Comparison of Crosslinking Efficiency in Dip and Roll-Deposited Coatings on Their Oxygen Barrier

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ABSTRACT: Coating techniques are key factors in determining coated film properties. In the present study, nanocomposite coatings of poly(vinyl alcohol) and a nanoclay, montmorillonite, were deposited layer-by-layer using roll (doctor blade, DB) and dip coating techniques, in an effort to compare the impact of these techniques on the crosslinking efficiency and oxygen barrier of the coated films. The barrier properties at different relative humidities were tested, and the extent of nanoclay intercalation as well as the films’ morphology was investigated. Barrier was further improved by crosslinking the coating with glyoxal and glutaraldehyde. Both techniques gave similar results but with a higher impact of relative humidity in roll coated films. Better results were achieved by tailoring the composition of those coatings to favor a higher density of hydrogen bonding in the coating.

1. INTRODUCTION

High oxygen barrier materials are in increasing demand for food packaging. Numerous food products have a shelf life that could be shortened due to an inadequate gas barrier of the package. Several technologies have been adopted to enhance the oxygen barrier. Silicone oxide (SiOx) coating results in a transparent coated film that is microwavable and has a low oxygen permeability as well as good resistance to water immersion.5 Its weak adhesion to plastic substrates and ease of oxygen permeability as well as good resistance to water immersion.5 It is mainly used with solution casting and extrusion, but a high filler loading cannot be reached, as the resulting agglomeration alters the composite’s properties.

The high aspect ratio of clays, such as montmorillonite (MMT) (more than 100), slows the diffusion of oxygen molecules through the polymer by increasing their diffusing path, known as tortuosity.6

To improve this tortuosity, the filler’s volume fraction and its aspect ratio are usually the considered parameters.8,9

The filler’s orientation has also an important impact on tortuosity, as demonstrated by Bhardwaj’s permeability model10 even though it is not usually considered for the modeling of nanocomposite permeability. A vertically oriented fillers, for example, would not improve the tortuosity in the film as does a perfectly horizontally oriented one.

An important factor to be considered when manufacturing nanocomposites is the chosen technique, considering its impact on these fillers’ properties. Polymer/clay nanocomposites, for instance, are often prepared by solution and melt intercalation. The main drawback is the clay platelets agglomeration during the processing11 that limits the amount of clay that can be incorporated in the nanocomposites, particularly in the melt state. This may result in an oxygen permeability.12

Supporting Information

Received: April 3, 2019
Accepted: June 18, 2019
Published: September 16, 2019
barrier not high enough for many applications. For a better barrier and acceptable film transparency, a good clay dispersion and intercalation must be achieved.

In some packaging applications, there is an increasing demand for alternative high-barrier materials due to the growing awareness about recyclability. Such materials could be obtained with nanocomposite coatings, as they result in a thinner structure than melt processed or cast nanocomposites films and an easier recyclability. These coatings have also a better barrier owing to the important fraction of clay that can be achieved. New techniques such as layer-by-layer (LbL) have succeeded in depositing thin nanocomposite coatings with good orientation, dispersion, and intercalation of clay platelets. This method consists in the successive deposition of thin layers (polymers and/or nanofiller) on a substrate with numerous types of interlayer interactions to hold these layers together (electrostatic interactions, hydrogen bonding, etc.). Depending on their composition, the thickness of these layers can reach hundreds of nanometers. LbL coatings have a higher gas barrier than conventional metal or mineral oxide coating techniques, as it enables a clay loading without aggregation.15

LbL deposition could be achieved with various processes, such as spin coating, spraying, and dipping, for which scaling up is still a challenge. Another technique that can be applied to LbL thin film deposition is a roll-to-roll process, such as blade coating (DB). This technique, derived from screen-printing, enables the deposition of thin films (hundreds of nanometers) quickly with low material consumption.17 For LbL nanocomposite coatings, the filler layer can be deposited separately from the polymer and not as a mix, like in the case of single-layer coatings. Due to such alternate deposition, it is possible to have a coating with a considerable amount of filler.13

LbL technique is widely applied to water-soluble polymers, which have high sensitivity to moisture. To further improve the oxygen barrier at high relative humidity, there is generally recourse to crosslinking. Dialdehyde crosslinkers (glutaraldehyde (GA), glyoxal (Gly), etc.) are among the most frequently used ones due to their high reactivity and increasing efficiency in crosslinking water-soluble polymers coatings, thus reducing their sensitivity to moisture.20,21 The focus of this work is on the impact of the chosen coating technique on the oxygen barrier at high relative humidity, which, to our knowledge has not been addressed before.

