Dyeing Properties of *Bombyx mori* Silks Grafted with Methyl Methacrylate and Methacrylamide

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ABSTRACT: To improve their dyeing and colorfastness properties, degummed *Bombyx mori* silks were chemically modified by a grafting technique with either methyl methacrylate (MMA) monomer or methacrylamide (MAA) monomer. Both commercial synthetic dyes, that is, acid and basic dyes, and natural dyes extracted from turmeric, without and with potassium aluminum sulfate mordant, were used in this study. Percentage dye uptake increased with the presence of poly(methyl methacrylate) or polymethacrylamide in the silk fibroin structure regardless of the types of the dyestuffs. Furthermore, compared to the degummed silk, the colorfastness to washing of the MMA-grafted and MAA-grafted silks dyed with acid, basic, and curcumin dyestuffs were greatly improved. Colorfastness to both acid and basic perspirations with acid and basic dyestuffs was slightly improved, whereas perspiration fastness remained unchanged for curcumin dyeing without and with the presence of the mordant. Also, the low-light resistances of the degummed and grafted silks dyed by curcumin dyestuff were notably improved by the MMA and MAA grafting technique. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1169–1175, 2006

Key words: dyes/pigments; graft copolymers; modification

INTRODUCTION

Silks possess many outstanding properties, including strength, dyeability, luster, handle, and moisture, that distinguish them from other natural and synthetic fibers. However, some textile properties of degummed silks, such as colorfastness properties, wrinkle recovery, rubbing resistance, and dimensional stability, also need to be improved. In recent years, the graft copolymerization of vinyl monomers has been regarded as a powerful method not only for increasing silk weight but also for improving the inferior textile properties of silk.[1–13] The physical and chemical properties of the grafted silks depend not only on the extent of grafting and/or weight gain but also on the characteristics of the functional group carried out by the monomer, which becomes an integral part of the silks.

Among vinyl monomers, methacrylamide (MAA),[1–5,8] methyl methacrylate (MMA),[6–9,11–13] and 2-hydroxyethyl methacrylate[3–5,8] have been extensively studied. Silks have been impregnated with MAA up to quite a high percentage of polymer add-on, and the comfort and drape properties of the silks have not been significantly affected by the MAA.[1–5,8] Copolymerization of silk fabrics with MMA has shown increases in wrinkle recovery and comfort and the maintenance of typical silk-like handle properties when the graft yield was in the range 30–60%.[6–9,11–13] Silks, copolymerized with both MAA and 2-hydroxyethyl methacrylate at low graft yields, have presented a noticeable increase in the moisture content and comfort of the silk fabric.[3,5]

Grafted silks unavoidably need to be dyed for textile applications. Generally, color is usually the first attribute noticed in a textile and is often an influential factor in customer decisions. Textile materials are also expected to exhibit a range of fastness properties in their application that ensure that they will withstand the effects of the environment in which they are placed, both in processing and in their useful lifetime. Dye uptake is the crucial parameter for dyeing process, and colorfastness properties are the most essential aspect for fabric exploitation.

Commonly, synthetic dyes are widely used due to their commercially availability, various color shades, and ease of use; however, environmental problems are still a major concern. On the contrary, natural dyes that present environmental compatibility, low toxicity, and few allergic reactions are growing in popularity. One example of natural 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*). This yellow colorant has been used as a natural dyestuff

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and also as a food colorant.[14,15] Nevertheless, a problem that arises with natural dyes is poor fastness properties, especially light fastness.[16,17]

Because the colorfastness properties of degummed silks have to be improved, the grafting process with vinyl monomers is considered an interesting technique. The influence of grafting on the dye uptake and colorfastness properties of MMA-grafted and MAA-grafted silks has not been reported; therefore, this study involved the investigation of the effects of grafting on the dye uptake and colorfastness properties to washing, acid and basic perspirations, and light of degummed, MMA-grafted, and MAA-grafted silks (*Bombyx mori*). Curcumin dyestuff, with and without a mordant used to improve dye affinity, was selected as a natural dyestuff to dye the MMA-grafted and MAA-grafted silks to compare with synthetic dyestuffs, that is, acid and basic dyes.

