Effects of Crosslinking Agents, Dyeing Temperature, and pH on Mechanical Performance and Whiteness of Silk Fabric

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ABSTRACT: The effects of bleaching and dyeing conditions on abrasion resistance, tear strength, and whiteness of silk fabrics were studied. Different crosslinking agents at various concentrations were introduced into the silk fabrics under various dyeing temperatures and pH. The results indicated that the oxidatively bleached silk fabric exhibited better mechanical properties than those of reductively bleached silk fabric. Sodium citrate was found to be the most suitable crosslinking agent for enhancing the abrasion resistance and tear strength of the silk fabrics with no significant effect on the whiteness. The mechanical property improvements of sodium citrate–dyed silk fabric were attributed to a chemical reaction between –COOH groups and amino acid side chains in silk fabric, the mechanism proposed in this work. Increasing sodium citrate resulted in improved mechanical properties and whiteness, but the opposite trend was found with increasing dyeing temperature. An optimum pH for dyeing the silk fabric in this work was 5.5.
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Key words: silk; crosslinking; bleaching; dyeing; mechanical properties

INTRODUCTION

Silk fibroin, like wool keratin, is formed by the condensation of α-amino acids into polypeptide chains, but the long-chain molecules of silk fibroin are not linked together by disulfide bridges as they are in wool.[1] Chemical treatments can cause modification of main peptide chains, and side chains of amino acids, which in turn influence the fiber's chemical, physical, and mechanical properties.[2] Permanent damages of wool keratin during processing usually occur because of irreversible shortening of the main peptide chains and rupture of disulfide crosslinks.[3] The damage to silk is also similar. Acid and alkali treatments cause severe damages to the protein fibers (i.e., silk and wool fibers), producing loss in strength, handle, and turning yellow. Peptide bonds and amide side chains are very sensitive to both acid and alkali hydrolyses during wet processes like bleaching and dyeing, especially at high temperatures.[1,4] Thus the optimal processing conditions ideally must not produce any damage to the main peptide chains.

Tsukada et al.[5] stated that the performance of silk includes many indicators such as crease recovery, rub resistance, colorfastness, wash and wear properties, and photo-yellowing. These properties can be usually improved by two different methods: (1) graft copolymerization such as methyl methacrylate (MMA), methacrylamide (MAA), 2-hydroxy-ethyl methacrylate (HEMA), styrene, ethoxy-ethyl methacrylate (ETMA), methacrylonitrile (MAN), and vinyltrimethoxysilane (VTMSi)[6]; and (2) use of chemical modifying agents such as epoxides, which improve the resilience, dyeability with acid dyes, and color fastness to washing.[7,8] This is attributed to the reactions of epoxides with tyrosine and both basic and acidic amino acids present in silk fibers. Dibasic acid anhydrides, including aliphatic (succinic, glutaric) and aromatic (phthalic, *o*-sulfobenzoic), have been known as effective chemical-modifying agents for improving crease recovery and reducing photo-yellowing of silk fabric without affecting the mechanical properties. The dibasic acid anhydrides will react with basic amino acids to produce chemical bonds in silk fabrics. The isocyanates and diisocyanates react with various amino acid side chains in proteins. These chemical modifications of the silk fabrics with isocyanates have been observed to enhance acid and alkali resistance.[9]

Bleaching wool fabrics generally decreases the abrasion resistance because disulfide bonds are damaged. Introducing protective agents and pre- and postsolvent treatments can improve such properties. Wool

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TABLE I
Physical Characteristics of Silk Fabric Used

Yarn of silk fabric sample	Yarn count (denier)	Setts (threads/in.)	Yarn twist	
			turns/in.	Type
Warp (single yarn)	53.53	92	8.35	S
Weft (twisted yarns)	147.56	56	3.45	Z

dyeing is normally carried out in boiled water to achieve levelness, good penetration of fibrous mass and individual fibers, optimum fastness properties, and excellent dye-bath exhaustion.[10] Dyeing fabrics at high temperature may damage the protein fibers. However, incorporating some fiber-protective agents that react with thiols and amine nucleophiles may prevent damage.[11] The damage to wool fibers can also be minimized by dyeing in the isoionic region under pH of 3.5–4.5.[10] In this pH region, the fiber structure has a maximum cohesion attributed to salt linkages between protonated amino groups and carboxylate anions, as well as minimized amide and disulfide bond hydrolysis.[11] Wool fiber protective agents, such as protein derivatives, formaldehyde-based products, and bifunctional reactive dyes, have been used to repair fiber damage. Examples of the protective agents are *N,N,N″*-triacroylaminohexahydrotriazine, *N,N′*-methylene bisquaternary aminoacrylamide, sodium hydrogent maleate, and Irgasol HTW. In addition, low-temperature dyeing with urea-based methods, formic acid–based methods, surfactant/auxiliary methods, and solvent-assisted methods are preferred to prevent damage to the fibers.[10]

In this article, abrasion resistance, tear strength, and whiteness of the silk fabrics were investigated under either an oxidative or reductive bleaching system, and dyeing processes. The effects of crosslinking agents and their concentrations in the dyeing process on the properties of the silk fabrics were evaluated. Finally, dyeing temperature and pH were varied to follow the changes in the mechanical performance and whiteness of the silk fabric.

