Tailoring barrier properties of thermoplastic corn starch-based films (TPCS) by means of a multilayer design

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Abstract

This work compares the effect of adding different biopolyester electrospun coatings made of polycaprolactone (PCL), polylactic acid (PLA) and polyhydroxybutyrate (PHB) on oxygen and water vapour barrier properties of a thermoplastic corn starch (TPCS) film. The morphology of the developed multilayer structures was also examined by Scanning Electron Microscopy (SEM). Results showed a positive linear relationship between the amount of the electrospun coatings deposited onto both sides of the TPCS film and the thickness of the coating. Interestingly, the addition of electrospun biopolyester coatings led to an exponential oxygen and water vapour permeability drop as the amount of the electrospun coating increased. This study demonstrated the versatility of the technology here proposed to tailor the barrier properties of food packaging materials according to the final intended use.

Keywords: TPCS, Electrospinning, Multilayer, Barrier properties, Biopolyesters.

1. INTRODUCTION

The use of biopolymers has received increased attention in the last decades as potential substitutes for conventional polymers in a broad range of applications. Among biopolymers, polysaccharides, like starch, are interesting renewable resources that have different applications. Indeed, the introduction of starch in the plastic sector has been motivated by its low cost and biodegradability and by the fact that it is available in large quantities (Xu *et al.,* 2005). However, starch cannot be processed through conventional plastic equipment without further modification because its degradation begins at a temperature lower than its melting point (Avérous, 2004). By the addition of water or other plasticizers such as glycerol or sorbitol, the native crystalline structure of starch is irreversibly disrupted (the so-called gelatinization phenomenon) and thus, the granular starch is transformed into a thermoplastic starch (TPS) which vary from a soft material (high plasticizer level) to a brittle material (low plasticizer level) depending on the moisture and plasticizer level (Jiménez *et al*., 2012).

The barrier to water vapor and oxygen are two essential properties to consider in starch-based materials because oxygen and water molecules can deteriorate food properties. Indeed, one of the main problems of starch-based films is their high water sensitivity arising from their hydrophilic character, which leads to strong plasticization (Yan *et al*., 2012). This effect negatively affects some characteristics such as the oxygen barrier properties, which are excellent at low hydration levels and plasticizer content but decrease as water sorption increases (Jiménez *et al*., 2013, Yan *et al*., 2012). Therefore, many research works have focused on improving starch performance either by blending it with other moisture resistant biodegradable polymers such as polylactic acid (PLA) and polycaprolactone (PCL) (Ali Akbari Ghavimi *et al*., 2015, Ayana et al., 2014, Cai *et al*., 2014, Matzinos *et al*., 2002, Ortega-Toro *et al*., 2015) or through the addition of dispersed nanoreinforcing agents to generate nanobiocomposites (Dean *et al*., 2008, Zeppa *et al*., 2009). However, from an industrial implementation point of view, it is important to highlight that complex multilayer structures are suggested as an alternative to improve the performance of biopolymers, being the most efficient form to constitute barrier materials (Fabra *et al*., 2013, 2014). Whilst this multilayer design has been widely used for synthetic materials, it has been scarcely developed for biodegradable food packaging systems due to technological problems associated to the scaling-up process and multilayer assembly. Nowadays, this methodology is being successfully exploited by means of electrohydrodynamic processing, also known as electrospinning, to improve the barrier and functional performance of biodegradable polymers thermodynamically immiscible with the additional advantages of forming electrospun coatings (Fabra *et al*., 2014) or bioadhesives (Fabra *et al*., 2015 ab) which show excellent adhesion between layers, avoiding the use of synthetic adhesives.

Taking advantage of the methodology already described, this paper reports, for the first time, a comparative study in which the effect of different amounts of electrospun biopolyesters coatings (polylactic acid –PLA-, polycaprolactone –PCL- and polyhydroxybutyrate –PHB-) has been analyzed and compared in terms of barrier efficiency.

2. MATERIALS AND METHODS

2.1 Materials

Polyhydroxybutyrate (PHB) pellets were supplied by Biomer (Krailling, Germany). PHB was reported to have 0-40 wt% of plasticizers and an unreported amount of non-toxic nucleating agents to improve melt processing (Hänggi, 2011). The semicrystalline polylactide (PLA) used was a film extrusion grade produced by Natureworks (with a Disomer content of approximately 2%). The molecular weight had a number-average molecular weight (Mn) of ca. 130,000 g/mol, and the weight average molecular weight (Mw) was ca. 150,000 g/mol as reported by the manufacturer. The polycaprolactone (PCL) grade FB100 was supplied by Solvay Chemicals (Belgium).

Corn starch (CS) was kindly supplied by Roquette (Roquette Laisa España, Benifaio, Spain) and glycerol (Panreac Quimica, S.A. Castellar Del Vallés, Barcelona, Spain) was used as plasticizer.

N,N-dimethylformamide (DMF) with 99% purity and trichloromethane (99% purity) were purchased from Panreac Quimica S.A. (Barcelona, Spain). 2,2,2-Trifuoroethanol (TFE) with 99% purity were purchased from Sigma-Aldrich (Spain). All products were used as received without further purification.

