Structure and Dyeability of *Bombyx mori* Silk Fibers with Different Filament Sizes

MASUHIRO TSUKADA,[1,*] MASAHIRO OBO,[1] HIROSHI KATO,[1] GIULIANO FREDDI,[2] and FABIO ZANETTI[2]

[1]National Institute of Sericultural and Entomological Science, Tsukuba City, Ibaraki 305, Japan, and [2]Stazione sperimentale per la Seta, via Giuseppe Colombo, 81, 20133 Milano, Italy

SYNOPSIS

This study deals with the analysis of structure, physical properties, and dyeing behavior of silk fibers with different filament sizes. Fine and coarse silk fibers were obtained from Akebono and Ariake cocoon varieties, respectively. Both samples exhibited a fairly similar x-ray crystallinity, while the degree of molecular orientation increased with decreasing the fiber size. Tensile strength and energy of fine silk fibers were significantly higher, while elongation at break did not change in relation to the fiber size. Fine silk fibers exhibited a slightly higher thermal stability, as shown by the upward shift of both the DSC decomposition temperature and the TMA final extension step at above 300°C. The TGA and DMA (E'') patterns remained unchanged regardless of fiber size. The amino acid analysis confirmed the absence of any difference of chemical structure between fine and coarse silk fibers, the content of acidic, basic, and other characteristic amino acid residues being exactly the same. Accordingly, both samples adsorbed the same amount of hydrochloric acid. Exhaustion dyeing tests with various direct, acid, and reactive dyes showed the occurrence of appreciable differences in the perceived color between fine and coarse silk fibers. The size of color difference was quantitatively evaluated by reflectance measurements and discussed in relation to silk fiber morphology, structure, as well as dyeing conditions. The kinetics of diffusion of two model dyes was not significantly affected by the different fiber size and structure. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

As a natural fibrous polymer, *Bombyx mori* silk is characterized by an intrinsic variability of fiber properties that affects both textile processing and end-use performance. The silk filament obtained from a single cocoon exhibits noticeable morphological and structural changes along its length, for instance, sericin content, filament size, longitudinal, and cross-sectional shape, degree of crystallinity and orientation, etc.[1–3] An appreciable degree of variability also exists from cocoon to cocoon in a single race, while the differences may be even larger if cocoons of different races are compared. These features mostly depend on the physico-chemical aspects of the spinning process carried out by the silkworm,[1] as well as on the physiology and biology of the silkworm itself and on rearing conditions[4] (temperature, humidity, type of diet, etc.).

In addition to the natural variability, processing conditions are known to exert a significant influence on the properties of silk. Early stage processes (cocoon drying, cooking, reeling and rereeling) consist in a sequence of thermal and mechanical treatments carried out in dry and wet conditions that may strongly affect the physical structure of silk fibers.[5,6] Therefore, a different behavior during processing is often observed for silk lots of different origin. The differences can be partly concealed during the subsequent processing stages, for instance, weaving, degumming, dyeing/printing, and finishing. However, it often occurs that they are emphasized, dyeing being the most critical phase for revealing defects related to changes in the inherent physical structure of silk fibers. A typical example is the appearance

of stripes showing different color intensity and hue on dyed silk fabrics.

Iizuka[1] conducted a systematic investigation on silk fibers obtained from a large number of silkworm races and found that the size of the silk filament plays the major role in determining the physical structure and mechanical properties of the fibers. This conclusion applies not only to silk fibers obtained from different cocoons, but also to different sections of the same cocoon filament, which may show changes in fiber size. These findings are important in determining processing conditions and end-uses of silk, because fiber size and structure are closely related to the functional performance and appearance of silk goods (handle, comfort, luster, etc.). For example, silk fibers with a very fine size, obtained from selected silkworm varieties, have been applied for the preparation of a conjugate silk-polyester yarn used for stocking manufacture.[7]

The aim of this study is to investigate the relation between structure and properties of silk fibers, with particular emphasis on the change in dyeing behavior as a function of the fiber size. The crystalline structure, molecular orientation, physico-mechanical and thermal behavior of two silk samples with different filament size were studied. The results of a large number of dyeing tests carried out with direct, acid, and reactive dyes selected among the most widely applied for silk dyeing are discussed in relation to the changes in fiber structure and morphology. These results may contribute useful scientific and technological information leading to improve the current silk processing techniques, as well as to understand the origin of some defects that often impair the quality of silk goods.

