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High-barrier and antibacterial films based on PET/SiO_x for food packaging applications

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Abstract

High-barrier and antibacterial materials have potential applications in the field of preservative packaging for fresh meat products. In this paper, UV irradiation and silane coupling agent (KH550) were used to modify the surface of SiO_x coating on polyester (PET)/SiO_x film to prepare the PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano-ZnO composite film, respectively. The contact angle test revealed that KH550 improved the surface hydrophilicity of SiO_x significantly compared to UV irradiation, and thus PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano ZnO composite films were successfully prepared and their physical and chemical properties were characterized. SEM images showed that the surface of the composite film was a smooth and layered structure. The mechanical performance testing of the films has revealed that mechanical performance of the PET was improved by SiO_x deposition while the coating (KH550, chitosan, and chitosan-nano ZnO) does not affect the mechanical performance of PET/SiOx. The oxygen resistance of PET/SiO_x films treated with KH550 was enhanced with the addition of chitosan and chitosan-nano ZnO coating, but the moisture resistance was slightly decreased. Furthermore, PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano ZnO composite films showed excellent growth inhibition against *Staphylococcus aureus* and *Escherichia coli*. The PET/SiO_x/chitosan-nano-ZnO films had exhibited the strongest inhibition of bacteria.

Keywords: SiO_x layer; chitosan; nano-ZnO; multifunctional films; food packaging.

Practical Application: Multifunctional film with high barrier and antibacterial activity based on PET/SiOx combining food-safe materials involving chitosan or nano-ZnO for application of meat products packaging.

1 Introduction

The current rapid development of e-commerce has resulted in a need for improvements in the requirements of the materials used to package fresh food (Cunha et al., 2020a, b). Especially for fresh meat products, not only should the packaging films have a better gas barrier (prevent oxidation and deterioration) and moisture barrier (ensure that moisture does not dissipate), it also should possess antibacterial properties (inhibit the growth of microorganisms on the surface of meat products) to ensure food safety and extend the shelf life of meat products.

SiO_x-based flexible packaging film has become a new trend among high barrier materials because of its environmental friendliness, excellent barrier property while not compromising the transparency of the base film. It is generally formed by physical vapor deposition or chemical vapor deposition of SiO_x on the surface of plastic films made using polyester (PET), polypropylene (PP) as substrate to obtain a high-barrier flexible composite film (PET/SiOx or PP/SiO_x), also known as soft glass (Baragetti et al., 2009; Qi et al., 2014). However, this type of film does not have antibacterial properties, which limits its application on preservative packaging for meat products.

Chitosan (CS) has been widely noticed as a natural bacterial inhibitor because of its strong broad-spectrum antibacterial properties and is readily available, safe, edible, and biodegradable (Elsabee & Abdou, 2013). By coupling CS coatings with polymeric substrates such as low-density polyethylene (LDPE) films or polyethylene terephthalate (PET) films, the substrates can be endowed with antibacterial properties (Vasile et al., 2013; Zemljič et al., 2013). Moreover, with the emergence of nanomaterials, many researchers have attempted to modify chitosan using nano-inorganic materials (e.g., SiO2, ZnO, TiO2, etc.) (Guo et al., 2020; Li & Li, 2010). In particular, ZnO nanoparticles have attracted much attention due to their low cost and excellent thermal stability, UV shielding, and inhibition of bacteria growth (Li et al., 2015). Furthermore, the nano ZnO had also been recognized as a generally safe substance by the FDA and GRAS. It has been reported that blending a certain amount of nano ZnO with chitosan can improve the mechanical properties, barrier properties and antibacterial properties of chitosan (Zhong et al., 2020).

In this paper, chitosan and chitosan-nano ZnO coating solution were combined with the PET/SiO_x based film to produce high barrier and antibacterial composite films. To improve the adhesion between SiO_x and the bacteriostatic coating, the surface treatment of PET/SiO_x was modified with UV irradiation or γ-aminopropyltriethoxysilane (KH550). The PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano ZnO composite films were then tested and characterized. The effects of surface treatment, chitosan, and chitosan-nano ZnO coating solutions on the mechanical properties, barrier properties, and bacterial growth inhibition of PET/SiO_x films were assessed.

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2 Materials and methods

2.1 Preparation of PET/ SiO_x/chitosan-nano ZnO composite film

A chitosan (Sinopharm Chemical Reagents Ltd.) solution was obtained by completely dissolving a certain amount of chitosan in 0.1% acetic acid concentration solution. Subsequently, an appropriate amount of nano ZnO with approximately 20 nm in diameter (Nanjing Hi-tech Nano Material Co., Ltd.) was added to the chitosan solution with thorough stirring and ultrasonic vibrations for 30 min. The pH was then adjusted to 5 with NaOH (0.1 mol /L) to obtain a chitosan nano ZnO coating solution with 1% nano ZnO concentration (compared to chitosan).

