

Article

Improvement of Paper Resistance against Moisture and Oil by Coating with Poly(-3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and Polycaprolactone (PCL)

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Abstract: Surface hydrophobicity and grease resistance of paper may be achieved by the application of coatings usually derived from fossil-oil resources. However, poor recyclability and environmental concerns on generated waste has increased interest in the study of alternative paper coatings. This work focuses on the study of the performances offered by two different biopolymers, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polycaprolactone (PCL), also assessing the effect of a plasticizer (PEG) when used as paper coatings. The coated samples were characterized for the structural (by scanning electron microscopy, SEM), diffusive (water vapor and grease barrier properties), and surface properties (affinity for water and oil, by contact angle measurements). Samples of polyethylene-coated and fluorinated paper were used as commercial reference. WVTR of coated samples generally decreased and PHBV and PCL coatings with PEG at 20% showed interesting low wettability, as inferred from the water contact angles. Samples coated with PCL also showed increased grease resistance in comparison with plain paper. This work, within the limits of its lab-scale, offers interesting insights for future research lines toward the development of cellulose-based food contact materials that are fully recyclable and compostable.

Keywords: compostable bioplastics; coatings; contact angle; grease resistance; paper; WVTR



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1. Introduction

Paper is a light, flexible, biodegradable, highly recyclable and compostable material, derived from renewable resources and its appreciable environmental compatibility often confirms it as the first choice by several food industries, both as primary and secondary packaging [1–3]. Nonetheless, the characteristic porous structure and hydrophilicity, lead to low barrier properties against possible food deterioration sources (moisture, gases, aromas), which are often not adequate to satisfy food products needs [3]. To overcome these weaknesses and improve final product properties, thus widening possible applications, different paper treatment technologies have been developed over time. Paper coatings with functional materials, and in particular, polyethylene and fluorinated compounds are among the most performing, cost-effective and hence widely used solutions because of the excellent barrier properties they offer. However, concerns related to the impact of plastic materials and fluorinated compounds (and derivatives) on the ecosystem and on human health have urged the search for alternative solutions. Moreover, food-grade paper contamination with food residues makes recycling often impossible. In the case of polyethylene coated papers, if the recycling of such a composite product already requires specialized facilities and systems and additional costs (the plastic layer can break down in flakes which tend to clog the fine screens, and by melting from roller heat, provoke paper breaking, meaning

downtimes and production losses), further issues are encountered at the time when food solid residues could remain anchored to the packaging: food residues can bypass filtration and fiber separation systems. This means they can interfere, by contamination, with paper sheet formation, or increase the organic load that treatment systems then have to handle (mechanical, physical, biological or physicochemical wastewater treatment). That is why paper mills are unwilling to receive such contaminated products [4,5]. According to CONAI (2020) [4], composting can be an alternative disposal for cellulosic materials contaminated with food, at least as long as the percentages entering in the organic waste stream remain at the actual level. At the same time, research on the development of bioplastics, suitable both as stand-alone film and as paper coatings, has moved forward: these materials may offer interesting functionalities contributing to the food products protection and shelf life extension and to sustainability [6]. The use of compostable bioplastics faces drawbacks at the industrial upscale. Traditional, fossil-based materials are often more cost-effective compared to bioplastics, and this represents an important challenge in a market that is particularly cost-conscious. Moreover, the compostable bioplastic end-of-waste management lacks standardization and awareness [5]. For this reason, the need to harmonize the test to verify the actual compostability of materials is urgent, especially in response to the development of new possible solutions. The UNI EN 13432 [7] standard establishes the criteria a material must comply to be defined as compostable. In 2021, the ASTM D6868 standard [8] was revised and updated and it defines the requirements for labeling of materials and products (packaging included), entirely designed to be composted in municipal and industrial aerobic composting facilities, wherein a biodegradable plastic film or coating is attached, either through lamination or extrusion directly onto the paper, to compostable substrates. It does not describe product contents nor their compostability or biodegradability performance. A satisfactorily compostable product must demonstrate proper disintegration during composting, adequate level of inherent biodegradation, and no adverse impacts on the ability of composts to support plant growth.

This work aims to develop and characterize the properties of paper coated with compostable bioplastics: in particular, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polycaprolactone (PCL) have been assessed. PHBV belongs to the polyhydroxyalkanoates (PHA) category, an aliphatic biogenic polyesters family, produced by bacterial fermentation and it is an isotactic copolyester obtained by copolymerization of hydroxybutyrate and hydroxyvalerate [9]. PCL is a semicrystalline biodegradable synthetic polyester obtained by a ring-opening polymerization (in presence of catalysts) of ϵ -caprolactone, which represents the monomeric unit [10,11]. Their biodegradability has been extensively studied and many different degradation times can be found; however, biodegradability is a material property that is influenced by many factors. A recent review [12] provides an overview of the main environmental conditions in which biodegradation occurs and then presents the degradability of numerous polymers. For example, strips of PHBV with a thickness of 1 mm showed a total mass loss of 100% after 70 days at 20–24 °C in industrial composting facilities; a complete degradation via composting can be observed for PCL within a few weeks. Figures on biodegradation of PHA and PHB can be found in another review [13] and the biodegradability in marine environment of PHA and PCL has been extensively discussed [14].

Many studies concerning the processing of these materials and the comparison with traditional plastic materials are available, but they are mainly focused on the development and evaluation of films, while the paper coating application still remains a little-explored research field. First, structural, diffusional and surface (water and oil affinity) properties of paper samples coated with PHBV at different thicknesses (in single and double layer) were evaluated; then, the optimization of PHBV and PCL coating solutions was attempted by addition of polyethylene glycol (PEG) (at 5%, 10% and 20% on biopolymer dry weight) to improve coating uniformity and spreadability. PEG may be defined as a natural-based plasticizer, whose ability to improve the mechanical properties of different biopolymers is well known [9,15]. PEG was used in the production of film via chloroform casting of

20% PEG and 80% PHB mixtures [16], reducing stiffness and increasing the elongation at break; PHB added with 10% of PEG (different MW) was used to produce film by compression molding [17–19]; similar results have been obtained for PCL films prepared by solvent casting and added with 10% PEG 400 and PEG 1500 [20]. In this work, different concentrations of PEG have been used, considering a range already investigated by other authors for different application: production of standalone film via solvent casting [21], via extrusion [22] or for the extrusion of PHBV on paper [23].

