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Low-Formaldehyde Hydrophobic Cum Crease Resistant Finishing of Woven Silk Fabric

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Abstract
In the present study, a low-formaldehyde based hydrophobic cum crease resistant finishing of woven silk fabric was developed with a comparison of three commercially available cross-linkers (i.e., Knittex RCT®, Fixapret ECO® and Reaknitt EC®). The treatment parameters of cross-liker types and their concentrations were investigated in relation to the crease recovery angle (CRA), contact angle, tensile strength and air permeability of the silk fabric. The highest CRA of 265° was observed for the Reaknitt EC® treated silk fabric and for the untreated silk fabric it was 165°. The contact angle generally increased with increasing of the cross-liker concentration; and amongst the all the cross-linkers considered, Fixapret ECO® treated fabric exhibited the highest contact angle of 134.59°, whereas that of untreated was zero. The finishing additionally improved the air permeability of treated silk fabric with fair whiteness. The treated silk fabrics, however, showed a loss in tensile strength with an increase in concentration for all three types of cross-linkers. Scanning electron microscopy showed the impregnation of the finish into the treated silk fabric.

Key words: *crease recovery, cross-linker, finishing, resiliency, hydrophobic, silk fabric.*

Introduction

Silk is one of the most luxurious and beautiful natural fibres, possessing excellent luster, wearing comfort, soft handle, good air permeability, excellent draping quality and aesthetic appearance in materials, and has been known as the 'queen of fibres' since its discovery [1]. Silk is produced in small quantities: about 130,000 tons per year and has remained a special fibre for use in high value textiles. The amino acid composition of silk protein is close to that of the human skin, hence it can also be used in biomedical applications such as sutures, prosthetic arteries and bandages [1]. However, recognised defects of silk fabrics include their tendency to crease easily during home laundering or when wet and in storage and in wearing. This disadvantage causes considerable inconvenience in the use of silk fabrics; therefore, world consumption of silk is directly influenced. Therefore modifying the properties of silk and expanding its new uses have attracted great attention in the world [2].

To solve the problem above, anti-wrinkle finishing agents are usually applied in after-treatment. Considerable effort has been made in trying to improve the inferior properties of silk such as stiffness, softness, wrinkle resistance, abrasion resistance, and shrink proofing through chemical modification [3 - 5]. These studies included graft copolymerization [6], dibasic anhydrides treatment [7], amino-formaldehyde resin finishing, polycarboxylic acid crosslinking and epoxide treatment [8]. In the early stages, trimethylol melamine was used as an anti-wrinkle finish [9], though it released formaldehyde. Subsequently non-formaldehyde finishing agents were developed, such as 1,2,3,4-butaneteracarboxylic acid [10], which is expensive and requires high temperature during treatment. Moreover in the textile sector, there has been continuous demand for water-repellent or hydrophobic coatings, especially for super-hydrophobic coatings which present water contact angles greater than 120° [11, 12].

Javid [13] used Knittex RCT®, a non-formaldehyde cross-linker, to cross-link the chitosan microcapsules on a cotton fabric surface by using the pad-dry-cure method. Fixapret ECO® contains extremely low levels of uncombined formaldehyde (less than 0.1%) and methanol. Khoddami [14] used Fixapret ECO® both as a cross-linking agent and anti-crease finish for cotton fabric treatment. Reaknitt EC® has not previously been reported as a cross-linker for silk fabric, to the best of our knowledge. Again none of the finishes considered in this study had been applied for either crease resistant or hydrophobic finishing of silk fabrics. Cai and Qiu [15] used an epoxy silicone cross-linking agent (EPSIA) to enhance the performance properties, especially crease resistance, of silk fabrics, especially their cease resistance. The purpose of the crease resistant finishing was to enhance the resilience with the hydrophobicity of silk fabrics.

It is believed that the finishing agent establishes covalent bonding with the fibroin polymers and extends cross-linking within the fibroins, which enhances the resilience of the deformed fibroins and results in enhanced crease resistance. It has been found that most of the finishing processes take place according to cross-linking theory [16].

A process for manufacturing an improved silk fabric is presented which includes wetting an untreated silk fabric with specially formulated low-formaldehyde hydrophobic cum crease resistant cross-linking agents. Based on the finishing techniques earlier developed for cotton, finishing recipes and conditions, the crease resistance and other important performance properties of the finished silk were studied.

