Research Article

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Sustainable nanocomposite films based on SiO₂ and biodegradable poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) for food packaging

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Abstract: Sustainable nanocomposites with transparent, biodegradable, and enhanced mechanical and barrier properties were prepared by the incorporation of SiO₂ into poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) films and subsequent solvent casting. The crystallinity of composites could be increased by 67% with appropriate contents of SiO₂, which proved that SiO₂ were effective nucleating agents for PHBH. And it was worth mentioning that the contributions of SiO₂ to the crystallization and thermal stability of composites are proved effectively by Avrami relationship and Horowitz and Metzger method. More importantly, compared with PHBH, it had not only an enhancement about 40% and 60% on the tensile strength and elastic modulus, respectively, but also half the reduction of the moisture and oxygen permeability which were much higher than the values of conventional plastics. The above, in conjunction with the low migration rate measured in food substitutes, illustrated unambiguously that the nanocomposites might be suitable for potential application in food packaging.

Keywords: PHBH, SiO₂, crystallization behavior, mechanical strength, barrier property

1 Introduction

The usages of plastic packaging materials in the fields of medicine, chemicals for daily use, and food are still far

more than other counterparts because of lightweight, low cost, strong plasticity, and excellent comprehensive performance at present (1,2). However, the development of traditional plastics is confronted with severe problems as the results of shortage of resources, pollution of environment, and transformation of economy (3,4). Many governments and enterprises have already called for restriction or new alternatives of nondegradable wrapping. And for the food industry, most food packaging materials also need to fulfill the requirements of nontoxicity, high barrier, and certain mechanical strength due to the special product characteristics, which promotes further development of this kind of packaging materials as well.

Biosynthetic polyhydroxyalkanoates (PHAs) are carbon source energy storage materials accumulated in cells or *in vitro* by bacteria in the absence of nitrogen, phosphorus and other nutrients, and excessive carbon source (5,6). The present main bacteria of producing PHAs are *Alcaligenes*, *R. eutropha*, *Acinetobacter* spp., *Alcaligenes latus*, and *Pseudomonas acidophila* (7,8). It is true that the excellent biodegradability of PHAs is attributed to its bacterial origin. PHAs are one of the key bioplastics that cannot be neglected in kinds of substitutes for packaging materials because of nontoxic, enhanced performance close to common plastics and biodegradable (9). And poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), as a third of generation of PHAs family, has been widely used in biomedicine, adhesive, and packaging materials due to reproducibility, biodegradability, and non-pollution in recent years (10). The application, however, is limited by poor thermal stability and weak crystallization level that cause low strength and barrier which are critical parameters in food packaging (11,12). Therefore, improving the above properties and enhancing the comprehensive performances of PHBH are the significant parts to further facilitate the development in packaging.

Adding nanoparticles into matrix, a simple and efficient strategy to improve the properties of plastics, has been studied extensively because of the high performance with strong sustainability and multifunction at pretty low nano-fillers (<2 wt%) (13–15). Inorganic SiO₂

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has been widely used in the modification of polymeric substances in recent years depending upon nontoxic, low price, excellent barrier, and good mechanical properties (16,17). It has been found that SiO₂ can not only play a good role in crystallization and thermal stability as a nucleating agent, but also increase the strength and barrier of polymers, which means the enhancement of comprehensive performance in composites (18,19).

In contrast, the sustainable SiO₂/PHBH nanocomposites are synthesized by the sample and effective solvent casting method using PHBH as matrix and SiO₂ as filler. The effectiveness of SiO₂ on the morphology, thermal stability, crystallization, mechanics, barrier, and migration of composites is investigated by corresponding characterizations and calculations in detail, which try to explain the relationship between structure and properties and learn more about this potential food packaging materials.

2 Experimental details

2.1 Materials

PHBH (11 mol% hydroxyhexanoate, $M_n = 6,00,000$ g/mol), given by Kaneka (Japan) generously, was received with purification. SiO₂ (99.5% metals basis) was purchased from Aladdin (China) with particle size about 15 nm. *N,N*-Dimethylformamide (DMF) was purchased from Fengchuan Chemical Reagents S & T, Ltd (China).