EXPERIMENTAL

Materials

Fine and coarse *Bombyx mori* silk fibers were obtained by reeling Akebono (Nichi 505-Nichi 506 × C505-C506) and Ariake (Nichi 509-Nichi 510 × C509-C510) cocoon varieties, respectively. Sericin was removed by degumming raw silk yarns with an aqueous solution containing 5 g/L soap and 2 g/L anhydrous sodium carbonate, at 95–98°C for 45 min. Yarn samples were thoroughly rinsed with warm and cold distilled water and dried at room temperature.

Exhaustion dyeing tests were carried out with different direct, acid, and reactive dyes purchased from Nippon Kayaku Co., Ltd. and Sumitomo Chemical Co., Ltd. Dyeing conditions and recipies conformed

the manufacturer suggestions. Dyed samples were taken out, rinsed carefully, and dried at room temperature before successive measurements.

Isothermal dyeing tests at constant dye concentration were carried out in a thermostatic bath (capacity: 11 L), under constant stirring (100 rpm). Commercial acid dyes, Acid Red PG (C.I. Acid Red 85) and Acid Orange II (C.I. Acid Orange 7), purchased from Nihon Kayaku Co., were used at a concentration of 75×10^{-5} eq/L. Dyeing conditions were pH 6 and 80°C for Acid Red PG, and pH 4 and 60°C for Acid Orange II. pH was adjusted with an acetic acid-sodium acetate buffer solution. The amount of silk yarn dyed was 0.6 g. The dyeing tests were carried out in duplicate. Dyed samples were taken out at different times (2, 5, 10, 15, 30, and 180 min), thoroughly rinsed with hot water, and dried at room temperature. The adsorbed dye was removed by extraction with a 50% pyridine aqueous solution at 60°C for 90 min, and the dye concentration (C_t) was determined spectrophometrically. The amount of dye adsorbed at 180 min was used as saturation value (C_∞).

Measurements

The x-ray diffraction intensity curves were obtained at a scanning rate of 1°/min, with a diffractometer Rigaku Denki Co., Ltd., using the CuKα radiation ($\lambda = 1.54$ Å). The voltage and current of the x-ray source were 40 kV and 20 mA, respectively.

The refractive indices parallel and perpendicular to the fiber axis were measured with the Beche's line method, using a polarized microscope under the monochromatic light (Na light) in standard conditions (20°C and 65% relative humidity). The conditions for measurements were described in detail elsewhere.[8]

The width of the degummed silk filament was measured by means of an optical microscope (Orthoplan, Leitz) connected to an image analysis system (ASM 68K, Leitz). Four hundred fibers per sample were measured.

Tensile properties were measured in standard conditions with a Tensilon UTM-II (Toyo Boldwin Co., Ltd.) tensile tester machine. The rate of strain was 20 mm/min on samples of 50 mm length. Each reported value is the average of 7 and 12 measurements for fine and coarse silk yarns, respectively.

Differential scanning calorimetry (DSC) measurements were performed on a Rigaku Denki Co., Ltd. instrument (model DSC-10A) at a heating rate of 10°C/min. The DSC range and sample weight were 2.5 mcal/s and 2 mg, respectively. The open

aluminium cell was swept with N_2 gas during the analysis.

A Rigaku Denki Co., Ltd. instrument (model CN-8361) for thermomechanical analysis (TMA) was used to detect the thermal contraction and expansion properties in the course of heating. The heating rate was 10°C/min, and dry N_2 gas provided the inert atmosphere. TMA full scale and the initial load applied to the sample were ± 500 μm and 1 g, respectively.

Thermogravimetric analysis (TGA) was run under N_2 on a Rigaku Denki Co., Ltd. instrument. The heating rate was 10°C/min and the temperature range studied was from 25 to 400°C. Sample weight and TGA full scale were both 5 mg.

Dynamic mechanical (DMA) properties were measured using a Toyoseiki Rheolograph Solid-S. The frequency of oscillation was adjusted to 10 Hz. The temperature range studied was from 25 to 260°C. Samples were heated at 2°C/min. The sample length was 15 mm, with an initial tension of 30 gf.

