Studies on Indian Silk. III. Effect of Structure on Dyeing Behavior

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ABSTRACT: This third in a series of articles deals with the analysis of the dyeing behavior of two mulberry and three nonmulberry varieties of silk. The results of the dyeing tests carried out were discussed in relation to the physical and chemical structure of the silk fibers. Noticeable differences in the dye uptake were observed among the different varieties of silk. Mulberry varieties showed higher dye uptake compared to that of all three nonmulberry varieties. Among the nonmulberry varieties, tasar shows higher dye uptake followed by eri and muga. Interestingly, dye uptake reduces significantly within a variety from the outer to the inner layers. The reduction within a variety was found to correlate well with the morphological parameters. Determination of morphology of fibers confirmed significant differences in structural parameters such as crystallinity, orientation, density, and birefringence, for example, between and within varieties. An increase in all these parameters was observed as one moves from the outer to the inner layers within a variety. The differences in the dye uptake of different varieties of silk correlated well with the physical as well as chemical structure of silk fibers. Dye uptake differences between the varieties were found to correlate with the end amino groups. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1116–1123, 2004

Key words: silk fibers; microstructure; dyes/pigments; structure–property relations; physicochemical properties

INTRODUCTION

Silk is a protein fiber and a wide range of dyes can be applied onto it, such as acid, basic, direct, metal-complex, and reactive dyes. Among these, acid and metal-complex dyes are the most popular, although recently reactive dyes are increasingly being used because of their excellent wet fastness, thus enabling machine washing.

It is a common knowledge that different silk fibers produced in different parts of the world differ not only in their chemical architecture but also in their morphological properties. Naturally, dye–fiber interaction is bound to vary from one variety to the other. Furthermore, the silk filament obtained from a single cocoon exhibits noticeable changes along its length, for instance, filament size, crystallinity, and orientation[1–3] and any variation in the microstructure is likely to result in differences in dye pick up along the filament length of the same cocoon. A consolidated and well-documented literature is not available that specifically relates to dye–silk interaction and morphological structure. Somashekharappa et al.[4] studied the changes in crystal size of mulberry (bivoltine and multivoltine) silk fibers after dyeing with acid and metal-complex dyes using WAXD studies. The crystal size values were found to decrease from 29.7 to 20.3 Å for acid-dyed fibers and from 29.7 to 21.5 Å for metal-complex–dyed bivoltine silk fibers. Similarly, in the case of multivoltine variety, the values decreased from 18.6 to 12.7 Å for acid-dyed fibers. No significant differences, however, were observed for metal-complex–dyed fibers. Tsukada et al.[5] investigated the dyeing behavior of mulberry silk fibers with different filament deniers. The results of the above study indicated the occurrence of large color differences between fine and coarse silk fibers regardless of the dye class and dyeing conditions. Dye uptake in fine fibers was less and this was attributed to the higher crystallinity and molecular orientation of the finer fibers. However, the authors hypothesized that a thorough investigation would be needed to establish the relationship between silk fiber structure and dyeability. In another study on the effect of grafting on *Bombyx mori* silk fibers, Tsukada et al.[6] reported that the dyeability increased after the silk was grafted with ethoxyethylmethacrylate polymer. This was attributed to modifications in the morphology of the amorphous region of the fiber because of the steric hindrance.

Some attempts have been made to study the dyeing behavior of mulberry silk using low temperature with ultrasonic techniques and using a redox system. In a

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TABLE I
Exhaustion of Acid Dye (Outer Layer)

