Utilization of Sericin on Modification of Cotton Dyeing using Acid Dyes

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Abstract
Silk fabrics are high quality commodities of woven (traditional and modern) fibers from silkworm cocoons. The research development has changed the paradigm of silk. Silkworm cocoons are no longer just used as fabrics; recently some studies have tried to develop their further usage using fibroin and sericin in many fields. Fibroin is a protein fiber (silk) while sericin is the adhesive. Sericin protein consists of 18 kinds of amino acids which mostly consist of a group of strong polar compounds such as hydroxyl, carboxyl and amino. Cotton fabrics will be slightly dyed with acid dyes because it cannot bind to the cotton and also because the negatively charged acid dyes will repel the hydroxyl groups of cellulose. It provoked a thought that sericin can be used as the agents to modify the cotton dye characteristics with acid dyes.

In this research, the utilization of sericin in the textile fields is examined by trapping sericin with a polymer network using the pad-dry-cure method. Sericin on the cotton surface will be dyed by the acid dyes. This experiment was performed using several sericin concentration (0, 10, 20 and 30 g/L). Adherence of sericin on cotton fabrics has been successfully performed by trapping it with a melamine formaldehyde polymer network, which is further confirmed by the morphology test results with the presence of coarse particles on the fiber surface and the content of amides. Sericin finishing process on a cotton fabrics has succeeded to increase absorption of acid dyes with sericin at an optimum concentration of 30 g/L and it has a low value color fastness to washing.

Keywords: Sericin, melamine formaldehyde, acid dyes, cotton.

Introduction

Natural silk fibers are obtained from silkworm coccoons. The type of silk worm that is widely used is the *Bombyx mori*. Silkworms have a perfect life cycle (holometabola metamorphosis) i.e. eggs, larvae (caterpillars), imago (moths) and pupae. In general, the pupa phase is a phase that is considered economical because the cocoon is formed and it can be utilized as the base material of silk fabric. Natural silk fiber consists of two protein types fibroin and sericin[1]. Fibroin is a fiber protein while sericin is the adhesive. Sericin encloses a very small filament fibroin fibers in a cocoon, weighing 20-30% of the total weight of the cocoon[1]. Sericin-release from cocoons in the silk industry is known as the degumming process. In this industry, sericin is discharged and becomes liquid waste disposed into the environment.

Sericin is a type of globular protein that dissolves in hot water. The proteins are composed of amino acids in a typical sequence. Sericin proteins consist of amino acids, most of which are strong polar groups such as hydroxyl, carboxyl and amino groups. *Bombyx mori* sericin is rich with serine 27.3%, aspartic acid 18.8% and glycine 10.7%[2]. Sericin is a protein with a hydrophilic surface of 70% and 30% hydrophobicity[2]. Sericin, which is produced by mulberry silkworms, has a molecular mass about 40-400 kDa[3].

Sericin protein molecules have properties such as anti-oxidant, anti-bacterial, UV-repellent properties, ability to absorb and to release moisture[4,5]. Based on its properties, it can be applied as recyclable biomaterials. The biomaterials have usage for medical, membrane, fiber for textiles of a special and nature cosmetic[1,4].

Acid dye is a substance used in textile dyeing. The naming of the acid dye derives from the use of an acid in the solution[6]. Acid dye is usually a sodium salt of sulfonic acid, or at least, it is an ionic carboxylic acid which turns into an anion in a solution[6]. It will dye the fibers in the cationic part. It is usually substituted with ammonium ion groups in fibers such as wool, silk and nylon. This fiber will absorb the acid. The acid will protonate the amino group of fibers, so they become cationic[6].

Dyeing involves exchange of the anion associated with an ammonium ion in the fiber with a dye anion in the bath. The cotton fibers are hydrophilic fibers whose structures are cellulose polymers with varying degree of polymerization (DP). The primary -OH group of cellulose is a functional group that acts to bond with the dyestuff. The use of acid dye causes less affinity to cotton fabric because of no cationic part in cotton.

