High-Strength, Low-Permeable, and Light-Protective Nanocomposite Films Based on a Hybrid Nanopigment and Biodegradable PLA for Food Packaging Applications

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ABSTRACT: Herein, a multifunctional filler, a dye (organic)—clay (inorganic) hybrid nanopigment (DCNP), was embedded into polylactic acid (PLA) to fabricate a colored biodegradable/biocompatible film, which is explored as a high thermomechanical resistant as well as a superior light and mass transport barrier for food packaging applications. In this respect, the DCNP was synthesized through a wet chemical process with a reaction yield of 76% and incorporated into a PLA matrix at various concentrations using a solution casting method. The morphological characterizations revealed partially intercalated/exfoliated structure for PLA–DCNP films. The samples filled with DCNP showed up to 20% and 12 °C improvements in storage modulus ($E'$) and glass transition temperature ($T_g$), respectively, compared to those with neat PLA. Incorporation of a small amount of DCNP into the PLA matrix significantly declined the water vapor and gas permeability of PLA by 36 and 54%, respectively. The optical property investigations indicated remarkable color characteristics and light protection performance of the samples containing DCNP. The results also showed better performance of the PLA–DCNP film compared to that of the PLA–Cloisite 20A sample at an identical filler loading. In conclusion, the desirable properties of the resulting films highlighted the potential application of such nanocomposite films as a promising option for food packaging materials.

INTRODUCTION

In response to increasing global concerns about long-lasting plastic pollution, biopolymers have attracted enormous attention in both academia and industry. Polylactic acid (PLA), a biocompatible and biodegradable polymer derived from renewable resources, has emerged as a compelling candidate to replace petroleum-based polymers in a wide range of applications. However, the use of PLA in food packaging has been limited by several major drawbacks, including low thermal and mechanical properties as well as high water vapor, gas, and light permeability of this macromolecule. Incorporation of different nanofillers into polymer matrices is known as one of the most straightforward, efficient, and cost-effective strategies to address the problems mentioned above. Organically modified montmorillonite, a two-dimensional nanofiller comprising stacks of 1 nm-thick clay platelets, can significantly improve thermal, mechanical, and barrier properties of PLA even at small content when the platelets are intercalated or exfoliated during the dispersion process. Furthermore, it has been reported that the uniformly dispersed clay layers within PLA can efficiently act as ultraviolet and visible light shielding agents to protect food containers and food inside against destructive light radiation. Colorants have been widely used in food packaging materials not only for coloration purpose but also for the preservation of foodstuffs against photodegradation. They are generally classified as organic and inorganic that each of which possesses their own benefits and drawbacks. Organic pigments are known for their high tinting strength but suffer from low light and heat stability as well as the high tendency to form aggregates while compounding. Despite having relatively better dispersibility in polymers and higher resistance against thermal degradation and photodegradation, inorganic pigments contain toxic heavy metals and show low color strength and dull shades. A dye–clay nanopigment (DCNP), a nontoxic hybrid coloring nanofiller synthesized via a cationic exchange reaction (CER) between mineral clays and organic dyes, can simultaneously present clay and colorant features. The DCNP with excellent tinting strength allows using a much lower amount of colorants to obtain a specific shade compared to that of conventional organic and inorganic pigments. Furthermore, the DCNP can disperse in polymer matrices easily and offer superior colorimetric properties and color fastness compared to those of its counterparts. Additionally, it has been recorded in the literature that the DCNP can be used as an excellent anticorrosive and mechanical property promoter in organic coating formulations. Despite these attractive advantages, the application of DCNP in food packaging and investigation of the functional properties related to this area are still remain unknown. Thus, in this...
study, a cationic dye, methylene blue (MB), was interconnected to a commercial organoclay, Cloisite 20A (C20A), through a cationic exchange reaction (CER) for synthesizing the dye–clay nanopigment (DCNP). PLA–DCNP and PLA–C20A nanocomposite films at various filler loadings were fabricated using the solution casting technique. The morphological, mechanical, barrier, and optical properties of prepared nanocomposites were comprehensively studied. Particular emphasis was given to explore the possibility of using PLA–DCNP nanocomposite films in food packaging applications.