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 as reference paper. According to technical sheet, it is obtained from a long-fiber sulphate pulp, with a grammage of 35 g/m², a thickness of 50 µm, a tensile strength of 3.5 and 1.5 kN/m, a tear resistance of 280 and 420 mN (respectively in machine and cross direction). Commercial polyethylene-coated paper and fluorinated paper were used as commercial references. Polyethylene coated paper (CCM Soc. Coop. Group, Modena, Italy) has a thickness of 73 µm and a grammage of 54 g/m², 9 g/m² of which represent the polymeric coating. Fluorinated paper (ACL, Azienda Cartaria Lombarda s.p.a., Malagnino, Italy) is superficially treated with fluorinated compounds, to grant an elevated grease resistance, and with epichlorohydrin, a polyamide polymer which cross-links during paper drying, partially hindering water penetration. Chloroform was used because of the good solubility of PHBV, PCL and PEG [24] in this solvent and to avoid paper modification during the coating. Only few solvents are suitable candidates for PHB, of which chloroform is one of the most compatible and most commonly used [24,25]. The good solubility of PCL in chloroform has been demonstrated in previous studies [26–28].

Coating paper solutions were prepared dissolving in chloroform two biopolymers: poly(-3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polycaprolactone (PCL). In the first case, the product used was PHI 003 (NaturePlast[®], Ifs, France). It is 94% biobased according to ASTM D6866 standard and industrially compostable according to ASTM D6400 standard. The product is a powder with a melt flow rate of 15–30 g/10 min (tested at 190 °C and with 2.16 Kg). PCL (Sigma-Aldrich, Mw ~80.000) has a melt flow rate in the range from 2.01 to 4.03 (tested at 160 °C and with 5.00 Kg) and a water content lower than 0.5%; melting point at 60 °C and relative density of 1.145 g/mL at 25 °C. As a plasticizer, in the second phase of the study, polyethylene glycol (PEG) 200 (Mw ~190–210; Fluka Analytical) was used.

2.2. Methods

2.2.1. Coating Solution Preparation

This work was organized in two sequential operational phases, starting from the preparation of the solutions. In the first set, coating solutions were prepared dissolving 5% *w/v* PHBV in previously heated chloroform, under continuous stirring in water bath for about 2 h at 55 °C. In the second set, in the purpose to obtain clearer solutions and a better solubilization of polymers, solvent was heated, always in water bath and under magnetic stirring, at 50 °C; then, the polymer was added (5% *w/v* of PHBV or PCL) and dissolved in chloroform under magnetic stirring at 60 °C for 50 min, and subsequently, at about 75 °C for 10 min. The solutions were cooled at room temperature under continuous stirring. A recovery system for the vapors condensation was used, to minimize the solvent evaporation losses. Any loss of solvent by evaporation was, however, restored to the initial volume. Solution of pure PHBV and PCL and solutions of each biopolymer added with plasticizer (PEG) at 5%, 10%, and 20% (on polymer dry weight basis) were prepared. A PEG stock solution in chloroform was previously prepared [29], which was added in due amounts to the bioplastic solutions, followed by stirring at room temperature for 10 min.

2.2.2. Sheets Coating

Paper sheets (210 × 297 mm) were coated via bar coating with a Compact AB3650 (TQC Sheen) automatic film applicator, working under a fume hood. The instrument allows different coating rates, which could affect continuity and uniformity of the coatings. Once coated, sheets were partially dried under fume hood, to remove the chloroform, and then placed in an oven at 40 °C for about 20 min. The samples were kept for 24 h at room temperature before testing. If a double layer was applied, the drying phase in the oven was performed only after the deposition of the second layer. The first set of samples was realized varying coating thickness with an application rate of 80 mm/s, except one sample coated at 50 mm/s. In Table 1 the different coating conditions and resulting samples are listed: nominal thickness refers to the thickness of the solution (wet coating), 3 replicate coated sheets were prepared for each formulation.

Table 1. Coating conditions and codification of samples from the first and second set.

Sample Code	Layers	Nominal Coating Thickness (µm)	Application Speed (mm/s)	Bioplastic	PEG (% w/w)
SET 1					
80s80	1	80	80	PHBV	-
80s50	1	80	50	PHBV	-
80d	2	80 + 80	80	PHBV	-
100s	1	100	80	PHBV	-
100d	2	100 + 100	80	PHBV	-
SET 2					
PHBV	2	80 + 80	80	PHBV	-
PHBVpeg5	2	80 + 80	80	PHBV	5
PHBVpeg10	2	80 + 80	80	PHBV	10
PHBVpeg20	2	80 + 80	80	PHBV	20
PCL	2	80 + 80	80	PCL	-
PCLpeg5	2	80 + 80	80	PCL	5
PCLpeg10	2	80 + 80	80	PCL	10
PCLpeg20	2	80 + 80	80	PCL	20

The second set of coated sheets were all obtained with double layer coatings, using the 80 µm application bar at 80 mm/s but with two different biopolymers, PHBV and PCL, also considering the addition of PEG as plasticizer at different concentrations (5, 10 and 20% w/w). In Table 1 the different samples are listed; 2 replicate coated sheets were prepared for each formulation.

2.2.3. Coating Grammage Determination

The coatings grammage was obtained by mass difference of 20 cm²—coated paper samples and uncoated paper samples of the same size.

Results reported in Table 2 are the mean ± standard deviation of 3 determinations.

2.2.4. Scanning Electron Microscopy (SEM)

The surface and structure of the samples were analyzed by scanning electron microscopy using a Nova NanoSEM 450 (FEI, Hillsboro, OR, USA) (available at CIGS, Centro Interdipartimentale Grandi Strumenti, of the University of Modena and Reggio Emilia) provided with LVD detector, under low vacuum conditions (80 KPa) and with an acceleration of 10 kV. Images were captured with different magnifications (500×–3000×) and tilts (0°–40°), thus enabling the visualization of both surface and cross section.

Table 2. Coating grammages.

Code	Coating Grammage (g/m ²)
SET 1	
80s80	2.82 ± 0.97
80s50	4.81 ± 1.14
80d	7.72 ± 1.31
100s	4.60 ± 0.88
100d	9.65 ± 0.82
SET 2	
PHBV	8.48 ± 1.15
PHBVpeg5	7.42 ± 1.71
PHBVpeg10	7.92 ± 1.16
PHBVpeg20	8.57 ± 1.45
PCL	8.30 ± 1.01
PCLpeg5	6.73 ± 1.32
PCLpeg10	5.42 ± 2.83
PCLpeg20	9.77 ± 0.79

2.2.5. Measurement of Water Vapor Transmission Rate (WVTR)

The measurement of the water vapor transmission rate (WVTR) of the different samples was performed in triplicate according to the ASTM E96 standard, with modifications. Two grams of anhydrous CaCl₂ were placed in 25 mL glass bottles (55 mm high, 10 mm internal diameter mouth) to achieve a 0% internal RH. They were positioned in an oven at 45 °C, to remain completely dry and to be progressively sealed with the paper samples glued on the top of the vials, with the coated part inwards to prevent water vapor tangential diffusion. The vials were weighed at zero time, then placed in a desiccator with 90% RH obtained by BaCl₂ saturated solution at 45 °C.

