

Investigation into the performance and mechanism of SiO₂ nanoparticles and starch composite films

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Nanomaterials are often introduced to improve the properties of polymers. In this article, the effects of SiO₂ nanoparticles with larger specific areas and special microstructural characters on the properties of starch films were investigated. Firstly, the ultrasonic mixing was used to disperse the SiO₂ nanoparticles under different dispersion times, and then the dispersed SiO₂ nanoparticles with various ratios were added into starch size. The effects of the dispersion time and the SiO₂ content on the mechanical properties of the SiO₂/starch composite size were analysed. It was found that the dispersion time and the SiO₂ content had significant effects on the tensile and abrasion behaviour of the nanocomposite films. The mechanism of the enhanced mechanical properties of the composite films was examined by analysing the size of the dispersed SiO₂ nanoparticles in the dispersion, the surface characters of the films and the structures of the fractured surfaces. And the morphology of the abraded surface was analysed by atomic force microscopy, scanning electron microscope and video zoom microscope.

Keywords: SiO₂ nanoparticles; starch; properties of nanocomposite film; mechanism

Introduction

Starch, as a glue size agent, has good film-forming properties and less desizing pollution. It can adhere to natural fibre easily. However, it also has higher molecular weight and its molecule chains consist of ringed glucose residues, which have high stiffness and high glass-transition temperature. Each glucose residue has three hydroxyl groups, with high density within molecule chain. There is a high interaction force among molecules and it is difficult for chain segment to move. These properties of starch have a negative influence on the behaviour of starch sizing and films (Zhou, 2004).

SiO₂ nanoparticles are white amorphous powder with unsaturated residual bond and different linkage hydroxyl groups on their surface. Their molecular appearance has three-dimensional chain structure, which is also named three-dimensional net construction or three-dimensional silica construction (Wang, Huang, & Liu, 2003). With such special structure, SiO₂ nanoparticles show special physical and chemical performance, such as excellent absorbency against light, force, electricity, magnetism, radiation and so on. SiO₂ nanoparticles were used as additive to modify the properties of starch, which could bring the size films some special properties as nanocomposite masteries commonly possess (Nguyen & Baird, 2006). And in order to find the way to improve the sizing properties of starch, some

special test methods were adopted to measure the mechanism of starch modification.

Experimental

Sample preparation

The preparation process of the samples is shown in Figure 1.

Step 1. SiO₂ nanoparticles, with an average diameter less than 35 nm, a surface-area larger than 400 m²/g and the purity higher than 99.5%, were used in this study. Sodium hexametaphosphate was used to treat the nanoparticles. It was first dissolved in deionised water and then the nanoparticles were added. The percentage of the SiO₂ nanoparticles used was set at 1%, 2%, 3%, 4%, 5% and 6% by weight, respectively. The dispersion of the nanoparticles was prepared by ultrasonic mixing.

Step 2. The starch with less than 14.0% water content was modified in this study (TB-225). And it was mixed with the SiO₂ nanoparticles/water dispersion. The concentration of the mixture was controlled at about 6%. The mixed sizing agent was heated up to 95°C with a stirring speed of 120 rpm. Then, the sizing agent was kept for an hour until it achieved its full gelatinisation.

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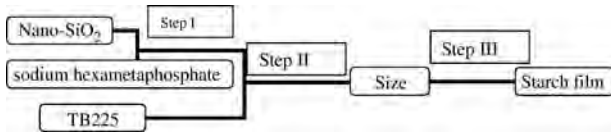


Figure 1. Preparation process of the starch/SiO₂ nanocomposite films.

Step 3. When the gelatinised size was cooled down to about 50°C, the size of 400 mL was taken and cast to a glass plate to form a film. The film was dried at a temperature of 20°C and a humidity of 65%. Finally, all the prepared films were conditioned at 20°C and 65% relative humidity for 24 hours before the mechanical tests.