Variety	*E* (%)
Mulberry (bivoltine)	89.82
Mulberry (crossbreed)	90.30
Tasar	59.10
Muga	57.02
Eri	58.38

study on dyeing of mulberry silk[7] using ultrasound (frequency 20 MHz, output 120 W), it was shown that the dye uptake was increased by 55–95% at a temperature of 35–45°C at shorter time periods (15–30 min). The increase in dye uptake was attributed to the breaking up of dye aggregates and removal of air from the fiber capillaries, thus accelerating the diffusion of the dye. Similar results were obtained on mulberry silk fabrics dyed with acid, basic, and metal-complex dyes.[8] Dyeing of mulberry silk at low temperature using a hydrogen peroxide/glucose redox system was reported by Luo.[9] Results of the study showed that exhaustion and fixation of acid dyes improved because of the increase in the number of dye sites through the action of free radicals, assisting in covalent fixation. The mechanism of improvement in exhaustion and fixation of acid dyes using the above redox system was attributed to the decrease in pH of the dye solution as a result of the decomposition of glucose with hydrogen peroxide.[10]

Most of the studies are confined to mulberry silk. This prior work suggests that the microstructure and mechanical properties of silk show large differences between the different varieties of silk.[11] Significant variations are observed along the filament length within a cocoon as well. All these variations would be expected to result in differences in dye pick up among the different varieties as well as along the filament length within a cocoon.

Based on the above considerations, an attempt was made in this article to study the dyeing behavior of different varieties of silk using acid and disperse dyes and to determine whether any structural correlation is possible both between varieties and within a variety. The results of the dyeing tests were analyzed in relation to the physical and chemical structure of silk fibers. Disperse dyes, although not used commercially, are structurally sensitive and were thus used in the present study to establish structural dependency, if any.

EXPERIMENTAL

Materials

The following five varieties of Indian silk were used for the study: mulberry (bivoltine), mulberry (crossbreed), tasar, muga, and eri.

Sample preparation

The filaments were reeled from the cocoons and degummed according to previously described procedures.[11]

Chemicals used

Acetic acid (LR), ammonium sulfate (LR), ninhydrin (AR), pyridine (LR), sodium propionate (LR), methyl cellosolve (LR), propionic acid (LR), and glycine (AR) (all chemicals were from Merck, Darmstadt, Germany) were used for this study.

Fiber characterization

In a previous study in this series,[12] these silk fibers were characterized using various techniques such as, for example, WAXD, birefringence, density, and sonic modulus. Some of the earlier structural data were used in this article for correlating dyeing behavior.

Estimation of end amino groups

The end amino groups of different varieties of silk were determined using the ninhydrin method as described by Chavan and Nallankilli.[13]

TABLE II
Dye Content on Fiber (Acid Dye, Texacaid Fast Red A)

Variety	Dye uptake (mg/100 g fiber)			Percentage change
	Outer layer	Middle layer	Inner layer	
Mulberry (bivoltine)	2640	2470	2350	11.00
Mulberry (crossbreed)	2700	2600	2570	5.00
Tasar	1786	1665	1605	10.00
Muga	1700	1560	1512	11.00
Eri	1770	1630	1590	10.00

TABLE III
X-ray Crystallinity (X_c) and Density (ρ) Values for Different Varieties of Silk[a]

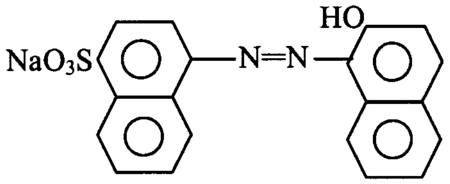
Type of silk	X_c (%) Outer layer	X_c (%) Middle layer	X_c (%) Inner layer	ρ (g/cm^3) Outer layer	ρ (g/cm^3) Middle layer	ρ (g/cm^3) Inner layer
Mulberry (bivoltine)	29.20	37.81	48.82	1.350	1.361	1.365
Mulberry (crossbreed)	28.17	34.95	47.22	1.342	1.350	1.356
Tasar	28.86	30.92	45.71	1.300	1.340	1.348
Muga	26.92	32.37	45.85	1.332	1.340	1.348
Eri	24.23	30.17	43.61	1.280	1.290	1.295

[a] From Refs. 11 and 12.

