Physical, Chemical, and Dyeing Properties of *Bombyx mori* Silks Grafted by 2-Hydroxyethyl Methacrylate and Methyl Methacrylate

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ABSTRACT: To obtain silk weight gain and to improve silk properties, *Bombyx mori* silks were grafted with either 2-hydroxyethyl methacrylate (HEMA) or methyl methacrylate (MMA). The moisture regain of the HEMA-grafted and MMA-grafted silks depended on the hydrophilicity of the used monomers. The acid and alkaline resistances of the HEMA-grafted and MMA-grafted silks were clearly improved. Both commercial synthetic dyes, that is, acid and reactive dyes, and a natural dye extracted from turmeric, with potassium aluminum sulfate as a mordant, were used in this study. The results suggested that the dye uptake increased in the presence of poly(2-hydroxyethyl methacrylate) or poly(methyl methacrylate) in the silk fibroin structures when acid and curcumin dyes were used. The washfastness level of the HEMA-grafted silk dyed by acid and reactive dyes was similar to that of the degummed silk. However, the colorfastness to washing of the MMA-grafted silk dyed by an acid dye was improved when the polymer add-on concentration was 65%. In addition, the washfastness for both grafted silks was improved when they were dyed with natural curcumin dyestuff. The acid and alkaline perspiration fastness properties remained unchanged for the HEMA-grafted and MMA-grafted silks when acid, reactive, and curcumin dyes were applied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1526–1534, 2007

Key words: dyes/pigments; fibers; graft copolymers; modification

INTRODUCTION

Bombyx mori silks are excellent fibers conventionally used for making yarn, cloth, and decorative articles because silks present many outstanding attractions, including strength, dyeability, luster, and moisture absorption, that distinguish them from other natural and synthetic fibers. However, silks still lack some important characteristics, such as colorfastness, abrasion resistance, and dimensional stability, and these properties need to be improved. In recent years, graft copolymerization has become a well-known technique for imparting new properties or heightening existing properties in the parent polymer with minimum degradation of the original properties.[1] The nature of the grafted copolymer is dependent on the type of grafting monomer and the degree of grafting.[2]

There has been much research focused on grafting techniques for silk fibroin with different types of vinyl monomers, that is, methyl methacrylate (MMA),[3–6] methacrylamide (MAA),[5,7,8] 2-hydroxyethyl methacrylate (HEMA),[5,7–9] and ethoxy ethyl methacrylate (ETMA).[10] It has been found[3–10] that silks grafted by vinyl monomers show improvements in the thermal stability and wrinkle recovery, whereas the crystallinity of the silk fibroin remains unchanged. Nevertheless, the mechanical properties of grafted silks slightly drop with an increase in the polymer add-on. Maji et al.[3] reported that the moisture regain of MMA-grafted silk decreased because of the hydrophobicity of the MMA monomer. When potassium sulfate and tri-*n*-butylborane were used as the initiators for grafting silks with MMA monomer, the greater polymer add-on caused a greater weight-average molecular weight of poly(methyl methacrylate) (PMMA).[6] Tsukada et al.[7] studied the structures and properties of tussah silks grafted with HEMA and MAA, and the results suggested that a very high weight gain of 175% could be obtained, but a high weight gain caused noticeable granules on the surface of the grafted silks. In addition, the moisture regain of not only HEMA-grafted silks but also MAA-grafted silks was higher than that of the degummed silk.[5] The effects of three different

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types of initiators, that is, ammonium persulfate (APS), 2,2′-azobis(2-amidinopropane) dihydrochloride, and 2,2′-azobisisobutyronitrile, on the properties of MMA-grafted, MAA-grafted, and HEMA-grafted silks were also examined.[5] Furthermore, ETMA-grafted silks also showed the appearance of ETMA oligomers on the surface of ETMA-grafted silk, especially when the percentage of the polymer add-on was more than 40%.[10]

In general, silks used for textile applications have to be dyed for customer attraction. Textile fibers are expected to present good fastness properties to ensure that they remain in their natural state after the dyeing process and normal daily life usage. The dye uptake is, therefore, the important parameter for the dyeing procedure, whereas the colorfastness properties are the most essential aspects for fabric exploitations.