Test methods

Strength test

The size films were cut into pieces with a length of 220 mm and width of 10 mm. Strength test was taken by ZWICK material tester. The clamp distance was 100 mm and the draw rate was 50 mm/min. There were 30 samples tested for each type of the film. And the average value of tensile strength of the films was calculated by:

$$\sigma = \frac{F}{H \times W} \quad (1)$$

σ is the tensile strength (N/m²), F means sample's average tensile force (N), H is sample's thickness (m) and W is the sample's width (m).

Abrasion test

Abrasion test was carried out by a Zweigle abrasion tester (G552) with 800 mesh size sand paper and a pressure of 250 g. Ten samples were tested for each type of films and the abrasion property was evaluated by abrasion loss. Abrasion loss was calculated by using the formula 2. Lower value of the abrasion loss indicates better wear resistance.

$$G = \frac{m_0 - m_1}{S} \quad (2)$$

G is the abrasion loss (kg/m²), m_0 is the sample's weight before rubbing (kg), m_1 is the sample's weight after rubbing (kg) and S is the abrasion area (m²).

Microscopic observations

To understand how SiO₂ nanoparticles affect the properties of starch films, microscopic observations were used to examine the dispersion of SiO₂ nanoparticles, the surface structures of the nanocomposite film, the structures of the fractures and the surface morphology of the worn surface. In this study, atomic force microscopy (AFM), scanning electron microscope (SEM) and video zoom microscope (VZM) were used.

Results and discussion

Physical properties of the nanocomposite films

The effect of dispersion time on the physical properties

Test data of film's physical properties by different ultrasonic dispersion time are presented in Table 1. The results show that the abrasion resistance and tensile strength of the starch films increased as the ultrasonic dispersion time extended. The decrease in abrasion loss indicated the better abrasion resistance. Both the coefficient of variation of abrasion and abrasion loss reached their maximum value when dispersion time was 10 min. The coefficient of variation of the tensile strength decreased as the dispersion time increased. The data show that abrasion resistance became relatively steady as dispersion time increased. The results revealed that proper dispersion could enhance the mechanical performance of the film.

The effect of SiO₂ nanoparticle content on physical properties

The effect of SiO₂ nanoparticle content on physical properties is presented in Table 2. The results show that physical properties of the starch films varied with the contents of SiO₂ nanoparticle. As the starch film was containing 3% to 4% SiO₂ nanoparticles, the abrasion resistance and tensile strength of the starch films looked good.

It was also found that SiO₂ nanoparticles, as a filling agent, could effectively improve the physical properties of starch films and it is believed that polyvinyl alcohol as textile sizing materials in textile industry could be replaced completely or partially.

Table 1. Test data of film's physical properties by different ultrasonic dispersion time.

Test index	SiO ₂ dispersion time (min)						
	10	20	30	40	50	60	>70
Tensile strength ($\times 10^6$) (N/m ²)	26.01	26.95	28.29	31.88	34.13	31.72	33.22
Coefficient of variation of tensile strength (%)	6.81	7.53	5.54	6.63	6.38	4.17	4.76
Abrasion loss ($\times 10^{-2}$) (kg/m ²)	0.805	0.731	0.618	0.543	0.528	0.589	0.560
Coefficient of variation of abrasion loss (%)	7.86	6.49	4.63	6.75	2.75	3.55	2.86

Table 2. The data of film performance.

Test index	Contents of SiO ₂ (%)						
	0	1	2	3	4	5	6
Tensile strength ($\times 10^6$) (N/m ²)	25.93	28.86	29.37	33.66	36.24	26.06	26.80
Coefficient of variation of tensile strength (%)	5.73	6.23	4.83	2.37	5.69	7.00	3.45
Abrasion loss ($\times 10^{-2}$) (kg/m ²)	0.689	0.535	0.526	0.511	0.508	0.563	0.588
Coefficient of variation of abrasion loss (%)	5.96	6.98	4.83	4.26	4.65	4.29	5.01

Mechanism analysis

The dispersion of SiO₂ nanoparticles

The SiO₂ nanoparticles were dispersed by ultrasonic mixing for 10 min, 20 min, 50 min and 60 min, respectively. Figure 2 shows the AFM micrographs of the dispersed SiO₂ nanoparticles, which was prepared on the mica slide.