EXPERIMENTAL

Materials

Raw silks (*B. mori*) were obtained from Jim Thompson (Nakorn Ratchaseema, Thailand). Reagent-grade MMA and MAA monomers including formic acid were obtained from Merck, Co., Ltd. (Samutprakarn, Thailand). Ammonium persulfate (APS) was used as the initiator. Alkali solutions of both sodium carbonate and sodium bicarbonate including Sandopan 60 soap solution were used for degumming. Acid dye (Erionyl Yellow A-R, C.I. Acid Orange 67) and basic dye (Maxilon Yellow 4GL, C.I. Basic Yellow 87) were from Ciba Specialty Chemicals (Samutsakorn, Thailand). Curcumin (*Curcuma longa,* C.I. Natural Yellow 3) was obtained locally, and the mordant used for natural colorant dyeing was potassium aluminum sulfate from ACS Xenon (Bangkok, 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 by immersion of the silks in a reaction system at pH 3 (adjusted with formic acid) containing 0.05 mol/L APS initiator and 0.8 mol/L MMA or MMA monomer. The liquor-to-material ratio during the treatment was maintained at 1:100. The temperature was gradually raised from room temperature to 80°C within 30 min and then maintained at this level for different periods of time. The grafted silks were thoroughly rinsed with acetone and then water and then vacuum-dried. The percentage polymer add-on was calculated from the weight difference of the dried silks before and after the graft treatment.

Dyeing

The degummed, MMA-grafted, and MAA-grafted silks were dyed with the exhaustion method with commercial acid and basic dyestuffs to examine 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 silk weight was maintained at 30:1. The initial temperature was 30°C, and the dyeing temperature was then raised to 90°C within 30 min; the silks were further dyed at this temperature for 45 min. Finally, the dyed silks were washed with water and dried at room temperature. The dyeing conditions and recipe conformed to manufacturer suggestions. Furthermore, the natural colorant extracted from turmeric was prepared[15] by 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 with a dyeing temperature of 60°C for 10 min, and the material-to-liquid ratio was maintained at 1:30. Dyeing was also done without and with potassium aluminum sulfate mordant (8% owf) for the curcumin dyeing procedure (metamordant). In addition, the percentage dye uptake was examined from the increase in the weight gain before and after the dyeing processes, and three measurements were carried out to calculate and average the percentage dye uptake values. Statistical analysis of the obtained data was also performed with the Tukey test to determine significant differences ($p \leq 0.05$) among the treatment means.

Mechanical properties

The mechanical property measurements were carried out in a universal testing machine (Lloyd Instrument) together with WINDAP software. The standard conditions were a load cell of 100 N, a crosshead speed of 30 mm/min, and a gauge length of 25 mm. Fifteen specimens were tested to obtain average values of Young's modulus, tenacity, and percentage elongation at yield. The diameters of the degummed and grafted silks were measured by optical microscopy (Nikon), and 25 fibers per sample were measured to obtain average values.

IR spectroscopic study

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

Colorfastness

Colorfastness of the silk samples was tested to washing, acid and basic artificial perspiration solutions,

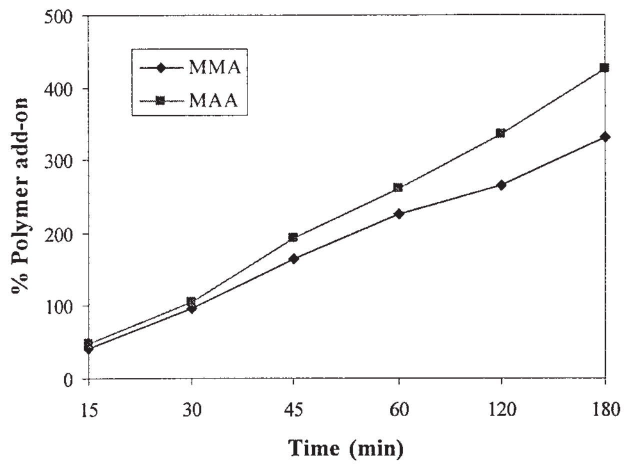

Figure 1 Polymer add-on percentage with grafting time for *B. mori* silk with either MMA or MAA monomer.

