

Effects of Quercetin and Organically Modified Montmorillonite on the Properties of Poly(butylene adipate-co-terephthalate)/Thermoplastic Starch Active Packaging Films

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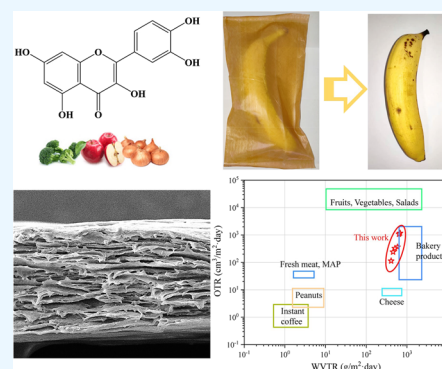
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ABSTRACT: The poly(butylene adipate-co-terephthalate) (PBAT)/thermoplastic starch (TPS) film stands out owing to its acceptable price, low impact on the environment, and excellent mechanical properties. The main objective of this study was to improve the antioxidant properties of the PBAT/TPS film by incorporation of quercetin (Q) through the extrusion blow process. Another specific objective was to incorporate the organically modified montmorillonite (OMMT) to prolong the release of Q and improve the poor barrier properties of the PBAT/TPS/Q film. The films were analyzed in terms of their morphology, mechanical properties, gas and water barrier properties, and antioxidant and anti-UV properties. Optimization of the OMMT content resulted in a fiber-like, co-continuous morphology of the PBAT/TPS/Q film. The incorporation of quercetin enhanced the antioxidant and anti-UV properties of the PBAT/TPS film, while OMMT improved the mechanical properties, ultraviolet barriers, and gas and water barrier properties. The results show that the films incorporating Q and OMMT provided the oxygen and water barrier by up to 94 and 54%, respectively. Also, the amount of polymer required for 50% 2,2-diphenyl-1-picrylhydrazyl (DPPH) inhibition is as low as 0.03 g, and the UV transmission rate was reduced by about 50%. Moreover, PBAT/TPS/Q/OMMT films successfully delayed the decay of the banana and blueberry due to their excellent antioxidant properties and suitable water vapor permeability.



1. INTRODUCTION

The trend in the food packaging market is to replace common plastics with more sustainable and biodegradable films with good antioxidant and mechanical properties to extend the preservation time of fruits and vegetables.¹ Poly(butylene adipate-co-terephthalate) (PBAT) is among the most promising substitutes for low-density polyethylene owing to its excellent biodegradability and facile synthesis.^{2,3} Nevertheless, high cost and low barrier properties limit the applicability of PBAT in packaging films.⁴ A potential solution to overcome these limitations is to incorporate natural fillers in the PBAT matrix.⁵

Starch is a highly abundant natural filler with good processability in thermoplastic composites.⁶ Starch is an energy source for many microorganisms, which improves the biodegradation rate of PBAT composites.⁷ The addition of polar plasticizers such as glycerol and sorbitol⁸ breaks up the semi-crystalline structure of starch and yields thermoplastic starch (TPS) with similar melt processability as common plastics.^{9–11} Recent studies have reported the preparation and characterization of PBAT/TPS composite films with various compositions, where compatibility between two phases was enhanced by the modifications of the starch surface.^{12,13}

Moreover, natural fibers, cellulose, and nano-clays have been added to enhance the mechanical strength, barrier properties, and hydrophobicity of PBAT/TPS films.^{14,15}

Active packaging materials (APM) are materials with good mechanical properties that reduce microbial growth, delay oxidation, and extend the shelf life of food. The formulations of APM usually contain health-promoting natural product antioxidants such as essential oils, natural pigments, chitosan, nisin, and ϵ -polylysine hydrochloride.^{16,17} Sabrina and co-workers^{18,19} formulated thermoplastic cassava starch/PBAT films containing curcumin as APM that prevent oil degradation. Sakanaka and co-workers²⁰ and Shirai and co-workers²¹ showed that the microencapsulation of oregano oil into the PBAT/TPS film yields biodegradable food APM with good antioxidant properties. Lim and co-workers²² incorpo-

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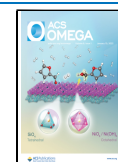


Table 1. Formulations of Studied Powders

samples	TPS	TPS/Q	TPS/Q/OMMT-0.9 vol %	TPS/Q/OMMT-1.75 vol %	TPS/Q/OMMT-2.61 vol %	TPS/Q/OMMT-3.34 vol %
starch (phr)	100	100	100	100	100	100
glycerol (phr)	35	35	35	35	35	35
Q (phr)	0	1	1	1	1	1
OMMT (phr)	0	0	5	10	15	20
proportion of OMMT in powder (wt %)	0	0	3.5	6.8	9.9	12.8
proportion of OMMT in composites (wt %)	0	0	1.42	2.74	3.97	5.13
proportion of OMMT in composites (vol %)	0	0	0.90	1.75	2.61	3.34

rated ϵ -polylysine hydrochloride into the starch/PBAT film which improved thermal stability, UV barrier, and oxygen barrier properties, while hydrogen bonding between polar molecules of starch and ϵ -polylysine hydrochloride lowered the water barrier properties. The byproducts of food consumption such as Pinhão coat extract are rich sources of antioxidants, and Silva et al.²³ used this feedstock to improve the antioxidant capacity of the TPS/PBAT film.

