.), respectively.

cutin, when combined with plasticizers like glycerol, may help maintain water vapor barrier properties. However, increasing the cutin content to a 1:1 ratio appears to compromise the barrier performance, regardless of glycerol addition. The increase in WVP observed in films with a 1:1 PCL: cutin ratio (PCL1 and PCLG1) may be attributed to the excessive presence of cutin interfering with the structural integrity of the PCL matrix. At higher concentrations, cutin may reduce polymer compatibility, disrupt PCL crystallinity, or create microstructural discontinuities that facilitate water vapor diffusion. However, despite statistical significance, the absolute differences in WVP among the samples remain relatively modest. The average WVP values ranged from 3.15E-04 ± 6.13E-05 $g \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot Pa^{-1}$ for PCL to 4.90E-04 ± 1.07E-04 $g \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot Pa^{-1}$ for PCLG1, with standard deviations indicating partial overlap in variability. These findings imply that while formulation influences the water vapor barrier, the differences are not drastic and should be interpreted in the context of practical application thresholds. When moving from neat films to coated paper samples, however, the interpretation of WVP becomes problematic.

As already demonstrated and discussed in Section 3.2, the application of barrier layers often leads to partial penetration of the coating into the porous fiber matrix of the paper, producing ill-defined interfaces and non-uniform thicknesses that cannot be precisely measured or clearly separated into distinct layers. Since WVP calculations require normalization by a homogeneous and well-defined barrier layer, such conditions undermine their reliability. For this reason, while WVP was calculated for the standing alone films, WVTR was measured for the coated paper samples, as it provides a direct assessment of the total water vapor transmission through the entire coated structure and thus a more accurate and representative evaluation of the barrier performance in practical applications (Han et al., 2010; Lahtinen and KuusipaLo, 2008).

Table 3 displays the WVTR values for UCP samples and samples coated with the experimental coating formulations. The data clearly indicate that the WVTR of the samples significantly decreased in the presence of the coatings.

A notable reduction in WVTR value of about 39 % (from 4348 ± 69 $g \cdot day^{-1} \cdot m^{-2}$ to 2654 ± 154 $g \cdot day^{-1} \cdot m^{-2}$, at 38 °C and 90 %RH) was achieved with a single layer of PCL, confirming the results of previous work (Lo Faro et al., 2021): this reduction was further enhanced when cutin was added to the coating formulations.

Specifically, a WVTR reduction up to 90 % compared to uncoated paper was observed for PCL6d sample, which demonstrates an optimal combination and synergy of cutin with PCL in a double-layer coating. The PCLG6d sample follows a trend similar to that of the PCL6d sample, with no statistically significant differences observed between the two.

Interestingly, it was anticipated that samples with a higher percentage of cutin, such as PCL1s, PCL1d, and their respective counterparts with the addition of glycerol, would yield lower WVTR values. However, this expectation was not met; conversely, samples containing a ratio of polymer:cutin of 1:0.6 exhibited the lowest WVTR values. A similar phenomenon has been reported by Arrighetti et al. (2024), where the incorporation of cutin into PLA did not consistently result in decreased WVTR values despite increased percentages of added cutin. This phenomenon is due to cutin, which acts as a fluidizing agent, reducing coating viscosity and increasing solution mobility, allowing deeper penetration into the paper pores.

The initial layer of coating effectively fills the pores present in the cellulose structure of the paper, which is due to the fiber distribution. Applying a second layer enhances this effect, resulting in a significant reduction in WVTR values observed for the samples tested. Cutin is essential to this process, as its composition, which is rich in fatty acids and waxes, aids in occluding the natural pores in the paper, thereby diminishing water vapor permeability.

This observation is further corroborated by the statistical analysis performed using MANOVA, which enables the assessment of the influence of each variable on the reduction of WVTR values. As presented in Table 3, the p-values obtained from the MANOVA analysis indicate that all individual variables and their interactions have a statistically significant effect. In particular, cutin and the presence of multiple layers exhibit p-values lower than 0.01, highlighting their strong influence in reducing WVTR values.