Research on the attachment of sericin may be carried out by binding sericin to the other polymer by means of crosslinking agent so that the sericin is covalently bonded to the polymer structure, as it did by binding sericin on polyvinyl alcohol by genipin[7] and polyester crosslinks with gluteraldehyde substances[8]. Melamine formaldehyde is a molecule that can polymerize to form a network of polymer. The polymer network is expected to trap macromolecules located at the bottom. If sericin macromolecules containing many cationic groups can be attached to the cotton fabrics, it will be able to modify the dyeing of cotton fabrics by acid dye.

Material and Methods

Materials: The materials prepared for the experiment are: Mullbery silkworm coccoons obtained from *Pusat Pembibitan Ulat Sutera* (PPUS) Candiroto Temanggung, 100% cotton woven fabric, melamine formaldehyde resin (Stabitex ETR), magnesium chloride, acid dyes Eronyl Blue A-R, sodium chloride, Teepol, acetic acid 1%, ECE Phosphate Reference Detergent (B) and multifiber.

Methods

Preparation of sericin powder[9]: Dry silkworm cocoons were cut into small pieces, then boiled using a high-pressure container. High pressure-high temperature dyeing (HT-HP) machine was used at 120°C for 1 hour. Sericin extracted solution was then filtered using Whatmann 41 paper. The sericin solution, provided from the degumming process and had been filtered, was then added with cold ethanol in the ratio of ethanol/water 3/1 (v/v). Then, the solution was cooled at 4°C for 24 hours to enhance the precipitation. Supernatant was then separated and the precipitate was frozen using liquid nitrogen. Afterwards, sericin was formed into a powder by lyophilization using a freeze dryer Operon -55°C.

Finishing Process: Sericin was dissolved using water at 60°C with concentrations of 0, 10, 20 and 30 g/L. Then, 50 g/L Stabitex ETR and 10g/L magnesium chloride were added to the sericin solution. The solution was prepared with a total volume of 100 mL. Cotton fabric was soaked in solution until wet and then padded with 80% wet pick up. The fabric was then dried at 100°C for 2 minutes and then cured at 160°C for 1 minute.

Dyeing Process: Cotton fabrics was dyed with Liquor Ratio 1:50 using High Temperature-High Pressure (HT-HP) machine dyeing. The immersion was carried out with Eronyl Blue A-R 2.5%, NaCl 10 g/L, wetting agent (Teepol) 1 g/L. Then, the solution was adjusted to pH 3 using 1% acetic acid. The dyeing process was carried out at 60°C for 30 minutes. After the dyeing process was complete, the fabric was washed using soap (Teepol) at a temperature of 50°C for 10 minutes, then rinsed with hot water for 3 times, each lasted 10 minutes respectively. The process continued with cold water rinsing and dried by air hanging.

Fabric Tensile Strength Test: The tensile strength test of the fabric was carried out according to SNI 0276: 2009 with ribbon thread methods. It was intended to know the maximum load that can be retained by a fabric test sample until the fabric is broken. The test was performed using a Tensolab 5000 machine. The test sample (warp and weft respectively) with size of 3.0 x 15 cm which had been trimmed to the length of the fabric until the threads on the width of the fabric are measured to be exactly 2.5 cm and clamp symmetric at the top and bottom with a 7.5 cm spacing. The direction of the long section was the same with the pull direction and the fabric was pulled to break.

Fabric stiffness test: Fabric stiffness test was conducted based on SNI 08-0314-1989. It is intended to obtain the rigidity of fabric by using tool stiffness tester. The test specimen in the form of ribbons of 2.5 x 20 cm was supported by the peripheral plane, the specimen was then shifted toward the elongated end and the ribbons were curved to form 41.5 ° because of their own weight. Bending stiffness was calculated from the length of the curve and the weight of the fabric per unit area. The calculation of the length of the arch was read directly from the scale. The length of the arch for each direction of the warp and the feed were calculated based on the average curve length using the following formula:

$$K = 0.1 \times B \times P^3$$

where K = Flexural (mg.cm), B = Fabric weight (g/m^2) and P = Long arch (cm)

Sericin Attachment Analysis by Fiber Surface Morphology Test: A small section of sericin treated fabric was cut and sputter coated with palladium for 40 second (JEOL JEC-3000FC) to prevent charging. The surface morphology of the fiber was then obtained with Scanning Electron Microscope (JEOL JSM 6510)

Sericin Attachment Analysis by Functional Group Test: The functional group test on the refined cotton fabrics was made using FTIR ATR Shimadzu. The samples to be scanned were prepared by inserting the sample on the plate, then they were measured for infrared spectrum with wave number 400 - 4000 cm^{-1}.