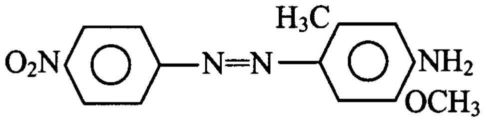
Dyeing

The following commercially available dyes were used:

1. Texacid Fast Red A (acid dye)



2. Foron Scarlet S-3GFL (disperse dye)



Dyeing with acid dyes

All the silk varieties were dyed with the acid dye Texacid Fast Red A. The dye bath contained 4% dye on the weight of the fiber (owf). The material-to-liquor ratio was maintained at 1 : 40. The dye bath pH was kept at 4.2 using acetic acid and ammonium sulfate. To understand the differences in dye uptake within a variety, different layers such as the outer, the middle, and the innermost layers were dyed separately. For information, the fifth layer for mulberry (bivoltine), the third for mulberry (crossbreed), the third for tasar, the third for muga, and the third for eri were designated as the middle layers, respectively. The dyeing was started at room temperature and the temperature was gradually increased to boiling at a rate of 2°C/min. The dyeing was continued for 2 h at the boil. The samples after dyeing were washed thoroughly in cold water and dried at room temperature.

Dyeing with disperse dyes

Foron Scarlet S-3GFL was used for dyeing all the varieties of silk. The dye bath contained 4% dye owf. The dyeing was started at room temperature and the temperature was gradually increased to boiling at a rate of 2°C/min. The dyeing was carried out for 2 h at the boil. The material-to-liquor ratio was maintained at 1 : 40. The pH of the dyeing bath was kept at 4.0 using acetic acid in the dye bath. In this case, too, the different layers were dyed separately. After dyeing, the samples were washed thoroughly in cold water and rinsed in a mixture of acetone and water (50 : 50) to remove any dye adsorbed on the surface. The samples were dried at room temperature.

Evaluation of dyed samples

Determination of exhaustion

Percentage exhaustion (E) of the dye was determined by measuring the absorbance of the dye bath before and after dyeing, using a Biochrom 4060 UV–vis spec-

TABLE IV
Crystallite Orientation Function (f_c), Birefringence (Δ_n), and Sonic Modulus (S_ϵ) Values for Different Varieties of Silk

Type of silk	f_c Outer layer	f_c Middle layer	f_c Inner layer	Δ_n Outer layer	Δ_n Middle layer	Δ_n Inner layer	S_ϵ (g/cl) Outer layer	S_ϵ (g/cl) Middle layer	S_ϵ (g/cl) Inner layer
Mulberry (bivoltine)	0.40	0.44	0.49	0.054	0.055	0.056	164.89	170.46	206.03
Mulberry (crossbreed)	0.32	0.36	0.41	0.051	0.052	0.052	153.06	166.9	192.27
Tasar	0.32	0.35	0.42	0.041	0.042	0.042	105.94	107.54	114.84
Muga	0.35	0.38	0.43	0.040	0.041	0.042	102.65	108.10	114.63
Eri	0.23	0.26	0.28	0.034	0.035	0.035	101.7	106.01	109.22

TABLE V
Correlation Coefficient *R* Value of Acid Dye Uptake with Physical Structural Parameters

Within variety	Crystallinity (X_c)	Crystallite orientation function (f_c)	Density (ρ)	Birefringence (Δ_n)	Sonic modulus (S_ϵ)
Mulberry (bivoltine)	0.987 (−)	0.988 (−)	0.997 (−)	0.996 (−)	0.883 (−)
Mulberry (crossbreed)	0.963	0.975	0.982	0.904	0.857
Tasar	0.822 (−)	0.913 (−)	0.986 (−)	0.783 (−)	0.853 (−)
Muga	0.921 (−)	0.947 (−)	0.981 (−)	0.815 (−)	0.826 (−)
Eri	0.934 (−)	0.932 (−)	0.975 (−)	0.878 (−)	0.834 (−)
Global	0.427 (+)	0.842 (+)	0.876 (+)	0.866 (+)	0.421 (+)

trophotometer (Pharmacia LKB, Uppsala, Sweden), and was computed as

$$E\ (\%) = \frac{A_i - A_f}{A_i} \times 100$$

where E is exhaustion, A_i is the absorbance of the initial dye bath, and A_f is the absorbance of the dye bath after dyeing.