The vials were weighted daily for 4 days of storage. The WVTR value (g 24 h⁻¹ m⁻²) was calculated using the following formula:

$$\text{WVTR} = \Delta W / (\Delta t \times A) \quad (1)$$

where: “ $\Delta W / \Delta t$ ” represents the weight gain as a function of time (g 24 h⁻¹), obtained as the slope of the linear regression of the mass gain versus time; “ A ” corresponds to the exposed surface of the film (7.85×10^{-5} m²). The reported WVTR data are the average of three replicates.

2.2.6. Oil and Grease Resistance

Oil and grease resistance was determined according to the ASTM F119-82 standard, with modifications [30]. Test specimens (60 × 60 mm) were placed on ground-glass plate (50 × 50 mm). Then, a cotton flannel (20 mm in diameter) was placed on specimens with 50 g weights (20 mm in diameter at the base) on them, and the assembly was conditioned in an oven at 40 °C for 30 min. It was subsequently removed, and after removing the weights, 150 µL of sunflower oil was pipetted on the flannel piece. Then, the weights were re-assembled and conditioned again in the oven at 40 °C. At convenient time intervals, the bottom of the ground glass plate was checked with the assembly in the oven. The time at which the first trace of wetting is visible at the position of the weight was recorded. Three specimens for each sample were used.

2.2.7. Water and Oil Contact Angle Measurement

Contact angle values were determined by means of an OCA 15EC contact angle meter and using OCA 20 (Dataphysics) software by the sessile drop method. For each type of sample, 1 × 3 cm paper strips were positioned on a film holder. Contact angle measurements were taken depositing 3 µL of water, and 7 µL of oil on the sample surface. For the contact angle measurement of each type of paper, 9 replicates were taken for water,

while 5 for oil, the average of which was considered. The contact angle was measured immediately after the drop deposition.

2.2.8. Statistical Analysis

Data were submitted to analysis of variance (ANOVA) using IBM Statistics SPSS 20 software and post hoc analysis by Tukey's test.

3. Results and Discussion

3.1. SEM Surface Analysis

The surface and cross-section of the uncoated paper and PHBV-coated paper samples obtained in step 1 were analyzed by means of scanning electron microscopy (SEM). The uncoated paper sheets show a typical fiber network and a flat surface due to the calendering treatment (Figure 1a); PHBV coatings (Figure 1a–d) determined the filling of void space of the network; however, the surface was characterized by the presence of lumps, whose dimensions and density seemed to increase both in double layer coatings and in single layer coating of 80 μm at 50 mm/s (Figure 1c,d).

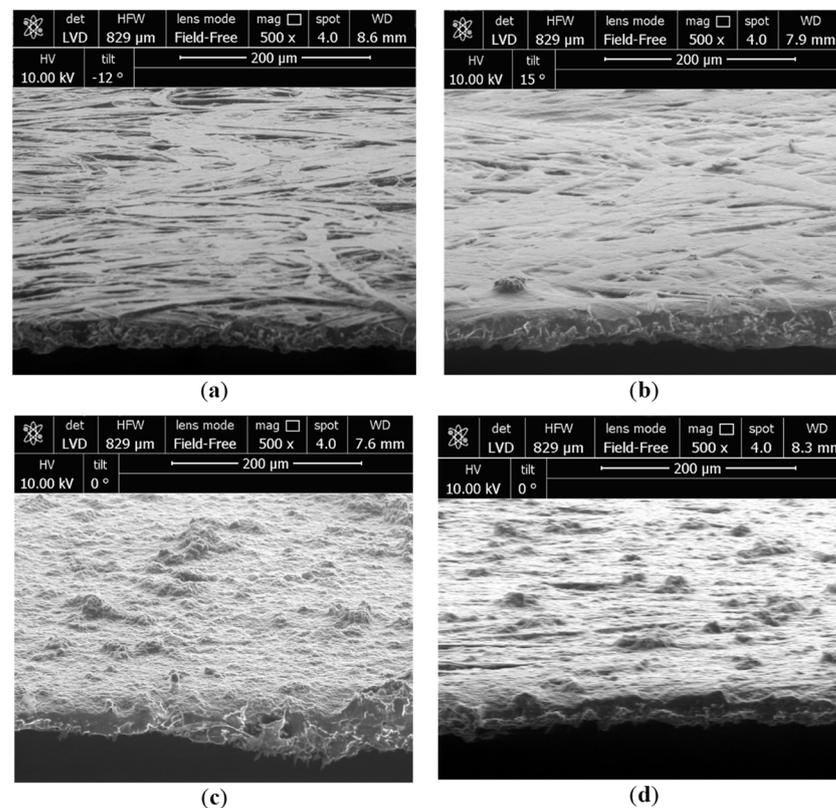


Figure 1. (a) Uncoated paper (calendered side) (UCP); (b) PHBV 80 μm single layer at 80 mm/s (80s80); (c) PHBV 80 μm double layer at 80 mm/s (80d); and (d) 80 μm single layer at 50 mm/s (80s50). See Table 1 for coating conditions.

Other authors [23,31] characterized PHBV paper coatings by SEM, but the different techniques, polymers and base support used do not allow a reliable comparison of results.

A second set of tests was conducted by changing the coating preparation conditions, obtaining an improvement of the solubilization. The PHBV solutions appeared more homogeneous and transparent compared to the ones obtained in the first set; PCL completely solubilized in chloroform and the solutions were more transparent and homogeneous than PHBV ones.

The new coated samples obtained were also observed by SEM and a significant improvement of surface homogeneity was noticed, especially in samples with 10% and

20% PEG. The comparison of PHBV-coated paper samples obtained in the first and second step allows to assume the effectiveness of the optimized solubilization strategy and the role of PEG in improving coating distribution and spreadability (Figure 2a,c).