The Color Depth Testing of the Dyed Fabric: This test was aimed to determine the amount of dyestuff absorbed in the dyed fabric. The color depth value was expressed in the K/S value and the reflectance value (% R) was based on the workings of the spectrophotometer. K/S of the dyed samples was then measured with a spectrophotometer (Minolta 3600d).

Color Fastness to Washing: The test for colour fastness to washing (SNI ISO 105-C06: 2010 with A1M number washing condition) was performed to determine the quality of dyeing between sericin and acid dye. 4 x 10 cm specimen was attached with multifiber fabric by sewing along one of the shorter edge and it was further more washed on Launder O-meter machine with 4 g/L ECE Phosphate Reference Detergent (B) with a volume of 150 mL each tube using the number 10 pieces of steel marbles. Washing was performed at 40°C for 45 minutes to analogize household washing as much as 5 times. After that it was rinsed and dried. The specimen was then washed under temperature conditions and friction of certain steel marbles to obtain the result of the color change of the fabric within a predetermined time. Specimen colour changing and staining on multifiber were assessed by comparing them to the grey scale.

Results and Discussion

Melamine Formaldehyde Polymerization: The results of the stiffness and tensile strength of the fabric processed in refinement with sericin can be seen in sequence in figure 1, figure 2 and figure 3. Figure 1 shows that the stiffness value (mg.cm) on cotton fabrics that was not applied by the finishing process (blank sample) has a stiffness value of 11.70 mg.cm, while the cotton fabric which contains the melamine formaldehyde resin and the sericin gives higher stiffness value. Finishing was performed using the same melamine formaldehyde concentration of 50 g/L for each sericin concentration.

Cotton fabric containing only melamine formaldehyde resin has the total stiffness value of 19.70 mg.cm. For fabrics containing melamine formaldehyde resin and sericin, the total stiffness value is 18.25 mg.cm for sericin concentration of 10 g/L, 18.24 mg.cm for sericin concentration of 20 g/L and 18.35 mg. cm for sericin concentration of 30 g/L. This suggests that the fabric of the refinement process has been successfully attached by a network-polymerized melamine-formaldehyde molecule. These network polymers are rigid, thus giving an effect to the stiffness of the coated fabric being increased.

Figure 2 and 3 provides the data from the tensile strength with ribbon thread methods. Figure 2 shows the tensile strength on warp direction (kg) and figure 3 provides the tensile strength on weft direction (kg). Cotton fabrics without treatment have a lower tensile strength value compared to cotton fabrics with the special treatment. This is due to the presence of other molecules/materials attached to the fabric with the special treatment. The melamine formaldehyde resin on the fabric surface will polymerize to form a network polymer and will provide a stronger effect on the tug so that the fabric has a higher tensile strength value than the cotton fabric. The relatively similar tensile strength value (on the fabric with sericin variation) is due to the use of the same melamine formaldehyde concentration in each sericin concentration .

The Morphology of Fiber Surfaces on Finishing Fabrics: The results of the Scanning Electron Microscope (SEM) testing on figure 4 (i) show that the surface of the unprocessed cotton fabrics without the modification using sericin has a smooth surface morphology on the fiber and there are only few small spots on some areas of the fiber surface. Compared with modified cotton using sericin and acid dyes dyed in figure 4 (ii) and figure 4 (iii), The results present very clear morphological differences. There are coarse particles indicated as sericin content attached to the fiber surface. The process of melamine formaldehyde polymerization forming network polymer occurs by a heating process at 160°C for 1 minute.

Sericin in the finishing solution is trapped in a melamine formaldehyde network polymer to the surface of the cotton fabric. This proves that the process of modifying cotton fibers using sericin has morphological change effect on the fiber surface.