2.2 Preparation of SiO₂/PHBH biocomposites

The colorless, transparent, and homogeneous SiO₂/DMF solution in different proportions was obtained by stirring (600 rpm, 1 h) and ultrasonic treatments (500 w, 1 h). Then the purified PHBH was dissolved in the dispersion after stirring (60°C, 600 rpm, 1 h) and ultrasonic treatments (500 w, 1 h) once again. And finally, the sticky miscible solution was cast in a glass mould and dried under atmosphere (70°C, 4 h) and vacuum pressure (60°C, 12 h) to obtain the SiO₂/PHBH nanocomposites with thickness of about 0.05–0.09 mm. The preparation of pure PHBH membrane as a control was same as procedures above. Samples with 0.5, 1, 1.5, 2, and 2.5 wt% content of SiO₂ were denoted as 0.5-SiO₂/P, 1-SiO₂/P,

1.5-SiO₂/P, 2-SiO₂/P, and 2.5-SiO₂/P, respectively. The schematic diagram in preparation is shown in Figure 1.

2.3 Characterization

The cross-section of PHBH nanocomposites was observed by SEM (Joel 2100F, FEI) at 5 kV after fractured cryogenically in liquid nitrogen. The functional groups were analyzed through FTIR (Nicolet i55, Thermo Fisher Scientific) and the parameters of scanning wavelength, frequency, and resolution were 600–4,000 cm⁻¹, 16, and 4 cm⁻¹, respectively. The thermal stability was recorded on a TA, TGA Q 50 thermogravimetric analyzer under a flow of nitrogen at 10°C/min from room temperature to 600°C. The performance of crystallization was investigated by XRD (D/max-2500), DSC (TA, DSC Q20), and POM (Leica DM 400). The mechanical strength was performed on the specimens of rectangle shape (150 × 10 × 0.05 mm), using universal testing machine (Instron 3369 series) with a strain rate of 12.5 mm/min at room temperature in the light of ASTM D882-2010.

According to ASTM D 1434, the oxygen permeability was measured by permeability tester (GDP-C, Brugger Feinmechanik GmbH). The water vapor permeability (WVP) was gained by moisture permeability tester (W3/031, Jinan) on the basis of ASTM D 1653 at 38°C and 90% RH, respectively. And the oxygen permeability and the WVP were calculated by Eq. 1 and 2, respectively:

$$OP = \frac{OTR \cdot t}{\Delta P} \quad (1)$$

$$WVP = \frac{WVTR \cdot t}{\Delta P} \quad (2)$$

Figure 1: Schematic diagram of SiO₂/PHBH nanocomposites.

where OTR and WVTR – oxygen transmission rate and water vapor transmission rate, and both were obtained directly from equipment; t – thickness of specimen; ΔP – pressure difference pressure on both sides of film.

The surface contact angle was acquired by the contact angle tester (VCA optima, AST). The migration level was tested by immersing the 15 cm² samples into water and different proportions of alcohol (10%, 50%, and 95%, v/v) which were used as substitutes for food at 40°C for 10 days according to the Commission Regulation EU 10/2011. And all samples were dried before testing.

3 Results and discussion

3.1 Morphology and structure of SiO₂/PHBH nanocomposites

There are obvious concave–convex islands on the SEM cross-section of pure PHBH in Figure 2a, with tiny holes and rough structure (20). The white SiO₂ particles are dispersed uniformly in PHBH matrix, and the sea-island structure disappears gradually on the increasing section of SiO₂. But it is shown that the aggregates of SiO₂ (some reunites are even larger than 100 nm) and crazes on the fracture surface after brittle failure are found in Figure 2f. This can be explained by the interaction between SiO₂ and PHBH. The intermolecular forces between two phases promote the dispersion of particle in matrix when the content of SiO₂ is moderate (<2 wt%). However, the intramolecular forces aggravates the aggregates due to the high surface polarity of SiO₂ with the further increase of SiO₂ (21–23).

In the FTIR spectra of Figure 2g, SiO₂ shows the absorption peaks at 3,451 cm^{−1} (surface absorbed water) and 1,631 cm^{−1} (surface OH groups) and a broad asymmetric stretching vibration peak of Si–O–Si near 1,082 cm^{−1} (24). The strength of amorphous carbonyl (stretching vibration peak at 1,717 cm^{−1}) increases gradually after adding SiO₂ and reaches the maximum at 2 wt% because of intermolecular hydrogen bonds conducive to the formation of C=O. And the poor compatibility caused by agglomeration may lead to the weakening of peak strength when the content of SiO₂ is 2.5 wt%. With the increase of SiO₂, the peak value at 2,921 cm^{−1} (symmetric vibration peak of CH₃) increases gradually, while decreases at 2,985 cm^{−1} (asymmetric vibration peak of CH₃). This is most likely that the destruction of hydrogen bonds between C=O and CH₃ promotes the balance of bonding energy in

CH₃ and the formation of symmetric peak more easily (25). Based on the above discussion, we have inferred the possible connection between SiO₂ and PHBH as shown in Figure 2h.