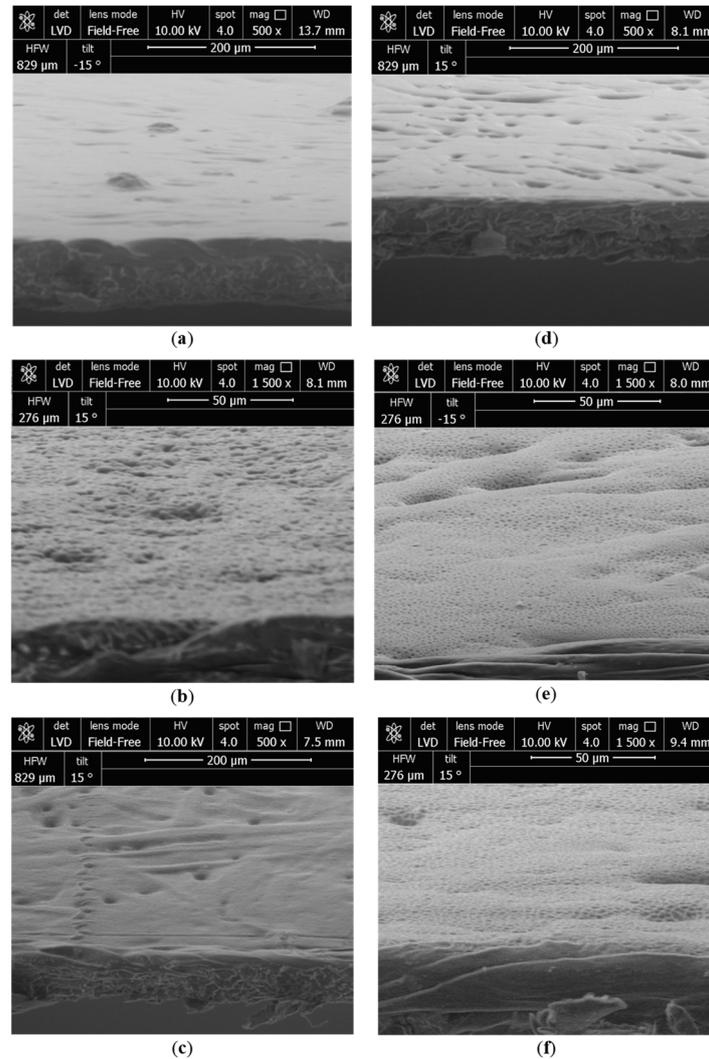


Figure 2. (a) PHBV without PEG; (b) PHBV with PEG 10%; (c) PHBV with PEG 20%; (d) PCL without PEG; (e) PCL with PEG 10%; and (f) PCL with PEG 20%.

PCL coatings show a characteristic surface, more regular and homogeneous compared to PHBV ones, although several discontinuities in the coatings were observed, but it is not clear if they are pores or simple depressions in the coating. The presence of pores in PCL coatings (of the same type used in this work, but dissolved in ethylacetate at 10%) on paperboard, was observed in a previous study too [32] and this structural characteristic was related to a lack of interaction between coating and base support. The addition of plasticizer seemed to progressively mitigate this phenomenon (Figure 2d–f). In both PHBV with PEG at 10% and PCL with PEG at 10% and 20% coatings (shown at 1500 \times magnification for this reason), a surface presenting bubbles (PHBV) and sponge-like structure (PCL) was observed. The fast evaporation of the solvent in combination with the plasticizer could justify this particular structure (Figure 2b,e).

The SEM images of the cross section in Figure 3, demonstrate that coating layer and base paper are not clearly distinguishable.

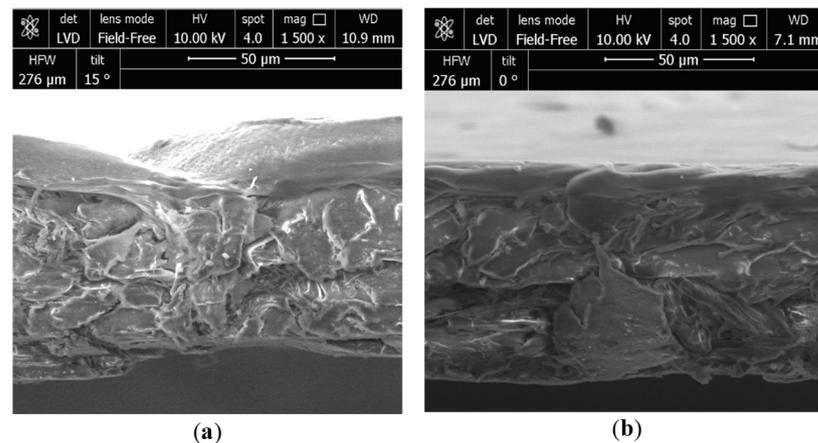


Figure 3. Cross section of pure PHBV (a) and PCL (b) of the second set.

3.2. WVTR Measurements

Water vapor transmission rate (WVTR) is one of the main characteristics of food packaging materials, being always included in technical sheets; it may be considered as an indicator of the food packaging material sensitivity toward water vapor and low WVTR values are often requested to assure an acceptable shelf life for many food products. The diffusional performances of biopolymers, such as PHBV and PCL, have been extensively measured and considerable scientific literature can be found [33–35]. In a recent review [36] on the barrier performance of biodegradable polymers, PHBV and PCL, together with other biopolymers, have been classified as a function of their diffusion performances. PHBV has been considered a medium barrier grade, for both oxygen (16–160 cc·mil/m² day atm) and water vapor permeability (16–40 g·mil/m² day kPa), while PCL has been classified as a poor barrier against oxygen (>1600 cc·mil/m² day atm) and water vapor (>120 g·mil/m² day kPa). In another recent study [37], different commercial biopolymers, PHBV and PCL included, were transformed into films via extrusion and the permeation performances were measured. The results obtained for water vapor permeability (WVP) were the following: PCL, around 2.0 g 100 mm m⁻² day⁻¹ mbar⁻¹; PHBV, 0.5 g 100 mm m⁻² day⁻¹ mbar⁻¹, the latter being close to values of PET-BO. PHBV seems to be a good candidate for the improvement of paper performances. In a study on double-layer composites using PHB and cellulose paper, different amounts of PHB (2%, 5%, 10%, 15%) were deposited via solvent casting (using chloroform as solvent) on control paper [38]. The authors observed that the permeation decreased with the amounts of PHB due to its low permeation but only if the concentration reached the value of 10%, concluding that it is necessary for the biopolymer to form a continuous layer above the paper sheet in order to fill all of the valleys of its structure. PCL may be considered as possible coating layer; authors [32] who evaluated the water vapor transmission of uncoated and coated paper (via bar coating, with a wet coating thickness of 24 μm and a dry coating thickness of ~6 μm) concluded that the PCL layer determines a decrease in permeability of around 15% if compared with the control paper. In another study [39] on the abilities of different coating formulations (zein, WPI, PCL and chitosan) to decrease the water vapor transmission of paperboard, PCL coating resulted to be effective at significantly ($p \leq 0.05$) reducing the WVTR of the cellulosic substrate from 513 to 320 g/m² 24 h, i.e., a percentage decrease around 37%. Literature data for different biopolymer types coated on papers and paperboards can be found, in terms of their barrier properties, but sometimes is not easy to compare the data because of the different substrate used and coating techniques, as well as coat weight and function of coating, together with different methods of calculation and units used [40].