With respect to dyestuffs, synthetic dyes are commercially available because of the various color shades available and the ease of use, but the major concern is environmental problems. Natural dyes, as a result, become options because they present environmental compatibility, low toxicity, and low allergic reactions for fabric wearers. One of the popular, naturally bright yellow dyes is curcumin [1,7-bis (4-hydroxy-3-methoxyphenyl)-1, 6-heptadiene-3, 5-dione)], which is extracted from the root of turmeric, a perennial herb (*Zingiber officinale*). The yellow colorant has been used as a natural dyestuff and also as a food colorant.[11,12] Nevertheless, the main problem with natural dyes is poor fastness properties.[13,14]

Only a few researchers have reported on the dyeing properties of grafted silks.[8,10] Tsukada et al.[10] reported an improvement of the dye uptake when ETMA-grafted silk was dyed with an acid dye. Furthermore, fastness to washing and perspiration of degummed silk dyed with acid, basic, and curcumin dyes could be improved through grafting with MMA and MAA monomers with a grafting yield of approximately 45%.[15] Nevertheless, there has been no research on the dyeing properties of cultivated silk (*B. mori*) grafted by HEMA. In general, HEMA is one of the most important vinyl monomers because it is the usual choice for daily-wear contact lenses on account of its biocompatibility and hydrophilic properties. Because of the hydrophilic properties of HEMA, it can be used as a grafting monomer for silk fibroin that will lead to comfort during the wearing of silk fabric. Therefore, this study was focused on the dyeing properties, that is, the dye uptake, color measurement, and colorfastness, of HEMA-grafted silk versus those of MMA-grafted silk. Moreover, the physical and morphological properties of HEMA-grafted and MMA-grafted silks were also investigated.

EXPERIMENTAL

Materials

Raw silks (*B. mori*) were supplied by Jim Thompton (Nakorn Ratchaseema, Thailand). Reagent grades of HEMA and MMA monomers, including formic acid, were obtained from Merck Co., Ltd. (Thailand). APS was used as the initiator. Alkali solutions of both sodium carbonate and sodium bicarbonate as well as a Sandopan 60 soap solution (Thailand) were used for degumming. The acid dye (Erionyl Yellow A-R, C.I. Acid Orange 67) and reactive dye (Cibacron Yellow W-R, C.I. Reactive Yellow 205) belonged to Ciba Specialty Chemicals (Thailand). Curcumin (*Curcuma longa*, C.I. Natural Yellow 3) was obtained locally, and the mordant used for the natural colorant dyeing was potassium aluminum sulfate from Fluka Co., Ltd. (Thailand).

Degumming and grafting

Raw silks were first degummed in an aqueous solution containing 0.05 mol/L sodium carbonate, 0.05 mol/L sodium bicarbonate, and soap at 80°C for 30 min. Grafting was performed through the immersion of the silks in a reaction system at pH 3 (adjusted with formic acid) containing 0.05 mol/L APS (initiator) as well as 0.8 mol/L HEMA or MMA monomer.[5,8] The material-to-liquor ratio during the treatment was maintained at 1:20. The temperature was gradually raised from room temperature to 80°C within 30 min and then maintained at this level for different periods. The grafted silks were thoroughly rinsed with acetone and then water and were vacuum-dried. The weight gain was calculated from the weight difference for the dried silks before and after the graft treatment.

Dyeing

The degummed, HEMA-grafted, and MMA-grafted silks were dyed with an exhaustion method with commercial acid and reactive dyestuffs to observe the dyeing characteristics of the silks. The concentration of the dyeing solution was kept at 3% owf, and the ratio of the dye solution to the silk weight was maintained at 30:1. For acid dyeing, the initial temperature was 30°C, the dyeing temperature was then raised to 90°C within 30 min, and the silks were further dyed at this temperature for 45 min. Ammonium acetate (1 g/L) was added, and a slightly acidic condition (pH 5–6) was used. The reactive dyeing process started with dyeing at 60°C for 45 min, followed by washing with cold and warm water until no change in the color was obtained. Sodium phosphate (0.3 g/L), sodium carbonate (2 g/L), and sodium chloride (1 g/L) were added, and a slightly basic condition (pH 6–7) was used. Finally, the dyed silks for both the acid and reactive dyes were dried at room temperature. The acid and reactive dyeing conditions and recipes conformed to the manufacturer's suggestions. Furthermore, a natural colorant extracted from turmeric was prepared[15] through the immersion of turmeric in a 75% ethanol solution, a suitable solvent for curcumin extraction, with a 1:20 material-to-liquid ratio for 1 h. The resulting filtrate was then used for further dyeing. The curcumin dyeing process was carried out at the dyeing temperature of 60°C for 10 min, and the material-to-liquid ratio was maintained at 1:30. Potassium aluminum sulfate as a mordant (8% owf) was used during the dyeing procedure (metamordant) for curcumin dyeing.