EXPERIMENTAL

Materials

Silk fabric

The silk fabric used was a plain-weave fabric, weighing 94 g/m^2, supplied by Alongkorn Thai Silk Ltd. (Sakon Nakron, Thailand). The physical characteristics of the silk fabric used are provided in Table I.

Crosslinking agents

Four different crosslinking agents were used in this investigation: sodium citrate (SC), adipic acid (AA), fumaric acid (FA), and bis(4-fluoro-3-nitrophenyl)sulfone (BFNS), whose chemical structures are shown in Figure 1.

Processes

Bleaching process

This was carried out in either an oxidative or a reductive bleaching system. The oxidative bleaching solution used was an alkaline hydrogen peroxide solution, which contained 22 mL/L of 30% hydrogen peroxide solution, 6 g/L tetrasodium pyrophosphate, and 1 drop/L of Tween 20. The bleaching was performed at pH 8.5 and a temperature of 60°C for 1 h at a fabric to liquor ratio of 1 : 20. The bleached samples were then washed with running tap water, rinsed with distilled water, and air-dried. For the reductive bleaching system, the solution had 1.5 g/L thio-urea dioxide, 2.5 g/L EDTA, and 1 drop/L of Tween 20. The pH used for reductive bleaching was 6.5, whereas the liquor ratio, bleaching temperature, operation time, and washing and drying performances were the same as those used in the oxidative system.

Dyeing process

All bleached silk fabric specimens were blank-dyed at a liquor ratio of 20 : 1 either with or without a crosslinking agent. The dyeing procedure is described in detail elsewhere.[11] The buffer solution used consisted of sodium acetate/acetic acid. A Roaches Bea-

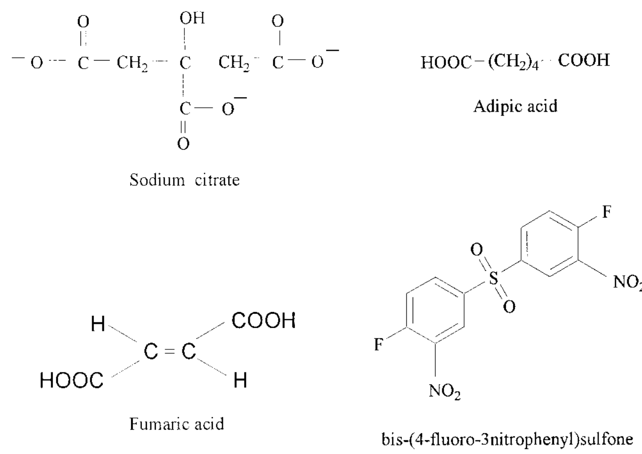

Figure 1 Chemical structures of crosslinking agents used.