Materials and methods

Materials

The fishing treatments were carried out on 100% raw silk fabric purchased from a local silk market. The construction properties of the silk fabric included the following: surface density 42.9 g/m^2, warp count 10.7 tex (55.3 Ne), weft count 10.7 tex (55 Ne), weft tensile strength 0.36 kN, warp tensile strength 0.22 kN, ends per cm 61,4 and picks per cm 31,5. Cross-linkers Knittex RCT® (modified dihydroxyethyleneurea, DHEU), Fixapret ECO® (modified dimethyloldihydroxyethyleneura, DMDHEU) and Reaknitt EC® (modified DMDHEU) were kindly donated by the local suppliers of Huntsman (USA), BASF (Switzerland) and CHT (Bezema) Chemicals, respectively.

Degumming of silk fabric

Raw silk matrix is mainly composed of a double strand fibroin surrounded by a layer of sericin gum, both being proteins. The degumming process is actually the removal of sericin, which brings out the soft qualities of silk fibroin. The sericin is more accessible to chemicals than the fibroin, and hence is removed during pretreatments e.g., degumming. The silk fabric was stirred in a solution of NaOH (20% w/v) at room temperature for 2 h and then washed with a hydrochloric acid solution (1 % v/v), followed by excessive rinsing in distilled water. The degummed silk specimen was then air dried.

Fabric finishing

The degummed silk fabric was cut down to specific dimensions and padded twice in a finishing bath containing the cross-linker of specific concentration desired (90 - 150 g/l). The pH value for all baths was adjusted to 6.0 and a catalyst ($MgCl_2$, 20 g/l) was added accordingly. The pick-up rate of the padder was set at 75%. After padding, the silk fabric specimens were dried (at 120 °C for 60 s) and cured (at 150 °C for 60 s). All the experiments were conducted on a lab-sale jigger machine in triplicate and the data reported are the average of three readings.

Characterisation of finished fabric

Crease recovery is a measure of crease resistance, specified quantitatively in terms of the crease recovery angle (CRA). The CRA of both untreated and treated fabric specimens was measured by using the standard method of ASTMD125-2014 on a Shirley crease recovery tester. The contact angle is a quantitative measure of the wetting of a solid by a liquid, defined geometrically as the angle formed by a liquid at the three phase boundary where the liquid, gas and solid intersect. A low value of the degree indicates that the liquid spread, or wets, well while a high value indicates poor wetting. If the angle is less than 90°, the liquid is set to wet the solid. If it is greater than 90°, it is said to be non-wetting. A zero contact angle represents complete wetting. In the present work, the contact angles were measured by using a Theta Lite optical tensiometer (TL 100 and TL 101). The whiteness indices of both untreated and treated silk fabrics were determined by using a spectrophotometer (Color Eye 7000A, GretagMacbeth) according to the standard method of AATCC 110-2014. The air permeability of the silk fabrics was measured by using the standard method of ASTM D-737-2014. In short, a circular fabric specimen was clamped into the air permeability tester, and through the use of a vacuum the air pressure was made different on one side of the fabric. Airflow occurred from the side with higher air pressure, through the fabric, to the side with the lower air pressure. From this rate of air flow, the air permeability of the fabric was determined. The tensile strength of the silk fabric specimen was measured according to the standard method of ASTM D 5035-2014 by using a tensile testing machine (KG-300, Daiei Kagaku Seiki Seisa-Kusho Ltd). The surface morphology of the acrylic fabric was observed under a scanning electron microscope (SEM, JSM-5910, JEOL, Tokyo, Japan). The SEM measurements were made at an accelerating voltage of 10 kV.

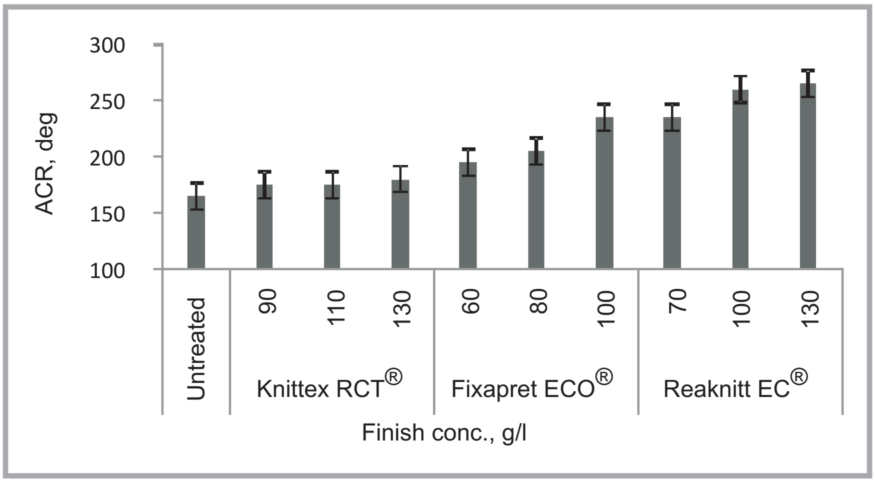

Figure 1. Comparison of crease recovery angles (CRA) under various treatments.