Quercetin (3,3',4',5,7-pentahydroxyflavone, Q) is a ubiquitous polyphenolic compound found in most fruits and vegetables. Several health-promoting effects of Q such as antioxidant, anti-UV, antibacterial, and anticancer activity have been demonstrated.^{24,25} The biomass-derived Q has been successfully incorporated into PVA and PLA by the solvent casting method, giving functional food packaging films.^{26–28} Compared with solvent casting, blown film extrusion is a more efficient and environmentally friendly technique. To the best of our knowledge, the application of a later method to produce active PBAT/TPS packaging films containing quercetin has not been reported in the literature.

In this study, we enriched the PBAT/TPS composite film with quercetin, intending to improve its antioxidant properties. We added the organically modified montmorillonite (OMMT) to inhibit the release rate of Q from the composite and prolong the antioxidant activity of the film and improve the intrinsically poor barrier properties of the PBAT/TPS composite. The changes in morphological, mechanical, rheological, gas and water barrier properties, and antioxidant and anti-UV properties upon the addition of quercetin and OMMT were systematically investigated. The fruit preservation activity of PBAT/TPS films with incorporated quercetin and OMMT was compared with commercially available PE films using banana and blueberry as model fruits.

2. EXPERIMENTAL SECTION

2.1. Materials. PBAT (Ecoworld, $M_n = 7 \times 10^4$ g mol⁻¹) was purchased from Jinhui Zhaolong High Tech Co., Ltd. (Shanxi, China). Hydroxypropyl distarch phosphate (HPDSP; 3.1% hydroxypropyl group content) was supplied by Puluoxing Starch Co., Ltd. (Hangzhou, China). Glycerol was purchased from Shanghai Titan Scientific Co., Ltd. OMMT (I.24 TL) modified using 18-amino stearic acid with a length/thickness ratio of 80 was ordered from Nanocor Inc. (USA). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was bought from Yuanye Bio-Technology Co., Ltd. (Shanghai, China). Quercetin (abbreviated as Q in the following) was acquired from Ark Pharm, Inc. (USA). Anhydrous ethanol was supplied by MREDA Technology Co., Ltd. (Beijing, China). Hydrochloric

acid was purchased from Jinrong Chemical Co., Ltd. (Hebei, China).

2.2. Preparation of Mixed Powder. The formulations of powders used in this work are listed in Table 1. In a typical preparation procedure, solids (starch, quercetin, and OMMT) were mixed using a high-speed mixer for 5 min at RT. Afterward, glycerol was slowly added, and the mixture was stirred for another 5 min at RT. Prior to extrusion with PBAT, each mixture was conditioned in PE bags at room temperature for at least 24 h.

2.3. Preparation of Blend Pellets. In the next step, PBAT and mixed powder in a 6/4 weight ratio were extruded and pelleted using the counter-rotating twin-screw extruder with screw diameter $D = 20$ mm and screw length 40 cm. The temperature profile of the extruder was set to 80/130/135/130/120 °C going from the feeding to the die zone. The final PBAT/TPS blends were produced by air cooling and granulation.

2.4. Blown Film. The pellets were extruded to blown film by a single screw extruder film-blowing (Kechuang, China, LSJ20), with $D = 25$ mm, a length of 30 D , and a die zone diameter of 30 mm. The rotating speed was 25 rpm and the temperature profile from the feeding to the die zone was set to 110/120/140/140 °C. The blow-up speed was 2 m/min. The thickness of the obtained films was measured by a digital micrometer (FUMA, Dongguan, China) at 10 different positions and averaged, and the thickness of blown films was about 25 ± 2 μm .

2.5. Characterizations. The OMMT dispersion state was analyzed using wide-angle X-ray diffractometry (WAXD) (Bruker D8 Advance) operating at 45 kV and 40 mA. The 2θ scan range was set to 3°~40°, with a 5°/min scanning rate and a Cu K α radiation wavelength of 1.54 Å.

The morphology of the films was analyzed using a field emission scanning electron microscope (SEM) (FEI Company, USA, Quanta 250 FEG) at an accelerating voltage of 10 kV. Cross-sections of the films in the machine direction were obtained by a fragile fracture with liquid nitrogen. To selectively remove the TPS phase, it was etched with 2 N HCl solution for 2 h. The prepared fracture surfaces were sputtered with gold for 2 min. Afterward, they were placed in the sample bin and vacuumed for 10 min before testing.

Fourier transform infrared (FTIR) spectra of the films were characterized by a PerkinElmer 782 instrument in the wavenumber range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹.

The tensile strength of films was tested according to ASTM D882 standards using a universal, microcomputer-controlled

CMT6104 machine (Mester Industrial Systems Limited Corp.) equipped with a 50 N load cell. The cross-head speed was 100 mm/min in the machine direction of the films and 20 mm/min in the transverse direction. The tearing strength of trouser-shaped specimens was measured at a speed of 100 mm/min. The reported values are the average and standard deviation of five measurements. Before testing, each sample was conditioned at 25 °C and 50% RH for 72 h.

The rheological properties of the blends were analyzed using a plate rheometer (Anton Paar, MCR-502, Austria). The viscosity and storage modulus of the blend materials are a function of the angular frequency and were measured at 140 °C in dynamic mode by setting two plates in parallel orientation with a 1 mm gap and 25 mm diameter. To ensure a linear viscoelastic response of tested composites, the low strain amplitude of 0.1% was maintained.