Silk fibroin fibers were hydrolyzed by heating at 110°C for 20 h, under vacuum in HCl 6 N. The hydrolyzed samples were filtered through a glass disk, dried in a rotary evaporator at 40°C, and dissolved in a buffer solution at pH 2.2 (1 mg/mL). The amino acid composition was determined by using a Hitachi L-8500 rapid amino acid analyzer.

HCl adsorption tests were performed by immersing silk fiber samples in different HCl solutions (0.01, 0.025, and 0.05 N) at 2°C for 4 days. The material-to-liquor ratio was 1 : 80. The amount of acid adsorbed was determined by titration with NaOH (Hiranuma TB-I autotitrator). The adsorption tests were carried out in duplicate.

The size of color difference (ΔE) was calculated according to the CIELAB system (ISO 7724/3-84), using the tristimulus values obtained from the reflectance measurements carried out with a Shimadzu Seishakusho spectrophotometer (model UV-3100S). L, A, and B values of coarse silk fibers were used as standard.

The concentration of standard dye solutions and dye extracts was determined with a Shimadzu Seishakusho spectrophotometer (model UV-3100S) at a wavelength of 510 and 484 nm for Acid Red PG and Acid Orange II, respectively.

RESULTS AND DISCUSSION

Crystalline Structure and Molecular Orientation

The structure of fine and coarse silk fibers was studied by means of optical and x-ray diffraction mea-

surements. While optical properties are a useful source of information about the overall fiber structure, including crystalline, laterally ordered,[9] and amorphous regions, x-ray data permit to elucidate some structural details specific of the crystalline domains.

The wide angle x-ray diffraction profile of both fine and coarse silk fibers (curves not shown) exhibited a prominent and broad 2 θ peak at 20.5°, corresponding to the crystalline spacing of 4.39 Å. This pattern is typical of silk fibroin with oriented β-sheet crystalline structure.[10] The degree of orientation and crystallinity were determined from the x-ray diffraction data and listed in Table I, together with the values of birefringence (Δn) and isotropic refractive index (n_{ISO}) calculated from the refractive indices parallel and perpendicular to the fiber axis.

Fine silk fibers exhibited a Δn value significantly higher than the coarse ones. Accordingly, a higher value of molecular orientation was obtained from x-ray diffraction measurements. These results suggest that fine fibers are characterized by a more advanced fibrous structure, for instance, the crystal axes in the crystalline regions and the individual molecules in the amorphous regions are better aligned along the fiber axis. These features might depend on several factors related to the spinning process carried out by the silkworm. Changes in spinning rate, shear rate, fibroin concentration, and size of silk glands (spinneret) have been reported to affect the structure and morphology of the newly spun filament.[1]

The values of x-ray crystallinity of fine and coarse silk fibers did not show significant changes in relation to the fiber size. The same comment applies to the values of n_{ISO}, an optical parameter that can be related to the fiber structure, such as crystal content, density, etc. Iizuka[1] observed large changes in crystallinity and size along the length of an individual cocoon filament. While the size decreases from the outer to the inner portions of the cocoon thread,

Table I Molecular Orientation and Crystallinity of Fine and Coarse Silk Fibers

	Fine Fiber	Coarse Fiber
Birefringence (Δn)	0.048	0.042
Isotropic Refractive Index (n_{ISO})	1.554	1.554
Molecular Orientation[a] (%)	91	86
Crystallinity[b] (%)	~ 23–24	~ 23–24

[a] Calculated from the x-ray diffraction curves.
[b] Calculated from the x-ray diffraction curves according to the Hermans' method.[11]

crystallinity increases. Moreover, there exists a noticeable variability from cocoon to cocoon. Because the silk yarn samples examined in this study were formed by adjacent fibroin filaments belonging to different cocoon layers, as well as to different cocoons, the inherent variability of each cocoon variety was averaged. We can, therefore, reasonably assume that fine and coarse silk fibers exhibited the same average value of x-ray crystallinity.

Tensile Properties and Fiber Size

The tensile behavior is an important factor in the assessment of the properties and functional performance of textile fibers. Studies on both natural and synthetic fibers gave experimental evidence that tensile strength increases with increasing molecular orientation.[12] The results listed in Table II are consistent with literature data. Fine silk fibers with a higher degree of molecular orientation displayed values of breaking load and tenacity significantly higher than coarse fibers. On the other hand, elongation at break remained unchanged regardless of fiber size. The behavior of both tenacity and elongation resulted in higher energy values for fine silk fibers, because they required a higher load to break. These experimental results agree with those reported by Iizuka,[1] who found that the finer the fiber size, the higher the tenacity of silk, with a negative linear correlation between the two variables.

