

Analysis of the Structural Characteristics of Nanoscale Silk Particles

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ABSTRACT: Nanoscale silk particles were prepared from silk fibers by a special pretreatment with the aid of specially designed machinery and techniques. Scanning electron micrographs showed that the particle sizes of the silk powders produced from silk fibers around 9–11 μm in diameter decreased from a microscale to a nanoscale after three stages of pulverization, and this was further confirmed with a laser particle size analyzer. Fourier transmission infrared analysis showed that there were no substantial changes in the chemical structure of the silk after the pulverization processes. The silk powders after the second and third pulverizations slightly differed from that of the silk fiber and the particles after the first pulverization with a greater amount of the primary aliphatic amines. Also, there were secondary

amides present in the silk fiber and the powders after the first and second pulverizations but absent in the powders after the third pulverization. Moreover, the silk powders after the third pulverization had a greater number of $\text{C}(\text{CH}_3)_3$ groups than the silk fibers and the powders after the first and second pulverizations. X-ray diffraction analysis showed that the crystallinity of the silk powders decreased when the particle sizes decreased, particularly to nanoscales. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 268–274, 2006

Key words: FTIR; nanotechnology; particle size distribution; X-ray

INTRODUCTION

Over the centuries, silk has been regarded as a highly valued textile fiber. Its qualities of strength, elasticity, softness, absorbency, affinity for dyes, and adaptability to various forms of twisting continue to satisfy various market demands. Despite facing keen competition from man-made fibers, silk has maintained its supremacy in the production of luxury apparel and specialized goods of the highest quality.¹ Silk has been used as a textile fiber for over 4000 years. Because of its high (tensile) strength, luster, and ability to bind chemical dyes, silk is still considered a premier textile material in the world today.²

The silk fiber has a triangular cross section. The double silk filaments lie with the flat sides of the triangles together, encircled by a sericin coating. The fiber is smooth and transparent and has a rodlike shape with occasional swelling or irregularities along its length. It is fine with a diameter of 9–11 μm . The length of the filaments ranges from 300 to 1000 m.

Individual filaments with a length of 3000 m have even been measured.³

In addition to applications in clothing, silk fibers have gained a great deal of attention because of their great potential and use as multifunctional materials in various fields, such as biomedical fields. As a result, many researchers, especially in Japan, have tried to develop new application areas for these fibers because of the application of their excellent intrinsic properties in the development of new materials in biotechnological and biomedical fields. For example, Masahiro et al.⁴ introduced a method to produce superfine silk powders with a particle size of around 10 μm , which could be used in plastic films or sheets, coating media, and fiber-treatment agents. Otoi et al.⁵ invented a method for crushing silk fibers into fine powders and obtained particularly useful powders to be used as additives for cosmetic preparations. Shoten⁶ also developed a technology for finishing yarn-dyed cotton fabrics with silk powders and marketed these cotton fabrics under the Powder Taste brand. Li and Xu⁷ reported the development of an apparatus to prepare fine powders from wool and silk.

Tsubouchi^{8,9} invented a way of generating superfine silk powders with an alkaline aqueous solution, and he proposed a method for manufacturing crystalline silk fibroin powder industrially by the mechanical comminution of silk yarn. He mentioned that this

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superfine crystalline silk fibroin powder could provide excellent formability, improve adhesive properties to skin or the like, and enhance the extensibility and sense of touch. It is also outstandingly suitable for making raw materials used in cosmetics, foundations, ink additives, resin composites, and paints. Li and Hu¹⁰ reported the development of a technique for pulverizing natural organic substances such as wool, cotton, and silk fibers into nanoscale, fibrous materials.

In these studies, the main focus is on the techniques used to prepare superfine and/or nanoscale powders from silk fibers. The structural characteristics of nanoscale silk particles, which are critically important in terms of the functional performance of nanomaterials, have not yet been reported. To fill this knowledge gap, this article reports an analysis of the structural characteristics of silk powders with particle sizes ranging from a microscale to a nanoscale during different stages of pulverization with a number of techniques, including scanning electron microscopy (SEM), laser particle analysis, Fourier transmission infrared (FTIR), and X-ray diffraction (XRD).

