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Investigating the Effects of Particle Size on the Growth of Silkworm and Fiber Properties with Feeding TiO_2 NPs

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ABSTRACT

The production method of functional silk by feeding the various nanoparticles is simple, it has attracted the attention of many researchers. However, many researchers have studied the concentrate of nanoparticles (NPs), there are few studies on the particle size. This study is aimed to confirm the effects in silkworm growth, cocoon quality, and mechanical properties of silk with feeding TiO_2 NPs of the various particle size. TiO_2 10nm, 50nm, 100nm powers individually are fed to silkworm, investigated the mortality and proliferation rate, cocoon mass and cocoon shell mass, mechanical characteristic of silk fiber. The experiments demonstrated that the larger the particle size of TiO_2 NPs, the greater the adverse impact on the growth and livability of silkworms. The stress of 523.35±42 MPa and strain of 19.73±1.8% of the TiO_2-10nm added silk were increased 35.9% and 19.5% on average, respectively. By the analysis of the Fourier transform infrared (FTIR) spectra, it was confirmed that this resulted in a more random coil/α-helix structure. The nanoparticles are acted as knots, forming the cross-linked network, resulting in lower crystallinity and higher strain, but the larger the particle, the fewer the number of knots, at the same time, it has a great impact on protein synthesis, and then the strength may be decreased. The effect in the silkworm body of TiO_2 NPs particle size has to be deeply studied, but this study has important significance to study in the production of the functional silk by feed additives.

Keywords: Silkworm Silk, TiO_2, Nanoparticles, Fiber Reinforcement, Particle Size

I. INTRODUCTION

Bombyx mori is not only an insect with high economic utility but also a lepidopteran insect with innate immunity. With the development of science and technology, silkworm chrysalis, silk, and silkworm sand have been well utilized. Among them, silk is the most widely used and has effective applications in the fields of textile, biomedicine, and cosmetics [1]. Silk has the advantages of light texture, heat preservation, moisture absorption, air permeability, and luster, but its mechanical properties and gloss are declined in the process of wearing and washing, so the modification of silk has been carried out all the time [2]. Some researchers used the dissolution regeneration method for dissolving the silk fibroin fiber into a solution and then spun it into silk fibroin fiber by spinning. Regeneration silk fiber had a smooth surface and uniform strength, but the mechanical properties were reduced. Therefore, they tried to add some reinforcing agents to the silk fibroin solution and obtained the fiber with improving the mechanical properties [3,4]. There are also chemical grafting methods, the principle of this method is to polymerize between the remained surface amino acid of silk fibroin and graft monomers under appropriate conditions, to form surface graft polymers on the silk fibroin, and then obtain regenerated fibers having the improving mechanical properties [5,6]. However, the modification method of chemical grafting leads to the fact that the grafted material only exists on the surface of silk and cannot go deep. Therefore, the essential modification of silk cannot be achieved. Moreover, the reaction environment of the chemical grafting method is in the organic solvent, which occurs polluting the environment. In addition to these methods, there are genetic modification methods [7], but transgenic modification engineering requires strict equipment and technical conditions, and transgenic technology is not stable, so it is not suitable for large-scale use. Recently, the method of feeding additive is appeared, which has attracted many experts' attention. This method is to spray additives on mulberry leaves or soak mulberry leaves in additive solution，and then additives can be absorbed into silkworm silk gland, to enter silk in the process of silk formation, achieve the improving properties of silk. Among additives, there are usually nanomaterials, a lot of studies were carried out using the nano additives containing Cu, TiO_2, Ag, graphene, etc., some achievements were gained [2,8-10]. But previous studies have done a lot of research on the concentration of nanoparticles, there are few studies on the effect of particle size on silkworm growth and fiber properties. Therefore, the effects of particle size on the growth and fiber properties of silkworms were studied with TiO_2 NPs as an additive.

II. MATERIAL AND METHODS

2.1 Preparing the silkworms and nanoparticles

In this paper, 3rd instar Bombyx mori silkworms were provided by Chun An Ling Chuan Sericulture Development Co., Ltd., Zhejiang Province，5th instar silkworms were used in all experiments. TiO_2 nanoparticles were 10nm, 50nm, 100nm provided by Wanjing New Material Co., China, Hangzhou. TiO_2 NPs powder was suspended in 0.5%(w/v) hydroxypropyl methylcellulose (HPMC) K4M solvent with 20h incubation and were then treated under the ultrasonic condition for 20 min and treated under the mechanical vibrate condition for 3 min. The concentration of TiO_2 NPs was 10 mg/L because this concentration has the best effect [11].