Functional Group Analysis on Finishing Fabric: FTIR-ART testing was performed to determine the presence of sericin on modified cotton fabrics. The presence of the sericin is confirmed by the presence of amide functional groups which previously do not appear on cotton fabrics. The existence of the functional group on the modified cotton fabric indicates that the sericin is attached to the cotton fabric. Based on figure 5, it can be seen that FTIR testing on modified cotton fabrics shows new peaks that is increasing at the peak of wave number 1600 and 1500 cm^{-1}.

Cotton fabrics that have been processed with sericin concentration of 30 g/L and modified cotton fabrics dyed with acidic dyestuffs, indicate the peak of wave numbers at 1543,05 cm^{-1} and 1541,12 cm^{-1}. They indicate the amide II functional group (N–H bending and the C–N stretching vibration of the amino group)[10]. There is also a rising peak when compared with cotton fabrics at the peak of the wave number 1649,14 cm^{-1} that denotes amide function group I. It shows C=O stretching vibration of the amino group[10]. Thus, it is proven that cotton fabrics which have been modified by sericin, provide the presence of sericin functional groups.

Color Depth Dyeing on Finishing Fabric: Based on figure 6, the color depth test on the modified cotton fabrics, by sericin then dyed with acid dyes, shows that the more sericin concentrations are used, the darker the colour will appear. The results of the color depth values were obtained at the wavelength 640 nm is 0.3043 on cotton fabric, 0.3774 on cotton fabrics using only melamine formaldehyde resin, 0.3919 on cotton fabrics with 10 g/L sericin, 0.4300 on cotton fabrics with 20 g/L sericin, and 0.4601 on cotton fabrics with a 30 g/L sericin concentration.

In the cotton fabric, the acid dyes that enter the fibers are very small. This is due to the absence of a positive charge contained in the cotton fibers are therefore, the acidic dyestuff cannot bind to the fabric. Cotton fabrics containing sericin may bind more acid dyes because, in sericin, there are various amino acids. It happens that the negatively charged acid dyestuff (-) may bind to the positively charged amino acid (+). The more sericin concentrations used, the more dyestuffs that bind to the positively charged amino acids attach to the cotton fibers.

Color Fastness to Washing: The color change value of the color fastness to washing of the cotton dyed by acid dyes can be seen in table 1. Cotton fabrics have a color change value of 3, the cotton modified using melamine-formaldehyde resins also have the value of 3 and the cotton fabrics modified by sericin with a concentration of 10 g / L, 20 g / L and 30 g / L has a color change value of 3/4. The value of low color fastness to washing is due to the sericin compound that is not resistant to detergents. Therefore, by testing the color fastness against washing with a 45 minutes' time which is equivalent to 5 times household washing, it results in a decrease in the color of the fabric.

The grey scale value for staining assessment on multifiber can be seen in table 1. Based on the data obtained, nylon fibers are stained more than other fibers with a gray scale value for staining on 4. For wool fibers, acrylates, polyesters, cotton and acetate rayon, they have grey scale values of 4/5 staining assessments.

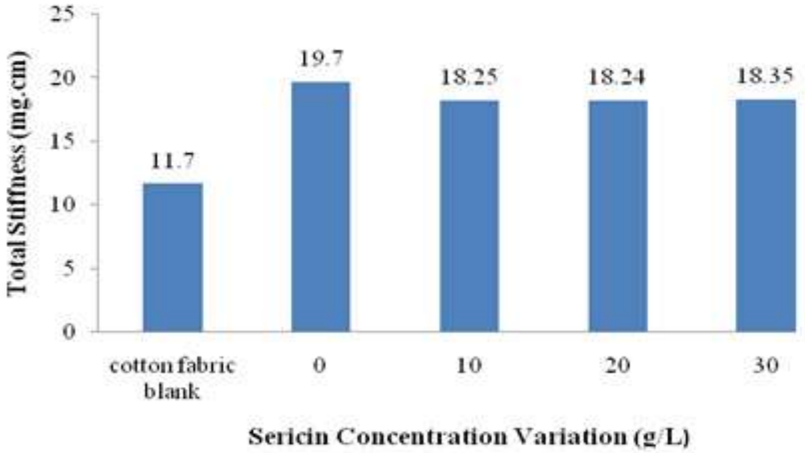


Figure 1: Relation between sericin concentration variation with fabric stiffness (mg.cm) of dyed cotton fabrics using acid dyes which contains melamine formaldehyde resin and sericin