The gas permeability of prepared films for oxygen, nitrogen, and carbon dioxide was tested by a gas permeability tester (VAC-V1, Jinan Languang) at 23 °C and 30% RH with an area of 38.48 cm² according to ISO 15105-1:2007 standard.

The water vapor permeability (WVP) was analyzed according to the GB/T 1037-2021 using a water vapor permeameter (C360M, Jinan Languang) operating at 38 °C and 90% RH. The films were conditioned at 23 °C and 50% RH for at least 4 h. All tests were carried out in triplicates and the result is the average of three independent measurements.

The transmittance of the films was measured in the UV–vis range from 200 to 800 nm by an ultraviolet–visible spectrophotometer (UV-3600, Shimadzu, Japan).

The antioxidant capacity of the films was studied by the DPPH-radical scavenging test.²⁹ The film samples were weighted (1, 0.8, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01, 0.008, 0.004, 0.002 g for each group), cut into small pieces, and then mixed with 20 mL of ethanol. The mixture was sonicated for 30 min at 40 °C. After that, the solution was centrifuged at 2000 rpm for 10 min and 2 mL of the supernatant was mixed with 2 mL of 30 ppm of ethanolic solution of DPPH. The reaction between antioxidants from packaging films and DPPH radicals occurs in the dark during 30 min of incubation at RT. In this process, hydrogen atom transfer from the antioxidant to DPPH radicals results in a stable, nonradical DPPH form which was accompanied by the color change from violet to yellow. This process was monitored at 517 nm using a UV-3600 spectrophotometer (Shimadzu, Japan). The blank probe was a mixture of 2 mL of ethanol and 2 mL of DPPH ethanolic solution. DPPH-radical scavenging activity was derived using eq 1:³⁰

$$\text{radical scavenging activity (\%)} = 1 - \frac{\text{Abs}_{\text{sample}}}{\text{Abs}_{\text{control}}} \times 100\% \quad (1)$$

where $\text{Abs}_{\text{sample}}$ is sample absorbance and $\text{Abs}_{\text{control}}$ is the absorbance of the control group. As a result, the amount of each material needed for quenching 50% of DPPH radicals (SR_{50} (g)) could be calculated and used to make a comparison of the antioxidant property. The results are expressed as an average \pm standard deviation of three measurements.

3. RESULTS AND DISCUSSION

3.1. Morphology. The dispersion state of clay highly influences the mechanical and barrier properties in polymer/composites. It can be characterized using XRD, which was

the technique used in this study to evaluate the dispersion state of OMMT in PBAT/TPS composites. Figure 1 shows the

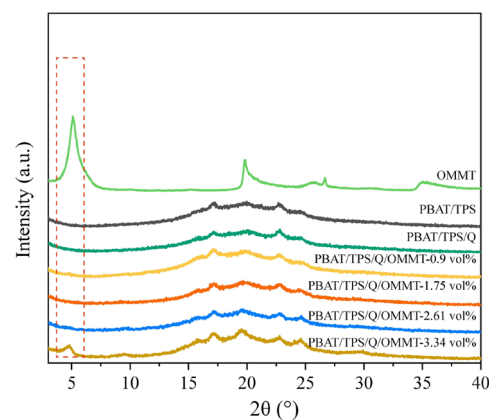


Figure 1. XRD patterns of neat OMMT and PBAT/starch films with quercetin and varying contents of OMMT.

XRD curves recorded for neat OMMT, PBAT/TPS, PBAT/TPS/Q, and PBAT/TPS/Q/OMMT films with OMMT loading from 0.9 to 3.34 vol %. The sharp diffraction peak of pristine OMMT at $2\theta = 5.12^\circ$ originates from the 001 diffraction plane with a basal spacing d_{001} of 1.725 nm. A similar peak is found at 4.84° in a composite having the highest concentration of OMMT (PBAT/TPS/Q/OMMT-3.34 vol %), which corresponds to $d_{001} = 1.824$ nm. This suggests that a part of OMMT has not been exfoliated. Polar plasticizer glycerol has two effects, plasticizing the semicrystalline structure of starch and at the same time facilitating the exfoliation of OMMT in PBAT/starch composites. When the OMMT content is 3.34 vol %, the amount of glycerol is not enough to allow all the OMMT to be exfoliated. Therefore, the films of PBAT/TPS/Q/OMMT-3.34 vol % can be observed at $2\theta = 4.84^\circ$ for the 001 diffraction plane of the OMMT. Other samples with a lower content of OMMT do not exhibit this diffraction peak, implying that the clay is exfoliated in the PBAT/TPS matrix. Chivrac et al.^{31,32} reported that glycerol as a plasticizer induces the fully exfoliated morphology of OMMT/starch nanocomposite obtained by melt extrusion. This is explained by the high affinity of glycerol to intercalate into OMMT platelets, which facilitates the exfoliation of OMMT in PBAT/starch composites.

