Self-cleaning and ethylene-scavenging properties of gelatin-TiO_2 and hydroxypropyl methylcellulose-TiO_2 photocatalytic biocomposites

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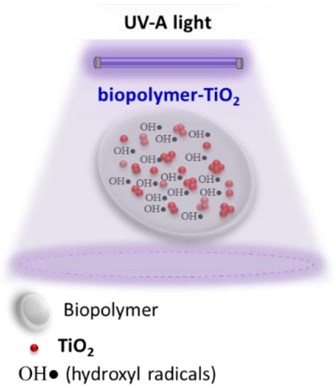

Photocatalytic composites based on biopolymers and titanium dioxide (TiO_2) exhibit potential applications as active food packages. Thus, the self-cleaning and ethylene-scavenging properties of gelatin-TiO_2 and hydroxypropyl methylcellulose (HPMC) -TiO_2 films were investigated to evaluate the influence of the biopolymer hydrophilicity on TiO_2 performance. Both films containing 1wt% TiO_2, HPMC-1%TiO_2 and Gel-1%TiO_2, presented self-cleaning properties, removing 12% and 18% of the oleic acid layer deposited on their surface at 25°C and RH = 58%, respectively. They also scavenged almost 40% of the ethylene loaded [5ppmv] into a batch reactor at 30°C and RH = 85%. However, Gel-1%TiO_2 exhibited a faster ethylene degradation due to the better TiO_2 dispersion into the gelatin than HPMC.

Introduction

Photocatalytic composites based on biopolymers and titanium dioxide (TiO_2) have been extensively investigated for active food packaging applications as antimicrobial and ethylene scavenger materials due to the generation of reactive oxygen species generation (ROS) that trigger the photodegradation reactions [1].

Ethylene is an important volatile organic compound (VOC) that accelerates the ripening of climacteric fruits. Because of this, its remotion at the beginning of the fruit ripening is essential to retard its autocatalytic production and extend the shelf-life of fruits [2].

Thus, this research aimed to study the influence of hydrophilicity of biopolymer matrices in self-cleaning and ethylene-scavenging properties of TiO_2 immobilized into hydroxypropyl methylcellulose (HPMC) and gelatin-based films.

Material and Methods

Commercial HPMC (Methocel E19®, Dow Chemical Company, USA) and bovine gelatin type B (Gel), bloom 250 (Gelnex®, Brazil) were used as hydrophilic and hydrophobic biopolymer matrices, respectively. Glycerol (99%, Neon, Brazil), titanium dioxide (TiO_2, anatase, particle size 10 nm were used as the plasticizer and the photocatalyst, respectively, whereas distilled water and acetic acid (99%, Navelab, Brazil) were used as solvents.

The composite films (HPMC-TiO_2 and Gel-TiO_2) containing 0, 0.5, 1.0, and 2.0 wt% TiO_2 and 25 wt% of glycerol in relation to biopolymers (4 wt% in dispersion) were fabricated by casting, and characterized as to their relative opacity at λ = 400 - 650 nm, activation and activity of the photocatalyst using water, oleic acid (OA) [$20 \mu g.cm^{-2}{}_{film}$] and ethylene [5ppmv] as model substrates under UV-A light [λ_{peak} = 365 nm], with irradiances (I) of 2.96 mW cm^{-2} at 25°C and RH = 58% for the water and OA and 9.80 mW cm^{-2} at 30°C and RH and 85% for the ethylene. The OA degradation was evaluated by gravimetry and contact angle (θ), whereas the ethylene degradation was assessed by gas chromatography.

Results and Discussion

A higher increase in the relative opacity as the TiO_2 content for the HPMC-TiO_2 films is observed in **Figure 1** and **Table 1**, attributed to the lower TiO_2 dispersity in the hydrophilic matrix. This result confirms the hydrophobic character of the photocatalyst in the dark. In both matrices, 2wt% TiO_2 was the photocatalyst concentration with the highest relative opacity values associated with the matrix saturation and TiO_2 agglomeration, causing the light scattering and increase in the whiteness index.

The HPMC- and Gelatin-based films containing 1wt% TiO_2 exhibited photocatalyst activation when exposed to the UV-A light [I = 2.96 $mW.cm^{-2}$] at 25°C, significantly decreasing the contact angle due to the rising of film hydrophilicity (result not shown). Thus, HPMC-1%TiO_2 and Gel-1%TiO_2 were used as photocatalyst biocomposites to degrade OA (**Figure 2**) and ethylene (**Figure 3**).