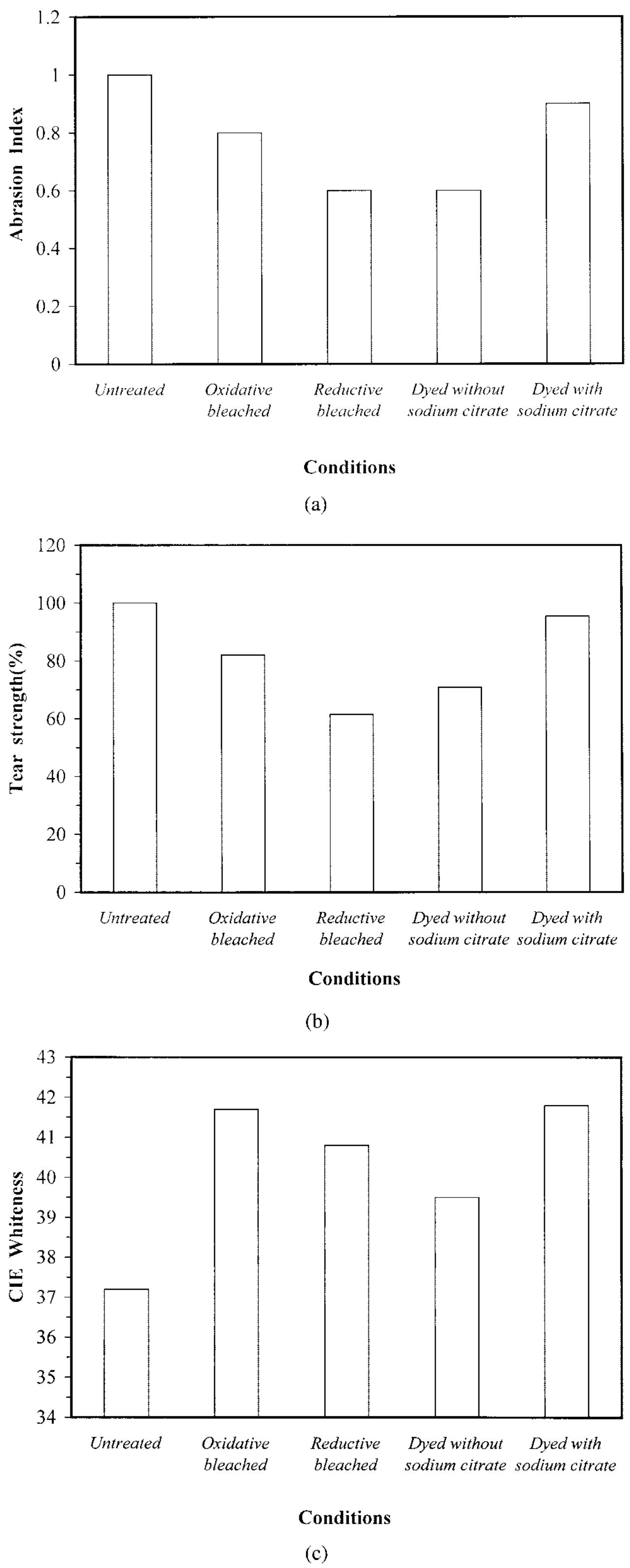

Figure 2 Effect of bleaching and dyeing with and without crosslinking agent on mechanical properties and whiteness of silk fabrics: (a) abrasion resistance; (b) tear strength; (c) whiteness.

ker dyer, a single-bath apparatus (model TPC-1001; Pyrotecs, Staffordshire, UK) was used for blank dyeing throughout the investigation. All the fabrics were introduced into the dyeing machine at room temperature (25°C). The temperature was then gradually increased at 1.5°C/min to reach the required temperature, and the fabric was then left at the required temperature for 1 h before being washed and rinsed with distilled water, and air-dried. The mechanical and whiteness properties of the resulting fabric were then examined.

Experimental variables

In this article, the mechanical and whiteness properties of silk fabric were investigated under the following aspects:

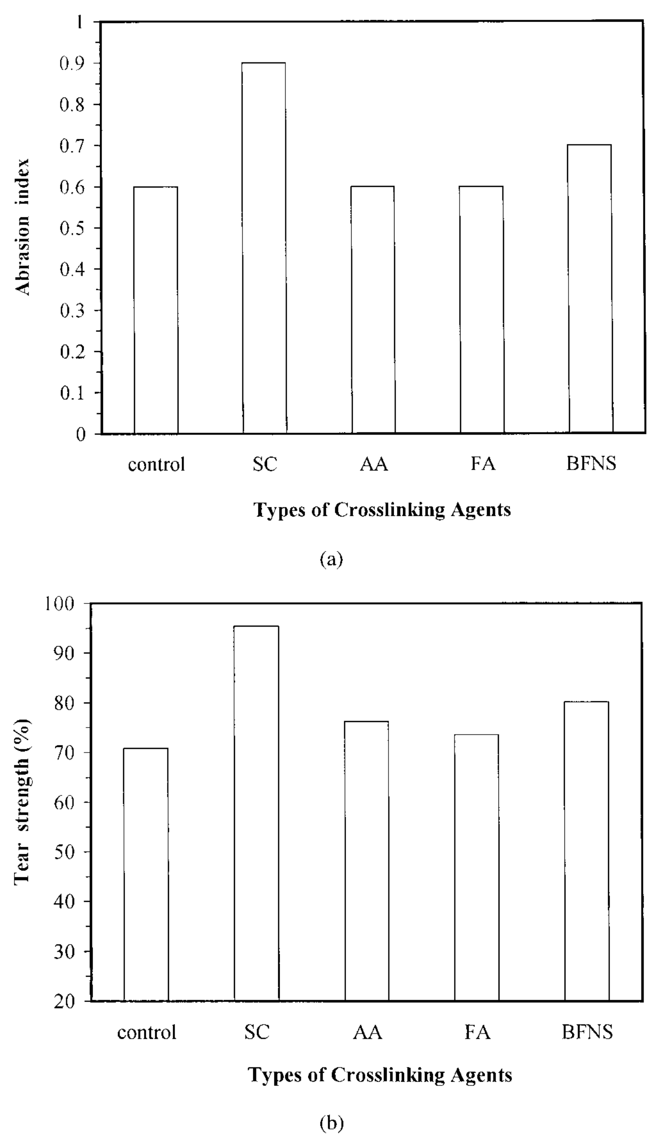

Figure 3 Effect of crosslinking agent types on mechanical properties of silk fabrics: (a) abrasion resistance; (b) tear strength.