Other authors have reported the phenomenon where the presence of cutin significantly contributes to the reduction of the WVTR value, as also described by Mroczkowska et al. (2024) who found that, regardless of whether cutin was incorporated into the selected polymer matrix or applied as a stratified layer on top of the designed polymer, its presence resulted in a significant decrease in the WVTR compared to the control sample.

Fig. 5 shows the relationship between WVTR and the thickness of coated paper samples containing cutin in their formulation (the paper coated only with PCL was not included). A clear inverse correlation was observed (R^2 = 0.892), with WVTR decreasing as sample thickness increased. This trend supports the observation that formulations with a 1:0.6 PCL:cutin ratio tend to form thicker coatings, which in turn exhibit lower WVTR values. The higher thickness is likely due to the favorable distribution of cutin at this ratio, and the effect is further enhanced in double-layered samples. These results confirm that not only composition but also coating thickness—closely linked to formulation behavior—plays a key role in improving barrier performance.

Table 3
Mean values with standard deviation of the data collected for contact angle values with oil and water, mechanical property values (Young's modulus, tensile strength, elongation at break and seal strength) grammage, thickness, and WVTR values. Results of the ANOVA of all samples reported as p-values. ns = $p > 0.05$; * = $p \leq 0.05$; ** = $p \leq 0.01$; *** = $p \leq 0.001$. Results of Tukey's HSD test is reported as lowercase letters ("a" > "b" > "c", etc.), respectively. Different letters identify significantly different samples. 1: The Tukey's HSD test was conducted for all samples after ANOVA. 2:The Tukey's HSD test was conducted for only samples formulated with cutin in the coating formulation after MANOVA.

	samples	**UCP**	**PCL**	**PCLG6s**	**PCL6s**	**PCLG6d**	**PCL6d**	**PCLG1s**	**PCL1s**	**PCLG1d**	**PCL1d**	*pvalue*
WVTR ($g \cdot day^{-1} \cdot m^{-2}$) 38 °C 90 %RH		4348	2654	1150	874	477	405	1902	1798	1052	1156	
		±69	±154	±97	±44	±56	±12	±206	±238	±145	±128	
	1	a	b	d	e	f	f	c	c	de	d	***
	2			b	c	d	d	a	a	bc	b	
Grammage (g/m^2)		34.50	45.20	51.10	47.30	59.40	65.10	48.20	47.30	54.80	63.20	
		±1.00	±2.15	±3.14	±3.62	±4.55	±4.07	±3.39	±2.71	±4.78	±5.55	
	1	e	d	cd	d	b	a	d	d	c	ab	***
	2			de	e	bc	a	e	e	cd	ab	
Thickness (mm)		0.0347	0.0411	0.0558	0.0538	0.0750	0.0721	0.0422	0.0409	0.0552	0.0593	
		±0.0018	±0.0033	±0.0029	±0.0020	±0.0055	±0.0069	±0.0022	±0.0026	±0.0074	±0.0055	
	1	d	cd	b	b	a	a	b	cd	b	b	***
	2			b	b	a	a	c	c	b	b	
Water CA (Degrees)		127.01	105.51	66.21	79.79	60.14	73.26	73.23	72.76	66.58	82.35	
		±1.47	±2.71	±1.22	±2.46	±2.60	±2.62	±0.81	±1.81	±3.84	±1.51	
	1	a	b	e	c	f	d	d	d	e	c	***
	2			c	a	d	b	b	b	c	a	
Oil Ca (Degrees)		66.37	39.83	44.80	49.60	39.43	40.79	39.87	34.87	39.27	54.96	
		±2.68	±5.49	±1.85	±1.44	±1.81	±2.87	±1.15	±1.94	±2.03	±2.19	
	1	a	e	d	c	e	e	e	f	e	b	***
	2			c	b	d	d	d	e	d	a	
σ (MPa) MD		62.83	82.58	6.73	7.27	6.00	6.45	78.88	79.56	67.30	61.24	
		±3.07	±9.05	±0.45	±0.32	±0.95	±0.28	±5.12	±4.07	±2.84	±3.49	
	1	bc	a	d	d	d	d	a	a	b	c	***
	2			d	d	d	d	a	a	b	c	
σ (MPa) CD		32.34	47.03	3.35	4.04	3.55	3.43	44.32	45.43	38.12	37.02	
		±1.21	±2.84	±0.52	±0.13	±0.44	±0.15	±3.34	±2.87	±2.03	±1.08	
	1	d	a	e	e	e	e	b	ab	c	c	***
	2			c	c	c	c	a	a	b	c	
E (MPa) MD		7690	8949	771	871	690	683	9620	9189	7772	6942	
		±294	±1499	±114	±30	±84	±60	±510	±598	±382	±365	
	1	bc	a	d	d	d	d	a	a	b	c	***
	2			d	d	d	d	a	a	b	c	
E (MPa) CD		2786	4221	186	325	203	184	4481	4327	3259	2806	
		±142	±402	±31	±23	±31	±39	±142	±256	±197	±89	
	1	d	b	e	e	e	e	a	ab	c	d	***
	2			d	d	d	d	a	a	b	c	
ε (%) MD		1.39	1.48	1.63	1.51	1.62	1.67	1.44	1.52	1.51	1.50	
		±0.11	±0.14	±0.12	±0.10	±0.30	±0.11	±0.14	±0.11	±0.07	±0.13	
	1	c	abc	ab	abc	ab	a	cb	abc	abc	abc	**
	2			d	d	d	d	a	a	b	c	
ε (%) CD		3.00	3.31	3.43	3.65	3.64	3.77	3.23	3.38	3.38	3.65	
		±0.19	±0.41	±0.83	±0.27	±0.90	±0.28	±0.59	±0.37	±0.24	±0.24	
	1	b	ab	ab	ab	ab	a	ab	ab	ab	ab	*
	2			ab	ab	ab	a	b	ab	ab	ab	
Seal Strength (N/25 mm)		-	3.65	4.63	5.27	5.42	7.92	3.79	4.18	6.17	6.82	
		-	±1.19	±0.69	±0.77	±1.31	±0.41	±0.62	±0.23	±0.83	±1.38	
	1	-	e	ed	cd	cd	a	e	ed	bc	ab	***