Dye uptake

The percentage of the dye uptake of the silks was obtained through the measurement of the differences in the absorbance, at the wavelength of maximum absorption, of the dye bath concentration before and after dyeing with an ultraviolet–visible (UV–vis) spectrophotometer. The dye uptake was calculated with the following equation:

$$\text{Dye uptake } (\%) = (A_0 - A_t)/A_0 \times 100$$

where A_0 and A_t are the absorbances of the dye solution at the beginning and end of the dyeing process, respectively.

Morphology

A Leo 1455 VP scanning electron microscope (Carlzeiss, Germany) was employed to study the surface morphology of the degummed and grafted silks. The samples were sputter-coated with a thin layer of gold to prevent electrical charging during the observation. The surface characteristics were examined and operated at a 6-kV accelerating voltage.

IR spectroscopic study

Fourier transform infrared spectra of silk samples were recorded on a Spectrum 2000 GX spectrometer (PerkinElmer) with a KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4000–650 cm^{-1} with 16 scans per sample.

Moisture regain

The degummed and grafted silks were placed in a controlled room with a temperature of 21°C and a relative humidity of 65% until constant weights of the samples were obtained. The weight difference for the samples after drying in an oven at 105°C for 2 h was then calculated.[16]

Chemical resistance

The silks were immersed in 3*M* HCl and 0.1*M* NaOH solutions at 65°C for 1 h, and this was followed by washing in distilled water. The dried samples were then weighed, and the weight loss was calculated as a percentage.[16]

Color measurements

The color parameters L^*, a^*, b^*, C^*, and H° were measured with a Miniscan XE Plus spectrophotometer with a D65/10° illuminant evaluated with the Commission Internationale de l'Eclairage L^*–a^*–b^* system. In this system, L^* represents lightness, a^* represents redness if positive and greenness if negative, and b^* represents yellowness if positive and blueness if negative. In addition, C^* and H° show the chroma and color angle in the color space of the samples, respectively. Five measurements were carried out for each sample to obtain average color parameters.

Colorfastness

The colorfastness of the silk samples was determined with washing and acid and alkaline artificial perspiration solutions according to ISO 105 C01-C03 and ISO 105 E04, respectively. The determination of the colorfastness with washing and perspiration tests was carried out with both sample and standard (silk and cotton) fabrics that were sewn together and tested under the same conditions. For washing colorfastness, the sewn fabric was washed at 42°C for 30 min in a standard soap solution. Both fabrics were then separated and dried. For perspiration colorfastness testing, the sewn fabrics were immersed in either acid (pH = 5.5) or alkaline (pH = 8.0) artificial perspiration solutions at room temperature for 30 min. Then, they were transferred into a perspirometer for pressing, and the perspirometer was kept in an oven at 37°C for 4 h; then, the fabric was dried by air. The washing and perspiration fastness levels, observed against a grayscale, were classified as numbers ranging from 1 and 5, which referred to poor to excellent fastness, respectively. In contrast, the staining level on standard silk and cotton fabrics was labeled from 1 (the maximum stain) to 5 (the minimum stain).

RESULTS AND DISCUSSION

Silks grafted by HEMA and MMA vinyl monomers can be obtained via free-radical polymerization with APS as an initiator. Two chemical reactions can take place, that is, the grafting of monomers and macromonomers onto silk fibroin molecules and the polymerization of individual monomers leading to homopolymers. For the grafting technique, high polymer add-on and a low level of homopolymerization are essential for industrial applications.

Morphology

The surface morphology of silks can be examined with the scanning electron microscopy (SEM) technique. Figure 1 shows SEM micrographs of the degummed, HEMA-grafted, and MMA-grafted silks. The surface morphology reveals that the surface of the degummed silk was rather smooth, as shown in Figure 1(a), but rough surfaces for the HEMA-grafted and MMA-grafted silks were obtained. The surface of the HEMA-grafted silks was apparently composed of a polymer film coated on the silks [Fig. 1(b)]; however, the surface of the MMA-grafted silks presented granules of oligomer particles [Fig. 1(c)]. The observed surface morphology was due to the grafting process, which caused bonding between the silk and the vinyl monomers.