The sizes of the dispersed SiO₂ nanoparticles were measured by the AFM software and the results are listed in Table 3.

Figure 2 and Table 3 indicate that the SiO₂ nanoparticles dispersed better as the dispersion time increased. The size of SiO₂ nanoparticles was more than 100 nm when the dispersion time was less than 20 min, while the size of

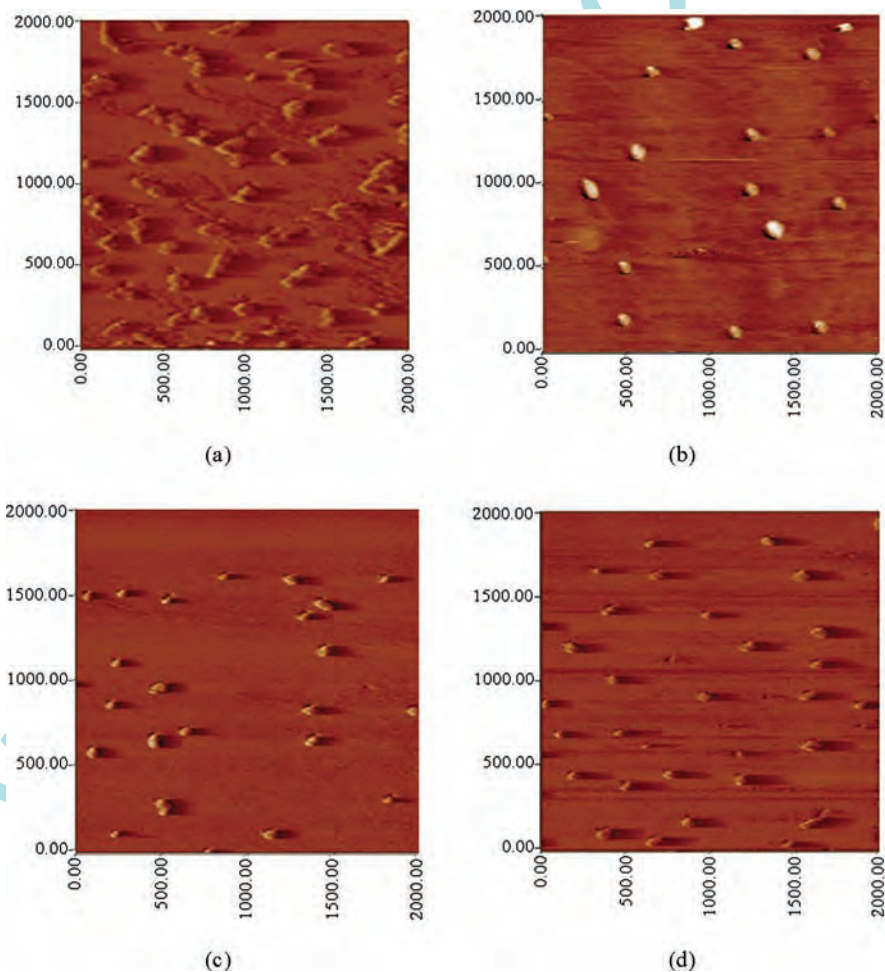


Figure 2. Atomic force microscope micrographs of the dispersed SiO₂ nanoparticles (the range of scan is 2000 nm). (a) Ultrasonic dispersion time, 10 min; (b) ultrasonic dispersion time, 20 min; (c) ultrasonic dispersion time, 50 min, and (d) ultrasonic dispersion time, 60 min.

Table 3. The diameters of the dispersed SiO₂ nanoparticles.

Dispersion time (min)	10	20	50	60
Particle diameter (nm)	115	102	67	52

the SiO₂ nanoparticles was reduced to about 50 nm as the dispersion time was increased to 60 min.

The surface analysis by atomic force microscope

There is a sharp probe fixed on AFM. It has a nanosize tip which is mounted on the end of a flexible cantilever to lightly scan across a specimen surface. The microscope is operated by measuring attractive or repulsive forces between the tip and the surface of the specimen. Meanwhile, the forces cause the tip to deflect. This deflection can be recorded by using a laser. It focuses on the top of the can-

tilever and reflects to photodetectors. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to the nanoscales (Yu & Chen, 2001).