2.2 Feeding TiO_2 NPs and degumming cocoon

Firstly, mulberry leaves were soaked in the experimental solvent for the 20s and then dried in a place without sunlight. Prepared leaves were fed to four experimental groups containing a control group of larvae, each group had 50 larvae, treated leaves were supplied to silkworm three times a day. And the body weight was tested until they reached full maturity. After, the silk quality and survival rate were evaluated with the cocoons of each group. Cocoons were dried at 110 °C for 1 h, 2 h at 85 °C in vacuum condition. The dried cocoons were boiled under the 0.5 wt% Na_2CO_3 solution at 100 °C for 20 min, this process was repeated three times, finally, washed with deionized water, and dried in a cool place [9,10].

2.3 Characterization

The surface of degummed silk was scanned by Scanning Electron Microscopy (SEM, S-4800, Hitachi, Japan). The diameter of silk fiber can be observed by the optical microscope, but it was tested using the weight/length method because the cross-section is triangular. We measured 20 single degummed silk fibers and obtained the averaged value. For measuring the mechanical properties of silk, 20 samples were prepared in every group and measured by the XQ-2 electronic single fiber strength tester at 22 ± 2 °C and 60 ± 5% relative humidity. The extension rate of the tester was 10 mm min^{-1}, the gauge length was 20 mm. Each test was repeated 50 times and averaged. And then the secondary structure of silk fiber was analyzed using Fourier transform infrared (FTIR) spectra (Nicolet 5700 Fourier transform spectrometer) with a resolution of 4 cm^{-1}, KBr pellets were employed in this test, quantitative analysis of tested results was performed by the software Peakfit 4.12 [12]. Finally, UV resistant properties of silk were investigated using the loss of the stress-strain properties after treating under the ultraviolet light condition, treatment machine was QUV/spray UV accelerating aging experiment machine (Q-Lab, USA). The samples were treated under ultraviolet light at the wavelength of 340 nm which had an intensity of 0.65W/cm^2 for 8 h. And then the mechanical properties of samples were tested using XQ-2 electronic single fiber strength tester, of the mechanical properties were calculated.

III. RESULTS AND DISCUSSION

3.1 Effects of feeding TiO_2 with the different particle sizes on the growth of silkworm

We fed the fifth instar silkworm larvae with treated leaves for each group. Four experimental groups containing the control group were named TiO_2-10, TiO_2-50, TiO_2-100, and control, respectively. The silkworm weights of each group were shown in Fig. 1, it was tested at once a day.

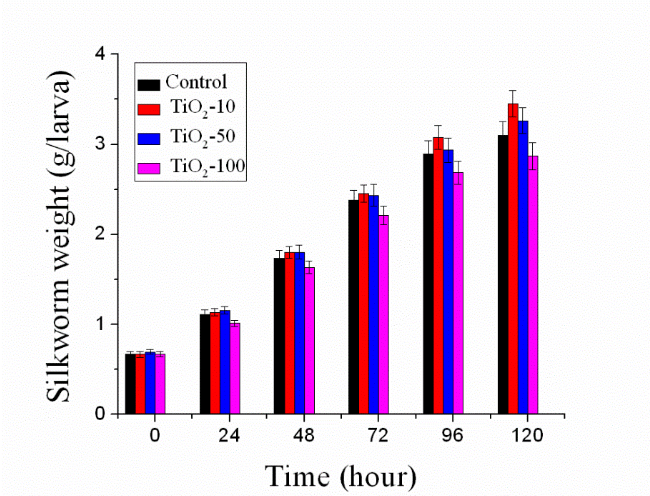

Fig. 1 Effect of the different particle sizes of TiO_2 on the weight of silkworm ($p < 0.05$)

The result showed that the increasing rate of silkworm weights appeared differently in every group. Especially, TiO_2-10 had an obvious increasing effect of weight and according to the increasing particle size, the effect lowed. It is explained that the larger the particle size of TiO_2 NPs, the greater the negative impact on the growth and the survival rate of silkworms. The reason for this may be explicated that the great particle size of TiO_2 NPs played a toxic role in silkworms.