IR spectroscopy study

The modifying agent used for the chemical modification of silk fibroin can be examined with the IR technique. IR spectra of the degummed and grafted silks are presented in Figure 2. The IR spectrum of the degummed silk in Figure 2(a) shows significant wave numbers at 3411, 2921, 1646, and 1517 cm^{-1} because of NH stretching, CH stretching, C=O stretching, and NH bending in amides (amide I and amide II), respectively.[4,9] The HEMA-grafted silk presents IR spectra similar to those of the degummed silk, except for the peak position of 3411 cm^{-1}, attributed to NH stretching, that shifted to a higher wave number. The IR spectrum in Figure 2(b) of the HEMA-grafted silk presents the other absorption bands at the wave numbers of 1728 and 1262 cm^{-1}, which refer to C=O stretching of the ester groups in poly(2-hydroxyethyl methacrylate) (PHEMA). Moreover, additional absorption bands at 1738 and 1252 cm^{-1}, assigned to C=O stretching and C—O stretching of ester groups of PMMA, respectively, can be observed for the MMA-grafted silk [Fig. 2(c)].

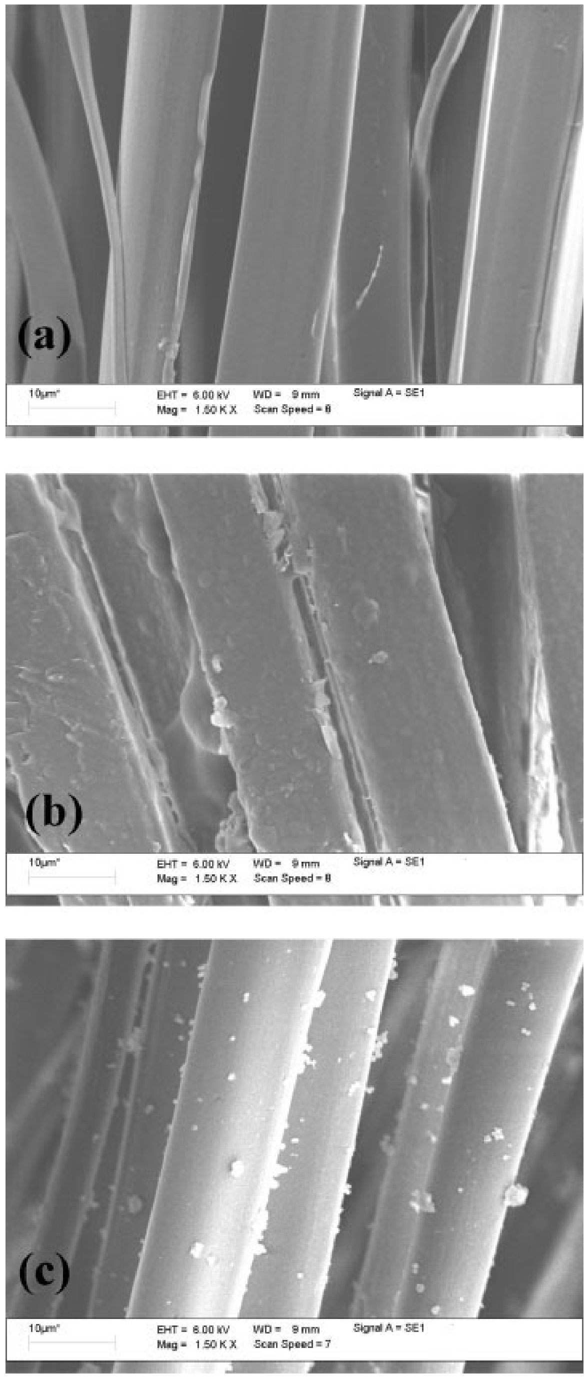

Figure 1 SEM micrographs of (a) degummed silk, (b) HEMA-grafted silk (75% grafting yield), and (c) MMA-grafted silk (65% grafting yield).

Moisture regain

Comfort during the wearing of silk fabrics is very important for textile applications. Comfort can be indirectly determined via the ability of the textile to absorb moisture. The moisture regain of the degummed, HEMA-grafted, and MMA-grafted silks is presented in Table I. Because of the hydrophilic characteristics of PHEMA, the moisture regain of the HEMA-grafted silk was much higher than that of the degummed silk. As expected, a greater content of PHEMA in the HEMA-grafted silk resulted in a slightly higher moisture regain. However, the MMA-grafted silk presented lower moisture regain than the degummed silk because of the hydrophobic nature of PMMA, which adhered to the surface of the MMA-grafted silk.