In this study, A CSPM3000 AFM made by Guangzhou Benyuan Nanoinstrument Company was used to scan the surfaces of the films. Scanning was carried out in contact mode and high-resolution images were obtained.

The results of AFM observation are presented in Figure 3. The images show the surface morphology of the films at a nanoscale. The starch film without any nanoparticles showed a relatively flat surface with some particle-like defects, as displayed in Figure 3(a). These defects are believed to be some undissolved components in the starch. In contrast, the starch film containing 3% SiO₂ nanoparticles showed much rougher surface, as exhibited in Figure 3(b). The AFM image also revealed that the nanoparticles were rather evenly distributed, although there are obvious aggregations in the image.

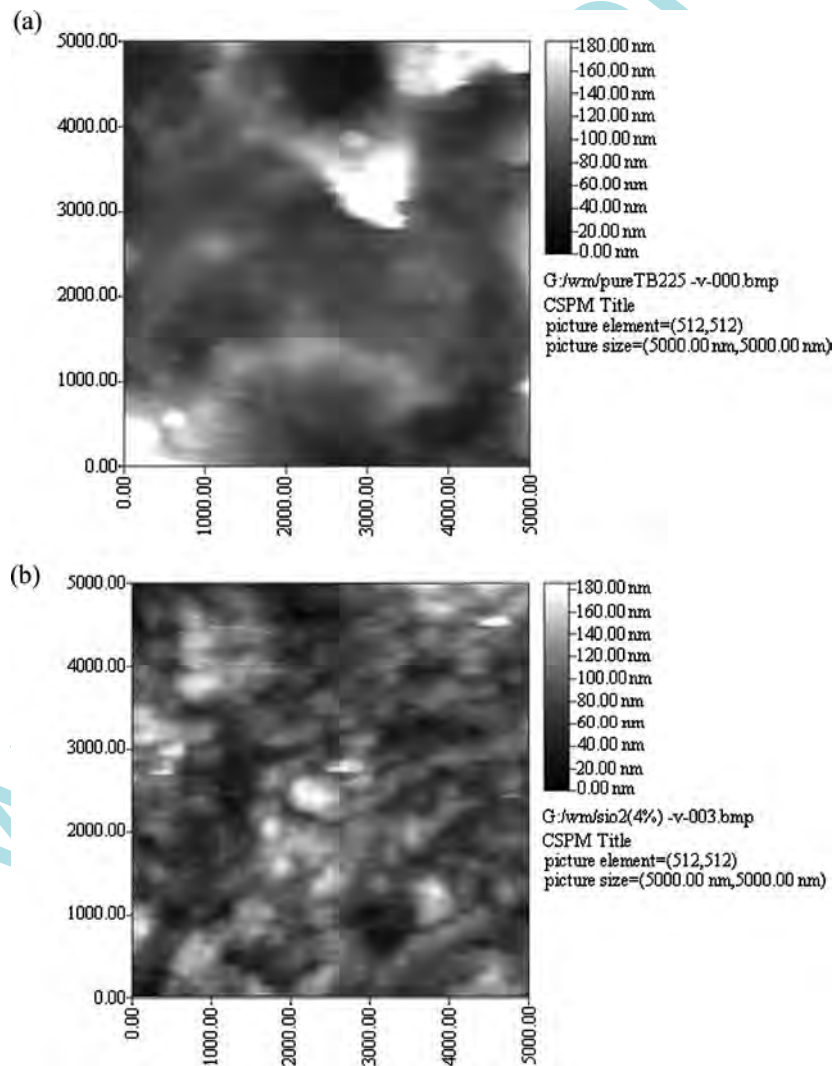


Figure 3. Atomic force microscope micrographs of the surface. (a) Pure starch film, and (b) starch film with 3% SiO₂.

