Polyvinyl Alcohol and Nano-Clay Based Solution Processed Packaging Coatings

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Abstract: Cost-effective, clean, highly transparent, and flexible as well as a coatable packaging material is envisioned to solve or at least mitigate quality preservation issues of organic materials, originating from moisture interaction under ambient conditions. Liquid phase processing of packaging coatings using nano-clay and polyvinyl alcohol (PVOH) has been developed and reported. Detailed analysis of the developed coating revealed moisture permeability of $2.8 \times 10^{-2} \text{g cm}^{-2} \text{m}^{-2} \text{day}^{-1}$ at 40 °C and 85% relative humidity (RH), which is in close accordance with Bharadwaj's theoretical permeability model. Moreover, the developed coatings are not only more than 90% transparent, when exposed to white light, but also exhibit excellent flexibility and even after going through 10,000 bending cycles maintained the same blocking effect against moisture.

Keywords: flexible barriers; flexible packaging; polyvinyl alcohol; nano-clay; moisture; permeability

1. Introduction

Packaging materials are designed to safeguard the product while it is in storage, transportation, or the distribution phase [1–3]. The basic requirement of this packaging material is to maintain the quality of the product by limiting chemical, physical, or biological changes [4]. Hence, packaging should have a barrier effect against environmental gases, moving in or out, and ultraviolet (UV) light [1,2,5]. In addition to these, packaging materials for food and other organic stuff should also have the ability to increase the shelf life [6] by providing a barrier against moisture and oxygen [7–9]. Miscellaneous materials (e.g., glass, polymers, ceramics, and metals) are in use in contemporary packaging.
applications. Among these, polymers have found wide application with a market share of 40% in the food industry [10] due to its cost-effectiveness, light-weight, and stability of its chemical and physical properties [10,11]. Transparency to visible light is another additive advantage of the food packaging [10], which polymers can also have. Moreover, these can be easily processed using simple coating techniques (i.e., spin coating, doctor blading, spray coating, etc.) [12–14].

All polymers, with the exception of a few (polystyrene, polycarbonates, etc.), offer high-quality barrier characteristics [3] that can further be improved against any specific permeating molecule by various factors. In general, there is no single polymer that possesses all of the properties required for packaging applications and hence multifaceted complex types of frameworks are used [7]. Ethylene-vinyl alcohol (EVOH), for example, exhibits excellent barrier properties against oxygen in dry conditions, which further amplifies in humid conditions (>75% RH) due to swelling of polymeric chains [15–17]. Although it is a good barrier against oxygen, it still has to be sandwiched between two hydrophobic polyethylene layers [18,19] for good results. Better barrier properties for packaging applications cannot be achieved via a monolayer of polymers, therefore, a direct mixing of polymers is preferred [20–22] either by blending [21] or by multilayered [23] coatings, but these have not only high production costs but are also difficult to recycle [24]. Therefore, interest has been developed in the recent past to produce novel monolayer packaging films with improved mechanical and barrier properties [24,25]. Due to the advantages of transparency and flexibility of a polymer matrix, quality barrier monolayer films have been developed by incorporating inorganic nanoparticles in them [5,11,24]. This enhances the barrier characteristics against permeating gases by offering a tortuous path [25–27] as the permeating molecules have to travel a long way along the axis of the particle until it finds the polymer or a defect to diffuse to the other side [26,28–31].

The reduction of permeation depends upon aspect ratio, orientation, concentration, compatibility, and uniform distribution of filler within the polymer matrix [28,29,32–34]. Numerous studies [35,36] have been carried out on systems containing nano-clays as gas barrier fillers in polymeric matrices whose results showed a direct effect of nano-clay on the permeation of moisture and oxygen. The hydrophobic nature of nano-clay makes its distribution uniform in water-soluble polyvinyl alcohol (PVOH) [37,38]. Gaume et al. [25] used sodium montmorillonite (MMT-Na+) clay as filling particles and reported a reduction in oxygen and moisture permeation by a factor of 2.7 and 1.7, respectively. However, the influence of clay on haze and the mechanical flexibility of the film is scanty. Therefore, the present research work was planned and carried out using a solution processing route to develop packaging films using PVOH and MMT-Na+ nano-clay coatings. PVOH is one of the well-known biodegradable polymers that can be processed easily [39,40] and exhibits low oxygen permeation and stability under UV irradiations [25,41,42] and hence has wide applications in flexible paper coatings. MMT-Na+ nano-clay, on the other hand, can uniformly disperse in PVOH because of its hydrophilic nature and has a platelet structure with an aspect ratio of 200–1000, which can effectively reduce the diffusion of gases and increase thermal and mechanical stability [25,29]. There have been many studies carried out on PVOH and nano-clay. In this study, the processing parameters were optimized to yield the desired results. Not only was the effect of clay concentration studied, but also the optimization of the thickness controlling parameters was carried out to produce a highly bendable/flexible barrier coating for the packaging industry with an economical and single-step easy procedure. Hence, a composite of PVOH and nano-clay (both being environmentally friendly materials) was developed and characterized mainly in terms of barrier characteristics, optical transparency, and flexibility.

