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# Effect of SiO<sub>2</sub> Nanoparticles on the Wear Resistance of Starch Films

## Abstract

Nanoparticles have been increasingly used to improve the properties of polymer materials. In this study, SiO<sub>2</sub> nanoparticles were added to starch for sizing applications in the textile industry. The effects of the content of SiO<sub>2</sub> nanoparticles on the abrasion properties of the starch film were measured using a wear tester. The wearing surfaces were observed with Scanning Electronic Microscope, an Atom Force Microscope and a High Magnification Optical Microscope in order to better understand the wearing mechanism. The results showed that the best wear resistance was achieved when the content of SiO<sub>2</sub> nanoparticles was about 3%. The wear resistance mechanism of starch film containing SiO<sub>2</sub> nanoparticles was analysed.

**Key words:** starch film, wear resistance, wearing mechanism, nanoparticles, SiO<sub>2</sub>.

ronmental pollution and difficulty in desizing. A growing challenge in the textile industry is to develop new types of sizing agents which contribute to the toughness, adhesion and softening of size films with a full or partial replacement for PVA. Nanotechnology - the engineering of applications on a molecular or even atomic scale opens up new avenues for progress in the textile industry.

Nanotechnology promises an unprecedented era of innovation across multiple disciplines and diverse applications [4]. The key to realising nanotechnology's potential is still the ability to assemble and manufacture nano-scale devices and structures with dimensions smaller than 100 nm. At such scales, material characteristics, such as colour, strength, conductivity and reactivity can differ substantially between the nano and macro scale due to the surface effect or quantum effect [1, 7]. The majority of all consumer products featuring nanotechnology belong to the nanoparticle class. Nanoparticles have found important uses in a wide range of industries. The synthesis of na-

noparticle/polymer blends has expanded greatly in recent years [3, 5]. When nanoparticles are ceramic, such blend materials have the advantage of combining a ceramic-type material with an organic polymer that can result in a material that may bridge the performance gap between the two systems [9].

In this study, SiO<sub>2</sub> nanoparticles were mixed with starch to improve the performance of starch size. The wear resistance of starch/SiO<sub>2</sub> films was analysed using wear tests. The surface morphology of the film was examined by a Scanning Electronic Microscope, an Atom Force Microscope and a High Magnification Optical Microscope to reveal the mechanism of wear resistance. It was expected that nanoparticles could be used in sizing agents to replace PVA.

## Introduction

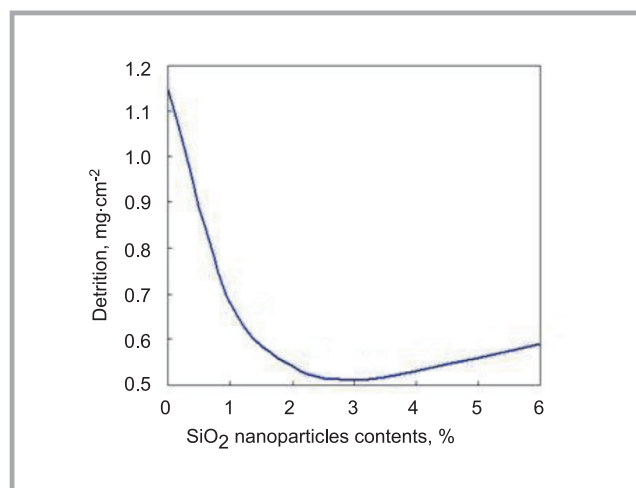
Spun or filament yarn needs to be protected against the stresses of weaving. This protection is provided by sizing agents which are dissolved in water and applied to the yarns. The sizing agent forms a thin film encapsulating the yarns for improved weaving performance and wear resistance. Therefore sizing is one of the most important processes in weaving preparation. Three types of sizes have been widely used in the textile industry, including starch, Poly Vinyl Acetate (PVA) and acrylic sizes [10]. Starch-based products are commonly used as sizing agents due to their abundance, low price, good adhesion to natural fibre, and causing less pollution to the environment. To improve the performance of starch size, PVA is often added to it due to the higher strength of PVA size. The addition of PVA, however, causes envi-

## Experimental

### Sample preparation

The nanoparticles used in this study were SiO<sub>2</sub>, obtained from Jiangsu Hehai Nan-

**Figure 1.** Relation between the mass loss of starch film and content of SiO<sub>2</sub> nanoparticles.



otechnology Co. Ltd, its average diameter was less than 35 nm, with a surface-area of more than 400 m<sup>2</sup>/g and purity of more than 99.5%. Sodium hexametaphosphate was used to treat the nanoparticles, whose content was 3% of the nanoparticles. Sodium hexametaphosphate was first dissolved in deionised water, and then the nanoparticles were added. The percentage of SiO<sub>2</sub> nanoparticles used was set at 1%, 2%, 3%, 4%, 5%, 6%, respectively, by weight. The dispersion of the nanoparticles was undertaken by ultrasonic mixing for 30 minutes; the frequency of the ultrasonic mixing was 59 kHz, and its power 0.3 W/m<sup>2</sup>.