3.2 Survival rate and cocoon quality

To study the effects of TiO_2 NPs with the particle size on the growth of the silkworm, recorded the survival rate of a silkworm, cocoon quality was evaluated by the cocoon mass, cocoon shell mass, the results were shown in Table 1. In this table, the fineness of degummed silk was used in calculating the strength of the fiber.

Table 1 Effect of TiO_2 NPs with the particle size on survival of silkworm, cocoon mass, cocoon shell mass, and fineness of degummed silk

Sample	Survival of silkworm (%)	Cocoon mass (g)	Cocoon shell mass (g)	Ratio of cocoon shell (%)	The fineness of degummed silk (dtex)
control	78.26	1.423±0.06a	0.273±0.02a	19.18±0.03a	1.25±0.04 a
TiO_2-10	93.57	1.579±0.05b	0.302±0.01b	19.15±0.02a	1.26±0.04 a
TiO_2-50	83.58	1.517±0.04b	0.291±0.01a	19.21±0.02a	1.25±0.04 a
TiO_2-100	75.77	1.387±0.06a	0.265±0.02a	19.11±0.03a	1.23±0.05 a

Ranks marked with different letters mean they are significantly different at the 5 % confidence level. Values represent means ± SD.

As shown in Table 1, the survival rate of the TiO_2-10 group was the highest in experimental groups, compared with the control group, which increased 20%. And the survival rate of the TiO_2-100 group was lower than the control group, which explains that the smaller the particle size of TiO_2 NPs, the better the positive impact on the growth of silkworm, and particle size is greater, resulting in a toxic role. And then the ratio of cocoon shell almost was fixed in each group, but the cocoon mass and the shell mass of TiO_2-10 were the highest, which was 10.9% higher than the control group. However, with the increase of the particle size, the effect gradually was weakened, and finally had a negative impact because of its toxic role. The fineness of degummed silk was tested by the traditional weight/length method, used in calculating the relative strength of silk fiber.

3.3 Surface morphology of degummed silk fiber

The surface morphology of fiber is shown in Fig. 2, which demonstrated that TiO_2 NPs do not affect the appearance of degummed silk. Because maybe explained that their concentrate is very low and absorbed TiO_2 NPs in silkworm is mainly go outside through excreta.

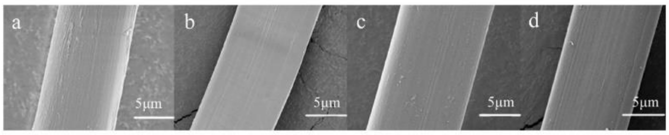

Fig. 2 SEM image of degummed silk fibers. **a** Control group. **b** TiO_2-10 group. **c** TiO_2-50 group. (d) TiO_2-100 group

3.4 Mechanical characteristics of degummed silk fiber

The stress–strain curves of the degummed silks were shown in Fig. 3. As shown in Fig.3, TiO_2 NPS has a considerable effect on the mechanical characteristics of silk fiber according to the particle size.

The breaking stress and strain of 524.35 MPa and 19.73% for TiO_2-10 silk remarkably exceed control silk with 385.8 MPa and 16.5%, like that, TiO_2-50 silk also exhibited high stress and strain with 503.36 MPa and 20.6%. It showed that the degree of influence decreased and then was lower than the control group according to the increasing particle size of TiO_2 NPs. Some researchers presented that the nanoparticles are acted as knots in the fiber, forming the cross-linked network containing the crystallites, resulting in lower crystal structure and higher strain [13]. With this mechanism, the smaller the particle size, the more the number of knots, the strength of the fiber may be increased. But the larger the particle, the fewer the number of knots, at the same time, it has a great impact on protein synthesis, and then the strength may be decreased. However, the detailed mechanism of TiO_2 on silkworm protein synthesis and the effect of particle size still needs to be further proved.