These findings highlight how the application method significantly influences barrier performance: formulations that performed best as films did not always yield the lowest WVTR values when applied as coatings. This discrepancy underscores the importance of evaluating both material composition and application context, as the interaction with the substrate and coating behavior can modified the final functional properties.

3.4. Grease resistance

All the coated samples of this work, including those covered only with PCL, showed a significant improvement in grease resistance, managing to resist even the most aggressive solution, as showed in Fig. 6. As extensively described in the literature (Sundar et al., 2020) PCL exhibits excellent oil resistance properties. This is attributed to its chemical characteristics, which make it a slightly oleophobic polymer, and this behavior is maintained also when cutin is used in mixture with PCL. Indeed, the addition of cutin does not alter the oleophobic properties, which remain unchanged, maintaining the excellent performance already demonstrated by the presence of PCL alone.

Packaging paper can undergo repeated folding to form sealed bags, using adhesives, heat sealing, or other closure methods, depending on the packaging requirements. However, such folds may compromise the integrity of the coating, leading to cracks or tears that could reduce its grease resistance at the bending points.

To assess whether the grease resistance of the coated samples remains effective after folding, Test Kit 12 was conducted specifically at the bending points of the folded sheets. This test aimed to evaluate the coating's integrity under mechanical stress and to determine whether folding compromises its grease-resistant properties at critical points.