Modified starch (TB-225) was used in this study, supplied by Zaozhuan Xianguyu Starch Co. Ltd. It was white powder with an ash content of less than 3.5%, the pH value of its 40% starch milk was 6.5 - 7.5, and its water content was less than 14.0%. The starch was mixed with the SiO<sub>2</sub> Nanoparticles/water suspension. The concentration of the mixture was controlled at about 6%. The mixed sizing agent was heated up to 95 °C and then stirred at 120 r.p.m, for an hour to achieve full gelatinisation. The gelatinized size was cooled down to around 50 °C. A size of 400 ml was accepted and cast on a glass plate to form a film, the average thickness of the film being 0.106mm. The film was then dried at a temperature of 20 °C and humidity of 65%. The films prepared were also conditioned for 24 hours at 20 °C and 65% relative humidity prior to the tests.

### Wear test

The size films were cut 220 mm long and 10mm wide. A wear test was carried out on a Zweigle wear tester (G552) with 800 mesh size sand paper, at a pressure of 250 grams. Ten samples were tested for each type of film, and the number of the tester movements about one sample was 1,000. The wear property was evaluated by the detritions of the wear test, which were calculated using the formula below. A lower value of the detrition indicates better wear-resistance.

$$G = (m_0 - m_1)/S \quad (1)$$

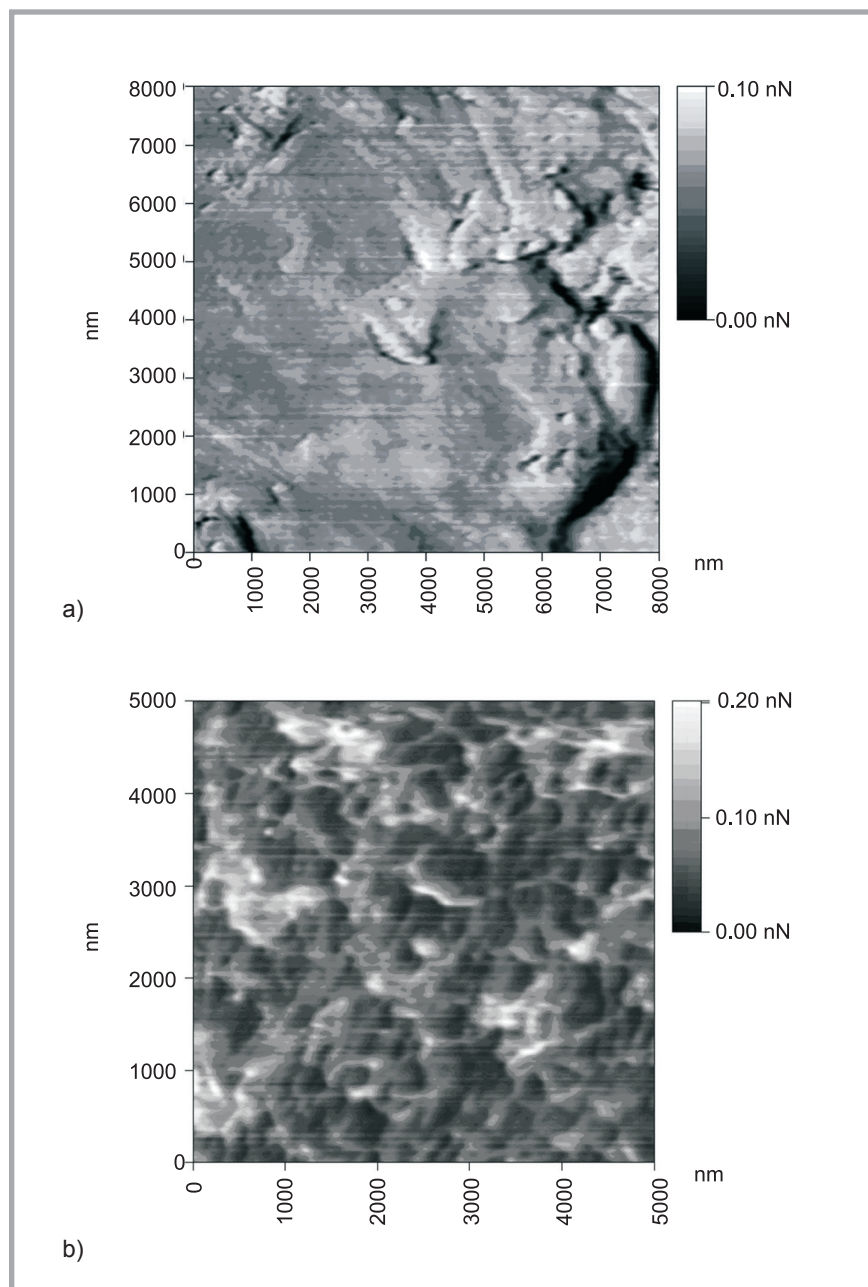
where  $G$  is the detrition in mg/cm<sup>2</sup>,  $m_0$  is the sample's weight before rubbing in mg and  $m_1$  is the sample's weight after rubbing in mg.  $S$  is the abrasion area in cm<sup>2</sup>.