and also light according to ISO 105 CO1–C03, ISO 105 E04, and ISO 105 B02, respectively. Colorfastness to washing and perspiration tests were carried out with both sample and standard fabrics, which 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 basic (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 a temperature of 37°C for 4 h; then, the fabric was dried in air. To observe colorfastness to light, standard fabrics were first dyed with each of the following dyes, C.I. Acid Blue 104, C.I. Acid Blue 109, C.I. Acid Blue 83, C.I. Acid Blue 121, C.I. Acid Blue 47, C.I. Acid Blue 28, C.I. Solubilized Vat Blue 5, and C.I. Solubilized Blue 8, in the standard levels 1–8, respectively. Then, both the dyed sample and standard fabrics were exposed to Xenon arc light with cardboard to protect the fabrics in each exposure time interval starting from level 1 to level 8. Color change before and after each colorfastness test was assessed against a grey scale and are reported as numbers between 1 (severely fading) and 5 (excellent fast) for colorfastness to washing and perspiration and between 1 (severely fading) and 8 (excellent fast) for colorfastness to light.

RESULTS AND DISCUSSION

Grafting silks with MMA and MAA monomers

Silks were grafted by MMA and MAA vinyl monomers, which could be polymerized through free radicals. At a temperature of 80°C, the APS initiator generated free radicals, which led to different free radicals, not only from vinyl monomers but also from structural chains of silk fibroin. As a result, two chemical reactions occurred, that is, polymerization of the individual monomers and also the grafting of monomers and macromonomers onto silk fibroins. For grafting techniques, a high weight gain, combined with a reduced level of homopolymerization, is a prerequisite for industrial applications. As shown in Figure 1, the percentage of polymer add-on of silk grafted with either MMA or MAA monomer obviously increased with increasing grafting time. Moreover, both the MMA and MAA monomers showed a similar trend of grafting ability. From the same grafting conditions, the MAA-grafted silk showed a slightly greater percentage of polymer add-on than MMA, probably due to the less bulky side group of polymethacrylamide (PMAA) and the similar chemical structures, or amide structures, of MAA and silk fibroin, which helped grafting take place more easily.

Mechanical properties of the MMA-grafted and MAA-grafted silks

For textile applications, the mechanical properties of a textile fiber are determined to obtain information about the fiber strength and stiffness. The raw silk presented average values of Young's modulus, tenacity, and percentage elongation at yield of approximately 1.9 GPa, 40 g/denier, and 21%, respectively. When the mechanical properties of the raw silk were compared with the degummed silk, the degummed silks exhibited a slight change in mechanical properties (1. 7 GPa, 43 g/denier, and 23%, respectively). This implies that the removal of sericin by the degumming process caused the softness of the silk by the indication of Young's modulus and elongation at yield.

Figures 2–4 illustrate the mechanical properties of the MMA-grafted and MAA-grafted silks with differ-

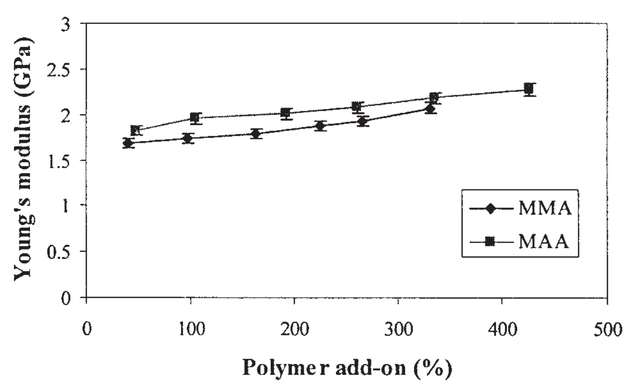

Figure 2 Young's moduli of the MMA-grafted and MAA-grafted silks with different polymer add-on percentages.

