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Silica-Chitosan Nanocomposite Coatings for Enhancing Hydrophilicity of Polyester Fabric

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Abstract. The hydrophilicity of polyester fabric surfaces has been modified using silica-chitosan nanocomposites. The silica-chitosan nanocomposite was synthesized by the sol-gel method from sodium silicate and various chitosan concentrations of 0 – 1.5% at a pH of 3 – 5. A single jersey knitted polyester fabric was coated by silica-chitosan nanocomposite using the pad-dry-cure method. It was found that the chitosan concentration and the solution pH controlled the formation of various size distributions of sphere nanocomposites with an average size of 96.0-201nm. The coated polyester fabric with sphere silica-chitosan exhibits a rough surface and produces a contact angle approaching 0°, facilitating the polyester fabric's speed-up water absorption and hydrophilic properties.

Keywords: Chitosan; Hydrophilic; Nanocomposite; Polyester; Sodium silicate

1. Introduction

Synthetic fibers such as polyester are the most popular and common fiber used in activewear and sportswear. It is cheap, easy to manufacture, and has excellent washing and wearing properties (Shishoo, 2005). Polyester fibers also have a good wicking rate and better dimensional stability (Ramakrishnan and Jagannathan, 2018). However, the fiber is generally hydrophobic and has a much lower water absorption capacity. Polyester deficiencies are usually overcome by improving the wicking ability through chemical treatment, which is achieved by applying a hydrophilic coating to each polyester filament. The resulting hydrophilic surface allows moisture to migrate along the outer surface of the filament.

Researchers have tried to modify the polyester surface's hydrophilicity, for example, by blending polyester with cellulosic (Zaman *et al.*, 2013; Troynikov and Wardiningsih,

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2011) and hydrolysis of the polyester surface using enzymes and surfactants (Gao *et al.*, 2017). Wu *et al.* (2014) modified the polyester surface using cutinase treatment. Natarajan and Moses (2012) used polyvinyl alcohol to modify the polyester hydrophilicity. Recently Chen, Haase, and Mahltig (2019) modified a polyester fabric surface using a silica-chitosan composite, which succeeded in enhancing the hydrophilicity of the polyester fabric surface by measuring the sink-in time. They use tetraethoxysilane (TEOS) as primary precursors for preparing a spherical shape of silica nanoparticles. However, considering the material cost, alkoxide may not be commercially viable in the textile industry.

Sodium silicate has been considered as an alternative inexpensive silica precursor to substitute expensive alkoxide compounds (Hwang, Lee, and Chun, 2021). Researchers have prepared diverse nanostructured silica from sodium silicate (Owoeye, Abegunde, and Oji, 2021; Chiang *et al.*, 2017; 2011; Jesionowski and Krysztafkiewicz, 2002). However, they synthesized sodium silicate precursor in an alkaline medium to produce non-agglomerated silica nanoparticles. In contrast, the synthesis of silica from sodium silicate in acid conditions tends to result in agglomeration (Zulfiqar, Subhani, and Husain, 2016).

Chitosan is a unique cationic polysaccharide that can easily be modified with chemicals, radiation, and enzymes (Barleany *et al.*, 2020; Usman *et al.*, 2018). It is a biodegradable biopolymer used in an environmentally friendly synthesis process (Lim *et al.*, 2021; Usman *et al.*, 2018; Kusrini *et al.*, 2015). As a biopolymer, chitosan is a useful polymer for synthesizing metal oxide and encapsulating small particles (Lim *et al.*, 2021; Matusiak, Grządka, and Bastrzyk, 2018). Recent interest in chitosan has increased due to its structure's presence of main amino groups that acts as crosslinker (Chen, Haase, and Mahltig, 2019; Haerudin *et al.*, 2010).

This study is aimed to synthesize silica-based chitosan nanocomposites using the sol-gel method from sodium silicate and chitosan. The relationship between pH and chitosan concentration in forming silica-chitosan composites was investigated. The effects of silica-chitosan nanocomposite coating on the polyester fabric surface were demonstrated.

2. Methods

2.1. Material

Knitted polyester fabric having a single jersey knitted design, mass per unit area 150.6 g/m^2, thickness 0.57 mm, yarn count 9.61 tex, 51 courses per inch, 43.67 wales per inch was used as a substrate for coating. The fabric samples were knitted on a single Fukuhara machine from 100% polyester filament yarn. Ethanol (99.9%) and acetic acid (98%) were obtained from Merck. Sodium silicate, chitosan, and distilled water were obtained from a local market. All chemical reagents were used without further purification.