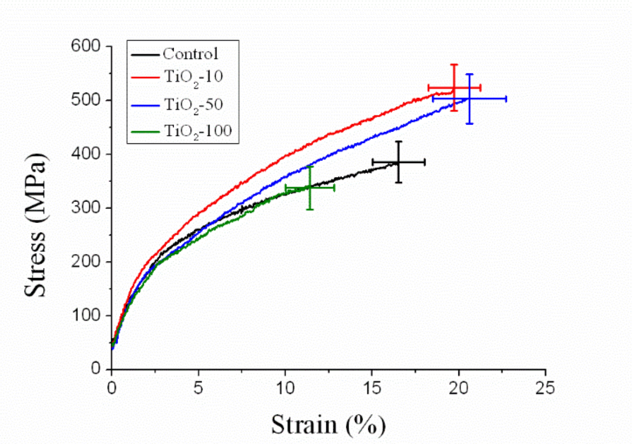

Fig. 3 Stress-strain curves of degummed silk

3.5 Secondary structure of silk fiber

The secondary structure of silk fiber is strongly related to its physical properties. FTIR has been early used in studying the secondary structure of silk fiber with the power tool. We selected TiO_2-10 and TiO_2-100 with the significant tendency in the experiment, compared with the control group. FTIR spectra of selected fibers were shown in Fig. 4, which indicated the peak position in the amide I band and III band. The characteristic peaks of silk fibroin in every experimental group have no considerable differences, it was explained that there was only a change secondary structure of the fiber, no strong covalent interaction between TiO_2 NPs and fibroin. To analyze the secondary structure, the assignment of absorption peak in the amide III band was performed in this paper.

The peaks centered at 1260 cm^{-1} and 1230 cm^{-1} are considered to be the β-sheet and the random coil / helical conformation, respectively [14]. The deconvolution of FTIR spectra in amide III band with the control, TiO_2-10, and TiO_2-100 were shown in Fig. 5. And then the contents of the secondary structure are shown in Fig. 6.