Estimation of dye content on fiber

The dye uptake of fiber was estimated on a Pharmacia LKB Biochrom 4060 spectrophotometer. The dyes were purified as according to the procedure described by Chavan.[14] Standard calibration curves of acid and disperse dyes were obtained by dissolving the dyes in 85% formic acid at room temperature. To determine the dye on the fiber, the dye was completely extracted from 10 mg of fiber in 20 mL of 85% formic acid by continuously shaking at room temperature for 10 min. Absorbance values for the solution of these extracts were recorded from which the dye on fiber was calculated using the calibration plot.

K/S spectra

The color strength (K/S) of the dyed samples was measured on a Jaypak X 4000 reflectance spectrophotometer. For this, the dyed filament samples were uniformly wound on white cardboard (3 × 3 cm). The K/S spectra were recorded and analyzed.

RESULTS AND DISCUSSION

Different varieties of silk have different chemical architectures as well as different morphological characteristics. The absorption and diffusion of dyes are known to depend on these factors. In this context, which of the above parameters plays a significant role

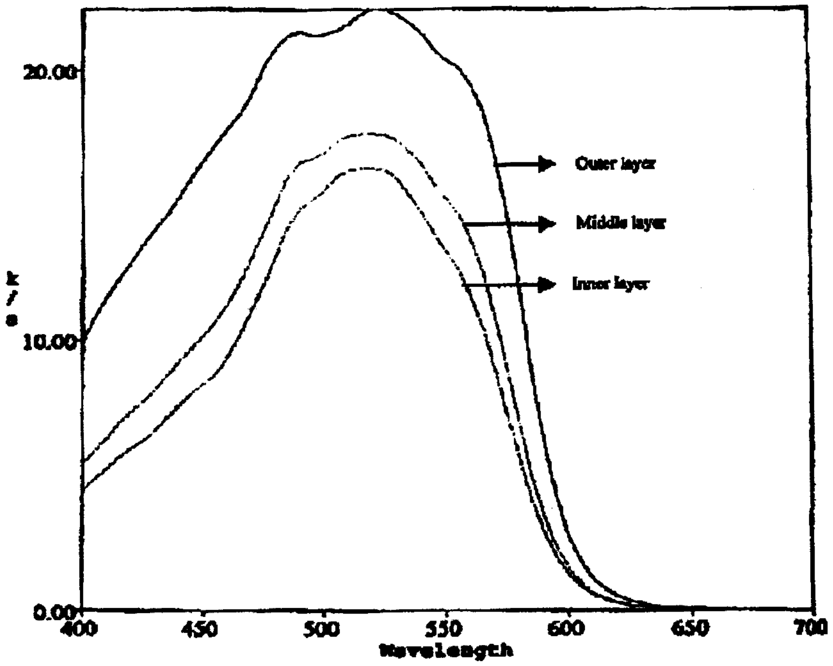


Figure 1 K/S plot of mulberry (bivoltine) silk fibers dyed by acid dye.

