Environmentally-Friendly RF Plasma Treatment of Thai Silk Fabrics with Chitosan for Antibacterial Property

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Abstract
A 13.56 MHz RF plasma discharge was successfully utilized to coat Thai silk fabrics with chitosan for antibacterial property. Uncolored and untreated Thai silk fabrics were activated in Ar plasma for 5 or 10 minutes with the RF power of 50, 100 or 150 W under the Ar pressure of 4×10^{-1} or 8×10^{-1} Torr. After plasma activation, specimens were submerged in a 1% (w/v) chitosan solution at room temperature. FTIR analysis confirmed the presence of chitosan. From SEM analysis, chitosan was observed to coat silk fibers almost everywhere. After having been washed up to 3 times, chitosan coating was still present. Unwashed and washed specimens exhibited an excellent antibacterial property against *Staphylococcus aureus*, as most can reduce > 93% of the bacteria. Thus, RF plasma treatment can effectively induce chitosan to strongly and durably coat onto Thai silk fabrics.

Keywords: 13.56 MHz RF plasma, Thai silk, Chitosan, Antibacteria

1 Introduction

Plasma treatment on textiles usually refers to the following three processes. The first is plasma polymerization, which is used to deposit a polymeric film on a substrate under the influence of plasma. The technique offers several advantages over conventional polymer synthesis techniques: ultra-thin, pin-hole free films with thicknesses of 500 Å to 1 μm can be synthesized; films can adhere to a variety of substrates such as polymers, glasses and metals; polymerization can be achieved without the use of solvents (vapor phase polymerization) [1]. Moreover, functional groups of monomers can be retained and a highly-crosslinked and dense coating can easily be synthesized. Synthesized films have been widely used in various applications such as anticorrosive surfaces, humidity sensors, electrical resistors, scratch resistance coatings, optical filters, protective coatings, chemical barrier coatings, etc [2]. The second plasma treatment process is plasma grafting after an activation of the surface by plasma discharge [3]. Similar to plasma polymerization, various monomers can be grafted/graft-polymerized onto various surfaces. Functional groups of monomers can result in the surface exhibiting desired properties such as hydrophobicity, flame retardancy and antibacterial ability without affecting the bulk property of the material. The third plasma treatment process is surface modification by plasma

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such as surface etching, which is usually performed by noble gases.

Common sources of energy to ionize the gas in the reaction chamber are direct current (DC), radio frequency (RF, typically 13.56 MHz) and microwave (typically 2.45 GHz). Reaction chamber design, feed gas composition and flow rate, RF frequency and power, plasma pressure, substrate temperature (lower temperature, higher deposition rate) and position in the chamber all influence the film deposition rate and physical and chemical properties of the film and the grafting [1].

Thai silk fabric has long been considered one of the popular specialties of Thailand. Various properties of silk fabrics can be improved for comfort wear, safety and hygienicity such as hydrophobicity, flame retardancy and anti-bacteria. Plasma treatment can be used to effectively enhance these surface-related properties because the process can be used to graft an appropriate material on the silk fiber surface without affecting the overall bulk mechanical properties. For example, hydrophobicity enhancement of Thai silk using SF_6 plasma was successfully performed in an inductively coupled plasma discharged system [3], [4]. Improvement of hydrophobic properties of Chinese silk and cotton by C_3F_6 plasma treatment was successfully performed [5]. A plasma induced graft polymerization was successfully utilized to coat silk fabrics with flame retardant material, followed by SF_6 plasma treatment for water repellent finishing [6]. Enhancement of hydrophobicity and tensile strength of Indian muga silk fiber by RF plasma discharge was successfully performed [7].

For surface enhancement in order to increase antibacterial ability, silk fiber surface was modified using anhydrides (succinic anhydride and phthalic anhydride) in different solvents (dimethyl sulfoxide (DMSO) and N,N-dimethyl formamide (DMF)) in order to chemically graft chitosan [8]. Grafted fibers were expected to exhibit an antibacterial property due to the presence of chitosan on the surface. Wool fabric was also grafted with chitosan using the same chemical grafting technique [9]. Chitosan is a biopolymer produced by alkaline deacetylation of chitin, which is the most abundant biopolymer in nature after cellulose. It is commonly extracted from shrimp and crab shells. Chitosan is highly bio-compatible and has been widely used in several countries as a natural preservative, as a coating for fruits and vegetables to preserve the freshness and as edible films for containing food, for example. As chitosan can induce *Trichoderma harzianum* such as Chitinase enzyme or β-1, 3-glucanase enzyme, which can dissolve septate hypha of fungi and cell walls of microbial organisms, this eventually results in their deaths. Thus, chitosan has also widely been used as anti-fungi and antibacterial agents for many agricultural products [10]–[15].

