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**Chitosan as a Consolidant for Fragile Silk**

### Abstract

Silk textiles in museum collections are often degraded and fragile, but no satisfactory treatment currently exists to strengthen or consolidate deteriorated silk. Recently, chitosan has been investigated as a consolidant for artifacts, including silk textiles. Chitosan is the N-deacetylated derivative of chitin, a linear polysaccharide found in the exoskeleton of crustaceans and other natural sources. Chemically, chitosan is (1→4)-2-amino-2-deoxy-β-D-glucopyranose, which has a chemical structure similar to cellulose, but with an amino or acetyl functional group substituting the hydroxyl group at carbon #2. Among its many properties, chitosan is non-toxic, anti-microbial, soluble in dilute acids, non-soluble in organic solvents, and capable of hydrogen and electrostatic bonding with organic substrates. Importantly, chitosan is capable of coating and strengthening textile fibres. Chitosan was applied to silk fabrics to test its effectiveness and suitability as a consolidant for textile conservation. Chitosan was dissolved in dilute acetic acid in distilled water to give 0.5% or 1% w/v solutions. The sample substrates were a new, white silk habutai fabric, and two naturally aged and degraded silk damask fabrics. Silk samples were treated by immersion in 1% or 0.5% chitosan solutions for 15 minutes followed by rinsing in distilled water for five minutes, or simply by immersion in 0.5% w/v chitosan without subsequent rinsing. Some samples were artificially aged by 100 hours of thermal aging at 50°C and 65% RH, and light aging under a bank of fluorescent lights. Tests were conducted to assess the strengthening effect of chitosan, and to see if treatment caused stiffening or colour change in the silk substrates. Samples were imaged by optical microscopy and scanning electron microscopy; tested for tensile strength, stiffness, pH, and colour change; spot-tested with solvents; and analyzed by Fourier transform infra-red spectroscopy and x-ray fluorescence.

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## Introduction

### Project Questions and Goals

Historic silk textiles in museum collections are often extremely fragile. Unfortunately, no satisfactory treatment method currently exists to strengthen, consolidate, and protect degraded silks. Recently, the natural polymer chitosan has been investigated as a consolidant for silk conservation (Conti et al. 2011). Chitosan is a natural organic polymer chemically similar to cellulose. It can form tough, clear, water-insoluble, and gas-permeable coatings on organic substrates. Results from studies in various fields suggest that chitosan can strengthen silk substrates; however, few have tested chitosan in the context of art conservation, so there is little information available to comment on its effectiveness and suitability as a conservation treatment. This project aimed to build upon preliminary investigations of chitosan as a silk consolidant, and determine whether it is indeed an appropriate conservation treatment. The hope was that chitosan would impart strength and cohesion to fragile, powdering silk textiles, without causing yellowing, stiffening, or other unwanted effects often associated with adhesives and consolidants.

### Silk Chemistry and Degradation

Silk fibres and textiles are characterized by their fineness, relatively high strength, and beautiful lustre. Most silk textiles found in museum collections are produced from the domesticated silkworm species *Bombxy mori*, or by other species in the *Bombycidae* family. *Bombxy mori* silk fibres are comprised of two continuous, creamy-white filaments of the protein fibroin extruded by the silkworm that are glued together by the protein gum sericin. As a natural proteinaceous fibre, silk is a polymer composed of amino acids linked together by peptide bonds. Fibroin contains a high proportion of alanine, glycine, and serine; these amino acids have small residue groups, and pack closely together to form an anti-parallel  $\beta$ -pleated sheet structure in the silk polymer. Crystalline regions of the silk fibre contain  $\beta$ -pleated polymer structures stabilized by hydrogen bonds and salt linkages. Amorphous regions contain a higher proportion of other amino acids, with bulkier residue groups. The amorphous matrix functions to consolidate crystalline regions of the protein, and maintains a highly oriented crystalline structure in the fibre overall; as a result, silk fibres are strong, but inelastic.

Sericin contains more polar amino acids residues than fibroin, and is therefore soluble in hot water, detergents, and alkaline solutions (Tímár-Balászy and Eastop 1998). Silk is usually washed in such solutions to de-gum the fabric, or remove sericin, as it causes silk to yellow upon exposure to light. Removing sericin also separates the two fibroin strands, and improves the fibre's luster and dyeability. Sericin offers fibroin some protection against light and ultra-violet (UV) radiation, so de-gumming renders silk fibres more susceptible to photo-degradation. In fact, silk is considered the natural fibre most vulnerable to deterioration by visible light and UV radiation. Chemical deterioration of silk occurs primarily in the amorphous areas of the polymer, which are more accessible to agents of deterioration like free-radicals, oxygen, moisture, and pollutants. When the amorphous regions are degraded, the overall crystalline structure of the polymer is lost, and the fibre weakens (Garside and Wyeth 2007).

Silk fibroin contains the light-sensitive amino acids phenylalanine, tryptophan, and tyrosine, which absorb UV radiation in the 220-370nm range (Boersma 2007). Visible light and UV radiation can therefore be absorbed by the silk polymer and furnish energy for deleterious photo-oxidation reactions, including the formation of free-radical compounds, oxidation, chain scission, and cross-linking. Oxidation reactions may produce chromophoric chemical groups in the silk polymer and turn silk fibres yellow or light pink in colour (Boersma 2007). Photo-oxidation may also cause chain-scission reactions that break apart polymer chains, lowering the degree of polymerization and weakening the material. Oxidation may also cause cross-linking reactions that form new bonds between polymer chains, resulting in brittle fibres.

Silk is also chemically damaged by concentrated acids and alkalis. Acid or alkaline-catalyzed hydrolysis reactions break peptide bonds in the silk polymer, resulting in chain scission, a subsequent decrease in the degree of polymerization, and weakening (Boersma 2007). In acidic environments, salt linkages, hydrogen bonds, and peptide bonds in the silk protein are broken, weakening the fibre. Alkaline environment render silk fibres more stiff and brittle, as salt linkages and hydrogen bonds are ruptured, and new chemical links are formed. Salts from skin contact and perspiration from wear will cause damage to silk costumes and textiles by these mechanisms.



Silk ages and degrades by physical processes as well. Organic polymers like silk age physically as the amorphous regions of the polymer gradually rearrange into more orderly, crystalline forms over time, rendering the fibres increasingly dense, stiff and brittle, and consequently more prone to physical damage from handling and movement (Bresee 1986). Like other organic materials, silk is hygroscopic, and will absorb and desorb moisture from its environment. Silk fibres swell as they absorb moisture at high relative humidity levels, and shrink in low humidity. Fluctuations in the relative humidity causes the abrasion of silk fibres when textile yarns rub against each other as they change dimension. Each cycle of environmental change causes additional damage to silk. Textile manufacturing methods like spinning and weaving also cause physical stress and abrasion. Creases, folds, and pleats in a textile will create localized stresses in those areas, making the fibres there especially vulnerable to physical breakage and chemical deterioration.

The processing methods of textile production can cause long-term deterioration to silk fibres and textiles. European silks from the 18<sup>th</sup> to early 20<sup>th</sup> centuries were regularly processed under harsh conditions. The processes of bleaching, weighting, mordanting, dyeing, and finishing all involved immersing silk in very hot and highly acidic or alkaline baths, all of which are damaging to silk (Hacke 2008). For example, bleaching by exposure to sulphur dioxide fumes is extremely harmful to silk. Since the 17<sup>th</sup> century, Western silks were commonly treated with metal salts, or weighted, to compensate for the weight lost by de-gumming (about 25% of the textile's mass), as silk was sold by weight rather than yardage. Weighting also altered the hand or drape of silk textiles, adding desirable body, glisten, and a characteristic rustle to fabrics. Common metal salt formulations included stannous chloride ( $\text{Sn(II)Cl}_2$ ); stannic chloride ( $\text{Sn(IV)Cl}_4$ ), called "pink weighting"; and stannic chloride plus phosphates and silicates, called "dynamite weighting" (Hacke 2008). Dynamite weighting produced silk with a heavy drape, popular in the 19<sup>th</sup> century, but was especially damaging. Dynamite weighted silks degraded quickly, even in storage; the metal salts catalyzed exothermic oxidation reactions, and the textiles could actually spontaneously combust (Boersma 2007). Iron, lead, magnesium, and zinc salts were also used as weighting agents or mordants. Iron salts were typically used as mordants for black and dark coloured dyes. Tannic acids, oils, waxes, starches, and other organic materials were also used as weighting silk, or as finishing agents for

silk textiles. The residues of metal salts, mordants, and other materials can damage silk by catalyzing oxidation and acid-hydrolysis reactions in the polymer. The metallic salts and finishes are chemically bound to silk fibres and cannot be removed from textiles. Garside, Wyeth, and Zhang (2010) argue the harsh processing baths used in weighting process are actually the major cause of the damage in weighted silks, rather than the metal residues themselves, noting not all metallic salts catalyze deleterious reactions or yield especially degraded silks.

Whether degraded by manufacturing processes, metal salts, light, age, or other factors, silk artifacts in museum collections are often very fragile. Aged silk threads and textiles are typically brittle, weak, and tend to powder and disintegrate. Old weighted silks are notoriously fragile, brittle, and break on their own, or with movement. Weighted silk textiles characteristically shatter and split, as degraded fibres have lost all tensile strength and extensibility. Such objects are tremendously vulnerable, as any movement can cause more silk fibres to break and disintegrate. Since the warp and weft yarns of a textile were typically processed and weighted differently, weighted silks tend to break along one grain direction (the more weighted yarns) before the other.

#### Adhesive Use in Textile Conservation

In the past, conservators debated the very use of adhesives in textile conservation; however, with increased experimentation and research into the properties and stability of adhesives, their use has generally become accepted, albeit restricted to certain circumstances (Keyserlingk 1990). For example, extremely fragile textiles such as shattering silks may be damaged by the physical stress of a sewing needle and thread, so an adhesive repair may be a more appropriate treatment to stabilize the artifact. Adhesive repairs may be used when stitched repairs would be visually obtrusive, especially for textiles with painted surfaces, where a sewing needle would puncture and disrupt the paint film. Fibres in very poor condition that break or disintegrate with movement require impregnation with an adhesive or consolidation to impart them with enough strength to be handled. Archaeological textiles may be so degraded that without consolidation, they would disintegrate (Stauffer 2011). Therefore adhesives and consolidants have important uses in textile conservation, though they tend to be used only when sewing repairs or immobilization of the artifact are not satisfactory options.

Adhesives are approached with caution in textile conservation because unstable materials can yellow, cross-link, and become brittle or insoluble over time. The adhesives may fail, delaminate, become tacky, or appear glossy over time, all of which are unacceptable when associated with an artifact, especially textiles, which are meant to move, flow, and drape (Karsten and Kerr 2002). The requirements for adhesives used in textile conservation treatments include: chemical compatibility with the substrate; the ability to wet and adhere to the substrate; not cause visual change such as yellowing; improvement of tensile strength of substrates; flexibility; reversibility; solubility in appropriate solvents; chemical stability; and resistance to aging (Tímár-Balászy and Eastop 1998). Additional desirable features of adhesives include ease of handling and application; low viscosity for good penetration; and non-toxicity.

Adhesives tend not to be directly applied to textile artifacts in conservation treatments. Instead, the adhesive is typically applied to a support fabric attached to the artifacts as a backing or overlay. A stable thermoplastic adhesive, such as a polyvinyl acetate resin, or the acrylic adhesives Lascaux 360HV or 498 HV, is brushed or sprayed onto a new, clean support fabric. Silk crêpe or Te-tex polyester textiles are used for sheer and unobtrusive supports. The adhesive-impregnated support is attached to the artifact by heat or solvent-reactivation of the adhesive. Commonly, a heated spatula is run over the support fabric to heat-seal it to the artifact. The adhesive-impregnated support fabric provides the textile with cohesion and physical support, without having the adhesive fully impregnate the artifact. Such treatments are less invasive than total immersion or saturation of an artifact with an adhesive or consolidant; are more easily reversible; and therefore better protect artifacts from the potential deleterious effect of unstable adhesives. Even so, if unsuitable adhesives and application methods are used, the support is at risk of blistering, delamination, discolouration, stiffness, and tackiness (Karsten and Kerr 2002).

Currently, these are no satisfactory conservation treatments that protect and stabilize degraded silks. Adhesive supports or encasement with new fabrics can physically protect fragile silk textiles, but the condition of the silk is not improved, and further deterioration is not prevented. Various consolidation methods have been tried to protect silk, including impregnation with various gums, starch, caoutchouc-latex,

seaweed, casein, gelatin, beeswax, paraffin wax, shellac, natural resins, synthetic compounds such as cellulose ethers and esters (including methylcellulose, carboxymethylcellulose, and hydroxypropylcellulose), soluble nylon, polyvinyl acetates, polyvinyl alcohols, polyvinyl butyrals, polyethylene glycol, Beva 371, and various acrylic adhesives (Tímár-Balászy and Eastop 1998). Unfortunately, some aspect of the treatment was always unsuitable, such as yellowing, stiffening, or embrittlement of the adhesive or textile. For example, polyvinyl alcohol cross-links over time and becomes insoluble upon the application of heat (so becomes irreversible), and nylon becomes insoluble at high relative humidity and shrinks upon drying, risking distortion of the textile substrate (Landi 1998).

Thompson and Kataoka (2011) argue that the direct use of adhesives on textile artifacts can be effective and suitable as a conservation treatment, if carefully considered and carried out. The adhesives used in their treatments, wheat starch paste, cellulose ethers, and acrylic adhesives, are commonly used in other conservation fields and are trusted for their stability. In one case study, Klucel G (hydroxypropylcellulose) was used to consolidate powdering silk yarns. A 2% solution of Klucel G in deionized water plus ethanol was applied directly to the silk yarns with a paintbrush. Klucel G is used in paper conservation as an adhesive or consolidant; it can form strong, clear films or coatings on various substrates. The treatment was considered successful, as the silk yarns were strengthened, stopped powdering, and treatment did not cause visual change.