EXPERIMENTAL

Preparation of the silk powders

Applying the methodology developed by Li and Hu,¹⁰ we pulverized natural silk fibers into nanoscale particles in three steps, as described here briefly. After being cleared and dried, the raw silk fiber (Huzhou, China) was crushed into small pieces by a mechanical rotating crusher to a particle length of around 100–300 μm . The obtained powder was called the first pulverized silk powder.

Next, the obtained powder was mixed with pure water and pulverized by an ultrasonic crusher (JY92-IIID, Ningbo, China). After this pulverization step, the size of a majority of the silk particle in the suspension was smaller than 10 μm . The powder obtained after this step was microscale in size and was called the second pulverized silk powder.

Then, the pulverized silk powder suspension was filtered to remove large, uncrushed particles. Furthermore, the filtered suspension was pulverized by an Ultraturray® (T 25 Basic, IKA labortechnik, Germany) machine at first and then by a collision machine for final pulverization. After this process, the particles were smaller than 100 nm in diameter. The powder obtained after these steps was nanoscale in size and was called the third pulverized silk powder.

Characterization of the silk powders

We studied the morphology, particle size distribution, chemical structure, and crystallinity of the first, sec-

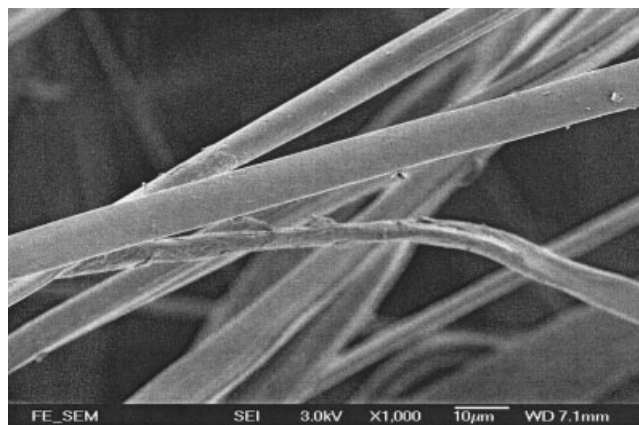


Figure 1 SEM image of silk fibers (original magnification = 1000 \times). The diameter of the fibers was 9–11 μm .

ond, and third pulverized silk powders by means of SEM, particle size analysis, FTIR spectroscopy, and XRD analysis, respectively.

The morphology of the pulverized silk powders was examined with SEM analysis, which was carried out with a JSM-6335F (JEOL, Japan) field emission scanning electron microscope after gold coating.

The particle size distributions of the first, second, and third pulverized silk powders were analyzed with a Beckman Coulter LS 13320 (Fullerton, CA) particle size analyzer, which was designed from conception to be fully compliant with ISO/DIN13320-1 (Particle Size Analysis—Laser Scattering Methods—Part 1: General Principles).

To study whether there were any chemical changes in the silk after pulverization, the FTIR spectra of the first, second, and third pulverized silk powders were studied. In this research, the KBr disc technique was used for the preparation of the pulverized silk powders for FTIR analysis. This method consisted of mixing finely divided 0.004-g pulverized silk powder samples with 0.4 g of powdered potassium bromide. The discs were formed in a die under a very high pressure and then were analyzed with a PerkinElmer 2000 FTIR (Wellesley, MA) spectroscopy system.

The crystallinity of the pulverized powders was determined by the XRD technique. The XRD experiments were conducted on the pulverized silk powders with a Philips Analytical PW3710 X-ray diffractometer (EA ALMELO, The Netherlands) with a copper-tube anode source at 40 kV and 35 mA. A 0.1-mm pinhole collimator was employed. Scattering XRD data were recorded with an XRD evaluation program (Advanced X-Ray Solutions Diffract Plus Release 2000 Eva, version 6.0, Bruker).

