Improving dyeing properties of silk grafted with methyl methacrylate and methacrylamide

The chemists at King Mongkut's Institute of Technology, Ladkrabang, Bangkok, Thailand worked on degummed *Bombyx mori* silk to improve its dyeing and colourfastness properties, 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 polymethyl methacrylate or polymethacrylamide in the silk fibroin structure regardless of the types of the dyestuffs. Furthermore, compared to the degummed silk, the colourfastness to washing of the MMA-grafted and MAA-grafted silks dyed with acid, basic and curcumin dyestuffs were greatly improved. Colourfastness 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 [Prachayawarakorn Jutarat and Kryratsamee Watthana, Dyeing properties of *Bombyx mori* silks grafted with methyl methacrylate and methacrylamide, *J Appl Polym Sci*, 2006, **100**(2), 1169-1175].

Adsorption and kinetic study of lac dyeing on silk

Lac dye is a natural reddish dyestuff extracted from stick lac which is a secretion of the insect *Coccus laccae* (*Laccifer lacca* Kerr). The insect *C. laccae* is often found in South and Southeast Asia, especially in Thailand and India. In Thailand, the lac insect grows most commonly on the Rain tree, ***Samanea saman* (Jacq.) Merr.** (syn. *Pithecellobium saman* Benth.). Lac dye is used extensively as a natural food additive, in cosmetics and as a colourant for silk and cotton dyeing. In the North and the Northeast of Thailand, it is used as a natural red dyestuff for cotton and silk dyeing but the fastness properties and reproducibility to give consistency in production are still problems to be solved. As part of the approach to tackle these problems, fundamental physical studies on the dyeing process are important.

Adsorption and kinetic studies of lac dyeing of silk were investigated by scientists of Thailand and Australia using, as optimal conditions, a *p*H of 3.0, a material to liquor ratio (MLR) of 1:100, an initial dye concentration of 450 mg/litre and 60 min contact time. The progress of dye adsorption was monitored at λ_{max} 487 nm by visible spectroscopy. The experimental data fitted well to the Langmuir and Freundlich isotherms with a high correlation coefficient (R^2). The pseudo second-order kinetic model was indicated with the activation energy of 47.5 kJ/mol. It is suggested that the overall rate of lac dye adsorption is likely to be controlled by the chemical process. The values of the enthalpy ($\Delta H^{\#}$) and entropy of activation ($\Delta S^{\#}$) were 44.7 kJ/mol and −175.7 J/mol K, respectively. The free energy of activation ($\Delta G^{\#}$) at 30°C was 97.9 kJ/mol. The activation parameters with and without erythrolaccin in the lac dye were similar, consistent with erythrolaccin only having a slight effect on the lac dyeing of silk. The free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) terms for the lac dyeing were also determined and the negative values of ΔG and ΔH obtained indicated that the lac dye adsorption process is a spontaneous and an exothermic one. The results from this kinetic study will assist in gaining a better understanding of the adsorption mechanism of this dyeing process [Chairat Montra, Rattanaphani Saowanee, Bremner John B and Rattanaphani Vichitr, An adsorption and kinetic study of lac dyeing on silk, *Dyes Pigments*, 2005, **64**(3), 231-241].

Lac dye

Natural dyes as photosensitizers for dye-sensitized solar cell

Dye-sensitized TiO_2 solar cell (DSC) has become an attractive and cheap device for the conversion of solar light into electrical energy since Grätzel and O'Regan firstly reported the prototype of this solar cell in 1991. DSC is assembled with an anode of conductive glass coated with platinum, a cathode of TiO_2 porous film on a conductive glass substrate anchored a monolayer of dyes and an electrolyte of certain organic solvent containing a redox couple, such as iodide/ triiodide. Many efforts have focused on sensitizer dyes, since dye plays a key role

Erythrina variegata

in harvesting sunlight and transferring solar energy into electric energy. So far, several organic dyes and organic metal complexes have been employed to sensitize nanocrystalline TiO_2 semiconductors, and one of the most efficient sensitizer is transition metal coordination compound (ruthenium polypyridyl complex). In nature, the fruit, flower and leaf of plants show various colour from red to purple and contain various natural dyes which can be extracted by simple procedure. It

Rosa xanthina

has been emphasized by many researches to obtain useful dyes as photosensitizers for DSC from natural products. The scientists of China investigated natural dyes extracted from black rice, capsicum, ***Erythrina variegata*** **Linn.** flower, ***Rosa xanthina*** **Lindl.**, and kelp, the interaction between the dye molecule (the core molecular groups of natural dyes) and TiO_2 porous film.