Consolidation of silk textiles has also been attempted with Parylene, or poly(p-xylylene) polymers, particularly Parylene C. The solid dimer of Paralyne C, poly-chloro-p-xylene, is vaporized in a light vacuum and deposited onto the artifact as a thin film in the form of a poly-chloro-p-xylene polymer (Tímár-Balászy and Eastop 1998). The polymer is colourless, insoluble, and resistant to chemical attack. Consolidation with Parylene C increased the strength of fragile silks, but also their stiffness. Parylene C is stable in the dark, but exposure to UV radiation causes the polymer to oxidize, yellow, stiffen, and lose its protective function (Halvorson 1991; Halvorson and Kerr 1994). Additionally, the treatment is irreversible. Parylene consolidation is therefore not an entirely satisfactory or suitable conservation treatment for fragile silks.

Recently, many natural polymers have been investigated as consolidants for silk. These include bacterial cellulose (Wu et al. 2012); silk fibroin in combination with ethylene glycol diglycidyl ether (fibroin-EDGE) (Zhao et al. 2011); and chitosan salts (Conti et al. 2011; Vargas 2005). Conti et al. (2011) also investigated the use of a silicon dioxide sol-gel modified with polyethylene glycol 1000 as a silk consolidant. Chitosan is a cellulose-like polysaccharide that can coat and consolidate fibres. Conti et al. (2011) tested the use of chitosan as a consolidant for fragile archaeological silk textiles, applying chitosan to silk as 0.1%, 0.3%, 0.5%, and 1% w/v aqueous solutions of acetic acid at pH 5, either by immersion or ultrasonic application. Tensile testing, scanning electron microscopy, and spectrophotometry showed that silk treated with chitosan had increased flexibility and breaking strength compared to untreated silk. The drape of the silk was not altered if the chitosan solution concentration was below 1%, and if the silk was rinsed in water after chitosan application. The change in the whiteness values of the silk substrates (colour change) due to treatment was considered negligible. Conti et al. (2010) claim that chitosan interacts with silk fibres rather than the textile on a gross scale. The low molecular weight of chitosan and its film-forming ability allows it to coat individual fibres, and not form globules of material on the textile surface. High magnification scanning electron microscopy images showed chitosan “bridges” formed between silk fibres, cited as the source of increased strength, flexibility, and overall integrity in the silk. This was only a preliminary study of chitosan consolidation; tensile testing was conducted on single silk threads only, not fabrics, and no artificial aging tests were reported on. In a similar experiment by Vargas (2005), artificially aged silk embroidery threads were treated with chitosan salts, artificially aged again, and evaluated for tensile strength, flexibility, pH, colour change, and UV stability. Both carboxymethyl chitosan and chitosan acetate salts improved the tensile strength of silk yarns with minimal yellowing, but chitosan acetate increased the stiffness of yarns.

Chitosan has also been investigated as a size and antimicrobial agent for paper artifacts (the antifungal properties of chitosan are well-known and exploited in various bio-medical and industrial applications of the material). Del Pilar Ponce-Jiménez et al. (2002) applied chitosan acetate, butyrate, and propionate salts to filter paper, and compared their performance against three cellulose ether sizes. Chitosan salts provided

paper samples with better fungal resistance than cellulose ethers. The chitosan salts also increased the tensile strength and fold endurance of paper samples, though not as much as the cellulose ethers. Chitosan salts were also more acidic than the cellulose ethers. Basta (2003) applied 0.2% and 0.4% chitosan in 1% acetic acid aqueous solutions to rosin-alum sized paper using sodium hydroxide or sodium silicate precipitators. The 0.4% chitosan and sodium silicate treatment condition improved the durability of degraded alum-rosin sized paper, even after accelerated aging. In a similar study, Ardelea et al. (2009) found that carboxymethyl chitosan improved the bursting and tensile strength of aged paper. These studies suggest chitosan has consolidating, strengthening, and other positive effects on organic substrates.

### Chitosan Chemistry and Applications

Chitosan is a de-acetylated derivative of chitin (Pillai, Paul, and Sharma 2009). Chitin is a natural linear chain polysaccharide found in the exoskeletons of crustaceans and insects, the cell walls of fungi, and other natural sources. Chitosan is produced in large amounts as a by-product of the food industry by treating crustacean shells with acid. Chitosan is obtained by treating chitin with sodium hydroxide. Chemically, chitin is  $\beta$ -(1 $\rightarrow$ 4)-2-acetamido-2-deoxy- $\beta$ -D-glucose, or N-acetyl-glucosamine (Dutta, Dutta, and Tripathi 2004). The structure and function of chitin is analogous to that of cellulose, but the hydroxyl functional group at carbon #2 in cellulose is substituted by an acetamide group ( $-\text{NHCOCH}_3$ ) in chitin, and by an amino group ( $-\text{NH}_2$ ) in chitosan (Pillai, Paul, and Sharma 2009; Kumar 2000). Chitosan is (1 $\rightarrow$ 4)-2-amino-2-deoxy- $\beta$ -D-glucopyranose (or de-acetylated chitin, or poly(D-glucosamine)), but since the degree of deacetylation varies, it may best be described as a copolymer of  $\beta$ -(1 $\rightarrow$ 4)-D-glucosamine and N-acetyl-D-glucosamine (Kumar 2000).

Chitosan can be modified at its functional groups (the amino and hydroxyl groups) to alter its properties and functionality, just as cellulose can be modified to produce cellulose ethers, esters, and polymers. Unlike cellulose, chitosan is hydrophobic. It is not soluble in most organic solvents, but is soluble in dilute acidic aqueous solutions below pH 6 (Pillai, Paul, and Sharma 2009). Due to its chemistry, chitosan is compatible with organic substrates, including silk. Its amino and hydroxyl functional groups can form hydrogen bonds with polar substrates (Conti et al. 2011). Chitosan is cationic, and

can form stable electrostatic bonds with negatively charged substrates (Kumar 2000). Additionally, chitosan is non-toxic and has anti-bacterial and anti-fungal effects.

Chitosan is used for various industrial purposes. Since chitosan is non-toxic, anti-microbial, bio-compatible, bio-degradable, and non-allergenic, it is used in many biomedical applications, including wound dressings, tissue engineering, and suturing material. It is also has uses in food processing, agriculture, ophthalmology, photography, water treatment, textile processing, and textile finishing (Dutta, Dutta, and Tripathi 2004). Chitosan is also found in cosmetic products such as shampoos, as cationic chitosan can coat negatively charged hair fibres, increasing their softness and mechanical strength (Dutta, Dutta, and Tripathi 2004). Chitosan is used in textile processing to increase the wet strength and dye reception of cotton, and can be used as a finishing agent for wool by coating wool scales to prevent felting (Lim and Hudson, 2003). Chitosan is also used as an antimicrobial finish for silk and cotton textiles (Periolatto, Ferrero, and Vineis 2012). These various textile finishes perform well and withstand multiple washings, demonstrating chitosan's stability and compatibility with natural fibre substrates.

Chitosan has many attractive qualities, such as the ability to bond to and coat silk fibres, impart them with strength, and provide them with microbial resistance. Because of its polysaccharide structure, chitosan can form films on organic substrates that are strong, durable, elastic, and gas and moisture-permeable. Chitosan is also an abundant natural material, and is non-toxic to humans. The application method is safe, as it does not require the use of organic solvents, only dissolution in dilute acids (acetic acid is commonly used as it is readily available). Initial tests of chitosan consolidation in conservation suggest chitosan imparts organic substrates with strength, without causing colour change, but sometimes causes an increase in substrate stiffness. Tests of chitosan in industrial settings (such as using chitosan to improve dye uptake and microbial resistance in textiles) found that treated silks were stiffer than untreated silks (Phattanarudee, Chakvattanatham, and Kiatkamjornwong 2009).

Some studies have found that chitosan is not resistant to UV-induced photo-oxidation. Andradý, Torikai, and Kobatake (1996) found that UV irradiation of chitosan caused chain scission, fibre weakening, and an increase in the amount of carbonyl groups in the polymer due to oxidation, but UV exposure did not cause cross-linking in the

chitosan polymer; similar results were obtained by Bajer and Kaszmarek (2010). These findings suggest chitosan may be vulnerable to yellowing due to the formation of chromophoric carbonyl groups and embrittlement by chain scission when exposed to UV light and photo-radicals. So, while chitosan may strengthen and consolidate fragile silk textiles, it may also stiffen the fabrics and cause yellowing with age and light exposure. These qualities would disqualify chitosan as a suitable treatment for silk textiles and other artifacts. It is important to note, however, that these effects were observed in experiments using chitosan for industrial applications, where testing conditions were presumably more extreme than those encountered in museums or used in conservation studies. Chitosan may be stable in the mild environmental conditions in museums, especially if light is limited and filtered to remove UV radiation.

When considering a new treatment method for conservation, the question of reversibility arises. Chitosan is soluble in acidic solutions below pH 6 (Conti et al. 2011), so theoretically, it could be removed from an artifact, and the treatment could be considered reversible. As Appelbaum (1987) notes, however, reversibility may not always be practical, or the most important tenant to follow when deciding on treatments. If an artifact is so fragile that it requires consolidation, removal of the consolidant (reversal of the treatment) would likely cause substantial damage to the object, if not complete destruction. In some cases, invasive and essentially irreversible treatments like consolidation and impregnation may be necessary to stabilize an artifact. Even adhesive-impregnated backings may not be easily removed from a textile, as some adhesive residue may remain on textile fibres, but this may be acceptable if the treatment stabilizes the artifact. Future treatments and examination of an artifact should be not hindered by conservation treatments, so if not reversible, treatments should at least allow re-treatment of an artifact. Conti et al. (2011) emphasize the hypothetical re-treatability of silk textiles consolidated with chitosan. Chitosan treatment would not interfere with other future treatments, as it is not soluble in organic solvents or neutral pH water, solvents typically used in textile treatments. Consolidated textiles could still be cleaned by chemical or mechanical means, and other adhesive could still be used, without interfering with the chitosan consolidation.



## Experiment Outline

The goal of this experiment was to determine whether consolidation with chitosan is an appropriate conservation treatment for fragile silk textiles. The experiment followed the chitosan application procedure from the Conti et al. (2011) study, with some modifications. Chitosan was applied to new and aged, silk textile, with some samples left un-treated as control conditions. Testing was carried out on textile strips, rather than individual threads, as in the Conti et al. study. Additionally, some samples underwent artificial aging to see how chitosan responded to environmental factors and irradiation, and to determine whether chitosan treatment offered any protection to the silk textile against thermal and photo-deterioration.

The chemical, physical, and optical effects of the chitosan consolidation treatment were assessed by the following: imaging silk samples with optical microscopy and scanning electron microscopy (SEM); testing for mass change, tensile strength, stiffness, pH, and colour change; analyzing by Fourier transform infra-red spectroscopy (FTIR) and x-ray fluorescence (XRF), and conducting chemical spot-tests. Optical microscopy and SEM imaging was utilized to provide highly magnified images of the silk fibres. Reflected light microscopy showed the gross textile structure of the samples, and polarized light microscopy showed the optical properties of silk fibres and chitosan. High magnification and resolution SEM images were able to show how chitosan was deposited onto individual silk fibres. Colour measurements of silk samples were taken to determine whether treatment caused colour change. The mass of samples before and after treatment was measured to determine the amount of chitosan deposited on silk substrates, and to gauge the effects of treatment. Tensile testing of silk samples evaluated the strengthening and physical effects of chitosan. Stiffness testing of silk samples assessed whether treatment increased the stiffness of fabric substrates. The pH of silk samples was measured to determine whether the mild acidic solution used to dissolve and apply chitosan to the silk affected their pH, and specifically, to see if treatment made silk substrates acidic. Chitosan-treated silk and cast chitosan films were spot-tested with organic solvents to check for dissolution or other effects that may occur with solvent use in hypothetical future conservation treatments. FTIR analysis was done on silk and chitosan samples to determine the chemical differences between treated and untreated

silks. Wyeth et al. (2005) note that sharp bands in an IR spectrum of silk indicates a crystalline orientation of fibroin in silk fibres, and wider bands indicate amorphous and degraded fibroin regions, which could help characterize silk samples. XRF analysis offered a non-destructive method to characterize the silk fabrics by testing for metallic elements possibly used as dyes, mordants, or weighting agents, for example lead, iron, or tin (Luxford, Thickett, and Wyeth 2011). Altogether, these tests and analyses were carried out to evaluate the effectiveness and suitability of chitosan as a consolidant material for silk textiles. Particular focus was placed on the treatment's ability to strengthen silk textiles, and whether chitosan caused the fabric substrates to change colour or stiffen.

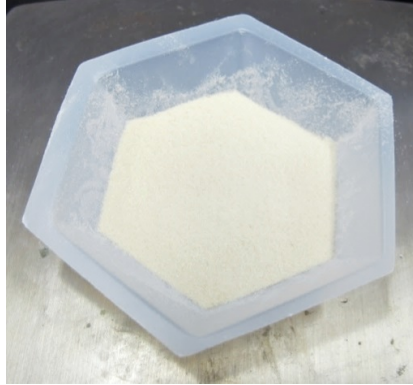
## **Experimental**

### **Experimental Overview**

Chitosan was dissolved in dilute acetic acid. Three silk fabrics were treated by immersion in 0.5% or 1% w/v chitosan for 15 min. and rinsing in distilled water for 5 min., or by immersion in 0.5% chitosan without rinsing. Some samples were artificially aged. Samples were examined by optical microscopy and SEM; tested for mass change, tensile strength, stiffness, pH, and colour change; spot-tested; and analyzed by FTIR and XRF. Statistical analysis (t-tests and ANOVA tests) was done on the data from colour, mass, tensile, stiffness, and pH tests in Microsoft Excel to assess the effects of treatment.