There is no literature report on grafting of chitosan onto Thai silk or any other silk using a 13.56 MHz RF plasma treatment process, thus, this work offers a new approach to coat fabrics. At this point, a question may arise as to whether it will be possible to graft chitosan onto a surface using RF plasma discharge. Chitosan was reported to be successfully grafted onto a multiwall carbon nanotubes (MWCNTs) surface using RF plasma [16]. The grafting procedure was performed by first treating the MWCNTs in N_2 plasma in a grafting reactor. The surface-activated MWCNTs were subsequently dipped in a 80°C, 1.50 g/L chitosan solution. The active carbon sites on the carbon nanotube surface can react with chitosan. The chitosan functional groups of $–CH_2OH$, –OH, and $–NH_2$ can form C–O–C, C–O–C and C–NH–C bonds between chitosan and MWCNTs [16]. Moreover, chitosan was successfully grafted onto nylon textiles by placing open-air plasma activated nylon textiles in a chitosan solution [17].

The objective of this experimental work was to effectively and durably graft Thai silk fabrics with chitosan using the environmentally-friendly RF plasma treatment process in order to increase the antibacterial property. The only required chemicals for grafting are chitosan, acetic acid and NaOH, making this process highly environmentally-friendly. The chitosan-grafted fibers were analyzed for the presence of chitosan using scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR). Antibacterial properties were evaluated by AATCC TM 100: 2004 protocol (conventional antibacterial diagnostic on textile materials) for S*taphylococcus aureus*. *S. aureus* is common on human skin and although not always pathogenic, could cause skin diseases, especially in atopic dermatitis. Additionally, *Staphylococcus* spp. including *S. aureus* could cause body smell and color on textile. Hence, antibacterial finish not only protects human skin but also prevents undesired body odor and prolongs textile color. Finally, to assess the durability

of the chitosan coating, grafted fabrics underwent a series of laundering durability test, and the antibacterial ability was evaluated.

2 Experimental Results

The RF power supply system consisted of a 13.56 MHz RF power generator made by DryTek model 2600422. The output power was connected to an automatic matching network made by YSE System model AMN-200. The automatic matching network was required to match the impedance of the generator with that of the load in order to minimize reflected power back to the generator. For all the runs, the reflected power was detected to be less than 5 watts.

The gas supply system consisted of a UHP Ar gas tank connected to a Unit Instruments mass flow controller. A rotary mechanical vacuum pump was used to maintain vacuum in the system. A convectron vacuum gauge and a reader were employed to measure the vacuum level in the chamber. A combination of the gas flow rate and the position of the isolation valve placed between the pump and the plasma chamber established the desired vacuum level in the chamber. Figure 1 shows the RF power supply system and Figure 2 shows the plasma chamber.

The glass plasma chamber had the inner diameter of 21 cm and the length of 31 cm. The two stainless steel flanges can be tightened together with screws. A viton o-ring was used as a gasket between the two flanges. A silicone grease rated for ultra-high vacuum was used to coat the o-ring and contact surfaces in order to ensure vacuum tightness. The substrate holder and the high potential plate placed parallel to each other were made of copper with the dimensions of 15 cm × 22 cm. They were fixed and separated from each other by 1 cm using high-purity alumina rods. A stainless steel gas supply line was inserted into the chamber and the opening of the line was between the substrate holder and the high potential plate in order to ensure that the argon plasma was sufficiently and uniformly generated in the substrate holder area.