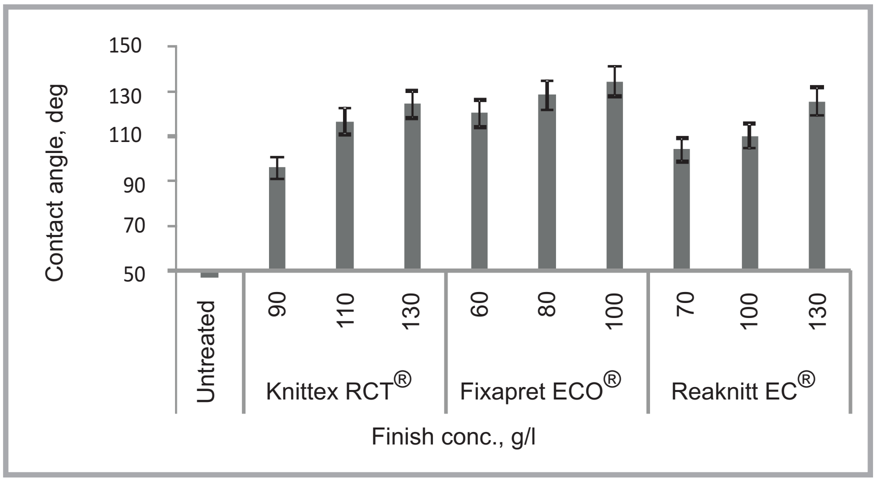

Figure 2. Comparison of contact angles under various treatments.

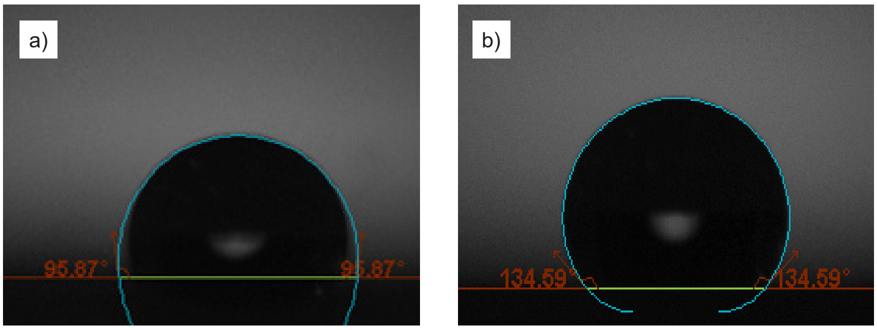

Figure 3. Micro-images of water drop on (a) Knittex RCT® and (b) Fixapret ECO® treated silk fabrics; range of contact angles observed under various setups.

Result and discussion

The application of most chemical finishes to silk fabric mostly results in substantial changes in the performance properties of the treated fabric. In the present study, the impregnation of cross-linking finishes onto silk fabric was conducted under the pad-dry- cure process, optimised for the type and concentration of the cross-linking agents. ***Figure 1*** (see page 117) shows that the CRA gradually increases with increasing the concentration for all types of cross-linkers. The effect of the concentration on the CRA was the most prominent in the case of Reaknitt EC® finishing until the maximum CRA of 265° was observed at 130 g Reaknitt EC®/l, in contrast to the CRA of 165° of unfinished silk fabric. This effect was not significant in the case of Knittex RCT®, where the range of CRA was 175° - 180° under the process conditions. The increased CRA with increasing the concentration of the cross-linker is attributed to the increased cross-linking among fibroin molecules of the silk matrix, which subsequently increases the CRA. Cai and Qiu [15] observed that the dry crease recovery angle of EPSIA treated silk fabric increased by 14%. The fabric specimen without a crease resistant finish hindered the cross-linking of fibroin molecules, which resulted in a low CRA.