RESULTS AND DISCUSSION

SEM

Figure 1 shows that the length of the original silk fibers was on a millimeter scale, and their diameter was

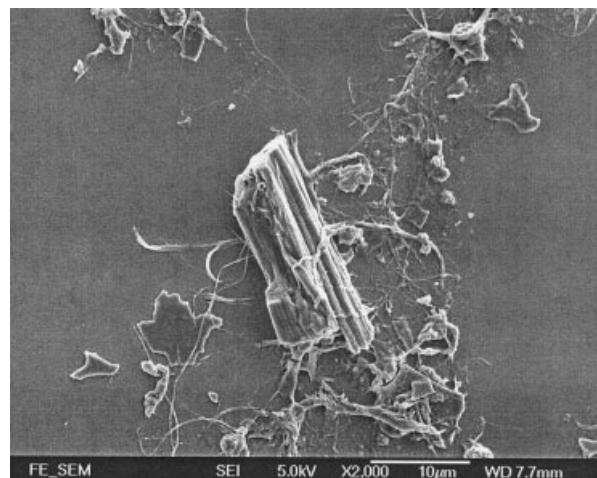


Figure 2 SEM image of the first pulverized silk powder (original magnification = 500 \times).

around 9–11 μm . The silk fibers had a smooth surface. Figure 2 shows that after the first pulverization process, the fibers were smashed into particles up to 30 μm long. The surface of the silk fibers became rough after the first pulverization process. Figure 3 shows that the second pulverized silk powder (ca. 0.1–10 μm) was obtained after the second pulverization process. Most of the second pulverized silk powder was in either a ribbon or spherical form. Figure 4 shows that all the third pulverized silk powder was a nanoscale, spherical powder.

Particle size analysis with a laser particle size analyzer

The aforementioned SEM images showed that after the second and third pulverization processes, microscale and nanoscale silk powders were generated, respectively. These SEM pictures only visually showed the images of silk powders located in a specific area and did not provide a quantitative analysis for the actual particle size distribution of the powders. As a result, the particle size distributions of the first, second, and third pulverized silk powders were analyzed with the Beckman Coulter LS 13320 particle size analyzer.

Figure 5 shows that the particle size of the first and second pulverized silk powders ranged approximately from 1 to 20 μm and from 0.1 to 5 μm , respectively. The powders with a diameter of less than 0.1 μm were classified as nanoscale silk powders. This confirmed that most of the third pulverized silk powder was on a nanoscale.

The resulting particle size distributions of the pulverized silk powders needed to be confirmed by observation through SEM images to determine the morphology of the silk particles. The laser diffraction technique of the LS 13320 particle size analyzer is based on

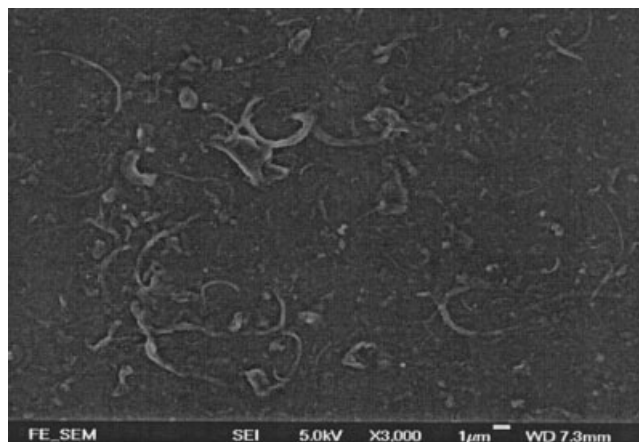


Figure 3 SEM image of the second pulverized silk powder (original magnification = 3000 \times).

the phenomenon that particles scatter light in all directions with an intensity pattern that depends on the particle size. All these instruments assume that the particles are spherical. For nonspherical particles, an equivalent-sphere size distribution is obtained because the technology makes the assumption of spherical particles in its optical model. Therefore, the resulting size distribution may differ from those obtained by methods based on other physical principles, such as sedimentation and sieving. This deconvolution is found according to the Fraunhofer theory of light scattering.¹¹ Xu and Di Guida¹² pointed out that for nonspherical particles for which the diameters were ill defined and theoretical models of scattering patterns were seldom available, the results obtained from the application of any spherical model would certainly have unexpected bias or error.