### **Chitosan Solution Preparation**

Approximately 75%-85% de-acetylated, low molecular weight chitosan was ordered from Sigma-Aldrich Canada. The chitosan was a dry solid powder composed of small, lightweight, pale yellow flakes (fig. 1). The method of preparing and applying chitosan to silk, by dissolving in dilute acetic acid and immersion, was taken from Conti et al. (2011). A 0.5% w/v chitosan solution was prepared by dissolving 5 g of chitosan to 1 L of dilute aqueous acetic acid at pH 5. Dry chitosan was added to 800 ml of distilled water in a large glass beaker on a Fisher Scientific Isotemp magnetic stir plate, and 1% percent acetic acid was added drop-wise until the pH reached 5.00, as measured by an Omega PHH-7X pH meter. More distilled water was added to bring the solution up to 1000 ml. The beaker was covered with Saran Wrap to prevent evaporation and left to mix overnight. The chitosan did not fully dissolve into solution; the mixture remained cloudy and contained solid particles of chitosan. Testing a small aliquot of the mixture in a separate beaker showed that the chitosan particles would dissolve upon the addition of more acetic acid. Glacial acetic acid was added drop-wise to the mixture until all chitosan dissolved into solution. The final pH of the solution was 4.16. Once the chitosan dissolved, the solution immediately became clear and viscous (fig. 2). The chitosan solution was clear, pale yellow, and slightly viscous, but was not tacky like an adhesive. A 1% chitosan solution was also prepared by adding glacial acetic acid drop-wise to chitosan in distilled water, until all the chitosan dissolved. The chitosan solutions were poured through a plastic funnel lined with fine polyester mesh fabric to filter out any remaining solids, and transferred into sealed glass containers for storage until use.



*Fig. 1. Dry chitosan.*



*Fig. 2. Chitosan dissolved into solution.*

### Sample Characterization

White silk habutai #609 was purchased from Testfabrics Inc. to serve as the main sample material. This fabric has a plain weave and no obvious front or back or directionality, and is commonly used as a sample fabric in textile conservation experiments (Karsten 1998; Halvorson and Kerr, 1994). Additionally, two lengths of naturally aged silk fabric were sent to the author by Dr. Nancy Kerr, Professor Emeritus Human Ecology at the University of Alberta. Both were mid-20<sup>th</sup> century historic reproduction silk textiles produced by the manufacturer Scalamandr , and were once on display at the Isabella Stewart Gardner Museum in Boston, Massachusetts. One fabric was a red Scalamandr  damask silk (fig. 3) that was on display as wall upholstery from 1959-87. This fabric was mildly abraded overall and had many tears in the warp yarns. The silk was weak and friable, especially along the warp direction. It could easily be torn apart by hand. The right side of the fabric was a dull red colour and showed substantial light fading, compared to the vibrant red colour on the back. Much of the red dye had faded from the front warp yarns. The second aged fabric was a blue-green Scalamandr  damask silk (fig. 4) called “Mt. Vernon Blue,” which was on display either from 1951 onwards, or between 1962-73. This fabric had a few areas of mild abrasion and spots of discolouration overall. A blue patch in the centre of the fabric suggested an object had been placed on the textile and blocked light in that area, while the rest of the fabric was exposed to light, and faded to a light green colour. The characteristics and condition of all three silk samples used in this experiment are summarized in table 1.



**Fig. 3.** Red Scalamandr  silk



**Fig. 4.** "Mt. Vernon Blue" Scalamandr  silk

**Table 1.** Sample Silk Characterization

Fabric	Weave:	Thread Count (yarns/cm)	Mass (g/m <sup>2</sup> )	Condition
<b>Testfabrics #609 white silk habutai</b>	Plain	Warp: 50 Weft: 42	33.96	New; excellent condition.
<b>Red Scalamandr� silk</b>	Damask	Warp: 84 Weft: 30	170.12	Aged; poor condition, fragile, light exposure, and dye fading.
<b>Blue Scalamandr� silk</b>	Damask	Warp: 40 Weft: 40	137.57	Aged; fair condition; light exposure, and dye fading.

#### Sample Preparation

The Testfabrics #609 silk was washed in 0.5% Orvus WA Paste (an anionic, pH neutral, synthetic detergent commonly used for wet cleaning textiles) in hot tap water for five minutes, then rinsed with deionized water until no more suds formed. The silk was air-dried on a tabletop, and ironed at medium heat (the silk setting) to remove wrinkles.

Fabric swatches 10 x 25 cm in size, with the long direction parallel to the textile warp, were cut from all sample fabrics. The swatches were cut large enough to provide separate specimens for all desired tests (tensile, stiffness, pH, colour change, XRF, FTIR, microscopy, and SEM), with an allowance for potential fabric shrinkage during treatment, and fraying. All swatches were cut at least 5 cm away from the selvage edges of the textiles to avoid areas of different fabric structure and tension. The cut swatches were distributed into one of four experimental conditions (outlined in table 2) following a Latin Square design, so that samples in each condition had no warp threads in common, and any natural variation in the textile would be evenly distributed across all conditions. Figure 5 shows the cutting layout and distribution of swatches for the Testfabrics #609

silk fabric. Forty swatches were cut from the #609 silk, 10 per experimental condition. Because a limited amount of fabric was available, 27 swatches were cut from the blue silk fabric, and 17 from the red silk, which were also divided into the four experimental conditions following a Latin Square design.

**Table 2.** Experimental Conditions

Code:	Chitosan Treatment:	Artificial Aging:
A	No treatment	None
B	No treatment	Thermal and light aging
C	15 min immersion in 0.5% w/v chitosan + 5 min distilled water rinse	None
D	15 min immersion in 0.5% w/v chitosan + 5 min distilled water rinse	Thermal and light aging

Selvage	A	B	C	D	A	B	C	D	A	B	Selvage
	40	39	38	37	36	35	34	33	32	31	
	C	D	A	B	C	D	A	B	C	D	
	30	29	28	27	26	25	24	23	22	21	
	B	C	D	A	B	C	D	A	B	C	
	20	19	18	17	16	15	14	13	12	11	
D	A	B	C	D	A	B	C	D	A		
10	9	8	7	6	5	4	3	2	1		

**Fig. 5.** Testfabrics #609 cutting layout and swatch distribution  
A/B/C/D: Experimental condition assignment; #: swatch number

### **Modified Treatment Methods**

Initial observations of chitosan-consolidated silks suggested that treatment had little effect, and that very little chitosan was deposited on the silk samples. Initial test results showed little difference between control and treatment condition samples. In order to emphasize the effects of chitosan, two additional treatment methods were devised: 1) immersion of silk samples in 1% w/v chitosan solution for 15 minutes followed immediately by rinsing in distilled water for five minutes, and 2) immersion in 0.5% w/v chitosan solution for 15 minutes *without* rinsing afterwards. All treatment conditions used in the experiment, with revised code names, are outlined in table 3. Due to the limited

amount of remaining silk fabric, specimens were cut out more economically for the second batch of treatment conditions. Ten 250 x 200 mm (1 x 8 in.) fabric specimens were cut from the Testfabrics #609 silk and the blue Scalmandré silk, and three from the red Scalmandré silk. The same specimens were used for stiffness testing, colorimetry, and tensile testing (in that order, since tensile testing was destructive). Fabric remnants from trimming the specimens to the size and torn samples from tensile testing were used as specimens for FTIR analysis, microscopy and SEM imaging, and pH testing. Due to time constraints and equipment availability, these samples could not be artificially aged.

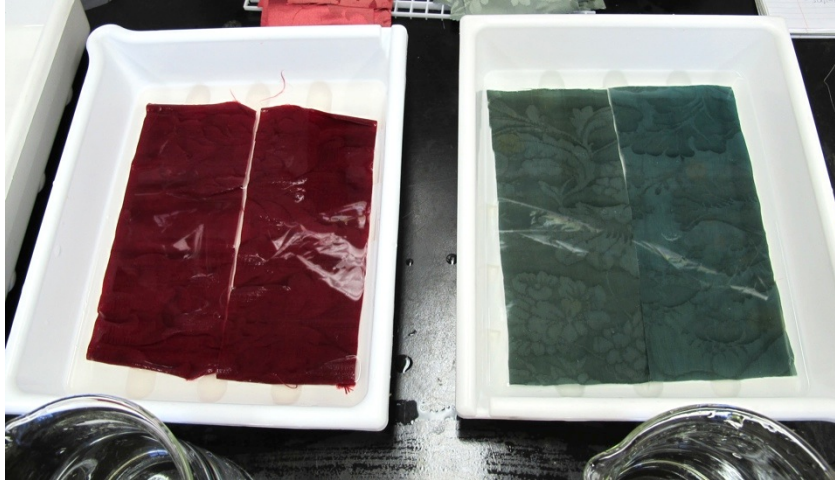
**Table 3.** Treatment Conditions

<b>Code:</b>	<b>Chitosan Treatment:</b>	<b>Artificial Aging:</b>
<b>Ø</b>	None	None
<b>Ø*</b>	None	Thermal and light aging
<b>0.5% Ch</b>	0.5% chitosan + rinsing	None
<b>0.5% Ch*</b>	0.5% chitosan + rinsing	Thermal and light aging
<b>0.5% Ch-X</b>	0.5% chitosan without rinsing	None
<b>1% Ch</b>	1% chitosan treatment + rinsing	None

#### Chitosan Treatment Method

The 0.5% and 1% chitosan solutions were poured into shallow plastic trays. The silk swatches were laid in the chitosan solution and the trays was gently rocked back and forth to ensure the samples were fully immersed and saturated with the consolidant (fig 6). Following the Conti et al. methodology (2011), each swatch was immersed in the chitosan solution for 15 minutes, and then immediately rinsed in distilled water for five minutes. The 0.5% Ch-X condition samples were not rinsed. To rinse the samples, swatches were removed from the chitosan baths using plastic tongs, dipped into a beaker of distilled water, then immersed in a large bath of distilled water for five minutes. The rinse baths were changed periodically to keep the water clean. After rinsing the swatches were laid flat and allowed to air-dry unrestrained. The first batch of samples was laid to dry on white cotton towels to help absorb moisture. Some cotton fibres did stick to the consolidated silk fabric if the samples were blotted with the towels; otherwise, the samples did not adhere to the towels. The second batch of samples were laid flat on

silicon release Mylar to air-dry. In both treatment rounds, the Testfabrics #609 silk samples were treated first, and the red and blue silks were treated afterwards in separate trays to avoid dye transfer (though the dyes were stable and did not bleed).



*Fig. 6. Silk specimens immersed in chitosan solution during treatment.*

### Artificial Aging

About half of the silk samples were aged by light and thermal aging to determine the stability of chitosan to environmental exposure. The samples assigned to artificial aging were the untreated  $\emptyset$  condition and the chitosan-treated 0.5 Ch\* condition silks. The artificial aging conditions were based on other textile conservation studies (Halvorson and Kerr 1994; Luxford and Thickett 2011) and chosen to induce degradation.

### ***Thermal Aging***

Samples assigned to artificial aging were loaded into a Despatch LEA I-69 oven. The silk swatches were hung from metal racks inside the oven in a random arrangement, with space between samples to allow air circulation. The samples were aged in the oven at 50°C ( $\pm$  2°C) and 65% RH ( $\pm$  4%) for 100 hours. Initially, the settings for thermal aging were to be higher, at 80°C and 75% RH for one week duration, but the historic silk samples (especially the red silk) were more fragile than anticipated, so the temperature and relative humidity levels were lowered to ensure all samples could withstand manipulation and testing after aging.



***Light Aging***

After thermal aging, the same samples were subjected to visible light and UV exposure. The silk samples were laid out flat, right side facing up, and in a random arrangement, under a bank of fluorescent lights. The light bank contained 12 fluorescent lights with removable UV filters. It is normally used for light-bleaching paper, but was used for light aging because of its high lux and UV output and large surface area to hold samples. The light intensity was approximately 13,000 lux with 164  $\mu\text{W}/\text{lm}$  UV when the UV filters were removed, as measured by an Elsec 764 UV+ monitor. The silk samples were exposed to the unfiltered lights for 100 hours to correspond to the thermal aging procedure. Following the reciprocity principle (Luxford and Thickett 2011), 100 hours of exposure was equal to 8.9 years of museum lighting exposure, assuming 50 lux exposure for eight hours a day, every day. The light bank was open to the environment. The ambient temperature and relative humidity levels were 22.2°C and 30.1% RH, as measured by the Elsec monitor.

***Light Aging Reciprocity Calculation***

$$8 \text{ hours} \times 50 \text{ lux} \times 365 \text{ days} = 146,000 \text{ lux hours}$$

$$13,000 \text{ lux} \times 100 \text{ hours} = 1,300,000 \text{ lux hours}$$

$$1,300,000 \text{ lux hours} \div 146,000 \text{ lux hours/year} = 8.9 \text{ years}$$

**Testing Methods*****Optical Microscopy***

Specimens from all three silk fabrics, treatment conditions Ø, 0.5% Ch, 1% Ch, and 0.5% Ch-X, were observed with an Olympus BH2-UMA reflected light microscope. Reflected light microscopy was used to examine the gross structure of the silk specimens. Photomicrographs of specimens at 50x, 100x, and 200x magnification were captured with a Moticam 2300 camera using Motic Images Plus 2.0 ML software.

Dry chitosan flakes, cast chitosan film, and individual silk fibres from all three fabrics and the conditions noted above, were also observed with by polarized light microscopy. Chitosan films were prepared by pouring 1% and 0.5% w/v chitosan solutions into plastic trays and allowing them to evaporate to dryness. The chitosan and fibre specimens were mounted on Fisherbrand glass microscope slides with Cargille

Meltmount 1.662 mounting medium ( $n=1.662$ ) and Fisherbrand glass coverslips. The specimens were observed using an Olympus BX51 polarized light microscope. Photomicrographs of specimens were captured with an Olympus DP72 digital camera at 50x, 100x, and 200x magnification.

### ***Scanning Electron Microscopy***

Scanning electron microscopy was utilized to provide highly magnified images of the silk samples with higher resolution than optical microscopy could achieve in order to see chitosan deposition on individual silk fibres (Conti et al. (2011) reported that treated silk samples contained chitosan “bridges” between fibres, visible by SEM). The specimens examined were Testfabrics #609 Ø, 0.5% Ch, 1% Ch, and 0.5% Ch-X conditions; red silk 1% Ch and 0.5% Ch-X conditions; and blue silk 1% Ch-X and 0.5% Ch-X conditions. The cost of this technique limited the number of specimens that could be examined. To prepare specimens, 5 x 5 mm pieces of fabric were cut from the silk samples and mounted onto metal discs using Nisshim Em Co. Ltd. double-sided conductive carbon tape. The samples were then sputter-coated with gold to be made conductive for SEM imaging. The samples were examined with a JEOL 840 Scanning Electron Microscope at 10kv energy. Images representative of each specimen were captured at 150x, 1000x, and 5000x magnification.

