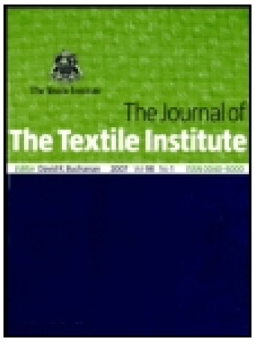

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Dyeing of male silk fibers with reactive dyes

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A study of the dyeing behavior of male silk fibers (obtained from silk cocoons spun by male worms) was undertaken. Normal silk (composed of filaments made by male and female worms) was also dyed for comparison purposes. Physical and chemical characteristics of silk which may affect dyeing behavior were also investigated using scanning electron microscope (SEM) and Fourier transform infrared (FT-IR) spectroscopy. From the results obtained in this research work, it can be concluded that male silk fibers tend to be finer than the normal silk fibers. The male silk fibers' dye uptake was tested and found to be lower than that of normal silk. Adjustment of exhaustion salt and dyeing temperature to higher levels had significant improvement on dye uptake and K/S value for male silk.

Keywords: male silk; reactive dyes; morphology; structure; exhaustion

Introduction

Silk is a natural fiber obtained from silk worms. Silk filament has superior natural luster, handle, and draping properties compared to many other textile fibers. Silk also possesses high strength, smoothness, flexibility, and good moisture absorbency characteristics. The warmth retention capacity, excellent wearability and luxurious appearance have allowed silk to withstand tough competition posed by man-made fibers. However, as a natural fiber, silk is characterized by an intrinsic variability of fiber properties that affects its processing and end-use performance (Zhao, Feng, & Shi, 2007). A study by Tsukada, Masahiro, Hirosh, Giuliano, and Fablo (1996) showed that the diameter of silk filament affects the physical, mechanical and dyeing properties of silk. Monti, Taddei, Freddi, Asakura, and Tsukada (2001) used the Raman spectroscopy to study the conformational features of silk. Such a study and expected future studies in this area are likely to shed more light on the properties of silk. Apart from studying the characteristics of silk, attempts have also been made to modify the properties of silk. A study by Vollrath (1999) has shown that the use of genetic sequencing of the silk spiders' protein, RNA, and DNA can lead to the optimization of the properties of silk. Further studies on the use of gene engineering to study the characteristic of silk fiber have been undertaken by Mori and Tsukada (2000). In the aforementioned research, the silk protein was modified by use of gene engineering (gene targeting) of a foreign gene into the fibroin gene of silkworms. This study further reports that the use of selective marker for screening of gene-targeting events and utilization of a recombining activity would lead to successful production of tailor-made silk fiber. This implies that genes with the needed silk fiber characteristics can be selected and hence produce silk of optimized characteristics.

While physical and chemical properties of silk are important, processing parameters also affect the behavior and hence the end-use performance of silk. Ping et al. (2006) have reported that the nature and type of degumming, which is a process of removing sericin from the silk filament, may affect the mechanical properties of silk. Studies of the behavior of silk fiber during dyeing have also attracted several researchers. This could be partly due to the fact that silk is used in the luxury apparel industry. Hiraku, Hiroaki, Toshikatsu, Hajime, and Fujiyoshi (1999) have investigated effects of variation in the diet of the silk worm to the dyeing behavior of silk. Two sets of silk worms, one fed on the normal mulberry diet and the other on a tofu-cake diet were reared and the silk produced by them was investigated. The study reported that the chemical structure of silk can be altered by the diet of the worm. This may lead to changes in the dyeing behavior of silk. The above-mentioned results were confirmed by Kushal and Murugesh (2004) who studied silk produced by worms fed on a mulberry and non-mulberry diets. The mulberry silk exhibited lower intrinsic viscosity and more amino groups compared to

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the non-mulberry silk, resulting in higher dye uptake for the mulberry silk. In summary, the studies of silk characteristics have included a general overview of the properties of silk and the factors that affect them (silk properties). Attempts to modify silk properties have also been reported by use of gene engineering, diet control, and modification of the processing parameters of silk fiber. Yu, Gu, Nie, Li, and Mu (2007), however, introduced a paradigm shift in the study of silk fiber when they reported that silk filaments can be classified based on the gender of the worm. In the aforementioned research the cocoons made by the male and female worms were separated and named male and female silk respectively while the unseparated silk was named normal silk. Compared to the normal silk, male silk exhibited superior physical and mechanical properties which included fineness, tensile strength, and length of the filament. The introduction of male silk has opened new areas of study. Due to the fact that the male silk filament exhibits different physical and mechanical properties, there is a need for investigations to be done concerning its behavior during processing with an aim of optimizing its manufacturing processes. This paper investigates the dyeing of male silk filament using reactive dyes. Normal silk was also dyed for comparison purposes.

