Potent environmental-friendly virucidal medical textiles against coronavirus to combat infections during the COVID-19 pandemic

Chayanisa Chitichotpanya\textsuperscript{1,2}, Phasinee Khwanmuang\textsuperscript{1}, Wariya Yamprayoonswat\textsuperscript{3}, Supanit Porntheeraphat\textsuperscript{3}, Anan Jongkaewwattana\textsuperscript{4} and Pisutsaran Chitichotpanya\textsuperscript{5}

Abstract
The sudden outburst of Coronavirus disease 19 or COVID-19 has raised serious awareness about viral contamination on the environment, which is one of the major causes of the disease. Transmission via contaminated surfaces has been recognized as a significant route for spreading the virus. To suppress and control the spread of SARS-CoV-2, potent virucidal finishing agents for decontamination of medical textiles are urgently required. In this study, an environmental-friendly, economical, non-toxic, and practical finishing on medical textiles with potent virucidal activity was proposed with the combined concepts of a new green synthesis of TiO\textsubscript{2}@Ag core-shell nanostructures using ascorbic acid reduction and UV-curing process. In order to evaluate efficiency of virucidal activity, effects of the amount of TiO\textsubscript{2}@Ag NPs and contact time were
determined against the coronavirus following ISO 18184:2019 standard. The finishing agent exhibited an excellent 99.9% virucidal efficacy. The stability of virucidal activity and mechanical properties were determined under repeated washing. The finished fabrics had the ability to retain their virucidal activity and tensile strength through 20 washes. The results suggested that the finishing agent had great potential as a potent and non-toxic virucide against the coronavirus for medical textile applications.

Keywords
Titanium dioxide, silver nanoparticles, antiviral activity, covid-19, medical textile

Introduction
Medical textiles are used in the manufacturing of personal protective clothing for healthcare workers (HCWs) or medical applications, specifically to mitigate the risks from exposure to hazardous substances and pathogens, and hence the risk of cross-infections. Several different types of medical textile products include aprons, gowns, coveralls, masks, as well as drapes and bedding textiles for healthcare settings. Unfortunately, the virus has been found to persist in on textile surfaces for up to 2 days, therefore protective textiles for the Covid-19 pandemic is urgently necessitated. A strategy to control the viral contamination on the medical textiles is to impart the antiviral functions to the materials through functional finishing. So far, few researchers have attempted to develop these antiviral textiles. For instance, cuprous oxide impregnated medical textiles were found to reduce infectious titers of the HCoV-229E by more than 99% in 2 h of exposure. Chlorinated, nonwoven fabrics exhibited a promising antiviral efficiency, achieving 7 log PFU reductions of a virus (T7 bacteriophages) within 5 min of contact. Additionally, functionalized carbon nanomaterials have been shown to exhibit antiviral activity against SARS-CoV-2 and the human coronavirus HCoV-229E.

Besides its well-known antibacterial and antifungal broad-spectrum activity, several studies have reported the potent antiviral activity of silver nanoparticles (AgNPs) and titanium dioxide (TiO2) against viruses such as the respiratory syncytial virus (RSV), the influenza virus, the Norovirus, the Hepatitis B virus (HBV), the Human immunodeficiency virus (HIV), the SARS-CoV, and the SARS-CoV-2. However, recent studies have shown the development of viral and bacterial resistance to AgNPs. The deposition onto or doping of AgNPs into TiO2 exhibits the synergistic effect of Ag-TiO2 under visible light, producing excellent antibacterial activity (Figure 1). The enhanced antibacterial efficiency can be explained by a combination of the reactive oxygen species (ROS) generated by the TiO2, and the release of Ag+ from the photocatalytic activity.