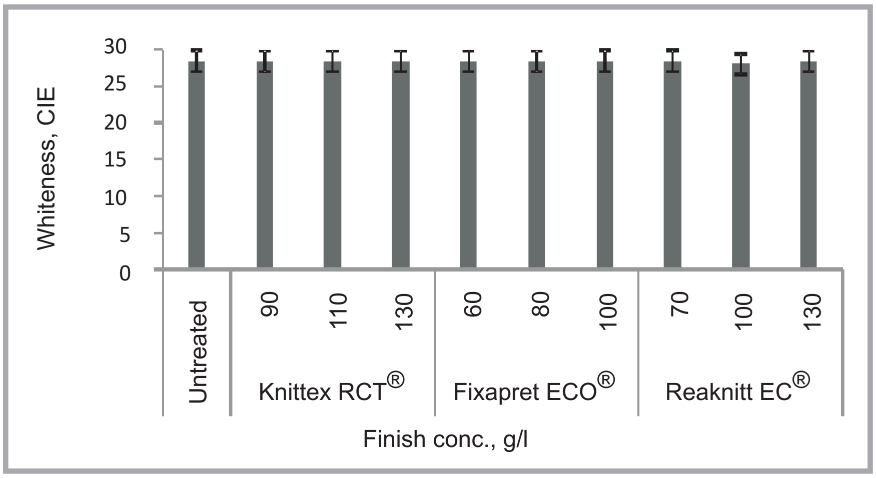

Figure 4. Comparison of whiteness of silk specimens under various treatments.

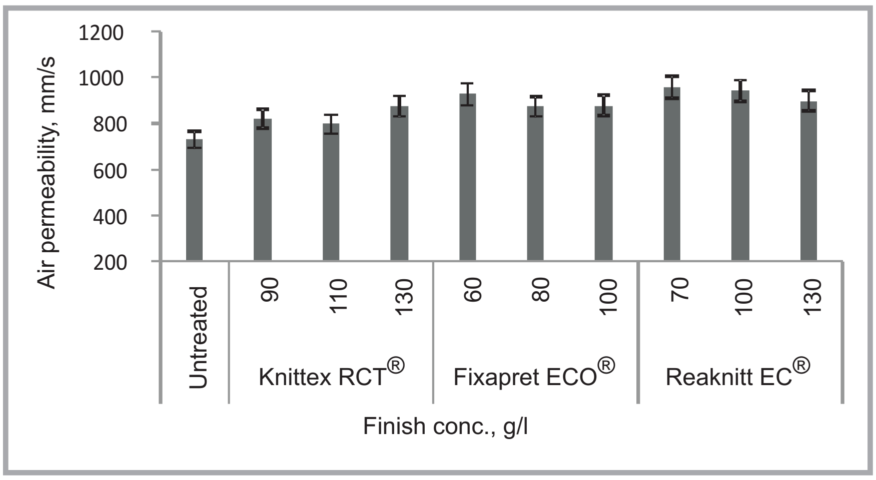

Figure 5. Comparison of air permeability of silk specimens under various treatments.

In practice, hydrophobicity and hydrophilicity are relative terms. If the contact angle of water is less than 30°, the surface is designated as hydrophilic; and hydrophobic if the contact angle is greater than 90°. The contact angle measured the water wetting properties of the fabric specimens. The higher the contact angle, the higher the hydrophobicity of the specimen. ***Figure 2*** (see page 117) shows that the untreated specimen showed no contact angle value because the degummed specimen was too hydrophilic. Large amounts of polar amino acids account for the hydrophobicity of the silk fabric [17]. When different types of separate cross-linkers were applied on the silk fabric at different concentrations, the surface wetting behaviour of the treated fabrics changed accordingly. The results show that the application of any cross-linker considered at any concentration under study resulted in a hydrophobic silk fabric; although of different extent, with the exception of Knittex RCT® at 90 g/l (***Figure 2***). The effect of cross-linker concentration on the water contact angle was positive in the case of Knittex RCT® and insignificant in the case of Fixapret ECO®, whereas a negative effect was observed for Reaknitt EC®. The lowest contact angle of 95.87° and the highest of 134.59° were observed at 110 g Knittex RCT®/l and 70 g Reaknitt EC®/l, respectively (***Figure 3***). This hydrophobic behavior of the treated silk fabric is due to the covering of hydrophilic polar amino acid groups preset in the silk matrix [17]. The finish gives a stable chemical structure over the surface of the fabric, thus inhibiting the penetration of water into the fabric surface.