2.2. Preparation of films

2.2.1 Preparation of thermoplastic corn starch films (TPCS)

Corn starch and glycerol, as plasticizer, were dispersed in water using a polymer: glycerol: water ratio of 1:0.3:0.5 (w/w/w) and the dispersion was melt-mixed in a Brabender Plastograph internal mixer at 130ºC and 60 rpm for 4 minutes. The mixture was then spread evenly on Teflon and placed in a compression mould (Carver 4122, USA) at a pressure of 30000 lbs and 130ºC for 5 minutes.

2.2.2 Preparation of multilayers TPCS systems

TPCS films were coated with PHB, PLA or PCL mats produced by means of the electrospinning technique. PHB solutions in 2,2,2-trifluorethanol having a total solids content of 10 wt.% were used to generate the electrospun fibres. The PLA and PCL electrospinning solutions were prepared by dissolving the required amount of the biopolymer, under magnetic stirring, in a solvent prepared with a mixture of trichloromethane (TCM):N,N-dimethylformamide (DMF) in order to reach a 5 or 12 % in weight (wt.-%) of PLA and PCL, respectively. The TCM:DMF ratio used for PLA and PCL was 85:15 and 65:35, respectively.

PHB, PLA or PCL fibre mats were directly electrospun onto both sides of the TPCS films by means of a Fluidnatek® electrospinning pilot plant equipment from Bioinicia S.L. (Valencia, Spain) equipped with a variable high-voltage 0-60 kV power supply. Biopolyester solutions were electrospun under a steady flow-rate using a motorized high throughput multinozzle injector, scanning vertically towards a metallic grid used as collector, in which the neat TPCS film was attached. The distance between the needle and the collector was 20, 24 and 31 cm for PHB, PLA and PCL, respectively, and the experiments were carried out at ambient temperature. The voltage of the collector and injector were set at 24 kV and 19 kV, respectively.

Different deposition times (0, 2, 10, 20, 40, 60 and 90 minutes), were evaluated in the TPCS film to see how deposition time affected barrier properties. The total amount of electrospun material (mg cm^{-1}) was estimated by weighing the TPCS film before and after collection of the electrospun material.

With the aim of obtaining transparent and continuous outer layers based on PHB, PLA or PCL, an additional heating step was applied. Coated TPCS films were placed between hot plates at 160ºC to melt and homogenize the PHB or PLA phase and 60ºC to melt the PCL layer.

2.3. Characterization of films

2.3.1. Scanning Electron Microscopy (SEM)

A Hitachi S-4800 microscope (Hitachi High Technology Corp., Tokyo, Japan) was used to observe the morphology of films cross-sections. Cross-sections of the samples were prepared by cryo-fracture of the films using liquid N_2. The samples were mounted on bevel sample holders with double-sided adhesive tape, and sputtered with Au/Pd under vacuum. Samples were observed using an accelerating voltage of 10 kV and a working distance of 12–16 mm. Layer thicknesses were measured by means of the Adobe Photoshop CS3 extended software from the SEM micrographs in their original magnification.

2.3.3. Barrier properties

2.3.3.1 Water Vapour Permeability (WVP)

The WVP of TPCS and multilayer structures was determined by using the ASTM (2011) gravimetric method using Payne permeability cups (Elcometer SPRL, Hermelle/s Argenteau, Belgium) of 3.5 cm diameter. For each type of samples, measurements were done in triplicate and water vapour permeability was carried out at 25ºC and 0-100% relative humidity gradient, which was generated by using dry silica gel and distilled water, respectively. The cups were weighed periodically (0.0001 g) after the steady state was reached. Cups with aluminium films were used as control samples to estimate solvent loss through the sealing. Water vapour transmission rate (WVTR) was calculated from the steady-state permeation slopes (8 points) obtained from the regression analysis of weight loss data *vs*. time (Eq. 1), and weight loss was calculated as the total cell loss minus the loss through the sealing.

$$WVTR = \Delta m / (\Delta t \cdot A) \qquad (Eq.\ 1)$$

where $\Delta m/\Delta t$, is the weight of moisture loss per unit of time (Kg/s); A, the film area exposed to moisture transfer (m^2).

Water vapour permeance was calculated using equation 2 as a function of p_1 (water vapor pressure on the film's inner surface) and p_2 (pressure on the film's outer surface in the cabinet).

$$\text{Permeance} = \text{WVTR} / (p_1 - p_2) \quad \text{(Eq. 2)}$$

Water vapour permeability (WVP) was obtained by multiplying the permeance by the average film thickness as specified in equation 3:

$$\text{WVP} = \text{permeance} \cdot \text{thickness} \quad \text{(Eq. 3)}$$

Films thickness was measured in at least 5 different points using a digital micrometer (Mitutoyo, Spain) with ± 0.001 mm accuracy.

2.3.3.2 Oxygen permeability (O_2P)

The O_2P was derived from oxygen transmission rate (OTR) measurements recorded, in triplicate, using an Oxygen Permeation Analyzer M8001 (Systech Illinois, UK) at 80% RH and 23ºC. A sample of each multilayer film (5 cm^2) was placed in the test cell and pneumatically clamped in place. The samples were previously purged with nitrogen in the humidity equilibrated samples, before exposure to an oxygen flow of 10 mL min^{-1}. In order to obtain the oxygen permeability (OP) (Eq. 4), film thickness was considered in each case.

$$\text{OP} = \text{permeance} \cdot \text{thickness} \quad \text{(Eq. 4)}$$

2.3.4. Contact Angle Measurements

Measurements of contact angle were performed at room conditions (*ca*. 23ºC and 53% RH) in a Video-Based Contact Angle Meter model OCA 20 (Data Physics Instruments GmbH, Filderstadt, Germany). Data were obtained by analysing the shape of a distilled water drop after it had been placed over the film for 5 s. Image analyses were carried out by SCA20 software. At least, eight replicates were made for each sample.