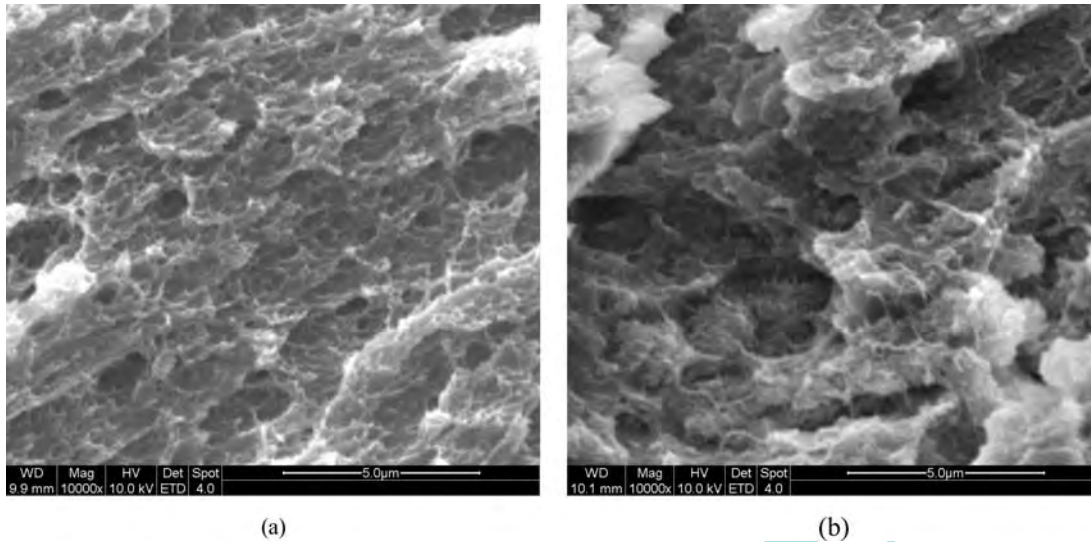


Figure 4. Scanning electron microscopes of the fractured surfaces. (a) Pure starch film, and (b) starch film with 3% SiO₂.

Fracture analysis by scanning electron microscope

The images which were the fractured sections of the films obtained by SEM (Quanta 2000, made by Holland FEI Company) are shown in Figure 4. All of the samples were plated with gold in the vacuum film plating machine before the SEM imaging.

The images clearly show the different cuticular structures of the fractured sections of the films. Figure 4(a) reveals that the starch film without any nanoparticles had a relatively flat surface with crystalloid and less plastic deformation. But the film with 3% nanoparticles shows a very rough fracture and much more caverned structure, which is displayed in Figure 4(b). According to fracture mechanics, the abruption process of the film could be regarded as a process of the crack expansion. From the formula of energy releasing fracture theory as follows (Li, Hu, & Zhu, 1998):

$$dW = dU + dA + dT$$

dW is the crack expansion and the variable work of load, dU is the variable work of the system's elasticity, dA is the variable of plastic work and dT is the variable of surface energy.

The film with 3% nanoparticles needed more energy and had larger tensile strength. Because of the plastic deformation and caverned structure, it would break.

Observation of abrasion surfaces by video zoom microscope

The images in Figure 5 show the surfaces of the films after abrasion test. It was clearly observed that grooves with

various depths and widths were formed on the worn surface of the starch film, as presented in Figure 5(a). It can also be seen from Figure 5(a) that a lot of exfoliations were formed at the surface. The formation of small grooves and exfoliations clearly revealed the phenomena of typical adhesion-abrasion. The grooves and scratches were much clearer than that of the film contained 6% SiO₂ nanoparticles, as shown in Figure 5(c). In this case, only some smaller exfoliations were observed. All these revealed the typical scratching abrasion. In comparison with Figures 5(a) and 5(c), Figure 5(b) shows much shorter and smaller grooves on the surface of the film containing 3% SiO₂ nanoparticles. This observation confirmed the lubrication effect of the nanoparticles.

It can be concluded from the optical images that Figure 5(b) had the best abrasion resistance, followed by Figure 5(a), but Figure 5(c) showed the lowest abrasion resistance during scratching abrasion, and Figure 5(b) had the best abrasion resistance, followed by Figure 5(c), but Figure 5(a) showed the lowest abrasion resistance during adhesion-abrasion.