In practice, most people neglect the difference between the real shapes of particles and the model and customarily take the reported mean values and

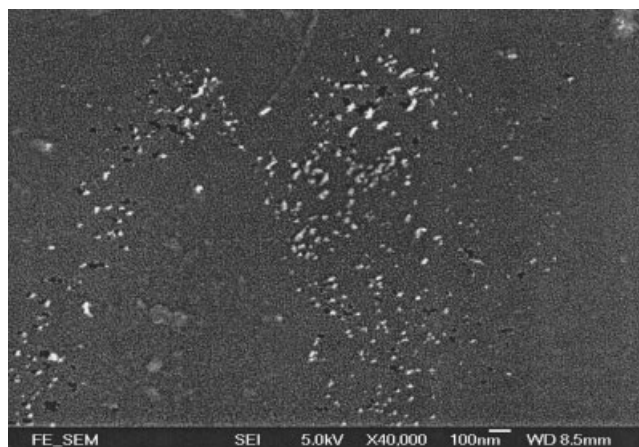


Figure 4 SEM image of the third pulverized silk powder (original magnification = 40,000 \times).

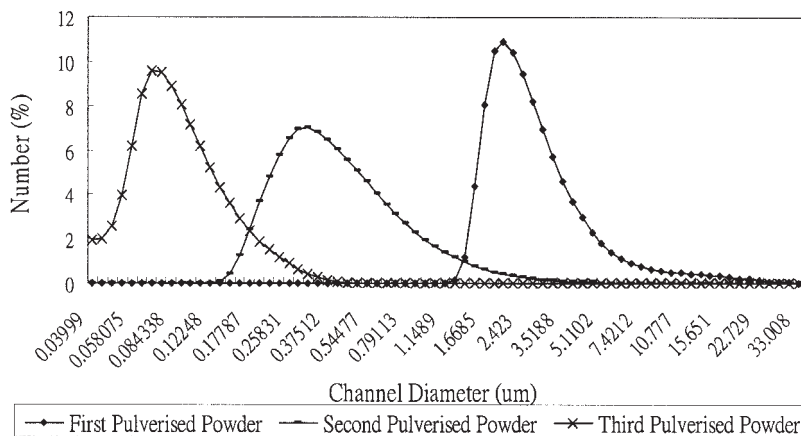


Figure 5 Particle size distribution of the first, second, and third pulverized silk powders.

size distributions for granted without realizing that these are only apparent sizes and actually are not equivalent sizes. In certain extreme cases, the results obtained by the application of the spherical model to nonspherical particles will be very different from the truth.

The SEM image of the first pulverized silk powders in Figure 2 shows that there were particles around 5–30 μm long. The particle size distribution in Figure 5, however, can hardly identify such particles. This difference may be attributed to a number of potential causes: (1) the powders in a specific area of the SEM images were randomly selected, (2) the particles were assumed to be spherical in the particle size analyzer, and (3) the particle size analysis was based on the counting of the number percentage of the powders. The first pulverized silk powder might have consisted of only a limited number of large particles (ca. 20–30 μm) in such an amount that was negligible for counting the number percentage as most of the first pulverized silk powder was around 1–10 μm .

The SEM image of the third pulverized silk powder shows that most of the particles were almost spherical, and the diameters were less than 100 nm; this was consistent with and validated the measurement results from the laser particle size analyzer.