### ***Colour Change***

The colour of all silk samples was recorded using the CIE 1976  $L^*a^*b^*$  colour space system. The  $L^*$  value denotes the colour lightness (positive value) or darkness (negative value); the  $a^*$  value denotes redness (positive) or greenness (negative); and the  $b^*$  value denotes yellowness (positive) or blueness (negative). The  $L^*a^*b^*$  values of all silk specimens was recorded using a Minolta Chromo Meter CR-300 following the procedure outlined in ASTM standard E1347: *Standard Test Method for Color and Color Difference Measurement by Tristimulus Colorimetry* (2011c). The D65 light source was used for all determinations. The colorimeter was calibrated with a Minolta CR-A43 calibration tile before each set of samples was tested.

The 25 x 200 mm fabric strip used for stiffness testing also served as specimens for colour measurements. All specimens were laid flat on a piece of white Coroplast for consistency during testing. The red silks were all tested in the ground area of the damask

pattern, on the front side of the fabric. Because fewer red silk specimens were made, each was tested multiple times to give at least 10 sets of colour measurements for each condition. The blue silk samples were all tested on the back side of the fabric, as the colour on the front of the fabric was uneven due to differential fading. Two readings were taken at the same location for every set of  $L^*a^*b^*$  measurements, with the colorimeter head rotated  $90^\circ$  to account for directionality in the textiles (ASTM 2011c). All recorded  $L^*$ ,  $a^*$ , and  $b^*$  values were averaged to give mean values for each experimental condition. These mean values were used to calculate the  $\Delta E^*$  values, or global colour change, between control and treated silks, following ASTM standard D2244: *Standard Practice for Calculations of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates* (2011a). The CIE 1976  $L^*a^*b^*$  Colour Difference Formula was used to calculate colour change, which has the equation:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where the  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  values are determined by:

$$\Delta L^* = L^*_B - L^*_S$$

$$\Delta a^* = a^*_B - a^*_S$$

$$\Delta b^* = b^*_B - b^*_S$$

where B = test batch specimen value (treatment condition), and S = standard or control specimen value (untreated control condition).

### ***Mass Change***

All fabric swatches from the first round of testing (control conditions and 0.5% w/v chitosan and rinsing conditions) were weighed on a Sartorius BP210S analytical scale before treatment, and after treatment and artificial aging. The mass of each swatch was recorded to four decimal places. Mass differences were calculated for all specimens.

### ***Tensile Testing***

The tensile strength of all silk specimens was determined following the ASTM standard D5035: *Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)* (2011b). The cut strip method was used since consolidation might have made raveled strips difficult to prepare (i.e. if the yarns were stuck together). Fabric specimens were cut 25 x 200 mm (1 x 8 in.) in size, with the long dimension parallel to

the fabric warp. Tensile testing was done on an Instron Universal Tensile Testing Machine (fig. 7) equipped with 1000 lb. load cells and metal-faced pneumatic grips (fig. 8). Each test began with the grips 3 in. (7.6 cm) apart. The grips pulled a fabric sample apart at a constant 2 in./min (5 cm/min) rate of extension. A computer running Instron 1.0 software plotted and recorded the force applied to the sample versus time. The test ended when the sample tore. Results were discarded if the sample slipped through the machine grips or tore at the grip. The ASTM standard called for a rate of extension that would break samples in  $20 \pm 3$  seconds (2011b). The 2 in./min rate gave a breakage time within 25 seconds for the Testfabrics #609 silk, but since the fabric samples were given slack between the grips and data collection started before extension began to give clear zero readings for force values, the true breakage time was approximately 20 seconds. The same rate was used for the red and blue silks for consistency, but they tore in less time (the red silk in 2-3 seconds, and the blue silk in 7-9 seconds). The highest force value of each test was taken as the ultimate tensile strength. Extension was calculated by multiplying the time of force increase by the rate of extension. Stress-strain curves were generated by plotting stress (force values converted to Newtons, divided by sample cross sectional area) by engineering strain (time values converted to extension).

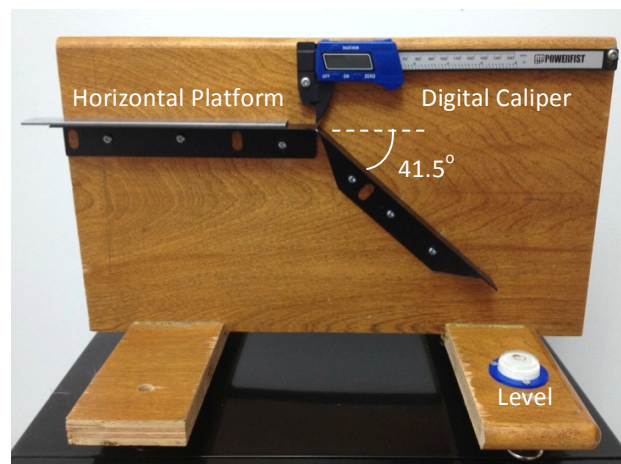


***Figs. 7, left: Instron Universal Tensile Testing machine.  
Fig. 8, right: Detail of a silk specimen in the machine grips.***

### ***Stiffness Testing***

Fabric stiffness was determined following ASTM standard D1388: *Standard Test Method for Stiffness of Fabrics*, using option A, the cantilever bending method (2008). A cantilever bending tester was built for the test (fig. 9) following the ASTM standard.

Fabric specimens were cut 25 x 20 mm (1 x 8 in.) in size, with the long dimension parallel to the fabric warp. The cantilever tester was leveled using its adjustable feet and integrated bubble level. A fabric specimen was placed on the smooth, horizontal metal platform of the cantilever tester. A 25 x 200 mm metal bar was placed on top of the fabric strip. The metal bar was slowly pushed forward to move the bar and the fabric strip off the edge of the horizontal platform until the fabric drooped and hit a metal blade positioned 41.5° to the horizontal platform. As the metal bar was moved to push the fabric strip, it also pushed the tip of a 6" Powerfist digital caliper positioned to measure the length of the fabric strip overhang. When the fabric strip touched the angled platform, the overhang length was read off the caliper to 0.1 mm. Each specimen was tested twice on both the front and back sides. The four values were averaged to give a single overhang length value for each specimen.



**Fig. 9.** Cantilever bending tester.

Stiffness testing determined the bending length and flexural rigidity of fabric specimens. The bending length was determined by the equation:

$$c = O/2$$

where  $c$  = bending length in mm, and  $O$  = length of fabric overhang in mm.

Flexural Rigidity was then calculated by the equation:

$$G = 1.421 \times 10^{-5} \times W \times c^3$$

where  $G$  = flexural rigidity in  $\mu\text{joule/m}$ ;  $W$  = fabric mass per unit area in  $\text{g/m}^2$ ; and  $c$  = bending length in mm. The bending length was determined in the previous equation; each silk fabric was measured and weighed to determine its mass per unit area.

### ***Silk pH***

The pH of all silk samples was determined using the aqueous cold extraction method outlined by Vuori and Tse (2005), where fabric samples are immersed in room-temperature distilled water in a 1g : 50 ml ratio for one hour before testing. This method was found to be suitable for testing the pH of textiles using small specimens sizes, and is in accordance with CGSB standard 4.2 no. 74-M91, *Textile Test Methods: Determination of pH of the Aqueous Extract* (1991). Specimens were cut from all fabric samples and conditions and trimmed until they weighed 0.1 g, as determined by an Ohaus Adventurer SL analytical scale, then immersed in 5 ml of distilled water in a small plastic cup for one hour. An Omega PHH-7X electronic pH meter was used to measure the pH of the liquor. The pH meter was calibrated using Oakton Standard Buffer solutions for pH 4.00 and 7.00. Three determinations were made to obtain the pH of each specimen. A first extract of liquor was poured into a small beaker and the pH meter was immersed in the liquid. The displayed pH value was recorded to 0.1 units once the reading stabilized. A second and third extract were tested in the same way. The pH values from the second and third determinations were averaged to obtain the pH value of the specimen, and the first determination value was discarded. The pH meter was not rinsed between determinations, but was rinsed in distilled water between testing different experimental conditions.

### ***Solvent Spot Testing***

Cast chitosan films and #609 Testfabrics silk 1% Ch and 0.5% Ch-X condition samples were spot tested with acetone, ethanol, mineral spirits, Stoddard solvent, and distilled water. Chitosan film was prepared by pouring excess 0.5% and 1% chitosan solution into plastic trays and allowing them to evaporate to dryness. A single drop of reagent was deposited onto the surface of the fabrics or chitosan films using an eyedropper. The specimens were observed under a 40x stereomicroscope until the reagent evaporated.

### ***Fourier-Transform Infra-red Spectroscopy***

The infra-red spectrum of all silk samples and chitosan were recorded using a Nicolet FTIR Spectrometer with a "Golden Gate" single pass ATR (Attenuated Total Reflection) sampling accessory, at 32 scans and  $4\text{cm}^{-1}$  resolution. Spectra were recorded for dry chitosan powder, cast chitosan films, and all three silk samples, conditions Ø,

0.5% Ch, 1% Ch, and 0.5% Ch-X. All specimens were tested directly using the “Golden Gate” accessory. To determine whether a small peak in the spectra of the treated silks was due to chitosan or acetic acid in the chitosan solution, untreated silk samples were washed in dilute acetic acid for 15 minutes, and then rinsed in water for five minutes (to replicate the treatment procedure, but without any chitosan). The IR spectra of these acid-washed silk samples were recorded for comparison against the chitosan-treated silks.

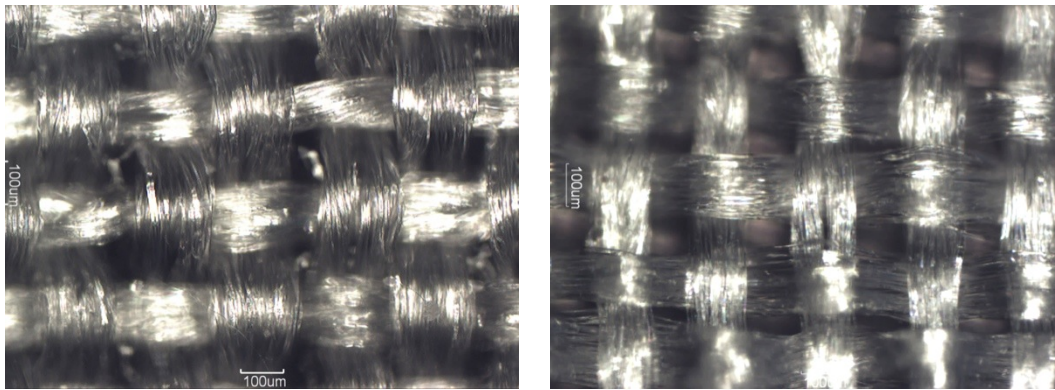
### ***X-Ray Fluorescence***

All three silk fabrics were analyzed by XRF to determine whether any metallic elements were present in the textiles as dyes, mordants, weighting agents, or other additives. Silk samples were tested with a Bruker Tracer III Hand-held XRF analyzer with 40 keV source, with approximately 20 seconds collection time. Multiple readings were taken on each sample ensure the results were representative of the entire sample.

## Results and Discussion

### Optical Microscopy

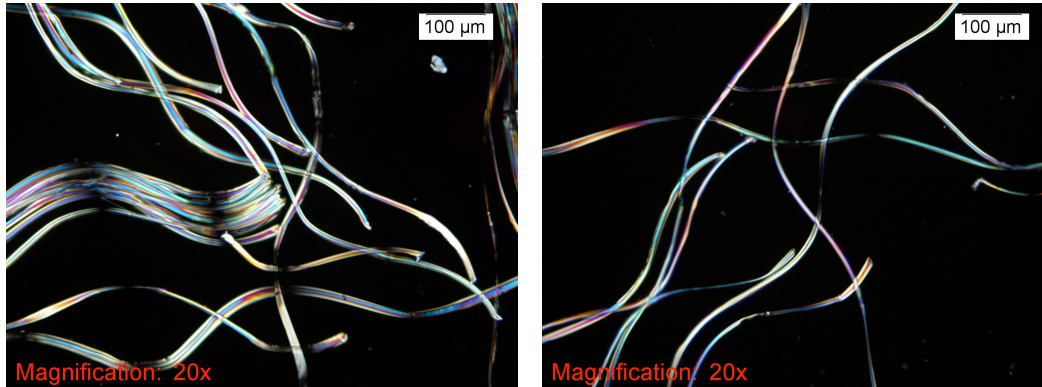
No visible difference was discernable between silk samples in different experimental conditions using reflected light microscopy at 50x, 100x, and 200x magnification (figs. 10a-b). All silk fibres appeared smooth and lustrous. There was no visual indication that a consolidant, coating, or any additional material was present on chitosan-treated samples. Chitosan could not be seen at this magnification and resolution.



**Fig. 10a**, left: #609 Ø silk (reflected light 100x)..  
**Fig. 10b**, right: #609 0.5% Ch-X silk (reflected light 100x).

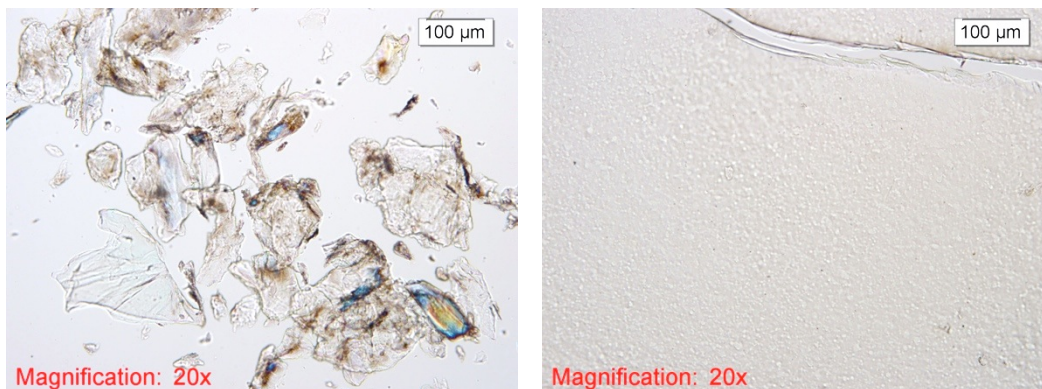
All silk fibres appeared long, thin, and smooth, with a triangular cross section, typical of *Bombyx mori* silk, when observed by polarized light microscopy. The Testfabrics #609 silk fibres had a regular, even cross-section, and smooth surface. The blue and red Scalamandr  silk fibres had irregular and uneven profiles and a rough surface texture, all likely due to their age and poor condition. The refractive index of all fibres was determined to be less than 1.662 using the Becke line test. All samples showed undulose extinction under cross-polarized light. There was no noticeable difference between treatment and control condition samples at 40x to 1000x magnification (figs. 11a-b). Again, no chitosan could be seen on the fibres, nor were there any perceptible changes in optical properties of the silk fibres because of chitosan consolidation.