Besides influencing the tensile behavior of silk, the size is known to affect other fiber properties, such as handle, luster, and dyeability. The relation between size and dyeability can be expressed in terms of specific surface, for instance, surface area relative to the fiber mass. On a weight basis, the size of coarse silk fibers was about twice than that of fine fibers (Table II). In order to estimate the respective values of specific surface, we measured the filament width (Table II). Assuming a triangular shape for the cross-section and a density of 1.349 g/cm^3,[3] a single silk filament can be regarded as a triangular prism, whose surface area and mass can be easily calculated. The values of specific surface were 4404 and 3068 cm^2/g for fine and coarse silk fibers, respectively. This difference might be considered large enough to influence not only the kinetics of dye adsorption during dyeing, but also the optical appearance of dyed silk fibers.

Thermal Behavior

Thermal analysis is a useful tool for monitoring important processing and end-use properties of textile fibers. Besides other factors, the response to a thermal treatment may depend on the structure and morphology of all phases forming the fibrous polymer.

The DSC thermograms of silk fibers (Fig. 1) are characterized by a broad endothermic transition attributed to the thermal decomposition of silk fibroin with oriented β-sheet crystalline structure.[13] The shape and intensity of the endotherm did not change in relation to the fiber size. However, the peak temperature slightly moved upwards with decreasing the fiber size, occurring at 306 and 312°C for coarse and fine silk fibers, respectively. This behavior might be due to the different molecular orientation of the silk samples examined. In fact, the higher the molecular orientation and crystallinity, the higher the decomposition temperature of silk. While amorphous silk fibroin membranes decompose at about 280°C, crystallization to β-sheet structure usually enhances the peak temperature to about 290–295°C.[14,15] Only

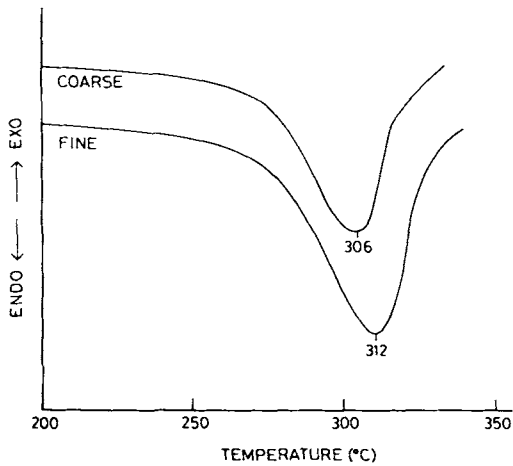## Table II   Tensile Properties of Fine and Coarse Silk Fibers

	Fine Fiber	Coarse Fiber
Width of silk filament (μm)	11.7 ± 0.3	16.8 ± 0.4
Size (d)		
Bave	2.3	4.2
Yarn	196	193
Breaking load[a] (g)	628 ± 13	561 ± 12
Tenacity (g/d)	3.2	2.9
Elongation at break[b] (%)	23.5 ± 0.8	22.4 ± 0.9
Energy[c] (gf × mm)	5127 ± 323	4677 ± 256

Significance level of $t(17, 95\%)$ = 2.11.
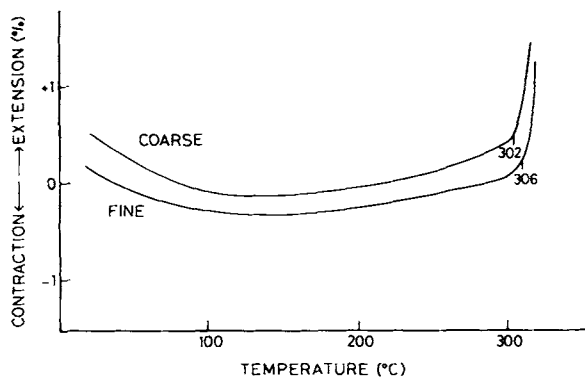[a] $t(17, 95\%) \gg 2.11$.
[b] $t(17, 95\%) \cong 2.11$.
[c] $t(17, 95\%) > 2.11$.