After hydrolysis of PBAT/TPS composites in HCl to remove starch and OMMT, the SEM images were recorded on cross-sectional cryo-fractured surface of films in the machine direction (Figure 2). The TPS phase in PBAT/TPS and PBAT/TPS/Q films appears as finely dispersed, elongated, partially connected droplets. Upon incorporation of OMMT, the morphology of the PBAT/TPS/Q system gradually changed to a fiber-like structure with the increasing content of OMMT. Moreover, both PBAT and TPS phases turn into the fibrillar form, indicating a completely continuous structure controlled by the OMMT content. This type of morphology enhances the barrier properties of PBAT/starch composite films. The mechanism that governs the formation of a continuous structure is driven by the exfoliated OMMT structure.^{33,34}

The hydrogen bonding (HB) between starch and the $-\text{Si}-\text{OH}$ groups on the surface of layered OMMT is studied in more detail using FTIR spectroscopy. According to Figure 3,

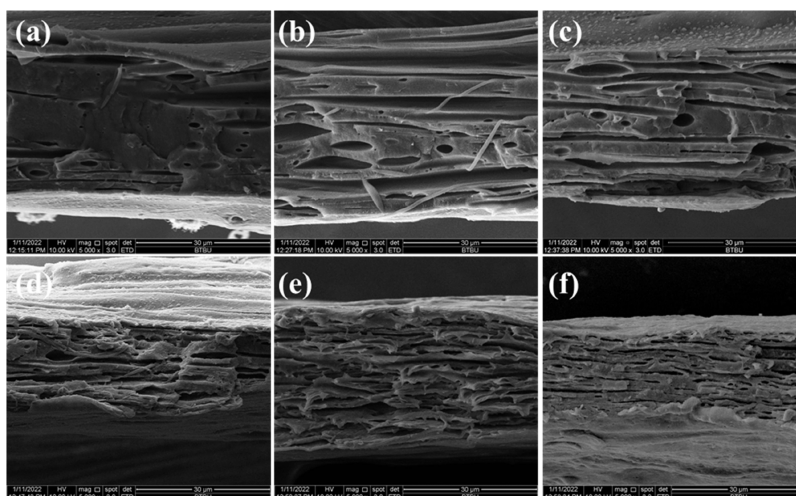


Figure 2. Influence of OMMT concentration on the morphology of PBAT/TPS films. The cross-sectional cryofractured surface recorded in the machine direction for films: (a) PBAT/TPS, (b) PBAT/TPS/Q, (c) PBAT/TPS/Q/OMMT-0.9 vol %, (d) PBAT/TPS/Q/OMMT-1.75 vol %, (e) PBAT/TPS/Q/OMMT-2.61 vol %, and (f) PBAT/TPS/Q/OMMT-3.34 vol %.

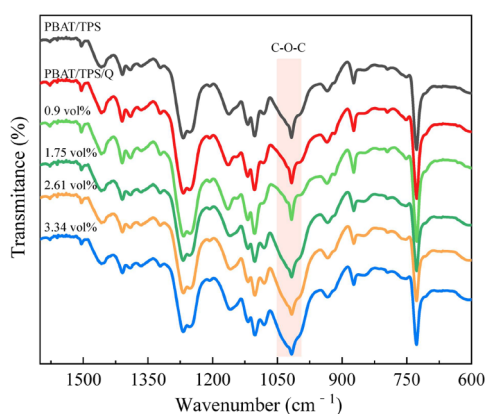


Figure 3. FTIR spectra of PBAT/starch films loaded with quercetin and different amounts of OMMT.

no peaks were formed or disappeared, indicating that the two phases bind exclusively via noncovalent interactions. The HB interactions are observed from the shift in the absorption peak at 1017.2 cm^{-1} that originates from C–O stretching vibrations in glycosidic bonds of starch.³⁵ The addition of 1.75 vol % OMMT decreases the wavenumber of this vibration to 1016.7 cm^{-1} and broadens the peak, which is a typical trend for the FTIR spectra of hydrogen-bonded vibrations as the peak frequency is directly proportional to the force constant of the chemical bond.³⁶

3.2. Mechanical Properties. The effect of quercetin and different amounts of OMMT on the mechanical properties of

PBAT/TPS films were tested by measuring the tensile and tearing strength of all composites. These properties were measured in two directions relative to the extruder: machine direction (MD) and transverse direction (TD). The tensile strength, elongation at break, and tearing strength of six composites are listed in Table 2. The results are in accordance with the trends in morphology changes, where the formation of PBAT and TPS fibers induced by OMMT improves tensile strength and tearing strength in the MD. As elongation at break in the TD is significantly lower compared to MD, it can be concluded that HB orients polymer chains along the MD axis during the extrusion process.^{37,38}

3.3. Rheological Properties. The rheological properties of polymer blends such as complex viscosity (η^*) and storage modulus (G') depend on the molecular structure and intermolecular interactions between the constituents. Herein, we measured the dependence of η^* and G' on angular frequency (ω) of PBAT/TPS and PBAT/TPS/Q blends loaded with different amounts of OMMT using a rotational rheometer at $180\text{ }^\circ\text{C}$. Figure 4 shows that OMMT improves the rheological properties of composites in the entire frequency region. This is explained by the formation of network structures that shift viscoelastic responses from liquid-like to solid-like. The same effect has been observed previously for PLA enriched with OMMT.³⁹ At low frequencies, neat PBAT/TPS and PBAT/TPS/Q films exhibit properties that obey linear viscoelastic theory.⁴⁰ However, the linear behavior gradually decreases at higher OMMT loadings and turns into a solid-like response in the low-frequency region. This result