### Surface characterisation

The film samples were examined before and after abrasion using an atomic force

**Table 1.** Data of the film wear test.

Test index	Contents of SiO <sub>2</sub> , %							
	0	1	2	3	4	5	6	
mass loss, mg/cm <sup>2</sup>	1.15	0.68	0.54	0.51	0.53	0.56	0.59	
mass loss, CV%	5.38	6.29	5.06	4.45	4.78	4.56	5.29	



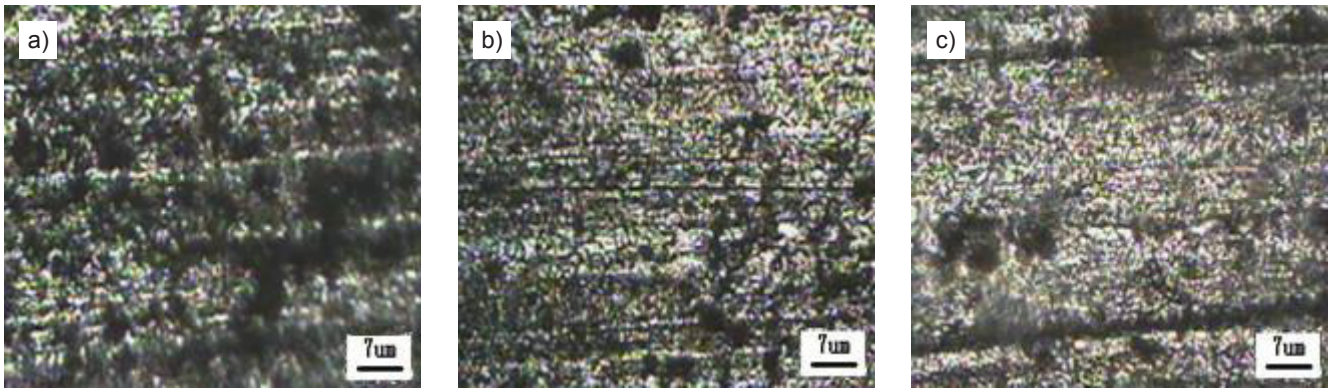
**Figure 2.** AFM micrographs of the surfaces of (a) starch film and (b) starch-3% SiO<sub>2</sub> nanoparticles.

microscope (AFM), a high magnification optical microscope (HMOM) and scanning electron microscopy (SEM).