The dye-sensitized solar cells (DSC) were assembled by using these natural dyes as sensitizers. The I_{SC} from 1.142 mA to 0.225 mA, the V_{OC} from 0.551 V to 0.412 V, the fill factor from 0.52 to 0.63, and P_{max} from 58 μW to 327 μW were obtained from the DSC sensitized with natural dye extracts. Based on investigation on the structure and properties of dye molecules, it was found that black rice extract possesses the best photosensitized effect in the extracts of five kinds of natural dyes chosen, which is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule on black rice extract and the TiO_2 film on cathode in DSC. The blue-shift phenomenon from absorption spectrum to photoaction spectrum of DSC sensitized with black rice extract is due to the intensity and gap energy match of incidence light. Because of the simple preparation technique, widely available and low cheap cost natural dye as an alternative sensitizer for dye-sensitized solar cell is promising [Hao Sancun, Wu Jihuai, Huang Yunfang and Lin Jianming, Natural dyes as photosensitizers for dye-sensitized solar cell, *Solar Energy*, 2006, **80** (2), 209-214].

Quinone and flavonoid dyes as insect feeding deterrents for wool

Wool (obtained from different breeds of sheep) is susceptible to insect damage from clothes moths and carpet beetle larvae. Continuous damage can result in significant economic losses, especially in warehouses and showrooms. Some insect larvae eat wool to obtain sulfur, which is an essential factor in insect growth. Several conditions, including food, temperature, and moisture, influence the growth of the insects, especially larvae.

There are two major approaches to controlling clothes moths and carpet beetles: (1) no-chemical methods and (2) chemical methods. No-chemical methods use extremely high temperature or electromagnetic radiation frequencies to kill insects. Chemical methods include the use of several natural and synthetic insecticides, biological control, chemical modification of wool, laundering with strong soap solutions, and dry-cleaning. Chemical methods are more popular, common and easy to apply.

Another important category of natural products that have potential use is natural dyes, such as chestnut, cochineal, fustic, indigo, madder, logwood and walnut, which comes from plant's leaves, roots and flowers, and insects. Natural dyes can be dyed on wool to provide brilliant colours, and they are related quinones- and flavonoids-containing products. Naturally occurring quinones and flavonoids are known to have insecticidal or insect-repellent properties. Natural dyes would provide an alternative to synthetic insecticides, which are more detrimental to the health and safety of humans and the environment. By properly selecting the dyestuffs for wool textiles that have inherent resistance to insects, the need for insecticidal chemicals could be greatly reduced. It also would reduce the cost of manufacturing because conventional insect repellency treatments would not be needed. Therefore, the scientists at Department of Apparel, Textiles and Interior Design, Kansas State University Manhattan, Kansas evaluated eight natural dyes and the combination of dyes and mordanting agents for insect repellency and/or insecticidal effect against black carpet beetle, *Attagenus megatoma* F. Seven of the natural dyes were applied in conjunction with five mordanting agents, whereas the indigo was applied by a conventional reduction/oxidation method.

For the experiment the fabric used was a medium-weight (g/m^2) wool flannel which was prescoured prior to mordanting and dyeing processes to remove surface impurities that would influence treatment and/or insect testing. The scouring solution contained 0.1% (w/w) AATCC soap and 10% (w/w) sodium carbonate. The five mordanting agents selected for evaluation were aluminum (aluminum sulfate), chrome (potassium dichromate), copper (copper sulfate), iron (iron oxide) and tin (stannous chloride). A premordanting procedure was used in which the specimens were mordanted prior to dyeing. The dyestuffs included three naturally occurring quinones (cochineal, madder and black walnut) and six flavonoids (chestnut, fustic, indigo and logwood).

