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Relationship between processing, surface energy and bulk properties of ultrafine silk particles

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ABSTRACT

Silk particles of different sizes and shapes were produced by milling and interactions with a series of polar and non-polar gaseous probes were investigated using an inverse gas chromatography technique. The surface energy of all silk materials is mostly determined by long range dispersive interactions such as van der Waals forces. The surface energy increases and surface energy heterogeneity widens after milling. All samples have amphoteric surfaces and the concentration of acidic groups increases after milling while the surfaces remain predominantly basic. We also examined powder compression and flow behaviours using a rheometer. Increase in surface energy, surface area, and static charges in sub-micron air jet milled particles contributed to their aggregation and therefore improved flowability. However they collapse under large pressures and form highly cohesive powder. Alkaline hydrolysis resulted in more crystalline fibres which on milling produced particles with higher density, lower surface energy and improved flowability. The compressibility, bulk density and cohesion of the powders depend on the surface energy as well as on particle size, surface area, aggregation state and the testing conditions, notably the consolidated and unconsolidated states. The study has helped in understanding how surface energy and flowability of particles can be changed via different fabrication approaches.

1. Introduction

Silk has a long history of use not only in luxury textiles, but also as a suture material [1]. In recent years, powders from silk fibres have been used in cosmetic applications due to their moisturising, UV absorbing, antibacterial, and antioxidant properties [2,3]. Silk powder has potential applications in coating textiles and other material surfaces. It can be also used as a filler in synthetic fibres and polymeric products. Incorporation of silk powder improves moisture management, handling, dyeing and functional properties in such products [4]. More recently, various forms of silk materials have received considerable interests for potential biomedical, biotechnological, and healthcare applications, thanks to their good biocompatibility, biodegradability and biomechanical properties [5–7]. Among biomedical applications of silk, powdered silk can be used as a resorbable vehicle for biomolecules for diagnostic and tissue engineering applications [7]. Particles have also been used as fillers in composite scaffolds for growing bone tissues [8,9]. Particles may be used as smart sorbents due to their ability to rapidly bind dyes and transition metal ions at ambient temperature [10].

Silk powder can be produced either by dissolving silk fibres followed by liquid–solid phase transfer or by a top-down approach of milling. There are prohibitive challenges associated with the bottom up approach of regeneration due to slow production rate, difficulty in scaling-up and use of harmful chemicals and extent of silk degradation [11]. The top-down approach of milling overcomes many such problems and commercial silk powders are therefore produced mostly by milling. However, as viscoelastic silk fibres are difficult to mill into fine particles, pre-treatments such as chemical hydrolysis, exposure to thermal or radiation energy are often needed to reduce fibre strength and impart brittleness to facilitate milling. In contrast, we have used a combined wet milling/spray drying approach and demonstrated that ultrafine silk particles could be produced without pre-treatments and the particles retained much of the original composition and structures of parent fibres [12,13].

The processing and applications of silk powders require a good understanding of their bulk properties such as cohesiveness, flowability, spreadability, aggregation, and dispersion. For example, flow characteristics are important for their prospective processing and applications such as drug delivery via dry formulations, fluidisation in a coater, filling

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into a powder container or tablet dies from a hopper, or even dispersion in a liquid. Similarly, avoiding aggregation is critical in particle production stages such as wet grinding and spray drying. Good compressibility and flowability will be useful for their applications in moulding or 3D printing. Many bulk properties of powders are dependent on their surface free energy. The surface energy of a particle is the analogue of the surface tension of a liquid. A high surface energy means a more reactive surface, which has important implications in processes involving interfacial interaction, as happens in wetting, coating, mixing, compaction, cohesion and adhesion [14,15]. In other words, surface energy determines the interactions between particles themselves as well as with other surfaces such as binders, polymers, and tissues [16]. However these properties of silk particles have not been well understood. For the first time we have reported quantitative measurements of these properties using two advanced techniques, namely inverse gas chromatography and powder rheology. We have measured surface energy of silk particles to understand how this energy is influenced by the particle size, shape and particle fabrication techniques. Such understanding is relevant for fabricating particles to suit different application needs.

Measurements of surface energy of particles involve determination of long and short-range intermolecular forces, which are commonly described as London dispersive and acid/base interactions respectively. Unlike flat surfaces of materials in which surface energy can be determined by contact angle measurements, in powder materials such measurements are difficult to perform. Compressing powder into pellets for contact angle measurements may change their surface properties. In this work, we have used a Surface Energy Analyser (SEA), which works on the principle of Inverse Gas Chromatography (IGC), a suitable technique for measurement of surface energy of powders. SEA can determine long range dispersive (non-polar) interactions such as van der Waals interactions using non-polar (series of n-alkanes) gaseous probes. By using polar gaseous probes, the specific short range (polar) interactions can be determined, which involve charge redistribution as exemplified by the formation of weak chemical bonds, such as the hydrogen bonds [17].