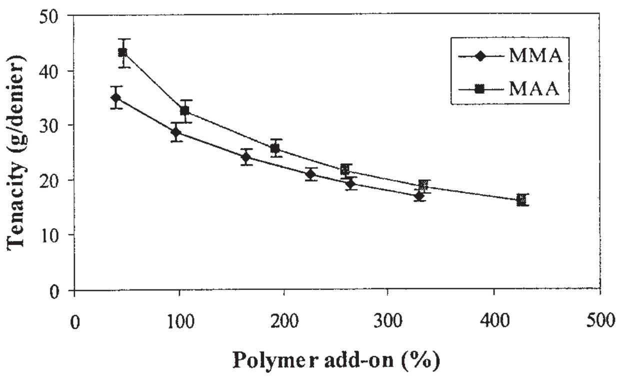

Figure 3 Tenacities of the MMA-grafted and MAA-grafted silks with different polymer add-on percentages.

ent percentages of polymer add-on. The Young's moduli (Fig. 2) of both of the grafted silks showed an increasing trend with polymer add-on due to the increment of fiber stiffness. This was because graft copolymerization occurs in the amorphous region of silks through chemical bonding between silk polymer chains with vinyl monomers.[3,11] Consequently, the grafted silks become stiffer, which inhibits the elastic deformation process occurring in the amorphous area, than those of the ungrafted silks.

However, the tenacities of the MMA-grafted and MAA-grafted silks decreased rapidly with increasing polymer add-on; after that, the decline in tenacity was slower (Fig. 3). A similar trend was also observed, as shown in Figure 4, for elongation ability. The reason is that the copolymerization produced a nonhomogeneous phase inside the grafted silks, which results in the creation of a large number of sites of stress concentration. Therefore, the ability of fibroin chains to slip or chains to move during plastic deformation in the crystalline region, accounted for fiber fracture, is enhanced.

Because of the comparable softness and mechanical properties between the degummed silk and the MMA-grafted and MAA-grafted silks (with 42 and 48% polymer add-on, respectively), further characterization and tests were carried out on these silks.

IR spectroscopic study

Chemical modification of silk entails incorporation into the protein substrate of the chemical group characteristics of the modifying agent. As shown in Figure 5(a), the IR spectrum of the degummed silk presented fibroin absorption bands at 1510 and 1650 cm^{-1}, assigned to the C═O stretching and N—H stretching of amide I and amide II, respectively. Other peak positions were located at 2926 and 3413 cm^{-1}, which were attributed to the C—H stretching and N—H stretching deformations, respectively.[18] New IR absorption bands of the MMA-grafted silk are presented in Figure 5(b) at wave numbers of 1146 and 1236 cm^{-1}; they were responsible for the C—O stretching of the ester group of poly(methyl methacrylate) (PMMA). Another dominant peak at 1733 cm^{-1} was due to C═O stretching from the PMMA molecule.[18] Figure 5(c) illustrates the absorption bands at 1516 and 1636 cm^{-1} assigned to the C═O stretching and N—H bending of the primary amide of PMAA.

Dyeing properties

Good dyeing properties are essential for textile dyeing procedures and for the use of the resulting dyed material. The degummed silk was dyed with commercial acid and basic dyes and natural dye extracted from turmeric with and without the mordant.

Dyeing ability

Table I presents percentage dye uptake, as examined from the weight gain of the degummed, MMA-grafted, and MAA-grafted silks before and after the dyeing procedures, with the three different dyestuffs. As clearly shown, both of the grafted silks showed a greater percentage dye uptake than the degummed silk for all of the synthetic and natural dyestuffs. This was probably due to the grafting process taking place in the amorphous region of the silk fibroin, which led to a greater possibility of the dye molecules penetrating into the silk amorphous structure and to greater interaction between the dye molecule and the grafted silk fibroin.

The mechanism of ionic dyeing for both acid and basic dyes first occurs through dyestuff penetration into the silk structure, especially in the amorphous area. For ionic dyeing, which is normally used for dyeing silks, ions of dye molecules are then attracted to oppositely charged ions of silk, and at the same

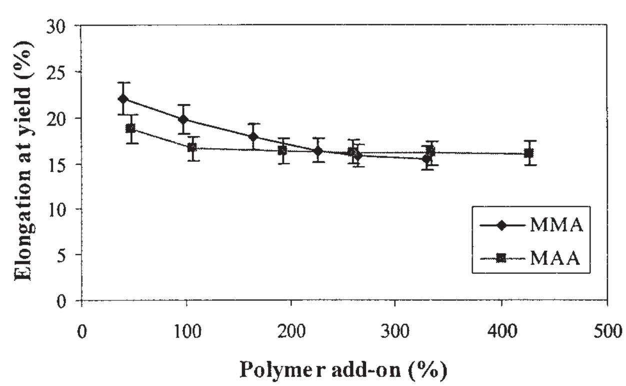

Figure 4 Elongations at yield of the MMA-grafted and MAA-grafted silks with different polymer add-on percentages.