2. Experimental
2.1. Materials

PVOH (27,000 g/mol) was obtained from Sigma-Aldrich GmbH (St. Louis, MO, USA) and used as received. Nano-clay (Sodium montmorillonite–MMT-Na+) with a monoclinic
structure was purchased from BYK GmbH (Wether, Germany). Polyethylene terephthalate (PET) Melinex ST504 was acquired from DuPont Teijin Films, Chester, VA, USA, and was used as the substrate.

2.2. Processing of Films

Pristine PVOH (10 wt.%) was mixed with de-ionized water and continuously stirred on a hot plate at 90 °C until a clear and homogenous solution was obtained. MMT-Na+ nano-clay was added to this PVOH solution with a concentration ranging from 2–10 wt.% of the matrix and then mixed thoroughly for a few hours at 60 °C followed by ultrasonication for 30 min before coating. It should be noted that the mixing of nano-clay in PVOH solution becomes very hard with an increasing clay content beyond 5 wt.%. Maintaining the uniform distribution of clay within the matrix needs extra effort and extra mixing time. The prepared solution was applied using a doctor blade (Zehntner, Sissach, Switzerland) on a PET substrate, which was maintained at 30 °C followed by drying in an oven at 80 °C. Finally, the dried films were taken off from the PET and characterized as free-standing films.

2.3. Characterization of Films

Microdefects and surface quality of the film were analyzed using the “Olympus MX51” microscope (Olympus, Tokyo, Japan). Transparency of the films under visible region was examined by “Shimadzu UV-1800” spectrophotometer Shimadzu UV-1800 spectrophotometer (Shimadzu Company, Tokyo, Japan). ATR-FTIR (attenuated total reflectance-Fourier transform infrared) analysis of the films was made using “Bruker ALPHA-P” (Bruker, Billerica, MA, USA) at a scan rate of 64 with 4 cm$^{-1}$ resolution. Water vapor transmission rate (WVTR) measurements were performed using the water method with a permeability cup (qualifying ASTM E96 standard, from Thwing-Albert Instrument Company GmbH, West Berlin, NJ, USA) that can measure WVTR values down to 0.1 g/(m$^2$·day) and following the procedure documented by Wu et al. [43]. WVTR was then calculated from a slope of the weight loss curve using Equation (1).

$$\text{WVTR} = \frac{G}{A \times t}$$  

where $G/t$ is the weight loss per day and $A$ is the exposed area of the film.

The flexibility of the barrier films was measured with a bend testing machine equipped with a counter, having one fixed end and another moving back and forth, maintaining a customized bending radius. For this test, a film with a 40 mm width, 80 mm length, and thickness ~100 µm were prepared and for WVTR measurement, the sample was cut from the middle of similar films.

3. Results and Discussion

Figure 1 shows the optical micrographs of PVOH/MMT-Na$^+$ films at various wt.%. The micrographs showed no significant defects in the developed films. However, some tiny black dots were present, which can be referred to as agglomerated nano-clay particles.

The IR spectra of pristine PVOH and PVOH/MMT-Na$^+$ films are shown in Figure 2. The IR spectra of PVOH/MMT-Na$^+$ film showed the summation of characteristic peaks of pristine PVOH and MMT-Na$^+$ nano-clay. The presence of a typical Si–O stretching band of montmorillonite around 970 cm$^{-1}$ was absent in the pristine PVOH spectrum. However, the peak close to 1000 cm$^{-1}$ in pristine PVOH refers to the C–O stretching band, which is in complete alignment with the work done by Reis et al. (2006) [24] in pure PVOH, which appears in PVOH/MMT-Na$^+$ films and whose intensity increases linearly with the percentage of nano-clay (from 2–10 wt.%) in PVOH. These results are in good agreement with the results reported in the literature [25].
In general, the spectra (Figure 3a) showed that the transmission of white light was not affected by the presence of nano-clay and the transparency level of 92% was almost unchanged. However, the transparency of pristine PVOH (i.e., 92%) slightly dropped to 89% as the wt.% of the nano-clay (Figure 3b) increased in it, which can be attributed to diffused transmittance (Figure 3c). This increase in diffused transmittance suggests that haze is generated, which creates scattering and this effect is more pronounced as we move from the visible to UV region. An increase of 11% in diffuse transmittance, for example, was observed for 6 wt.% PVOH/MMT-Na+ at a wavelength of 400 nm (Figure 3c).