All samples coated with PCL neat and with cutin-containing formulations were tested. As illustrated in Fig. 7, clear bending lines (orthogonal) are visible, yet no discontinuities in the PCL and cutin coating were observed. Even after the bending treatment, the coated

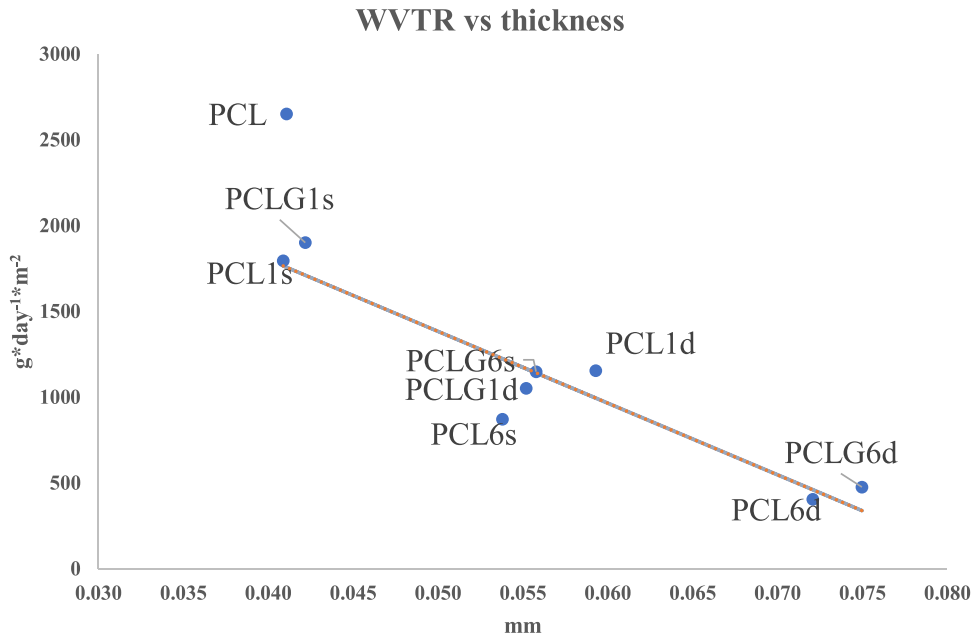

Fig. 5. WVTR values (g·day^{-1}·m^{-2}) at 38 °C and 90 %RH as a function of sample thickness (mm). The regression line was calculated considering only the samples containing cutin in the coating formulation (y = –41838x + 3478; R^2 = 0.892).

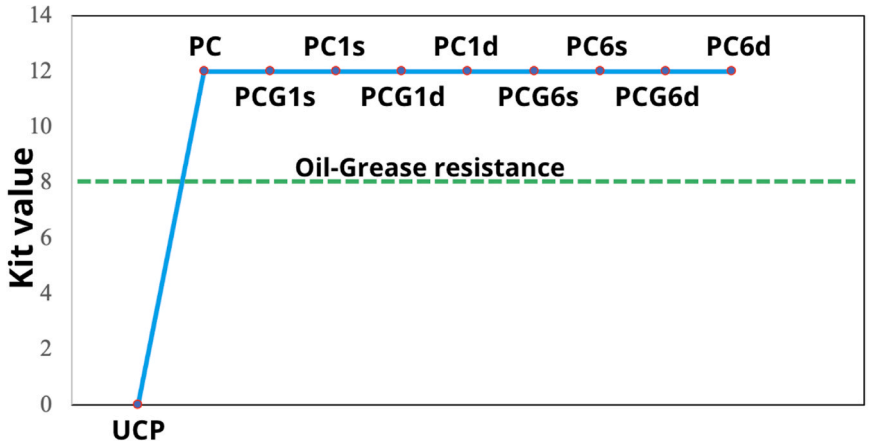

Fig. 6. Oil-Grease resistance values of samples submitted to the 'Kit 12' test.

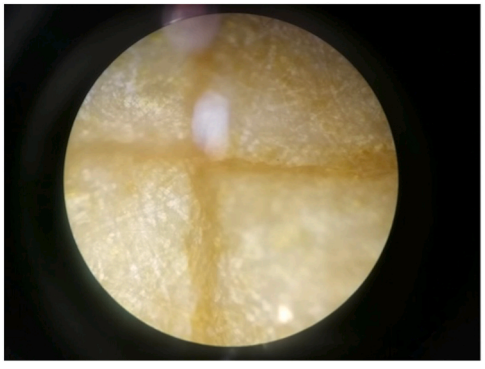

Fig. 7. Image of a PCL-cutin-coated paper sample after the folding test.

samples retained their maximum grease resistance, confirming the integrity of the coating and its ability to resist fats and oils.