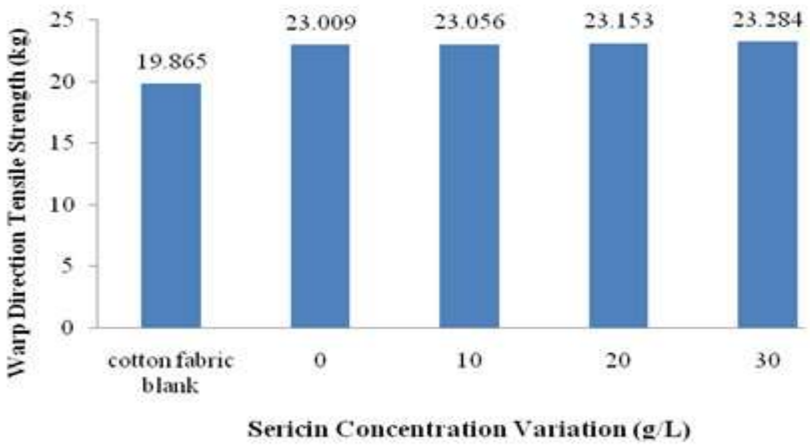


Figure 2: Relation between the variation of sericin concentration with the fabric tensile strength in warp direction (kg) of dyed cotton fabrics using acid dyes which contains melamine formaldehyde resin and sericin

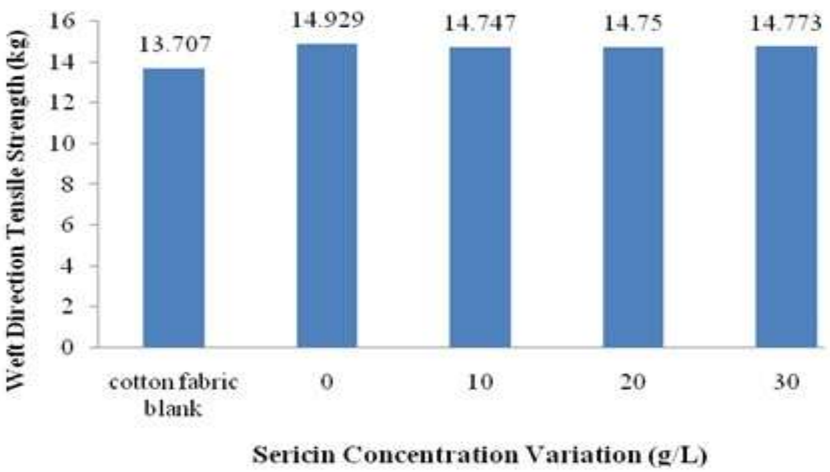
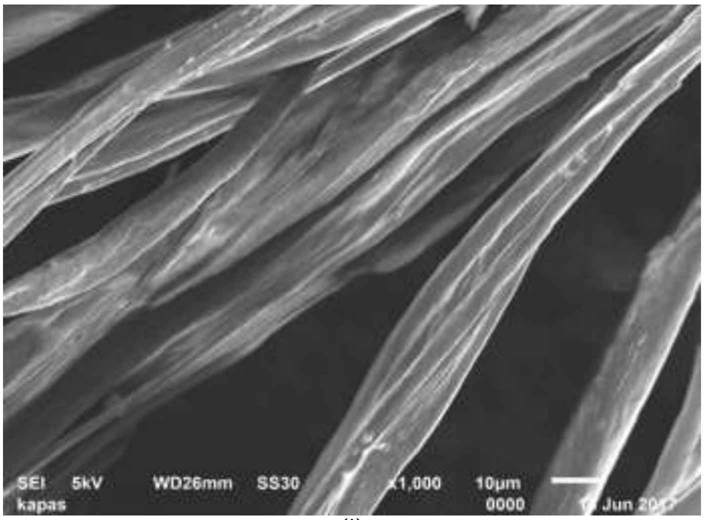
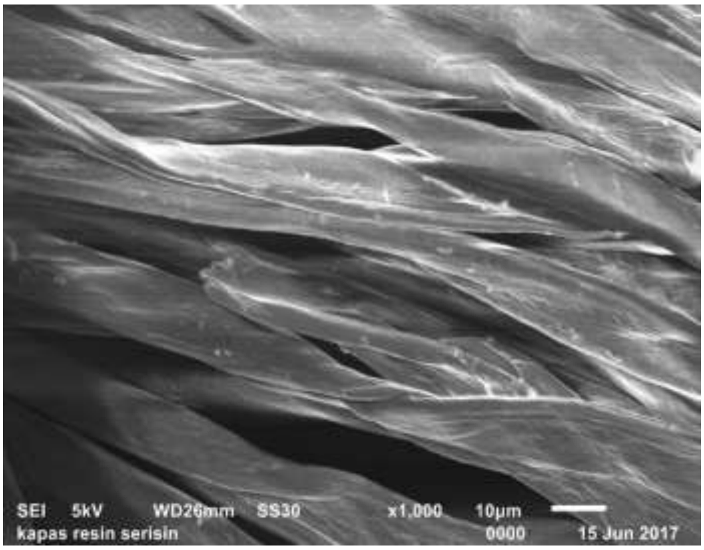