2.2. Preparation of precipitated silica-chitosan

Precipitated silica-chitosan was prepared by mixing sodium silicate with ethanol and distilled water under continuous magnetic stirring. The solution was then divided into three equal parts. Acetic acid was titrated to each solution to adjust the pH value to 3, 4, and 5. Chitosan solution with concentrations of 0%, 0.5%, 1%, and 1.5% was added to the different pH of sodium silicate solutions. Finally, white precipitated silica-chitosan was collected by centrifugation and filtering and then dried in an electric oven at 50^{o}C for 2 h.

2.3. Coating silica-chitosan on polyester fabric

Five pieces of polyester fabrics were coated with silica-chitosan nanocomposite using a pad-dry-cure method. The polyester fabric was padded for double-nip and double-dip in a 100 mL bath with a wet pick-up ratio of 70%. The silica-chitosan-treated polyester fabric was then dried at 100^{o}C for 1 min and cured at 150^{o}C for 2 min.

2.4. Characterization of silica-chitosan nanocomposite

The silica-chitosan nanocomposite and coated fabric surface morphology were observed using a Hitachi TM SU-3500 Scanning electron microscope (SEM). The functional groups of nanocomposites were analyzed using a Shimadzu Prestige 21 Fourier-transform infrared (FTIR) Spectrophotometer. The microstructure of the samples was measured using a Bruker X-ray diffractometer (XRD) at 40 kV with a Cu-Kα radiation source (λ = 1.5418 Å).

2.5. Characterization of the coated fabric surface

The polyester fabric surface was evaluated, including water contact angle and absorption. The wettability or absorbency of polyester fabrics was examined before and after treatment using the AATCC test method 79 (AATCC, 2018). In brief, a drop of water is dropped from a fixed height onto the surface of a test specimen. The time required for the specular reflection of the water drop to disappear is measured and recorded as sink-in time. The water contact angle on polyester fabric before and after treatment was measured using a Kyowa KYOWA interFAce Measurement and Analysis System. The volume of the water droplet was set at 2 µL.

3. Results and Discussion

3.1. The morphology of silica-chitosan nanocomposites

SEM examined the surface morphology of the silica and silica-chitosan products; representative images are shown in Figure 1. At pH 3, the silica product synthesized without chitosan (pH 3 Ch 0) depicted a loose spherical particle of various sizes from 50 nm to 200 nm. With increasing chitosan concentration (pH 3 Ch 0.5 – 1.5), the surface morphology did not change, but the silica-chitosan product decreased the size (96.0 nm – 120.3 nm) and was narrowly distributed. The surface morphology of the silica-chitosan product prepared at pH 4 and 5 have the same trend as the surface morphology of the silica-chitosan product prepared at pH 3.

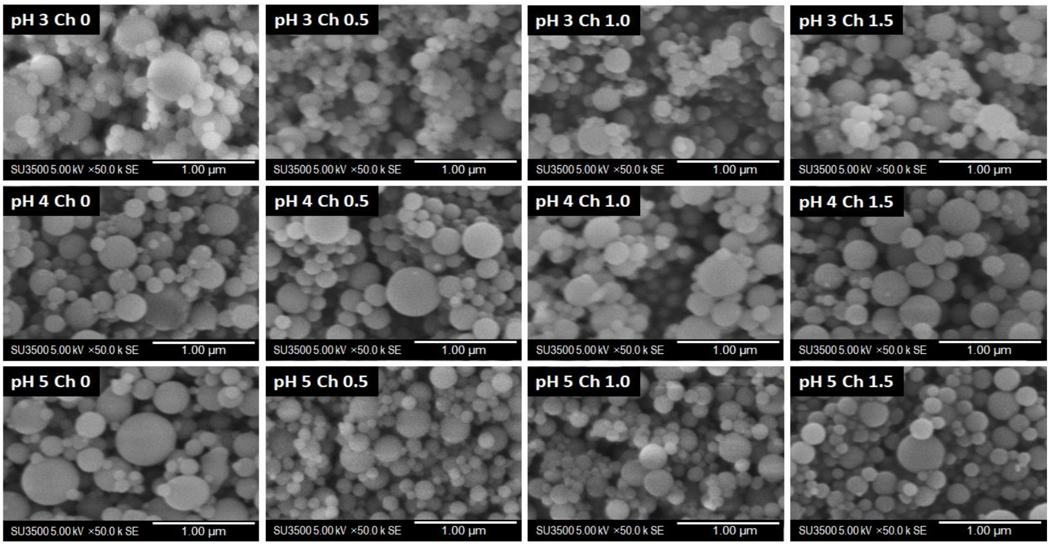

Figure 1 SEM images of silica and silica-chitosan particles synthesized at different pH and chitosan concentrations