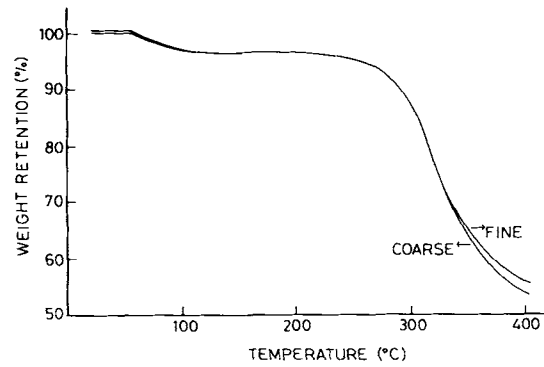**Figure 1**   DSC thermograms of fine and coarse silk fibers.

Figure 3   TGA curves of fine and coarse silk fibers.

well-oriented and crystallized silk fibroin materials, such as the fibers spun by the silkworm, decompose at a temperature higher than 300°C. The value of peak temperature may range from 310 to 315°C, in relation to the origin and to the intrinsic properties of the fibers, the molecular orientation being one of the most important parameters.

The dimensional changes of fine and coarse silk fibers as a function of the temperature were studied by means of TMA measurements (Fig. 2). The TMA profiles are characterized by an initial region of shrinkage from room temperature to about 100°C, essentially due to the loss of moisture, followed by a region of slight but continuous extension until about 300°C. The final abrupt extension, coinciding with the thermal degradation of the fibers, occurred at 302 and 306°C for coarse and fine silk fibers, respectively. This pattern is consistent with the above DSC data, confirming that fine silk fibers with a higher degree of molecular orientation displayed a fairly higher thermal stability.

Figure 3 shows the TGA curves of silk fibers with different size. The percentage of weight retention decreased sharply beyond 300°C, due to thermal degradation. The curves of fine and coarse silk fibers coincided, because TGA response mainly reflects the chemical constitution rather than the physical microstructure of fibrous polymers. Though changes in TGA behavior as a function of crystallinity and molecular orientation of fibers have been reported,[16] the difference between fine and coarse silk fibers is probably too small to give rise to changes detectable by TGA analysis.

Figure 4 shows the temperature dependence of the dynamic loss modulus (E'') of fine and coarse silk fibers. The changes in loss modulus can be related to major transitions of silk fibers, such as the glass transition temperature (T_g),[17] as well as to the thermally induced molecular motion of the fibroin chains in the crystalline regions.[18] Fine and coarse silk fibers did not show significant differences of dynamic mechanical behavior. Magoshi et al.[17] reported that the loss modulus of silk fibroin is significantly affected by the degree of crystallinity, the loss peak shifting to higher temperature following

Figure 2   TMA curves of fine and coarse silk fibers.
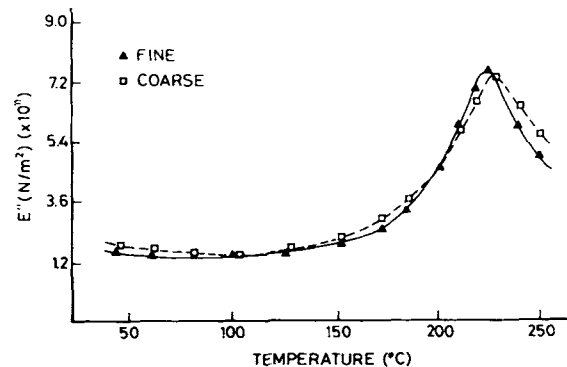
Figure 4   Dynamic loss modulus curves (E'') of fine and coarse silk fibers.

Table III   Amino Acid Composition of Fine and Coarse Silk Fibers

Amino Acid (mol %)	Fine Fiber	Coarse Fiber
Aspartic acid	1.64	1.65
Threonine	0.88	0.89
Serine	10.65	10.66
Glutamic acid	1.23	1.22
Glycine	45.09	45.06
Alanine	29.28	29.29
Valine	2.49	2.48
Cystine	n.d.	n.d.
Methionine	0.15	0.16
Isoleucine	0.75	0.79
Leucine	0.52	0.51
Tyrosine	4.95	4.97
Phenilalanine	0.72	0.73
Lysine	0.35	0.34
Histidine	0.19	0.18
Arginine	0.50	0.51
Proline	0.61	0.56

random coil→β-form conformational transition and crystallization of amorphous silk fibroin membranes. Accordingly, fine and coarse silk fibers with the same degree of crystallinity displayed a closely similar dynamic mechanical behavior. The influence of molecular orientation in restricting the chain movement and rising the loss peak temperature has been demonstrated for synthetic[12] but not for silk fibroin fibers. The results reported in this study seems to exclude a strong effect of molecular orientation on the dynamic loss modulus of silk fibers. However, this conclusion should be limited to the samples examined and to the experimental conditions adopted. Further investigations are needed to elucidate this aspect of the thermal behavior of silk fibers with variable degrees of molecular orientation.