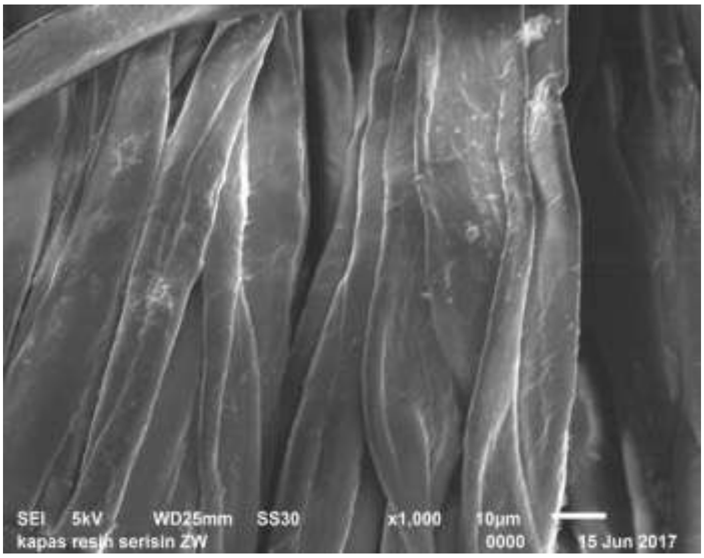
Figure 3: Relation between the variation of sericin concentration with the fabric tensile strength in weft direction (kg) of dyed cotton fabrics using acid dyes which contains melamine formaldehyde resin and sericin



(i)



(ii)



(iii)

Figure 4 : Fiber surface morphology (i) cotton blank, (ii) cotton modified by 30 g/L sericin and (iii) dyed cotton (acid dyes) modified by 30 g/L sericin