Flexibility and transparency, the key parameters in the processing, are related to the protection and visual effect of products. The good bending of PHBH membrane can be seen from Figure 2i, which means the better flexible operations. The clarity of pattern under 5 layers of composite with high light transmittance is hardly affected by adding SiO₂ into PHBH.

3.2 Thermal stability of SiO₂/PHBH nanocomposites

It can be seen from Figure 3 that the thermolysis of PHBH nanocomposites belongs to one-stage thermal decomposition. The pyrolysis of pure PHBH occurs mainly in the range of 236–325°C and reaches the mass loss rate of more than 90%, while the temperature range and loss rate for composites are between 218°C and 400°C and at about 80%, respectively. Apparently, the thermal stability of packaging film can be obviously improved because of the appearance of SiO₂, and it shows a trend of first rising and then dealing with the increase of amount.

T_{on} (temperature at 1 wt% mass loss) of pure PHBH membrane is 236°C from Figure 3c, and the decomposition attributes to the brokenness of PHBH chain, resulting in shorter segments and butenic acid (26). Compared with pure PHBH, T_{on} and T_{max} (temperature at maximum loss rate) of composites both shift to low temperature. It is probably because the interaction between the bound water on the surface of SiO₂ and ester groups in PHBH reduces the degradation temperature, which indicates that SiO₂ is grafted onto PHBH successfully. And the trend of T_{end} (temperature at constant mass) towards high temperature and the extension of range of thermal degradation also indicate the improvement of thermal stability. E_a (degradation activation energy), obtained by Eq. T1, also follows the variation (go up first then go down), which is consistent with the change trend of T_{on} and T_{end} and can hint the promotion of thermal stability for nanocomposites as well as the presence of SiO₂. And the variation of linear slope under high fitting degree proves that even more in Figure 3d. The presence of SiO₂ limits the movement of PHBH segments and delays the decomposition of composites. Meanwhile, SiO₂, as a thermal barrier, can inhibit efficiently heat transfer to PHBH (27).

Figure 2: Cross-section of: (a) PHBH, (b) 0.5-SiO₂/P, (c) 1-SiO₂/P, (d) 1.5-SiO₂/P, (e) 2-SiO₂/P, and (f) 2.5-SiO₂/P in SEM. (g) FTIR spectra and bonding mechanism of SiO₂/PHBH composites. (i) Photographs of nanocomposites.

3.3 Crystallization of SiO₂/PHBH nanocomposites

The cold crystallization temperature T_{cc} of the composites decreases from 54°C to 49°C, indicating that the addition of SiO₂ promotes the regular arrangement of PHBH chain at lower temperature and accelerates the crystallization rate (28). But it has little effect on the glass transition temperature T_g . With the addition of SiO₂, the melting enthalpy ΔH_m and crystallinity X_c of composites increase first and then decrease, and both reach maximum at 2 wt%. The higher melting point of SiO₂ than that of PHBH can

promote PHBH to form stable nucleation on the surface of nucleating agent and favor the heterogeneous nucleation, resulting in crystallizing at lower temperature and enhancement of crystallization density. However, the excessive SiO₂ will obstruct the chain movement of PHBH, inhibit arrangement in order, and finally reduce the crystallinity. And the deviation of melting temperature to low temperature after adding SiO₂ shows that the thickness of primary crystals becomes thinner (29,30).

Isothermal crystallization kinetics includes judging crystallization rate and studying the nucleation mechanism which are often explained by Avrami relationship:

Figure 3: (a) TGA, (b) DTG, and (c) plots of T_{on} , T_{max} , T_{end} , and E_a , and (d) $\ln[\ln(W_0/W_T)]$ vs $T - T_s$ during pyrolysis of SiO_2 /PHBH nanocomposites. Note: T_{on} – temperature at 1 wt% mass loss; T_{max} – temperature at maximum loss rate; T_{end} – temperature at constant mass; E_a – degradation activation energy, calculated by Horowitz and Metzger method as shown in the following: $\ln \left[\ln \left(\frac{W_0}{W_T} \right) \right] = \frac{E_a(T - T_s)}{RT_s^2} (T_1)$ where: W_0 is the initial weight before tested; W_T is the actual weight at temperature T ; R is the gas constant; T_s is the temperature at 36.79% weight loss.