3.5. Water and oil contact angle

The values of contact angle were evaluated for water and castor oil, the latter chosen because it is the basis of the solutions used in the test "Kit-12", the reference method to evaluate the repellency of paper against oils and fats.

As presented in Table 3, the UCP and PCL samples exhibited a contact angle with water greater than 90°, whereas all samples containing cutin in their coating formulations displayed contact angle values below 90°. Consequently, none of the experimental samples demonstrated hydrophobic behavior, as materials are classified as hydrophobic when their contact angle with water exceeds 90°. One possible explanation for the decrease in the contact angle observed in the coated samples could be the changes in surface roughness. As also reported by Mroczkowska et al. (2024), the application of a cutin-based coating resulted in an alteration of surface roughness compared to uncoated samples, which influenced the contact angle values with water. Following similar observations, it can be postulated that the decrease in contact angle values, remaining below 90°, is likely linked to alterations in surface roughness.

Focusing on the influence of the coating, it is evident that glycerol is

a critical factor (Table 4). Samples containing glycerol (PCLG6s, PCLG1d, and PCLG6d) showed significantly lower contact angle values compared to their counterparts without glycerol (PCL6s, PCL1d, and PCL6d).

This behavior can be attributed to the chemical structure of glycerol, which contains -OH groups that impart hygroscopic and hydrophilic characteristics (Pulla-Huillca et al., 2021); as it has also been demonstrated by Chakraborty et al. (Chakraborty et al., 2019), the addition of glycerol to PCL results in a reduction of the contact angle with water. Therefore, the presence of glycerol in the formulations negatively affects the contact angle value. Removing glycerol from the formulation allows the contact angle to approach 90°, as observed in the PCL1d sample, where the absence of glycerol and the presence of a double layer increase the water contact angle.

It is interesting to note that oil CA values and results obtained from KIT 12 cannot be correlated. Indeed, contact angle measurements with castor oil indicate that the presence of coatings did not enhance this property in the paper samples. This finding contrasts sharply with results from the 'Kit 12' test, which showed maximum resistance to oil and grease across all samples. Such discrepancies between the two testing methods have been previously observed (Lo Faro et al., 2023), highlighting differing outcomes for the same samples. However, while the two tests analyze related properties, they provide different information about the samples. Specifically, the 'Kit 12' test is used to evaluate grease resistance or the ability of a surface to prevent the penetration of oily substances, while the contact angle with oil provides more specific, localized information about surface tension and the surface's affinity for oil. However, since the 'Kit 12' test is the official method for assessing grease resistance in paper and cardboard, we can confidently assert that our samples demonstrate high resistance in this regard. We can assume that the slight decrease observed in the CA with castor oil was due to the same cause affecting CA with water, i.e. the roughness of coated paper surface, which determines a change in the shape of the drop in contact with the surface based on physical arrangement rather than on a chemical interaction.

3.6. Mechanical behavior

The mechanical properties of paper were assessed in machine (MD) and cross direction (CD). Young's modulus (E) and elongation at tensile strength (σ) typically decrease from MD to CD due to the higher alignment of fibers in the MD, resulting in greater resistance and reduced deformability in that direction. As shown in Table 3, the data collected confirm this trend regardless of coating presence, indicating a specific fiber orientation in the paper.

Tensile strength analysis revealed that samples coated with a polymer:cutin ratio of 1:1 maintained values comparable to the control in both machine (MD) and cross directions (CD). Conversely, a 1:0.6 ratio led to a marked decrease, likely due to differences in coating stratification. SEM images (Fig. 3) confirm that in 1:0.6 samples, the coating remained superficial, failing to penetrate the fibers, thereby reducing tensile strength regardless of single or double-layer application.