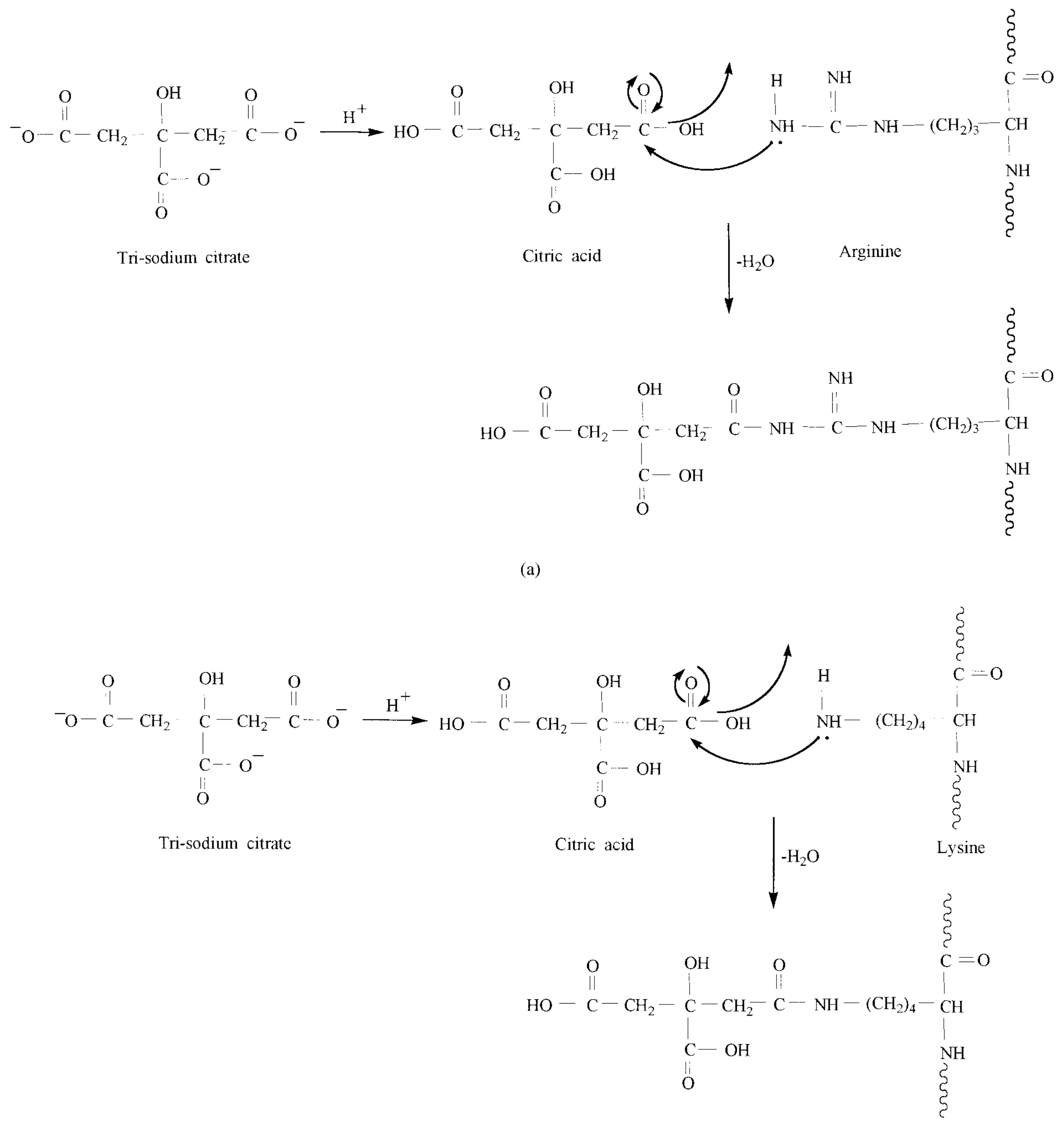

Figure 4 Chemical reaction mechanism of sodium citrate with silk protein: (a) sodium citrate with quanidino group of arginine; (b) sodium citrate with amino group of lysine.

TABLE II
CIE Whiteness of Silk Fabrics for Different Crosslinking Agents

	Crosslinking agent				
Property	Control	Sodium citrate	Adipic acid	Fumaric acid	Bis(4-fluoro-3-nitrophenyl) sulfone
CIE whiteness	39.5	41.8	41.0	41.1	−116.5