$$\log [-\ln(1 - X_t)] = n \log t + \log k$$

$$X_t = \frac{\int_0^t \left(\frac{dH}{dt} \right) dt}{\int_0^\infty \left(\frac{dH}{dt} \right) dt} \quad (3)$$

n can be obtained from the slope of line and elaborate the crystallization mechanism. The apparent shorter complete time of PHBH than nanocomposites in Figure 4c means the acceleration of crystallization rate. And in Figure 4d, the n value of PHBH and nanocomposites is 1.84 and 2.03–2.17, respectively, suggesting the 3D crystallization growth and heterogeneous nucleation of composites at the presence of SiO_2 .

Similar diffraction location can be found in all samples in Figure 4e, indicating that the crystal structure has unchanged. The calculated value of crystallinity and grain size are different from those of DSC and POM, but the trend with content of SiO_2 is consistent, which proves that SiO_2 is beneficial to the crystallization of PHBH once again.

It can be seen from Figure 4g that the cross extinction of spherulites in all samples is very obvious, accompanied by alternation of light and shade as well as periodic concave and convex fluctuations caused by the twisting of lamellae along the radius direction of spherulites. Horizontally, the size and number of spherulites increase gradually over time. Longitudinally, the number increases first and then decreases with the adding of SiO_2 . However, the size of spherulites is opposite, and both of them can reach maximum and minimum at 2 wt%, respectively, consistent with the results of XRD and DSC. A little SiO_2 provides more nucleation sites for crystallization and increases the number of crystals, while the hydrogen bond between SiO_2 and PHBH shortens the molecular chains and refines the spherulites (31,32). But the heterogeneous nucleation and formation of hydrogen bond will be inhibited by the agglomeration caused by excessive SiO_2 . From the statistic of size growth in Figure 4f, it can be found that the addition of SiO_2 can only affect the crystallinity and the size of crystal, but has little effect on the growth rate (33).

Figure 4: Crystallization behavior of SiO₂/PHBH nanocomposites: (a) DSC and (b) related parameters of DSC, plots of (c) X_t vs time and (d) $\log[-\ln(1 - X_t)]$ vs $\log t$, (e) XRD, (f) diameter variation of spherocrystal, and (g) photos of POM.

3.4 Mechanical of SiO₂/PHBH nanocomposites

The elongation at break of composites decreases with the increase of SiO₂ and reaches the minimum at 2 wt%, which is 29.8% lower than that of pure PHBH. The reduction in toughness is caused by the enhancement of rigidity and crystallinity after SiO₂ is introduced into PHBH (34).

Both the elastic modulus and tensile strength increase first and then decrease as SiO₂ increases. The maximum of elastic modulus and tensile strength is 935.29 and 19.41 MPa, which is 60.6% and 40.1% higher than that of pure PHBH, respectively. The larger specific area and more active points promote the formation of hydrogen bond, thus resulting in the better stress transfer from PHBH to SiO₂ and the improvement of mechanical properties. The narrowing of range in chain activity and increasing defects points caused by excessive SiO₂ make it difficult to absorb the external impact force, and finally reduce the strength (35). Moreover, the craze of 2.5-SiO₂/P in SEM cross-section also indicates the generation of stress concentration. The tensile strength and elastic modulus of PHBH modified by SiO₂ have been improved greatly (Figure 5), so it can be used in packaging materials with high mechanical strength for electrical appliances, automotive parts, food, and pharmaceutical products (36).

3.5 Barrier properties and migration level of SiO₂/PHBH nanocomposites

It is obvious from Figure 6a that the oxygen permeability of composites reduces after adding SiO₂. The oxygen permeability has the biggest decline at 0.5 wt%, which decreases from $12.36 \times 10^3 \text{ mL } \mu\text{m}/\text{m}^2 \text{ day atm}$ of pure PHBH packaging film to $6.58 \times 10^3 \text{ mL } \mu\text{m}/\text{m}^2 \text{ day atm}$ and reaches minimum at 2.5 wt%. It is most likely that the enhancement of oxygen resistance is attributed to the heterogeneous nucleation of SiO₂, which improves the crystallization and regularity of polymer (37). Moreover, SiO₂ can fill the porous on the surface of PHBH effectively and improve the compactness of film. But the voids of polymer have been basically filled by SiO₂, so the later changes are not obvious as before.