Table 2. Mechanical Properties of PBAT/Starch Films Loaded with Quercetin and Different Amounts of OMMT

samples	tensile strength (MPa)		elongation at break (%)		tearing strength (kN/m)	
	MD	TD	MD	TD	MD	TD
PBAT/TPS	8.0 ± 0.69	2.3 ± 0.15	631.9 ± 23.16	91.9 ± 25.16	54.0 ± 9.27	27.4 ± 8.32
PBAT/TPS/Q	8.3 ± 0.30	2.3 ± 0.27	645.0 ± 27.53	84.5 ± 17.07	62.9 ± 1.99	32.4 ± 4.42
PBAT/TPS/Q/OMMT-0.9 vol %	9.7 ± 0.96	2.3 ± 0.07	658.0 ± 78.45	68.8 ± 12.92	69.3 ± 11.88	33.9 ± 2.33
PBAT/TPS/Q/OMMT-1.75 vol %	10.0 ± 0.41	2.2 ± 0.31	644.3 ± 22.17	60.9 ± 4.84	71.3 ± 6.25	36.5 ± 9.55
PBAT/TPS/Q/OMMT-2.61 vol %	10.9 ± 0.99	2.6 ± 0.74	607.1 ± 22.32	58.8 ± 7.86	73.3 ± 26.60	41.7 ± 3.89
PBAT/TPS/Q/OMMT-3.34 vol %	11.5 ± 0.28	3.0 ± 0.28	569.8 ± 24.12	49.6 ± 25.71	81.3 ± 9.16	46.9 ± 7.74

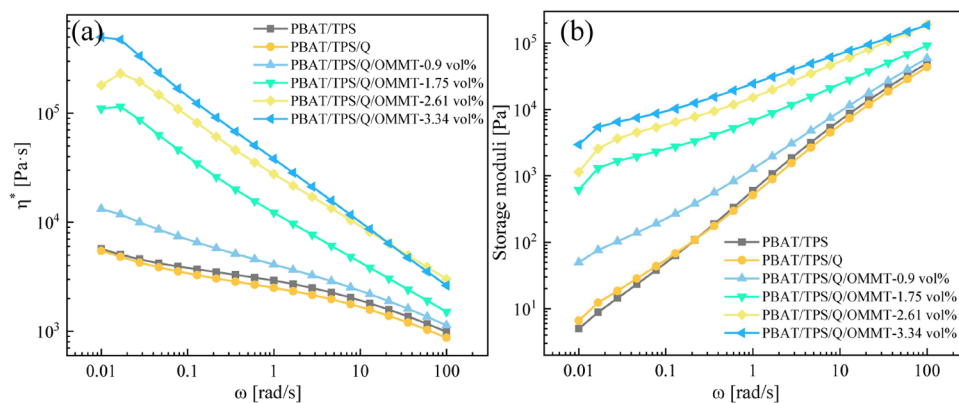


Figure 4. (a) Complex viscosities (η^*) and (b) storage moduli (G') of PBAT/TPS blends loaded with quercetin and different amounts of OMMT.

Table 3. Gas Transport Performance of Films^a

samples	permeability (Barrer)			selectivity (α)		
	O ₂	N ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /O ₂
PBAT/TPS	1.61	0.48	13.44	3.36	28.13	8.35
PBAT/TPS/Q	1.12	0.30	7.26	3.72	24.22	6.48
PBAT/TPS/Q/OMMT-0.9 vol %	0.46	0.13	3.84	3.54	29.52	8.34
PBAT/TPS/Q/OMMT-1.75 vol %	0.26	0.073	2.32	3.50	31.51	9.00
PBAT/TPS/Q/OMMT-2.61 vol %	0.15	0.044	1.40	3.49	31.81	9.33
PBAT/TPS/Q/OMMT-3.34 vol %	0.10	0.028	0.86	3.52	30.18	8.60

^a1 Barrer = 1×10^{-10} cm³ cm/cm² s cm Hg.

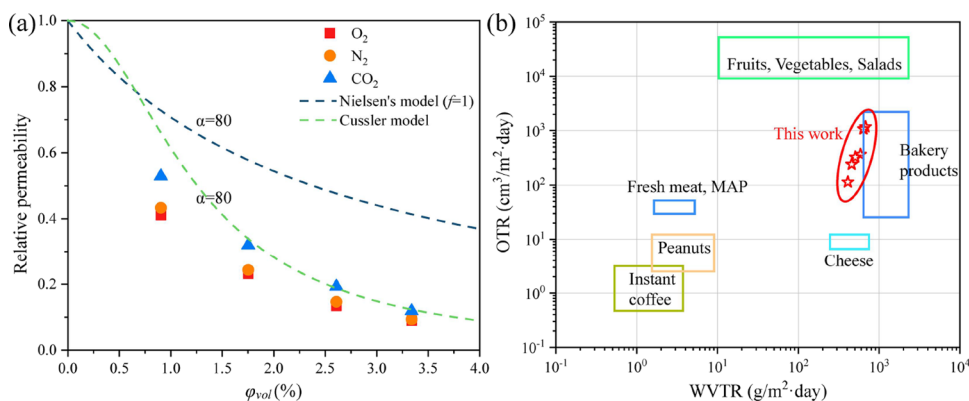


Figure 5. (a) Comparison between the experimental P/P_0 and the data predicted using the Nielsen model and Cussler model, (b) optimum values of OTR and WVTR for different food packaging materials, and the comparison with the values for PBAT/TPS/Q/OMMT films developed in this work.

indicates that OMMT reinforces the PBAT/TPS composite and restrains the flexibility of polymer chains.