Figure 4 shows the WVTR values calculated in this work for coated samples (first set) and for commercial reference samples.

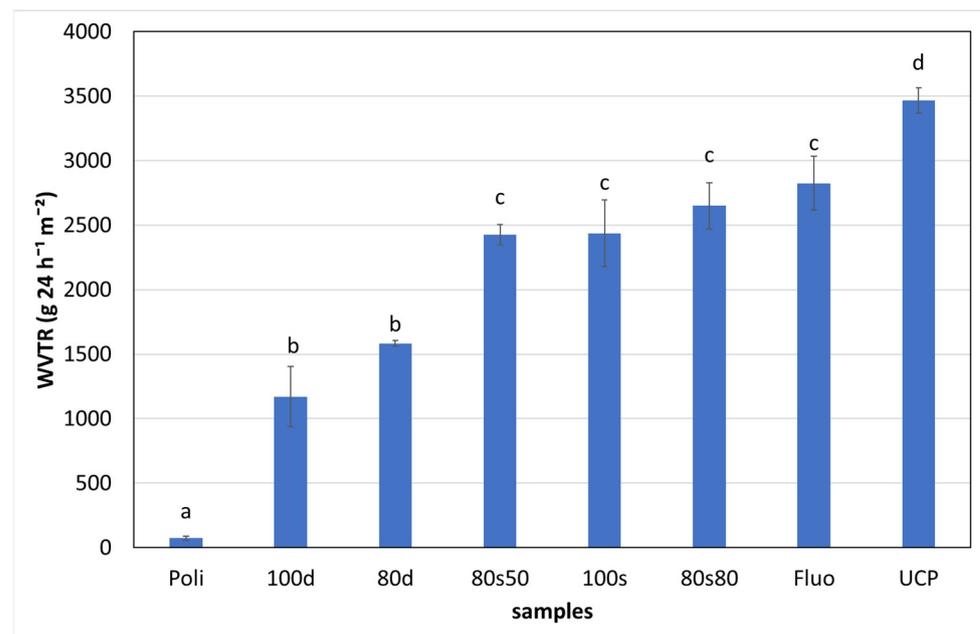


Figure 4. WVTR values ($\text{g } 24 \text{ h}^{-1} \text{ m}^{-2}$) of PHBV coating at different thickness. Bars represents the average value of three determinations, error bars report standard deviation. Different letters indicate statistically significant differences ($p < 0.05$). “UCP” refers to base paper, “Fluo” to fluorinated paper, while “Poli” to polyethylene-coated paper. See Table 1 for other samples codification.

As expected, the polyethylene-coated paper (Poli) is characterized by an extremely low WVTR (average value of $71.91 \text{ g } 24 \text{ h}^{-1} \text{ m}^{-2}$). Conversely, the fluorinated treatment (Fluo) slightly improved the barrier against water vapor (average value of $2825 \text{ g } 24 \text{ h}^{-1} \text{ m}^{-2}$) compared to the uncoated calendered paper (sample UCP) (average value of $3468 \text{ g } 24 \text{ h}^{-1} \text{ m}^{-2}$). Compared with base paper, WVTR value of PHBV coated samples significantly decreased, as a function of both coating thickness and number of layers. Single layer $100 \mu\text{m}$ (100 s) coating resulted to have a lower WVTR than single layer of $80 \mu\text{m}$ coating obtained at 80 mm/s (80s80). Comparing both single layer of $80 \mu\text{m}$ coated samples, but with different application speeds, the lower speed (50 mm/s) corresponds to a lower WVTR. This suggests a more uniform coating distribution and a higher penetration capacity in the paper support. In accordance with this assumption, grammage data (Table 2) show higher values at a lower coating speed.

The WVTR data for the first set samples were plotted in a graph (Figure 5) versus coating grammages, showing a linear inverse relationship ($R^2 = -0.986$; $\alpha < 0.01$).

The lowest WVTR values reached were 80d and 100d, and they resulted statistically different from single layer-coated samples (namely, 80s50, 100s and 80s80).

In the second set, calendered paper was coated with PHBV and PCL, also considering the influence of PEG addition as plasticizer (from 0% to 20% w/w of polymer). By comparison of WVTR values of PHBV 80d sample (first set) and PHBV (second set) it could be assumed that the modification of coating solution preparation allowed a better distribution on the paper sheet, with positive effect on moisture barrier performances (Figure 6).

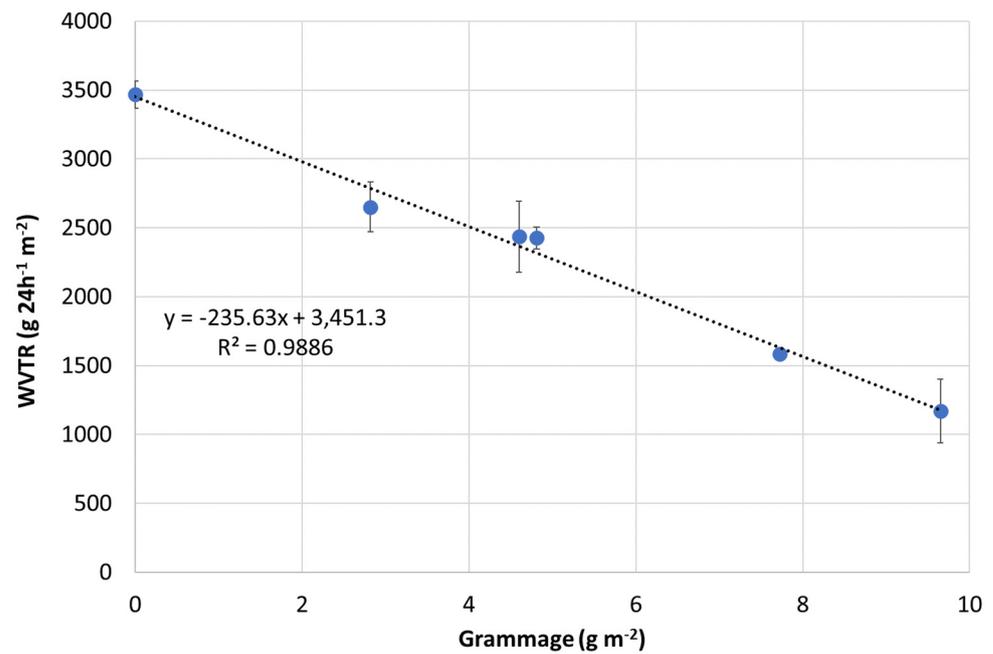


Figure 5. Linear correlation between coating grammage and WVTR of first set samples. Grammage equal to 0 corresponds to uncoated paper sample.