The casting method was used to apply a certain amount of either the chitosan solution or the chitosan-nano-ZnO solution to the surface of the PET/SiO_x film (KH550 modified) and dried at room temperature. PET/SiO_x film and PET base film are provided by Beijing Institute of Graphic Communication. The sample films were labeled as follows: PET film (PET), PET/SiOx film (P-S), PET/SiO_x film (P-SK), PET/SiO_x/chitosan film (P-SK-C), PET/SiOx/KH550/chitosan-nano ZnO film (P-SK-CZ). The thickness of the composite film was about 13.2 μm.

2.2 Surface modification of PET/SiOx film

The surface of PET/SiO_x film was modified by UV irradiation or 20% concentration of KH550 (Nanjing Chuang Shi Chemical Co.) to increase the compatibility between SiO_x and chitosan-ZnO, respectively. The KH550 was applied by the homogenizer, and the coating time was 5 s, the homogenization time was 20 s, and the homogenization speed was 1000 r/min.

2.3 Characterization of PET/SiO_x/chitosan-nano ZnO composite film

The contact angle test was performed on the PET/SiO_x film surface before and after treatment using a contact angle measurement instrument (FANGRUI TCY-3, Shanghai, China). The average contact angle of six different measurements was taken as the final result.

The surface and cross-sectional morphology were observed through scanning electron microscope (S-4800, Hitachi Inc., Japan); the mechanical properties of the film were measured by electronic universal testing machine (SANS JTM4104, Shenzhen, China) referring to GB/T16421-996, and the final test result is the average of 6 samples; the water vapor permeability rate (*WVT*) of the film was determined by water vapor permeability tester (W-E-11A, Labthink Inc., China), and the oxygen permeability rate (*OT*) was determined by oxygen permeability tester (OX2/230, Labthink Inc., China). The final result is the average of the 3 samples taken.

The antibacterial characterization of the films was tested using the absorptiometry method (Li et al., 2018, 2020). The films were immersed in a bacterial solution containing *Staphylococcus aureus* or *Escherichia coli* in the logarithmic phase and were incubated in a 37 °C water bath with vibration (rotational speed 50 r/min). The absorbance of the bacterial solution at 600 nm (OD 600) was measured hourly using the UV spectrophotometry (T6, Beijing P&C Instrument Co., China). PE films were used as the control check (CK).

3 Results and discussion

3.1 Surface modification of SiO_x coatings

As shown in Figure 1, the contact angle of the film surface decreased slightly (from 84° to 71°) with the increase of UV irradiation time, and the contact angle of the film surface decreased from 84° to 44° after KH550 coating. Therefore, compared to UV irradiation, the KH550 treatment improves the hydrophilicity of the SiO_x coating surface better and thus helps to enhance its adhesion to the chitosan solution. Follow-up experiments showed that PET/SiO_x and PET/SiO_x/KH550/chitosan-nano ZnO films could be successfully prepared by performing surface modification on PET/SiO_x with KH550.

3.2 Morphology of the composite film

Figure 2 shows the microscopic morphology of the composite film cross-section. It is found that from Figure 1 the morphology of PET/SiO_x and PET/SiO_x/chitosan films cross-section surfaces were smooth with layered structure.

3.3 Mechanical performance of the composite film

Table 1 shows the results of the mechanical performance tests of composite films. As shown in Table 1, the surface deposition of SiO_x led to an increase in the tensile strength and elongation at break of PET. Whereas, the coating of PET/SiO_x with KH550 or chitosan and chitosan-nano ZnO coating solution had no significant effect on the tensile strength and elongation at break of PET/SiO_x film.

3.4 Barrier properties of composite films

Table 2 shows the test results of *WVT* and *OT* of composite films. It is apparent in Table 2 that the surface deposition of SiO_x reduces the *WVT* of the PET film. This indicated that the SiO_x coating can effectively improve the water-resistance of the PET film. When the film of PET/SiO_x was modified with