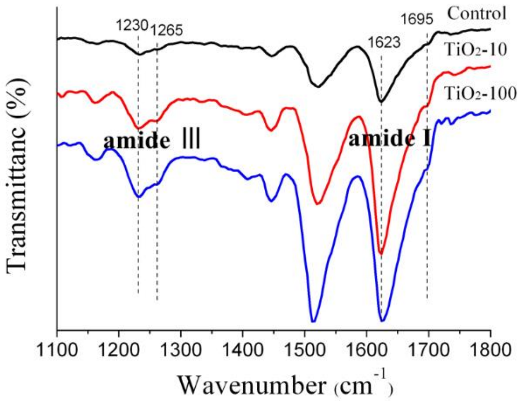

Fig. 4 FTIR spectra of degummed silks

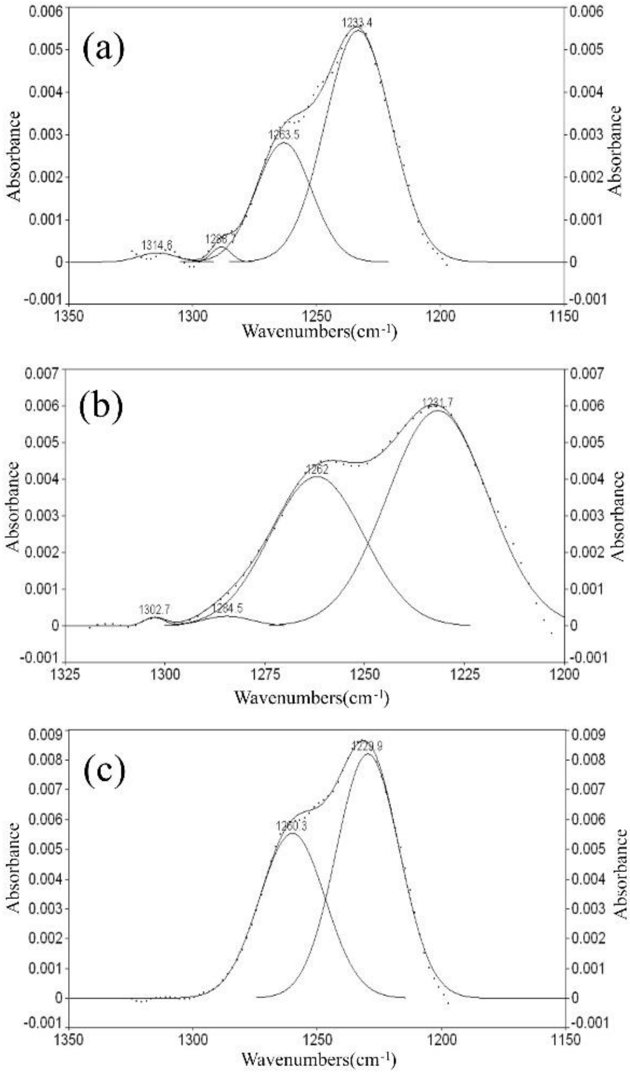

Fig. 5 Deconvolution of FTIR spectra in amide III band. **(a)** Control. **(b)** TiO_2-10. **(c)** TiO_2-100

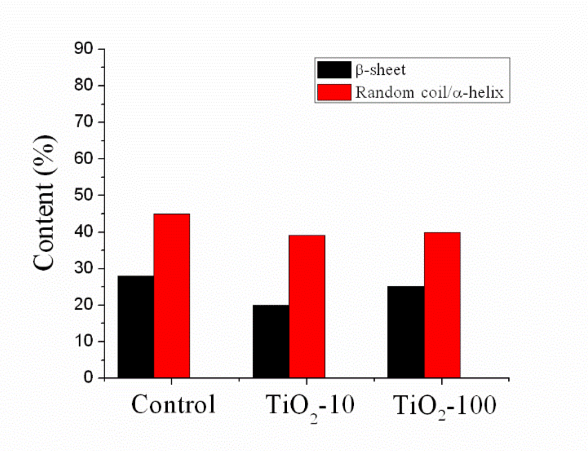

Fig. 6 The content of secondary structure in degummed silks

As shown in Fig. 6, the TiO_2-100 silk contained the lesser with β-sheet conformation and the greater number of chains in random coil or helical conformation compared with the control fiber. This may be explained that the TiO_2 NPs hindered the transformation from random coil/α-helix to β-sheet, the larger the particle size, the more obvious it is. However, when the increasing of random coil/α-helix exceeds a certain limit, the stress and strain of silk are decreased.

3.6 Ultraviolet resistant properties of silk fiber

The stress-strain loss rate with the control, TiO_2-10, and TiO_2-100 silks were plotted in Fig. 7. As expected, the breaking strength and elongation of UV irradiated silks were lower than untreated silks because UV may break the protein chain.

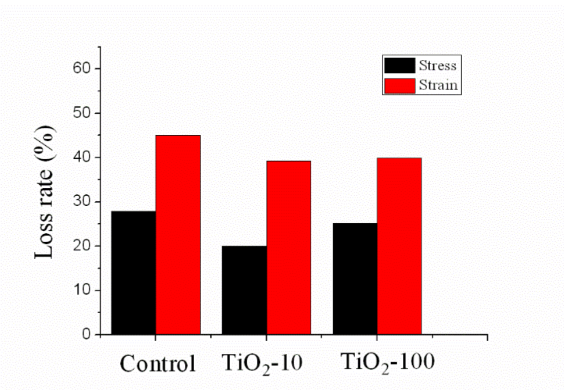

Fig. 7 The stress and strain loss rate of UV irradiated silks

The stress and strain loss rate of 20%, 39.1% for TiO_2-10 silk were improved compared with 27.9%, 45% of the control silk, respectively. But according to the increasing particle size of TiO_2 NPs, ultraviolet resistant properties of silk fiber were lowed, it may be concerned with its change of the secondary structure.

IV. CONCLUSIONS

In summary, absorbed TiO_2 NPs in silkworm can occur a change in protein synthetics of silkworm body, when the particle size is small, have no negative effect on the growth and survival rate of silkworms and the quality of cocoons. And compared with the control group, the stress of 524.35±42 MPa and strain of 19.73±1.8% for modified silk by the feeding TiO_2-10nm were increased 35.9% and 19.5% on average, respectively.

It may be concerned with the more random coil/α-helix conformation, which was tested by the analysis of the secondary structure of silk fiber using FTIR spectra. The study also demonstrated that the degree of influence depends on the particle size of TiO_2 NPs. But in the future, the action mechanism in the silkworm body of TiO_2 NPs has to be deeply studied.

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