In this study, LbL coatings of PVA and MMT were deposited on a PET substrate through two techniques, blade and dip coating with the aim of comparing their efficiency in improving the coating’s oxygen barrier at high relative humidity. To reduce the sensitivity to moisture, the nanocomposite coatings were crosslinked with two dialdehydes, glyoxal, and glutaraldehyde. The effect of crosslinking on their permeability was investigated, and the oxygen permeability of those coatings as a function of the relative humidity was reported. Coatings morphology was analyzed using atomic force microscopy (AFM) and the intercalation of clay platelets was characterized by X-ray diffraction (XRD).

2. EXPERIMENTAL SECTION

2.1. Materials. PVA (Mw = 140 000–186 000 g/mol) was purchased from Sigma Aldrich (Saint Louis, Missouri). Natural sodium montmorillonite (MMT) platelets (Cloisite NA+), nanoclay, with a density of 2.86 g/cm³, were supplied by BYK (Gonzales, Texas) and used as received. Silicon plates, supplied by EL-Cat Inc. (Ridgefield Park, New Jersey), and poly(ethylene terephthalate) (PET) films, supplied by ProAmpac (Terrebonne, QC, Canada), were used as substrates for LbL deposition. Poly(ethylene imine) (PEI) (5% aqueous solution), supplied by MICA Corporation (Shelton, CT), was used as a primer for all of the samples. The crosslinkers glyoxal (Gly, 40% aqueous solution) and glutaraldehyde (GA, 25% aqueous solution), were purchased from Sigma Aldrich (Saint Louis, Missouri).

2.2. Preparation of Thin Films. PVA solutions and MMT suspensions were prepared with deionized (DI) water. PVA solutions were heated at 80 °C for 2 h. A PEI solution (0.6% in DI water) was used to deposit a primer layer whether blade coated or dip coated for 20 min and rinsed with DI water.

2.2.1. Dip Coating. The coating deposition cycle is a repetition of dipping in PVA and MMT solutions, rinsing, and drying steps, as illustrated in Figure 1a. To increase the coverage of the surface, the dipping time was 5 min for the first bilayer and the rinsing time was 1 min. For the next layers, the dipping and rinsing times were reduced to 1 min and 30 s, respectively. To achieve chemical crosslinking, films were dipped in the GA or Gly solution (5% aqueous solution) after half of the bilayers had been deposited and then at the end, once all the 15 bilayers had been deposited.

2.2.2. Roll (Blade) Coating. PVA and MMT layers were deposited alternately by spreading the solution using the doctor blade (Harper Scientific (Charlotte, NC); Figure 1b). As for dipping, a crosslinker layer was applied twice, once half of the bilayers had been deposited and at the end, after the final bilayer.
2.3. Characterization. X-ray diffraction (Philips X’pert) was used in the wide-angle mode (wide-angle X-ray diffraction (WAXD)), in the range from 2 to 10° at a rate of 0.02°/s to determine the MMT interlayer spacing d(001) according to Bragg’s law. The source is copper Cu Kα radiation (λ = 1.54056 Å).