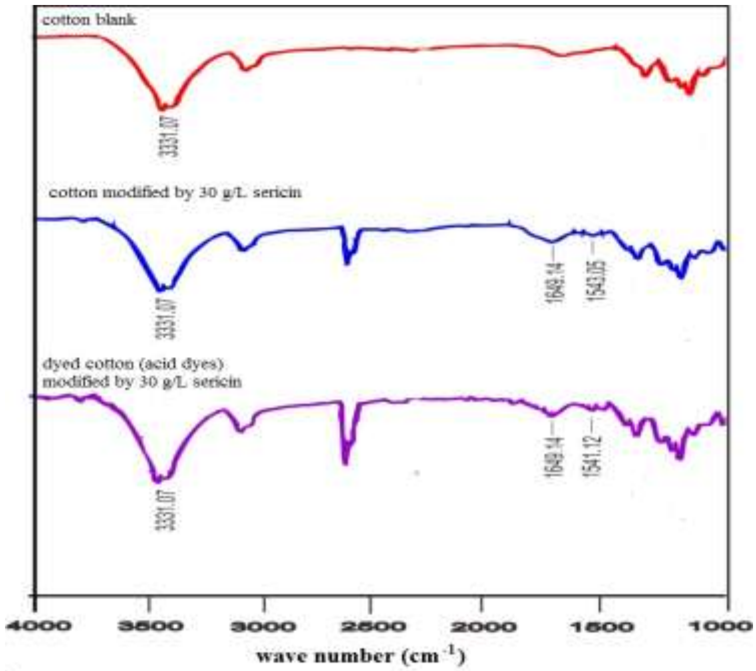


Figure 5: The results of the functional group test of cotton fabric and modified sericin cotton fabric using FTIR-ATR

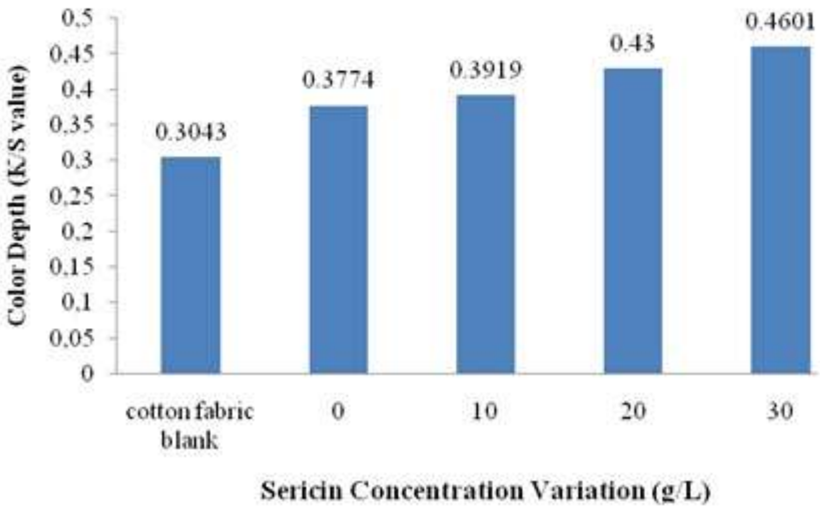


Figure 6: Relation between the variation of sericin concentration with the color depth (K/S) of dyed cotton fabrics using acid dyes which contains melamine formaldehyde resin and sericin

Table 1
The grey scale value of dyed cotton fabrics using acid dyes which contains melamine formaldehyde resin and sericin color change and staining to multifiber by color fastness to washing test

	Sericin Concentration Variation (g/L)	Color change Value of Dyed Sample	Staining Value to Multifiber					
			Wool	Polyacrylic	Polyester	Nylon	Cotton	Acetate Rayon
1	Cotton blank	3	4/5	4/5	4/5	4	4/5	4/5
2	0	3	4/5	4/5	4/5	4	4/5	4/5
3	10	3/4	4/5	4/5	4/5	4	4/5	4/5
4	20	3/4	4/5	4/5	4/5	4	4/5	4/5
5	30	3/4	4/5	4/5	4/5	4	4/5	4/5

Conclusion

Based on this research, it can be concluded that the process of attachment of sericin on cotton fabrics can be done by pad-dry-cure method using melamine-formaldehyde polymer. The modification process on cotton fabrics using melamine-formaldehyde resin and sericin may affect morphological properties of the cotton fibers.

Melamine formaldehyde affects the increasing of stiffness and tensile strength of the cotton fabric. The optimum condition for the modification of cotton dyeing is on using acid dyes of 30 g/L sericin concentration and it has a good value of low color fastness to washing.

Acknowledgement

We would like to thank CV Wisata Sutera Padepokan Dayang Sumbi Bandung, Pusat Pembibitan Ulat Sutera (PPUS) Candiroto Temanggung and PT Pulcra Chemicals for all their assistance to this research.

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