



# Article Polyvinyl Alcohol and Nano-Clay Based Solution Processed Packaging Coatings

Ali Dad Chandio <sup>1</sup>, Iftikhar Ahmed Channa <sup>1,2</sup>, Muhammad Rizwan <sup>1</sup>, Shakeel Akram <sup>3</sup>, Muhammad Sufyan Javed <sup>4,5</sup>, Sajid Hussain Siyal <sup>6,\*</sup>, Muhammad Saleem <sup>7</sup>, Muhammad Atif Makhdoom <sup>2</sup>, Tayyaba Ashfaq <sup>8</sup>, Safia Khan <sup>9</sup>, Shahid Hussain <sup>10,11</sup>, Munirah D. Albaqami <sup>12</sup> and Reham Ghazi Alotabi <sup>12</sup>

- <sup>1</sup> Department of Materials and Metallurgical Engineering, NED University of Engineering and Technology, University Road Karachi, Karachi 75270, Pakistan; alidad@neduet.edu.pk (A.D.C.); iftikharc@neduet.edu.pk (I.A.C.); materialist.riz@gmail.com (M.R.)
- <sup>2</sup> Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany; atif.ceet@pu.edu.pk
- <sup>3</sup> College of Electrical Engineering, Sichuan University, Chengdu 610065, China; Shakeel.Akram@scu.edu.cn
- <sup>4</sup> School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China; safisabri@gmail.com
- <sup>5</sup> Department of Physics, COMSATS University Islamabad, Lahore 54000, Pakistan
- <sup>6</sup> Department of Metallurgy and Materials Engineering, Dawood University of Engineering and Technology, Karachi 74800, Pakistan
- <sup>7</sup> Department of Physics, The Islamia University of Bahawalpur Punjab, Bahawalpur 63100, Pakistan; saleem.malikape@gmail.com
- <sup>8</sup> Department of Chemistry, Government College University Faisalabad, Faisalabad 38000, Pakistan; tayyabaa961@gmail.com
- <sup>9</sup> Department of Chemistry, Quaid-i-Azam University Islamabad, Islamabad 45320, Pakistan; safiakhan715@gmail.com
- <sup>10</sup> School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China; shahid@ujs.edu.cn
- <sup>11</sup> Departamento de Quimica Organica, Universidad de Cordoba, Edificio Marie Curie (C-3), Ctra Nnal IV-A,
  - Km 396, E14014 Cordoba, Spain
- <sup>12</sup> Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; muneerad@ksu.edu.sa (M.D.A.); 438202971@student.ksu.edu.sa (R.G.A.)
- Correspondence: sajid.hussain@duet.edu.pk

**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  $2.8 \times 10^{-2} \text{ g} \cdot \text{cm/m}^2 \cdot \text{day}$  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



Citation: Chandio, A.D.; Channa, I.A.; Rizwan, M.; Akram, S.; Javed, M.S.; Siyal, S.H.; Saleem, M.; Makhdoom, M.A.; Ashfaq, T.; Khan, S.; et al. Polyvinyl Alcohol and Nano-Clay Based Solution Processed Packaging Coatings. *Coatings* **2021**, *11*, 942. https://doi.org/10.3390/ coatings11080942

Academic Editor: Yingyi Zhang

Received: 3 July 2021 Accepted: 30 July 2021 Published: 6 August 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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<sup>+</sup>) 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<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup>) 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<sup>-1</sup> 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<sup>2</sup>·day) and following the procedure documented by Wu et al. [43]. WVTR was then calculated from a slop of the weight loss curve using Equation (1).

$$WVTR = \frac{G}{A \times t}$$
(1)

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  $\sim$ 100  $\mu$ m 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<sup>+</sup> 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<sup>+</sup> films are shown in Figure 2. The IR spectra of PVOH/MMT-Na<sup>+</sup> film showed the summation of characteristic peaks of pristine PVOH and MMT-Na<sup>+</sup> nano-clay. The presence of a typical Si–O stretching band of montmorillonite around 970 cm<sup>-1</sup> was absent in the pristine PVOH spectrum. However, the peak close to 1000 cm<sup>-1</sup> 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<sup>+</sup> 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].