3.4. Gas and Water Vapor Transport Properties. The structure of composite blends also influences their gas and water permeability. The effect of OMMT content on O₂, N₂, and CO₂ permeability is summarized in Table 3. Compared to pristine PBAT, the PBAT/TPS film has a higher permeability to oxygen (P_{O_2} 1.61 vs 0.94 Barrer⁴), which is a consequence of interfacial gaps formed between the interfaces of the TPS phase dispersed in the PBAT matrix.^{41,42} Besides gas permeability, gas selectivity is another important parameter for films, especially for packaging fruits and vegetables in a modified atmosphere.⁴³ The selectivity expressed as the ratio of gas permeabilities is also shown in Table 3. The results show that the addition of quercetin reduces the gas permeability of PBAT/TPS. The possible reason for this trend is the tighter packing of polymer chains as a result of HB between the

phenolic –OH groups of quercetin and polar chains of starch polymers,⁴⁴ as well as π – π interactions between quercetin and benzene rings of PBAT chains. The addition of OMMT significantly improves the gas barrier properties. For example, the PBAT/TPS/Q/OMMT film with 2.61 vol % of clay has a low oxygen permeability of 0.13 Barrer, which is an 87% reduction compared with the PBAT/TPS/Q film. This demonstrates excellent dispersion of OMMT in composite films and confirms previous findings from XRD and SEM.

To study the effect of OMMT on gas barrier properties of PBAT/TPS/Q/OMMT films in a more quantitative manner, the experimental data were fitted into Nielsen's model⁴⁵ and Cussler's model⁴⁶ to correlate gas permeability with the volume fraction and morphology of layered flakes. The first model accurately predicts gas permeability for films with the random distribution of flakes and weak interactions between the filler and polymer matrix. The second model is applicable

for composites with a more ordered structure, and we aimed to fit the relative permeability for O₂, N₂, and CO₂ in both models to quantify the effect of the OMMT filler. The fitting of experimental P/P_0 data for three gases and predicted data from two models is shown in Figure 5a. The following equations describe the abovementioned models:

Nielsen model:

$$\frac{P}{P_0} = \frac{1 - \phi_{\text{vol}}}{1 + \frac{\alpha}{2}\phi_{\text{vol}}} \quad (2)$$

Cussler model:

$$\frac{P}{P_0} = \left(1 + \frac{\alpha^2 \phi_{\text{vol}}^2}{1 - \phi_{\text{vol}}} \right)^{-1} \quad (3)$$

where P and P_0 are the permeabilities of the films with OMMT and PBAT/TPS/Q, respectively, ϕ_{vol} represents the volume fraction of the OMMT, and α is the length-to-thickness ratio of OMMT. The ϕ_{vol} can be calculated as³⁷

$$\phi_{\text{vol}} = \frac{\frac{\phi_{\text{wt}}}{\rho_{\text{OMMT}}}}{\frac{\phi_{\text{wt}}}{\rho_{\text{OMMT}}} + \frac{1 - \phi_{\text{wt}}}{\rho_{\text{PBAT/TPS/Q}}}} \quad (4)$$

where ϕ_{wt} denotes the mass fraction of the OMMT and ρ_{OMMT} and $\rho_{\text{PBAT/TPS/Q}}$ represent densities of the OMMT and PBAT/TPS/Q film, which are taken as 1.35 and 2.1 g/cm³, respectively.⁴⁸ Using these data, we were able to convert the weight content of OMMT to volume content. Finally, the α value of 80, determined by TEM in our previous work,⁴⁹ was taken.

While relative gas permeability for the PBAT/TPS/Q/OMMT film significantly deviated from the Nielsen model, the data fitted closely to the Cussler model, indicating that OMMT is highly exfoliated and evenly distributed in polymer films.

WVP is an important parameter of moisture-proof food packaging films, and high WVP is not suitable for this application. On the other side, some fruits with a fast breathing rate require films with a good water vapor transmission rate (WVTR) to allow diffusion of generated water vapor and prevent rotting. Table 4 shows WVP and WVTR values of

Table 4. Water Vapor Transport Performance of Different PBAT/TPS Films

samples	WVTR g/(m ² ·day)	WVP (10 ⁻¹³ g·cm/cm ² ·s·Pa)
PBAT/TPS	678.67	9.64
PBAT/TPS/Q	640.45	8.77
PBAT/TPS/Q/OMMT-0.9 vol %	587.37	6.85
PBAT/TPS/Q/OMMT-1.75 vol %	507.08	6.05
PBAT/TPS/Q/OMMT-2.61 vol %	457.07	4.99
PBAT/TPS/Q/OMMT-3.34 vol %	410.26	4.42

different PBAT/TPS films prepared in this work. The addition of OMMT induces the formation of continuous fibrillar structures that improves both parameters, but to a lesser extent compared with oxygen permeability. The high hydrophilicity of starch can explain this trend. For example, the WVP of the film with 2.61 vol % of OMMT is reduced by 50% compared with that of PBAT/TPS/Q film. The WVP of PBAT-based composites requires further optimization as commercial