Chemical resistance

Acid and alkaline resistances can be expressed in terms of the percentage of weight loss of the silks af-

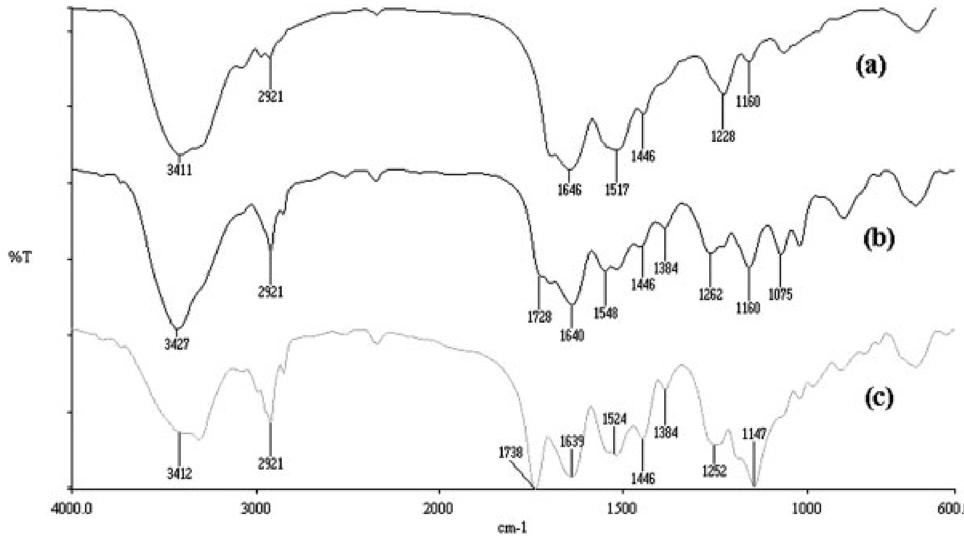

Figure 2 IR spectra of (a) degummed silk, (b) HEMA-grafted silk (75% grafting yield), and (c) MMA-grafted silk (65% grafting yield).

ter the immersion of samples in specific solutions for a specific time. Table I shows that the weight losses of both HEMA-grafted and MMA-grafted silks after acid and alkaline immersion clearly decreased, probably because the grafting technique caused a denser structure in the amorphous region; consequently, the acid and alkali could not penetrate the grafted silks as easily as the degummed silk.

Dyeing properties

In general, dyeing properties are unavoidably significant for textile utilization for both manufacturers and customers. The degummed silk was dyed with commercial yellow acid dyes and reactive dyes including a natural dye extracted from turmeric with a mordant.

Dye uptake

The dye uptake was examined on the basis of absorbance values obtained with a UV–vis spectrophotometer. The absorbance values were measured at the wavelength of the maximum absorption for each dye. The dye uptake increased for the HEMA-grafted and MMA-grafted silks dyed by acid and curcumin dyes, as shown in Table II. The results suggest that more physical interactions between the grafted silks and the acid or curcumin dyes can form. For acid dyeing, the cation of silk can attack the anion of the acid dye; therefore, ionic bonding can mainly be formed. When curcumin dyestuff, the natural yellow colorant in the flavonoid group, is applied, dipole–dipole interactions can be mainly formed between HEMA and MMA side groups and the curcumin dyestuff containing carbonyl, hydroxyl, and methoxy groups.[14]

In contrast, a chemical reaction is expected with the use of a reactive dye. It is widely accepted that silks can chemically react with reactive dyes at —OH or $—NH_2$ functional groups of silk structural fibroin and that a grafting process can take place at hydroxyl (—OH), amine ($—NH_2$), or carbonyl (⟩C=O) groups of silk fibroin. The results in Table II show that both HEMA-grafted and MMA-grafted silks presented lower dye uptake than degummed silk when the reactive dye was applied. This could be because the grafting process caused the reduction of functional groups reacting with the reactive dye. In addition, the bulky group of the grafted mono-

TABLE I
Moisture Regain of the Degummed, HEMA-Grafted, and MMA-Grafted Silks

Sample	Weight gain (%)	Moisture regain (%)	Weight loss (%)	
			Acid	Alkaline
Degummed silk	—	4.7 ± 0.1	4.9 ± 0.1	3.6 ± 0.6
HEMA-grafted silk	27.6 ± 4.7	6.6 ± 0.1	4.2 ± 0.5	3.4 ± 0.2
	74.8 ± 4.4	7.0 ± 0.1	4.1 ± 0.4	3.2 ± 0.6
MMA-grafted silk	11.5 ± 1.0	4.3 ± 0.2	3.1 ± 0.3	1.5 ± 0.3
	65.3 ± 1.9	4.1 ± 0.1	2.0 ± 0.2	1.1 ± 0.5

TABLE II
Percentage Dye Uptake of the Degummed, HEMA-Grafted, and MMA-Grafted Silks with Acid, Reactive, and Curcumin Dyestuffs