2.4. Statistical Analysis

Statistical analysis was performed using the analysis of variance procedure (ANOVA) with StatGraphics Plus version 5.1 (Statistical Graphics Corp.). Fisher's Least Significant Difference (LSD) test was applied to detect differences of means, and $p<0.05$ (95% significant level) was considered to be statistically significant.

3. RESULTS AND DISCUSSION

3.2 Microstructure of multilayer films

Since it is well-known that barrier properties of biopolymers are strongly related to their morphology, SEM was used to evaluate the films' homogeneity, layer structure, presence of pores and cracks, surface smoothness and thickness. SEM micrographs of the surface images of the multilayer TPCS-based films are shown in Figure 1. TPCS film presented homogeneous and smooth surfaces, without visible pores and cracks (see Figure 1). Besides, it was clearly observed that annealing the PCL, PLA and PHB fibres favoured the formation of a continuous coating layer which could contribute to improve the barrier properties of the TPCS films.

The cross-section image of the TPCS film showed a compacted structure with absence of intact starch granules, demonstrating the effectiveness of the destructuration and thermo-compression processes (*cf.* Figure 2A). Representative images of the multilayer structures prepared with PCL, PLA or PHB are shown in Figures 2, 3 and 4, respectively. The first clear observation of these multilayer films was that all samples exhibited a laminate-like structure in which relatively homogeneous biopolyester coatings were formed onto both sides of the TPCS films. Furthermore, the adhesion between the outer layers and the TPCS film was very good and only a weak delamination occurred after cryo-fracturing the material in some of the samples.

From the cross-section micrographs, it is also interesting to note that the thickness of the outer layer depended on the biopolyester used and thus, on the electrospinning solutions and the morphology of the electrospun fibres. Therefore, the amount of the coating layer was estimated by weighting the TPCS before and after the electrospinning process and it was observed that, for a given amount of the electrospun layer, the thickness of the coating was governed by the polymer concentration used in the electrospinning solution and the diameter of the electrospun fibres (Pérez-Masiá *et al*., 2013; Chalco-Sandoval *et al*., 2014). A lineal relationship was observed between the thickness and the deposited amount of the electrospun coating, as it will be detailed below (see Figure 5). In this sense, for a given amount of the electrospun layer (*i.e*. 5 $mg{\cdot}cm^{-2}$), PHB provided thicker layers and PLA the thinnest ones. As it was previously reported by Pérez-Masiá *et al*., 2013, PLA fibres were thinner than those obtained for PCL and PHB, in identical electrospinning conditions as the ones applied in the present work. Therefore, after the annealing process, PLA fibres were better compacted than PCL and PHB thus providing thinner layers. Besides, when comparing the thicker ones (PCL and PHB), an excellent interfacial adhesion between PCL and thermoplastic starch (TPS) melt phases have been reported elsewhere (Ortega-Toro *et al*., 2015, Cai *et al*., 2014) in composite PCL/TPS films which could also contribute to the increased attractive forces through hydrogen bonding interactions between the ester carbonyl of PCL and the –OH groups of starch, thus, reducing the thickness of the outer PCL layers when compared to the PHB layer thickness. This interaction could lead to lowering the interfacial tension between both materials, leading to compatibilization (Cai *et al*., 2014). This could also explain the good adhesion between PCL and TPCS layers.

3.3 Barrier properties

Figures 5 and 6 show the water vapour (WVP) and oxygen permeability (O_2P) values of the neat TPCS films and the developed multilayer structures. Water and oxygen barrier properties of the uncoated TPCS films developed in this work were in the same order as those reported in the literature for films prepared by melt-compounding (Ortega-Toro *et al*., 2015). However, comparing with the literature data, these films were less permeable than their counterparts prepared by solvent casting (Jiménez *et al*., 2012; Müller *et al*., 2011, Pushpadas *et al*., 2008). Thus, one can firstly conclude that the processing method used during film-formation played an important role in the final properties of the films. This can be ascribed to the fact that the casting process involved long drying times which contributed to the formation of a more open microstructure due to the solvent evaporation phenomenon, creating channels throughout which water molecules could easily diffuse. However, using the compression-moulding method, polymer chains were more compacted giving rise to a denser structure. A similar trend was observed comparing other biopolymer matrices such as PHA (Fabra *et al*., 2013) or PLA (Byun, Kim and Whiteside, 2010; Rhim, Hong, and Ha, 2009; Sánchez-García and Lagaron, 2010ab).

Figure 5 displays the water vapour permeability values of the developed multilayer structures. As mentioned on above, the thickness of the outer layers linearly increased as the mg (PCL, PLA or PHB) $\cdot cm^{-2}$ increased, whatever the biopolyester used.