Figure 1. Optical micrographs of PVOH/MMT-Na<sup>+</sup> films with (a) 2 wt.% nano-clay, (b) 4 wt.% nano-clay, and (c) 6 wt.%.



Figure 2. FTIR-ATR spectra of pristine PVOH and PVOH/MMT-Na<sup>+</sup> films.

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<sup>+</sup> 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/(m<sup>2</sup>·day)) and polyvinyl butyral (~70 g/(m<sup>2</sup>·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/m<sup>2</sup>·day was observed for a 25  $\mu$ m 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<sup>+</sup> films. (b) Kinetics of total transmittance decrease for PVOH/MMT-Na<sup>+</sup> films with a concentration @ 450 nm. (c) Diffused transmittance of pristine PVOH and PVOH/MMT-Na<sup>+</sup> films.



**Figure 4.** Weight loss versus time using a cup sealed with pristine PVOH films having different thicknesses at 40 °C and 85% RH.

**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/(m <sup>2</sup> ·Day))
25	$90 \pm 5.2$
50	$47\pm4.2$
75	$29\pm3.4$
100	$20.5\pm2.5$

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  $\mu$ m.

Figure 6 shows the graphs of the weight loss measurement of moisture through PVOH/MMT-Na<sup>+</sup> (2 to 10 wt.%) and pristine PVOH of 100  $\mu$ m 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/m<sup>2</sup>·day was reported by the 10 wt.% PVOH/MMT-Na<sup>+</sup> 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.



PVOH/MMT-Na<sup>+</sup> (6 wt.%)

PVOH/MMT-Na<sup>+</sup> (8 wt.%)

PVOH/MMT-Na<sup>+</sup> (10 wt.%)

**Figure 6.** Weight loss versus time using a cup sealed with pristine PVOH and PVOH filled with MMT-Na<sup>+</sup> nano-clay films (100  $\mu$ m thick) at 40 °C and 85% RH.

Films	WVTR (g/m <sup>2</sup> ·Day)	Permeability (g·cm/(m <sup>2</sup> ·Day))
Pristine PVOH	$20.5\pm2.5$	$2.05  imes 10^{-1}$
PVOH/MMT-Na <sup>+</sup> (2 wt.%)	$10 \pm 1.3$	$1.1  imes 10^{-1}$
PVOH/MMT-Na <sup>+</sup> (4 wt.%)	$6\pm0.5$	$6 imes 10^{-2}$

 $4\pm0.3$ 

 $3.2\pm0.3$ 

 $2.8\pm0.2$ 

 $4 imes 10^{-2}$ 

 $3.2 imes 10^{-2}$ 

 $2.8 imes 10^{-2}$ 

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

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<sup>+</sup> 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.

$$\frac{P_s}{P_p} = \frac{1 - o_s}{1 + \frac{L}{2W} o_s(\frac{2}{3})(S + \frac{1}{2})}$$
(2)

where  $P_s$  and  $P_p$  represent the permeability of the composite and permeability of the polymer, respectively.  $ø_s$  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<sup>+</sup> films.

To check the barrier quality of PVOH/MMT-Na<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup> films.

# 4. Conclusions

A solution-processed route was adopted for the development of a good barrier film using pristine PVOH and MMT-Na<sup>+</sup> 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<sup>+</sup> 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<sup>+</sup> 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.