Permeability to oxygen was measured via a MOCON OXTRAN 2/21 (Minneapolis) at 25 °C, 0% relative humidity, and 1 atm pressure, in accordance with the ASTM D-3985-81. For tests with an adjustable relative humidity (RH), a MOCON OXTRAN 10X apparatus (Minneapolis) was used at 25 °C and a RH up to 70%. Water vapor permeability (WVP) was determined at 25 °C via a MOCON PERMATRAN-W model 101K for 100% RH. Water contact angle was measured at room temperature, with distilled water as the probe liquid with a Contact Angle Goniometer OCA20 from dataphysics. The time chosen to calculate the contact angles by the software was 5 s after a drop touches the sample surface. Five readings were measured for each sample and an average of these values was reported and used for the results discussion. The thickness of the coatings was determined with a Dektak 3030 profiler using silicon plates as substrate. Morphology and roughness of the surface of the coated layer were examined using an atomic force microscope (AFM) (Nanoscope V Dimension Icon/Fastscan AFM, Bruker) operated in the tapping mode in air. All of the imaging was acquired using Intermittent Peak Force tapping using 125 μm TESP-V2 Air probes with the tip radius of 8 nm. The average roughness of the samples was determined by measuring the roughness at 6 different points. The average roughness values are reported with the standard deviations. The surface microstructure was examined by comparing the phase images of different samples for 5 μm × 5 μm scan windows.

3. RESULTS AND DISCUSSION

Dip coating is a widely used technique for fundamental studies of LbL, whereas blade coating mimics better the industrial coating process and can be helpful in scaling up the LbL deposition process. Blading technique is faster than dipping, taking approximately half the time compared to dipping due to fewer steps. This technique is also more cost-effective, as it requires less material for each layer. The use of DB enables a better control on the deposited volume of the material. These techniques result in coatings with different morphologies and properties as discussed in the following sections.

3.1. Oxygen and Moisture Barrier. Oxygen transmission rates (OTR) of PET films coated with LbL deposited assemblies were measured at 23 °C and 0% RH. A 15-bilayer coating reduced the neat PET permeability considerably (Table 1). This high barrier is due, on one hand, to an important nanoclay loading (½ >50 wt %) in the LbL coatings, which enhances the tortuosity in the film. On the other hand, the high density of hydroxyl groups in the PVA structure coupled to their strong hydrogen bonding. Whether intermolecular or with MMT, can be responsible of a considerable reduction of the free volume in the coatings, thus reducing the permeability.

Blade coating results in a better surface homogeneity than dip coating as illustrated in Figure 1c. The heterogeneous surface of dipped coatings is due to the progressive coverage of the substrate with each dipping step, commonly known as island growth. For the first dipping cycles, the substrate surface is partially covered with “islands” of polymers. The homogeneity of the layers as well as a complete coverage of the substrate is eventually obtained with more dipping cycles. This difference in the surface coverage explains the better oxygen barrier of blade-coated films with a permeability almost one third that of dip-coated films at 0% RH.

Table 1. Oxygen Permeability of Coated PET and Coatings Only

| Coating Type                        | Oxygen Permeability (cm³·m⁻²·day⁻¹·atm⁻¹) |
|-------------------------------------|--------------------------------------------|
| PET                                 | 3072                                       |
| 15 PVA dipped coating               | 1616.5                                     |
| 15 PVA bladed coating               | 405                                        |
| 30 PVA dipped coating               | 309                                        |
| 15 (PVA + MMT) dipped coating       | 47.59                                      |
| 15 PVA + 15 MMT dipped coating      | 8.17                                       |
| 15 PVA + 15 MMT bladed coating      | 3.47                                       |

Neat PET (16 μm) has a higher permeability than conventional barrier polymers like PVA (1.5 cm³·μm⁻²·day⁻¹·atm⁻¹). Coating with 15 PVA layers only reduced this permeability by 50% with dipping and by 80% with blading (Table 1). Increasing the number of PVA layers (30 instead of 15) further reduced the permeability by 90%, whereas adding MMT layers, instead, in a 15-bilayer structure (15 PVA + 15 MMT) resulted in the highest reduction, 99%, for both dip and blade coatings. To compare the permeability of a PVA-MMT bilayer coating and a coating with layers of mixed PVA and MMT, a mixture of PVA and MMT was prepared by dispersing MMT in the PVA solution while keeping the same concentration as used for bilayer coating. The permeability of the mix coating was 10 times higher, which is mainly due to the poorer dispersion of MMT and a low intercalation of PVA.