Although pristine PVOH is water-soluble, however, its film shows resistance against moisture and the WVTR exhibited by the PVOH films was comparable to commercially used packaging polymers such as low-density polyethylene (~100 g/(m²·day)) and polyvinyl butyral (~70 g/(m²·day)) [3]. However, the PVOH films have several other advantages that include easy processing, biodegradability, and a high barrier against the diffusion of oxygen. Figure 4 shows a decreasing trend in weight loss of water through films of pristine PVOH films by increasing their thicknesses. Using Equation (1) and weight loss measurements, the WVTR values were calculated as shown in Table 1. Table 1 shows
that a WVTR of 90 g/m²·day was observed for a 25 µm thick pristine PVOH film at test conditions of 85% RH and 40 °C, which decreased linearly with thickness.

Figure 3. (a) UV–Vis spectra of pristine PVOH and PVOH/MMT-Na⁺ films. (b) Kinetics of total transmittance decrease for PVOH/MMT-Na⁺ films with a concentration @ 450 nm. (c) Diffused transmittance of pristine PVOH and PVOH/MMT-Na⁺ films.
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![Weight loss versus time using a cup sealed with pristine PVOH films having different thicknesses at 40 °C and 85% RH.](image-url)

**Table 1.** Moisture permeation of the pristine PVOH films with different thicknesses. For statistical analysis, at least five samples were tested for each thickness variation.

| Film Thickness (µm) | WVTR (g/(m²·Day)) |
|---------------------|-------------------|
| 25                  | 90 ± 5.2          |
| 50                  | 47 ± 4.2          |
| 75                  | 29 ± 3.4          |
| 100                 | 20.5 ± 2.5        |

This can be attributed to the fact that the regular and orderly formation of a defect-free thicker film of the pristine PVOH takes time, taking longer paths for the moisture molecules to diffuse from one side to another. When these WVTR data are plotted against film thickness, a linear graph was obtained (Figure 5), which indicates that barrier properties (inverse of WVTR) of pristine PVOH against moisture is directly proportional to film thickness. Therefore, an improvement of ~77% was observed in the barrier quality of the films by increasing the film thicknesses from 25 to 100 µm.

![Figure 6](image-url)  

**Figure 6.** Graphs of the weight loss measurement of moisture through PVOH/MMT-Na⁺ (2 to 10 wt.%) and pristine PVOH of 100 µm thick films. Using Equation (1) and weight loss measurements, the WVTR values were calculated and tabulated along with the values of permeability, as shown in Table 2. Table 2 shows that the lowest moisture permeability value of 2.8 g/m²·day was reported by the 10 wt.% PVOH/MMT-Na⁺ film at test conditions of 85% RH and 40 °C, which increases linearly with decreasing wt.% of nano-clay. This means that the moisture permeation value of pristine PVOH can be further reduced by 86% under the same test conditions by the addition of 10% nano-clay. This further reduction in moisture permeability can be attributed to a result of the intercalation of the nano-clay platelets. Moreover, the dispersion of the nano-clay platelets creates hindrances to the diffusing molecules [44], therefore, these hindrances are referred to as the tortuous path, and hence the permeation is decreased.
Figure 5. Blocking effect of pristine PVOH films with different thicknesses along with the linear fitting curve.

Figure 6. Weight loss versus time using a cup sealed with pristine PVOH and PVOH filled with MMT-Na+ nano-clay films (100 µm thick) at 40 °C and 85% RH.