The specimen for each run had a rectangular size of about 5 × 10 cm, cut from a large piece of woven Thai silk fabric purchased from Huay Kian Silk Fabric Weaver Moo 10, Chiang Rai Province, Thailand. The fabric had not been colored or treated in anyway;

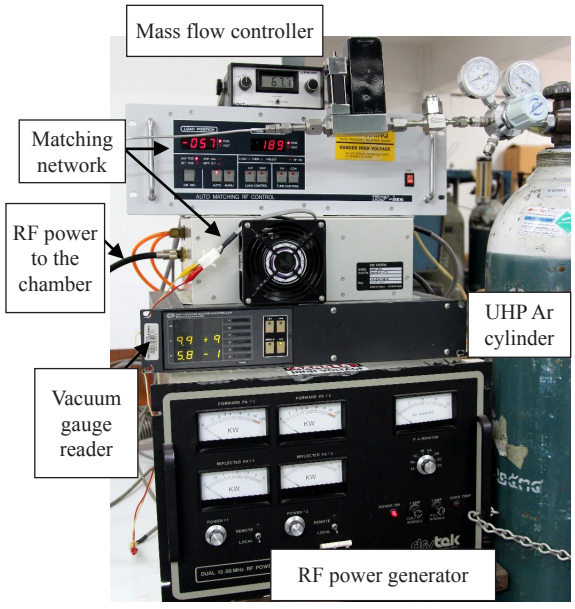


Figure 1: RF power supply system.

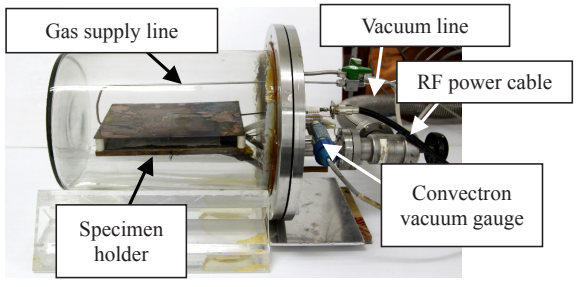


Figure 2: Plasma chamber.

it was made from 100% natural Thai silk. Prior to placing the specimen on the specimen holder, it was thoroughly cleaned with methyl alcohol several times in order to remove any oil attaching to the surface. Afterwards, it was placed in a forced-convection oven at 50°C for 20 minutes to achieve complete dryness.

For each run, 2 cleaned and dried specimens were placed on the specimen holder. Plasma treatments were performed under 4×10^{-1} or 8×10^{-1} Torr of argon pressure, the RF power of 50, 100 or 150 watts and the treatment time of 5 or 10 minutes.

After the treatment, the specimens were quickly removed from the specimen holder and were immediately

submerged and stirred in a 1% (w/v) chitosan solution at room temperature for 2 minutes. The solution was prepared by dissolving 1 wt% of chitosan into a 2% (v/v) acetic acid solution, which was adjusted to a pH of 5.6 by addition of NaOH. The food-grade chitosan was purchased from Bonafides Marketing Company, Thailand, which had a molecular weight in the range of 500–1,000 kDa. Afterwards, the specimens were removed from the solution and were placed in a forced-convection oven at 50°C to achieve complete dryness. To ensure adequate coating, specimens were then subjected to the same plasma treatment process and chitosan submersion. At the end, they were washed with deionized water several times to ensure that non-grafted chitosan was completely removed.

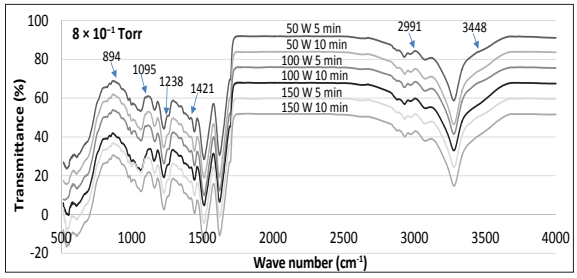
Specimens underwent FTIR and SEM analysis for the presence of chitosan. The laundering durability test was performed by pouring tap water into a 5-liter beaker and mixing with ordinary detergent at 1 g/L concentration. The temperature was controlled at 35–36°C and the test was performed for 30 minutes per TIS-121 (3–1975) standard.

For testing of antibacterial property and to ensure that coated materials were chitosan, specimens were sent to Textile Testing Center, Thailand Textile Institute in Bangkok, Thailand, for quantitative evaluation of *Staphylococcus aureus* ATCC 6538 following the standard AATCC TM 100-2004 protocol [18]. In summary, the test specimens were sterilized before testing by using the autoclave at 121°C, 15 psi for 15 minutes. 1.0 ± 0.1 ml of the *Staphylococcus aureus* inoculum was loaded on the swatches of 4.8 ± 0.1 cm in diameter, cut from the test fabrics (treated and untreated). After inoculation, the specimens were incubated at 37 ± 2°C for 24 hours. Then, the bacteria were eluted from the specimen swatches by shaking in known amounts of neutralizing solution. The percentage bacteria reduction can be calculated according to Eq. (1):