So far, there have been a few studies that were conducted and reported based on effectiveness of silver-doped TiO2 against virus. The Ag/TiO2 film was proved to be extremely effective against H1N1 virus and enterovirus type 71, with almost a 100% virucidal efficacy. This film was found to be significantly more active than pure TiO2.
In addition, Ma et al.\textsuperscript{23} demonstrated that different types of TiO\textsubscript{2} particles decorated with AgNPs had important impacts on photocatalytic and antibacterial activity by comparing Ag-TiO\textsubscript{2} with three nanostructures: AgNPs deposited onto TiO\textsubscript{2} (Ag-TiO\textsubscript{2}), AgNP/TiO\textsubscript{2} nanocomposite, and a TiO\textsubscript{2}@Ag core-shell nanostructure (Figure 2). The TiO\textsubscript{2}@Ag core-shell nanostructures were found to exhibit the highest photocatalytic and antibacterial activity, reflecting the concentration of AgNPs on the TiO\textsubscript{2} surface. To date, there have not been any studies of antiviral activity on any viruses, let alone the coronavirus, of the TiO\textsubscript{2}@Ag core-shell nanostructures. During the COVID-19 outbreak, the Thai government raced to speed up care amid the overwhelming demand for field hospital beds. Due to its cost-effective and ease of maintenance, polyester (e.g. poly(ethylene terephthalate), PET) textiles are one of the most important used textiles in healthcare settings during this crisis. To take this study into practice for the purpose of reducing infection in field hospitals, the virucidal activity of finished medical textiles was tested against coronavirus. Therefore, the objectives of this study is to evaluate the virucidal efficacy of TiO\textsubscript{2}@Ag core-shell nanostructures finished on PET fabrics against the coronavirus following ISO 18184:2019 standard as well as its stability after multiple standard washings.

TiO\textsubscript{2}@Ag core-shell NPs were deposited on polyester fabrics using UV-curable waterborne polyurethane (UV-curable WPU) as a polymeric binder to ensure adhesion and durability of antiviral textiles.\textsuperscript{24,25} Our virucidal functional finishing formulation offers several environmental-friendly benefits: (1) TiO\textsubscript{2}@Ag core-shell nanostructures were synthesized via a new green process using ascorbic acid reduction. (2) UV-curable WPU as a polymeric binder was used because of its eco-friendly, non-toxic, and non-flammable nature. (3) UV-curable WPU consumes less energy due to shorter curing time, leading to a significant cost saving.

**Materials and methods**

**Materials**

Silver nitrate (AgNO\textsubscript{3}) was sourced from Sigma-Aldrich (Bangkok, Thailand) and titanium dioxide (Degussa P-25) from Evonik Degussa. L-ascorbic acid and sodium hydroxide (NaOH) were purchased from RCI-Labscan (Bangkok, Thailand). A PET plain
A commercial radiation curable WPU was obtained from Allnex (Thailand) Ltd. (Bangkok, Thailand). The surrogate coronavirus used in this study is porcine epidemic diarrhea virus (PEDV) strain AVCT12 that has been modified to harbor the mCherry fluorescent protein in the open reading frame of the ORF-3 gene. The virus was rescued by reverse genetics has previously described. Virus propagation was performed in human hepatocarcinoma (Huh-7) cells as described. The virus titer was normalized to 10⁵ TCID50/ml before using in all subsequent experiments.

**Experimental**

**Synthesis of Ag seed TiO₂ (AST) powder**

AgNPs seeded TiO₂ was prepared using ascorbic acid reduction. L-ascorbic acid solution 6x10⁻⁵ M, 50 mL was adjusted to pH 11 by NaOH 0.1 M. Then, 0.200 g. of TiO₂ was added into ascorbic acid solution, and sonicated by ultrasonic probe 1800 watts (BANDELIN electronic, 60% of power) for 2 min. Next, 5.0 mL of 0.01 M AgNO₃ was added into TiO₂ colloid and stirred for 120 min. The colloid was decant and then washed with deionized water (DI water) 25 mL for 3 times. And, the AgNPs seeded TiO₂ was dried by freeze dry machine for 24 h.