Dyeing Properties

As a protein fiber, silk is a polyampholite with cationic and anionic groups. Therefore, it can be dyed and printed with various basic, acid, metal complex, and reactive dyes. Of these, the acid dyes are the most widely used and have received most attention from the scientific and technological point of view. Because it is expected that the uptake of acid dyes is closely related to the presence and amount of ionizable amino and carboxyl groups carried by basic and acidic amino acid residues, we compared the amino acid composition of fine and coarse silk fibers (Table III). The results of the chemical analysis

show that there are no differences between the two samples, the content of acidic, basic, and other characteristic amino acid residues being exactly the same.

The adsorption of simple acids has often been used as a model to investigate the mechanism of acid dye uptake.[19] When silk is immersed in an aqueous solution, the net charge of the protein depends on the ionization of its amino and carboxyl groups, which in turn, is pH dependent. Table IV lists the values of hydrochloride acid adsorption of silk fibers with different size. At pH values $\leq$ 2, the amino groups of lysine, histidine, and arginine are completely dissociated, while the carboxyl groups of aspartic and glutamic acid are undissociated. Therefore, the net charge is positive, the maximum amount of acid bound being determined by the number of basic groups present. The results obtained show that fine and coarse silk fibers adsorbed the same amount of HCl regardless of fiber size and HCl concentration. These findings are in agreement with the results of amino acid analysis, suggesting the absence of difference of chemical structure between the two fiber samples. The adsorption of HCl in excess of the amino group content is consistent with literature data,[19] and might have been caused either by the possibility that amide groups act as basic sites at very low pH and adsorb hydrogen ions, or by the formation of new free amine groups due to hydrolysis of the peptide bond in strong acidic conditions.

Table V lists the results of a series of exhaustion dyeing tests carried out on fine and coarse silk fibers by using different direct, acid, and reactive dyes, as well as different dyeing conditions. The size of color difference was quantitatively expressed by calculating the ΔE values, according to the CIELAB color space equations.[20] ΔE ranged from 0.2 to 5.7, indicating the occurrence of large color differences between fine and coarse silk fibers, regardless of the

Table IV   Acid Adsorption (HCl) of Fine and Coarse Silk Fibers

	Fine Fiber	Coarse Fiber
Equivalent number of basic groups[a] (mEq/g)	0.137	0.136
Equivalent number of acidic groups[a] (mEq/g)	0.379	0.379
Adsorption of acid (mEq/g)		
HCl 0.01	0.152	0.160
HCl 0.025	0.192	0.200
HCl 0.05	0.288	0.276

[a] By amino acid analysis (see Table III).

**Table V   Size of Color Difference between Fine and Coarse Silk Fibers**

#[a]	Color Index	ΔE	ΔL[b]	ΔA[b]	ΔB[b]	ΔC[b]	ΔH
1	Direct red 242	2.187	−0.189	−1.877	−1.107	−2.168	0.224
2	Direct blue 200	2.146	1.951	−0.473	0.759	−0.787	0.425
3	Direct black 17	0.667	0.281	0.250	−0.551	0.605	0.011
4	Direct black 154	1.289	1.075	−0.595	−0.392	0.623	0.345
5	Acid red 52	1.300	0.042	0.643	−1.129	1.010	0.816
6	Acid yellow 110	1.352	0.713	−1.147	0.075	0.345	1.096
7	Acid blue 129	3.788	1.706	−2.446	2.337	−2.889	1.764
8	Acid violet 48	5.175	3.778	−2.490	2.511	−3.416	0.915
9	Acid red 111	1.761	−1.101	−1.177	−0.710	−1.368	0.134
10	Acid black 109	0.968	−0.123	0.104	−0.954	0.951	0.127
11	Acid red 256	2.320	−2.249	−0.557	−0.122	−0.552	0.143
12	Acid black 155	0.749	−0.518	0.521	−0.146	0.491	0.228
13	Acid brown 297	2.793	−2.706	0.545	0.432	0.654	0.236
14	Acid blue 229	3.050	−1.909	0.459	−2.334	2.373	0.167
15	Acid red 114	1.777	1.417	−0.563	−0.911	−0.774	0.741
16	Acid black 109	1.489	1.033	0.170	−1.059	1.070	0.076
17	Acid red 256	5.728	5.269	−2.047	−0.930	−2.008	1.009
18	Acid black 155	0.224	0.181	0.120	0.055	0.063	0.115
19	Acid brown 297	4.212	4.150	0.502	0.518	0.640	0.333
20	Acid blue 229	1.956	1.510	0.072	−1.241	1.217	0.254
21	Reactive red 22	0.743	0.419	−0.094	−0.606	−0.148	0.595
22	Reactive blue 231	4.079	2.199	0.502	3.399	−2.815	1.970
23	Reactive orange 13	2.290	1.730	−1.249	−0.832	−1.494	0.138