FTIR spectroscopy analysis

The FTIR spectra of the pulverized silk powders shown in Figure 6 confirmed that there were no very great changes in the chemical structure of silk after the pulverization processes. However, the FTIR spectra of the silk fiber and the pulverized silk powders differed from one another only slightly within the ranges of 1020–1240, 1200–1305, and 1350–1475 cm^{-1} . The FTIR spectra illustrated that the second and third pulverized silk powders had a stronger absorbance band within 1020–1240 cm^{-1} than the silk fiber and the first pulverized silk powders, and this might be due to the greater number of primary aliphatic amines present in the second and third pulverized silk powders. The silk

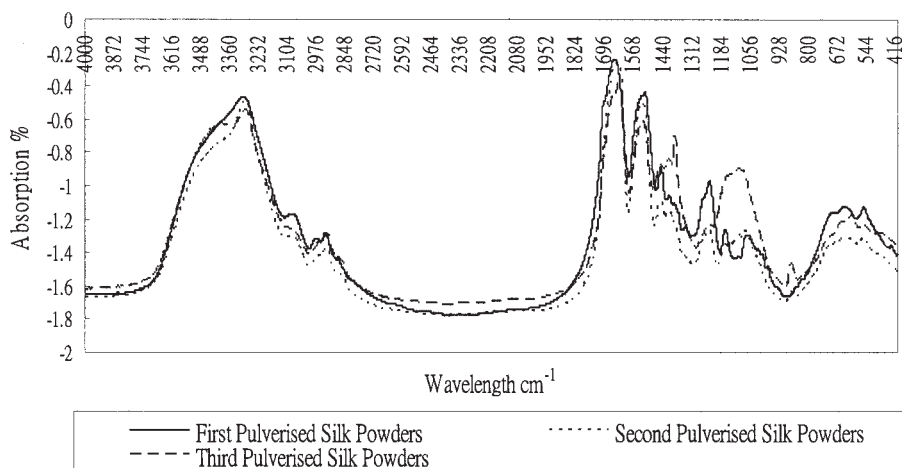


Figure 6 FTIR absorption spectra of the first, second, and third pulverized silk powders.

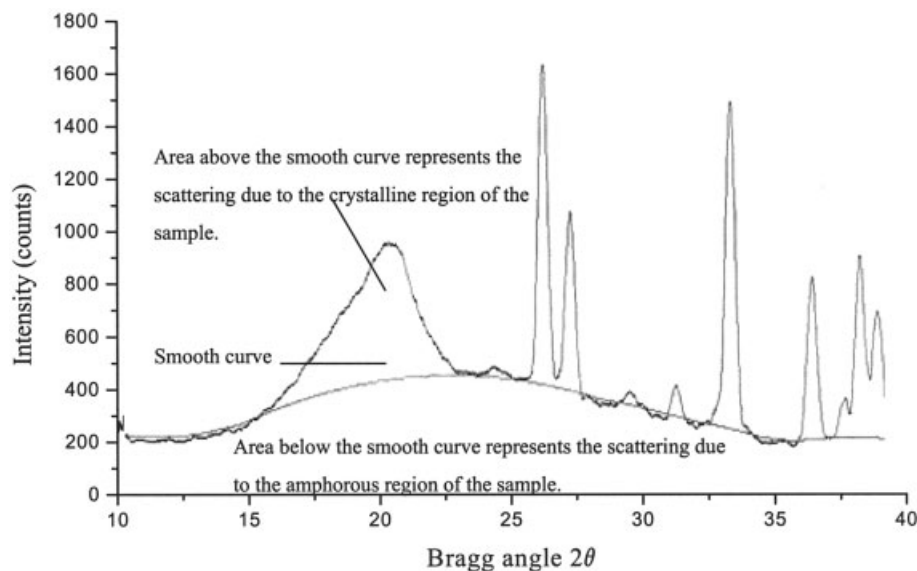


Figure 7 XRD pattern of the first pulverized silk powder with 2θ ranging from 10 to 40° .

fiber and the first and second pulverized silk powders had medium absorption in the region of $1200\text{--}1305\text{ cm}^{-1}$, whereas the third pulverized silk powder did not. This might be due to the presence of the secondary amides in the silk fiber and the first and second pulverized silk powders, but they were absent in the third pulverized silk powder. That the absorbance band within the region of $1350\text{--}1475\text{ cm}^{-1}$ for the third pulverized silk powder was stronger than that of the silk fiber and the first and second pulverized silk powders might be the result of the greater concentration of $\text{C}(\text{CH}_3)_3$ groups of the third pulverized silk in comparison with that of the silk fiber and the first and second pulverized silk powders.¹³