#### References

- 1. Siracusa, V. Food packaging permeability behaviour: A Report. Int. J. Polym. Sci. 2012, 2012, 302029. [CrossRef]
- Figura, L.O.; Teixeira, A.A. Food Physics, Physical Proerties-Measurements and Applicartions; Springer: Berlin/Heidelberg, Germany, 2008; Volume 39, pp. 561–563.
- 3. Channa, I.A.; Distler, A.; Egelhaaf, H.; Brabec, C.J. Solution Coated Barriers for Flexible Electronics. In *Organic Flexible Electronics, Fundamentals, Devices, and Applications*; Cosseddu, P., Caironi, M., Eds.; Woodhead Publishing: Sawston, UK, 2020.
- Channa, I.A.; Distler, A.; Zaiser, M.; Brabec, C.J.; Egelhaaf, H. Thin film encapsulation of organic solar cells by direct deposition of polysilazanes from solution. *Adv. Energy Mater.* 2019, *9*, 1900598. [CrossRef]
- 5. Cooksey, K. Important Factors for Selecting; Packag: Boston, MA, USA, 2004; pp. 1–12.
- 6. Geueke, B.; Groh, K.; Muncke, J. Food packaging in the circular economy: Overview of chemical safety aspects for commonly used materials. *J. Clean. Prod.* **2018**, *193*, 491–505. [CrossRef]
- Channa, I.A. Development of Solution Processed Thin Film Barriers for Encapsulating Thin Film Electronics; Friedrich Alexander University of Erlangen Nuremberg: Bavaria, Germany, 2019.
- 8. Raheem, D. Application of plastics and paper as food packaging materials? An overview. *Emir. J. Food Agric.* **2013**, 25, 177. [CrossRef]
- 9. Eustace, I.J. Some factors affecting oxygen transmission rates of plastic films for vacuum packaging of meat. *Int. J. Food Sci. Technol.* **2007**, *16*, 73–80. [CrossRef]
- 10. Majid, I.; Nayik, G.A.; Dar, S.M.; Nanda, V. Novel food packaging technologies: Innovations and future prospective. *J. Saudi Soc. Agric. Sci.* **2018**, *17*, 454–462. [CrossRef]
- 11. Silvestre, C.; Duraccio, D.; Cimmino, S. Food packaging based on polymer nanomaterials. *Prog. Polym. Sci.* **2011**, *36*, 1766–1782. [CrossRef]