**Fig. 11a**, left: #609 Ø fibre (cross-polarized light 200x)  
**Fig. 11b**, right: #609 1% Ch fibres (cross-polarized light 200x).

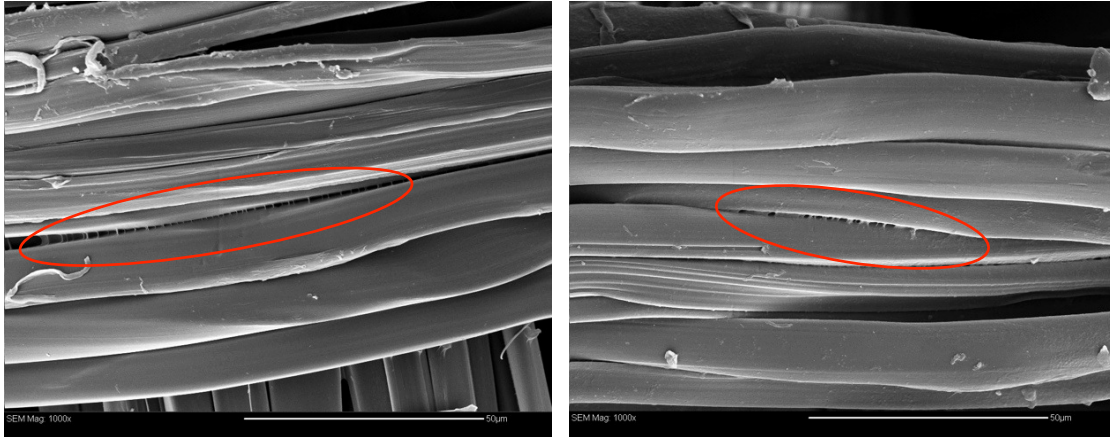
Dry chitosan flakes viewed under polarized light were translucent and colourless to pale yellow-brown in colour (fig. 12). The flakes had a rough surface texture and were irregularly shaped, ranging from less than 50 µm to a maximum of 200 µm across. The refractive index was determined to be less than 1.662 using the Becke line test. The chitosan flakes were anisotropic, showing extinction every 90° under cross-polarized light. The cast chitosan films were translucent and pale yellow in colour; thin; flexible; crinkly; strong; and resembled cellophane film. The chitosan films appeared smooth to the eye but at 100x magnification and higher, it was apparent the films had a bumpy, pocked-marked surface (fig. 13). The films were anisotropic, with roving areas of extinction under cross-polarized light and microscope state rotation.



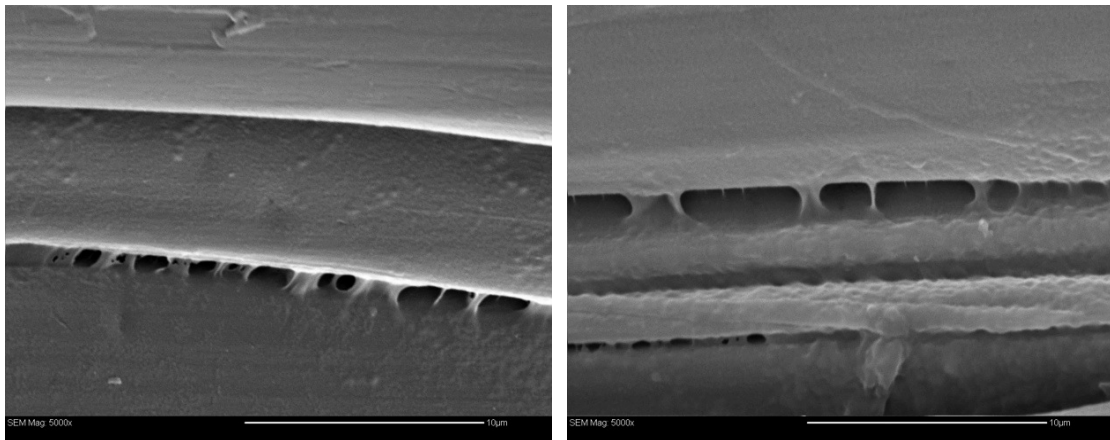
**Figs. 12**, left: Dry chitosan flakes (polarized light 200x).  
**Fig. 13**, right: Cast chitosan film (polarized light 200x).

### Scanning Electron Microscopy

Chitosan could not be seen on silk fibres using low power magnification, but was seen on some samples using scanning electron microscopy. No visual evidence of chitosan was seen on the #609 silk 0.5% Ch and 1% Ch condition samples using SEM. The specimens looked the same as the untreated silk samples. The 1% Ch condition samples were noticeably stiff and rough to the touch, so it was clear some chitosan was indeed deposited on the silk fabric, yet no chitosan could be seen on the fibres. It is possible a chitosan coating was deposited onto the silk fibres, but was too even and thin to see. The #609 silk 0.5% Ch-X condition sample did show evidence of chitosan deposition in the form of small strands of material or “bridges” between fibres, visible at 1000x magnification and higher (figs. 14a-d). Conti et al. (2011) found the same chitosan “bridges” in consolidated silk samples. These bridges appear to be extensions of a thin layer of chitosan coating the surface of silk fibres. The #609 silk fibres had a smooth and uniform surface texture, even when chitosan bridges were found between fibres. In contrast, the red and blue silk samples had irregular and rough surface textures with longitudinal cracks along fibres (all likely due to the age and poor condition of the fabrics). Many chitosan bridges were found in the treated red and blue silk samples. Some red and blue silk fibres had bumpy, textured surfaces, which were interpreted as areas of increased chitosan deposition. Overall, more chitosan was found on the 0.5% Ch-X samples than the other conditions, and in the aged red and blue Scalmandré silks than the new Testfabrics #609 silk samples.



**Fig. 14a**, left: #609 0.5% Ch-X fibres (SEM 1000x). Chitosan bridges are circled.  
**Fig. 14b**, right: Blue 0.5% Ch-X fibres (SEM 1000x). Chitosan bridges are circled.



**Fig. 14c**, left: Blue 0.5% Ch-X fibres (SEM 5000x).  
**Fig. 14d**, right: Red 0.5% Ch-X fibres (SEM 5000x).

### Colour Change

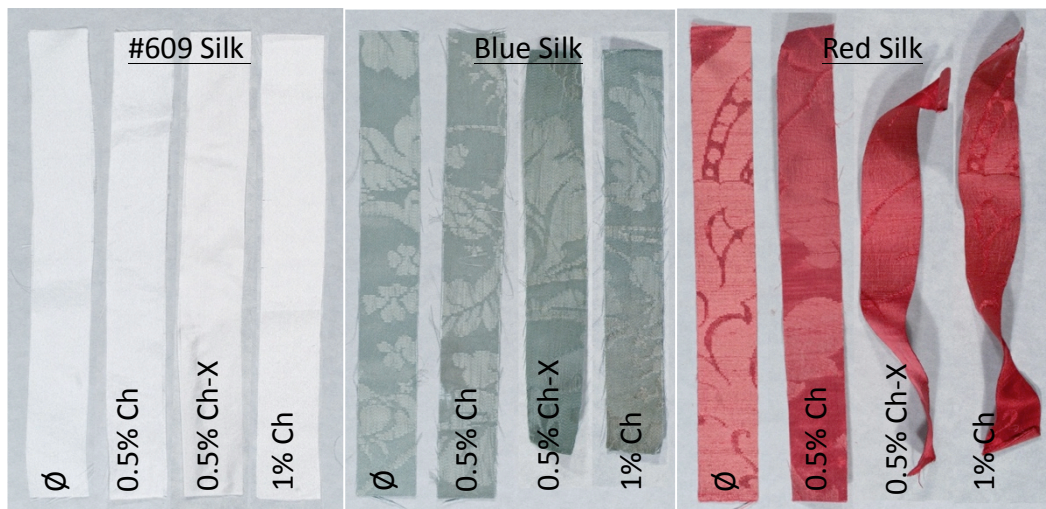
Colour measurement results are summarized in table 4 (bolded items indicate  $\Delta E^* > 1.00$ , or noticeable colour change) and in Appendix A. Figure 15 shows side-by-side comparisons of silk samples. Chitosan treatment did cause colour change in the silk fabric substrates. Dry chitosan flakes, the chitosan solutions, and the cast chitosan films all had a pale yellow colour, but the treated silks did not appear noticeably more yellow. In fact, the  $b^*$  values of many treated silk samples decreased very slightly compared to the control conditions, meaning the colour became less yellow and more blue. The only exceptions were the artificially aged Testfabrics #609 samples, both treated and control conditions, which did yellow slightly. The greatest change in all chitosan-treated samples occurred in the  $L^*$  or lightness values. All chitosan treated silk were darker, or had lower

L\* values, than the control conditions. The changes in a\* values were minor and variable across samples and conditions and showed no clear pattern.

**Table 4.** Measured Colour Differences

Sample	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$	N
#609 $\emptyset$	-	-	-	-	40
#609 $\emptyset^*$	-0.37	-0.90	+0.88	0.95	40
#609 0.5-CH	-0.01	-0.09	+0.39	0.40	40
#609 0.5-CH*	-0.21	-0.12	+0.81	0.85	40
#609 0.5-CH-X	-0.27	+0.02	+0.11	0.29	40
#609 1-CH	-0.07	-0.05	-0.01	0.088	40
Sample	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$	
Red $\emptyset$	-	-	-	-	14
<b>Red <math>\emptyset^*</math></b>	+0.32	-1.21	-0.06	<b>1.251</b>	10
<b>Red 0.5-CH</b>	-4.10	+0.98	-0.15	<b>4.218</b>	10
<b>Red 0.5-CH*</b>	-2.59	-1.07	-0.32	<b>2.825</b>	10
<b>Red 0.5-CH-X</b>	-4.36	+0.70	-0.59	<b>4.452</b>	10
<b>Red 1-CH</b>	-5.71	+1.19	-0.25	<b>5.838</b>	10
Sample	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$	
Blue $\emptyset$	-	-	-	-	20
Blue $\emptyset^*$	-0.43	-0.26	-0.50	0.711	20
<b>Blue 0.5-CH</b>	-3.90	+0.19	-1.13	<b>4.07</b>	20
<b>Blue 0.5-CH*</b>	-3.10	+0.49	-0.62	<b>3.20</b>	20
<b>Blue 0.5-CH-X</b>	-5.08	+0.77	-0.24	<b>5.14</b>	20
<b>Blue 1-CH</b>	-4.70	+1.08	+0.17	<b>4.83</b>	20

*Bold #:  $\Delta E^* > 1.00$  (noticeable colour difference)*



**Fig. 15.** Comparison of silk sample treatment conditions. Blue and red silks darkened and curled.

No change in  $L^*$ ,  $a^*$ , or  $b^*$  values or  $\Delta E^*$  was greater than 1.00 in any of the white Testfabric #609 samples, thus no noticeable colour change can be said to have occurred. Indeed, it was difficult to discern any difference between experimental conditions by eye. Both artificially aged samples did yellow slightly and had  $\Delta E^*$  values greater than 0.5, which may be considered a just-noticeable colour change. The Testfabrics #609 artificially aged control and treated samples both showed similar colour changes, slight decrease in  $b^*$  values or yellowing, suggesting chitosan did not protect the silk from photo-oxidation by light and UV exposure. In the blue and red silk samples, however, the aged 0.5% Ch\* condition showed less colour change than the unaged 0.5% Ch condition; chitosan possibly had a protective or sacrificial effect in these samples.

All treated red and blue silk samples showed noticeable colour change, with  $\Delta E^*$  values over 1.00. The colour difference in these treated silks was discernable by eye; the samples all appeared darker and duller in colour. A test was conducted to see whether water or acetic acid alone would cause colour change in the fabrics, for example, by dye bleeding or an interaction of the dyes with acetic acid. Scraps of the Scalmandré silks were immersed in a beaker of distilled water or dilute acetic acid for 15 minutes, then rinsed in distilled water for five minutes. The fabric dyes did not bleed or discolour, thus it appears chitosan was responsible for the colour change of the fabrics.

### Mass Change

The mass change of silk samples after treatment is summarized in table 5. The #609 silk samples showed little change in mass. Treated samples did gain approximately 2% mass, but the results were variable and not statistically significant. The red and blue silk samples both showed a statistically significant decrease in mass after treatment and aging. The red silk 0.5% Ch and 0.5% Ch\* condition samples showed an average 5.5% and 5.95% loss in mass, respectively. Rather than gaining mass by chitosan deposition, it seems lint and soluble degradation products in the fabric were washed away during treatment, decreasing the mass of the samples. This did not occur in the Testfabrics #609 silk samples, as they were in good condition and were washed before testing, whereas the aged silks were not. Mass differences could also be attributed to the silk's response to ambient relative humidity, absorption of water during treatment, or a loss of fibres and fibres due to handling. Ultimately, weighing was not an effective way to determine how

much chitosan was deposited on the silk samples. Chitosan has a low density (0.15-0.3 g/m<sup>3</sup>), and it seems very little material was deposited onto silk fibres by treatment.