To reveal the particle size distribution of the silica and silica-chitosan, the particle images in Figure 1 were analyzed using ImageJ software. Figure 2 shows the particle size distribution of the silica and silica-chitosan products prepared at pH 3 – 5. It can be seen from Figure 2 that the silica and silica product prepared at low pH tends to have a narrow particle size distribution. This is because the pH value strongly influences the hydrolysis and condensation reactions in the sol-gel process. Under acidic conditions, the hydrolysis reaction rate is faster than the condensation reaction rate to produce a small particle size (Barker et.al., 2022; Budnyak et al., 2015). Therefore, the average particle size of the silica (119.5 nm) and silica-chitosan (96 - 120.3 nm) compared at pH 3 is smaller than the silica (182 nm and 165.5 nm) and silica-chitosan (126.6 – 144.2 nm and 177.6 – 201.4 nm) prepared at pH 4 and 5, respectively. It is also clearly noticed in Figure 2 that the average size of silica prepared without chitosan is larger than that prepared by adding chitosan. Increasing the concentration of chitosan tends to enhance the size of silica-chitosan. The higher the concentration of chitosan involved in the reaction, the larger the size of the silica-chitosan formed. In an acidic environment, the chitosan acts as a crosslinker that connects the formed silica particles (Pieróg, Gierszewska-Drużyńska, and Ostrowska-Czubenko, 2009). The amine group of chitosan (NH_2) is protonated to be positively charged to form -NH_3^+ ion, while silica is negatively charged. The interactions between the negatively charged silicon oxide surface and the positively charged polymer chains formed silica-chitosan nanocomposite (Chen, Haase, and Mahltig, 2019; Budnyak *et al.*, 2015).

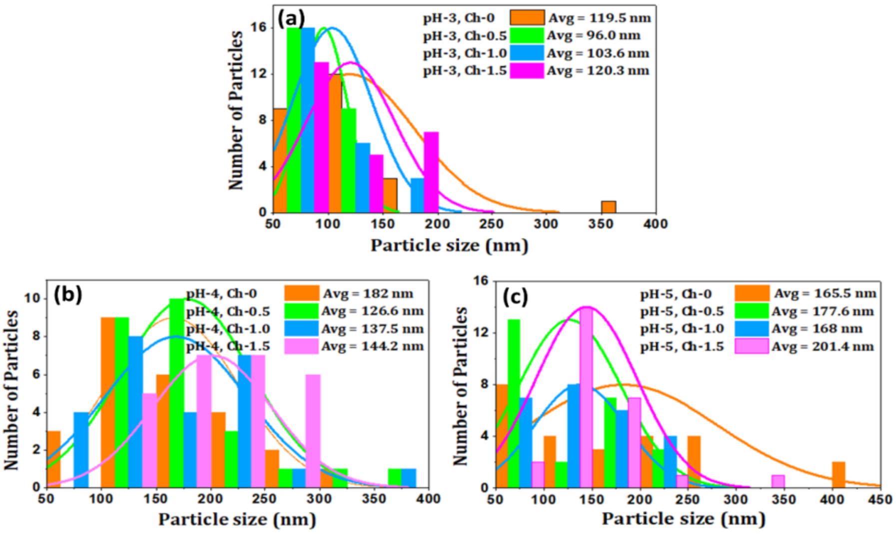

Figure 2 Particle size distribution of silica and silica-chitosan prepared at (a) pH 3, (b) pH 4, and (c) pH 5

3.2. *FTIR of silica-chitosan nanocomposites*

Figure 3 shows the FTIR spectra of the silica and silica-chitosan nanocomposite with chitosan concentration and pH variations. The FTIR spectra pose similar peak vibrations for all samples, indicating that changing pH and adding chitosan does not alter the silica backbone. A large vibration area peak at 3424 cm^{-1} corresponds to O-H and N-H stretching. A small peak at 1638 cm^{-1} relates to the possible interaction between the hydroxyl group of silica and the amine group of chitosan (Imani *et al.*, 2022). Sharp peaks at 1092 cm^{-1} and 789 cm^{-1} are attributed to asymmetric and symmetric stretching vibration Si-O-Si. The peak at 941 cm^{-1} indicates a functional group of Si-OH stretching vibration (Ryu and Lee, 2018; Shariatinia and Jalali, 2018), and the peak at 457 cm^{-1} indicates the existence of O-Si-O symmetric deformation vibration (Mahmoud *et al.*, 2012).