XRD analysis

The XRD evaluation program (Advanced X-Ray Solutions Diffract Plus Release 2000 Eva, version 6.0, Bruker) allowed convenient data transfer and analysis. The method for determining the crystallinity percentage was based on the estimation ratio of the crystalline material to the amorphous material in the sample. It was obtained from the modified XRD intensity profiles by the drawing of a smooth curve through the minima of the principal diffraction effects and the comparison of the areas below and above the curve over an angular range of $2\theta = 10\text{--}40^\circ$. The smoothing curve was generated with the function "Background" of the program Eva.

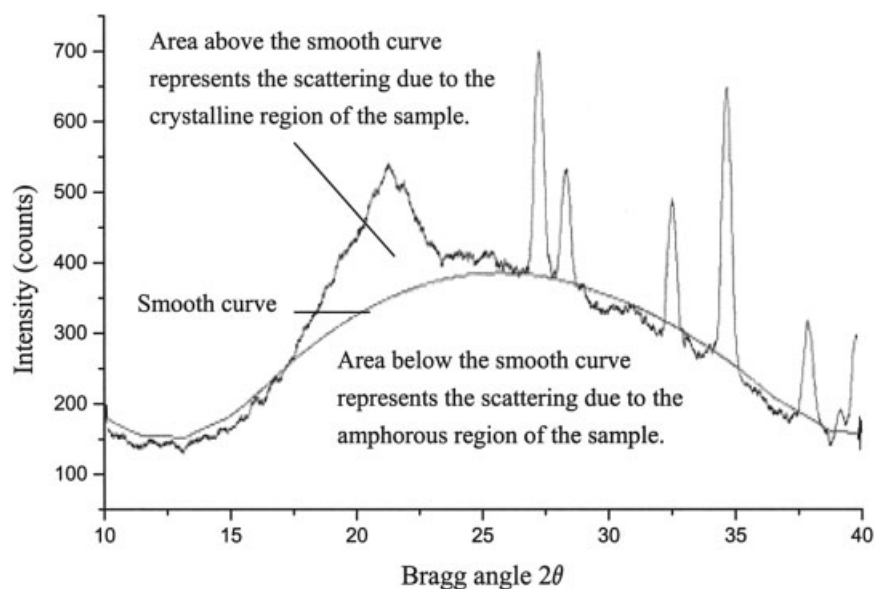


Figure 8 XRD pattern of the second pulverized silk powder with 2θ ranging from 10 to 40° .

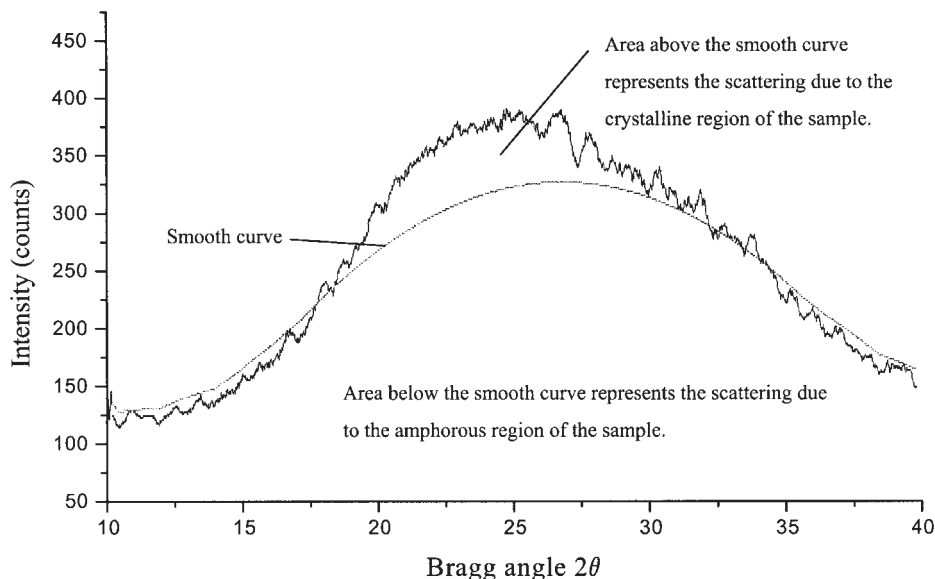


Figure 9 XRD pattern of the third pulverized silk powder with 2θ ranging from 10 to 40° .