Experimental

Materials and preparation

Reeled male silk and normal silk in filament form was supplied by Jiangsu Minxing Cocoon Silk Stock Company, China. The silk samples were degummed as follows: the raw silk was boiled for 45 minutes in 99.5% boric acid (0.2 mol/l) at a temperature range of 98–100°C. Borax (99.5%) was used to buffer the liquor. The samples were rinsed using de-ionized water. This degumming method is comparatively mild and hence minimizes the damage to the raw silk (Ping et al., 2006). Except where otherwise stated, the degummed silk samples were used for the experiments which included the study of silk physical and structural characteristic and the dyeing behavior of silk.

Testing the physical and chemical characteristics of silk

Scanning electron microscope (SEM) Hitachi TM-1000 (Japan) was used to study the cross-sectional structure and morphology of silk. The silk samples were gold sputtered to give the samples electronic conductivity under a vacuum. The SEM microscope was operated at a 15-kV accelerating voltage. While the SEM gave the images of the male and normal silk filaments, it was deemed necessary to determine the size (diameter) of the silk filament using an electron microscope. An average of 20 readings was taken for the male and normal silk filament samples.

The chemical characteristics of silk were analyzed using the Fourier transform infrared (FT-IR) spectroscopy Nicolet 5700 (USA). KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4000–200 cm^{-1} with 16 scans per sample were used. The silk crystallinity was tested using D/MAX2550PC X-ray detector diffraction system.

Dyes and dye assistants

Dyeing was carried out using a water bath shaker (Dye plus DL-2003) dyeing machine. In all the dyeing experiments red reactive dye (Argazol Red BF-3B 150%) and yellow reactive dye (Argazol Yellow BF-3B 150%) were used. The dyes were supplied by Argus (Shanghai) Textile Chemicals Company Ltd. Other chemicals used in the experiments were 99.0% anhydrous sodium sulphate used as exhaustion salt and 99.8% sodium hydrogen carbonate ($NaHCO_3$) used as fixation alkali.

Dyeing silk using reactive dyes

The dyeing procedure for both male silk and normal silk was designed based on the dye manufacturers' recommendations. Two types of reactive dyes were used in this research work. These dyes were expected to give red and yellow shades when applied to silk fibers. The dye bath was prepared using the set percentage of dye on the weight of the fiber (o.w.f.) and dyeing commenced at 40°C, half of the salt to be used was added at start for exhaustion. The temperature was raised at the rate of 1°C per minute up to the optimum dyeing temperature, the second half of the salt was added at the mid of temperature rise. $NaHCO_3$ was used for dye fixation. After dyeing the samples were soaped in 1 g/l of ionic soap with liquor ratio of 1:50 for 15 minutes at a temperature of 90°C, then washed thoroughly in cold water and dried at 60°C in the oven.

Evaluation of the dyeing process

Determination of the dye percentage exhaustion (*E%*), dye reactivity (*R%*), and dye total fixation (*TF%*) was done using Unico UV-2000 spectrometer (USA). The absorbance of the dye bath before and after dyeing was recorded. The absorbance of the soap solution before and after soaping was recorded. The computation was as follows (Nan, Wei, Zhang, Tang, & Yang, 2009):

$$E\,\% = \frac{A_0 - A_1}{A_0} \times 100 \qquad (1)$$

$$R\,\% = \frac{A_0 - A_1 - A_2}{A_0} \times 100 \qquad (2)$$

$$TF\,\% = E \times R \times 100 \qquad (3)$$

where A_0 is the absorbance of the initial dye bath, $A_1$is the absorbance of the dye bath after dyeing, and A_2 is the absorbance of the extracted dye in the soap liquor after soaping.

Evaluation of the dyed samples

Light scattering and light absorption of visible light determine the color of an opaque object. The color depth of a dyed fabric which is proportional to the amount of dye in the fabric can be expressed using the following equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (4)$$

where K is the coefficient of absorption, S is the coefficient of scattering, and R is the decimal fraction of the reflectance of the dyed substrate. K/S value was used to measure the amount of dye in the dry silk filaments. It was determined using Datacolor Spectraflash 650 (USA) spectrophotometer.