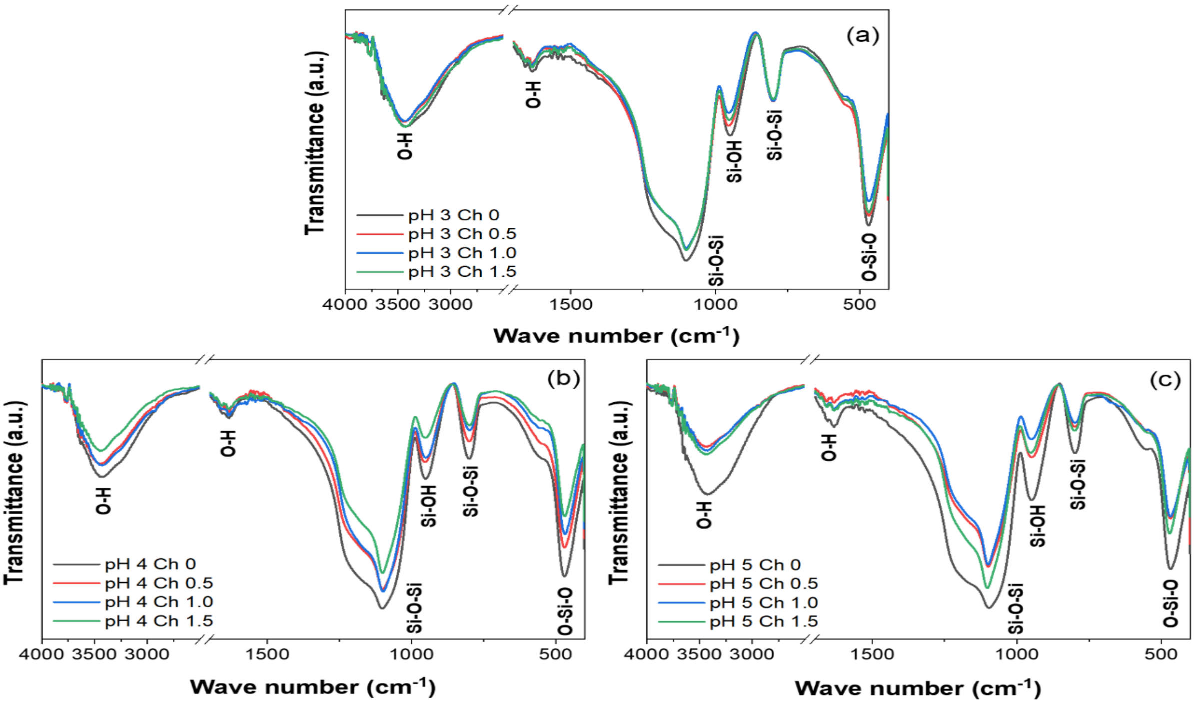

Figure 3 FTIR spectra of silica and silica-chitosan

The silica and silica-chitosan product synthesized at pH 3 have relatively the same peak intensities, while the samples synthesized at pH 4 and 5 have changed the peak intensities. Therefore, peak intensities of OH vibration change slightly in the sample. Chitosan is easily soluble in acidic solutions with a pH of less than 6. At pH 2-3, silica has a zero charge point where the concentration of the positively charged group is the same as the negative charge. Therefore, it is possible that at pH 3, even though different concentrations of chitosan are added, the intensity in the FTIR spectra is not changed. In acid conditions, the silica surface is generally negatively charged (Matusiak, Grządka, and Bastrzyk, 2018). At pH 4 and 5, silica surfaces tend to be more negatively charged than at pH 3.

On the other hand, the polymer chain of chitosan has a positively charged -NH_3^+ group. The interaction between the negatively charged SiO_2 surface and the positively charged chitosan became possible due to the increasing negative charge on the silica surface at pH 4 and 5 and the increasing positive charge from adding chitosan. As a result, the intensity of the OH and Si-O-Si, Si-OH, and O-Si-O groups in the FTIR spectrum changes.

3.3. Morphology of the silica-chitosan coated polyester fabric

The polyester fabrics were coated with silica-chitosan nanocomposite using a pad-dry-cure method. The surface morphology of the untreated and treated polyester fabric is shown in Figure 4.