A similar trend was observed for Young's modulus, with 1:0.6 samples exhibiting greater susceptibility to deformation, while 1:1 samples retained rigidity akin to the control. This behavior is attributed to enhanced penetration in 1:1 formulations, fostering stronger fiber-coating interactions, as supported by SEM observations and literature (Lavoine et al., 2014; Tanpichai et al., 2020; Zakaria et al., 2015).

Regarding elongation at tensile strength, no statistically significant differences were detected among experimental groups, indicating that this property remained unaffected by the polymer:cutin ratio.

Although the material being designed is primarily dedicated to wrap food, it was intended to test the sealing behavior of the experimental materials (coating on coating), thus adding a function to the paper, i.e. the possibility to realize hermetic packages.

Data shows that even using PCL alone as coating material, it is possible to seal the coated paper and the seal strength (Fig. 8) of this material is around 4 N/25 mm. In fact, PCL due to its low glass transition temperature (Sundar et al., 2020; Najarzadeh et al., 2014; Tabasi et al., 2015; Moll & Chiralt, 2024; Joo et al., 2021) (Tg −62°C, melting point 55–60°C) can be considered a good sealing material on the same level as ethylene vinyl acetate (Tg −33°C; melting point 55°C) (EVA, Properties), whose seal strength (for a thickness of 25 μm) is on average 28 N/25 mm.

Considering that the exposed layer of PCL on the paper surface is about only 0.006 mm of thickness (calculated by subtracting the thickness of uncoated paper to the PCL coated one), it is explained the low value of seal strength obtained. Looking at the results obtained with other coatings, it is evident that the addition of cutin, especially in double-layer samples, has further improved this function. On the other hand, the presence of glycerol does not seem to have significant benefits, regardless of the type of coating (single or double layer), and in some cases has even reduced this property. This is confirmed by statistical analysis conducted by the Tukey test (Najarzadeh et al., 2014; Joo et al., 2021).

It is important to emphasize the improvement of the property in double-layer samples, since a higher strength value, expressed in Newtons, was recorded in all cases. In particular, glycerol-free double layer samples in the coating formulation (PCL6d and PCL1d) were identified with the letter 'a' by Tukey's test (Fig. 8), suggesting that these represent the optimal solution. In addition, the amount of cutin does not affect the weldability between the two samples, as also indicated by the statistical analysis.

Similarly, double layer samples containing glycerol (PCLG6d and PCLG1d) exhibit similar behavior to equivalent glycerol-free samples.

The importance of the thickness of the sealing layer is thus demonstrated by the seal strength data obtained with coatings of greater

Table 4
MANOVA results using "Cutin", "Glycerol" and "Layer" as statistical factors were shown. Results of the Multifactorial-ANOVA (MANOVA) only of samples with cutin, reported as p-values and considering the parameters cutin, glycerol and layer and their interaction. ns = $p > 0.05$; * = $p \leq 0.05$; ** = $p \leq 0.01$; *** = $p \leq 0.001$.

		Cutin	Glycerol	Layer	Cutin Glycerol	Glycerol Layer	Cutin Layer	Cutin Glycerol Layer
WVTR	38 °C 90 % RH	***	**	***	**	**	**	**ns**
Grammage		**	**	***	**ns**	***	**ns**	**ns**
Thickness		***	**ns**	***	**ns**	**ns**	**ns**	**ns**
Water CA		***	***	***	***	***	***	***
Oil CA		**	***	**	**	***	***	***
σ	MD	***	**ns**	***	*	**	***	*
σ	CD	***	**ns**	***	**ns**	**ns**	***	**ns**
E	MD	***	***	***	***	**ns**	***	**ns**
E	CD	***	***	***	***	***	***	**ns**
ε	MD	**	**ns**	**ns**	**ns**	**ns**	**ns**	**ns**
ε	CD	**ns**	**ns**	**ns**	**ns**	**ns**	**ns**	**ns**