**Green synthesis of TiO₂@Ag core-shell nanostructure**

AST powder 0.02 g. was added into ascorbic acid solution pH 11 and sonicated by ultrasonic probe (BANDELIN electronic, 30% of power) for 60 s. Then, 100–500 μL of 0.01 M AgNO₃ was added into AST colloid and stirred for 24 h. Next, the TiO₂@Ag core shell was centrifuged (5000 rpm/min, 15 min), and washed with DI water 25 mL for 3 times. Finally, the TiO₂@Ag core-shell was dried by oven at 80°C for 24 h. Then, the particle sizes and zeta potentials of core-shell were determined using Zetasizer instrument (Model nano ZS, Malvern Instruments Ltd, UK). Their oxidation states were investigated by X-ray Photoelectron Spectroscopy (XPS). In addition, their morphology was
investigated by Transmission Electron Microscope (TEM, JEM 2100F, JEOL Inc., USA). For TEM measurement, 20 µL of core-shell dispersed in DI water was dropped on formvar-coat Cu grids. The excess solution was removed by filter paper, and then the samples were evaporated at 80°C for 15 min.

**Preparation of virucidal medical textiles**

TiO$_2$@Ag/WPU nanocomposite solutions were prepared with WPU content of 20% wt. Scoured polyester fabric samples were sprayed with TiO$_2$@Ag/WPU solutions and cured via spray applicator equipped with UV as shown in Figure S1 (see Supplementary Materials). The specification of spray applicator equipped with UV-curing system are as the following: 6 Nozzles (a distance of 200 mm between each nozzle) with a spray width of 130 mm, a spray angle of 65°, a distance of 275 mm between the nozzle and the fabric, and droplet sizes of 15–40 µm; UV-curing time of 60 s; UV-A, B, C: an electric power of 464.0 watts and an output power of 128.4 watts.

**Antiviral assay (ISO 18184:2019 standard)**

Fabric samples treated with TiO$_2$@Ag/WPU nanocomposite as well as untreated control were cut to 1.5 cm x 1.5 cm dimension and irradiated with UV-C in the biosafety cabinet on both sides for 5 min each (Figure S2, see Supplementary Materials). Subsequently, samples were placed individually in a 24-well plate. Viral sample (100 µl) was dropped on top of the sample to cover the surface area of the fabric for different contact time points ranging from 30, 45, 60, and 120 min at room temperature. At the end of each time point, the well was supplemented with 1 ml of culture media (Opti-MEM) to release the virus. The media containing residual virus was then used to adsorb onto confluent Huh-7 cell monolayer in a 24-well plate for 30 min at 37°C. After the incubation, the media was removed and cells were washed five times with 1x phosphate buffered saline (PBS). Cell monolayers were then cultured in Opti-MEM containing trypsin (2 µg/ml). At 24–48 h after infection, cells were monitored for the mCherry expression under the fluorescence microscope. Syncytial formation with the mCherry expression was scored as indication of virus replication.

**Cell toxicity test**

Fabric samples were incubated with Opti-MEM for 120 min. Subsequently, the media was added onto Huh-7 cell monolayer for 1 h. Cells were washed with 1xPBS twice before supplemented with Opti-MEM containing 10% fetal bovine serum (FBS). Cells were monitored for changes in morphology daily until 72 h.

**RT-PCR of PEDV viral RNA**

Cell supernatants from infected monolayers were harvested at 24 h after infection and subjected to viral RNA extraction (Geneaid) following manufacturer’s instruction. Equal
volume of RNA was subjected to one-step RT-PCR using primer specific for PEDV N sequence. PCR product was analyzed by gel electrophoresis.

**Whiteness index and mechanical properties**

A spectrophotometer (GretagMacbeth LLC, Switzerland) was used to investigate the CIE Whiteness Index (WI) of the functionalized fabrics. The apparatus settings were the following: illuminant D65, 10° standard observer, including specular and UV. The samples were measured three times and average values were calculated.

The tensile strength and % elongation at break of fabric samples were determined using an Instron tensile tester (Instron 5567) following ASTM D 5035-95. The fabric stiffness was measured using a Handle-O-Meter tester (Model 211–300) following ASTM D6828-02. The samples were measured five times and average values were calculated.