Interestingly, the WVP values decreased exponentially as the mg coating layer·cm^{-2} increased (y=*b*·e^{ax}) and thus, it was shown that the addition of biopolyester coatings significantly reduced the WVP of the neat TPCS film. The exponential equation represents the WVP behaviour whose initial value is *b* and whose rate of decay at any time equals *a* mg coating layer· cm^{-2} its value at that time. It is well-defined that if 0< e^{ax} <1, the function decays as x (x= mg ·cm^{-2}) increases and thus, thus, greater values of *a* lead to faster rates of decay. PHB was more efficient in reducing water vapour permeability of TPCS films than PCL and PLA biopolymers. This agrees with the greater water vapour permeability values of the neat PLA and PCL films (1.2 and 1.4 kg Pa^{-1} m^{-2} s^{-1}, for PLA and PCL respectively) (Ambrosio-Martin *et al.*, 2014; Bychuk, Kil'deeva and Cherdyntseva, 2014) as compared to the WVP obtained for a neat PHB film (0.16 kg Pa^{-1} m^{-2} s^{-1}) (Plackett and Siró, 2011). Coefficients *a*, *b* and R^2 are given in Table 1. The greater barrier efficiency on TPCS films is reflected through the lower ~~*a* and~~ *b* and greater *a* values. Due to the abrupt permeability decrease for the multilayer structures prepared with PHB as compared to the neat TPCS film, the regression coefficient from the exponential model considering the whole mg PHB·cm^{-2} range was only ~0.93, so another fit only considering data of multilayer samples (without taking into account the permeability of the neat TPCS film) was carried out, which allowed us to make better predictions. The obtained values indicate that it is possible to use smaller amounts of PHB electrospun outer layer than PLA or PCL to achieve the same barrier efficiency. Concretely, for a given amount of electrospun coating (i.e. 5 mg ·cm^{-2}), the WVP of TPCS films dropped down to *ca.* 83, 88 and 91% for PCL, PLA and PHB multilayer structures, respectively. Accordingly, the greatest reduction was observed when coating the TPCS film with the greatest amount (expressed as mg·cm^{-2}) of electrospun PHB fibres, where the WVP dropped down to *ca*. 99 %.

A similar trend was observed for oxygen barrier properties, measured at 80% RH (*cf.* Figure 6). The addition of electrospun coatings significantly reduced the oxygen permeability and, the total amount of electrospun coating was also exponentially related with oxygen barrier properties, being the PHB the biopolyester which provided the greatest reduction in O_2P values. The coefficients a, b and R^2 of the fitting model are given in Table 2. Once again, the greater barrier efficiency on TPCS films was evidenced by the lower b values found for the multilayer structures prepared with PHB. In fact, for a given amount of electrospun coating (*i.e.* 5 $mg \cdot cm^{-2}$), the oxygen permeability of multilayer structures was improved up to ~ 91% for PLA and PCL and ~ 95% for PHB as compared to the neat TPCS film. For oxygen barrier, the exponential model was also reported considering only the data of PLA and PHB multilayer structures (without the neat TPCS film), which allowed to make better predictions.

Thus, barrier results highlighted the suitability of this methodology to develop fully biodegradable multilayer structures with improved barrier performance which could be adapted depending on the final intended used.

3.4 Contact angle

The wettability properties of the TPCS films and the coated multilayer structures were determined by direct measurement of contact angles of a water drop deposited on the upper surface of the samples in order to investigate the effect of the PCL, PLA and PHB coating layers on the surface water affinity. Contact angle was measured for the neat TPCS and for multilayer structures prepared with the lowest and highest deposition times. Since the deposition time did not match with the amount of biopolyester deposited onto each side of the TPCS film, contact angle of multilayer structures prepared with 3.2 $mg \cdot cm^{-2}$ electrospun coatings were also measured for comparative purposes. The results are displayed in Table 3 and Figure 7, showing that all of them (PCL, PLA and PHB) were quite effective (significantly greater contact angle values) in protecting the TPCS inner layer from moisture. It might be noted that the resulted contact angle values of the developed multilayer structures were in the same range as for the neat PLA and PCL biopolymers (de Campos *et al*., 2013; Chan *et al*., 2013; Darie *et al*., 2014) although lower to contact angles reported in the literature for neat PHB films (Zhijiang *et al*., 2016). This difference could be ascribed to the intrinsic plasticizer content in the original PHB pellets. As mentioned before, PHB was originally reported to have between 0 and 40 wt% plasticizer in order to improve melt processing (Hänggi, 2011).

4. CONCLUSIONS

Multilayer technology is a common and efficient technique used to improve the physicochemical properties, mainly barrier, of the hydrophilic materials. In this work, TPCS multilayer systems containing electropun biopolyester outer layers based on PCL, PLA or PHB have been developed. The incorporation of electrospun biopolyester coating layers effectively improved water vapour and oxygen barrier properties of the TPCS films, although the PHB was the most efficient in reducing both water and oxygen permeability values.