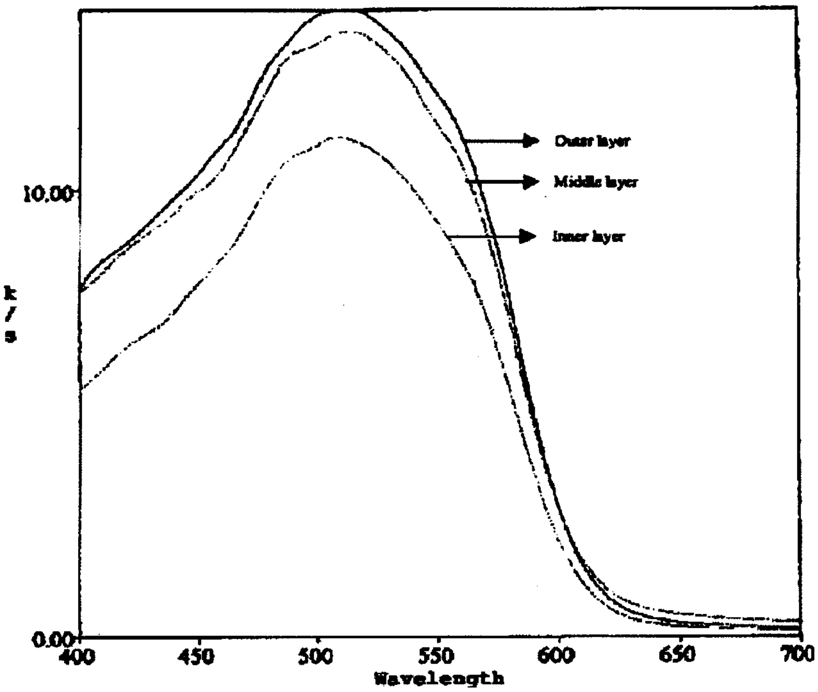


Figure 2 K/S plot of tasar silk fibers dyed by acid dye.

in the case of silk, is a question of considerable interest.

Response of different silks to acid dye uptake

The percentage exhaustion of acid dye on different silk fibers is presented in Table I. This study was conducted on the outer layers of all the varieties of silk. It may be observed from the results that the acid dye exhausts very well on both the mulberry varieties showing exhaustion values of about 89%. On the other hand, all three nonmulberry varieties show comparatively lower exhaustion values. Among the three varieties, tasar has the highest value (59.1%) followed by eri (58.3%) and muga (57.0%), although this difference is not significant. The results of dye uptake of different varieties of silks expressed as milligrams/100 grams of fiber are presented in Table II. Both the mulberry varieties show higher dye uptake compared to that of nonmulberry silks. The results confirmed the mea-

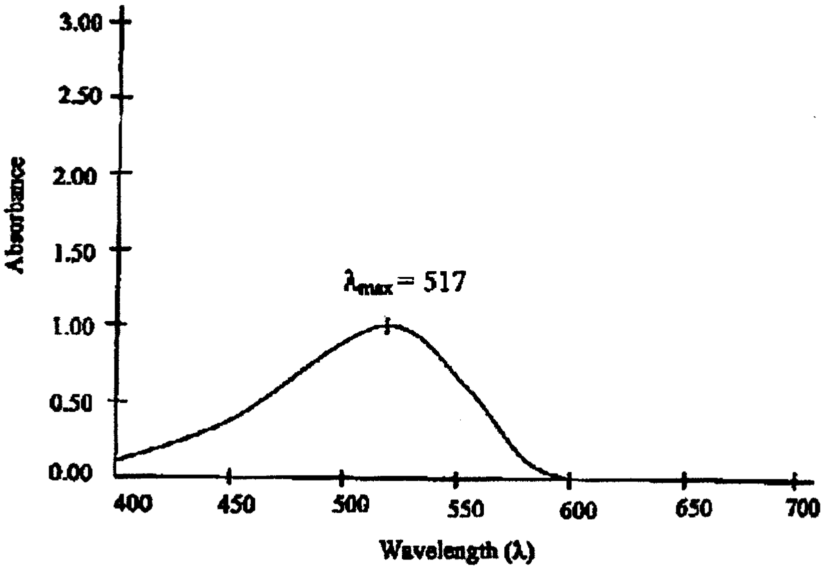


Figure 3 Solution spectrum of acid dye.