Sample	Weight gain (%)	Dye uptake (%)		
		Acid dye	Reactive dye	Curcumin dye
Degummed silk	—	37.5 ± 3.5	39.6 ± 3.9	14.6 ± 2.2
HEMA-grafted silk	27.6 ± 4.7	45.5 ± 3.8	5.0 ± 0.5	17.3 ± 2.8
	74.8 ± 4.4	50.3 ± 4.1	10.8 ± 0.3	29.8 ± 2.9
MMA-grafted silk	11.5 ± 1.0	45.8 ± 4.2	17.9 ± 0.5	27.5 ± 3.1
	65.3 ± 1.9	49.9 ± 5.3	N/A	32.6 ± 2.5

N/A = not applicable because of the hydrophobicity of the silks.

mers brought about difficulty for the chemical reaction, leading to a decrease in the dye uptake of the HEMA-grafted and MMA-grafted silks.

Color parameters

Color differences in textile samples can be classified with a spectrophotometer. Table III presents color parameters obtained after color measurements, that is, L^*, a^*, b^*, C^*, and H°, for the degummed and grafted silks dyed with acid, reactive, and curcumin dyes. All the grafted silks dyed with the acid dye showed similar a^* and b^* values, but the L^* and C^* values for the HEMA-grafted and MMA-grafted silks were higher than those for the degummed silk, showing greater brightness and chroma in the grafted silks. For the reactive dye, the L^* and a^* values were approximately equal for all samples, and b^* for both grafted silks was higher than that of the degummed silk; the HEMA-grafted silk with 75% polymer add-on presented the greatest b^* value, which indicated the most yellowness in the sample. In addition, the values of C^* were in the following order: HEMA silk > MMA silk > degummed silk. Furthermore, the L^*, b^*, and C^* values for both grafted silks dyed by curcumin dyestuff were higher than those of the degummed silk.

Colorfastness properties

The ability of dye molecules to remain within the fiber structure is an important aspect when a dyed textile fabric is used. Better fastness properties result in the same color shade as that of the original state after the fabric is used for a period of time. The important colorfastness properties are colorfastness to washing and colorfastness to perspiration. The colorfastness level and staining level on standard silk and cotton fabrics of the degummed, HEMA-grafted, and MMA-grafted silks are presented in Tables IV and V, respectively.

TABLE III
Color Parameters of the Degummed, HEMA-Grafted, and MMA-Grafted Silks with Acid, Reactive, and Curcumin Dyestuffs

Dyestuff	Sample	Weight gain (%)	Color parameter				
			L^*	a^*	b^*	C^*	H°
Acid dye	Degummed silk	—	44.0	36.1	79.3	83.5	68.9
	HEMA-grafted silk	27.6 ± 4.7	47.3	36.8	80.8	88.8	70.6
		74.8 ± 4.4	48.2	38.3	82.4	91.3	64.5
	MMA-grafted silk	11.5 ± 1.0	46.3	35.9	79.0	85.8	69.9
		65.3 ± 1.9	46.4	35.3	79.1	86.6	67.5
Reactive dye	Degummed silk	—	53.9	31.9	77.6	83.9	62.9
	HEMA-grafted silk	27.6 ± 4.7	54.9	29.5	86.7	91.6	62.9
		74.8 ± 4.4	55.5	31.6	91.5	96.7	63.9
	MMA-grafted silk	11.5 ± 1.0	55.7	29.2	83.4	87.7	64.1
		65.3 ± 1.9	N/A	N/A	N/A	N/A	N/A
Curcumin	Degummed silk	—	51.3	14.3	78.5	80.8	79.8
	HEMA-grafted silk	27.6 ± 4.7	54.6	15.6	81.9	83.4	79.3
		74.8 ± 4.4	56.5	17.5	82.1	84.3	76.6
	MMA-grafted silk	11.5 ± 1.0	56.4	16.7	81.1	83.8	77.7
		65.3 ± 1.9	57.2	17.2	85.3	87.7	78.4

N/A = not applicable because of the hydrophobicity of the silks.