- 12. Kim, H.M.; Lee, H.S. Water and oxygen permeation through transparent ethylene vinyl alcohol/(graphene oxide) membranes. *Carbon Lett.* **2014**, *15*, 50–56. [CrossRef]
- Nazarenko, S.; Meneghetti, P.; Julmon, P.; Olson, B.; Qutubuddin, S. Gas barrier of polystyrene montmorillonite clay nanocomposites: Effect of mineral layer aggregation. J. Polym. Sci. Part B Polym. Phys. 2007, 45, 1733–1753. [CrossRef]
- 14. Granstrom, J.; Roy, A.; Rowell, G.; Moon, J.S.; Jerkunica, E.; Heeger, A.J. Improvements in barrier performance of perfluorinated polymer films through suppression of instability during film formation. *Thin Solid Films* **2010**, *518*, 3767–3771. [CrossRef]
- 15. Müller, K.; Bugnicourt, E.; Latorre, M.; Jorda, M.; Echegoyen Sanz, Y.; Lagaron, J.; Miesbauer, O.; Bianchin, A.; Hankin, S.; Bölz, U.; et al. Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields. *Nanomaterials* **2017**, *7*, 74. [CrossRef]
- 16. Mokwena, K.K.; Tang, J. Ethylene vinyl alcohol: A review of barrier properties for packaging shelf stable foods. *Crit. Rev. Food Sci. Nutr.* **2012**, *52*, 640–650. [CrossRef]
- 17. Hammann, F.; Schmid, M. Determination and quantification of molecular interactions in protein films: A review. *Materials* **2014**, 7, 7975–7996. [CrossRef] [PubMed]
- Schmid, M.; Dallmann, K.; Bugnicourt, E.; Cordoni, D.; Wild, F.; Lazzeri, A.; Noller, K. Properties of whey-protein-coated films and laminates as novel recyclable food packaging materials with excellent barrier properties. *Int. J. Polym. Sci.* 2012, 2012, 562381. [CrossRef]
- Schmid, M.; Zillinger, W.; Müller, K.; Sängerlaub, S. Permeation of water vapour, nitrogen, oxygen and carbon dioxide through whey protein isolate based films and coatings—Permselectivity and activation energy. *Food Packag. Shelf Life* 2015, *6*, 21–29. [CrossRef]
- 20. Reig, C.S.; Lopez, A.D.; Ramos, M.H.; Ballester, V.A.C. Nanomaterials: A map for their selection in food packaging applications. *Packag. Technol. Sci.* 2014, 27, 839–866. [CrossRef]
- 21. Ahmad, A.; Jini, D.; Aravind, M.; Parvathiraja, C.; Ali, R.; Kiyani, M.Z.; Alothman, A. A novel study on synthesis of egg shell based activated carbon for degradation of methylene blue via photocatalysis. *Arab. J. Chem.* **2020**, *13*, 8717–8722. [CrossRef]
- Yeo, J.H.; Lee, C.H.; Park, C.-S.; Lee, K.-J.; Nam, J.-D.; Kim, S.W. Rheological, morphological, mechanical, and barrier properties of PP/EVOH blends. *Adv. Polym. Technol.* 2001, 20, 191–201. [CrossRef]
- 23. Siracusa, V.; Ingrao, C.; Giudice, A.L.; Mbohwa, C.; Rosa, M.D. Environmental assessment of a multilayer polymer bag for food packaging and preservation: An LCA approach. *Food Res. Int.* **2014**, *62*, 151–161. [CrossRef]
- 24. Hahladakis, J.N.; Iacovidou, E. Closing the loop on plastic packaging materials: What is quality and how does it affect their circularity? *Sci. Total Environ.* **2018**, *630*, 1394–1400. [CrossRef] [PubMed]
- 25. Gaume, J.; Taviot-Gueho, C.; Cros, S.; Rivaton, A.; Thérias, S.; Gardette, J.L. Optimization of PVA clay nanocomposite for ultra-barrier multilayer encapsulation of organic solar cells. *Sol. Energy Mater. Sol. Cells* **2012**, *99*, 240–249. [CrossRef]
- Strawhecker, K.E.; Manias, E. Nanocomposites based on water soluble polymers and unmodified smectide clays. *Polym. Nanocompos.* 2006, 206, 20–33.
- Ahmad, J.; Bazaka, K.; Anderson, L.J.; White, R.; Jacob, M. Materials and methods for encapsulation of OPV: A review. *Renew. Sustain. Energy Rev.* 2013, 27, 104–117. [CrossRef]
- 28. Atai, M.; Solhi, L.; Nodehi, A.; Mirabedini, S.M.; Kasraei, S.; Akbari, K.; Babanzadeh, S. PMMA-grafted nanoclay as novel filler for dental adhesives. *Dent. Mater.* 2009, 25, 339–347. [CrossRef]
- 29. Nikolaidis, A.K.; Achilias, D.S.; Karayannidis, G.P. Synthesis and characterization of PMMA/organomodified montmorillonite nanocomposites prepared by in situ bulk polymerization. *Ind. Eng. Chem. Res.* **2011**, *50*, 571–579. [CrossRef]
- 30. Seethamraju, S.; Ramamurthy, P.; Madras, G. Performance of an ionomer blend-nanocomposite as an effective gas barrier material for organic devices. *RSC Adv.* **2014**, *4*, 11176–11187. [CrossRef]
- 31. Hong, S.I.; Lee, H.; Rhim, J. Effects of clay type and content on mechanical, water barrier and antimicrobial properties of agar-based nanocomposite films. *Carbohydr. Polym.* **2011**, *86*, 691–699.
- Kurtz, S. Photovoltaic Module Reliability Workshop 2012: February 28–March 1, 2012; Office of Scientific and Technical Information (OSTI): Zhenjiang, China, 2013.
- Carosio, F.; Colonna, S.; Fina, A.; Rydzek, G.; Hemmerlé, J.; Jierry, L.; Schaaf, P.; Boulmedais, F. Efficient gas and water vapor barrier properties of thin poly(lactic acid) packaging films: Functionalization with moisture resistant nation and clay multilayers. *Chem. Mater.* 2014, 26, 5459–5466. [CrossRef]
- Tsai, T.-Y.; Lin, M.-J.; Chuang, Y.-C.; Chou, P.-C. Effects of modified clay on the morphology and thermal stability of PMMA/clay nanocomposites. *Mater. Chem. Phys.* 2013, 138, 230–237. [CrossRef]
- 35. Dabbaghianamiri, M.; Duraia, E.-S.M.; Beall, G.W. Self-assembled Montmorillonite clay-poly vinyl alcohol nanocomposite as a safe and efficient gas barrier. *Results Mater.* **2020**, *7*, 100101. [CrossRef]
- 36. Tsurko, E.S.; Feicht, P.; Habel, C.; Schilling, T.; Daab, M.; Rosenfeldt, S.; Breu, J. Can high oxygen and water vapor barrier nanocomposite coatings be obtained with a waterborne formulation? *J. Membr. Sci.* **2017**, *540*, 212–218. [CrossRef]
- Abdullah, Z.W.; Dong, Y.; Han, N.; Liu, S. Water and gas barrier properties of polyvinyl alcohol (PVA)/starch (ST)/ glycerol (GL)/halloysite nanotube (HNT) bionanocomposite films: Experimental characterisation and modelling approach. *Compos. Part B Eng.* 2019, 174, 1. [CrossRef]
- 38. Rangreez, T.A.; Mobin, R. 13-Polymer composites for dental fillings. In *Woodhead Publishing Series in Biomaterials [Internet]*; Woodhead Publishing: Sawston, UK, 2019; pp. 20–24.