RESULTS AND DISCUSSION

Characterization of DCNP. The elemental analysis results of C20A and DCNP are detailed in Table 1. The results showed the presence of 0 g and 1.1 g of sulfur per 100 g of C20A and DCNP, respectively. Owing to the fact that each molecule of MB contains one sulfur atom, the amount of MB in 100 g of DCNP was calculated to be 35 mmol. By dividing the MB content of DCNP (i.e., 35 mmol/100 g DCNP) by the initial mole of MB in CER (i.e., 46 mmol/100 g C20A), the CER yield between the clay and dye was found to be 0.76. The amount of dimethyl dihydrogenated tallow ammonium chloride (2M2HT) in C20A before CER with MB was determined to be 65 mmol/100 g clay, which was lower than that reported by the manufacturer. Similar observations were reported by other studies. After the CER, the concentration of 2M2HT fell to 44 mmol/100 g DCNP, confirming the replacement of the organic modifier with MB. Generally, cationic dyes due to some chemical factors concerned with their chemical structures have much higher binding strength for CER with clays compared to that for alkylammonium ions. The presence of resonance, donor heteroatoms, and polar moieties in the structure of MB, as well as its planar chemical structure, can explain this phenomenon. The first three mentioned factors in MB structure promote dipolar interactions such as hydrogen bonding between MB and clay; hence, MB has more affinity to be inserted in clay layers compared to the organic ammonium modifier. Additionally, the planarity of MB leads to efficient penetrating and packing of the dye into the clay gallery. The higher total concentration of the intercalants in DCNP (the total amount of 2MHT and MB was 79 mmol/100 g DCNP) than that in C20A (the total amount of 2MHT was 65 mmol/100 g C20A) suggested the nonstoichiometric exchange of 2MHT and MB in CER. It seems that the replacement of such a bulky organic modifier with two long hydrogenated tallow chains provides more available negative sites and space in clay layers for MB.

Morphology of PLA films. The X-ray diffraction (XRD) patterns of C20A and DCNP are presented in Figure 1. An intense reflection peak at 2θ = 3.46° in the diffraction pattern of C20A corresponds to a d-spacing value of 2.55 nm. After CER between C20A and MB, the reflection peak experienced a shift from its original position toward a higher angle, 2θ = 3.84°, with a d-spacing value of 2.30 nm that can be ascribed to the replacement of the bulky organic modifiers with the smaller dye and molecular reorientation of organic compounds inside clay layers. The reflection peaks disappeared after incorporating 3 wt % C20A and 1, 3, and 5 wt % DCNP in PLA at different loading concentrations. However, a broad shoulder at around 2θ = 2° with a d-spacing value of 4.40 nm was observed for the films containing 3 wt % C20A and 5 wt % DCNP. These observations suggest the simultaneous existence of exfoliated or disordered intercalated platelets through the polymer matrix. By comparing PLA films filled with C20A and DCNP at an equal concentration (i.e., 3 wt %), it was observed that the shoulder is more intense for C20A, which could be attributed to better delamination of DCNP in the PLA matrix compared to that of C20A. The interaction of ester functional groups in PLA chains with polar substituents of MB can enhance the compatibility of DCNP with PLA and results in more uniform dispersion of DCNP compared to that of C20A. Visual investigation of DCNP dispersion in PLA was performed by high-resolution transmission electron microscopy (HRTEM) to precisely depict the dispersion state and support XRD findings. The micrograph of PLA–DCNP3 at low magnifications (Figure 2A) only showed random dispersion of variously sized DCNP tactoids in the PLA matrix. Noted that dark lines in Figure 2 show DCNP platelets through the light gray PLA matrix. However, at high magnifications (Figure 2B,C), the presence of individual DCNP platelets (black arrows) and intercalated DCNP tactoids with ordered/disordered morphology (red arrows) through the polymer background was discernible. These observations suggest partially intercalated and exfoliated morphology of the DCNP/PLA sample, which is in good agreement with XRD results.