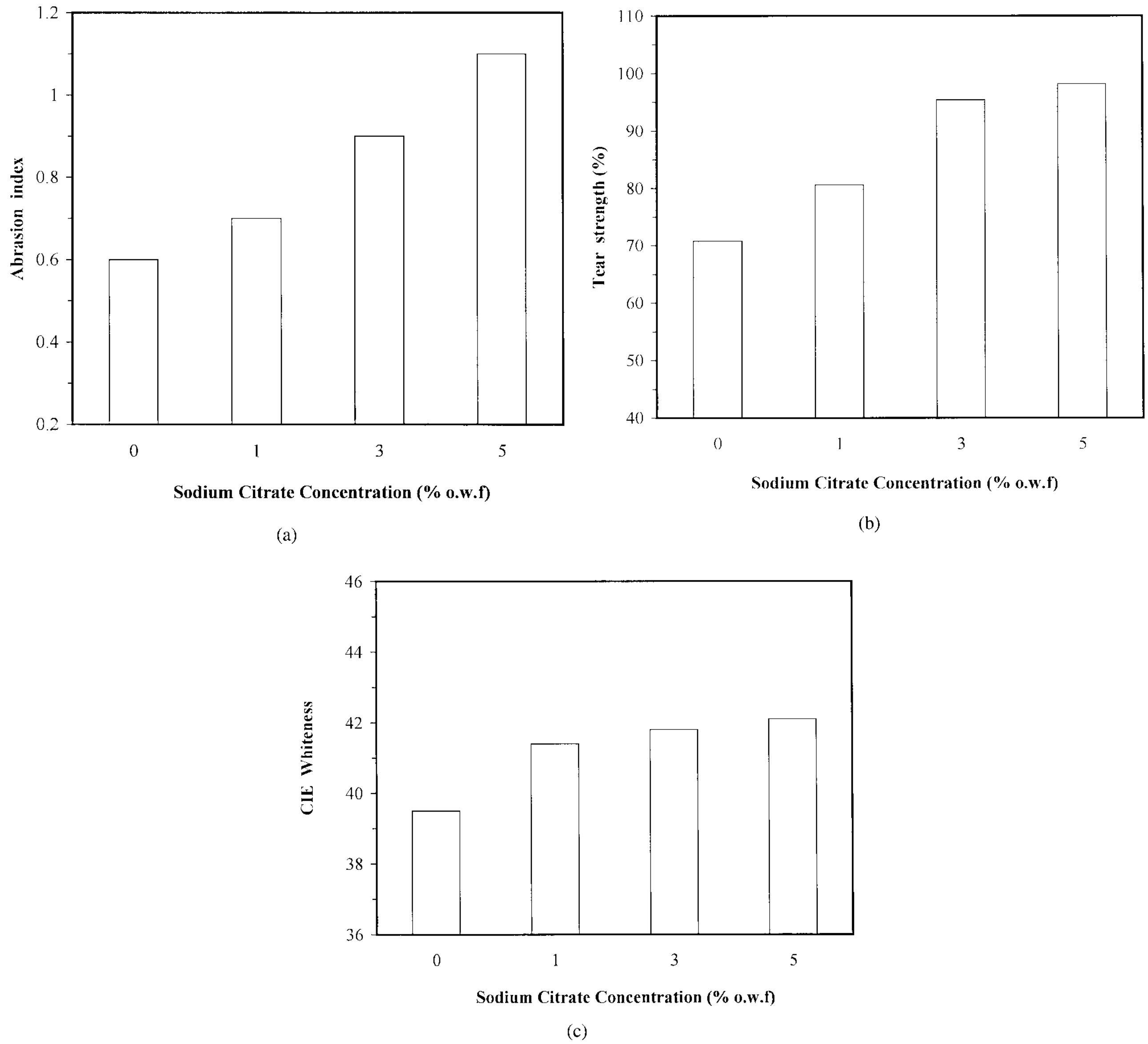

Figure 5 Influence of sodium citrate concentration on mechanical properties and whiteness of silk fabrics: (a) abrasion resistance; (b) tear strength; (c) whiteness.

1. *Type of bleaching and dyeing processes*. The fabrics were either oxidative or reductive bleached, and then dyed either with or without crosslinking agent.
2. *Type of crosslinking agents*. Four different types of crosslinking agents, including SC, AA, FA, and BFNS, were introduced into the dye bath. The crosslinking agent used was at 3% owf (on weight of fabric), and dyeing temperature and pH were kept constant for this purpose, to seek the most suitable crosslinking agent for the silk fabric.
3. *Amount of crosslinking agent added*. The best crosslinking agent was selected for the concentration study. Concentrations were varied from 0.0 to 5.0% owf, to determine the optimum concentration of the crosslinking agent to be added into the dye bath.
4. *Dyeing conditions*. Dyeing temperature and pH were varied from 80 to 110°C and 3.0 to 7.0, respectively.

Mechanical properties and whiteness of fabric

The performance of bleached and dyed silk fabrics was evaluated with respect to abrasion resistance (abrasion index), tear strength, and whiteness compared to that of untreated silk fabric. All fabric specimens were conditioned at 65% relative humidity at a temperature of 20°C for 24 h before testing.