LDPE has about two orders of magnitude lower WVP (7.3 × 10⁻¹⁵ g·cm/cm²·s·Pa) compared with PBAT/TPS/Q/OMMT films (Table 4). Table 5 summarizes the comparison of the barrier performance PBAT/TPS/Q/OMMT films developed in this work with the other reported PBAT/TPS active packaging films. The results show that the WVP of active packaging films has a great correlation with the starch content. Generally, the lower the TPS content, the smaller the WVP. Figure 5b illustrates the optimum values of OTR and WVTR for different foods and compares them with the results for PBAT/TPS/Q/OMMT films.⁵⁰

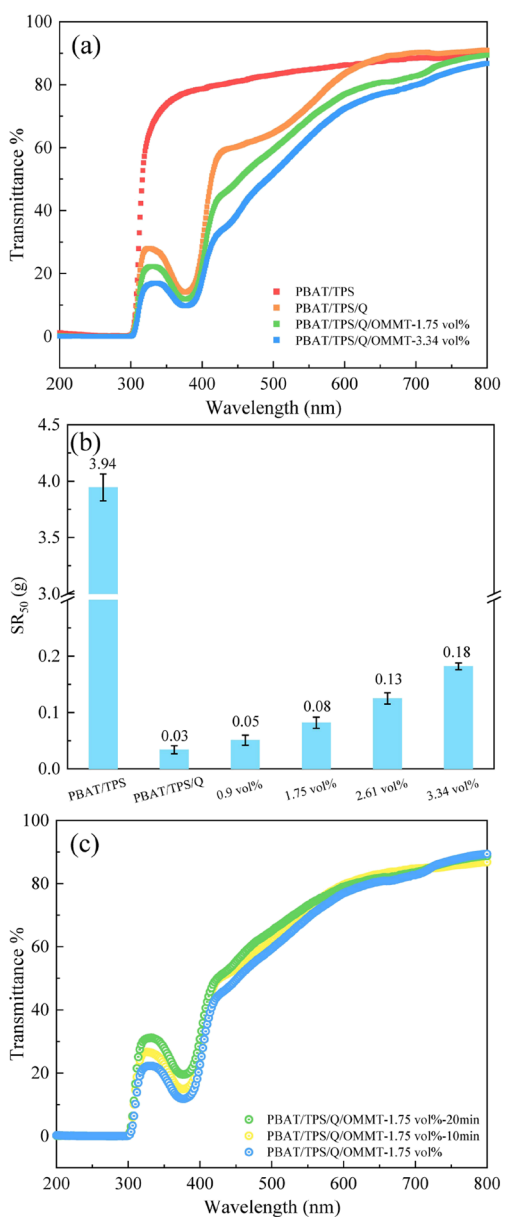
3.5. Antioxidant and Anti-UV Properties. UV radiation is among the most important factors that reduce food quality. Therefore, novel active packaging materials should be endowed with light absorption properties in the UV part of the electromagnetic spectrum. According to Figure 6a, neat PBAT/TPS film is highly transparent for UV radiation between 300 and 400 nm. The addition of quercetin and OMMT significantly reduces the UV transmittance, which is attributed to UV light absorption of phenolic chromophores and the shading effect of OMMT. It can be concluded that PBAT/TPS/Q/OMMT films have exceptional UV-blocking performance.

To extend the shelf life of foods, antioxidants are often incorporated into the structure of active packaging materials.^{53,54} The antioxidant activity of such films can be determined using free radical scavenging assays such as DPPH or ABTS assays. In this study, the antioxidant activity of PBAT/TPS/Q/OMMT films was analyzed using the DPPH test. The amount of each material needed for quenching 50% of DPPH radicals is shown in Figure 6b. The lower values mean better antioxidant activity of the film. The lowest activity is observed for quercetin-free PBAT/TPS films where the main DPPH elimination mechanism is physisorption on the surface of the material. The addition of quercetin, a well-known polyphenolic antioxidant,^{55,56} significantly increased the antioxidant activity as the amount of polymer needed for 50% DPPH inhibition reduced from 3.94 to 0.03 g. Following the addition of OMMT, the antioxidant activity of the film gradually decreases. To investigate the reason, the film containing 1.75 vol % OMMT was immersed in ethanol different times and its UV-vis spectrum was characterized. As shown in Figure 6c, with the extension of immersion time, the UV absorption intensity of the film between 300 and 400 nm was weakened and the transmittance was enhanced. This indicates that quercetin will gradually leach from the film over time, thus reducing the UV absorption capacity of the film. Therefore, the incorporation of OMMT decreases the quercetin release rate from the blend. However, all these materials still possess much higher antioxidant activity compared with the pristine PBAT/TPS film. In the layered structure of the polymer, the diffusion path for quercetin is long and tortuous which prevents the rapid release of antioxidants. The controlled release of quercetin from PBAT/TPS/Q/OMMT films is favorable for the prolonged shelf life and also improves food safety and quality.⁵⁷