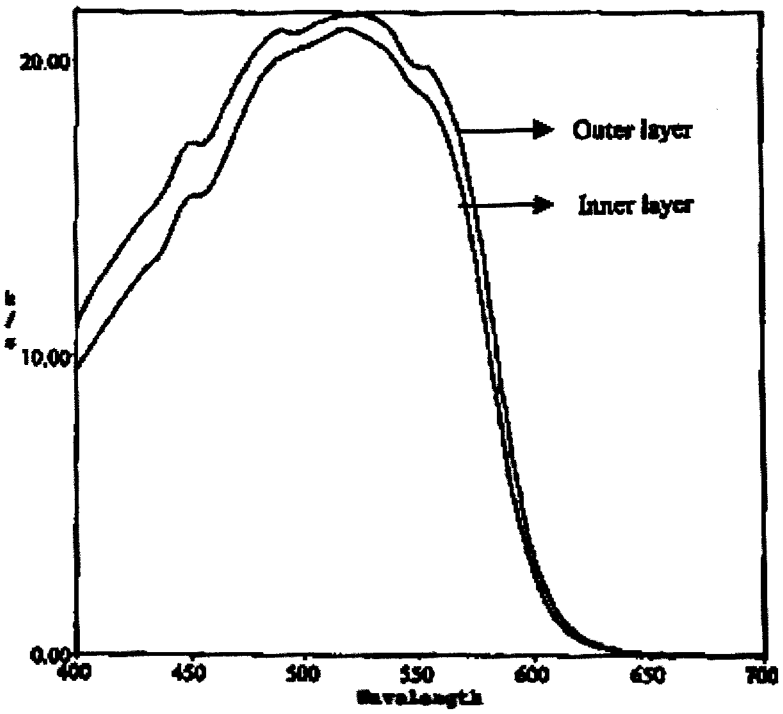


Figure 4 K/S plots of acid-dyed mulberry silk fibers washed with acetone : water (50 : 50) mixture.

sured exhaustion values for mulberry and nonmulberry silks. As was observed from exhaustion (%) data, the mulberry (crossbreed) variety exhibits higher dye uptake compared to that of the bivoltine variety.

All three nonmulberry silks showed lower dye uptake than that of mulberry silks. Here too tasar showed the highest value followed by eri and muga. Muga silk showed the least dye uptake compared to that of the other nonmulberry silks. Within the nonmulberry variety, however, the difference was not very significant.

It is interesting to note the differences in dye uptake among the layers within a cocoon. The dye uptake decreases significantly from the outer to the innermost layers in all the varieties of silk. The percentage reduction from outer to innermost layers is about 10% for mulberry (bivoltine), 5% for mulberry (crossbreed), 10% for tasar, 11% for muga, and 10% for eri. It may be noted that the variation is least in the mulberry (crossbreed) variety. From the above, it is clear that the dye uptake follows a definite pattern with respect to the reduction along the length of the fiber, irrespective of the origin. It may be safely assumed that the fiber's fine structure must be playing a decisive role.

To ascertain the effect of physical structure on the dye uptake, correlations must be established among some important characteristics such as crystallinity, orientation, birefringence, and density, for example. In previous studies in this series[11,12] it was established that there are significant differences in the density, crystallinity, and orientation of the fibers as one moved from the outer to the inner layers of a cocoon, irrespective of the variety of silk. The relevant data are reproduced in part in Tables III and IV. It may be observed that the crystallinity, crystalline orientation function, birefringence, sonic modulus, and density all increase from the outer to the innermost layers, irrespective of the nature of silk. It is but natural that the

TABLE VI
End Amino Groups on Different Varieties of Silk

Variety	Amino groups (meq/100 g)
Mulberry (bivoltine)	3.68
Mulberry (crossbreed)	3.74
Tasar	2.32
Muga	2.20
Eri	2.30

TABLE VII
Intrinsic Viscosity of Different Varieties of Silk[a]

Variety	Intrinsic viscosity (dL/g)
Mulberry (Bivoltine)	0.25
Mulberry (crossbreed)	0.19
Tasar	0.71
Muga	0.76
Eri	0.69

[a] From Ref. 11.