Apart from measurement of surface energy in static conditions, powder bulk properties under dynamic conditions have been measured using powder rheometry. These measurements provide data on compressibility, flow energy and frictional energy (shear forces) during particle movement, which relate to particle flowability, and the degree of particle cohesion. Powder rheometer measurements were obtained in both consolidated and unconsolidated forms. Understanding bulk properties and the ability to predict cohesion and flow properties of powders are important for two reasons. First, such knowledge helps in designing particles for specific applications. Second, it helps process control during powder production such as minimising batch to batch variations. Finally, the relationships between the bulk and surface properties were analysed by interpreting dynamic properties measured by the powder rheometer using the surface energy data form SEA.

2. Material and methods

2.1. Silk degumming

Eri silk cut cocoons were purchased from Fabric Plus Ltd. (India). Eri silk is less popular for textile applications as its cocoons are not reelable into continuous filaments. However Eri is more disease resistant than other commercial silkworm silk varieties, and its host plants are available in wide climatic conditions. Therefore it is an attractive silk for biomaterials applications. Moreover Eri is relatively easy to mill into powders compared to other silkworm silk varieties [18]. Hence we have used Eri silk in this study. They were degummed in a laboratory dyeing machine (Thies Gmbh, Germany) using laboratory grade sodium carbonate 2 $g \cdot l^{-1}$ and sodium dodecyl sulphate (Sigma Aldrich) 0.6 $g \cdot l^{-1}$ at 100 °C with a material (g) to liquor (l) ratio 1:25 for 120 min. To reduce fibre strength for improving milling time for part of the material, intensive degumming was performed using sodium carbonate with concentration 10 $g \cdot l^{-1}$ and temperature of 120 °C.

2.2. Milling

Milling was performed as reported previously [12]. Briefly, degummed silk fibres were chopped in a cutter mill (Pulverisette 19, Fritsch Gmbh, Germany), fitted with a 1 mm grid and operating at 2888 rpm. Chopped snippets were then wet milled for 6 h in a stirred media mill (1S Attritor, Union Process, USA). In the case of intensively degummed silk, the milling time was 3 h. The stirrer speed was set at 280 rpm and 20 kg of yttrium doped zirconium oxide balls of 5 mm diameter were used as the milling media. The batch size was 200 g of snippets in 2 L of deionised (DI) water. Cooling water (approximately 18 °C) was circulated through the vessel jacket to keep the product temperature low during milling. After wet milling, the slurry was spray dried (B-290, Buchi Labortechnik AG, Switzerland) to recover the silk powder using the following conditions: inlet temperature 130 °C, pump setting 25% (18–20 $ml \cdot min^{-1}$), and aspirator setting 100% (42.5 $m^3 \cdot h^{-1}$). A proportion of the spray dried powder was kept for characterisation and the remaining powder was air jet milled (2 inch Sturtevant micronizer, USA) with a grinding air pressure of 110 psi. Powder was fed into the air jet mill at a rate of 200 $g \cdot h^{-1}$ utilizing a powder hopper feeder (K-Tron, USA). Table 1 shows the nomenclature of the different samples used in this study.

2.3. Particle size distribution

Particle size distributions were measured using a Mastersizer 2000 (Malvern Instruments, UK) fitted with Hydro 2000S. The dispersion medium was DI water. Data analysis was performed by the Malvern software using the following material parameters: refractive index of eri silk 1.542, imaginary refractive index (absorbency) of 0.1. Each sample was measured four times.

2.4. Scanning electron microscopy

The morphology of gold sputter coated particles was observed under a scanning electron microscope (Zeiss LEO 1530 FEG-SEM, Germany) at 5 kV accelerated voltage and 6–7 mm working distance.

2.5. Surface energy analysis

All analyses were carried out using the surface energy analyser (SEA, Surface Measurement Systems, UK). SEA works on the principle of inverse gas chromatography (IGC). A known volume of a known vapour is passed through a column containing the materials (in this case silk fibres and powders) under investigation. The time required for elution of vapour probes depends on the interaction with the solid surface and the elution peaks obtained give information about the surface properties of the material. SEA allows an accurate measurement at extremely low partial pressures of probe gases. It can operate in the Henry range (linear portion of the isotherm) where only high-energy sites in the absorbent are accessed by the probe molecule and there is no solute–solute (probe–probe) interaction [19]. It allows the detection of very small differences between materials.

Table 1
Materials used in the study.

Type of silk materials	Nomenclature
Degummed Fibre	F
Silk fibre–degumming–cutting–attritor milling 6 h–spray drying to get powder	AM
Air-jet milling of AM powder	AM-AJM
Silk fibre–intensive degumming–cutting–attritor milling 3 h–spray drying to get powder	ID-AM