Results and discussion

The physical characteristics of silk

The physical morphology of normal and male silk observed using SEM are given in Figure 1. The male silk fiber appears to be finer than the normal silk. To verify this apparent difference the fiber diameter was measured using an electron microscope. The result obtained from the aforementioned experiment indicated that male silk has a finer diameter of 15.40 μm. The diameter for the normal silk filament was 19.44 μm. The crystallinity of silk fibers was tested using X-ray diffraction meter and the results are depicted in Figure 2. The degree of crystallinity of male silk was 50.47±2.74%, against that of normal silk which was 48.53±1.46%.

Tsukada et al. (1996) reported that for a given type of silk finer filaments will be characterized by a fibrous structure with better orientation of amorphous and crystalline regions along the fiber axis than thicker filaments. The results obtained in this research work indicate that the male silk is finer than the normal silk. Therefore compared to normal silk, the male silk will be expected to have a better orientation of the amorphous and crystalline regions. A high orientation of the male silk structure is likely to adversely affect diffusion of the dyes into the filament.

The chemical characteristics of silk

The chemical characteristics of male and normal silk fibers was investigated using the FT-IR spectroscopy and the results are given in Figure 3. The Amide I and Amide II absorption bands of normal silk appeared at 1641 and 1516 cm^{-1}, respectively. For male silk, the Amide I and Amide II absorption bands appeared at 1651 and 1526 cm^{-1}, respectively. Also there was a marginal shift in the wavelength of the hydroxyl group from 3415 cm^{-1} for normal silk to 3420 cm^{-1} for male silk which is accompanied by broadening of the peak. While the above-recorded results may not be

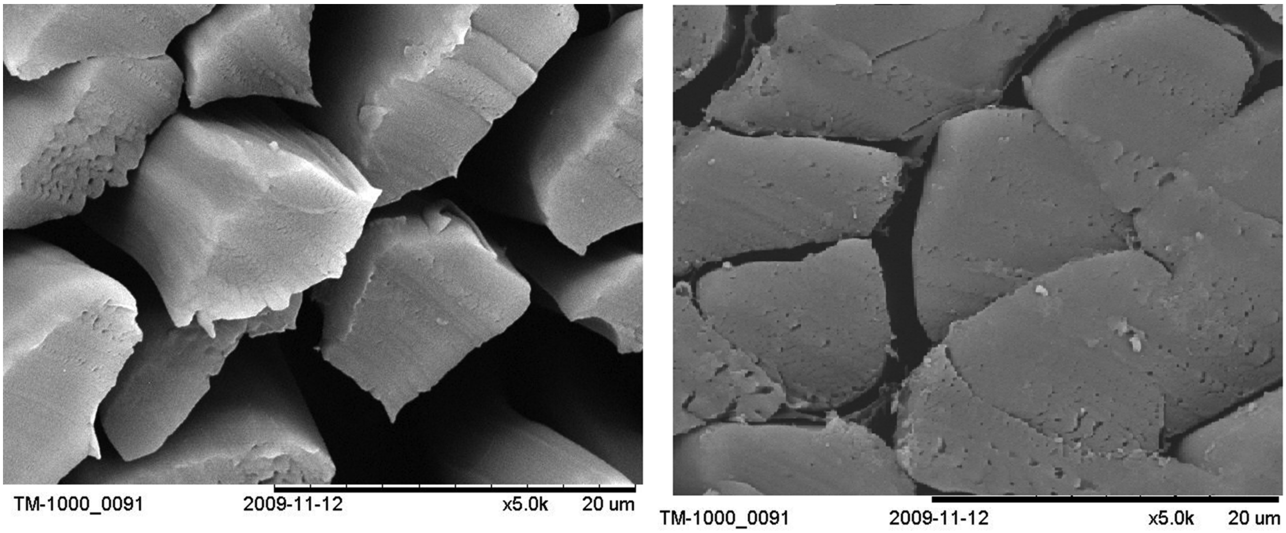

Figure 1. SEM cross-sectional views (× 5000 magnification): (a) male silk fiber, and (b) normal silk fibers.