**Table 5.** Mass Change in Silk Samples

Sample	Average Mass Change (g)	$\sigma$	Change (%)	N
#609 $\emptyset$	0.0016	0.0430	+0.18	10
#609 $\emptyset^*$	0.0128	0.0178	+1.50	10
#609 0.5% Ch	0.0163	0.0238	+1.94	10
#609 0.5% Ch*	0.0194	0.0282	+2.306	10
Red $\emptyset$	-0.0049	0.0042	-0.12	4
Red $\emptyset^*$	-0.0641	0.0111	-1.51	4
<b>Red 0.5% Ch</b>	<b>-0.2342</b>	<b>0.0637</b>	<b>-5.509</b>	4
<b>Red 0.5% Ch*</b>	<b>-0.2548</b>	<b>0.0466</b>	<b>-5.953</b>	5
Blue $\emptyset$	-0.0122	0.0757	-0.353	7
Blue $\emptyset^*$	-0.0724	0.0889	-2.12	6
Blue 0.5% Ch	-0.0320	0.0958	-0.915	7
<b>Blue 0.5% Ch*</b>	<b>-0.1611</b>	<b>0.0665</b>	<b>-4.624</b>	7

*Bold #:  $P < 0.05$*

### Tensile Testing

Tensile testing results are summarized in table 6. Stress-strain curves generated from tensile test data are included in Appendix B. Chitosan treatment had little to no effect on the ultimate tensile strength (the maximum force applied to the samples until breakage) of any silk fabric. The only statistically significant difference in tensile strength due to chitosan treatment occurred in the #609 silk 0.5% Ch-X condition samples, where the ultimate tensile strength actually decreased by 9.65% compared to the control condition. Chitosan treatment also lowered the pH of this sample condition; the acidity of the chitosan solution likely degraded and weakened the fabric. For all other silk samples the tensile strength results were highly variable, and there were no statistically significant differences between the control condition and treatment conditions. The blue and red samples had especially variable results because of the damask weave of the fabric, as the distribution of warp and weft yarns was not uniform in all areas, forming stronger and weaker areas in the fabric (unlike the uniform weave of the Testfabrics #609 silk habutai).

**Table 6.** Tensile Testing Results

Sample	Average Tensile Strength (kg)	$\sigma$	Change (%)	Extension Change (%)	N
#609 $\emptyset$	17.7202	0.7566	-	-	10
#609 $\emptyset^*$	16.6741	0.8040	-5.90	-8.87	10
#609 0.5% Ch	17.7085	0.8864	-0.0665	+3.65	10
#609 0.5% Ch*	16.9796	0.9174	-4.18	-6.49	10
<b>#609 0.5% Ch-X</b>	<b>16.0095</b>	<b>1.3827</b>	<b>-9.65</b>	<b>-19.86</b>	10
#609 1% Ch	18.0616	0.8703	+1.93	+9.13	10
Red $\emptyset$	1.0527	0.3957	-	-	4
Red $\emptyset^*$	0.7642	0.1765	-27.4	+8.64	4
Red 0.5% Ch	0.9463	0.4787	-10.1	+28.40	4
Red 0.5% Ch*	1.2433	0.3347	+18.1	<b>+105.43</b>	5
Red 0.5% Ch-X	1.0075	0.1683	-4.30	+35.31	5
Red 1% Ch	0.9801	0.2276	-6.90	+35.31	5
Blue $\emptyset$	3.4569	0.74973	-	-	6
Blue $\emptyset^*$	2.7290	1.1619	-21.1	-21.55	5
Blue 0.5% Ch	3.6337	0.81704	+5.12	+6.07	6
Blue 0.5% Ch*	3.1724	1.0708	-8.23	+16.98	6
Blue 0.5% Ch-X	3.4807	0.59845	+0.689	-4.04	10
Blue 1% Ch	3.7898	1.0034	+9.63	-16.41	10

*Bold #:  $P < 0.05$*

Chitosan caused some minor differences in the modulus of silk samples, although results were variable across the different silk fabrics. The Testfabrics #609 silk 0.5% Ch-X condition was more brittle than the untreated control condition, though the tensile strength was similar. The #609 silk 0.5% Ch and 1% Ch conditions showed little difference in the modulus compared to the control condition. The blue silk 0.5% Ch condition was more flexible than the control, but the 0.5% Ch-X and 1% Ch conditions were more brittle. The red silk 0.5% Ch-X condition was more brittle than the control, and 0.5% Ch condition was more flexible, with little change in the 1% Ch condition. Essentially, consolidation with 0.5% chitosan and rinsing may render silk fabric slightly more flexible, but consolidation without rinsing may render silk textiles more brittle.

These results indicate chitosan does not have a strengthening effect on silk on the gross textile scale. Chitosan did however seem to have a mild consolidating and stabilizing effect on individual silk yarns and fibres. The cut edges of treated silk samples did not fray, as they readily did before treatment. Chitosan seemed to lightly hold the

yarns together, though they could still easily be pulled apart by hand. Additionally, the treated blue and red silk sample fibres no longer powdered and shed lint as they did before treatment.

### Stiffness Testing

Stiffness testing results are summarized in table 7. All silk samples in the 1% Ch and 0.5% Ch-X conditions exhibited a dramatic and statistically significant increase in flexural stiffness, with 0.5% Ch-X conditions yielding the highest increases. All samples from these conditions were noticeably stiff, rigid, and rough to the touch. The Testfabrics #609 0.5% Ch condition showed little change in stiffness or drape compared to the control, but did feel slightly rough to the touch, suggesting some chitosan was deposited. The red and blue silk 0.5% Ch conditions increases in stiffness, but the measurements were variable and had large standard deviations, partly due to testing issues.

**Table 7. Stiffness Testing Results**

Sample	Average Flexural Stiffness	$\sigma$	Change (%)	N
#609 $\emptyset$	1.77	0.245	-	10
#609 $\emptyset^*$	1.82	0.316	+2.43	10
#609 0.5% Ch	1.80	0.227	+1.31	10
#609 0.5% Ch*	1.93	0.277	+8.90	10
<b>#609 0.5% Ch-X</b>	<b>23.2</b>	<b>5.05</b>	<b>+1210</b>	10
<b>#609 1% Ch</b>	<b>3.23</b>	<b>1.95</b>	<b>+81.8</b>	10
Red $\emptyset$	12.5	5.41	-	4
Red $\emptyset^*$	18.6	7.95	+48.9	4
Red 0.5% Ch	21.2	4.58	+70.3	4
Red 0.5% Ch*	17.2	4.00	+37.8	5
<b>Red 0.5% Ch-X</b>	<b>25.5</b>	<b>3.18</b>	<b>+105</b>	3
<b>Red 1% Ch</b>	<b>12.3</b>	<b>1.78</b>	<b>-0.943</b>	3
Blue $\emptyset$	7.06	1.04	-	7
Blue $\emptyset^*$	5.64	0.495	+20.1	6
Blue 0.5% Ch	14.7	3.15	+108	7
Blue 0.5% Ch*	12.4	1.60	+75.2	7
<b>Blue 0.5% Ch-X</b>	<b>69.2</b>	<b>11.9</b>	<b>+881</b>	10
<b>Blue 1% Ch</b>	<b>53.9</b>	<b>17.6</b>	<b>+664</b>	10

*Bold #:  $P < 0.05$*



The Testfabrics #609 silk samples were not distorted by chitosan treatment, but the shape of the blue and red silk samples was affected (see fig. 15). The treated blue silk samples curled up slightly at the ends, and the treated red silk samples curled and twisted. The red silk 0.5% Ch-X and 1% Ch samples twisted dramatically, and held that shape. Even silk samples stuck to a glass plate to dry restrained curled and twisted once they were removed from the plate. To see whether this distortion was caused by chitosan or simply by wet treatment, strips of red silk were washed in distilled water or dilute acetic acid for 15 minutes, rinsed in distilled water for five minutes, and laid flat to air-dry. The fabric strips dried flat without any distortion, indicating the distortion was indeed caused by chitosan treatment. An attempt to humidify and flatten the samples was not very successful, as the silk was rendered slightly hydrophobic by the chitosan. Since the samples would not lay flat they were difficult to test on the cantilever bending tester. The stiffness testing results for the red silk samples were therefore highly variable and did not represent the perceived stiffness of the specimens. Notably, the plain weave #609 silk did not curl, but the two damask weave silk fabrics did. The red silk fabric was the thickest and most dense fabric, and curled and twisted the most. Factors such as fabric weave, density, or condition may influence the distortion caused by chitosan treatment.

### Silk pH

Results from pH testing are summarized in table 8. The purpose of pH testing was to determine whether the slightly acidic chitosan solution caused the silk substrates to become acidic. Chitosan is soluble in dilute acids below pH 6, but the chitosan solutions prepared in this experiment did not fully dissolve into solution until pH 4-4.2.

**Table 8.** Silk pH Test Results

Sample	pH	$\sigma$	Change (%)	N
#609 $\emptyset$	6.09	0.51	-	10
#609 $\emptyset^*$	5.74	0.65	-5.74	10
#609 0.5% Ch	5.66	0.47	-7.90	10
#609 0.5% Ch*	5.66	0.59	-7.03	10
<b>#609 0.5% Ch-X</b>	<b>5.37</b>	<b>0.12</b>	<b>-11.9</b>	10
#609 1% Ch	5.78	0.30	-5.07	10
Red $\emptyset$	2.94	0.02	-	4
Red $\emptyset^*$	2.76	0.01	-6.33	4
<b>Red 0.5% Ch</b>	<b>3.83</b>	<b>0.14</b>	<b>+30.1</b>	4
<b>Red 0.5% Ch*</b>	<b>3.57</b>	<b>0.12</b>	<b>+21.3</b>	5
<b>Red 0.5% Ch-X</b>	<b>4.82</b>	<b>0.11</b>	<b>+63.8</b>	4
<b>Red 1% Ch</b>	<b>4.86</b>	<b>0.13</b>	<b>+65.1</b>	4
Blue $\emptyset$	3.31	0.11	-	6
Blue $\emptyset^*$	3.19	0.04	-3.50	5
<b>Blue 0.5% Ch</b>	<b>4.33</b>	<b>0.12</b>	<b>+30.9</b>	7
<b>Blue 0.5% Ch*</b>	<b>4.11</b>	<b>0.12</b>	<b>+24.3</b>	7
<b>Blue 0.5% Ch-X</b>	<b>5.01</b>	<b>0.07</b>	<b>+51.5</b>	10
<b>Blue 1% Ch</b>	<b>5.10</b>	<b>0.06</b>	<b>+54.3</b>	10

*Bold #:  $P < 0.05$*

The pH of untreated Testfabrics #609 silk was near neutral, and was only slightly lowered by chitosan treatment, though the results were not statistically significant. Predictably, aging lowered pH values for all untreated silks. The only statistically significant pH difference was for the 0.5% Ch-X condition, where the pH decreased from 6.09 (control) to 5.37 (treated). If silk samples were not rinsed after immersion in the mildly acidic chitosan solution, some acetic acid likely remained in the silk and lowered the pH, whereas any acid in the rinsed condition samples was washed away or neutralized. The aged red and blue silks were acidic to begin with, at approximately pH 3, but the chitosan treatment did not make them more acidic. All red and blue silk samples yielded statistically significant higher pH values after treatment. The aqueous chitosan solution and rinsing method likely washed out acidic degradation products present in the aged silks, raising their pH values.

Disconcertingly, all of the 0.5% Ch-X and 1% Ch condition silk samples had a strong, lingering smell of acetic acid after treatment, even when dry. This suggested the silk was off-gassing acidic compounds, yet the pH values for these samples were not extremely acidic. All measured pH values for chitosan-treated silks were within the

isoelectric range for silk, pH 3-7 (Tímár-Balázszy 1998). Still, the pH of the 0.5% Ch-X condition Testfabrics #609 silk was lowered by chitosan treatment, and corresponded to a decrease in tensile strength, suggesting the silk was damaged by the treatment, likely by the acidity of the chitosan solution.

### Solvent Spot Testing

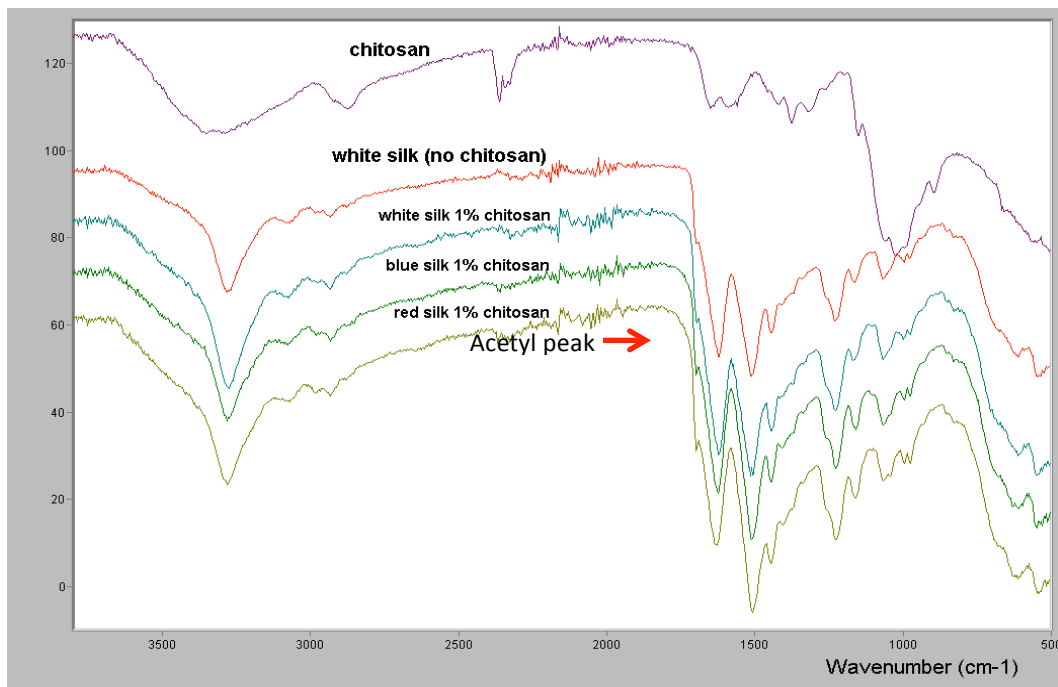
Results of solvent spot testing are summarized in table 9. Dried chitosan films and chitosan-treated silks were not affected by acetone, ethanol, mineral spirits, or Stoddard solvent. There was no apparent dissolution of chitosan, or change in the feel or appearance of silk samples after the application of the reagents. All organic solvents readily wet the treated silks and chitosan films, then evaporated without any visible changes. Distilled water in contrast did have an effect on both the chitosan films and treated silks. Drops of distilled water initially sat on the surface of the film and silk without any wetting, then wet the substrates after a few seconds. Chitosan is a hydrophobic material, and seems to have imparted the silk substrate with this property. The chitosan film eventually softened and swelled where it was in contact with water, but the water still did not easily spread across the film on its own. When the water evaporated, the chitosan film was shrivelled, hard, and had a darker colour than before. The chitosan-treated silk was also eventually wet by distilled water, and then the water then slowly spread through the fabric by capillary action along silk yarns. Once the silk dried, there was no noticeable change in the silk's appearance, stiffness, or texture. Treated silk samples did not appear or feel any different after extraction in water during pH testing either. Washing treated silks in water did not seem to remove chitosan from the samples.