Abrasion resistance test

The abrasion resistance test was performed using a Martindale Wear and Abrasion Tester (James H. Heal

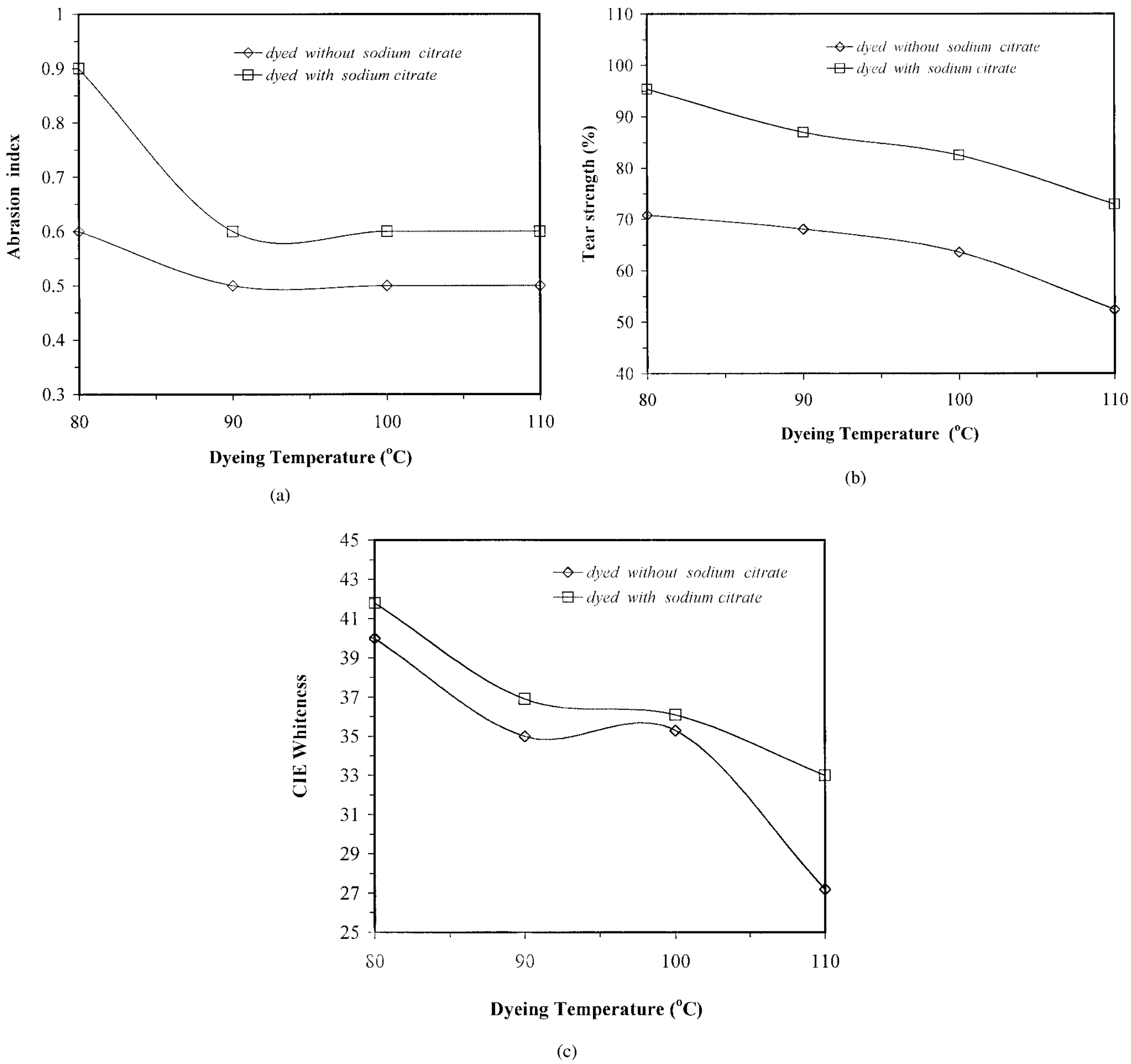

Figure 6 Effect of dyeing temperature on mechanical properties and whiteness of silk fabrics: (a) abrasion resistance; (b) tear strength; (c) whiteness.

and Co., Halifax, UK). The test procedure followed British Standard method (BS-5690: 1991).

Tear strength

Tear strength of silk fabric was evaluated using an Elmendorf tearing tester (Model EL-6400 W; Daiei Kagaku Seiki, Japan), and the test procedure was in accordance with ASTM D-1424: 1983.