TABLE IV
Colorfastness Properties of the Degummed, HEMA-Grafted, and MMA-Grafted Silks with Acid, Reactive, and Curcumin Dyestuffs

Fastness property	Sample	Weight gain (%)	Colorfastness level: Acid dye	Reactive dye	Curcumin
Washing	Degummed silk	—	4	4–5	3
	HEMA-grafted silk	27.6 ± 4.7	4	4–5	3–4
		74.8 ± 4.4	4	4–5	3–4
	MMA-grafted silk	11.5 ± 1.0	4	4–5	3–4
		65.3 ± 1.9	4–5	N/A	3–4
Acid perspiration	Degummed silk	—	4	4–5	4–5
	HEMA-grafted silk	27.6 ± 4.7	4	4–5	4–5
		74.8 ± 4.4	4	4–5	4–5
	MMA-grafted silk	11.5 ± 1.0	4	4–5	4–5
		65.3 ± 1.9	4–5	N/A	4–5
Alkaline perspiration	Degummed silk	—	4	4–5	4–5
	HEMA-grafted silk	27.6 ± 4.7	4	4–5	4–5
		74.8 ± 4.4	4	4–5	4–5
	MMA-grafted silk	11.5 ± 1.0	4	4–5	4–5
		65.3 ± 1.9	4–5	N/A	4–5

N/A = not applicable because of the hydrophobicity of the silks.

Colorfastness to washing

Colorfastness to washing is very important for both dyeing and finishing processes. A washfastness test was performed through the washing of the standard and sample fabrics in a standard solution at a controlled temperature and time; after that, the color change was observed against a grayscale, and the washfastness level was reported from 1 to 5, as shown in Table IV. The washfastness property of the HEMA-grafted silks with grafting yields of 28 and 75% dyed with the acid dye was at the same level as that of the degummed silks. Because the washing fastness level of the degummed silks was already at an excellent level, the fastness to washing could be maintained by the grafting process using HEMA monomers. In addition, the staining level on the silk and cotton standard fabrics was indicated to be fair, as presented in Table V.

On the contrary, the MMA-grafted silk with a percentage grafting yield of 65% dyed with the acid dye showed a better washfastness level than the

TABLE V
Staining Level on White Standard Fabrics of the Degummed, HEMA-Grafted, and MMA-Grafted Silks with Acid, Reactive, and Curcumin Dyestuffs

			Staining level					
			Acid dye		Reactive dye		Curcumin	
Fastness property	Sample	Weight gain (%)	Silk	Cotton	Silk	Cotton	Silk	Cotton
Washing	Degummed silk	—	3	3–4	4–5	4–5	1	1–2
	HEMA-grafted silk	27.6 ± 4.7	3	3–4	4–5	4–5	1	1–2
		74.8 ± 4.4	3	3–4	4–5	4–5	1	1–2
	MMA-grafted silk	11.5 ± 1.0	3–4	3–4	4–5	4–5	1	1–2
		65.3 ± 1.9	4	4	N/A	N/A	1	1–2
Acid perspiration	Degummed silk	—	3–4	4	4–5	4–5	1	1–2
	HEMA-grafted silk	27.6 ± 4.7	3–4	4	4–5	4–5	1	1–2
		74.8 ± 4.4	3–4	4	4–5	4–5	1	1–2
	MMA-grafted silk	11.5 ± 1.0	3–4	4	4–5	4–5	1	1–2
		65.3 ± 1.9	3–4	4	N/A	N/A	1	1–2
Alkaline perspiration	Degummed silk	—	3	4	4	4	1	1–2
	HEMA-grafted silk	27.6 ± 4.7	3	3–4	4–5	4–5	1	1–2
		74.8 ± 4.4	3	3–4	4–5	4–5	1	1–2
	MMA-grafted silk	11.5 ± 1.0	3–4	3–4	4–5	4–5	1	1–2
		65.3 ± 1.9	3–4	3–4	N/A	N/A	1	1–2

N/A = not applicable because of the hydrophobicity of the silks.

degummed silk (Table IV) because of the ionic interaction between the carbonyl group of the MMA monomer and the anion of the dye molecule; therefore, the movement of the dye molecules was inhibited. In addition, staining on the standard silk and cotton fabrics could be minimized with the 65% weight gain of the MMA-grafted silk (Table V). However, a low grafting level of approximately 12% MMA did not result in an improvement in the fastness to washing of the MMA-grafted silk (Table IV).

Because a reactive dye can form a covalent bond with silk fibroin, the degummed, HEMA-grafted, and MMA-grafted silks presented excellent levels of fastness to washing, as shown in Table IV. Besides, all the silk samples showed the least staining ability on standard silk and cotton fabrics when the reactive dye was used, as indicated in Table V.

When curcumin was used, the colorfastness to washing (Table IV) of both grafted silks could be improved because the HEMA-grafted and MMA-grafted silks could interact with the curcumin dyestuff and form complex compounds between the dye, monomer, and mordant. Moreover, the improvement of the colorfastness level to washing for both grafted silks implied that, during the washing action, the color maintenance capability was improved with the presence of PHEMA and PMMA molecules within the amorphous region of the grafted silk fibroin. On the contrary, great staining on the standard fabrics for all silks dyed with curcumin was obtained, as indicated by staining levels of 1 or 1–2 (Table V), even though the colorfastness level for washing was increased through grafting with HEMA and MMA monomers.