[a] Dyeing tests # 1–14 and # 15–20 were conducted in acidic and neutral bath conditions, respectively.
[b] L, A, and B values of coarse silk fibers were used as standard.

dye class and dyeing conditions. Because ΔE does not give any information on the nature of the color difference, we should refer to its components (ΔL, ΔA, ΔB), that indicate the relative position of coarse (standard) and fine (sample) fibers in the CIELAB space. ΔL is a quantification of the difference in lightness, for instance, its value is positive if fine fibers are lighter than coarse fibers, negative if darker. The bar diagram of Figure 5 shows that in most cases fine silk fibers appeared lighter than the coarse ones (positive ΔL values), the extent of the difference changing from dye to dye. The lighter appearance of fine silk fibers may be simply considered as an optical effect due to the finer fiber size. However, some acid dyes applied in acidic bath conditions (tests 10–14) resulted in darker colors (negative ΔL values), while the same dyes applied in neutral bath (tests 16–20) gave lighter colors. These results sug-
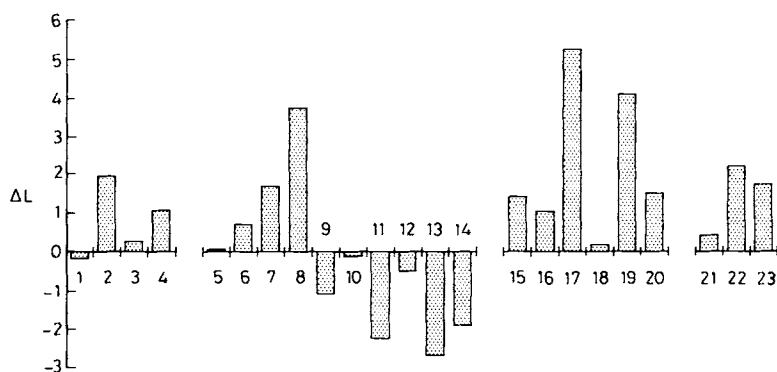
Figure 5   Difference of lightness (ΔL) between fine and coarse silk fibers. Positive and negative ΔL values mean that fine silk fibers are lighter and darker, respectively, than coarse silk fibers. Refer to Table V for dyeing test number.

gest that not only the fiber size, but also the dyeing conditions may affect the final result of the dyeing process.

Additional information on the nature of the color difference are given by other parameters listed in Table V. ΔC and ΔH indicate the difference in chroma and hue, respectively, between dyed samples. A positive ΔC value means that a sample has a higher chroma (amount of pure chromatic color or brightness of color) than the standard. ΔH is indeterminate with regard to the sign and its value indicates the size of any hue difference. Also, these data confirm that the difference between fine and coarse silk fibers was sometimes quite large. Moreover, it was clearly detectable by visual inspection, so that its occurrence on a textile material in form of dark or lightly colored stripes might have been a source of controversy.