- Tian, Y.; Zhu, P.; Zhou, M.; Lin, Y.; Cheng, F. Effect of Microfibrillated cellulose loading on physical properties of starch/polyvinyl Al-cohol composite films. J. Wuhan Univ. Technol. Mater. Sci. Ed. 2020, 35, 825–831. [CrossRef]
- 40. Gao, X.; Tang, K.; Liu, J.; Zheng, X.; Zhang, Y. Compatibility and properties of biodegradable blend films with gelatin and poly(vinyl al-cohol). *J. Wuhan Univ. Technol. Sci. Ed.* **2014**, *29*, 351–356. [CrossRef]
- 41. Carrera, M.C.; Erdmann, E.; Destéfanis, H.A. Preparation of Poli (Vinylalcohol)/Organoclay Nanocomposites by Casting and in Situ Polymerization. In Proceedings of the 15th European Conference on Composite Materials, Venice, Italy, 24–28 June 2012.
- 42. Reyes, Y.; Peruzzo, P.J.; Fernández, M.; Paulis, M.; Leiza, J.R. Encapsulation of clay within polymer particles in a high-solids content aqueous dispersion. *Langmuir* 2013, *29*, 9849–9856. [CrossRef] [PubMed]
- 43. Wu, P.; Fisher, A.; Foo, P.; Queen, D.; Gaylor, J. In vitro assessment of water vapour transmission of synthetic wound dressings. *Biomaterials* **1995**, *16*, 171–175. [CrossRef]
- 44. Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T.C. Polypropylene/montmorillonite nanocomposites. Review of the synthetic routes and materials properties. *Chem. Mater.* **2001**, *13*, 3516–3523. [CrossRef]
- 45. Bharadwaj, R.K. Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules* **2001**, *34*, 9189–9192. [CrossRef]
- Channa, I.A.; Distler, A.; Scharfe, B.; Feroze, S.; Forberich, K.; Lipovšek, B.; Brabec, C.J.; Egelhaaf, H.-J. Solution processed oxygen and moisture barrier based on glass flakes for encapsulation of organic (opto-) electronic devices. *Flex. Print. Electron.* 2021, 6, 025006. [CrossRef]
- 47. Channa, I.; Chandio, A.; Rizwan, M.; Shah, A.; Bhatti, J.; Shah, A.; Hussain, F.; Shar, M.; AlHazaa, A. Solution processed PVB/mica flake coatings for the encapsulation of organic solar cells. *Materials* **2021**, *14*, 2496. [CrossRef]