**Washing fastness**

The stability of antiviral activity and tensile strength of finished fabrics after repeated standard washing (AATCC test method 61–1996) were evaluated after washing for 10 and 20 cycles.

**Results and discussion**

**Green synthesis of TiO₂@Ag core-shell nanostructure**

A new eco-friendly synthesis process of TiO₂@Ag core-shell nanostructure, using ascorbic acid was presented. TiO₂@Ag was prepared via the growth of AgNPs on TiO₂NPs surfaces, using ascorbic acid reduction. A schematic of the preparation process was shown in Figure 3. First, the agglomerated TiO₂NPs were separated using ultrasonic probe to form smaller groups 163.2±1.5 nm in size. Next, the TiO₂NPs were dispersed in ascorbic acid solution of pH 11, resulting in a negative charge on the surface of TiO₂. AgNO₃ was added. Ag⁺ were dispersed, distributed close to the negatively charged side of the TiO₂NPs and converted to Ag⁰ nuclei by ascorbic acid reduction. Ag⁰ nanoclusters were formed and adsorbed onto the TiO₂NPs surfaces, creating Ag seed TiO₂ (AST). The AST was then re-dispersed in ascorbic acid solution and AgNO₃ was added. The Ag⁰ nanoclusters on the TiO₂NPs surface grew and changed to AgNPs, forming TiO₂@Ag.

For creating Ag seed TiO₂ (AST) step, 5.0 mmol of AgNO₃ was added into TiO₂NPs colloids. The color of TiO₂NPs changed from white to light violet that corresponded to nuclei of AgNPs generation on TiO₂ surfaces. Then, AST was precipitated and used as initial AgNP creator for synthesized TiO₂@Ag. To prepare TiO₂@Ag, AST was re-dispersed in ascorbic acid solution and then AgNO₃ at different concentrations was added for growing AgNPs on TiO₂ particles. Four different AgNO₃ concentrations including 0.10, 0.15, 0.25, and 0.50 mmol were investigated. The sample with concentration greater than 0.50 mmol of AgNO₃ presented the silver platelet of micro-particles in colloid during AgNPs growing process. The formation of AgNPs on the TiO₂ surface led to the color
change due to surface plasmon resonance (SPR). Figure 4(a) show the color of AgNPs that was formed using ascorbic acid. It presents dark violet with a size of nm 5.51±1.5 in diameter. These AgNPs was size smaller than that of Qin et al. reported. For the formation of AgNPs onto TiO2 surface, the NPs changed from white to violet, darkening as the AgNO3 concentration increased, due to the formation of AgNPs increased (Figure 4(b)).

Table 1 showed the amount of AgNPs adsorbed on TiO2NPs surface of AST and TiO2@Ag (AA) with different AgNO3 concentration. These amounts were determined by the chemical extraction. The 20.0 mg of samples were soaked in 5%v/v of nitric acid 20.0 mL for 24 h. AgNPs were converted to Ag⁺ by oxidation process. The equations are illustrated as follow:

\[ 4\text{Ag(s)} + 4\text{H}_3\text{O}^+ + \text{O}_2 \rightarrow 4\text{Ag}^+ + 6\text{H}_2\text{O} \]

After extraction, the concentration of Ag⁺ in the solution was determined using a Graphite Furnace Atomic absorption Spectrometer (GF-AAS). As a result, the amount of AgNPs on the TiO2NPs increased from 0.90 to 2.76%wt with an increase in AgNO3.
addition (0.10–0.50 mmol). While the AgNO3 addition increased, the charge changed from $\pm 33.4$ to $\pm 27.1$ mV. These charges suggested that TiO2@Ag NPs were stable in the medium. With increasing AgNO3 content, the charge of nanocomposite led to positive side due to decreasing degree of uniformity of Ag deposited onto TiO2NPs, as agreeing well with Miyagi et al.\textsuperscript{30}