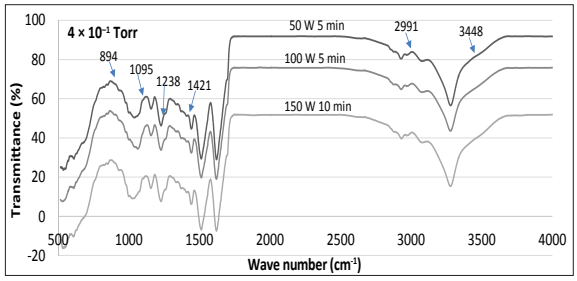
$$\% \text{ Reduction } (R) = 100\ (C\text{-}A)/C \qquad (1),$$

where (A) = the number of bacteria recovered from the inoculated treated test specimen swatches in the jar after 24 hours contact time,

(C) = the number of bacteria recovered from the inoculated untreated control swatches in the jar at 0 hour contact time.



(a) 8 × 10^{-1} Torr



(b) 4 × 10^{-1} Torr

Figure 3: FTIR spectra.

3 Results and Discussion

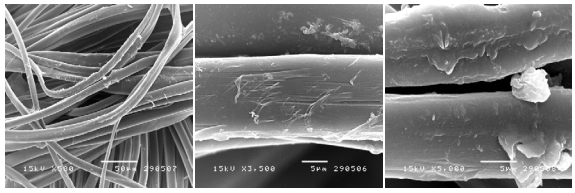
Figures 3(a) and 3(b) show the FTIR spectra of the 8 × 10^{-1} Torr and 4 × 10^{-1} Torr case. Each spectrum was slightly shifted downward in order to allow for visual observation of each of them, as they are almost indistinguishable from one another.

The observed characteristic peaks for chitosan were at 1238, 1421 and 2991 cm^{-1}. Characteristic peaks at 894, 1095 and 3449 cm^{-1} were not observed. Peaks were not sharp, indicating that only a small amount of chitosan was coated on silk.

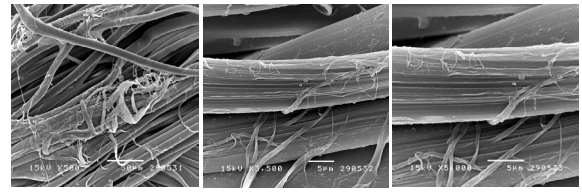
For physical appearances, after undergoing plasma activation and chitosan coating, all silk specimens exhibited the same color. Thus, the plasma treatment process did not alter the physical appearance of the silk fabrics.

Figures 4(a)–4(l) show scanning electron micrographs of chitosan-coated silk fibers before and after the laundry process. Figure 4(m) shows uncoated silk fibers for comparison.

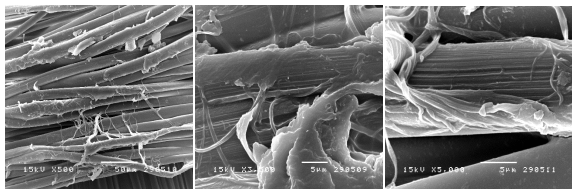
For all treatment conditions, SEM images show that silk fibers were coated with chitosan almost everywhere. All of the studied coating conditions yielded similar results despite different treatment times, RF powers and Ar gas pressures. After washing up to



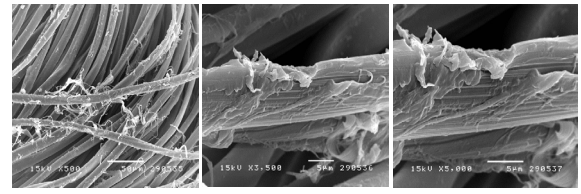
(a) 50 W, 5 min, 8×10^{-1} Torr, unwashed



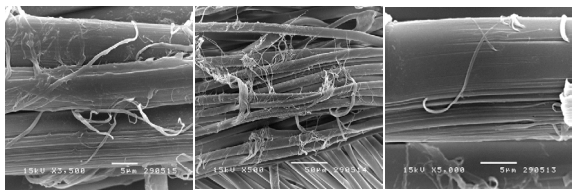
(e) 150 W, 5 min, 8×10^{-1} Torr, unwashed