The CIE whiteness indices (***Figure 4***) show that the treated specimens retained their whiteness above 90% of that of the unfinished silk specimen. The air permeability determines how much air is permeable through the fabric specimen. The higher the air permeability, the higher the comfort of the fabric specimen. ***Figure 5*** shows that on ap-

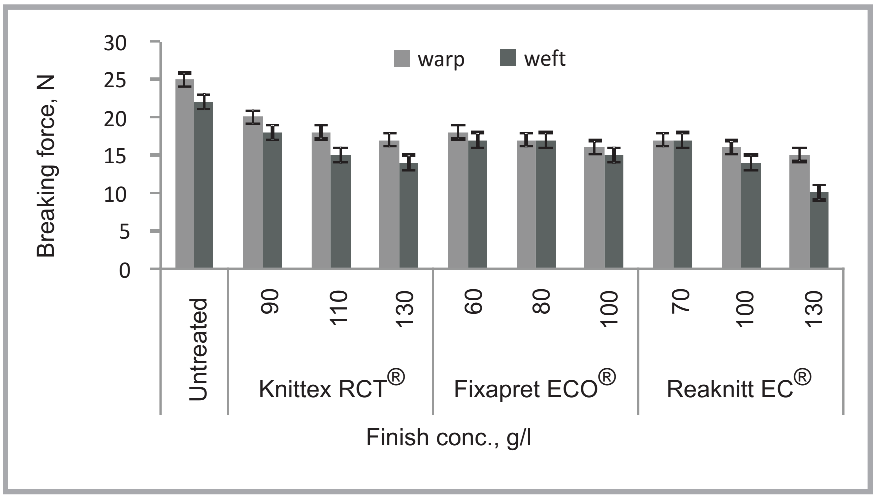

Figure 6. *Comparison of tensile strengths of silk specimens under various treatments.*

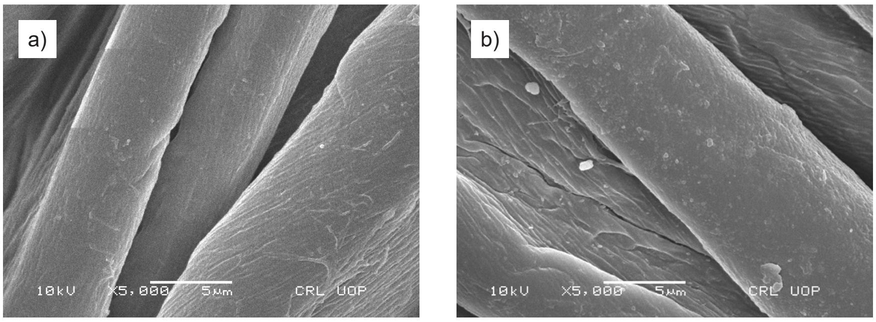

Figure 7. *Representative SEM images of (a) untreated and (b) Fixapret ECO® treated silk fabrics. Magnification: 5,000×.*

plication of any type of finish considered the air permeability improved as compared to that of the untreated specimen.

The tensile strengths, both in the warp- and weft-directions, of the treated silk specimens generally decreased with all type of finishes applied as compared to the untreated silk specimen. ***Figure 6*** shows that the tensile strength decreased with increasing of the concentration of either finish. However, tensile strength losses were comparatively less in the case of Knittex RCT®. The finished silk fabric retained up to 80% of its original tensile strength in the warp- and 82% in the weft-directions at a Knittex RCT® concentration of 90 g/l. Cai and Qiu [15] also observed that the tensile strength of EPSIA treated silk fabric decreased, which was due to the finish causing the fabric to stiffen, thus inhibiting the slippage or movement of fibres over each other when an external force is applied. Since the slippage of the fibres causes the external load to dissipate, and in the absence of which the fabric will break more easily. Hence, these results show that there was a significant reduction in the inter-fibre or inter-yarn frictional force with the treatment of all types of cross-linkers, besides being capable of enhancing the wrinkle recovery angle.

SEM images of both untreated and treated silk fabrics are presented in ***Figure 7***. The surface of untreated fabric is quite smooth and even, whereas that of the treated fabric becomes more rugged, and there is obvious deposition after finishing, which indicated that the finish coating was formed on the fabric surface.

Conclusions

Three types of commercially available cross-linkers were investigated to improve the crease resistance and hydrophobicity of silk fabric with minimum tensile strength losses. Both the resilience and hydrophobicity of the treated silk fabric were considerably improved as compared to untreated silk fabric. Nevertheless a decrease in tensile strength of the treated specimens was observed. The cross-linkers considered were either a zero or low-formaldehyde cross-linker. This provides the opportunity for producing better quality, low-formaldehyde resilient hydrophobic silk textiles with improved air permeability and fair whiteness.

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