The optimal condition was determined to be pH 3 with 0.5 % chitosan (pH 3 Ch 0.5) based on an analysis of the morphology of the silica chitosan nanocomposite, particle distribution, and functional groups. It shows the presence of a layer on the surface of the fabric coated with silica-chitosan. The presence of a layer on the surface of the polyester affects the surface roughness, so it influences its wetting ability.

The presence of silica-chitosan particle aggregates on the polyester fabric surface suggests that silica-chitosan nanocomposites adhere to the polyester fabric surface, most likely by van der Waals interactions. The polyester chain has a hydroxyl group at the end, enabling it to bond to the hydroxyl group of the silica-chitosan.

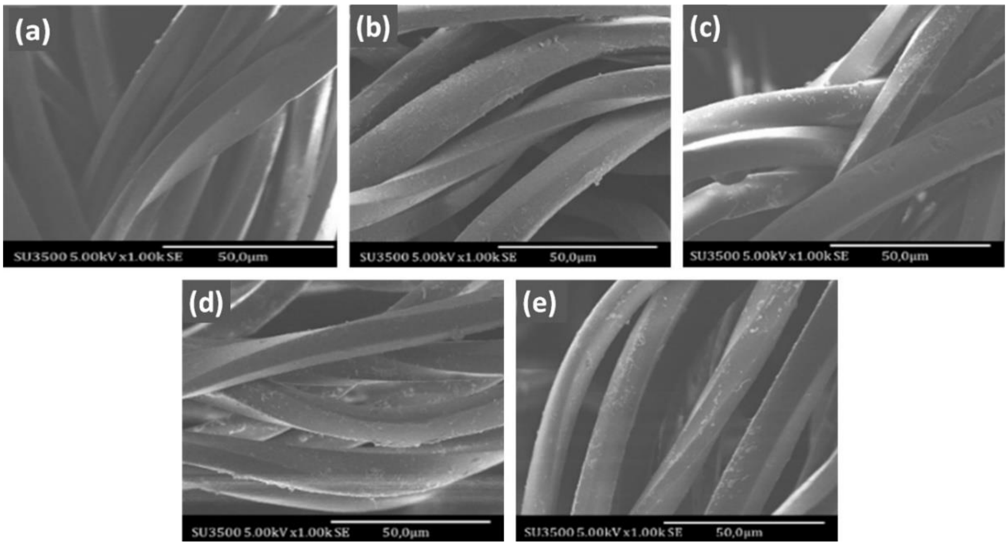

Figure 4 SEM images of (a) untreated polyester fabric surface and treated polyester fabric surface at pH 3 with (b) no chitosan, with chitosan of (c) 0.5%, (d) 1.0%, and (e) 1.5%

Figure 5 shows a prediction of the reaction between silica and silica chitosan nanocomposite in the polyester layer. As predicted in the reaction, the hydroxyl group on silica (Si-OH) will bond to the polyester hydroxyl group at the end of the polymer chain (a). Figure b illustrates the hydroxyl group of chitosan bonds to the hydroxyl group of silica (Si-OH), and the hydroxyl group of silica bonds to the hydroxyl group of polyester after forming the silica chitosan nanocomposite. These findings indicate that the addition of hydroxyl groups to the surface of polyester can enhance its hydrophilic characteristics.