Dynamic Mechanical Properties of PLA Films. Figure 3A,B displays the temperature dependence of storage modulus (E') and tan δ of the samples. The values of E' at 20 °C, glass transition temperature (Tg), and the intensity of tan δ peak for the samples are detailed in Table 2. After the incorporation of 1 and 3 wt % DCNP in PLA, the storage modulus of PLA increased from 1800 MPa to 2139 (19%) and 2157 (20%), respectively, which demonstrated the reinforcing effect of DCNP in the PLA matrix. The formation of intercalated/exfoliated morphology enhances the interfacial interactions between PLA molecular chains and DCNP layers. Consequently, the imposed stress on PLA chains can be effectively suppressed by rigid and high aspect ratio clay nanosheets of DCNP. However, further incorporation of DCNP up to 5 wt %
in PLA resulted in a deterioration of the storage modulus. The formation of aggregates and a decrease in the extent of intercalation/exfoliation of DCNP at high filler contents can explain the observed results. The temperature for the maximum value of tan δ represents the glass transition temperature of the samples. As can be seen from Figure 3B, the tan δ peak for the neat PLA occurred at 64 °C and shifted to higher temperatures with values between 1 and 12 °C after the incorporation of the fillers. These results may be explained by the fact that the dispersed clay layers in the PLA matrix can decrease the free volume and hinder the segmental motions of PLA molecular chains at the interface, thus leading to an increase in glass transition temperature.38–41 With the addition of the fillers in the PLA matrix, a drop in the intensity of the tan δ peak was observed for the samples, and this decrement was more amplified for DCNP and at higher filler concentrations. Generally, a decrease in the intensity of the tan δ peak reflects a lower degree of polymer chain mobility.42–45 Embedding high aspect ratio DCNP layers in the PLA matrix even at lower concentrations causes a strong interaction between the two components, restricting polymer chain motions. It is worth noting that PLA–DCNP films displayed higher $E'$ and $T_g$ values compared to those of neat PLA and filled PLA with C20A, which implied the excellent performance of DCNP in improving the dynamic mechanical properties. Additionally, the higher values of $T_g$ for PLA–DCNP films compared to that of the neat PLA film showed a favorable effect of DCNP on PLA thermal stability. PLA with low $T_g$ values ranging from 55 to 65 °C unlike other commonly used food packaging materials with high $T_g$ values such as poly(ethylene terephthalate) ($T_g = 67–81$ °C) and polystyrene ($T_g = 70–115$ °C) is technically limited to be used in thermally processed packages.46–49 If $T_g$ of the applied thermoplastic in food packaging is low (somewhere in the vicinity of its application temperature), that packaging will be in or close to its rubbery state and will have low mechanical strength. Consequently, it will be vulnerable and will easily lose its dimensional stability, particularly in more severe circumstances when such material as a container is exposed to hot foodstuffs in different heat treatments such as pasteurization and cooking. Moreover, due to the high mobility of the polymer molecules in the rubbery state, the immigration of the packaging materials from the matrix and contamination of foodstuffs would be more probable. Accordingly, to avoid such drawbacks, it is necessary for the material to have a $T_g$ adequately higher than the application temperature. A specific example in which the application temperature is lower than the glass transition temperature of PLA–DCNP films (up to 76 °C) is mild-temperature pasteurization of water, milk, juice, and beer that is usually performed in the temperature range of 60–75 °C.

**Barrier Properties of PLA Films.** Oxygen permeability (OP) and water vapor permeability (WVP) of the films are depicted in Figure 4. As can be seen from the figure, OP and WVP of PLA plummet by 36 and 54% after addition of 1 and 3 wt % DCNP. These significant improvements in barrier properties of PLA can fulfill the requirements in terms of permeability to expand PLA applications in food packaging materials.50–51 The improvement of barrier properties of PLA after incorporation of DCNP can be explained by the Nielsen tortuous path model.52–54 In fact, well-dispersed DCNP layers as barrier shields lengthen the diffusion pathway of oxygen and water vapor through the PLA matrix and decrease the gas and water vapor permeability of PLA.55–59 Another possible

**Figure 2.** HRTEM micrographs of the PLA film containing 3 wt % DCNP at (A) 30k, (B) 100k, (C) 250k magnifications. The black and red arrows point to the exfoliated and intercalated clay platelets, respectively.

**Figure 3.** Elastic modulus (A) and tan δ (B) vs temperature of the neat PLA film and the PLA films containing C20A and DCNP at different loading levels.

**Table 2.** Storage Modulus ($E'$) at 20 °C, Glass Transition Temperature ($T_g$), and Intensity of tan δ Peak Values of Samples

| sample code | $E'$ at 20 °C (MPa) | $T_g$ (°C) | intensity of the tan δ peak |
|-------------|---------------------|------------|-----------------------------|
| neat PLA    | 1800                | 64         | 0.155                       |
| PLA–DCNP1  | 2139                | 73         | 0.150                       |
| PLA–DCNP3  | 2157                | 76         | 0.125                       |
| PLA–DCNP5  | 1720                | 65         | 0.127                       |
| PLA–C20A3  | 2065                | 71         | 0.137                       |
DCNP concentration up to 5 wt % showed a negligible increase in \( \Delta E^* \) (i.e., approximately 2 units, it is worth noting that this small color difference between PLA–DCNP3 and PLA–DCNP5 is almost indistinguishable by the human vision system), reflecting that the hue was saturated at lower loading levels of the colorant. These findings highlighted that the PLA–DCNP film due to its excellent color performance is capable of providing a specific shade with less consumption of colorants, which is more economic. The contrast ratio of neat PLA was found to be 13.6 and considerably rose to 58.2 after addition of 5 wt % DCNP in the PLA matrix. At the identical concentration of DCNP and C20A (i.e., 3 wt %), an increase in contrast ratio was found to be more pronounced for DCNP. These observations revealed that DCNP provided much higher hiding power and light protection performance for food packaging materials compared to those of the organoclay.