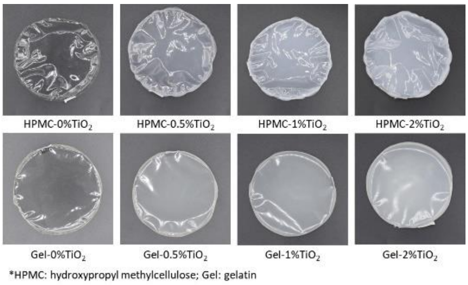

Figure 1. Image of HPMC-TiO_2 and Gel-TiO_2 films.

All films exhibited weight loss, indicating that biopolymer matrices have also been photodegraded, especially the HPMC matrix, because of its simpler structure than the gelatin protein structure. However, Gel-1%TiO_2 films presented a more accentuated degradation, characterized by an apparent reaction rate constant [0.186 ± 0.021 min^{-1}] higher than HPMC-1%TiO_2 films [0.034 ± 0.003 min^{-1}], when Langmuir-Hinshelwood model was fitted to the kinetic data.

Both films also catalyzed the ethylene photodegradation, removing almost 40% of the ethylene loaded into the batch reactor.

The most accelerated ethylene degradation by the Gel-1%TiO_2 films corroborates the better dispersion of the TiO_2 in the gelatin matrix, enhancing its efficiency. However, the plateau exhibited in both Kinect curves indicates possible carbonaceous fouling on the photocatalyst due to the biopolymer degradation.

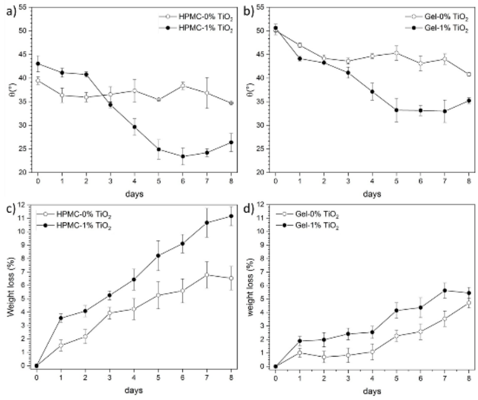

Figure 2. Contact angle evolution (a,b) and weight loss (c,d) of HPMC-TiO_2 and Gel-TiO_2 films for the oleic acid photodegradation.

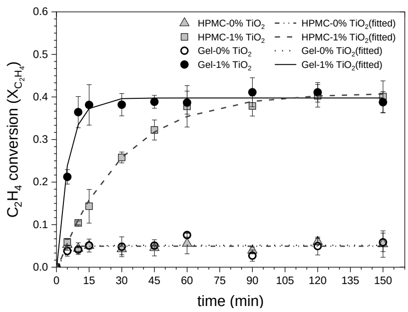

Figure 3. Photodegradation of ethylene by HPMC-TiO_2 and Gel-TiO_2 films.

Table 1. Whiteness index (WI) and relative opacity (RO) of HPMC-TiO_2 and Gel-TiO_2 films.

TiO_2 (wt%)	HPMC-TiO_2		gelatin-TiO_2	
	WI (%)	RO (AU.nm)	WI (%)	RO (AU.nm)
0	42.44 ± 2.28^a	0^d	50.25± 0.91^c	0^d
0.5	63.96 ± 2.65^b	61.36 ± 1.34^c	62.93± 3.05^b	45.88± 2.23^c
1	67.37 ± 2.25^b	83.82± 1.86^b	66.78± 2.85^{ab}	81.44± 1.43^b
2	70.10 ± 1.45^b	240.26 ± 2.06^a	73.75± 0.46^a	164.44± 2.82^a

Means within the same column and for the same group having different superscripts are significantly different at the level of $\alpha = 0.05$ ($p \leq 0.05$).

Conclusions

Both Gel-1%TiO_2 and HPMC-1%TiO_2 films exhibited photocatalytic activity to degrade liquid (oleic acid) and gas (ethylene) substrates, confirming their potential use as active food packages. The fastest ethylene degradation by the Gel-1%TiO_2 films can contribute to the most efficient ethylene remotion at the beginning of the ripening stage of climacteric fruits.

Acknowledgments

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