Whiteness

A spectrophotometer (Spectra-flash 500; Datacolor International) was used for determining the whiteness indices [International Commission on Illumination (Commission Internationale de L'Eclairage = CIE) whiteness] of the fabric sample. The experimental procedure is reported in detail elsewhere.[11]

RESULTS AND DISCUSSION

Effect of bleaching and dyeing conditions

Figures 2(a)–(c) show the effect of bleaching conditions and dyeing with and without sodium citrate as a crosslinker on abrasion resistance, tear strength, and whiteness of the silk fabrics, respectively. For abrasion resistance, the results clearly indicated that the oxidative bleaching decreased the abrasion resistance of the fabric samples compared to that of the untreated sample. This was because the peptide bonds, amide side chains of protein fibers, were sensitive to alkali hydrolysis,[1,11] which caused damage to the fibers during bleaching. The reductively bleached silk fabric showed a lower abrasion resistance than that of the oxidatively bleached fabric. For dyed silk fabric samples, it may be seen that dyeing the fabric with sodium citrate evidently conferred a remarkable improvement in fabric abrasion resistance. The explanation was that the sodium citrate introduced additional crosslinks between the silk protein or repaired some degraded chemical bonds in the fibers.[11] The tear strength result of the fabric in Figure 2(b) also showed very similar behavior to that of abrasion resistance. The results from Figure 2(a) and (b) clearly indicated that the suitable bleaching and dyeing conditions for improving the mechanical properties of silk fabrics were oxidative bleaching and dyeing with sodium citrate as a crosslinking agent.

With respect to whiteness property [Fig. 2(c)], the result clearly suggested that all bleaching (either oxidative or reductive) and dyeing conditions (with or without sodium citrate) improved the whiteness of the fabric samples compared to that of the untreated one. Fabric with oxidative bleaching and sodium citrate dyeing appeared to give the best whiteness property in this case. It was postulated that the change in color from white to yellow of the fiber was probably caused by a fiber degradation. Introducing sodium citrate into the dyeing system led to more crosslinks occurring in the fibers, and thus the fiber degradation decreased.

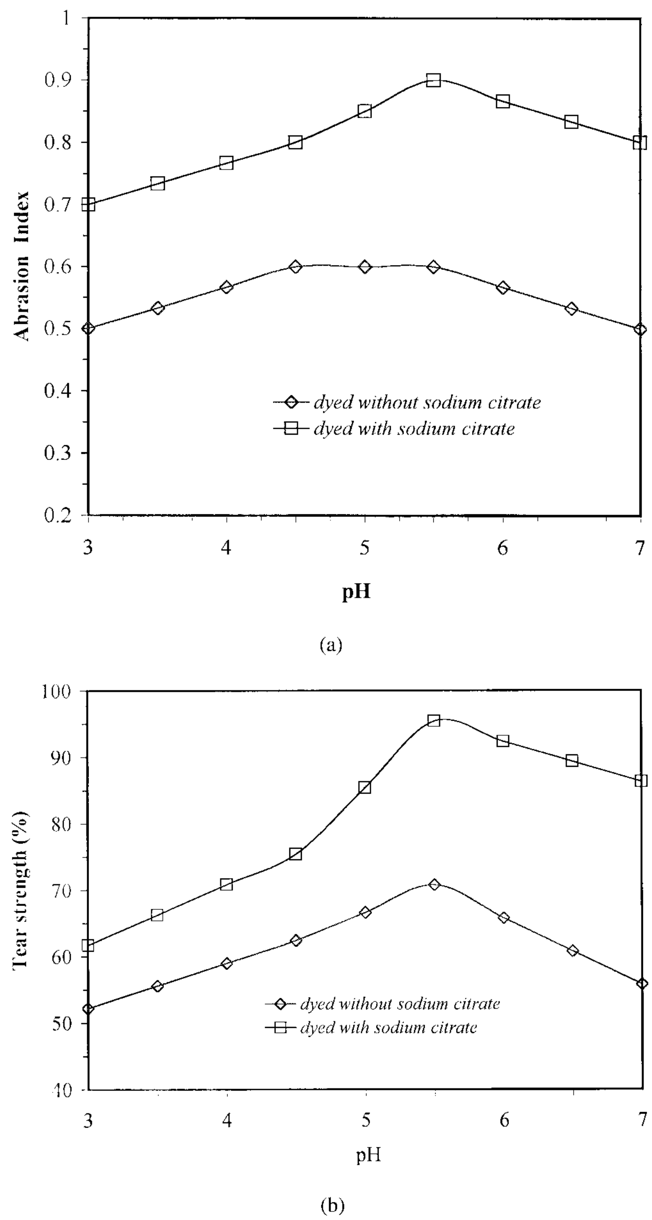

Figure 7 Effect of dyeing pH on mechanical properties of silk fabrics: (a) abrasion resistance; (b) tear strength.