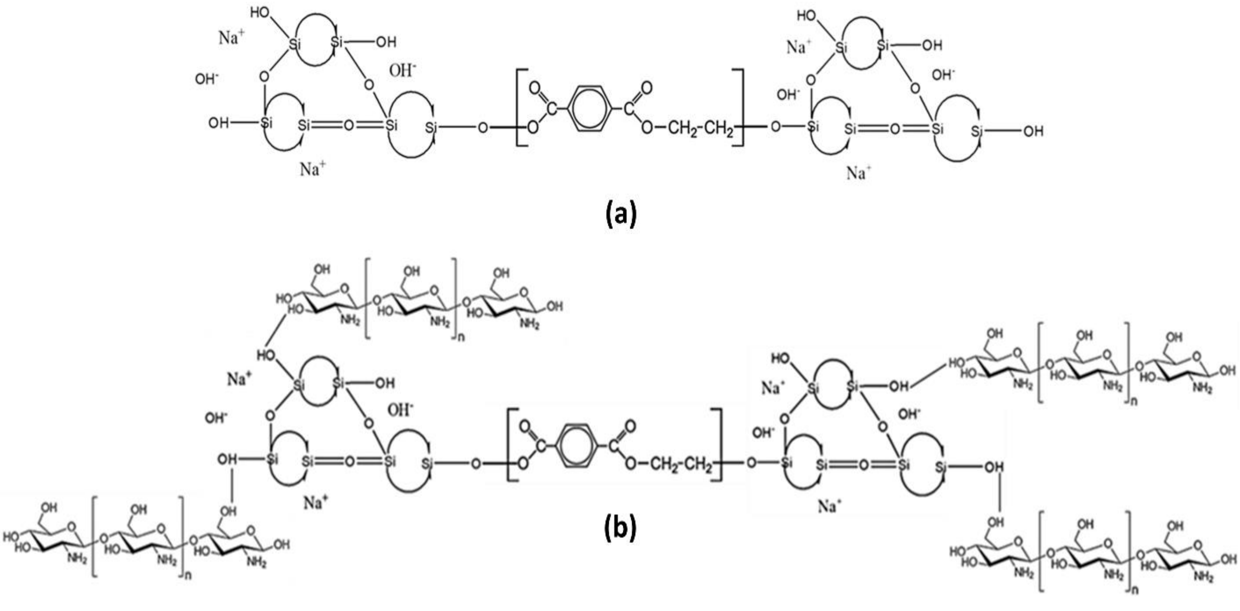

Figure 5 Schematic representation of the proposed reaction of polyester fabric surface with (a) silica nanocomposite, (b) silica-chitosan nanocomposite

3.4. Measurement of static and dynamic contact angles

Figure 6 shows images of water droplets on polyester fabric surfaces before and after treatment with silica-chitosan sol. The static contact angle was measured 3 seconds after a water droplet of 2 μL was placed on the fabric surface. Figure 6(a) shows the static contact angle of water droplets on untreated fabric is 122°. While dropping water droplets on treated fabric with silica-chitosan 0 – 1.5% resulted in zero degrees contact angle, which suggests that coating fabric with silica or silica-chitosan produced a hydrophilic polyester surface. Furthermore, the hydrophilicity of treated polyester with silica and silica-chitosan was tested by measuring the time elapse for a water droplet to disappear or be completely absorbed by the fabric.

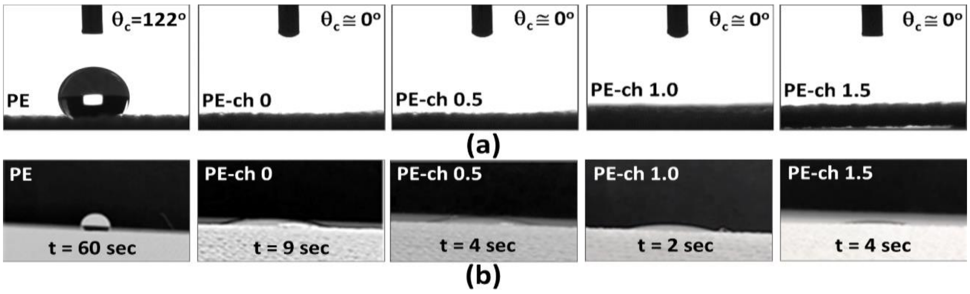

Figure 6 Water droplets on the polyester fabric surface, (a) static, and (b) dynamic contact angle

Figure 6(b) shows time elapses for a water droplet to disappear from the untreated and treated fabric surface. For the untreated fabric, the water droplet formed a ball-like water droplet with a contact angle of 122^0. The ball-like water droplet remained unchanged for 60 seconds, and then the water droplet suddenly disappeared. On the other hand, the treated fabric absorbed the water droplet as the droplet immediately touched the fabric surface. It requires 9 seconds for the water droplet to absorb completely into the fabric, while the silica-chitosan-treated fabric requires 2-4 seconds. It suggests that coating fabric with silica-chitosan enhances surface energy and hydrophilicity.

4. Conclusions

Chitosan and sodium silicate were used to create a silica-chitosan nanocomposite. This research investigated the morphology, particle distribution, functional groups, and prospective applications of silica-chitosan nanocomposites in modified polyesters. The pH condition and the chitosan concentration affected particle growth. The optimal conditions for making nanocomposites during the synthesis process were pH 3 and chitosan 0.5%. The application of a silica-chitosan nanocomposite coating to polyester fabrics has been proven to enhance the hydrophilic properties of polyester. Surface modification with silica-chitosan nanocomposites provides an opportunity in the process of functional textile modification but also presents a challenge for future research on the application of bio nanocomposites in the textile industry.

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