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Table 1. Values of *a, b* coefficients and R^2 in the relationship between WVP and mg (PCL, PLA or PHB) $\cdot cm^{-2}$

Coating layer	Model	*a*	*b*	R^2
PCL	exponential	-0.478	4.00E-17	0.992
PLA		-0.413	3.00E-17	0.928
without TPCS		-0.351	2.00E-17	0.983
PHB		-0.425	2.00E-17	0.936
without TPCS		-0.378	1.00E-17	0.947

Table 2. Values of *a, b* coefficients and R^2 in the relationship between O_2P and mg (PCL, PLA or PHB) $\cdot cm^{-2}$

Coating layer	Model	*a*	*b*	R^2
PCL	exponential	-0.478	4.00E-17	0.992
PLA		-0.413	3.00E-17	0.928
without TPCS		-0.351	2.00E-17	0.983
PHB		-0.425	2.00E-17	0.936
without TPCS		-0.378	1.00E-17	0.947

Table 3. Contact angle values of the neat thermoplastic corn starch-based films, the developed multilayer structures and the neat PHB, PLA and PCL films.

Coating layer	mg · cm^{-2}	θ (°)
		54.8 (3.5)^{a}
PCL	0.8	82.2 (2.5)^{b}
	3.2	81.9 (3.0)^{b}
	7	78.5 (4.4)^{b}
PLA	0.5	84.0 (3.8)^{b}
	3.2	84.1 (2.6)^{b}
	4.9	83.2 (3.6)^{b}
PHB	1.5	81.6 (2.6)^{b}
	3.2	84.2 (2.4)^{b}
	13.6	86.5 (3.1)^{b}
PHB		123 (3.5) (*)
PLA		86.9 (1.6) (**)
PCL		89.5 (1.9) (***)

(*)Zhijiang *et al.*, 2016 (**)Darie *et al.*, 2014 (***)Campos *et al.*, 2008

a-b: Different superscripts within the same column indicate significant differences among samples ($p < 0.05$).

Figure captions

Figure 1. Surface images of the neat TPCS film (A) and the developed multilayer films prepared with PCL (B), PLA (C) or PHB (D).

Figure 2. Cross-section images of the neat TPCS and multilayer films prepared with PCL at different deposition times (A) TPCS, (B) 20 min, (C) 40 min and (D) 90 min.

Figure 3. Cross-section images of the multilayer films prepared with PLA at different deposition times (A) 2 min, (B) 20 min, (C) 40 min and (D) 60 min.

Figure 4. Cross-section images of the multilayer films prepared with PHB at different deposition times (A) 20min, (B) 40 min, (C) 60 min and (D) 90 min.

Figure 5. Relationships between WVP values *vs.* the mg electrospun coating · cm^2 (black symbols) and thickness *vs.* the mg electrospun coating · cm^2 (white symbols).

Figure 6. Relationships between O_2P values *vs.* the mg electrospun coating · cm^2 (black symbols) and thickness *vs.* the mg electrospun coating · cm^2 (white symbols).

Figure 7. Images of water droplet in **c**ontact angle measurements of the uncoated TPCS film (A) and the developed multilayer films prepared with the highest deposited amount of PCL (B), PLA (C) or PHB (D).