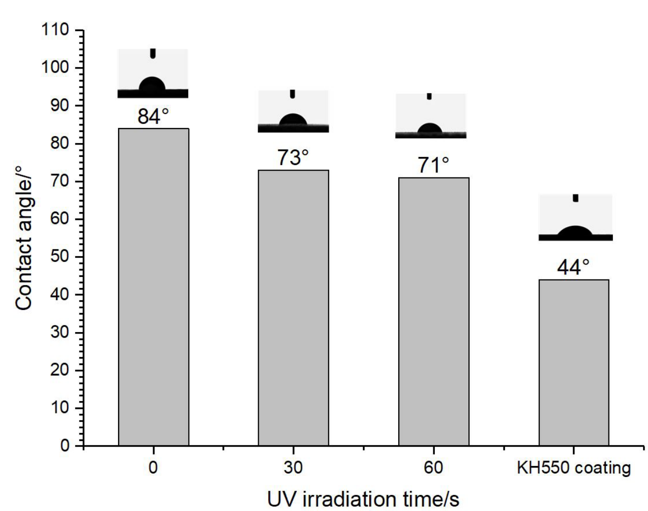
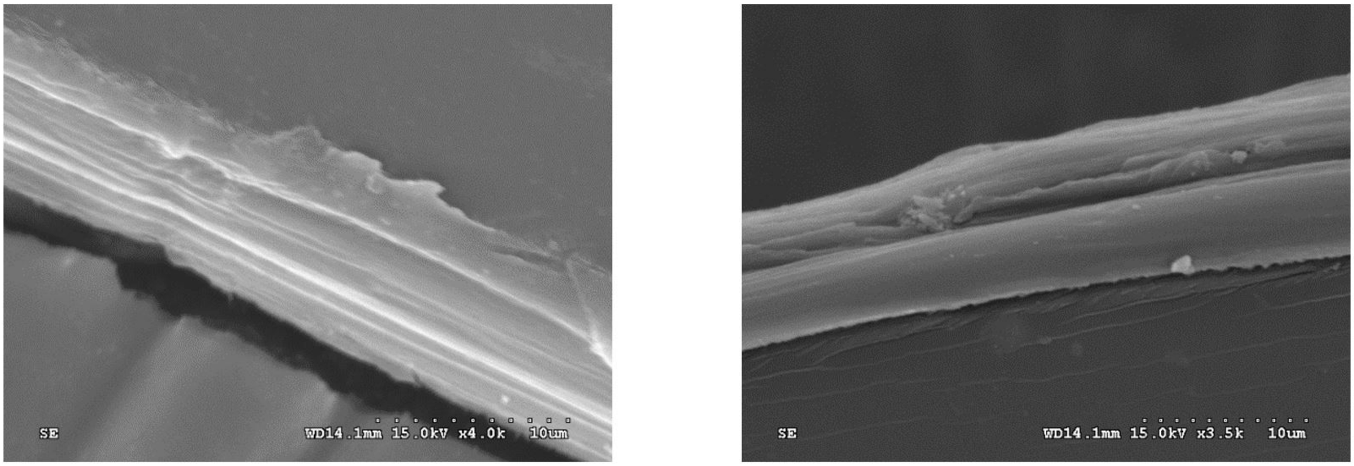


Figure 1. Water contact angle of PET/SiO_x before and after modification.



(a) (b)

Figure 2. Cross-section SEM of PET/SiOx (a) and PET/SiOx/chitosan (b) composite films.

Table 1. Mechanical performance of composite films.

	PET	P-S	P-SK	P-SK-C	P-SK-CZ
Tensile strength (Mpa)	106.17	116.33	115.47	114.16	117.90
Breaking elongation rate (%)	41.93	58.21	54.57	57.06	55.32

Table 2. *WVT* and *OT* of composite films.

	PET	P-S	P-SK	P-SK-C	P-SK-CZ
WVT (g/m^2.d)	37.50	21.32	7.66	11.36	11.66
OT (mL/m^2.d)	58.25	5.56	5.23	5.09	5.05

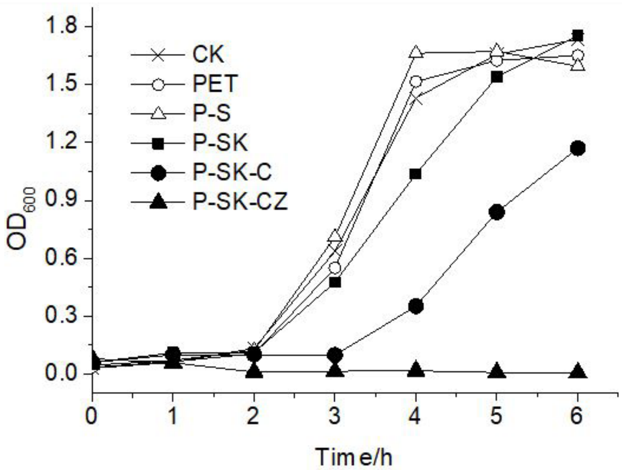
KH550, the *WVT* of the composite film was further reduced, which may be due to the silane coupling agent layer acting as a repair agent to cover the pinholes and defects on the SiO_x surface, thereby increased the water-resistance of the PET/SiO_x film (Moosheimer & Bichler, 1999; Singh et al., 2007). When the chitosan coating was applied further, the *WVT* of the composite film started to increase again, and this was due to the hydrophilicity of chitosan (Stoleru et al., 2016). Since ZnO is inorganic and easily absorbs water, the *WVT* of PET/SiO_x/chitosan-nano ZnO composite film slightly increased and the moisture barrier decreased as compared to PET/SiO_x/chitosan.