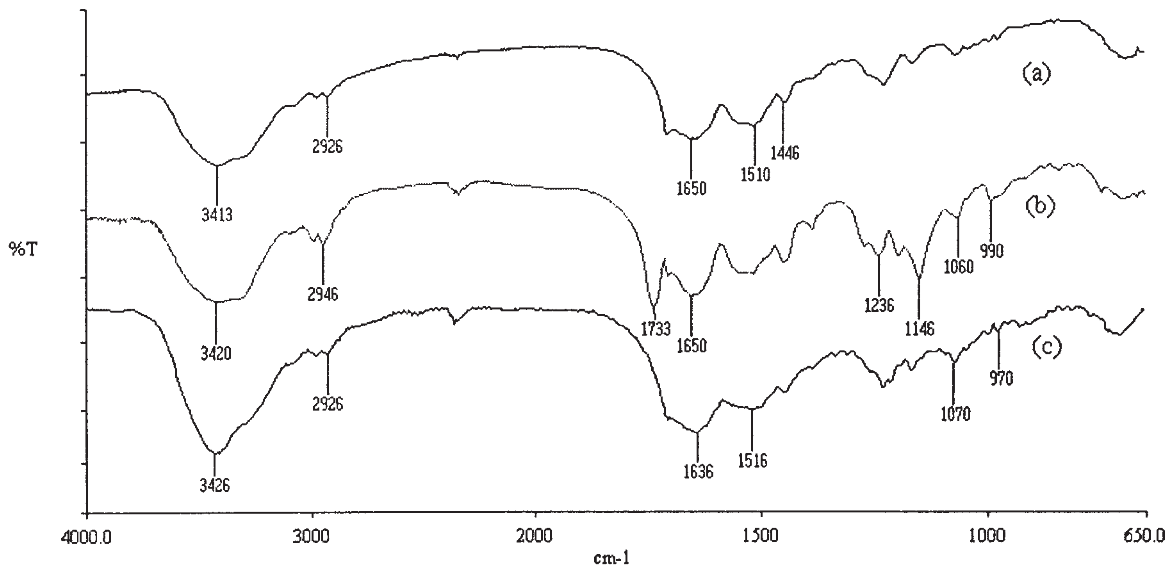

Figure 5 Fourier transform infrared spectra of (a) degummed silk, (b) MMA-grafted silk with 42% polymer add-on, and (c) MMA-grafted silk with 48% polymer add-on.

time, Van der Waal's forces between the similarly charged ions of the dye and silk are formed. As a protein fiber, silk is a polyampholite with cationic and anionic groups. 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; therefore, silks can be dyed with various acid and basic dyes. In the case of acid dye, silk possesses cations that can attract anions of the acid dye by ionic bonding. Oppositely charged ions are also found for basic dyeing.

Curcumin, the natural yellow colorant in flavonoid groups, is typically used for dyeing silk and cotton.[14] The percentage dye uptake, as shown in Table I, indicated that slightly greater dye uptakes were obtained from the MMA-grafted and MAA-grafted silks, regardless of the use of the potassium aluminum sulfate mordant. This is possibly because the MMA and MAA monomers, presented in the grafted silk molecular structures, caused not only the volume expansion of the amorphous region but also dipole–dipole interactions, hydrogen bonding, and Van der Waal's forces between the MMA and MAA side groups and the curcumin dyestuff, which contained carbonyl, hydroxyl and methoxy groups.[14]

Generally, mordants, salts of inorganic elements such as aluminum, iron, and copper, are used together with natural dyestuffs to improve not only interactions between natural dyestuffs and fibers by the formation of complex molecules but also colorfastness properties.[19] When the mordant was used during curcumin dyeing, the degummed and both of the grafted silks had greater percentage dye uptakes compared to that of those dyed without the mordant because complex molecules could be formed among the dyestuff, MMA-grafted or MAA-grafted fibroin, and mordant molecules.