TABLE VIII
Exhaustion of Disperse Dye

Variety	*E* (%)
Mulberry (Bivoltine)	23.67
Mulberry (crossbreed)	26.34
Tasar	16.20
Muga	12.59
Eri	13.55

dye uptake decreases. In the case of mulberry (bivoltine), for instance, crystallinity increases from 29.2 to 48.8% (Table III), whereas the dye uptake decreases from 2637 to 2348 mg/100 g of fiber (Table II). The negative correlation, with an *R* value of 0.987, established very high correlation with the crystallinity of the fiber. The negative sign signifies a reduction in dye uptake with an increase in crystallinity. For this fiber, density, crystallite orientation, birefringence, and sonic modulus all show a very good negative correlation with dye uptake with *R* values of 0.997, 0.988, 0.996, and 0.883, respectively (Table V).

To find whether the reflectance behavior of the dyed silk fiber follows a similar trend, K/S versus wavelength (λ) plots of the samples were analyzed and K/S values at λ_{max} were determined. Figures 1 and 2 depict the typical curves for mulberry (bivoltine) and tasar. These curves reveal that mulberry silk shows higher K/S values for all the layers compared to those of tasar. These curves also indicate that the outer layers take up more dye than do the inner layers, which clearly demonstrates the role played by the chemistry and microstructure of the fiber. It may be noticed that the λ_{max} value is the same for all the layers and both the silks; however, their curves are not true bell-shape curves. The appearance or sharpening of shoulders, particularly at higher dye concentration (or on outer layers), suggests some aggregation of the dye on the fiber. A similar response was also observed with other silks. Because the acid dye is water soluble, it was not natural to expect this. In fact, the solution spectrum of this dye gives a clear bell-shape curve (Fig. 3). To check whether this was surface deposition, the dyed mulberry sample was rinsed in acetone :thswater (50/50) mixture and reflectance spectra were run. The nature of this curve (Fig. 4) did not change, suggesting that the aggregation was formed on the fiber. This dye has only one solubilizing group and may have a tendency to aggregate at higher concentration. Such aggregates in wool have been reported with milling and supermilling dyes.

Anomalous dyeing behavior of silk

Although excellent correlation was found within all the varieties of silk between dye uptake and microstructural parameters, it was surprising to note that such correlation does not exist between different varieties. For instance, both mulberry varieties have higher density, crystallinity, orientation, and sonic modulus (Tables III and IV) compared to those of the nonmulberry varieties, which means that these should have low dye uptake. In fact, it is the reverse of this. The nonmulberry varieties seem to pick up less dye. All the observations point toward lesser dye pick up in the nonmulberry varieties, whether it is exhaustion, K/S, or dye content on fiber.

To see whether any general correlation existed between dye uptake and structure, irrespective of layer or nature of silk, global correlations were determined (Table V). There was a poor linear correlation and the correlation was positive, which failed to explain the effect of physical structure on dyeing behavior.

To gain better insight, it was decided to determine the end amino groups by the ninhydrin method. The results are presented in Table VI. It may be observed that the end amino groups for the mulberry variety are higher (3.68–3.74 meq/100 g) compared to those of the nonmulberry variety (2.20–2.32 meq/100 g). For acid dyes, this is a very important parameter because these are site-specific dyes. Interestingly the correlation coefficient *R* between dye uptake (outer layer) and end amino groups was positive and very high (0.998). This explains the higher dye uptake values obtained on mulberry silk.

However, one may ask why do the mulberry silks show higher numbers of end amino groups, because as such the basic amino groups are more numerous in nonmulberry silks.[11] To understand this further, the intrinsic viscosities (IV) of these silks were determined (Table VII). It is very clear that the IV for mulberry silks is very low (0.19–0.25 dL/g) compared to that of

TABLE IX
Dye Content on Fiber (Disperse Dye, Foron Scarlet S-3GFL)

Variety	Dye uptake (mg/100 g fiber) Outer layer	Middle layer	Inner layer	Percentage change
Mulberry (bivoltine)	555	453	336	39.47
Mulberry (crossbreed)	614	569	482	21.42
Tasar	394	292	205	48.18
Muga	321	234	175	45.45
Eri	351	205	190	45.83