The morphology of the TiO2@Ag was investigated using TEM. As shown in Figure 5(a), TiO2NPs with a size of 25–30 nm agglomerated into a small group 163.2 ± 1.5 nm in diameter. Figure 5(b) showed the AST, Ag\textsuperscript{0} nanoclusters (dark spot) dispersed evenly across the TiO2 particle surface. The Ag\textsuperscript{0} nanoclusters were small, with a uniform size of 1–3 nm. Figure 5(c)–(d) shows the formation of TiO2@Ag. Ag\textsuperscript{0} nanoclusters grew on the TiO2, increasing in size from 1 to 3 nm to 5 to 8 nm. As a result, the size of TiO2@Ag increased from 163.2 to 191.0 nm. The amount of AgNPs corresponded to the Ag\textsuperscript{0} nanoclusters seed. These seeds were initial sites that induced the growth of AgNPs. At the same amount of Ag\textsuperscript{0} nanoclusters seed, the increased of AgNO3 addition provided the large size of particle.

Further investigation, the oxidation state of Ti and Ag in the TiO2, AST, and Ag-TiO2 nanocomposite was investigated by XPS. Figure 6(a)-(c) showed the XPS spectrum of Ti (2p) of TiO2 component. There are two main peaks in the Ti (2p) binding energy region. Ti\textsuperscript{4+} located at binding energy of 458.8 and 464.8 eV for Ti (2p\textsubscript{1/2}) and Ti (2p\textsubscript{3/2}), respectively. The slitting between Ti (2p\textsubscript{1/2}) and Ti (2p\textsubscript{3/2}) levels is 6.0 eV, confirming a normal state of Ti\textsuperscript{4+} in the anatase of TiO2.\textsuperscript{31,32} And, the additional peak at 457.7 and

| No. | Sample | Added [AgNO\textsubscript{3}] mmol | [Ag] %wt | Particle size (nm) | Zeta potential (mV) |
|-----|--------|-----------------------------------|----------|-------------------|---------------------|
| 1   | TiO2   | —                                 | —        | 163.2 ± 1.5       | −33.4 ± 1.2         |
| 2   | AST    | 0.00                              | 0.90 ± 0.02 | 177.3 ± 3.6   | −31.5 ± 0.7         |
| 3   | AA 0.10| 0.10                              | 1.49 ± 0.02 | 176.5 ± 2.8     | −31.4 ± 0.3         |
| 4   | AA 0.15| 0.15                              | 1.54 ± 0.01 | 176.2 ± 1.2     | −29.1 ± 0.1         |
| 5   | AA 0.25| 0.25                              | 2.44 ± 0.02 | 181.0 ± 1.1     | −28.3 ± 0.2         |
| 6   | AA 0.50| 0.50                              | 2.76 ± 0.00 | 191.0 ± 1.9     | −27.1 ± 0.3         |

Figure 4. Appearances of (a) AgNPs and (b) TiO2@Ag dispersed in ascorbic acid solution at different AgNO\textsubscript{3} concentrations.
463.3 eV were attributed to present a small amount of Ti$^{3+}$, due to the incorporation of Ag$^0$, Ag$_2$O, and AgO on the TiO$_2$ 32-34, as shown in Figure 6(c). For the chemical state of Ag, the major components were in Ag$^0$ (metallic state) of AST and Ag-TiO$_2$ nanocomposite as seen in Figure 7(a)-(b). The binding energy of Ag (3d$_{5/2}$) located at 367.8 and 373.8 eV. The minor component, which appeared at 368.5 eV, was assigned to Ag-O (Ag$^{2+}$) due to the binding between a positive charge of Ag and the anionic oxygen of TiO$_2$. 31,32,34 Moreover, both samples presented the deconvoluted peak at 366.6 eV that corresponded to Ag (3d$_{5/2}$) of Ag$_2$O (Ag$^{+}$). 32 However, the results confirmed the major state of Ag onto TiO$_2$ was AgNPs (Ag$^0$).