Colorfastness properties

Colorfastness properties, which are concerned with dye retention within the fiber structure, are other key parameters for textile fabrics. Good colorfastness properties bring about a similar color shade in used

TABLE I
Dye Uptake for the Degummed and MMA-Grafted and MAA-Grafted Silks with 42 and 48% Polymer Add-On, Respectively

Dye	Dye uptake (%)		
	Degummed silk	MMA-grafted silk	MAA-grafted silk
Acid dye	4.55_a	5.40_b	6.00_c
Basic dye	2.20_a	4.75_b	5.70_c
Curcumin dye without mordant	7.80_a	8.70_b	8.45_c
Curcumin dye with mordant	9.25_a	10.30_b	10.79_c

Different subscript letters in the same row indicate significant differences ($p \leq 0.05$).

TABLE II
Colorfastness Levels for the Degummed, MMA-Grafted, and MAA-Grafted Silks with Acid, Basic, and Curcumin Dyestuffs

Colorfastness property	Colorfastness level		
	Degummed silk	MMA-grafted silk	MAA-grafted silk
Acid dyeing			
Washing	2	3	4–5
Acid perspiration	2–3	4	3–4
Basic perspiration	3	4	3–4
Light	5	6	6
Basic dyeing			
Washing	2	3	3–4
Acid perspiration	2–3	3	3–4
Basic perspiration	2	4	3–4
Light	4	5	5
Curcumin dyeing without mordant			
Washing	2	4–5	4–5
Acid perspiration	3	3	3
Basic perspiration	3	3	3
Light	2	5	4
Curcumin dyeing with mordant			
Washing	3	4–5	4–5
Acid perspiration	4	4	4
Basic perspiration	4	4	4
Light	3	5	4

The MMA-grafted and MAA-grafted silks had 42 and 48% polymer add-on, respectively.

fabrics as that of the original fabric after the fabrics are used for a period of time. The important colorfastness properties are colorfastness to washing, perspiration, and light.

Colorfastness to washing

Wash fastness, the ability of dyes to remain in the fiber when placed in water, is important during both dyeing and further textile finishing processes. We tested colorfastness to washing by washing both the standard and sample fabrics in a standard solution at a controlled temperature and time; then, the color change was observed against a grey scale. The colorfastness level was reported from 1 to 5. Both MMA-grafted and MAA-grafted silks presented greater levels of washing colorfastness than the ungrafted silks when acid and basic dyestuffs were applied (Table II); this suggests that the grafting process improved the washing colorfastness of the silks.

The reason for the improvement in the washing colorfastness of the MMA-grafted and MAA grafted silks may be because the silks contained PMMA and PMAA molecules in their amorphous regions, which led to higher free volumes inside the amorphous areas. In the grafted silks, the possibility of the dye molecules entering the amorphous region should have been greater than that of the degummed silk due to the presence of the polymers. In addition, the percentage dye uptake for the grafted silks was higher than that of the degummed silk (Table II), which indicated that the diffusion and migration of the dye molecules into the amorphous area was, to some extent, influenced by the existence of PMMA and PMAA. When dye molecules diffused into the amorphous boundary, the movement of the dye molecules was, therefore, inhibited not only by ionic bonds among the MMA or MAA, dyestuffs, and silk fibroin molecules but by also Van der Waal's force attractions of the hydrophobic or nonpolar parts between the dye molecule and the grafted silks.

Through the comparison of the silks grafted by the MMA and MAA monomers, we found that the washing colorfastness level for the MAA-grafted silk was slightly greater for both acid and basic dyestuffs, possibly due to greater polymer add-on and the resulting dye uptake of the MMA-grafted silk, which led to the greater possibility of the formation of ionic and physical interactions.