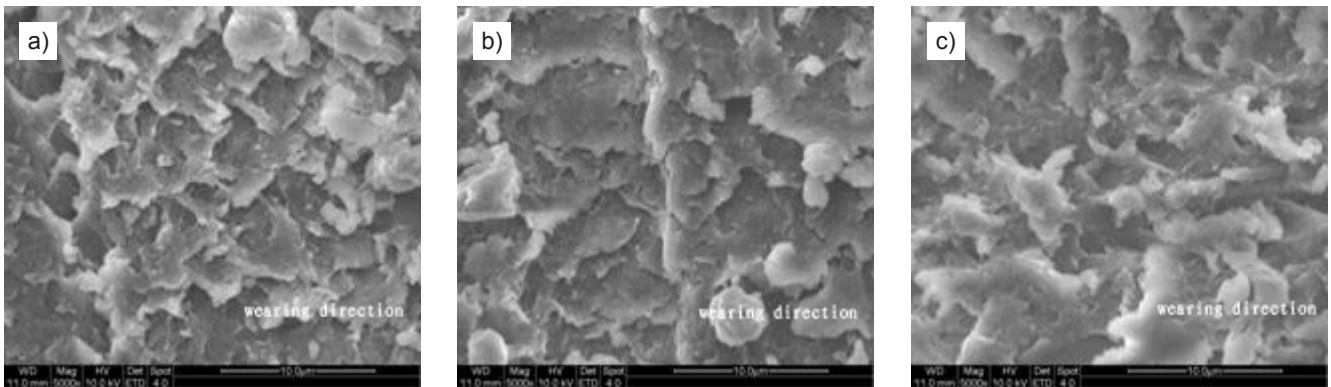
### (1) AFM

The AFM uses a sharp probe which has a nanosize tip mounted on a flexible cantilever to lightly scan across a specimen surface at the end of the cantilever [6]. The microscope operates by measuring

attractive or repulsive forces between the tip and specimen, where the forces cause the tip to deflect. This deflection can be recorded using a laser focused on the top of the cantilever and reflected on to photodetectors. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to nanoscales [9].



**Figure 3.** Optical microscopy images ( $\times 700$ ) of the worn surface of (a) starch film and (b) starch-3% SiO<sub>2</sub> nanoparticles and (c) starch-6% SiO<sub>2</sub> nanoparticles.



**Figure 4.** SEM microscope ( $\times 5,000$ ) of the worn surface of (a) starch film and (b) starch-3% SiO<sub>2</sub> nanoparticles and (c) starch-6% SiO<sub>2</sub> nanoparticles.

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 AFM was employed to examine the structures of the films at a nanoscale.

### (2) HMOM

In this study, a DZ3 High Magnification Optical Microscope made by Japan Union company was used to observe the films. The optical microscopy provided a tool to view a relatively larger area.

### (3) SEM

The wear behaviour of the film was also observed using a Quanta 200 SEM made by Fei Company. The samples were sputter coated with gold before the SEM observation. The observation was made in the SEM chamber at a high vacuum.

## Results and discussion

### Wear performance test

The wear performance of the starch/ SiO<sub>2</sub> nanocomposite films is shown in **Figure 1** (see page 96). It can be seen that the mass

loss of the film decreases as the content of nanoparticles increases from 0% to 3% and then rises when the content of nanoparticles is over 3%. The mass loss reaches the lowest level when the content of SiO<sub>2</sub> nanoparticles is about 3%, as illustrated in **Figure 1** (see page 96). Test data, and CV% (Coefficient of Variation) are shown in **Table 1** (see page 97). The addition of nanoparticles, however, could have a negative effect on the wear property of the film if the content of the nanoparticles is more than 3%. The results indicate that the wear performance of starch film can be effectively improved if a proper amount of SiO<sub>2</sub> nanoparticles is used. The effect of the content of SiO<sub>2</sub> nanoparticles on the wear performance of starch films can be attributed to the quasi-particle structure, small dimension, large surface-area, high surface energy and severe coordination shortage on the surface of the nanoparticles [10]. The nanoparticles are likely to bond with the hydroxyl group of starch macromolecules, and consequently the molecular forces between the nanoparticles and starch are strengthened. Meanwhile, SiO<sub>2</sub> nanoparticles can also approach unsaturated bonds of starch macromolecules and form some interaction with the elec-

trons of unsaturated bonds [2]. Such interaction contributes to the improvement in the wear resistance of starch films.

### Surface analysis

#### (1) AFM investigation

The results of AFM observation are presented in **Figure 2** (see page 97). The images show the surface morphology of the films at a nanoscale. The starch film without any nanoparticles shows a relatively flat surface with some particle-like defects, as displayed in **Figure 2.a**. These defects are believed to be some undissolved components in the starch. In contrast, the starch film containing 3% SiO<sub>2</sub> nanoparticles shows a much rougher surface, as exhibited in **Figure 2.b**. The AFM image also reveals that the nanoparticles are more or less evenly distributed; there are even obvious aggregations in the image. The roughened surface of the starch film containing SiO<sub>2</sub> nanoparticles significantly increases the surface area of the film, which plays a very important role in the wear performance of the material.