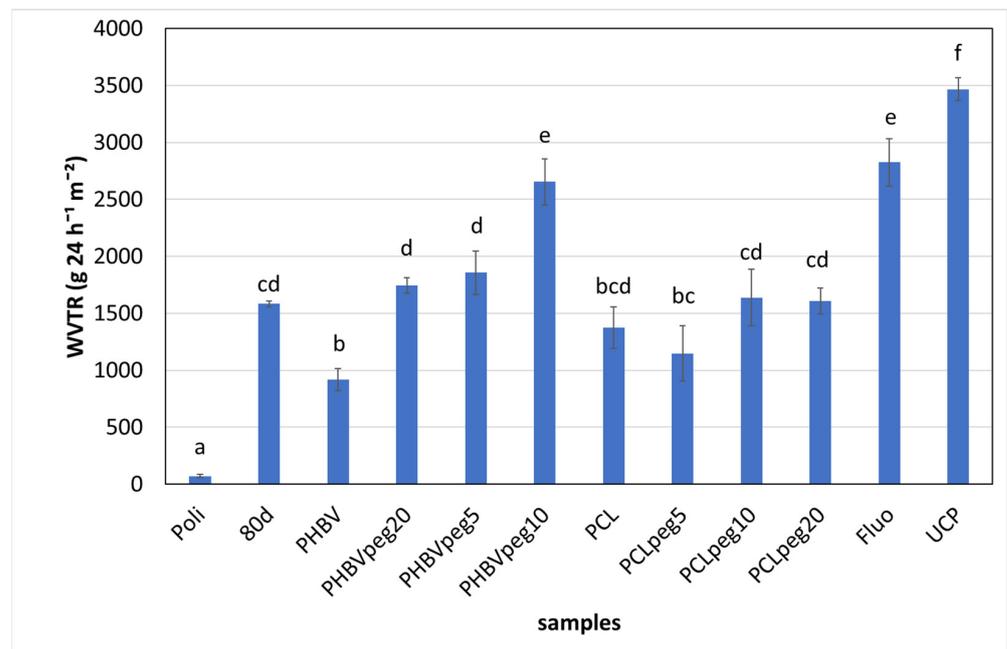


Figure 6. WVTR values ($\text{g } 24 \text{ h}^{-1} \text{ m}^{-2}$) of PHBV and PCL coated samples both pure and with PEG addition at different concentrations (set 2). Bars represent the average value of three determinations, error bars report standard deviation. Different letters indicate statistically significant differences ($p < 0.05$). “UCP” refers to base paper, “Fluo” to fluorinated paper, while “Poli” to polyethylene-coated paper. See Table 1 for other samples codification.

Concerning the addition of PEG to PHBV, a general increase of WVTR in presence of plasticizer can be observed. These results could be explained considering the hydrophilic nature of PEG and its plasticizing action, according with previous studies that attribute this behavior to a free volume increase (which promotes molecular diffusion) and to the PEG hydrophilic nature, which tends to increase sorption capacity, solubility and water

permeability of plasticized films [17]. In particular, WVTR values significantly increased in presence of plasticizer up to 10%, and then decreased at 20% PEG concentration, while maintaining a value higher than PHBV not plasticized and not significantly different compared with PHBV with 5% PEG. This trend agrees with a study about PHBV extruded films incorporated with PEG1000 at 5%, 10%, 20%. The WVTR decrease was explained in the study assuming a demixing between plasticizer and PHBV, which could, given the relatively low PHBV permeability, allow a reduction in water vapor permeability [22]. This hypothesis is not necessarily in contrast with the SEM structure observed for these samples, which appeared as more uniform compared to non-plasticized films and could be explained as the result of a beginning demixing between the two materials, not always detectable by SEM images. According to Figure 6, pure PHBV coating showed lower, although not significantly, WVTR values compared to PCL. It is possible that discontinuities observed at SEM on PCL coatings could facilitate water vapor permeation. In accordance with a previous study [41], this result could be further explained considering both that water vapor diffusion coefficient in an amorphous or semicrystalline polymer depends on molecular dynamic or amorphous regions segmental movements, and the different glass transition temperatures of the biopolymers (PCL has a lower T_g compared to PHBV), but the presence and arrangement of substituent groups (such as methyl or ethyl groups) as in PHBV case, which tend to have a minor chain flexibility on account of steric effect, and therefore, a lower WVTR, but the lack of information does not allow to elaborate additional considerations. Compared to PHBV-based coatings, plasticizer addition did not significantly affect WVTR in PCL coatings: the ones with 10% and 20% resulted to be more permeable (though not significantly) to water vapor compared to pure PCL. In general, coated samples, in particular PCL ones, showed an improvement of barrier to vapor compared to base paper; nevertheless, barrier properties can be further improved using other application techniques: processing method plays a key role in film production and can do the same in the case of coatings. Long drying required by solvent casting process can contribute to the formation of more open microstructures and channels for easy diffusion of water vapor molecules [42]. Biopolymers hot processing may allow to achieve denser and more resistant structures.

3.3. Oil and Grease Resistance

The determination of oil and grease resistance of food packaging materials, cellulosic included, is important in many applications, e.g., retail packing of fresh and cured meat, cheese, fish, but also when exchange of food components with packaging materials occurs, occasionally affecting the performances of the material itself (delamination). There is a discrete number of available and known tests to assess this performance, but they (including ASTM F119 applied in this work) are largely based on subjective statements, often not allowing to obtain measurements with a statistically meaningful physical value. Especially when grease barrier properties differences are low, a more precise and reproducible measurement method will be required: for instance, mixing oils used in the tests with coloring agent and determining colorimetric coordinates using a spectrophotometer), with the aim of making results independent from individual subjectivity [43].

Table 3 shows grease resistance times of all samples of this work. All the coatings improved base paper resistance (resistance ranging between 0 and 10 min), but performances were not comparable with fluorinated and polyethylene-coated papers, which did not show any failure after 72 h. Resistance times recorded for PHBV coated papers were generally lower than 20 min; only PHBVpeg5 showed resistance ranging between 40 and 60 min. The few studies available in literature report variable grease resistance data and ascribe this variability to the presence of cracks or to lack of uniformity in the material [23]. PCL coated samples showed in all cases a resistance of more than 4 h, but less than 12 h, except one sample showing a higher resistance between 12 and 24 h.

Table 3. Grease resistance times.