TABLE X
Correlation Coefficient *R* Value of Disperse Dye Uptake with Physical Structural Parameters

Within variety	Crystallinity (X_c)	Crystallite orientation function (f_c)	Density (ρ)	Birefringence (Δ_n)	Sonic modulus (S_ϵ)
Mulberry (bivoltine)	0.987 (−)	0.992 (−)	0.978 (−)	0.997 (−)	0.936 (−)
Mulberry (crossbreed)	0.912	0.983	0.965	0.983	0.912
Tasar	0.897 (−)	0.963 (−)	0.976 (−)	0.987 (−)	0.921 (−)
Muga	0.912 (−)	0.985 (−)	0.981 (−)	0.937 (−)	0.914 (−)
Eri	0.892 (−)	0.991 (−)	0.975 (−)	0.964 (−)	0.923 (−)
Global	0.288 (+)	0.289 (+)	0.384 (+)	0.616 (+)	0.627 (+)

nonmulberry (0.69–0.76 dL/g). This explains the higher number of end amino groups in mulberry: the lower the molecular weight (i.e., low IV), the greater the number of end groups.

Response of different silks to disperse dye

Disperse dyes are not commercially used for dyeing of silk because they are predominantly hydrophobic. Disperse dyes are not site specific, although they are structurally sensitive. It was considered of interest to study the response of the different varieties of silk to disperse dyes. A quick glance at Table VIII makes it clear that the exhaustion obtained with disperse dyes is very low compared to that obtained with acid dyes (Table I). This is expected because the substantivity of these dyes for silk is considerably less. Despite low values of exhaustion, the percentage exhaustion of this disperse dye on mulberry silk was significantly higher, a trend similar to that observed with acid dye. Similarly, the data on dye uptake (mg/100 g) (Table IX) also substantiate the fact that in all the varieties and all the layers, the dye uptake of mulberry registered a higher dye uptake, although in absolute terms the actual amount of dye on fiber was considerably less compared to the uptake values obtained with acid dyes.

As expected, within the variety, the dye uptake decreased from the outer to the inner layers. It may be noted, however, that the percentage reduction in uptake of disperse dye was much higher, around 21–48% (Table IX), compared to that for acid dyes, which was around 5–11% (Table II). This clearly points toward the high structural dependency of disperse dyes. The correlation coefficients *R* between disperse dye uptake and various structural parameters within a variety are listed in Table X. It may be observed that all the parameters show a very high negative correlation, irrespective of the variety of silk, suggesting a reduction in dye uptake with an increase in these parameters; that is, higher crystallinity, orientation, and density help reduce the dye uptake. However, the anomalous dyeing behavior as seen with the acid dyes is also seen here.

The correlation between the varieties is not only poor but also meaningless. For instance, all the nonmulberry varieties show lower dye uptake despite having lower crystallinity, density, and orientation. The reason may be attributed to the fact that the molecular weight (as suggested by the IV values) is high for all the nonmulberry varieties, which may lead to profuse entanglements, making the path of dye diffusion more difficult, thus leading to a reduction in dye uptake. A minor contribution from the different chemistry of the nonmulberry variety may not be ignorable. The hydrophobic/hydrophilic ratio of the amino acids present in mulberry (3.5) is higher than that of nonmulberry (2.27–2.85).[11] This may also contribute to the higher substantivity of disperse dye, a hydrophobic dye, for mulberry silk.

CONCLUSIONS

The microstructure and chemical architecture of silk fibers play a significant role in determining the dyeing behavior. The lower intrinsic viscosity in mulberry silk, leading to greater numbers of end amino groups, results in higher dye exchange capacity in these fibers. Within the same variety, in which the chemistry is the same, microstructure plays a predominant part. The nonmulberry silks exhibits lower dye uptake because of the higher intrinsic viscosity and fewer end amino groups present in these fibers.

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