**Determination of virucidal efficacy of TiO$_2$@Ag/WPU finished on fabric**

In order to determine the virucidal efficacy of these synthesized TiO$_2$@Ag NPs, TiO$_2$@Ag/WPUs, nanocomposite finishing solutions with different AgNO$_3$ concentrations (0.10, 0.15, and 0.25) were prepared using WPU content of 20%wt as a binder. Then, the sample fabrics were finished with these solutions (S0, SW, S0.10, S0.15, and S0.25). S0 represents untreated fabric samples, SW treated with only WPU, S0.10 treated with AA 0.10/WPU, S0.15 treated with AA 0.15/WPU, and S0.25 treated with AA 0.25/WPU. The antiviral activity test was performed against porcine epidemic diarrhea virus (PEDV)
Figure 6. Deconvolution of Ti (2p) XPS spectrum of (a) TiO$_2$, (b) AST, and (c) TiO$_2$@Ag
strain AVCT12 as a surrogate coronavirus. Effects of concentration of TiO$_2$@Ag nanocomposites and contact time on antiviral activity were determined.

**Cell toxicity test**

All fabric samples did not release toxic chemicals upon incubation with the media. Figure 8 showed cell morphology 72 h after incubating with media contacted with the sample.
Antiviral assay

The viral replication, based on the formation of red syncytia, was examined under the fluorescence microscope. As depicted in the Figure 9 and Table 2 below, S0 and SW could not inhibit virus replication at all contact time points, while S0.25, S0.15, and S0.10 showed varied degrees of inhibition. It is notable that S0.25 showed the highest efficiency of virus replication inhibition. Significant inhibition, as compared to S0 and SW, could be observed in S0.25 as early as 30 min of contact time, with the complete inhibition could be observed at 60 and 120 min. S0.15 showed moderate inhibition with the complete inhibition observed at 120 min of contact time. S0.10, despite showing some degree of inhibition, could not completely inhibit virus replication at all contact time points. Taken together, the sets of data indicate that S0.25 is the optimal fabric sample that can effectively inhibit our surrogate coronavirus replication with a 99.9% virucidal efficacy.

To further validate the inhibition of virus replication, supernatants were harvested from each sample at the contact time point of 60 and 120 min. Viral RNA was extracted from the supernatants and subjected to RT-PCR analysis using primers specific for PEDV N gene. As shown in Figure 10, while clear bands could be detected at both contact time points in S0 and SW samples, significantly reduced band intensity was detected in all samples. Samples that showed complete inhibition in the syncytium formation correlate with the intensity of the RT-PCR band. These data thus strengthen the conclusion that TiO$_2$@Ag NPs finished on the fabric samples could inactivate the coronavirus upon contact, rendering the virus unable to replicate in host cells.

Whiteness Index (WI) and Mechanical Properties

The WI, fabric stiffness, tensile strength, and %elongation at break of the S0, SW, S0.10, S0.15, and S0.25 are shown in Table 3. The WI is not affected by treatment with WPU as
WI values of S0 (WI = 82.46) and WI values of SW (WI = 82.15) are quite the same. However, S0.10, S0.15, and S0.25 exhibit changes in whiteness in comparison to the S0 and SW samples. As the content of TiO$_2$@Ag NPs increased, a slight reduction in WI

![Figure 9. Viral replication was examined under the fluorescence microscope.](image)

Table 2. Data of syncytia number in each well of treatment.

| Contact time (min) | S0  | SW  | S0.25 | S0.15 | S0.1 |
|-------------------|-----|-----|-------|-------|------|
| 30                | >50 | >50 | 25    | >50   | >50  |
| 45                | >50 | >50 | 10    | 20    | >50  |
| 60                | >50 | >50 | 0     | 10    | >30  |
| 120               | >50 | >50 | 0     | 0     | 5    |