Sample Code	Time (minutes)		
UCP	10	-	0
Fluo	>4320	>4320	>4320
Poli	>4320	>4320	>4320
80s80	20	20	20
80s50	10	30	20
80d	10	10	10
100s	10	10	40
100d	10	20	20
PHBV	10	20	20
PHBVpeg5	40	60	40
PHBVpeg10	20	20	20
PHBVpeg20	20	10	40
PCL	240–720	240–720	240–720
PCLpeg5	240–720	240–720	240–720
PCLpeg10	240–720	720–1440	240–720
PCLpeg20	240–720	240–720	-

3.4. Contact Angle Measurements

3.4.1. Water

As shown in Figures 7 and 8, fluorinated paper resulted far more hydrophobic than other samples, possibly because of the epichlorohydrin treatment. Contact angle values of first set samples resulted to decrease as number of layers and coating amount increase. This result could be explained by the Wenzel theory [44], assuming the effect of the relative roughness of coatings, and in particular, assuming a raise of the measured hydrophilicity as roughness of the material increases: as noted in SEM images, double layer coatings showed a higher roughness compared with single layers and resulted to be the most hydrophilic.

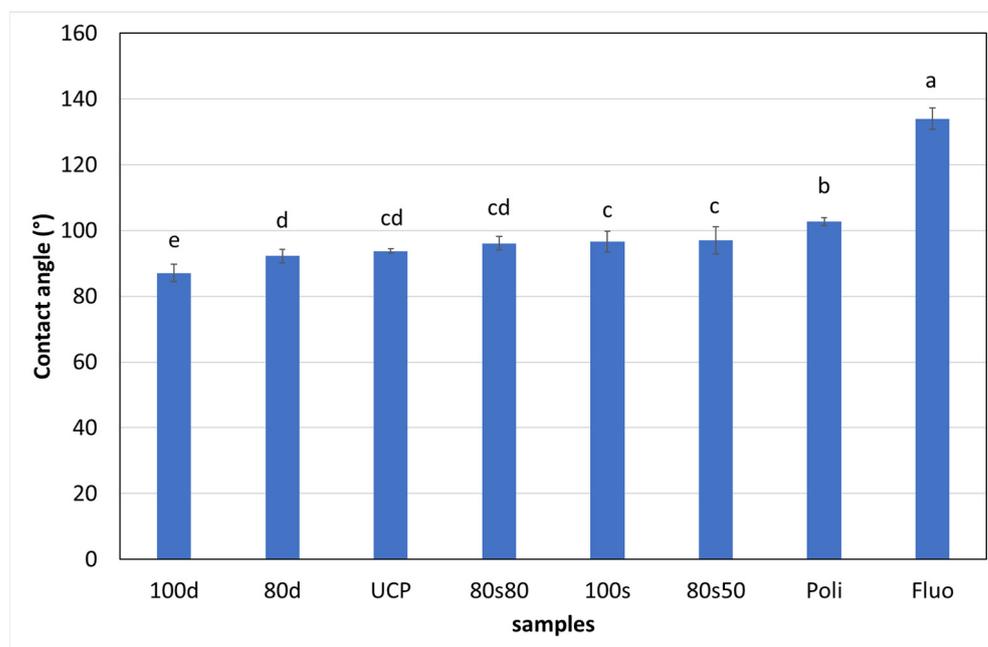


Figure 7. Average water contact angle values for first set samples. Error bars report standard deviation. Different letters indicate statistically significant differences ($p < 0.05$). “UCP” refers to base paper, “Fluo” to fluorinated paper, while “Poli” to polyethylene-coated paper. See Table 1 for other samples codification.

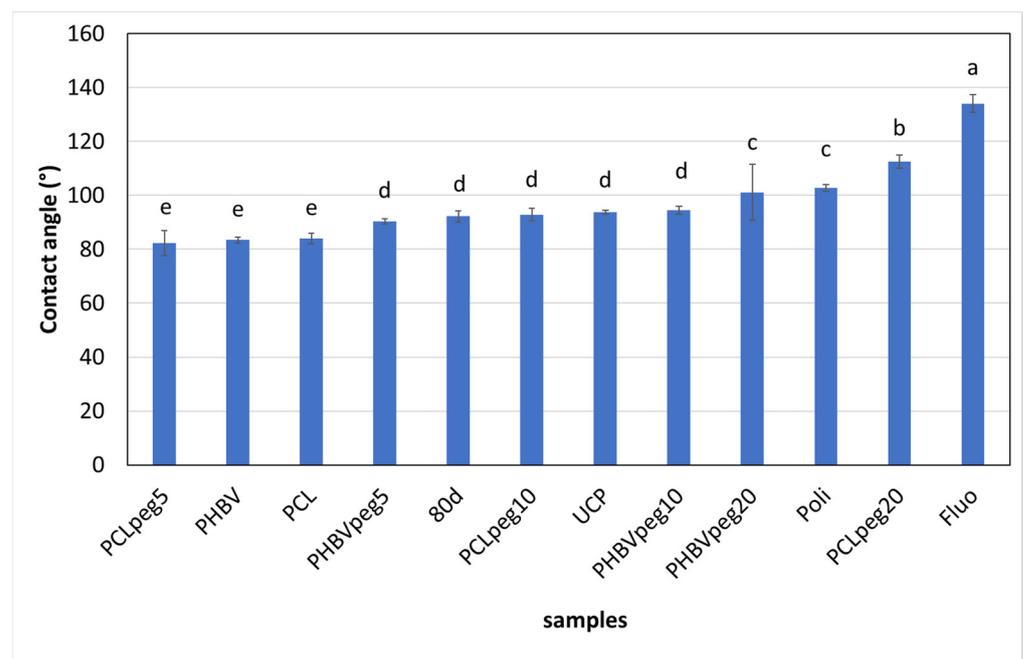


Figure 8. Average water contact angle values for the second set samples. Error bars report standard deviation. Different letters indicate statistically significant differences ($p < 0.05$). “UCP” refers to base paper, “Fluo” to fluorinated paper, while “Poli” to polyethylene-coated paper. See Table 1 for other samples codification.

Calendered paper showed a good hydrophobicity. The relatively high value detected for this paper could be related to a behavior that comes closer to the Cassie-Baxter model, assuming the contribution of air bubbles entrapped between interfiber gaps, given the high porosity of this material, but it is difficult to verify such a hypothesis (Figure 8) [44,45].

It is possible to notice a general upward trend of the contact angle (or a downward trend of wettability), by adding plasticizer. Given the relative hydrophilicity of PHBV and PEG, this result could be explained considering the Wenzel theory and the effect of surface roughness [44]. The use of plasticizer in the coating solution formulation could be associated with a better solution spreadability and a more uniform coating distribution. The SEM images seemed to support the effectiveness of PEG in this regard, as the coated surface appeared more uniform and less rough with increasing plasticizer concentrations. PCL contact angle values were higher than the ones found in literature for films based on the same PCL type used in this work (always at 5% w/v , but in trichloromethane and differently processed), equal to 64.5° [46].