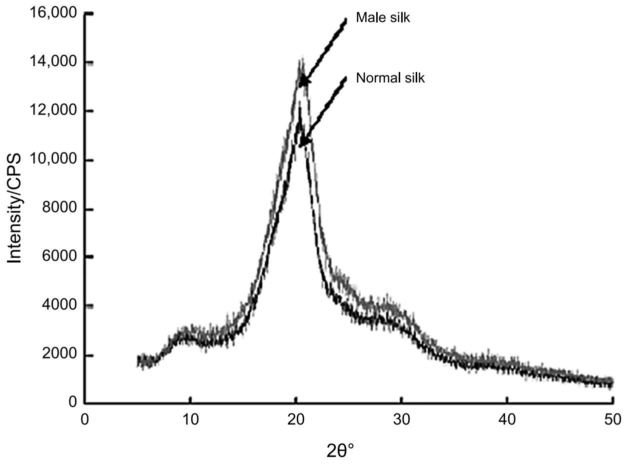

Figure 2. X-ray diffraction curves for male and normal silk.

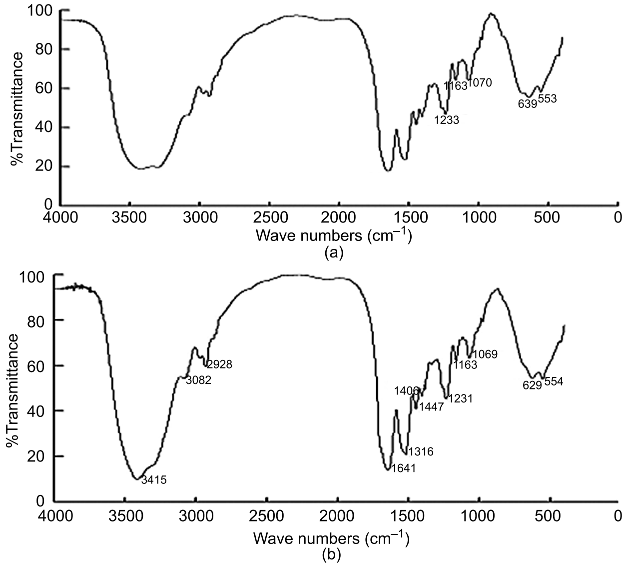

Figure 3. FT-IR images before degumming: (a) male silk fibers, and (b) normal silk fibers.

significantly different, it is important to note that no absorption bands have disappeared. This implies that the male silk fiber has the same chemical structure like normal silk. Therefore, male and normal silk fibers can be dyed using the same type of dyes.

Dyeing characteristics of male and normal silk

Dye exhaustion and fixation

The male and normal silk samples were dyed using the two types of reactive dyes as discussed in the Experimental section. The dye exhaustion results for normal silk dyed with red reactive dye (Red [n]), male silk dyed with red reactive dye (Red [m]), normal silk dyed with yellow reactive dye (Yellow [n]), and male silk dyed with yellow reactive dyes (Yellow [m]) are given in Figure 4. The normal silk fiber showed better dye exhaustion behavior than that of male silk fiber for the red and yellow reactive dyes. The results of the above study indicated that there is a color difference between male and normal silk fibers. To improve on the dye exhaustion, there is a need to make changes in the dyeing conditions that may influence the degree of association between the dye molecule and the fiber. This has been dealt with in the optimization of the male silk dyeing process.

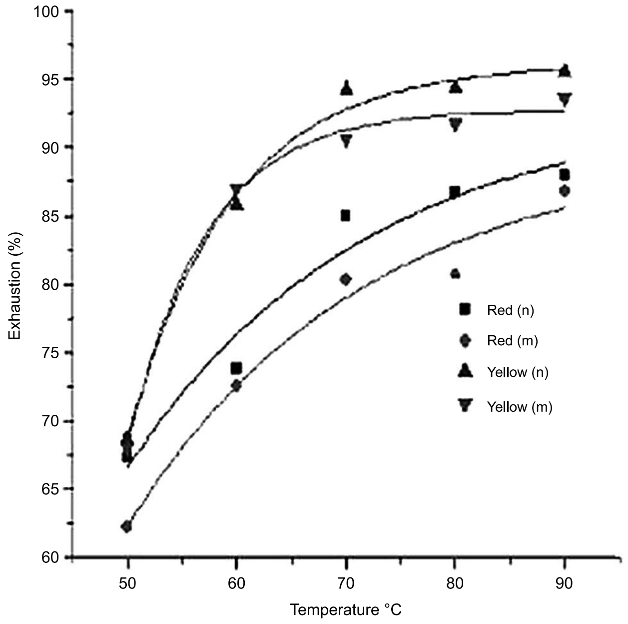

Figure 4. Exhaustion curves for male and normal silk.