The WVP decreases in general with the increase of SiO₂, which decreases from $3 \times 10^{-8} \text{ g/m day Pa}$ at PHBH to $1.1 \times 10^{-8} \text{ g/m day Pa}$ at 2 wt%. Like the principle of oxygen barrier, the effective filling and increased

Figure 5: (a) Stress–strain curves, (b) Young's modulus and tensile strength of SiO₂/PHBH nanocomposites.

crystallinity caused by SiO₂ promote the water barrier of polymer (38). And the possible schematic diagram of permeability inferred from the test results is shown in Figure 6b. However, the moisture permeability increases further at 2.5 wt% because of the superfluous OH groups on the surface of SiO₂. It can be used as a bridge to transport water vapor from one side of composites to the other side, thus the water permeability will increase slightly. The same trend is found on the surface contact angle of composites at Figure 6d. The research above shows that the oxygen and moisture resistance of PHBH nanocomposites have been improved greatly, which will be greatly beneficial to prolong the storage time of food and expand the packaging application of high barrier products.

It is essential to compare the values with representative results from currently used food packaging applications (39). And the SiO₂/PHBH film in the paper appears to have this competitive edge as shown by the low permeability compared with others in Figure 6e. This comparison proves again that our SiO₂/PHBH films are indeed potential packaging materials.

The migration properties of the nanocomposites in different food simulants are shown in Figure 6f and Table 1. The overall migration levels of PHBH in water, 10%, 50%, and 95% ethanol were 0.33, 0.67, 1.83, and 2.5 mg/dm², respectively. And after adding SiO₂, the overall migration levels of nanocomposites increased basically

Figure 6: (a) The oxygen and moisture permeability of SiO₂/PHBH nanocomposites. (b) Diagram of oxygen and water molecules passing through membranes. Photos (c) and statistical chart (d) of contact angle on SiO₂/PHBH nanocomposites. (e) Comparison of the permeability in this paper with representative results from the literature. (f) Overall migration properties of SiO₂/PHBH nanocomposites.

with the increase of content, but the total migration in different food simulants was below the standard (10 mg/dm² for overall migration level) except 95% ethanol (more than 1.5 wt% SiO₂). Meanwhile, the higher the alcohol content in the food simulant, the higher the overall migration. Similarly, as for the single migration

of SiO₂, the migration also increased with the increase of the addition, but the migration levels of all nanocomposites in different food simulants were less than the standard (60 mg/kg for specific migration limit) (40). The results indicated that the prepared nanocomposites could be used as food packaging materials.

Table 1: The overall migration levels and specific migration limits of SiO₂/PHBH nanocomposites

Food simulants		Water	10% ethanol	50% ethanol	95% ethanol
0.5-SiO ₂ /P	Overall migration (mg/dm ²)	0.83	1.50	2.33	5.17
	SiO ₂ migration (mg/kg)	0.235	0.26	0.465	1.18
1-SiO ₂ /P	Overall migration (mg/dm ²)	1	1.33	2.00	7.00
	SiO ₂ migration (mg/kg)	0.46	0.61	1.36	4.61
1.5-SiO ₂ /P	Overall migration (mg/dm ²)	1	1.17	2.17	7.33
	SiO ₂ migration (mg/kg)	0.765	1.035	2.205	10.725
2-SiO ₂ /P	Overall migration (mg/dm ²)	1.5	2.00	2.67	10.67
	SiO ₂ migration (mg/kg)	1.48	1.62	3.04	16.48
2.5-SiO ₂ /P	Overall migration (mg/dm ²)	1.33	2.33	3.83	11.17
	SiO ₂ migration (mg/kg)	1.975	2.35	4.3	35

4 Conclusions

In conclusion, the sustainable and homogeneous SiO₂/PHBH nanocomposites were synthesized by solvent casting method. The final evaluating results indicated that the addition of SiO₂ could not only accelerate the crystallization and increase thermal stability of composites due to the uniform dispersion and heterogeneous nucleation, but also improve greatly the macro-properties of nanocomposites in tensile strength, elastic modulus, and barrier (oxygen and water molecules) compared with pure PHBH. This, in conjunction with low migration measured in food simulant, will provide sound evidence that SiO₂/PHBH nanocomposites may be used as the attractive potential materials in related food packaging fields.

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