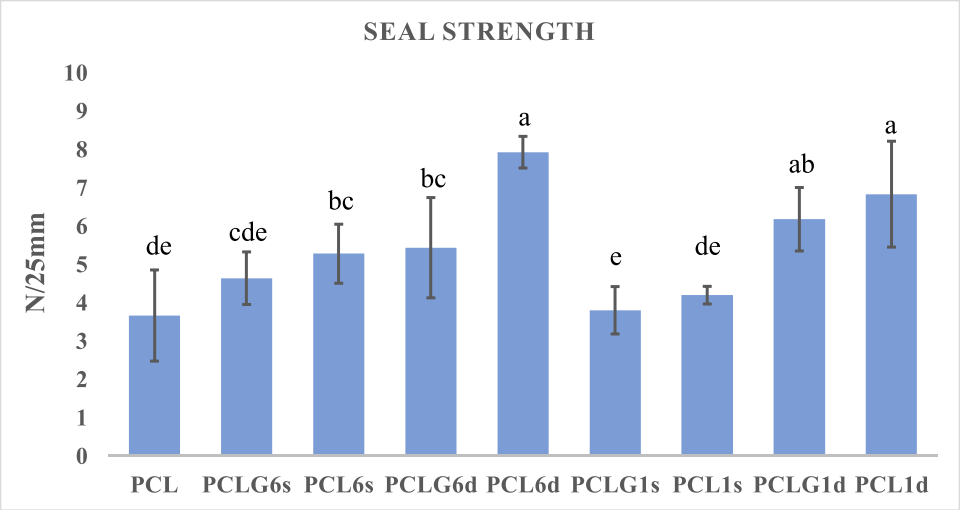

Fig. 8. Seal strength data of coating paper samples. Results of Tukey's HD from ANOVA test is reported as lowercase letters ("a" > "b" > "c", etc). Different letters identify significantly different samples.

thickness; in Fig. 9 the relationship between the thickness of the exposed coating is shown (calculated as the difference between the thickness of the coated paper and that of the control paper) of all samples without of glycerol and the seal strength. As can be seen, the samples coated in double layer with cutin (PCL:cutin ratio of 1.0:0.6 w/w) are those characterized by a greater thickness and also by a higher weld toughness.

3.7. Potential applications and limitations of coated paper substrates

Although the coated paper materials developed in this study do not exhibit high barrier performance to water vapor—showing, in the best-case scenario, an average WVTR value of 405 ± 12 g·day^{-1} ·m^{-2}·Pa^{-1} at 38 °C and 90 % RH—they may still be suitable for specific food packaging applications where moderate moisture protection is sufficient.

However, it should be emphasized that these coated papers are not suitable for products requiring long shelf life and stringent moisture protection. Despite the presence of barrier layers, the relatively high WVTR allows moisture to penetrate the substrate over extended storage periods, potentially leading to product degradation, loss of quality, or changes in texture and mechanical properties—particularly for moisture-sensitive goods.

On the other hand, such substrates could be effectively used as wrapping papers for low-moisture or semi-dry products—such as hard cheeses and sliced cured meats—where high water vapor barrier is not essential. In these applications, the material's excellent grease resistance (KIT value of 12) is a significant advantage, making it suitable for contact with high-fat foods while still providing a functional, partially protective layer. Additionally, they may be employed for short shelf-life items, such as fresh meat or fish, when used as overwraps in combination with other packaging systems (e.g., trays with polymer-based layers), helping to reduce plastic use while maintaining overall performance.

Given their heat-sealing properties, these coated papers might also be used for packaging of dry foods with low hygroscopicity, such as certain nuts or dried fruits, especially when paired with a secondary, higher-barrier material.