Measure of depth of color

The depth of color for the reactive red and yellow dyes applied on the male and normal silk fibers was measured using the spectrophotometer. The *K/S* value for silk samples dyed using the red and yellow dyes are given in Figure 5, which shows that the *K/S* value increased with the increase in the dye concentration. The rate of increase of the *K/S* value for the normal silk fiber tends to increase at a higher rate than that of the male fiber. This is more vivid when the dye concentration is over 3% o.w.f.

Optimization of male silk dyeing process

Since the dyes manufacturer's recommended dyeing conditions could not give the optimum results for dyeing male silk, experiments were carried out to establish the optimum condition for dyeing male silk.

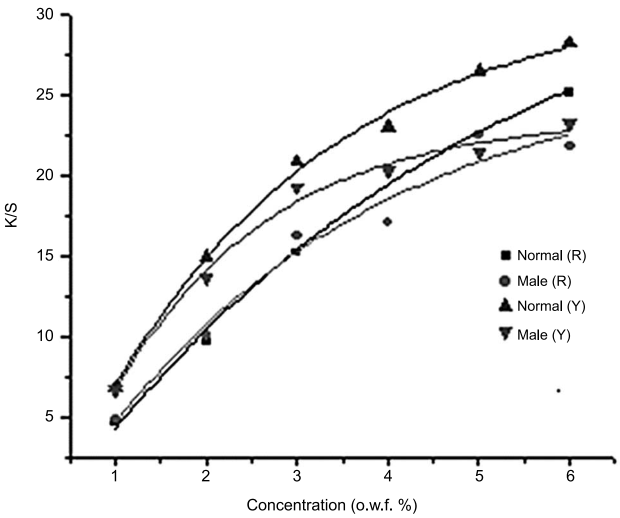

Figure 5. Effect of dye concentration on *K*/*S* value.

The experiments involved maximizing dye exhaustion, fixation, and depth of color while dyeing male silk.

Dye exhaustion and fixation

Experiments were carried out to establish optimum amount of salt required for dye exhaustion and fixation, and the results are listed in Tables 1 and 2. From Table 1, the percentage exhaustion of the reactive red dye at 20 g/l of sodium sulphate was very low and increased appreciably with the increase in the salt concentration. However, at 120 g/l salt concentration the dye exhaustion had only reached exhaustion from a level of 72.4% for 20 g/l of salt to 85.37%. The yellow reactive dye exhibited better 93.29% for 120 g/l of salt. With the increase in the amount of fixation agent, $NaHCO_3$ did not seem to show any significant improvement in the dye fixation of the red and yellow reactive dyes. Dye exhaustion for male silk fibers can be improved by using higher amounts of salt. Therefore, other factors remaining constant higher amounts of salt can be used to improve dye exhaustion when dyeing male silk using reactive dyes, but this also has a limit beyond which the luster of the fiber starts reducing. The fixation of the red and yellow reactive dyes seems to work well with 2 g/l of $NaHCO_3$ (Table 2). Increasing the amount of the fixation agent did not show any positive significant effects on the dye fixation. This could be due to the fact that the fixation agent is not involved in the adsorption of the dye. Once the dye has reacted with the dye site in the fiber, then the fixation agent comes to fix the already reacted dye. Since the chemical composition of the male silk is similar to that of normal silk, the fixation process is least affected.

Table 1. Optimization of exhaustion salt (Na_2SO_4).

Na_2SO_4g/1	%Exhaustion for red	%Exhaustion for yellow
20	43.54	72.40
40	57.89	82.28
60	66.15	88.10
80	73.01	89.15
100	80.89	91.90
120	85.37	93.29

Table 2. Optimization of fixation agent ($NaHCO_3$).