Figure 1

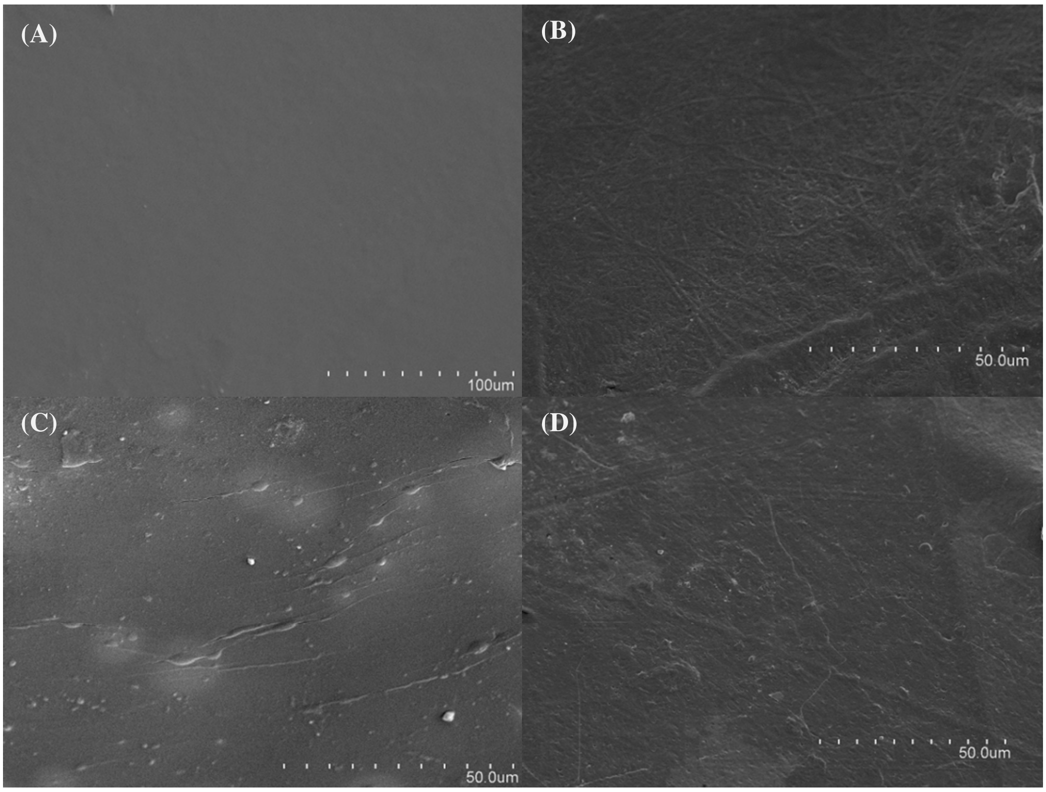


Figure 2

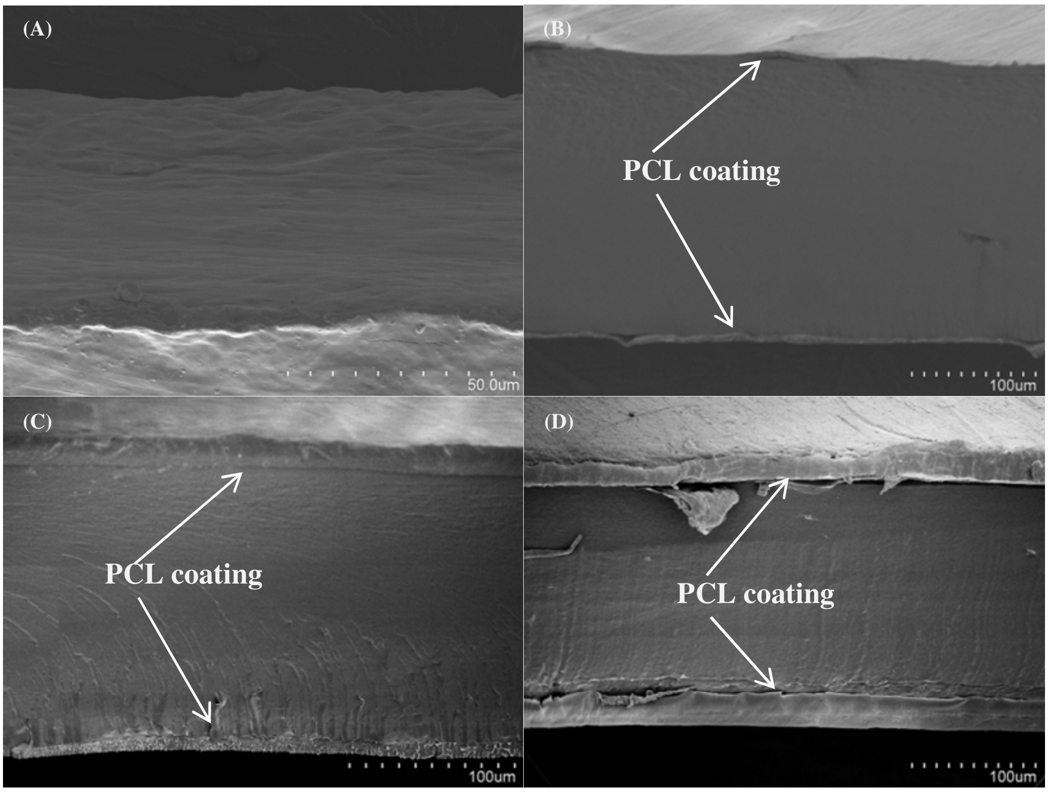


Figure 3

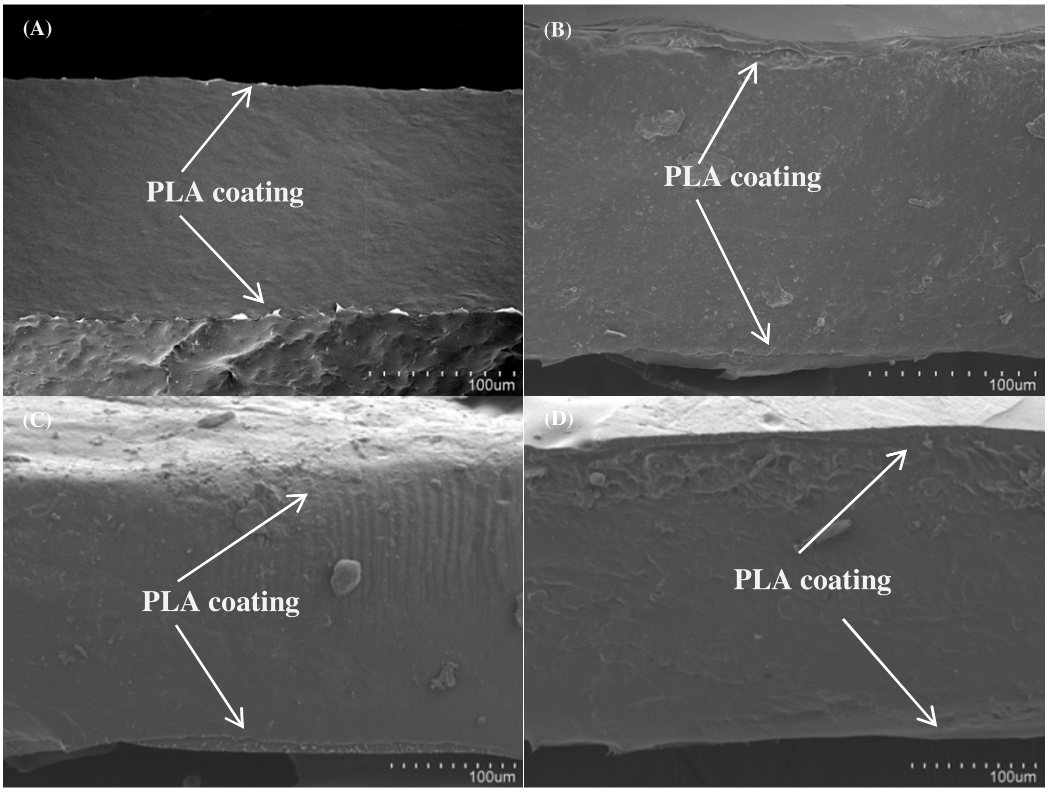