On the basis of the above observations and analyses, it is believed that the surface of the starch film showed plastic deformation and minor breakage due to the normal and tangential stress at the beginning of the abrasion, and then small pieces of the material were separating from the film matrix during abrasion and contact with the abrasive on the tester, resulting in the adhesion-abrasion. As a proper amount of the SiO₂ nanoparticles was added and well dispersed into the starch matrix, the nanoparticles formed strong interfacial forces with the starch matrix. The SiO₂ nanoparticles themselves had strong rigidity and good lubricant properties. Therefore, the addition of SiO₂

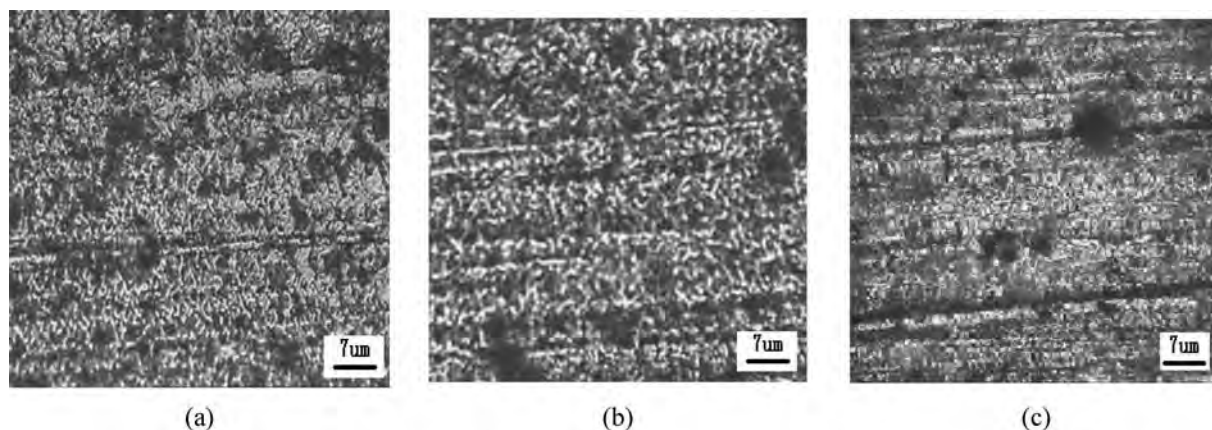


Figure 5. Images of the worn surface ($\times 700$). (a) Pure starch film; (b) starch film with 3% SiO_2 , and (c) starch film with 6% SiO_2 .

nanoparticles at a suitable level could strengthen the surface rigidity of starch film to resist the adhesion-abrasion. The well dispersion of the nanoparticles also lubricated the surface to reduce the scratch effect. When the content of the nanoparticles reached 6%, more aggregations were formed in the starch matrix. These large aggregations moved into the surface of the film during the abrasion process and scratched the surface of the film, resulting in more grooves on the film surface.

Another reason is that SiO_2 nanoparticles transferred to the surface of the film during the abrasion process to create a lubrication effect when the content of the nanoparticles was at a proper level (Yan, Xue, & Wang, 2002). The wear performance, however, could be weakened by the scratching effect of the nanoparticles if the content of the nanoparticles is too high.

Conclusions

This study has explored the effect of SiO_2 nanoparticles on the wear performance and tensile strength of the starch films. It was found that SiO_2 nanoparticles, as a filling agent, could effectively improve the wear performance and tensile strength of starch film. The best wear resistance and tensile strength of starch film could be achieved when SiO_2 nanoparticles were added into starch with an amount of 3% to 4%. The reason is that the nanoparticles were likely

to bond with hydroxyl group of starch macromolecules. Therefore, the molecular forces between nanoparticles and starch were strengthened.

Meanwhile, if the particle diameter of SiO_2 nanoparticles was smaller, the performance of starch film would be improved. And different ultrasonic dispersion time induced various dispersion effects of SiO_2 nanoparticles, which would affect the mechanical properties of the composite films accordingly.

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