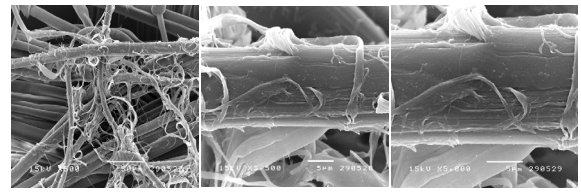
(b) 50 W, 10 min, 8×10^{-1} Torr, unwashed



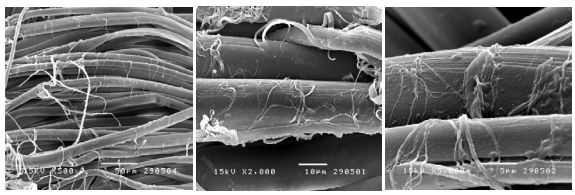
(f) 150 W, 10 min, 8×10^{-1} Torr, unwashed



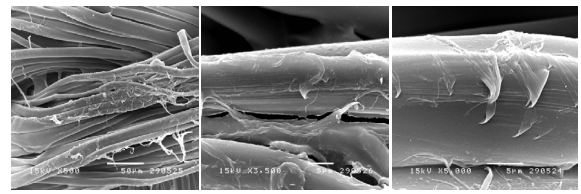
(c) 100 W, 5 min, 8×10^{-1} Torr, unwashed



(g) 50 W, 5 min, 4×10^{-1} Torr, unwashed



(d) 100 W, 10 min, 8×10^{-1} Torr, unwashed



(h) 100 W, 5 min, 4×10^{-1} Torr, unwashed

Figure 4: SEM images of silk specimens.

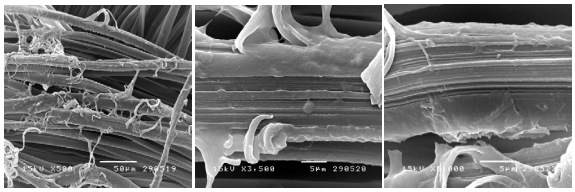
3 times, chitosan was still present, even though the fiber-like structure vanished. This can be interpreted that the fiber-like materials were weakly-bonded chitosan, and that even after 3 rounds of washing, chitosan was still strongly and durably coated onto Thai silk fibers. In real chitosan-coated silk garment, it is thereby likely that our coating method will resist laundry, and the hygienicity will still be present owing to the strong chemical bonding chitosan establishes with silk fibers. This excellent property cannot be accomplished by simply submerging silk fabric in a chitosan solution, as weakly-coated chitosan will simply be washed away during the first wash.

Table 1 shows results of the anti-*Staphylococcus* evaluation.

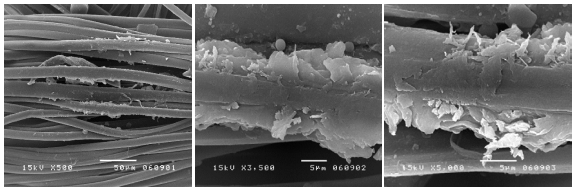
Table 1: Results of antibacterial evaluation

Treatment	Bacterial Reduction (%)		
	Unwashed	Washed 1 time	Washed 2 times
50 W, 5 min, 8×10^{-1} Torr	> 99.88*	93.44	99.25
50 W, 10 min, 8×10^{-1} Torr	> 99.88*	83.75	99.73
100 W, 5 min, 8×10^{-1} Torr	98.75	62.50	99.16
100 W, 10 min, 8×10^{-1} Torr	98.62	95.62	99.44
150 W, 5 min, 8×10^{-1} Torr	98.00	97.00	99.62
150 W, 10 min, 8×10^{-1} Torr	88.25	93.44	95.31
50 W, 5 min, 4×10^{-1} Torr	> 99.97*	85.00	97.88
100 W, 5 min, 4×10^{-1} Torr	99.92	93.75	99.81
150 W, 10 min, 4×10^{-1} Torr	98.19	96.25	99.76
Uncoated silk	0.00	0.00	0.00

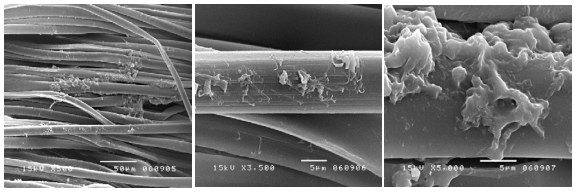
*According to AATCC TM 100-2004 protocol [18], report "0" counts at 100 dilution as "less than 100." Thus, for certain results, the % reduction (R) according to Eq. (1) must be reported as greater than certain values.