WI values of S0 (WI = 82.46) and WI values of SW (WI = 82.15) are quite the same. However, S0.10, S0.15, and S0.25 exhibit changes in whiteness in comparison to the S0 and SW samples. As the content of TiO$_2$@Ag NPs increased, a slight reduction in WI
was observed for all finished fabrics due to the surface plasmon resonance on the TiO$_2$@Ag NPs surface.\textsuperscript{20}

The TiO$_2$@Ag/WPU finishing solutions can improve the mechanical properties of PET fabrics in comparison to S0 and SW samples. It is suggested that both TiO$_2$@Ag and WPU contents had a slight effect on the tensile properties of the finished fabrics. The fabric stiffness were found to significantly increase after treated with WPU and further increased with increasing TiO$_2$@Ag NP contents. As nanofillers in the WPU matrix, TiO$_2$@Ag NPs restricted the mobility of polymer chains, resulting in the enhancement of the tensile property of the treated fabrics as well as the stiffness. This is achieved because TiO$_2$@Ag NPs have great binding affinity with –COO and –NH groups in WPU.

**Table 3.** Whiteness index, stiffness, tensile strength, and \% elongation at break of fabric samples.

| Samples | Whiteness index (WI) | Stiffness (g) | Tensile strength (MPa) | \% elongation at break |
|---------|----------------------|---------------|------------------------|------------------------|
|         |                      | Warp | Weft | Warp | Weft |
| S0      | 82.46 ± 1.89         | 135  | 9.81 ± 0.65 | 7.26 ± 0.54 | 31.12 ± 0.83 | 28.56 ± 0.77 |
| SW      | 82.15 ± 2.04         | 170  | 10.42 ± 0.32 | 8.03 ± 0.41 | 30.03 ± 1.06 | 27.99 ± 0.39 |
| S0.10   | 80.26 ± 1.77         | 178  | 10.63 ± 1.14 | 8.25 ± 0.47 | 29.23 ± 0.99 | 27.34 ± 1.04 |
| S0.15   | 79.93 ± 2.45         | 182  | 10.78 ± 0.85 | 8.46 ± 1.02 | 28.88 ± 1.09 | 27.11 ± 0.79 |
| S0.25   | 79.15 ± 1.59         | 188  | 10.86 ± 0.65 | 8.59 ± 0.69 | 27.96 ± 0.84 | 26.94 ± 0.86 |

**Figure 10.** RT-PCR analysis.

The TiO$_2$@Ag/WPU finishing solutions can improve the mechanical properties of PET fabrics in comparison to S0 and SW samples. It is suggested that both TiO$_2$@Ag and WPU contents had a slight effect on the tensile properties of the finished fabrics. The fabric stiffness were found to significantly increase after treated with WPU and further increased with increasing TiO$_2$@Ag NP contents. As nanofillers in the WPU matrix, TiO$_2$@Ag NPs restricted the mobility of polymer chains, resulting in the enhancement of the tensile property of the treated fabrics as well as the stiffness. This is achieved because TiO$_2$@Ag NPs have great binding affinity with –COO and –NH groups in WPU.
chains.\textsuperscript{33,35,36} It was apparent that TiO$_2$@Ag/WPU finishing lowered the %elongation of untreated PET fabric under tension in both warp and weft directions. The elongation at break slightly decreased with increasing contents of TiO$_2$@Ag NPs as the presences of these NPs resulted in less deformation than that of pure WPU.\textsuperscript{19,34}

**Washing fastness**

To determine the stability of antiviral activity and mechanical properties, the S0.25 sample was chosen to be investigated as it exhibited optimal antiviral activity. The S0.25 samples were prepared and washed for 10 and 20 cycles following AATCC test method 61-1996. The evaluation of antiviral activity and tensile strength under multi-washing are presented in Table 4.

After repeated standard washing, the S0.25 samples showed excellent washing fastness regarding both antiviral activity and tensile strength. The finished fabrics were found to retain their virucidal activity and tensile strength through 20 washes. It showed a high %reduction of 99.9 after 20 washing cycles, and suggested the strong adhesion between WPU and PET fibers. WPU therefore serves as good three-dimensional matrix for the high-density loading of TiO$_2$@Ag NPs.