Figure 5A,B illustrates the transmittance spectra of the PLA films in UVB (280–320 nm) and UVA (320–400 nm) regions. As shown in Figure 5A, a neat PLA film with a thickness of 100 \( \mu \text{m} \) showed an average UV transmittance of 23%, suggesting a relatively transparent film susceptible to UV light diffusion. Filling PLA with DCNP and C20A substantially dropped UV transmittance of PLA in a way that at 3–5 wt % filler contents the samples represented no UV transmittance, reflecting remarkable UV protection performance of PLA–DCNP samples. To get further insight into the effect of fillers on UV resistance properties of PLA, UV–vis spectrophotometry was also performed on the samples with a thickness of 10 \( \mu \text{m} \), and the results are displayed in Figure 5B. As can be seen, the neat PLA film with a thickness of 10 \( \mu \text{m} \) has an average transmittance of 90% in the wavelength range of 280–400 nm, which allowed most of the incident UVA and UVB rays to pass that means high transparency and poor UV protection performance of this sample. When fillers were added to PLA, however, the average transmittance values drastically decreased to 29–60% for PLA–DCNP samples and 42% for PLA–C20A samples. Such a substantial decrease in UV transmittance by only a 10 \( \mu \text{m} \) film indicated superior UV radiation barrier properties of filled PLA. However, from the figure, it was found that the UV opacity of PLA–DCNP was slightly better than that of PLA–C20A at an equal filler concentration. Two possible mechanisms can be proposed to explain the high UV protection performance of PLA–DCNP samples. High aspect ratio aluminaisolate platelets of DCNP as an appropriate protective shield in the PLA matrix can hinder the UV diffusion pathway. Furthermore, a part of UV beams can be absorbed or suppressed by the interaction of electromagnetic radiation with polar moieties of methylene blue and clay platelets. The high UV and visible light blocking performance of obtained PLA–DCNP films,

### Optical Properties of PLA Films

Color coordinates over the white tile in the CIELAB 1976 space, \( \Delta E^* \), and contrast ratio for the samples are summarized in Table 3. As can be seen from the table, \( b^* \) values, expressing the blue-yellow component of the samples, shifted from −4.0 for the neat PLA up to −29.1 for DCNP/PLA. The values of \( a^* \), indicating the green-red component of the samples, remained almost constant. These results quantitatively illustrated that the DCNP/PLA samples represented an obvious blue hue. The \( L^* \) value is representative of two optical properties of the samples at the same time. The first property is the samples’ lightness, and the second one is attributed to the transparency of them, which leads to better light transmittance through the films and smaller changes on the high lightness of the white substrate. \( L^* \) values progressively dropped from 91.8 for the neat PLA to 31.2 for the DCNP/PLA films. The high lightness of the neat PLA is due to its colorless and relatively clear appearance that leads to easy light transmittance, therefore negligibly affecting the white substrate color coordinates. On the other hand, low lightness of the DCNP containing samples is attributed to the intense selective light absorption and strong blue color of them, which hinder light transmittance and effectively hide the white substrate. Addition of 1 and 3 wt % DCNP in the PLA matrix resulted in a large \( \Delta E^* \) with the values of 32.6 and 62.1, respectively. A further increase of

| sample code | \( L^* \) | \( a^* \) | \( b^* \) | \( \Delta E^* \) | contrast ratio (%) |
|-------------|---------|---------|---------|---------------|------------------|
| neat PLA    | 91.8    | 1.1     | −4.0    | 13.6          |                  |
| PLA–DCNP1  | 62.8    | −1.6    | −18.6   | 32.6          | 20.6             |
| PLA–DCNP5  | 35.0    | 2.6     | −29.1   | 62.1          | 51.8             |
| PLA–C20A3  | 31.2    | 1.25    | −24.6   | 64.0          | 58.2             |

Figure 4. Oxygen permeability (OP) and water vapor permeability (WVP) of the PLA films.
comparable to that of polymer films containing different additives, enable use of PLA–DCNP films for packaging of many UV and visible light sensitive foods such as meat, vegetable oils, milk, and dairy products. It is worth mentioning that the durability (i.e., color fastness) of the nanopigment under the continuous intense UV exposure was found to be desirable in our previous studies.