Varying the relative humidity changed the barrier results for the two techniques. By increasing the humidity, the film is in contact with a considerable amount of water molecules that interact with free hydroxyl groups at the surface. This interaction affects the permeability by altering the free volume in the coating. On one hand, water molecules may disrupt hydrogen bonding by breaking the existing bonds and establishing hydrogen bonds with hydroxyl groups. This implies that a higher density of free hydroxyl groups may increase the permeability. On the other hand, the adsorption of water molecules results in the swelling of the coating, allowing a higher diffusing area for oxygen. Such a swelling can be limited by the presence of well-intercalated MMT platelets in the coating with a strong interaction with the polymer.

According to these two points, the better barrier of dipped coating at higher humidity can be related to its lower amount of free hydroxyl groups and its reduced swelling due to the higher amount of MMT in the coating (Figure S1). WVP results (Table 2) confirm this conclusion, as the blade-coated film has a higher permeability to the hydrophilic permeant, i.e., water vapor, implying a higher water adsorption due to free functional groups.

3.2. Crosslinking. Crosslinking with Gly and GA reduced the oxygen permeability by 4–5 times for dipping and 2–6 for blading. The better barrier of the Gly crosslinked film may be due to small Gly molecules (Figure 2), which enables a faster diffusion through the multilayer structure.
Thus densification was achieved by creating covalent acetal bridges between polymer chains, as the establishment of covalent bonds at both crosslinker ends is higher with Gly. The change in intensity coupled to the permeability results confirmed this densification density is higher with Gly.

Table 2. Oxygen Permeability at Different Relative Humidities and WVP of Coated Films

| Relative humidity (g/m²·day) | WVP 100% RH (g/m²·day) | Coating thickness (μm) |
|-------------------------------|-------------------------|------------------------|
| dipped coating                | 8.17 ± 15.65            | 173.29 ± 49.96         | 0.964 ± 5.4 |
| bladed coating                | 3.48 ± 4.66             | 215.5 ± 53.02          | 1.02 ± 5.6  |
| dipped coating crosslinked with Gly | 1.82 ± 4.16          | 45.81 ± 49.93          | 0.92 ± 5.6  |
| bladed coating crosslinked with GA | 2.23 ± 4.67          | 114.16 ± 50.1 ± 5.4   | 0.866 ± 5.4 |
| bladed coating crosslinked with Gly | 0.54 ± 0.51           | 456.3 ± 51.63          | 0.833 ± 5.6  |
| bladed coating crosslinked with GA | 1.71 ± 2.64          | 55.84 ± 52.16          | 0.883 ± 5.6  |

The results are shown in Table 2. At high RH, crosslinking with GA decreased the sensitivity to moisture for both types of coatings. Crosslinking with Gly, however, resulted in two distinct results, with a barrier improvement for the dip-coated film and a sharp permeability increase for the blade-coated film. Knowing that permeability in humid conditions depends on the interaction with water, this sharp increase of permeability with Gly could be explained by a higher amount of nonreacted Gly molecule in the film due to the short drying time. The presence of these nonbonded molecules in the coatings may disrupt the established hydrogen bonds. The barrier improvement with crosslinking for the dip- and blade-coated film crosslinked with GA is the result of the covalent bonding that reduces the fraction of the available hydroxyl groups. The crosslinking mechanism of PVA with dialdehydes has already been discussed in literature, and it is described as the establishment of covalent bonds at both crosslinker ends by creating covalent acetal bridges between polymer chains, thus densifying the coating (thinner coatings with crosslinking; Table 2, Figure 2).

To validate this mechanism for an LbL structure, FTIR spectra of the crosslinked and no coatings deposited by dipping were compared (Figure 3). The vibration band of PVA corresponding to C=O stretching shifted from 1096 to 1046 cm⁻¹, which may be due to inter- and intramolecular H-bonding interactions as well as bonding with MMT. The peak intensity increased with crosslinking, with a higher intensity for the Gly crosslinked coating. This change in intensity coupled to the permeability results confirm that the crosslinking density is higher with Gly.

The broad peak between 3000 and 3500 cm⁻¹ corresponds to the hydroxyl groups in the coating. With no acid used in the crosslinking reaction; in this study, both reaction steps are reversible. According to the FTIR spectra, there is a higher amount of hydroxyl group in the Gly crosslinked coating compared to the noncrosslinked and GA crosslinked coatings. As free functional groups of dialdehyde can be hydroxyl or carbonyl, Gly has more free hydroxyl than GA which is confirmed by the FTIR peak at 1700 cm⁻¹ in the GA spectrum, specific to carbonyl groups.