The insect resistance of eight naturally occurring quinones and flavonoids dyes applied to wool with five mordanting agents was studied in detail by using laboratory-reared black carpet beetles. The anthraquionone dyes, such as cochineal and madder, were found to be very effective in protecting the wool fabric against black carpet beetles. Madder resulted in the lowest weight loss and the best effect of insect deterrence against black carpet beetles. Among the flavonoids, chestnut, fustic, logwood and indigo dye when used on wool will not provide insect resistance. Among mordanting agents, alum, copper and iron can be used with the eight dyes without increasing insect susceptibility of the dyed wool products. Using chrome or tin as a mordanting agent for dyeing wool with cochineal is not recommended as it increases insect susceptibility. Thus, the naturally occurring mordant dyes provide an alternative to insecticides in protecting wool textiles from insect attack [Park Jung Hwa, Gatewood Barbara M and Ramaswamy Gita N, Naturally occurring quinones and flavonoid dyes for wool: Insect feeding deterrents, *J Appl Polym Sci*, 2005, **98**(1), 322-328].

Dyeing wool with lac

Recently, a revival interest in the use of natural dyes in textile coloration has been growing. This is a result of the stringent environmental standards imposed by many countries in a response to the toxic and allergic reactions associated with synthetic dyes. Conventional wisdom leads to the belief that natural dyes are friendlier to the environment than their synthetic counterparts. Natural dyes can exhibit better biodegradability and generally have a higher compatibility with the environment.

Lac is a unique dye material of animal origin being the secretion of a tiny insect *Laccifer lacca* Kerr thriving on certain host plants such as, *Palas* [***Butea monosperma* (Lam.) Kuntze**], *Kusum* [***Schleichera oleosa* (Lour.) Oken.**] and *Ber* (***Ziziphus mauritania* Lam.**). The use of lac dye in the dyeing of silk and leather seems to have been known to the Chinese some 4000 years ago. Lac is a mixture of at least five closely related laccaic acids, which are water soluble red dyes of anthraquinoid type structure.

Researchers at National Research Centre, Textile Research Division, El-Behos St. Dokki, Cairo, Egypt conducted a study to investigate the dyeing and fastness properties of wool fibres using lac as a natural dye. Different factors affecting dyeability and fastness properties were thoroughly investigated by both conventional and ultrasonic techniques. The extractability of lac dye using power ultrasonic was also evaluated in comparison with conventional heating. The results of dye extraction indicated that power ultrasonic is rather effective than conventional heating at low temperature and short time. The effects of dye bath *p*H, salt concentration, ultrasonic power, dyeing time and temperature were studied and the resulting shades obtained by dyeing with ultrasonic and conventional techniques were compared. Colour strength values obtained were found to be higher with ultrasonic than with conventional heating. The results of fastness properties of the dyed fabrics were fair to good. Dyeing kinetics of wool fibre with lac dye using conventional and ultrasonic conditions was also compared. The time/dye-uptake isotherms revealed the enhanced dye-uptake in the second phase of dyeing (diffusion phase) [Kamel MM, El-Shishtawy Reda M, Yussef BM and Mashaly H, Ultrasonic assisted dyeing III. Dyeing of wool with lac as a natural dye, *Dyes Pigments*, 2005, **65** (2), 103-110].