**CONCLUSIONS**

Colored biodegradable/biocompatible PLA nanocomposite films containing 1–5 wt % of dye–clay hybrid nanopigment (DCNP) were fabricated using a simple solution casting approach for application in food packaging materials. DCNP was successfully synthesized with a reaction yield of 76% via a cationic exchange reaction (CER) between a cationic dye (MB) and organically modified montmorillonite (C20A). The morphological studies of PLA–DCNP films showed the coexistence of the intercalated and exfoliated structure of DCNP/PLA nanocomposite films. It was also found a more uniform dispersion of DCNP within the PLA matrix compared to that of C20A. With the inclusion of DCNP in the PLA matrix, the dynamic mechanical properties, including storage modulus (E’), glass transition temperature (Tg), were greatly improved. The highest improvement in E’ and Tg was obtained at 3 wt % of DCNP loading level, while increasing the DCNP concentration to 5 wt % deteriorated the storage modulus of PLA. Oxygen permeability (OP) and water vapor permeability (WVP) of PLA–DCNP films were found to be much lower (i.e., 36% for OP and 54% for WVP) than those of neat PLA. These values also were higher than those of PLA–C20A at the same filler concentration. Optical property investigation of the samples revealed excellent color performance (high color strength and hiding power) and visible light protection performance of PLA–DCNP, especially at 3 wt %. UV protection performance of PLA–DCNP films with a sample thickness of 100 μm was found to be 100% and slightly higher than that of PLA–C20A. Overall, the presented results signaled that the colored PLA–DCNP film with excellent functional properties (i.e., high mechanical strength, barrier properties, blocking effect against destructive radiation, and biodegradability of the applied polymeric matrix) are well qualified to be potentially employed in food packaging applications.

**EXPERIMENTAL SECTION**

**Materials.** A film-grade polylactic acid, Ingeo biopolymer 4032D, was purchased from NatureWorks Co. Ltd. The selected grade is a semicrystalline PLA designed for use in the production of food packaging materials according to the manufacturer’s data sheet. A commercial montmorillonite organoclay, Cloisite 20A, modified with a bulky quaternary ammonium salt (dimethyl dihydrogenated tallow ammonium chloride, 2M2HT) and a modifier concentration of 95 mmol/100 g clay was supplied by BYK Additives, Germany. Analytical-grade chloroform, ethanol, hydrochloric acid, and methylene blue were obtained from Merck GmbH, Germany.

**Synthesis of DCNP.** Cloisite 20A, C20A, (10 g) was suspended into 500 mL of mixture of water/ethanol with a volumetric ratio of 25:75 using a magnetic stirrer under a stirring speed of 600 rpm for 12 h at ambient temperature. Methylene blue, MB, at a quantity equal to 46 mmol/100 clay (i.e., 50% of clay cationic exchange capacity, CEC = 92 mequiv/100 g clay) was dissolved in 200 mL of 0.1 M HCl. The dye solution was gently added to the stirring clay suspension, and then, the resultant mixture was stirred for 24 h at the same condition to complete the cationic exchange reaction between the clay and dye. Subsequently, the solid product was separated by filtration and washed with excess of distilled water. The filtrate was dried in vacuum at 60 °C for 12 h. Finally, the dried filtered cake was ground and sieved to obtain fine DCNP powder. Noted that, as previously stated, the optimum initial concentration of MB in CER, in which the resulting DCNP represents best functional properties along with an acceptable reaction yield, is 50% of clay CEC.

**Preparation of PLA Films.** To prepare PLA films containing C20A and DCNP, 1 g of PLA was first dissolved in 20 mL of chloroform using a magnetic stirrer under a stirring speed of 600 rpm for 2 h at ambient temperature. Then, the determined amounts of C20A and DCNP, based on Table 4, were slowly added into the PLA solution. The mixtures were stirred for 2 h followed by a sonication process using a Hielser UP400S ultrasonic sonicator, Germany, at a power of 50 W for 30 min. The dispersions were cast on a glass Petri dish and allowed to evaporate the solvent at ambient temperature for 48 h. The obtained films were finally dried in vacuum at 40 °C for 48 h to ensure complete evaporation of the residual solvent. The thicknesses of the final films were measured to be 100 ± 5 μm using a digital micrometer, Absolute Digimatic 547–401, Mitutoyo, Japan. The measurements were repeated on 10 random locations over the surface of each film.