As for noncrosslinked films, dip-coated films crosslinked with Gly and GA have a better barrier to a hydrophilic permeant (Table 2), suggesting that even after crosslinking, blade-coated films have a higher density of free functional groups.

To gain information about the hydrophilicity of those coatings, water contact angle (CA) was determined. Dip-coated films had a higher CA with water than blade coated films (Figure 4). Blade coated film crosslinked with Gly had the most hydrophilic character, which would explain the sharp increase in its permeability. Since hydrophilicity depends on the composition of the outermost layer, the CA is mainly affected by the free hydroxyl groups on the surface that are able to establish hydrogen bonds with water. The higher hydrophilicity of blade-coated films could be explained by a lower crosslinking density, as it is limited by the drying time. The hydrophilicity of those coatings correlates well with the permeability results at 70% RH (Figure 5), as dip-coated films have a higher CA and a lower oxygen permeability.

Crosslinked coatings with Gly have a similar roughness (37.7 ± 5.4 compared to 39.6 ± 8 nm; Figure S2) even though noncrosslinked dipped coating showed a higher roughness (40.4 ± 6 compared to 18.8 ± 5.6 nm for bladed coating).

Figure 2. Structure of crosslinkers, (a) glyoxal, (b) glutaraldehyde, and (c) potential reaction of a dialdehyde crosslinker with PVA.

Figure 3. FTIR spectra of crosslinked and no PVA-MMT coatings.
Knowing that an incomplete exfoliation of clay and the overlapping of its platelets may affect the coating roughness, clay intercalation and orientation were investigated. The MMT basal spacing of 1.14 nm (2θ peak at 7.73°) increased considerably for both types of coatings (Figure 6). The WAXD patterns for the PVA-MMT bilayers deposited by blade and dip coating show a better nanoclay intercalation for the dip-coated films (29.79, 17.89 Å compared to 23.19, 12.92 Å for blading). Considering the affinity between PVA and MMT, the wider interlayer spacing for platelets in dip-coated films may be explained by the better diffusion of PVA between the MMT platelets. The dipping method allows better mobility of PVA chains as well as longer time for diffusion. With blading, however, the volume of the deposited layers is imposed by the doctor blade, and its diffusion is limited by the film’s drying.

To compare clay platelets orientation, the Hermans orientation function, \( f_{CN} \), for each type of coating was determined (see the Supporting Information for calculation details). This function ranges from 1 to \(-1/2\), with 1 for an orientation parallel to the surface and \(-1/2\) for a vertical platelet orientation. Both techniques resulted in a good clay platelet orientation, with a slightly better orientation for blade coating (a value of 0.7 for \( f_{CN} \) compared to 0.675 for dipping) as some stress is applied when spreading the solution of PVA or MMT on the substrate.

Clay orientation varies considerably with the used process. Extrusion blow molding, for instance, results in a better orientation of clay than compression molding or casting. Compressed molded samples of poly(propylene) and modified clay (Cloisite 20A) have a \( f_{CN} \) of around 0.32 when compatibilized and 0.27 without compatibilization. Clay orientation in blown films is considerably higher with a \( f_{CN} \) that reaches 0.8 without compatibilization and can be tailored by the draw ratio (DR) (0.6 (DR = 1) to 0.749 (DR = 5)). Single-layer nanocomposite coatings can also have a similar orientation to LbL coatings. A PVA/Kaolin coating, deposited by a bench coater, has an orientation value of 0.76. This coating also has a similar permeability to the studied LbL coatings (0.7 ± 0.3 cm³·µm/(m²·day·atm) (50% RH)), which is due to its higher thickness (5.9 µm) and crystallinity (40%), as LbL coatings usually lack crystallinity.