Finally, the natural aesthetic and sustainable profile of these

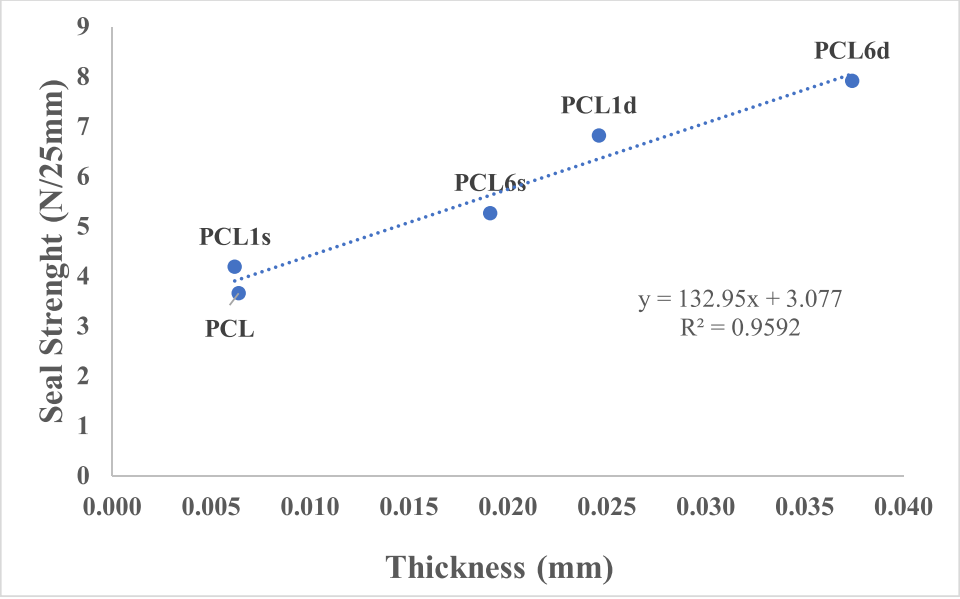

Fig. 9. Relationship between seal strength and coating thickness.

materials make them particularly appealing for the packaging of artisanal or gourmet bakery products, where barrier requirements are less stringent, and visual and environmental attributes of the packaging play a prominent role—e.g., artisan breads, muffins, or cakes intended for short-term consumption.

4. Conclusion

This study demonstrates the potential of biodegradable polymer coatings, specifically PCL and cutin, at improving the functional properties of paper-based food packaging. The findings confirm that these coatings significantly enhance moisture barrier properties, grease resistance, and mechanical strength, making them a promising sustainable alternative to conventional plastic coatings.

A key result was the 90 % reduction in WVTR for samples coated with a PCL–cutin ratio of 1:0.6, demonstrating cutin's strong barrier effect against moisture. All coated papers also showed excellent grease resistance, maintained even after folding, while seal strength reached up to 4 N/25 mm and further increased with cutin-based multilayers. Mechanical strength was generally preserved, with only a slight reduction observed at lower cutin contents due to partial penetration into the paper matrix. Glycerol, used as a plasticizer, provided no significant benefit and in some cases reduced mechanical and sealing performance.

The most promising formulation was found to be a double-layer coating with a polymer:cutin ratio of 1:0.6, which significantly reduced WVTR, maintained excellent grease resistance, and ensured adequate mechanical performance. Additionally, cutin, a naturally derived polymer from tomato processing by-products, proves to be a valuable eco-friendly resource for improving biodegradable packaging solutions, aligning with current sustainability goals and efforts to reduce plastic waste.

Future research should explore further optimization of these formulations, investigate scalability for industrial applications, and examine potential bio-based plasticizers that could enhance the flexibility and durability of the coatings. These advancements would further support the transition towards sustainable, high-performance food packaging materials, reducing environmental impact while ensuring optimal food protection.

CRediT authorship contribution statement

Patrizia Fava: Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Andrea Pulvirenti:** Writing – review & editing, Supervision, Conceptualization. **Fabio Licciardello:** Writing – review & editing, Validation, Methodology, Data curation. **Emanuela Lo Faro:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

On behalf of all authors, I confirm that there are no known financial, professional, or personal conflicts of interest that could have influenced the research presented in our manuscript entitled "**Polycaprolactone/cutin blends for the improvement of moisture barrier and grease resistance of paper for food use**", submitted for consideration in Food Packaging and Shelf Life.

Furthermore, we declare that:

No funding sources or sponsors had any role in the study design, data collection, analysis, or interpretation.

The authors have no affiliations or relationships that could be perceived as a potential conflict of interest related to this work.

If required, we are happy to provide additional information or clarification.

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Data Availability

Data will be made available on request.

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