Table 2. Moisture permeation of pristine PVOH and PVOH/MMT-Na+ films (100 µm thick) at 40 °C and 85% RH. For statistical analysis, at least five samples were tested for each measurement.

| Films                  | WVTR (g/m²·Day) | Permeability (g·cm/(m²·Day)) |
|------------------------|------------------|------------------------------|
| Pristine PVOH          | 20.5 ± 2.5       | 2.05 × 10⁻¹                  |
| PVOH/MMT-Na⁺ (2 wt.%)  | 10 ± 1.3         | 1.1 × 10⁻¹                   |
| PVOH/MMT-Na⁺ (4 wt.%)  | 6 ± 0.5          | 6 × 10⁻²                     |
| PVOH/MMT-Na⁺ (6 wt.%)  | 4 ± 0.3          | 4 × 10⁻²                     |
| PVOH/MMT-Na⁺ (8 wt.%)  | 3.2 ± 0.3        | 3.2 × 10⁻²                   |
| PVOH/MMT-Na⁺ (10 wt.%) | 2.8 ± 0.2        | 2.8 × 10⁻²                   |

The current experimental data are in good agreement with Bharadwaj’s model of permeation for nanocomposites [45–47]. This permeation model suggests that the tortuous path of gas is influenced by film thickness, fractional volume, and aspect ratio of the particles with the ordered parameter “S”. This ordered parameter is based on the orientation of the particles within the polymer matrix. In the present work, MMT-Na⁺ nano-clay with an aspect ratio of 500 was used as reported in the literature [25,44]. For a semi-exfoliated
structure and the calculations based on this aspect ratio using Equation (2), Bhardwaj’s model [26] fit well.

\[ \frac{P_s}{P_p} = \frac{1 - \phi_s}{1 + \frac{2\phi_s S}{W} (S + \frac{1}{2})} \]

where \( P_s \) and \( P_p \) represent the permeability of the composite and permeability of the polymer, respectively. \( \phi_s \) represents the volume fraction of the nano-clay. \( L \) and \( W \) represent the length and width of the clay platelets (\( L/W \) is the aspect ratio), and \( S \) is the order parameter.

Experimental results and the theoretical data suggested by Bhardwaj’s model are almost similar or in close tolerance, as shown in Figure 7, which corroborate the experimental results.

![Figure 7. Comparison of the experimental and theoretically calculated data of pristine PVOH and PVOH/MMT-Na+ films.](image)

To check the barrier quality of PVOH/MMT-Na+ films under bending conditions, these were subjected to a maximum of 10,000 bending cycles at a radius of 3 cm and the obtained results are shown in Figure 8. The graph shows that pristine PVOH maintained its barrier properties even after 10,000 bending cycles and a similar trend in barrier properties were demonstrated by respective PVOH/MMT-Na+ films under the same bending cycles. This suggested that the nano-clay platelets, even 10 wt.%, held strongly within the matrix of PVOH, therefore showed no loss in barrier quality [3].

![Figure 8. Moisture permeation versus bending cycles of pristine PVOH and PVOH/MMT-Na+ films.](image)
4. Conclusions

A solution-processed route was adopted for the development of a good barrier film using pristine PVOH and MMT-Na⁺ as dispersants, which is not only a cost-effective route but is also safe for the environment. The developed films exhibited high transparency of ~92% in the white light region and the presence of nano-clay did not affect the transparency of the films and gave similar results to that of the pristine PVOH films. The addition of nano-clay caused the scattering of light due to the agglomeration of particles and found only less than 2% in the visible region. Increasing the percentage of nano-clay from 2 wt.% to 10 wt.% in PVOH resulted in the reduction of moisture permeation to a maximum of 86% when compared with pristine PVOH film, but on the other hand, it becomes very hard to distribute the nano-clay uniformly in the matrix, hence, in that perspective composite, 6 wt.% of MMT-Na⁺ clay is the best choice. Barriers with 6 wt.% clay are not only easy to process, but also remain transparent and improve the barrier characteristics of PVOH against the diffusion of moisture by over 80%. The experimental data were also validated using Bharadwaj’s permeation model and the results were in good agreement with the theoretical calculations. The developed films also depicted excellent flexibility and even after 10,000 bending cycles, the same barrier quality was maintained. All the reported results make PVOH/MMT-Na⁺ films a potential candidate for various packaging applications such as optoelectronics, foods, etc.

Author Contributions: Conceptualization, I.A.C.; Data curation, T.A.; Formal analysis, S.H.S.; Funding acquisition, R.G.A.; Investigation, S.K.; Methodology, M.R.; Project administration, M.D.A.; Resources, M.A.M.; Software, S.A.; Validation, M.S.J.; Visualization, S.H.; Writing—original draft, A.D.C.; Writing—review & editing, M.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Researchers Supporting Project Number (RSP-2021/267) King Saud University, Riyadh, Saudi Arabia.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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