### 3.3. Effect of Concentration of Solutions on Permeability

Despite the barrier improvement, crosslinking is an additional coating step that does not generally use environmentally friendly materials. To decrease the moisture sensitivity of the noncrosslinked coatings, their composition was tailored. To this end, two approaches were separately considered: the amount of free hydroxyl groups is altered by improving the hydrogen bonding in the coating, and the volume fraction of MMT in the coating is increased. This can be achieved by increasing the concentration of the polymer solution and the MMT suspension. For the studied PVA-MMT nanocomposite coating, the concentrations of the polymer solution and the clay suspension affected differently the permeability results. At 0% RH, dipped and bladed coatings showed similar trend of permeability for low PVA solution concentration, as illustrated in Figure 7. Bladed coatings showed a slightly better barrier and reached a plateau at 0.3 wt %, whereas the permeability decreased further for dipped coating to reach the same permeability as the bladed coating at 0.5 wt %. The same trend is observed at 70% RH, with a plateau in the range of 0.3–0.5 wt % for bladed coatings but with a better barrier for dipped coatings.
A higher PVA solution concentration (0.5 wt %) increased the coating thickness, from 0.964 μm (for a 0.1 wt % concentration) to 1.668 μm, while the percentage per weight of the MMT in the coating was reduced by 4% (Table S1).

This is due to the deposition of the higher amount of PVA, as confirmed by FTIR (Figure S3), with a higher concentration of hydroxyl groups (3300 cm$^{-1}$) and C–O bonds (1070 cm$^{-1}$) in the coating. With the increase in the density of hydroxyl groups, there are more inter- and intramolecular hydrogen bondings in the coating, resulting in the shift of the hydroxyl peaks from 3378 to 3359 cm$^{-1}$.

Increasing the MMT suspension concentration did not have the same effect on permeability (Figure 8a,b). At high and low RH, the permeability of blade-coated films increased remarkably, whereas the permeability of the dip-coated films started to increase from 2 wt % MMT suspension concentration for both RH humidities and did not reach high values as in blade-coated films. Contrary to PVA, a high concentration of the MMT suspension did not lead to an improvement of the oxygen barrier. This could be due to platelet agglomeration, thus reducing the tortuosity in the coatings. The high loading of MMT in the film may also hinder the intermolecular hydrogen bonding of PVA, which explains the considerable increase in permeability with the higher concentration of clay suspension (Table S1).

As mentioned previously, the increase of permeability at high RH is due to the established hydrogen bonds between water and free hydroxyl groups and the possible rupture of pre-existing hydrogen bonds. Reducing this permeability was possible with higher concentration of PVA in the film due to a denser intermolecular interaction that lowers the number of available hydroxyl groups to interact with water. The barrier order shifted with the RH for these two techniques. A plausible explanation could be that at dry conditions, the deposited layers of PVA and clay are stuck together thus preventing the permeation of oxygen. At high relative humidity, however, the solubility of water molecule changes the fraction of free volume in the film. Tailoring the concentration of clay and polymer solutions could also shed light on the clay–polymer interface in the coatings. As clay–PVA interaction is based on hydrogen bonding, the more established bonds there are, the more the whole structure is maintained and the less water can penetrate. By increasing the PVA concentration, dip coating resulted in the lowest permeability at 70% RH. This confirms that the lower sensitivity of dipped coatings to humidity is due to the higher density of hydrogen bonds.

4. CONCLUSIONS

In this study, barrier properties of two types of coating were investigated. Bilayers coatings of PVA and MMT were deposited by the LbL technique on a PET substrate using blade and dip coatings. The presence of free hydroxyl groups at the surface caused a high sensitivity to moisture for both coatings. Crosslinking this LbL structure with dialdehydes reduced the oxygen permeability at high relative humidity. Although the permeability was reduced by up to six times, densifying the coating by creating covalent bonds between PVA and the crosslinker was not enough for a better barrier. Limiting free hydroxyl groups interaction with water by increasing the hydrogen bonding in the coating turned out to be a better alternative. By increasing the PVA concentration in the coating, the oxygen permeability was 26 times lower for dip-coated films and 19 for blade-coated ones. Increasing the volume fraction of clay was also considered as an alternative. Different concentrations of the MMT suspension were used,
and the resulting permeability led to the conclusion that MMT concentration had a limit above which clay platelet agglomeration increases the permeability. Finally, our results suggest that the coating technique has a significant impact on the coating surface structure, the extent of interlayer interaction, the clay properties and the permeability of the coatings.

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