Figure 4

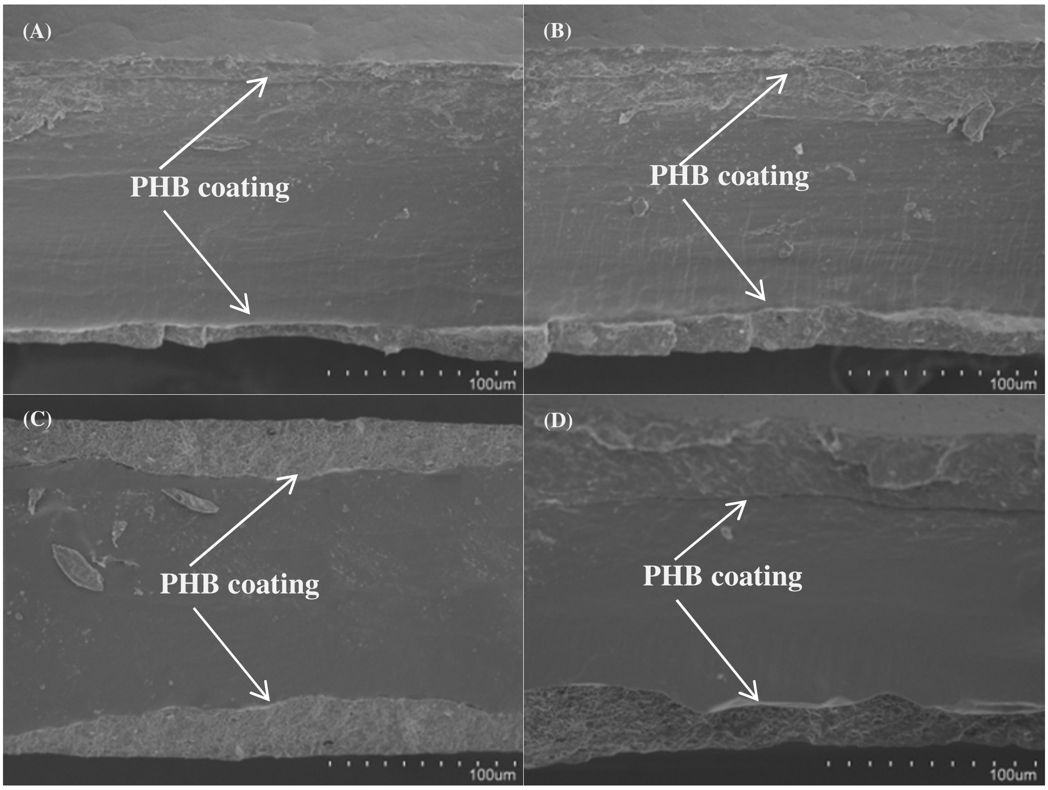

(A)
PHB coating
100um
(B)
PHB coating
100um
(C)
PHB coating
100um
(D)
PHB coating
100um