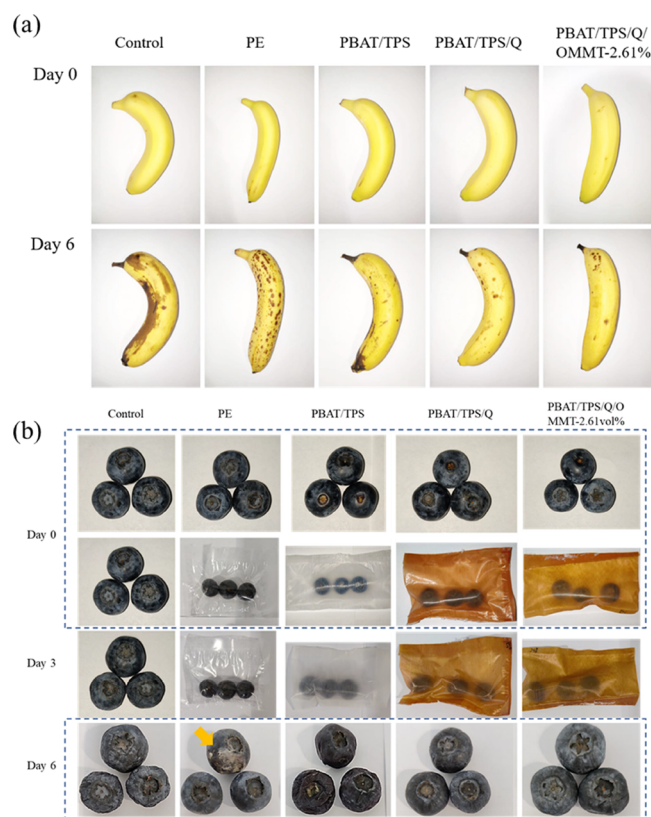
3.6. Application of PBAT/TPS/Q/OMMT Films in Fruit Packaging. Banana and blueberry were chosen as models to investigate the fruit preservation ability of PBAT/TPS/Q/OMMT films at room temperature. Bananas are highly prone to oxidation and fast ripening, and the loss in freshness is visible from the dark color of the peel. In the control experiments, the fruits were exposed to air and packed into

Table 5. Comparison of the Barrier Performance of PBAT/TPS/Q/OMMT Films Developed in This Work with the Other Reported PBAT/TPS Active Packaging Films

samples	TPS content (wt %)	WVP (10^{-13} g·cm/cm ² ·s·Pa)	test conditions
PBAT/TPS/Q/OMMT-3.34 vol % (this work)	40	4.42	38 °C, 90% RH
starch/PBAT/ α -tocopherol ⁵¹	60	12.2	25 °C, 42% RH
TPS/MTPS/PBAT ¹³	70	20	23 °C, 25% RH
starch/PBAT ⁵²	50	5.22	23 °C, 53% RH
starch/PBAT/ ϵ -PL ²²	32	4.03	38 °C, 90% RH

**Figure 6.** (a) UV light transmittance and (b) antioxidant activity of PBAT/starch films modified with quercetin and OMMT. (c) Comparison of UV light transmittance of PBAT/TPS/Q/OMMT-1.75 vol % after immersion in ethanol for different times.

commercial PE bags. Figure 7a shows the appearance of bananas at the beginning of the storage process and after 6 days. All films reduced the air oxidation of bananas compared to unpacked and LDPE-packed controls. This effect was the most pronounced for PBAT/TPS/Q/OMMT-2.61 vol %,

**Figure 7.** Appearance of (a) bananas and (b) blueberries during the storage in different packaging films.

implying that the addition of quercetin and OMMT improves the antioxidant properties of the packaging films.

Excess moisture at the surface of fruits favors the formation of various microorganisms and results in rotting. Therefore, it is necessary to obtain a packaging material that can easily spread out water vapor generated by the respiration of fruit. Blueberry was a model for monitoring the influence of WVTR on the storage time of fruit. The photographs of blueberries taken at different time intervals are shown in Figure 7b. The blueberry exposed to air was dry after 6 days, while the one stored in PE foil was moldy and decayed. The only blueberry sample that maintained the initial freshness after 6 days was the one kept in the PBAT/TPS/Q/OMMT film. These results suggest that the antioxidant and barrier properties of the PBAT/TPS/Q/OMMT film are beneficial for the prolonged shelf life of fruits.

4. CONCLUSIONS

In this study, the PBAT/TPS film with excellent antioxidant activity and UV protection was prepared by the incorporation of quercetin through blown film extrusion. Moreover, the addition of OMMT changed the morphology of polymer

chains to a continuous, fibrillar structure with improved gas and water barrier properties and prolonged release of quercetin. The OMMT phase changed from the fully exfoliated to the intercalated structure in a concentration-dependent manner. Hydrogen bonding between the starch polymer and silanol groups on the OMMT surface was the driving force for the formation of the network structure with enhanced mechanical properties. The excellent fruit preservation properties of the PBAT/TPS/Q/OMMT film were demonstrated using bananas and blueberries as model fruits and were superior compared to commercial LDPE films. The results of this study demonstrate the proof-of-concept for the development of active packaging materials for fruit storage based on PBAT/TPS composites functionalized by antioxidants and natural clay materials. Future research should be oriented toward the modifications that may result in more hydrophobic, moisture-resistance materials with water vapor resistance close to LDPE films.

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Notes

The authors declare no competing financial interest.

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