**Table 9: Solvent Spot Testing Results**

<b>Reagent</b>	<b>#609 0.5% Ch-X and #609 1% Ch Silk</b>	<b>0.5% &amp; 1% Chitosan Film</b>
<b>Acetone</b>	No effect	No effect
<b>Ethanol</b>	No effect	No effect
<b>Mineral Spirits</b>	No effect	No effect
<b>Stoddard Solvent</b>	No effect	No effect
<b>Distilled Water</b>	No wetting for ~1 sec, then wet fabric. No noticeable change once fabric dried.	No wetting for ~3 sec, then softened and swelled film. Dried film was shriveled, hardened, and darkened.

### Fourier-Transform Infra-red Spectroscopy

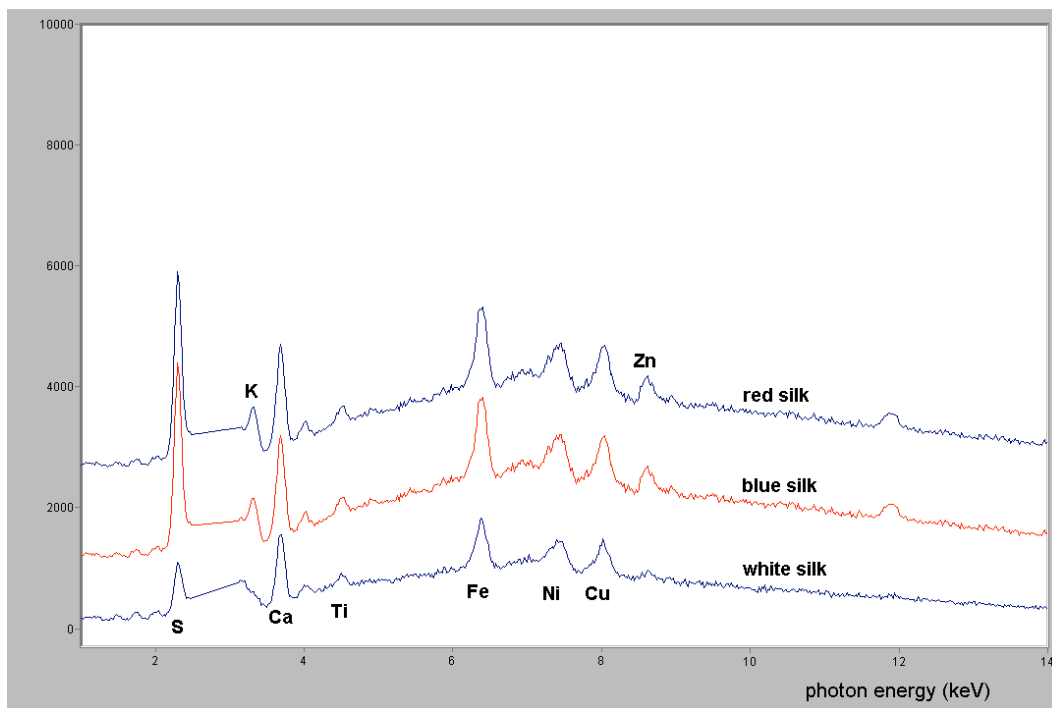
The spectra of treated silks were virtually the same as the untreated silks, and had no peaks that could be attributed to chitosan (fig. 16). The spectrum of chitosan powder and chitosan film had no peaks in common with the spectra of any of the silks. The only difference in the spectra of the treated silks compared to control condition silks was a small peak at  $1696.7\text{ cm}^{-1}$  attributed to an acetyl group. Silk washed in dilute acetic acid without chitosan showed the same peak, so the change was attributed to acetic acid in the chitosan solution, rather than the chitosan itself. Besides the acetylation of silk, there appeared to be no chemical change to the silk caused by chitosan treatment. The spectra of chitosan-treated silks did not actually show chitosan to be present in the samples, but some chitosan was deposited on fibres, as evidenced by SEM imaging and increased fabric stiffness. The amount of chitosan present on the silk may have been too small to be detected by FTIR, which has a threshold of about 1% weight of the sample. This implies chitosan would not impede IR analysis of silk fibres, but also that chitosan could not be detected on consolidated fibres using this analytical technique.



**Fig. 16.** FTIR spectra of silk samples versus chitosan.

### X-ray Fluorescence

The XRF spectra of all three silk fabrics indicated calcium, copper, iron, nickel, potassium, sulphur, titanium, and zinc were all present in small amounts (fig. 17). All these metals are naturally present in silk as trace elements. The aged blue and red silks had higher sulphur peaks than the new Testfabrics #609 silk, possibly due to their increased age, absorption of gaseous pollutants over time, or different manufacturing methods. Otherwise, the spectra were of all three silk fabrics were very similar. The relatively low intensities of all metals present in the spectra suggest no metallic weighting agents, dyes, mordants, pesticides, or other additives are present in the silk fabrics. If the metals present were due to such additives, their peaks would be much higher (Ballard et al. 2011). The aged silk samples used in this experiment are therefore not necessarily representative of weighted silk textiles.



**Fig. 17.** XRF spectra of #609 (white) silk, blue silk, and red silks.

## Additional Tests and Observations

### ***Treatment Reversibility***

Chitosan is soluble in dilute acids, so should be removable from silk substrates, making chitosan consolidation a reversible treatment. Cast chitosan films were dissolved by 1% acetic acid in distilled water. The films immediately softened and then easily dissolved upon immersion in the dilute acid solution. To test the removability of chitosan from silk, 1% and 0.5% Ch-X condition samples from all silk fabrics were immersed in 1% acetic acid solution for 10-15 minutes, rinsed in distilled water, and allowed to air-dry. The silks felt soft and pliable, as they did before chitosan consolidation, suggesting chitosan was indeed removed from silk substrates by rinsing in dilute acid. Since chitosan could not be detected by FTIR or seen using low power magnification (chitosan deposition could only be seen by SEM), there was no way to determine how much chitosan actually remained on the silk samples.

### ***Response to Water and Flattening Attempts***

Silk is a hygroscopic material, so normally moisture can be used to plasticize and re-shape distorted textiles. The untreated silk samples were hydrophilic and readily absorbed liquid water and moisture. Chitosan is hydrophobic, and seemed to have imparted this property to the silk substrates. The treated silk samples that warped due to chitosan consolidation were rendered hydrophobic and could not be flattened using normal textile conservation techniques. Treated silk samples resisted wetting when immersed in water. All treated silk samples initially resisted wetting during extraction in water during pH testing and during solvent spot-testing. Additionally, blue silk 1% Ch condition samples immersed in a bath of distilled water were not evenly wet. Some areas of the fabric did not absorb water, even after several minutes of immersion and agitation in the bath. Chitosan-treated red silk samples could not be humidified with moisture from a damp blotter through Gore-tex (a moisture-permeable membrane), or even by the direct application of hot steam from a clothes steamer. In both cases, the silk did not absorb moisture or become plasticized, so could not be flattened. When pressed flat under weights, the fabric sprung back to its curled and twisted shape. In a final attempt to flatten the twisted red silk, samples were wet with distilled water, pinned out flat onto a

board, and dried by fan (blocking out). When unpinned, the fabric immediately sprung back into its previous twisted shape.

### Methodology Issues

The artificial aging regime used in the experiment did not cause significant change or deterioration in the silk samples. It was hoped that the effects of aging would be more dramatic, to emphasize the effects of chitosan treatment. The aging regime could have been longer; used higher temperature, relative humidity, or light settings; or could have been conducted in multiple stages. These variations could not be realized in this experiment due to time and equipment limitations.

The method of immersing silk textiles in an aqueous solution of chitosan was chosen for simplicity in this preliminary test of chitosan consolidation, but would likely be impractical for the treatment of many artifacts. Wet cleaning is always a risky treatment for textiles, as there is a possibility of bleeding dyes, removing fabric finishes, damaging fibres by drying, and damaging non-textile materials in composite artifacts. Any textile artifact undergoing such a treatment must have dyes stable in water, acids, and chitosan. Furthermore, artifacts with multiple layers and complex fabric forms would have to be supported, interleaved, and restrained to ensure the artifact maintains its shape throughout treatment. Application of chitosan in an organic solvent is not possible, because chitosan is insoluble in organic solvents. An alternative application method, such as ultrasonic application (tested by Conti et al. (2011)) would likely be more practical for the treatment of real artifacts; spray application with a dahlia mister or spray bottle may also be suitable. These application methods would minimize the manipulation and excess moisture involved in total immersion in an aqueous solution, although rinsing is still recommended as part of the consolidation treatment, as the pH of silk samples was not lowered if they were immediately rinsed in distilled water after chitosan application.

All silk samples in the 1% Ch and 0.5% Ch-X treatment conditions smelled strongly of acetic acid after treatment. The chitosan solution used in the experiment was somewhat acidic, at approximately pH 4.2. The solution was brought to this pH to fully dissolve the chitosan into solution for application. If the acidity of the consolidant solution is problematic, there are possible modifications that can be made to the application method. One option might be to dissolve as much chitosan as possible at pH 5,

then filter out any remaining solids. The concentration and volume of the solution could be adjusted to dissolve the chitosan at a higher pH. Another type of acid could also be used to dissolve the chitosan. Rather than rinsing the silk substrate in distilled water after chitosan application, the silk could be rinsed with a mild alkaline solution to neutralize any remaining acidity, or a buffer could be added into the consolidant solution. Maintaining a neutral pH value would protect the silk polymer from acid hydrolysis.



## Conclusion

### Evaluation of Chitosan Consolidation

The purpose of this experiment was to determine whether chitosan was an effective and suitable consolidant for fragile silk textiles. The main areas of interest were the strengthening and consolidating effects of chitosan, and whether chitosan consolidation rendered the silk substrates noticeably stiff or yellow. Any other visual, chemical, or physical changes in the substrate caused by treatment were also of interest.

Overall, chitosan treatment did cause colour change in some silk samples. The red and blue silks became noticeably darker, rather than yellower, after consolidation. The effect was subtle, but unattractive and undesirable. The white #609 Tesfabrics silk samples did not demonstrate noticeable colour change, but the chitosan-treated samples still yellowed upon exposure to visible and UV radiation. Chitosan was not visually apparent on the surface of treated textiles or fibres at low power magnification, and was only visible using an SEM.

Most treated silks became stiff after treatment. Only the #609 silk 0.5% Ch condition showed no change in fabric drape, and all other treated silks became noticeably stiffer. The silks felt crisp, paper-like, and slightly rough to the touch. The #609 silk 1% Ch and 0.5% Ch-X conditions felt like stiff taffeta rather than fine, lightweight silk. Treated silk yarns were lightly held together and did not fray easily. Chitosan also consolidated individual yarns and prevented the aged silk fibres from powdering and shedding lint. Interestingly, the stiffening and consolidating effects of chitosan did not translate to an increase in strength. No chitosan treatment condition resulted in an increase in tensile strength, and the Testfabrics #609 silk 0.5% Ch-X condition actually became weaker and more brittle than the control condition. While the mild consolidating effect may benefit fragile, powdering silk fibres, chitosan treatment would not impart textiles with additional strength. Three-dimensional textiles like costumes or drapery would benefit from additional strength to support their own weight and withstand handling, so chitosan may not be an effective consolidant for such objects.

Some unexpected and negative effects of chitosan were observed after treatment. Silk samples in the 0.5% Ch-X and 1% Ch conditions had a strong, lingering smell of acetic acid after treatment, even when dry. This raised the concern of off-gassing acidic

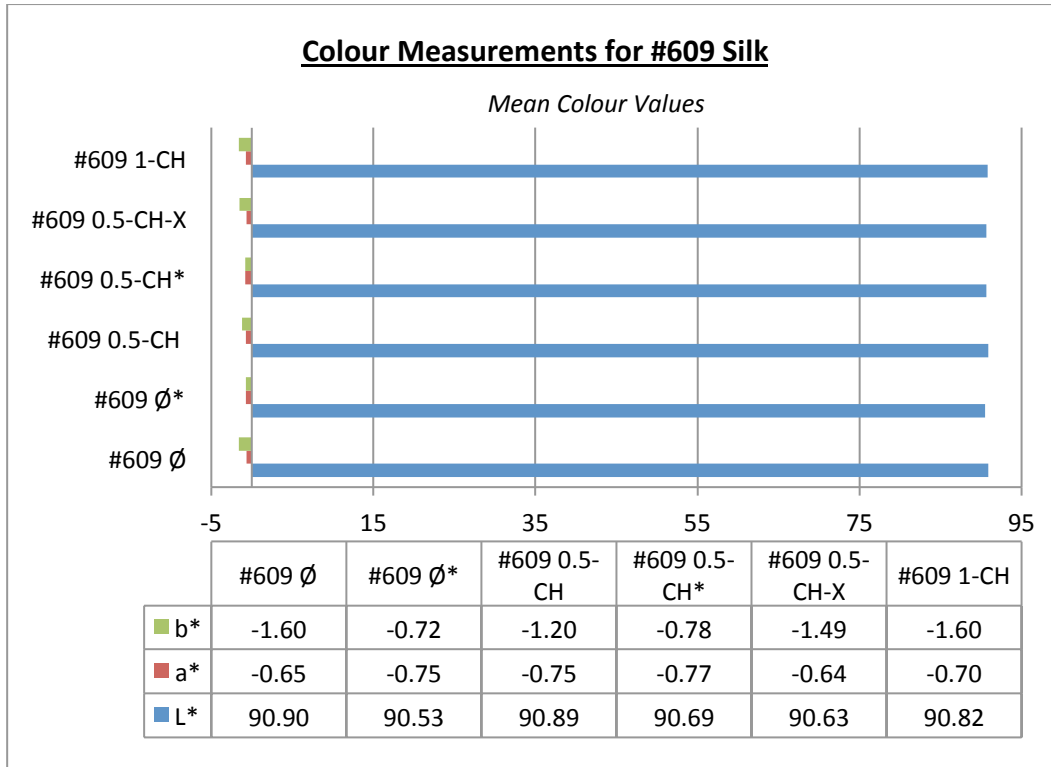
compounds, though the measured pH values for the silk samples were not extremely acidic. The Testfabrics #609 0.5% Ch-X condition samples were treated with chitosan and were not rinsed with water afterwards; these samples were more acidic, stiffer, weaker, and more brittle than the control condition samples, suggesting the acidity of the consolidant solution had a detrimental effect on the silk. In treatment conditions where consolidated samples were rinsed, the pH did not fall, but there was still no strengthening effect, suggesting chitosan imparted no beneficial physical effects to silk using this treatment method.