Colorfastness to perspiration

Each person excludes perspiration of a different chemical composition that depends on his body metabolism. In general, human perspiration can be divided into two different groups, that is, acid and alkaline types, so two dissimilar tests were performed for the dyed silks obtained from the degummed and grafted silks. Table IV presents numerical levels of colorfastness for acid and alkaline artificial perspiration solutions containing histidine monohydrochloride monohydrate, sodium chloride, and sodium orthophosphate.

When the acid dye was applied, the colorfastness levels to both acid and alkaline perspiration solutions of HEMA-grafted silk were on the same level as that of the degummed silk, and the staining levels were moderate (Table V). The colorfastness properties to acid and alkaline perspiration, as shown in Table IV for the MMA-grafted silk dyed with the acid dye with a grafting yield of 65%, showed better results than those of the degummed silk, probably because of the formation of ionic bonds between the MMA-grafted silk and the acid dye. On the other hand, the improvement of the acid perspiration fastness for the MMA-grafted silk with a 65% weight gain gave the same staining level to the standard fabrics as the MMA-grafted silk with a 12% weight gain, as presented in Table V. Nevertheless, the fastness to acid and alkaline perspiration for the MMA-grafted silk with a 12% grafting yield was similar to that of the degummed silk. Table IV also shows that all silks dyed by the acid dye presented lower fastness to acid and alkaline perspiration solutions than the silks dyed by the reactive dye because of the covalent bond formation when the reactive dye was used.

In the case of reactive and curcumin dyestuffs, the colorfastness to acid and alkaline perspiration for the degummed, HEMA-grafted, and MMA-grafted silks was found to be on the same excellent level (Table IV), regardless of the grafting yield, and this indicated that dye retention due to acid and alkaline perspiration solutions was maintained.

As for the staining level after acid and alkaline perspiration fastness tests, Table V shows that all the samples dyed with the reactive dye showed the highest staining level (the least stain), but the opposite results (the highest stain) were obtained when the curcumin dye was used. The staining levels for all the samples tested for acid and alkaline perspiration could be arranged in the following order: reactive dye > acid dye > curcumin dye.

Comparison of the properties for MMA-grafted, MAA-grafted, and HEMA-grafted silks

Grafting vinyl monomers into silk fibroin causes significant changes in the grafted silk properties. MMA-grafted and MAA-grafted silks presented higher Young's modulus values but lower tenacity and elongation at yield values in comparison with degummed silk; there was an increase in the stiffness for the grafted silks.[15] However, the moisture regain of the grafted silks depended on the hydrophilic characteristics of the vinyl monomers grafted onto the silk structures. In this research, the moisture regain of the MMA-grafted silk was lower than that of the degummed silk, but the opposite behavior was found for the HEMA-grafted silk. When the chemical resistance of the grafted silks was considered, the results suggested that both the MMA-grafted and HEMA-grafted silks showed better chemical resistance than the degummed silk. In addition, the colorfastness properties of the grafted silks depended on the monomers as well as the dyestuffs. The MMA-grafted and MAA-grafted silks presented greater colorfastness levels to washing and perspiration than the degummed silk when the acid dye was applied.[15] Nevertheless, no change in the colorfastness level to washing and perspiration was found for the HEMA-grafted silk with the acid dye. Furthermore, using the curcumin dyestuff with the mordant caused an improvement in the colorfastness to washing for the MMA-grafted, MAA-grafted, and HEMA-grafted silks.

CONCLUSIONS

The HEMA-grafted silk showed higher moisture regain and acid and alkaline resistances than the degummed silk, regardless of the weight gain. The dye uptake of both the HEMA-grafted and MMA-grafted silks increased when the acid, reactive, and curcumin dyes were applied. For the colorfastness properties, the HEMA-grafted silk dyed with acid and reactive dyes presented the same fastness level to washing and acid and alkaline perspiration as the degummed silk. In contrast, the colorfastness to washing of the MMA-grafted silk with a 65% weight gain was better than that of the degummed silk when the acid dye was applied. Poor staining properties of the degummed, HEMA-grafted, and MMA-grafted silks were clearly observed with the use of the curcumin dyestuff. Nevertheless, the washfastness of the degummed silks dyed with curcumin could be improved through grafting with HEMA and MMA monomers.

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