Characterization of anthocyanin extracts from maize kernels

The researchers at Mexico worked on the characterization of the pigments present in the kernel of four native maize varieties related to the races Arrocillo, Conico, Peruano and Purepecha to determine their possible use as natural dyes. Total anthocyanin content was determined by a conventional spectrophotometric method and anthocyanin analysis by high-performance liquid chromatography. The stability of the pigment at *p*H was also evaluated. The four maize samples contained anthocyanin in both the pericarp and aleurone layer. Total anthocyanin content among samples ranged from 54mg/100g to 115 mg/100g of sample. Anthocyanin profiles were almost the same among the four samples. Differences were observed only in the relative percentage of each anthocyanin. The anthocyanins identified are: cyanidin-3-glucoside, pelargonidin-3-glucoside, peonidin-3-glucoside, cyanidin-3-(6" malonylglucoside) and cyanidin-3-(3", 6"-dimalonylglucoside). Anthocyanin extracts showed similar behaviour in solutions with different *p*H. From *p*H 1-6 lambdamax values were maintained almost constant; however, above this *p*H value, a marked increase was observed in the bathochromic shifts, but the bluish colour did not continue to change above *p*H 8 [Moreno YS, Sanchez GS, Hernandez DR and Lobato NR, Characterization of anthocyanin extracts from maize kernels, *J Chromatogr Sci*, 2005, **43**(9), 483-487].

Extraction of natural dyes from coloured plant wastes

The production of natural dyes from natural resources has been found to be costly, hence, new strategies are required to establish technically and commercially competitive processes and resources. The use of cheap by-products from other agricultural activities, e.g. bark from the timber industry or leaves from abundantly available plants like deodar, jackfruit and eucalyptus and use of dyestuff-containing wastes released from the food and beverage industry free of charge has been suggested by researchers. In the traditional natural dyeing of textiles an important part of red/yellow dyes had been extracted from fruits and vegetables.

The scientists at Institute for Textile Chemistry and Textile Physics and Institute for Applied Ecology, Austria worked on various wastes released from the food and beverage industry and considered plant materials derived from Raspberries, Sour cherries, Black elder, Blackcurrant, Grapes, Red beet, Onions, Rhubarb, Black tea and Black carrots. During experiment a weighed amount of plant material was extracted with distilled water in a beaker. In the standard procedure the ratio mass of waste:volume of liquid was set at 1:20. The extraction was performed for approximately 60 min at 95°C. Photometry was used to quantify the extractable amount of coloured material and to estimate the minimum time required to complete dyestuff extraction. Samples were collected during extraction at intervals of 10 minutes.


Red beet


Black carrot


Onions

The extracts were applied as direct dyes and in the presence of iron(II) or alum mordants. The results prove the potential of such wastes as a source for natural dyestuff for woolen textiles. To obtain textile dyeing with acceptable fastness properties, however, rigorous selection of dyes and development of suitable processes is required. A considerable number of red natural dyes need further research to optimise the low level of fastness to light [Thomas Bechtold, Rita Mussak, Amalid Mahmud-Ali, Erika Ganglberger and Susanne Geissler, Extraction of natural dyes for textile dyeing from coloured plant wastes released from the food and beverage industry, *J Sci Food Agric*, 2006, **86**(2), 233-242].

Improving light fastness of natural dyes on cotton yarn

Researchers from France conducted studies to evaluate the light fastness of selected natural dyes [aerial parts of Weld (***Reseda luteola* Linn.**) and Woad (***Isatis tinctoria* Linn.**) and Madder roots (***Rubia tinctoria* Linn.**)] and the effect of some commonly used antioxidants and UV absorbers on the light fastness of these dyes. These dyes were selected because they were widely used for red (madder), yellow (weld) and blue (woad) colours in European, American and even Asian textiles until the 19th century. The photofading rate curves of madder and weld fixed on cotton correspond to Type II fading rate curves described by Giles. These results are in concordance with those of Cox-Crews. The woad presents a Type III fading rate curve, similar to the indigo fading rate curve presented by Cox-Crews. A poor light fastness of the three natural dyes in comparison with synthetic ones is established beyond question. Nevertheless, the use of some additives can improve this default of natural dyes. In all the cases, the use of UV absorbers or antioxidants improved the light fastness of dyed fabrics. The most effectives were the vitamin C and the gallic acid [Cristea Daniela and Vilarem Gerard, Improving light fastness of natural dyes on cotton yarn, *Dyes Pigments*, 2006, **70**(3), 238-245].