SiO<sub>2</sub> nanoparticles transfer to the surface of the film during the abrasion process to

create a lubrication effect when the content of nanoparticles is at a proper level [8]. The wear performance, however, can be weakened by the scratching effect of the nanoparticles if the content of nanoparticles is too high. The observation of a larger area by optical microscopy provides direct evidence of the lubrication or scratch effect.

### (2) HMOM investigation

The images in *Figure 3* show the observation of the surfaces of the films after the wear test. It is clearly observed that grooves of various depths and widths are formed on the worn surface of the starch film, as presented in *Figure 3.a*. It can also be seen from *Figure 3.a* that a lot of exfoliations are formed on the surface. The formation of small grooves and exfoliations clearly indicates the phenomena of typical adhesion abrasion. The grooves and scratches are much clearer as the content of SiO<sub>2</sub> nanoparticles reaches 6%, as shown in *Figure 3.c*. In this case, only some smaller exfoliations are observed. All these reveal typical scratching abrasion. *Figures 3.a*, *Figures 3.b*, and *Figure 3.c* show much shorter and smaller grooves on the surface of the film containing 3% SiO<sub>2</sub> nanoparticles. This observation confirms the lubrication effect of the nanoparticles.

It can be concluded from the optical images that the degree of abrasion of the film surface increases in the order the following order: film(b), film(a), film(c) during scratching abrasion, and the degree of abrasion of the film surface increases in the following order: film(b), film(c), film(a) during adhesion abrasion.

Based on the above observation and analysis, It is believed that the surface of the starch film first shows plastic deformation and minor breakage due to normal and tangential stress at the beginning of the abrasion, during which small pieces of the material are separated from the film matrix during abrasion and contact with the abrasive on the tester, resulting in adhesion abrasion. When a proper amount of SiO<sub>2</sub> nanoparticles is added and well dispersed in the starch matrix, the nanoparticles will form a strong interfacial force with the starch matrix. SiO<sub>2</sub> nanoparticles themselves have a strong rigidity and good lubrication properties. Therefore the addition of SiO<sub>2</sub> nanoparticles at a suitable level strengthen the surface rigidity of starch film to resist adhesion abrasion. Good dispersion of nanoparticles also

lubricates the surface to avoid a scratch effect. When the content of nanoparticles reaches 6%, more aggregations are formed in the starch matrix. These large aggregations move into the surface of the film during the abrasion process and scratch the surface of the film, resulting in more grooves on the film surface. SEM provides a much clearer examination of the surfaces of worn films.

### (3) SEM investigation

The images obtained by SEM examination are presented in *Figure 4*. The images clearly show similar cuticular structures of the surface after the wear test for three types of starch film. The cuticular layers are parallel to the wearing direction, indicating the feeling effect of the adhesion abrasion. The images reveal that starch film without any nanoparticles has more cuticular layers than those of film with 3% nanoparticles as well as film with 6% nanoparticles. Film containing 3% nanoparticles has the fewest cuticular layers among the three films, which confirms the observation by optical microscopy.

Starch itself has a lower strength and more easily fatigues after repeating wear, as presented in *Figure 4.a* showing a large quantity of cuticular layers and peeling marks. With the introduction of SiO<sub>2</sub> nanoparticles with the proper amount of 3%, the structure of starch film is strengthened and the performance of its wear resistance is enhanced. The image in *Figure 4.b* indicates plastic deformation by pressing and less adhesion abrasion. When the content of SiO<sub>2</sub> nanoparticles is increased to 6%, the congregation of nanoparticles causes the formation of some large aggregates of nanoparticles. The aggregates have less strength and are easily detached from the starch matrix. The nanoparticles dispersed in the starch matrix inhibit the effect of adhesion abrasion, which is why film with 6% SiO<sub>2</sub> nanoparticles still has fewer cuticular layers than starch film, as illustrated in *Figure 4.c*.

It should be pointed out that various types of abrasion normally happen at the same time during the abrasion process, and primary as well as secondary abrasions can change at different conditions.

## Conclusions

This study has explored the effect of SiO<sub>2</sub> nanoparticles on the wear performance of

starch films. It was found that SiO<sub>2</sub> nanoparticles as a filling agent can effectively improve the wear performance of starch film, and they can be used to completely or partially replace PVA in textile sizing materials in the textile industry. The best wear resistance of starch film can be achieved when SiO<sub>2</sub> nanoparticles are added to starch at an amount of 3%. The microscopic analysis using optical microscopy, scanning electron microscopy and atomic force microscopy provided an insight into the wear mechanism of the film.

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