$NaHCO_3$(g/l)	Total fixation for red	Total fixation for yellow
2	81.32	93.69
4	79.52	92.66
6	80.40	92.90
8	79.79	92.17
10	78.94	92.24
12	78.39	91.97

Dye bath temperature

The effects of temperature on dye exhaustion are given in Figure 6, where male silk was dyed using reactive yellow dye at three levels of temperature: 70°C, 80°C, and 90°C. The results shown in Figure 6 indicate that better dye exhaustion results are obtained at higher temperatures. There is a possibility of improving the fiber dye absorption with increase in temperature but since silk fibers are easily hydrolyzed when dyed at high temperatures especially in acidic or alkaline

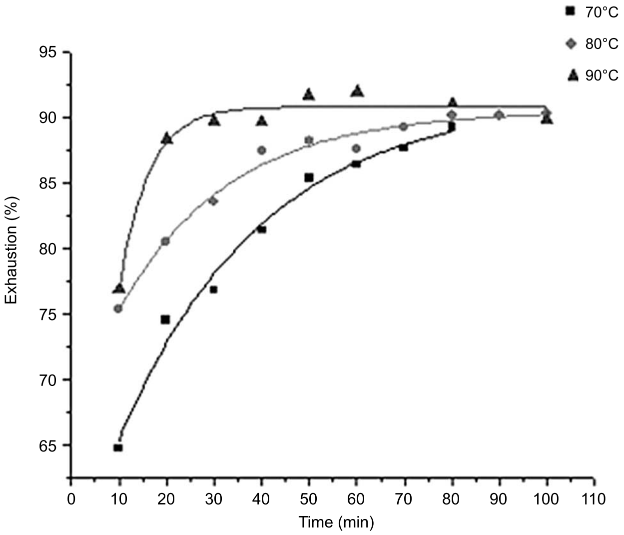

Figure 6. Dye exhaustion curves for male silk.

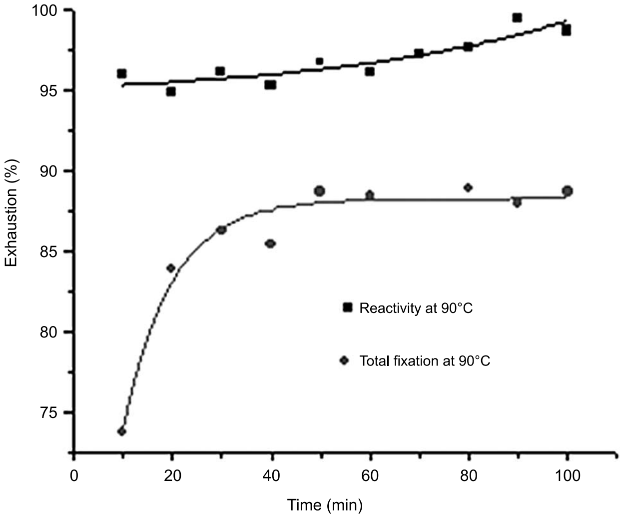

Figure 7. Dye exhaustion and reactivity for male silk.

medium, lower temperatures are usually preferred so the experiment is stopped at 90°C.

Dyeing time

The results of the study of the effect of dye exhaustion on dye reactivity (*R*%) and dye total fixation (*TF*%) are given in Figure 7. Dye total fixation increased with increase in dyeing time up to a level of 85% when it became stagnant. Reactivity, on the other hand, had a small but steady increase as dyeing time was increased. The reactivity curve is well above the total fixation curve. This could be an indication that the fibers reactivity is not affected by low dye exhaustion, but low dye exhaustion has an effect of reducing total fixation. From Figure 6 optimum dyeing time for male silk dyed using reactive dyes could be between 40 and 50 minutes.

Conclusion

A study of the behavior of male silk fiber when dyed using reactive dyes was undertaken. Normal silk was also dyed for comparison purposes. Physical and chemical characteristics of silk which may affect dyeing were also investigated. From the data obtained in this study, it can be concluded that male silk filaments are finer than the normal silk fiber. A study of the chemical characteristics of silk revealed that the Amide I and Amide II absorption bands for male silk appear to have marginally shifted to higher frequencies when compared with those in normal silk. There is also a slight shift in the frequency of the hydroxyl amino group of male silk to a higher frequency when compared to that of normal silk. The shift of the Amide I, Amide II, and hydroxyl groups appears to be insignificant. When dyed with reactive dyes the male silk fibers exhibited lower dye uptake. Adjustment of exhaustion alkali and dyeing temperature to higher levels had significant improvement on dye uptake and *K*/*S* value for male silk.

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