The XRD patterns of the samples were divided into crystalline and amorphous regions with a smooth curve, as shown in Figure 7. The area above the curve corresponded to the scattering due to the crystalline region of the sample, whereas the area below the curve responded to the amorphous region.

Figures 7–9 show the XRD intensity of the pulverized silk powders with 2θ ranging from 10 to 40° . The area above the smooth curve represents the scattering due to the crystalline region of the samples. The area above the smooth curve decreased with the smaller particle size of the powders, and this meant that the crystallinity of the powders decreased with their particle size too.

Figure 10 is a graph presenting the crystallinity and amorphous percentages of the powders, which were determined by a comparison of the areas above and below the smooth curve with the aid of the XRD evaluation program. The results showed that the crystallinity percentage of the silk powders decreased from 58.281% for the first pulverized silk powder to 27.085 and 21.821% for the second and third pulverized silk powders, respectively.

CONCLUSIONS

Particle size analysis and SEM images of pulverized silk powders showed that the particle sizes of the

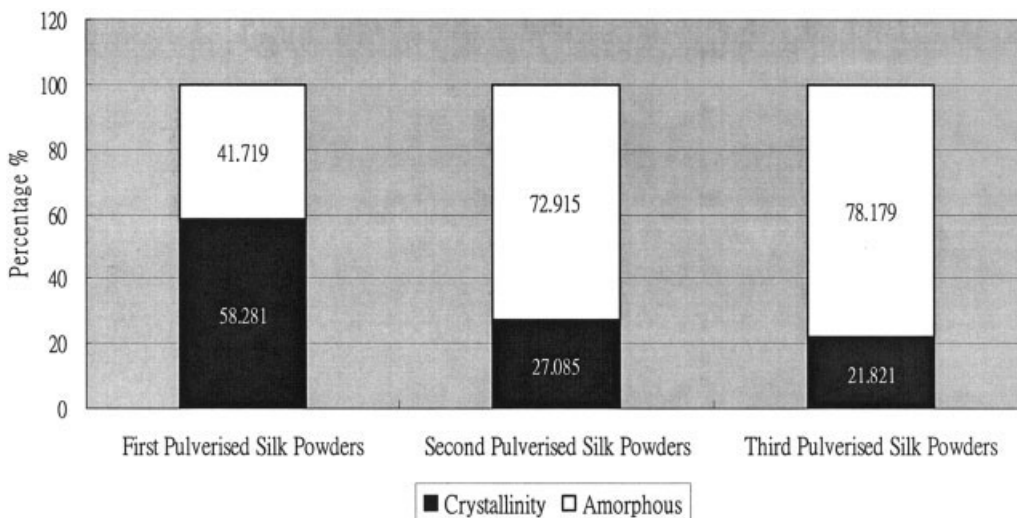


Figure 10 Crystallinity and amorphous percentages of the first, second, and third pulverized silk powders.

silk powders decreased from a microscale to a nanoscale with the progress of the three-stage pulverization. The FTIR spectra of the pulverized silk powders illustrated that there were no substantial changes in the chemical structure of the silk after the pulverization processes. The differences in the FTIR curves showed slight changes in the chemical structure between the samples, indicating that the second and third pulverized silk powders had more primary aliphatic amines than the silk fiber and the first pulverized silk powders. The silk fiber and the first and second pulverized silk powders contained secondary amides, whereas the third pulverized silk powder did not. Also, there were more $C(CH_3)_3$ groups in the third pulverized silk powder than in the silk fiber and the first and second pulverized silk powders. The XRD analysis showed that the crystallinity of the pulverized silk powders decreased with decreasing particle size.

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