Even if the trend is not as linear as for PHBV, the Wenzel theory could explain the significantly higher contact angle values detected for PCL with PEG at 10% and 20% samples, considering the progressive increase of smoothness observed for these coatings by the SEM images. Although PCL with PEG at 5% sample showed a contact angle value lower than pure PCL, the difference was not statistically significant. PHBV and PCL both with PEG at 20% samples showed the lowest wettability (highest contact angle values) among coated samples. In particular, PCLpeg20 reached a wettability level significantly lower compared to reference polyethylene-coated paper (Figure 9).

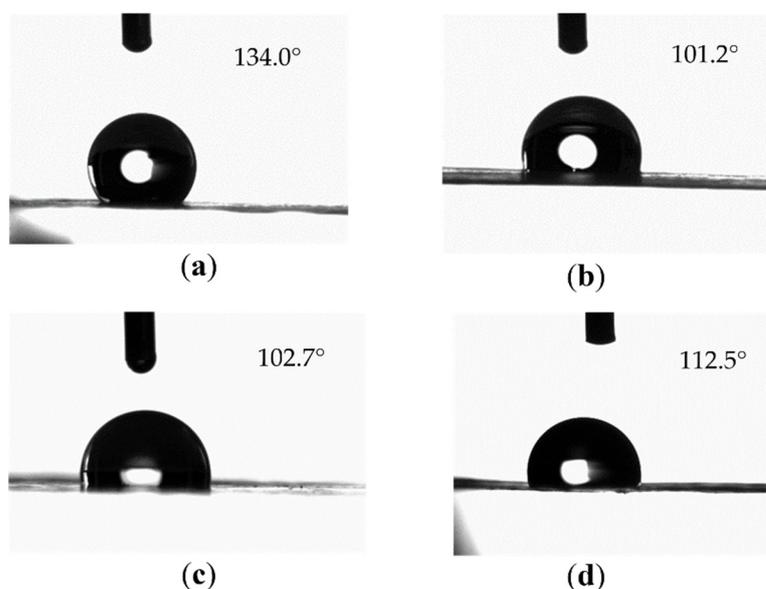


Figure 9. Water contact angles of (a) fluorinated paper (Fluo); (b) paper coated with PHBV with PEG 20% (PHBVpeg20); (c) polyethylene-coated paper (Poli); (d) paper coated with PCL with PEG 20% (PCLpeg20).

Furthermore, it is important to remember that unexpected results may occur, as the hydrophobic and hydrophilic surface chemistry physics is more complex than Wenzel and Cassie-Baxter models, which represent simplification of what is really going on. Rough surfaces contact angles study is still a vibrant research field [44].

3.4.2. Oil

Tables 4 and 5 show oil contact angle values of, respectively, first and second set and commercial reference samples. Oil contact angle values in both sets showed an elevated wettability (oleophilicity) of the coatings, expressed by low contact angle values (in the range from 11.3 to 37.3°), and therefore difficult to determine. As expected, given the low surface energy, fluorinated paper showed high contact angle values (average value of 101.9°) and particularly reduced wettability (high oleophobicity) (Figure 10).

Polyethylene-coated paper showed a low oil contact angle value (average value of 16.9°). Several coatings of the second set showed a higher oleophobicity than this commercial reference, with special regards for PCLpeg20, showing an average measured value of 37.3°.

Table 4. Oil contact angle values of first set samples.

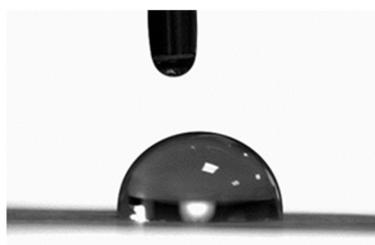
Sample Code	Mean Contact Angle Value
UCP	15.1 ± 3.8 ^{bc}
Fluo	101.9 ± 1.5 ^a
Poli	16.9 ± 0.2 ^b
80s80	14.0 ± 1.6 ^{bc}
80s50	11.3 ± 0.7 ^c
80d	12.6 ± 1.8 ^{bc}
100s	15.5 ± 3.2 ^{bc}
100d	12.4 ± 1.5 ^{bc}

Different superscript letters indicate statistically significant differences ($p < 0.05$).

Table 5. Oil contact angle values of second set samples.

Sample Code	Mean Contact Angle Value
UCP	15.1 ± 3.8 ^{de}
Fluo	101.9 ± 1.5 ^a
Poli	16.9 ± 0.2 ^d
80d	12.6 ± 1.8 ^e
PHBV	24.7 ± 1.6 ^c
PHBVpeg5	19.3 ± 1.0 ^d
PHBVpeg10	17.2 ± 1.7 ^d
PHBVpeg20	17.6 ± 2.3 ^d
PCL	18.9 ± 1.9 ^d
PCLpeg5	16.6 ± 0.8 ^{de}
PCLpeg10	27.0 ± 2.3 ^c
PCLpeg20	37.3 ± 1.9 ^b

Different superscript letters indicate statistically significant differences ($p < 0.05$).

**Figure 10.** Oil contact angle of fluorinated paper (Fluo).

4. Conclusions

To conclude, this work, within the limits of its lab-scale, offers insights for future research lines toward the development of cellulose-based food contact materials, with special attention to a greater sustainability compared to actual commercial solutions. The SEM analysis of the developed coated samples showed the disappearance of the typical fiber network of paper and allowed to observe a continuous layer of coating. The smoothness of the coating surface was used as an indicator of good biopolymer solubilization. Coated samples developed in this work showed a significant improvement of water vapor barrier compared to uncoated paper and also to commercial fluorinated paper. The significant reduction of WVTR is a promising feature of the developed coated paper samples, according to the importance of this parameter for food quality preservation. Biopolymer-coated paper samples showed improved grease resistance, still not comparable with fluorinated and polyethylene-coated commercial samples. Among samples, PCL-coated offered the best resistance, ranging from 4 to 12 h. PHBV and PCL coatings with PEG at 20% showed good water contact angles, thus a low wettability. The measured oil contact angles were generally much lower compared to fluorinated paper, however certain coating formulations (i.e., PCLpeg20, PCLpeg10 and PHBV) showed significantly higher surface oleophobicity compared to commercial polyethylene-coated paper.

Chloroform utilized in this study is a poorly biocompatible solvent; therefore, future developments should include the evaluation of more eco-friendly solvents, when possible, or other coating techniques, such as extrusion coating. The increasing availability and commercial variety of compostable biopolymers allow a more concrete technical feasibility. The real compostability of biopolymer-coated paper should, however, be verified.

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