Additionally, the red and blue silk samples treated with chitosan curled and warped when they dried. The red silk samples twisted dramatically and could not be flattened, an response unsuitable for a real artifact. The samples did not respond to humidification and flattening as textiles should; moisture was not readily absorbed by the silk fibres, likely due to the hydrophobic nature of chitosan, so the fabric could not be plasticized and flattened. Chitosan-treated silk samples also resisted wetting during pH testing, spot-testing, and immersion in water. This hydrophobic effect raises issues for re-treatability, as any treatment involving water or moisture would be difficult to or impossible to carry out on chitosan consolidated textiles, such as wet cleaning, blocking, or humidification and flattening. This limitation is inappropriate for artifacts. Chitosan consolidation does at least appear to be a reversible treatment; chitosan remained soluble in dilute acetic acid, and appeared to be washed out of silk using 1% acetic acid (though this method may not be suitable for all artifacts).

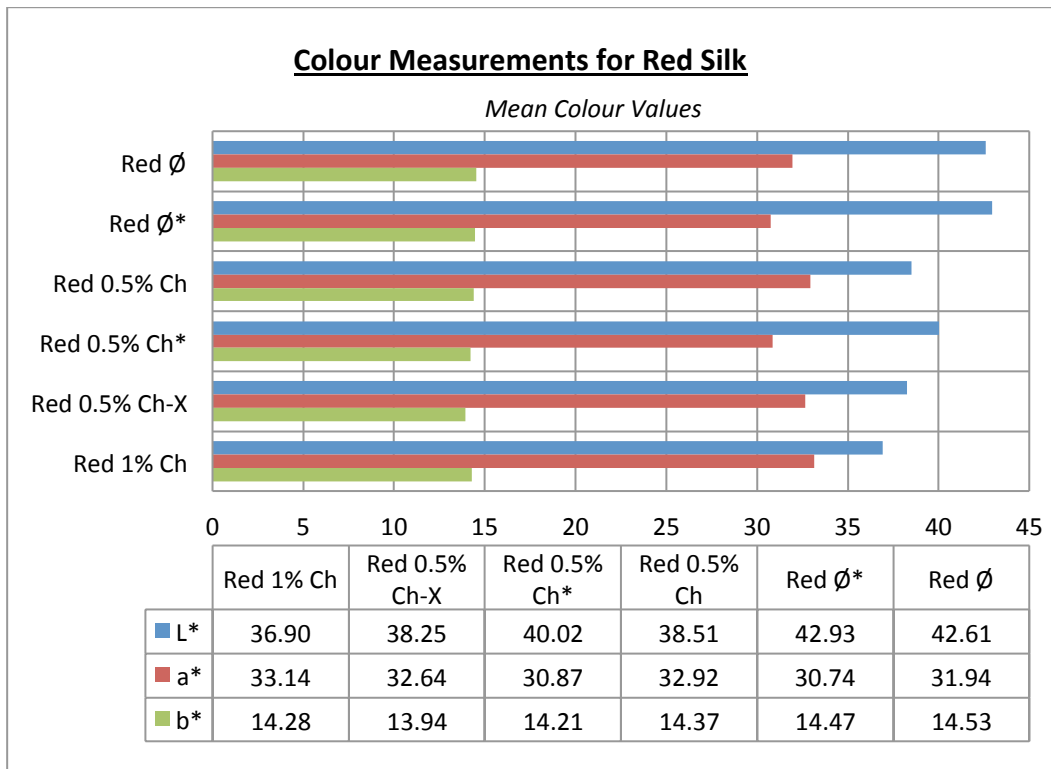
Ultimately, consolidation of silk textiles by immersion in chitosan dissolved in dilute acetic acid was unsuitable and ineffective as a conservation treatment. The treatment was ineffective in strengthening silk substrates, and the colour change, stiffening, and warping of silk substrates was unacceptable. The only positive effects of treatment were the consolidation of powdering fibres, and a mild cohesive effect between yarns that preventing the fabrics from fraying. Still, the undesirable effects of treatment, namely fabric warping and the hydrophobic nature of chitosan, outweigh these benefits. Overall, no treatment was preferable to the effects of chitosan consolidation. Consequently, the chitosan consolidation method practiced here cannot be recommended as a conservation treatment. Perhaps the method of dissolving chitosan in a dilute acid

was problematic; though proteins are somewhat resistant to mild acids, immersing an artifact in a dilute acidic solution is not an appealing treatment method, and seemed to have negative effects. Chitosan modified to be water or ethanol-soluble may be a better option for application to silk and other organic substrates, and is worth further investigation.

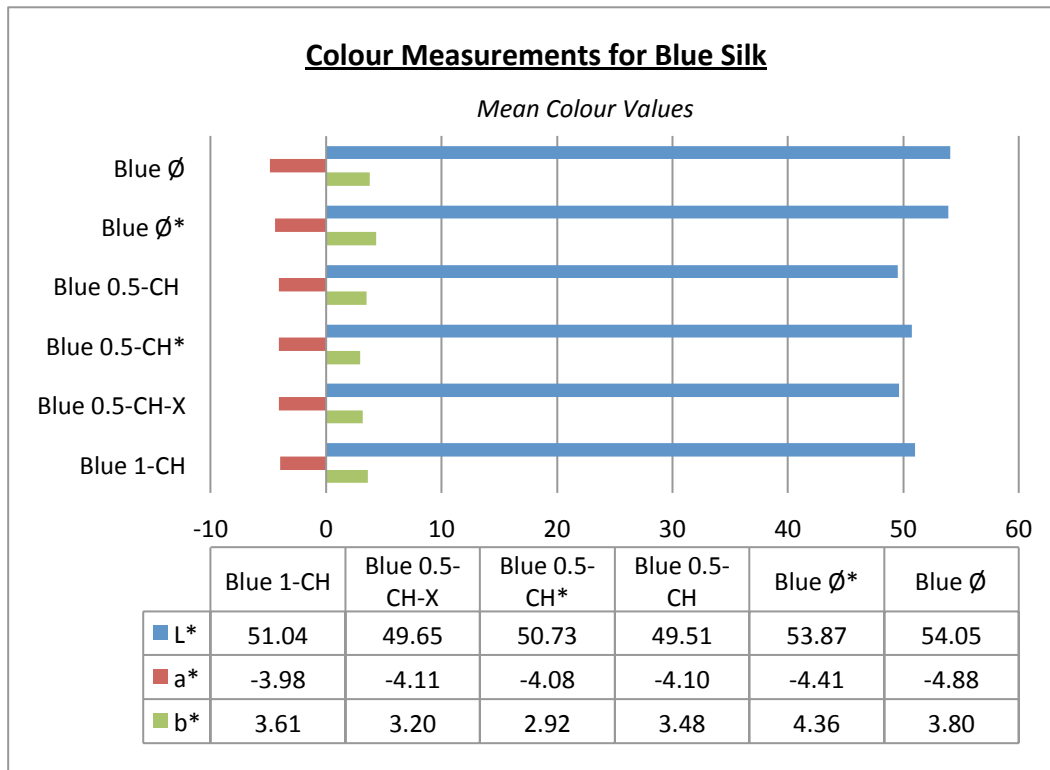
**Appendix A: Colour Measurement Results**



A-1. Averaged L\*, a\*, and b\* values for white #609 silk samples.

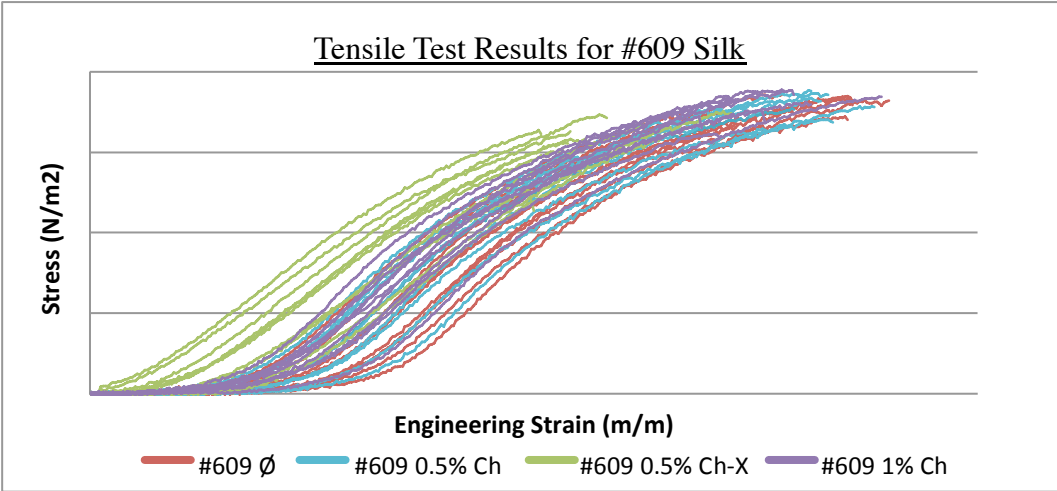


A-2. Averaged L\*, a\*, and b\* values for red silk samples.

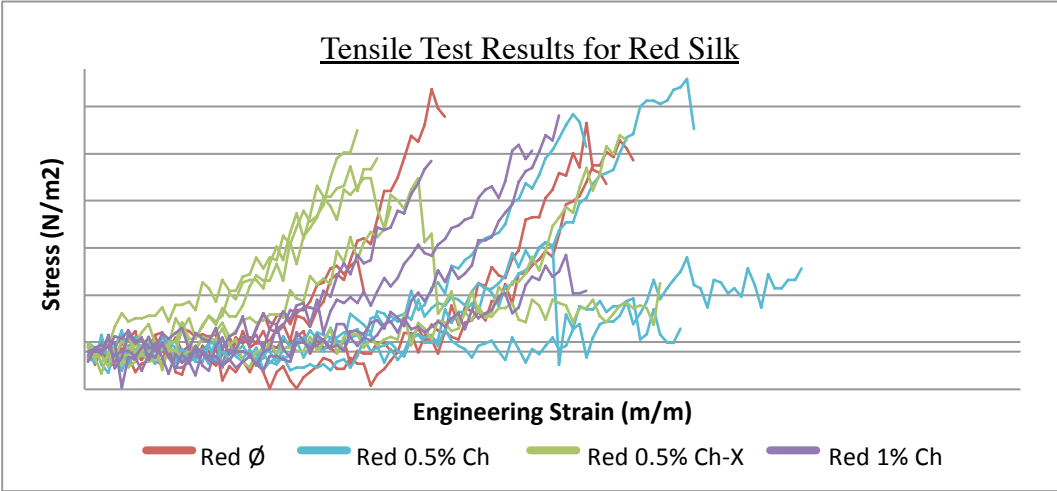


*A-3. Averaged L\*, a\*, and b\* values for blue silk samples.*

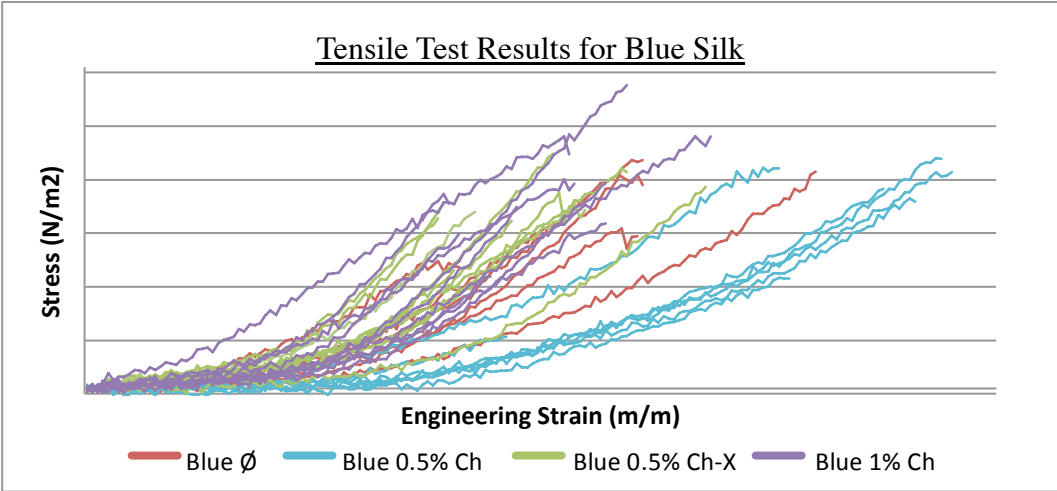
**Appendix B: Stress-Strain Curves**



*B-1. Stress-strain curves for #609 silk samples.*



*B-2. Stress-strain curves for Red silk samples.*



*B-3. Stress-strain curves for Blue silk samples.*

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