**CHARACTERIZATION**

**Characterization of DCNP.** Elemental analysis was performed to determine the reaction yield and the quantity of 2M2HT and MB in DCNP using a PerkinElmer 2400 series II CHNS/O elemental analyzer. By determining the mass percentage of sulfur in DCNP, the amount of MB reacted with clay was calculated. Then, the amount of 2M2HT between clay layers was calculated by subtracting the nitrogen content attributed to MB from the total nitrogen content of DCNP.

**Morphology of PLA Films.** The extent of intercalation and exfoliation of fillers in PLA was quantitatively and qualitatively examined using X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) techniques, respectively. XRD patterns were collected at scattering angles from 0.5 to 10° with a scanning rate of 0.02°/s on a Philips X’Pert MPD X-ray generator (tube Cu Kα, λ = 1.54 Å) at room temperature. The basal spacing of samples (d-spacing) was calculated using the Bragg equation. HRTEM micrographs of the PLA film filled with 3 wt % of DCNP (PLA–DCNP3) was the sample that showed the optimum properties were obtained by an FEI Tecnai F20 with an acceleration voltage of 200 kV. The cross section of the sample

| Sample name | DCNP (wt %) | C20A (wt %) | PLA (wt %) |
|-------------|------------|------------|------------|
| neat PLA    | 100        |            |            |
| PLA–DCNP1   | 1          | 99         |            |
| PLA–DCNP3   | 3          | 97         |            |
| PLA–DCNP5   | 5          | 95         |            |
| PLA–C20A3   | 3          | 97         |            |
was generated under cryogenic conditions using a Leica EM UC7 ultra-microtome equipped with a diamond knife.

**Dynamic Mechanical Properties of PLA Films.** The dynamic mechanical properties of the films were investigated using a Mettler Toledo DMA 1 dynamic mechanical analyzer. The experiments were carried out on 30 × 10 × 0.1 mm³ dimension specimens under tension mode at a scanning temperature range of 25–120 °C with a temperature ramp of 5 °C/min and frequency of 1 Hz.

**Gas and Water Vapor Permeability of PLA Films.** Oxygen permeability (OP) of the PLA films was evaluated using a Brugger Feinmechanik GmbH GDP-C gas permeability tester at 25 ± 1 °C and 45 ± 5% relative humidity (RH) according to ASTM D 1434. Briefly, the samples were clamped and sealed between two metallic chambers. The permeating gas was pumped toward the PLA films in a chamber with a higher gas pressure. The oxygen transmission rate (OTR) of the samples was indicated by monitoring the increase in gas pressure at another chamber with a lower gas pressure. Finally, the OP of the samples is calculated using eq 1

\[
OP = \frac{OTR \cdot L}{\Delta p}
\]  

where OTR, \( L \), and \( \Delta p \) are the oxygen transmission rate, film thickness, and difference in partial pressure of the gas on the two sides of the film, respectively. A dish method was used to determine the water vapor permeability (WVP) of the samples as described by ASTM E 96. The test specimens were placed at 25 ± 1 °C and 45 ± 5% RH and weighed every 6 h for 14 days. The weight change as a function of time was plotted for each sample. The WVP of the samples is calculated using eq 2

\[
WVP = \frac{G \cdot x}{A \cdot \Delta p \cdot t}
\]  

where \( G \) and \( t \) are weight change and time at the steady-state region of the plot, respectively, and \( A, x, \) and \( \Delta p \) are the cup mouth area, film thickness, and the water vapor pressure difference between the two sides of the film, respectively.

**Optical Properties of PLA Films.** Color coordinates of the samples were determined according to the CIELAB color scale under the D65 standard illuminant over a standard white tile \((L^* = 82.3, a^* = -0.1, \) and \( b^* = -0.6)\) using a GretagMacbeth Color Eye 7000A spectrophotometer. The instrument was adjusted in 8/d geometry and specular scattering all UV radiation in 280–400 nm (zero transmittance in 280–400 nm) even at low filler concentrations. Therefore, to make a tangible comparison, UV–vis tests were also performed on 10 μm-thick films to magnify the difference between transmittance spectra of the samples in the UV region and to highlight the UV blocking effect of the nanofillers.

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**Notes**

The authors declare no competing financial interest.

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