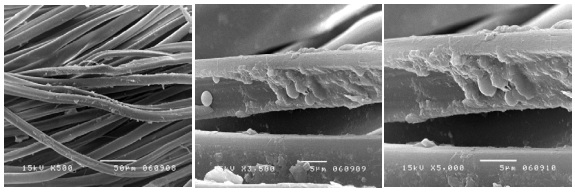
(i) 150 W, 10 min, 4×10^{-1} Torr, unwashed



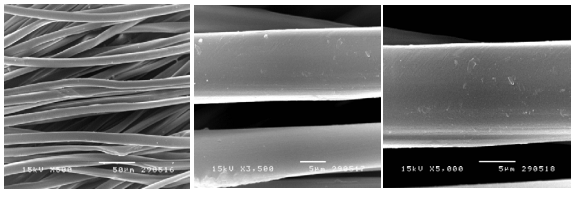
(j) 50 W, 5 min, 8×10^{-1} Torr, washed 1 time



(k) 50 W, 5 min, 8×10^{-1} Torr, washed 2 times



(l) 50 W, 5 min, 8×10^{-1} Torr, washed 3 times



(m) Uncoated silk fibers for comparison

Figure 4: SEM images of silk specimens. (continued)

Coated materials were undoubtedly confirmed to be chitosan as all of the coated silk specimens exhibited excellent antibacterial reductions and as the uncoated silk specimen could not tolerate any bacterial infection at all (0% bacteria reduction). Moreover, it can be observed that, for most specimens, the antibacterial capability slightly decreased after the first wash. This was expected, as weakly-bonded chitosan was washed away and less chitosan was present. However, for all specimens, the antibacterial capability actually increased after they underwent 2 rounds of washing. This result was not expected. It may be because detergent in newly-washed fabrics provides a short-term antibacterial effect. 2–3 continuous rounds of washing without wearing may accumulate this short-term detergent accumulation effect. In any case, unwashed specimens exhibited an excellent antibacterial capability as most of them can reduce > 98% of the bacteria. More importantly, after subjected to 1 or 2 rounds of washing, most specimens still exhibited > 93% antibacterial property. Thus, chitosan was strongly and durably coated onto Thai silk fabric, forming a strong covalent bonding with the silk fibers.

Similar to results from SEM analysis, no trend can be observed on the amount of coating vs. treatment time, RF power or Ar gas pressure. All of the studied coating conditions yielded excellent results, and this can be expected from SEM analysis illustrating numerous chitosan coating on all specimens. Thus, for as little as 50 W of RF power with 5 minutes of treatment time and the Ar gas pressure of 4×10^{-1} or 8×10^{-1} Torr, chitosan can be made to strongly and durably coat Thai silk fabrics.

4 Conclusions

This experimental work utilized a 13.56 MHz RF plasma to durably coat Thai silk fabrics with chitosan for antibacterial property. The treatment conditions were 5 or 10 minutes of plasma activation time, 50, 100 or 150 W of RF power and 4×10^{-1} or 8×10^{-1} Torr of Ar pressure. FTIR analysis confirmed the presence of chitosan as the observed characteristic peaks were at 1238, 1421 and 2991 cm^{-1}. Small peaks indicate that only a small amount of coated chitosan on silk fabric is required. From SEM analysis, chitosan exhibiting the fiber-like appearance was observed to coat silk fibers almost everywhere. After being washed up to 3 times, chitosan was still present, but the fiber-like structure vanished. This means that, in real chitosan-coated silk garment, this method allows entire-surface coverage of silk fabric by minimal amount of chitosan, and this chitosan-coated fabric can be washed several times: the hygienicity is still present due to the strong covalent bonding chitosan establishes with silk fibers.

Coated materials were confirmed to be chitosan as unwashed specimens exhibited an excellent antibacterial capability because most can reduce > 98% of *Staphylococcus* bacteria. After subjected to 1 and 2 rounds of washing, most specimens still exhibited > 93% antibacterial property.

All of the studied coating conditions yielded excellent results, and for as little as 50 W of RF power with 5 minutes of treatment time and 4×10^{-1} or 8×10^{-1} Torr of Ar pressure, chitosan can be made to effectively coat Thai silk fabrics, making the fabrics much more hygienic to wear.

The findings of this research work offer the new and highly environmentally-friendly coating process of silk with chitosan for potential uses in the textile industry to increase the commercial value of silk, because the only chemical required is the environmentally-friendly chitosan solution.

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