When the curcumin natural dyestuff was used, as shown in Table II, colorfastness to washing for the degummed silk was notably improved with the presence of the mordant, due to complex molecule formation between the silk fibroin, mordant, and curcumin.[19] In addition, colorfastness level to washing for both of the grafted silks dyed by curcumin without the mordant was clearly higher than that of the degummed silk, which implied that during the washing action, color maintenance capabilities were improved with the presence of PMMA or PMAA molecules within the amorphous region of the grafted silk fibroin, due to Van der Waal's forces, hydrogen bonding, and dipole–dipole interactions between the grafted silk and the curcumin dyestuff. Similar colorfastness to washing levels were also obtained for both of the grafted silks dyed with curcumin dyestuff in the presence of the mordant, which indicated that the improvement of colorfastness to washing could not be detected with the use of the mordant and the formation of the complex molecules because the washing colorfastness level was already excellent (4–5).

Colorfastness to perspiration

Human perspiration contains organic and salt solutions excreted from the human body. Each person possesses a different chemical composition of perspiration depending on his or her body metabolism. In general, human perspiration can be classified into two different types, that is, acid and basic types, so two dissimilar tests were performed for the dyed silks with and without the grafting process. Table II also presents numerical levels of colorfastness to acid and basic artificial perspiration solutions containing histidine monohydrochloride monohydrate, sodium chloride, and sodium orthophosphate. Grafting with MMA and MAA, including dyeing with acid and basic dyes, produced a slight increase in both acid and basic perspiration colorfastness properties in comparison with the ungrafted silks. The perspiration fastness results suggest that the presence of PMMA or PMAA molecules in the silk fibroin could slightly improve the acid and basic dye retention behaviors of the grafted silks.

For the curcumin dyeing, as shown in Table II, colorfastness levels to acid and basic perspirations for the degummed and both of the grafted silks were similar, which indicated that dye retention manners due to acid and basic perspirations were maintained for the degummed, MMA-grafted, and MAA-grafted silks dyed by curcumin without and with the mordant (Table II).

Colorfastness to light

When a dye molecule is exposed to light, one type of energy, the chemical structure of dye molecule may be changed, such as by chemical bonding dissociation, or auxochrome removal. As a result, color shading, leveling, and intensity can be affected. Some chromophores, for example, —C═O, can absorb UV radiation and result in Norrish chemical reactions that affect the color change.[20] Colorfastness levels of the degummed and grafted silks to light (Xenon arc) are shown in Table II. The MMA-grafted and MAA-grafted silks in the case of acid dye showed one greater level of colorfastness to light compared to the silks without grafting. The results indicate that PMMA or PMAA molecules grafted in the silk structure could prevent, to some extent, some chemical reactions after exposure to light. Also, the surface of the grafted silks appeared to be glossy due to the polymer coating. The glossy surface of the grafted silks tended to reflect light exposed onto the silk. As a result, some chemical reactions may have been partially interrupted, which led to the improvement in colorfastness to light for the grafted silks. Similar to acid dyeing, basic dyeing also showed an enhancement in light colorfastness levels in the grafted silks compared to the degummed silk, as presented in Table II.

In general, light fastness properties are one of the main drawbacks with natural dyestuffs due to the energy absorption of the presenting chromophore.[17] For the degummed silk, the use of the mordant for curcumin dyeing was found to improve its light fastness. As shown in Table II, a considerable enhancement in colorfastness level to light was remarkably achieved for both of the grafted silks dyed by curcumin dyestuff, regardless of the use of the mordant, possibly because the used monomer could reduce the energy from UV radiation to direct exposure on the chromophore of the curcumin dyestuff.

CONCLUSIONS

Mulberry silks were chemically modified by MMA or MAA vinyl monomers via a grafting technique, and the dyeing properties were examined with acid dye, basic dye, and a natural dye extracted from turmeric. High percentages of polymer add-on were obtained for both of the grafted silks, and the grafted silks exhibited greater dye uptake than that of the degummed silk. Also, improvements in colorfastness to washing, perspiration, and light were observed in the silk grafted by MMA or MAA dyed by acid and basic dyestuffs. Additionally, for curcumin dyeing, colorfastness to washing and light for the MMA-grafted and MAA-grafted silks was enhanced. However, colorfastness to both acid and basic perspiration with curcumin dyestuff was maintained by the grafting process, and the mordant affected the colorfastness properties of only the degummed silk.

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