Due to the complexity of the dyeing system, it is difficult to attribute the above dyeing behavior of fine and coarse silk fibers to a specific parameter. Changes in dye bath composition and pH may influence the degree of association of the dye molecules both in solution and in the pores within the fiber matrix, therefore affecting the adsorption and diffusion stages. For example, a higher molecular orientation and/or crystallinity might become a limiting factor for the diffusion of large aggregates formed by self-associated dye molecules. Changes in the ionization state of the fiber as a function of the pH may also modify the dye-fiber forces active during dyeing, especially the mutual electrostatic attraction, which plays an important role in dyeing protein fibers. Moreover, some morphological (specific surface) and structural (molecular orientation) features of the fibrous substrate might influence the kinetics of dye adsorption and diffusion,[21] causing an uneven distribution of the dye between fine and coarse silk fibers, especially when they are present in the same bath and compete for a limited amount of dye, as is the case of exhaustion dyeing.

The study of the isothermal diffusion of two acid dyes (C.I. Acid Orange 7 and C.I. Acid Red 85) in conditions of constant dyeing bath concentration was preliminarily attempted in order to investigate the dyeing behavior of fine and coarse silk fibers. By applying the equation for diffusion proposed by Vickerstaff[22] to the initial stages of dye uptake, the plot of C_t/C_∞ against $t^{1/2}$ resulted in straight lines (Fig. 6). The slope of the curve is proportional to the square root of the diffusion coefficient. The results show that the rate of diffusion was higher for the dye with the smallest molecular size (C.I. Acid Orange 7). No significant differences of dye diffusion
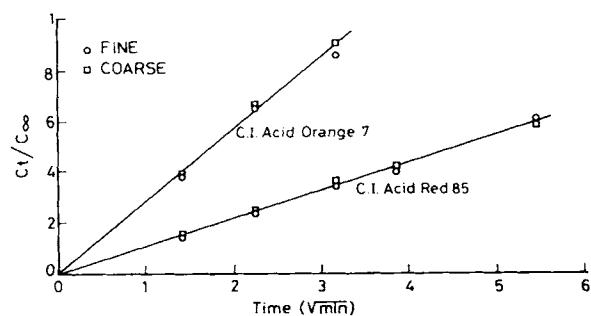

Figure 6 Diffusion of C.I. Acid Orange 7 and C.I. Acid Red 85 into fine and coarse silk fibers.

were observed between fine and coarse silk fibers, as shown by overlapping of the experimental data. These findings permit to presume that, in the experimental conditions adopted and with the dyes used, the difference of structure and morphology between the fibers was not so large as to influence adsorption of dye molecules at the fiber surface, as well as to impose a restraint on their diffusion within the fiber matrix by steric hindrance and/or by reducing the accessibility of internal adsorption sites. However, this hypothesis must be regarded as a subject still open to investigation. Because the number of factors that may conspire to influence the dyeing behavior is large, as shown by the results of the exhaustion dyeing tests, a complete understanding of their effect can only be allowed by the knowledge of the basic chemical and structual features of both dye molecule and fibrous polymer.

CONCLUSIONS

The results reported in this study show that changes in silk fiber size are often accompanied by differences of fine structure and properties. Fine silk fibers with a more advanced fibrous structure displayed better tensile performance (higher tenacity) and thermal stability than the coarse ones. These features fit the model of the relationship between fiber size and structure suggested by Iizuka,[1] the size being strongly dependent on silkworm race.

The different fiber structure and morphology is expected to exert a great influence on the dyeing behavior of silk. In fact, exhaustion dyeing tests resulted in such remarkable color differences that most samples would have been rejected if submitted to a color-matching test to assess the acceptability of dyed goods. Such differences would give rise to serious defects if appearing on adjacent areas of the same piece of fabric. Several factors might be con-

sidered responsible for the outcome of the dyeing process, such as dyeing conditions (time, temperature, pH, auxiliaries, etc.), chemical structure, size and shape of the dye molecule, affinity of the dye for the silk substrate, morphology (specific surface) and structure (molecular orientation) of silk fibers, etc. A preliminary study of the diffusion of two model dyes did not permit to ascertain to what extent the different specific surface and molecular orientation could affect the dyeability of fine and coarse silk fibers. Further studies are needed to investigate the relation between silk fiber structure and dyeability.

A large number of process parameters interact each other during dyeing, thus making it difficult to isolate an individual effect, especially under industrial conditions. Therefore, a correct technological approach to silk dyeing should imply awareness of the inherent variability of the fibrous substrate, accompanied by the implementation of suitable procedures for the selection of dyeing recipes and application conditions able to attain a uniformity of color distribution, in order to meet not only the expected standards but also consumer satisfaction.

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