Figure 5

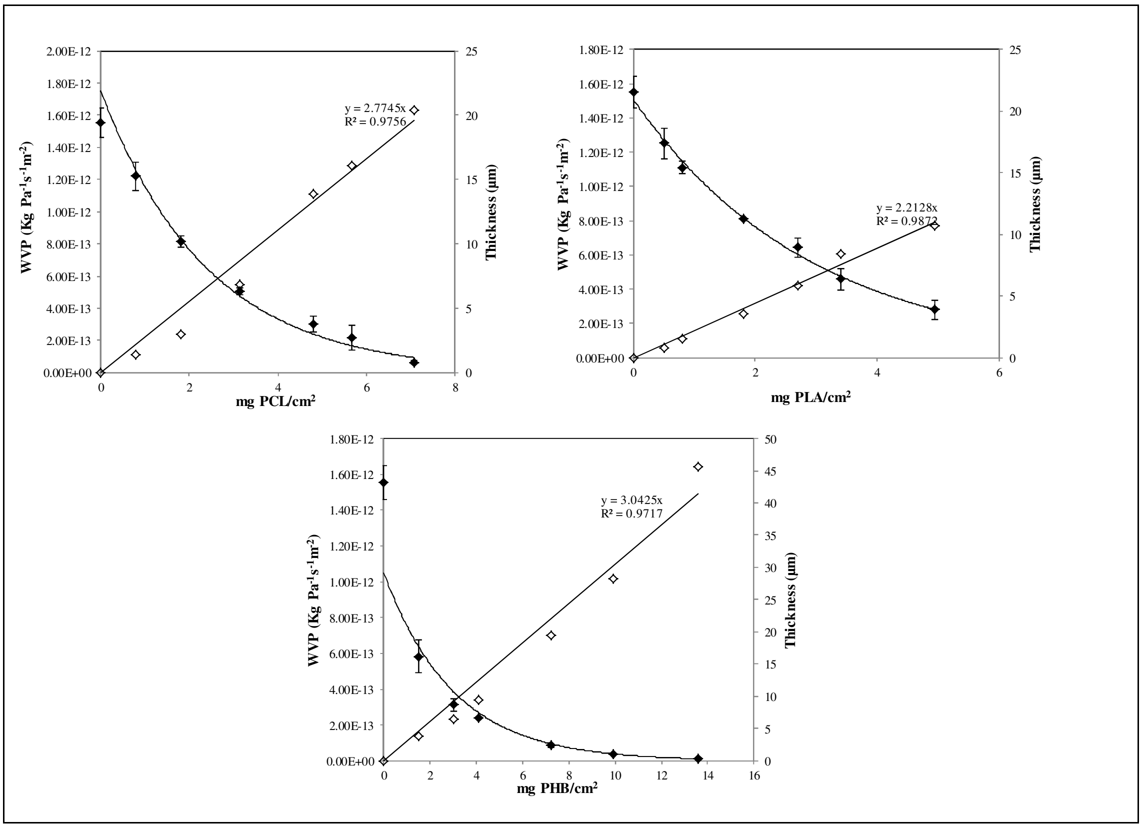
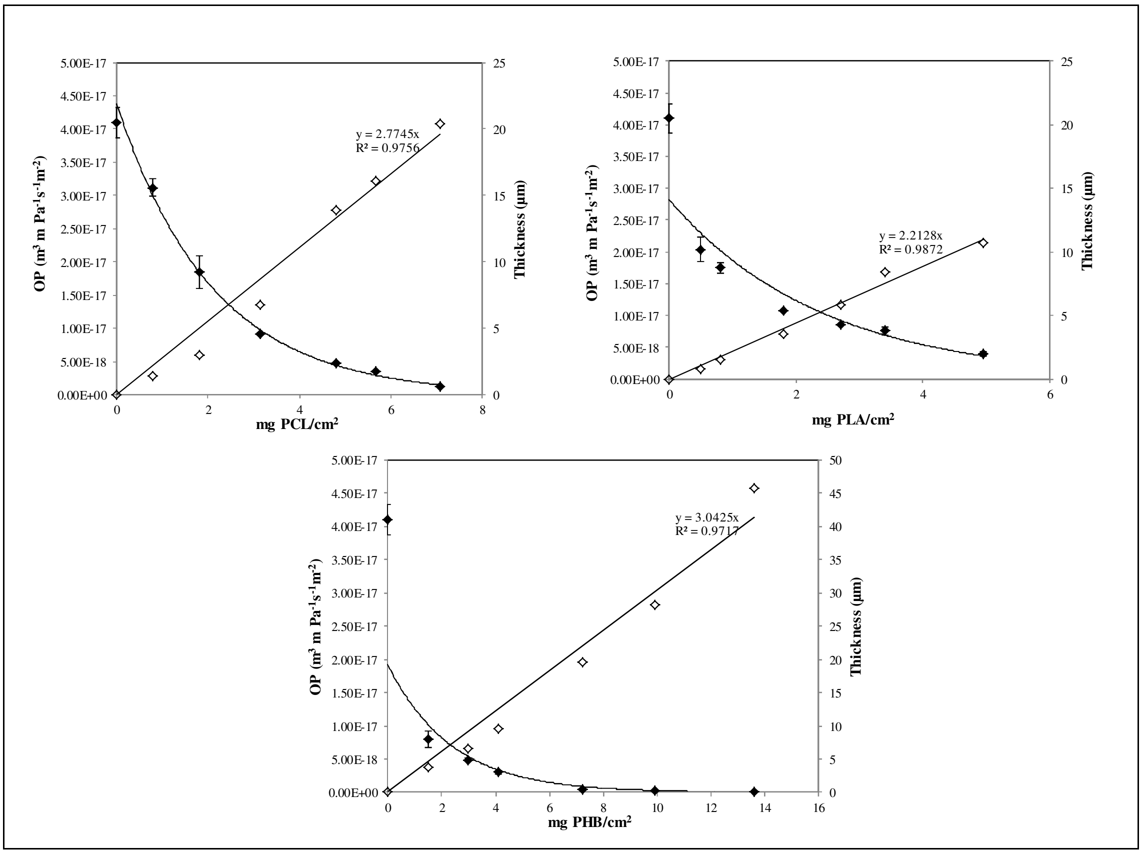

WVP (Kg Pa-1s-1m-2)
Thickness (µm)
mg PCL/cm2
y = 2.7745x
R² = 0.9756
mg PLA/cm2
y = 2.2128x
R² = 0.9873
mg PHB/cm2
y = 3.0425x
R² = 0.9717

Figure 6



OP (m³ m Pa⁻¹s⁻¹m⁻²)
Thickness (µm)
y = 2.7745x
R² = 0.9756
mg PCL/cm²
y = 2.2128x
R² = 0.9872
mg PLA/cm²
y = 3.0425x
R² = 0.9717
mg PHB/cm²

Figure 7