Furthermore, according to Table 2, the *OT* of PET was reduced from 58.25 mL/m^2.d to 5.56 mL/m^2.d by SiO_x coating. Therefore, SiO_x could effectively improve the oxygen barrier property of PET, and compared to the moisture barrier, the SiOx deposition layer improves the oxygen barrier of PET more significantly. Also, the oxygen barrier of PET/SiO_x was enhanced with KH550 modification. When the chitosan coating was applied further, the *OT* of the composite film continued to decrease, which indicated that the chitosan coating could further improve the oxygen barrier of PET/SiO_x, and the *OT* of the PET/SiO_x/chitosan film was 5.09 mL/m^2.d, which meets the standards for high barrier materials (Hering et al., 2020). Compared to PET, PET/SiO_x/chitosan films improved oxygen barrier by approximately 11 times, while PET/SiO_x/chitosan-nano ZnO films had about the same *OT* as PET/SiO_x/chitosan films.

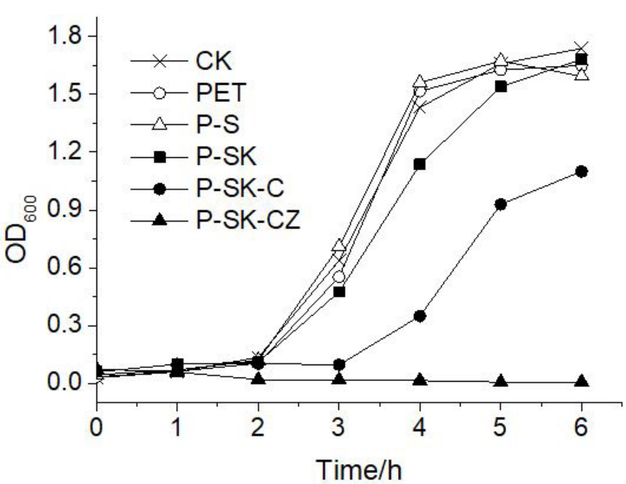
3.5 Antibacterial properties of composite films

The change of the absorptiometry value can reflect the multiplication of bacteria typically based on the wavelength of 600 nm absorbance (OD_{600}). An increasing trend of OD_{600} indicates that the bacteria are multiplying and growing well, while a decreasing wavelength or a constant wavelength shows that the bacteria are not multiplying well or dying and stop growing (Li et al., 2018).

The OD_{600} test results of the composite film against *Staphylococcus aureus* and *Escherichia coli* are as illustrated in Figure 3. Figure 3 shows that the PET, PET/SiO_2, and the control check curves almost overlap. This indicates that the PET and PET/SiO_2 films had no antibacterial property. The absorbance curves of the KH550-treated PET/SiO_2 films were slightly lower than the control check. This indicates that the KH550 had an antibacterial property. When chitosan and chitosan-nano ZnO were coated on PET/SiO_2 film, the OD value of the composite film decreased significantly where the lowest OD curve of PET/SiOx/chitosan-nano



(a)



(b)

Figure 3. Antibacterial property of composite films, (a) *Staphylococcus aureus*; (b) *Escherichia coli*. OD: Optical density, PET: Polyethylene terephthalate, CK: Control sample.

ZnO composite film reached 100% growth inhibition against *Escherichia coli* and *Staphylococcus aureus* within 2h. The results above show that both PET/SiOx/chitosan and PET/SiO_2/chitosan-nano ZnO films had great antibacterial property, and the addition of nano ZnO could significantly enhance the antibacterial effect of chitosan. This suggests a synergistic gain in chitosan inhibition by nano-ZnO. Consequently, PET/SiO_2/chitosan-nano ZnO composite films had the best antibacterial property.

4 Conclusion

The surface hydrophilicity of PET/SiO_x can be improved by coating with KH550, and its adhesion to chitosan coating solution can be improved to successfully prepare PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano ZnO composite films. Compared with the PET base film, the mechanical properties of the composite films were slightly improved. The SiO_x coating could effectively improve the barrier properties of the PET film; the KH550 coating could further improve the water and oxygen barrier properties of the PET/SiO_x films; whereas the chitosan and chitosan-nano ZnO coating, though reduced its water barrier property, could further improve the oxygen barrier property of the composite films. PET/SiO_x/chitosan and PET/SiO_x/chitosan-nano ZnO films have a good antibacterial effect on *Staphylococcus aureus* and *Escherichia coli*, and the addition of nano ZnO further enhances the antibacterial property of PET/SiO_x/chitosan. Besides, KH550 has antibacterial property to a certain extent, the mechanism of which needs to be further investigated.

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