Effect of crosslinking agent type

The oxidatively bleached silk fabric samples were used to evaluate the effect of various types of crosslinking agent on the fabric properties. The crosslinking agents used were sodium citrate, adipic acid, fumaric acid, and bis(4-fluoro-3-notrophenyl) sulfone, the concentration of each crosslinking agent added during the dyeing process being 3% owf. Figure 3(a) and (b) show the effects of crosslinking types on abrasion resistance and tear strength of the silk fabrics, respectively. The results indicated that the sodium citrate treatment offered the highest improvement in abrasion resistance and tear strength of the silk fabric compared to that of other crosslinkers. The differences in mechanical properties of the silk fabric in this case can be explained in terms of differences in chemical structures of the crosslinking agents used. Sodium citrate used was in the form of trisodium citrate, which had three $-COO^-$ groups, whereas adipic and fumaric acids had two groups. Under acidic conditions, these $-COO^-$ groups were protonated to produce –COOH in the solution to react with amino acid side chains to form new amide bonds, as molecular crosslinks, in the silk fibroin. The greater the number of –COOH groups, the greater the opportunity to form molecular crosslinks in the silk fibroin, thus increasing the mechanical strength of the fabric. The above-discussed chemical mechanism between trisodium citrate and the silk proteins is proposed in Figure 4(a) and (b). It can be clearly seen that the proposed mechanism was a condensation reaction of sodium citrate and silk amino groups that produced new amide bonds and water molecules.

Table II shows the whiteness property of oxidatively bleached silk fabric dyed with various crosslinking agents. The result of dyed fabric whiteness can be interpreted from the value of the CIE whiteness: the greater the CIE value, the whiter the fabric. The results showed that dyeing the fabrics with sodium citrate, adipic acid, and fumaric acid gave a similar whiteness to that of the control sample, whereas that with BFNS yielded a negative value, and its sample was observed to become yellow. This was probably attributable to a decomposition of BFNS itself during the dyeing process, which caused yellowness of the fabric. Therefore, the BFNS was not considered to be a good crosslinking agent.

Effect of sodium citrate concentration

Based on its performances as discussed in the previous section, sodium citrate was chosen and used for assessment of the effect of crosslinking agent concentration on the properties of silk fabrics. The results are shown in Figure 5(a) (abrasion resistance), Figure 5(b) (tear strength), and Figure 5(c) (whiteness). The results clearly illustrated that the abrasion resistance and tear strength progressively increased with increasing sodium citrate concentration. Increasing the sodium citrate amount resulted in an increase in the number of the reactive functional groups to form crosslinks (amide bonds) in the silk fibers, as discussed in Figure 4(a) and (b). It was also noticeable that the whiteness of the silk fabric was less affected by increasing concentration of the sodium citrate used. The reason was similar to that explained in Figure 2(c). In terms of magnitude of the property improvement and cost savings, an amount of 3% owf of sodium citrate was selected for further investigations.

Effect of dyeing temperature and pH

Figure 6(a)–(c) show the changes in abrasion resistance, tear strength, and whiteness properties of the oxidatively bleached fabrics dyed both with and without 3% sodium citrate for different dyeing temperatures. It may be observed in Figure 6(a) that the abrasion resistance of the fabrics decreased with increasing dyeing temperature from 80 to 90°C, but no difference was seen at temperatures higher than 90°C. Tear strength [Fig. 6(b)] monotonically decreased with increasing dyeing temperatures. The reduction in the mechanical performance of the fabrics was probably caused by damage or degradation of the fibers resulting from the increased temperature.[11] However, addition of 3% sodium citrate appeared to improve the mechanical performance of the silk fabrics, especially at low dyeing temperature, which is related with the proposed reaction of sodium citrate and silk protein as discussed earlier. Similarly, whiteness of the silk fabrics was observed [Fig. 6(c)] to decrease with dyeing temperature, but slightly improve with addition of sodium citrate.

Figure 7(a) and (b) show the effect of dyeing pH on abrasion resistance and tear strength of the oxidatively bleached silk fabric with and without sodium citrate. It was observed that the fabric abrasion resistance and tear strength increased with increasing pH from 3.0 to 5.5; beyond these values, such properties decreased. It was thought that the silk fabric at pH 5.5 may be in an isoionic region, at which the structure of silk fiber had a maximum cohesion attributed to the salt linkage between the protonated amino group and carboxylate anions, as well as minimized amide hydrolysis,[12] and thus increased mechanical strength of the fabric. Once again, an improvement in the mechanical properties was seen with the presence of sodium citrate. It should be noted that changing pH from 3.0 to 7.0 had only a slight effect on the change of whiteness of the silk fabric (results not shown in graph).

CONCLUSIONS

The effects of various crosslinking agents and concentrations, and dyeing conditions on abrasion resistance, tear strength, and whiteness of silk fabrics were examined. The results suggest that silk fabrics that were oxidatively bleached had better mechanical performance than those that were reductively bleached. The whiteness was improved with the bleaching. Sodium citrate was observed to be the most suitable crosslinker in this study, for enhancing the abrasion resistance and tear strength of the silk fabrics without affecting silk whiteness. The mechanical property improvements of sodium citrate–dyed silk fabric were illustrated through a reaction between –COOH and amino acid side chains in silk fabric, whose mechanism is proposed in this article. Increasing sodium citrate led to an improvement of mechanical properties and whiteness, but the opposite trend was found when increasing the dyeing temperature. An optimum pH for dyeing the fabric was 5.5.

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