**Conclusion**

We proposed an environmental-friendly, economical, non-toxic, and practical finishing on medical PET textiles with potent virucidal activity as a result of this study. It combines the concepts of a new green synthesis of TiO$_2$@Ag core-shell nanostructures using ascorbic acid reduction and UV-curing process. TiO$_2$@Ag NPs were successfully synthesized, and were shown to be 163.2 to 191.0 nm in diameter. Effects of the amount of TiO$_2$@Ag NPs and contact time on virucidal activity against coronavirus following ISO 18184:2019 standards were determined. The finishing agent exhibited excellent antiviral activity of 99.9\% virucidal efficacy. The effectiveness of which corresponded to the increasing amount of AgNPs adsorbed onto the TiO$_2$. The stability of virucidal activity and mechanical properties were determined under repeated washing, and the finished fabrics were found to retain their virucidal activity and tensile strength through 20 washes.

| Samples | Washing cycles | % Viral reduction | Tensile strength (MPa) |
|---------|----------------|-------------------|------------------------|
|         |                |                   |                        |
|         |                |                   | Warp                   |
|         |                |                   | Weft                   |
| S0      | 0              | N/A               | 9.81 ± 0.65            |
|         |                |                   | 7.26 ± 0.54            |
| SW      | 0              | N/A               | 10.42 ± 0.32           |
|         |                |                   | 8.03 ± 0.41            |
| S0.25   | 0              | 99.9              | 10.86 ± 0.65           |
|         | 10             | 99.9              | 10.75 ± 0.88           |
|         | 20             | 99.9              | 10.69 ± 0.82           |
|         |                |                   | 8.38 ± 0.91            |

Table 4. Washing fastness to virucidal activity and tensile strength of finished samples.
The results suggested that this finishing agent had high potential as a virucide against coronavirus for medical textile applications.

**Acknowledgements**

The authors gratefully acknowledge Thailand Center of Excellence for Life Sciences (TCELS) [grant no. TC48/63] and the Thailand research fund [grant no. IRG5980007] and for the financial support.

**Declaration of conflicting interests**

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

**Funding**

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the Thailand Center of Excellence for Life Sciences (TCELS) [grant no. TC48/63] and the Thailand research fund [grant no. IRG5980007].

**ORCID iDs**

Chayanisa Chitichotpanya  [https://orcid.org/0000-0003-1149-8396](https://orcid.org/0000-0003-1149-8396)
Wariya Yamprayoonswat  [https://orcid.org/0000-0001-7793-3819](https://orcid.org/0000-0001-7793-3819)

**Supplemental Material**

Supplemental material for this article is available online.

**References**

1. Karim N, Afroj S, Lloyd K, et al. Sustainable personal protective clothing for healthcare applications: a review. *ACS Nano* 2020; 14: 12313–12340.
2. Chin AWH, Chu JTS, Perera MRA, et al. Stability of SARS-CoV-2 in different environmental conditions. *Lancet Microbe* 2020; 1: e10. DOI: 10.1016/S2666-5247(20)30003-3.
3. Borkow G, Salvatori R and Kanmukhla VK. Drastic Reduction of Bacterial, Fungal and Viral Pathogen Titers by Cuprous Oxide Impregnated Medical Textiles. *J Funct Biomater* 2021; 12: 9.DOI: 10.3390/jfb12010009.
4. Ma Y, Wisuthiphaet N, Bolt H, et al. N-Halamine polypropylene nonwoven fabrics with rechargeable antibacterial and antiviral functions for medical applications. *ACS Biomater Sci Eng* 2021; 7: 2329–2336. DOI: 10.1021/acsbiomaterials.1c00117.
5. Galante AJ, Yates KA, Romanowski EG, et al. Coal-derived functionalized nano-graphene oxide for bleach washable, durable antiviral fabric coatings. *ACS Applied Nano Materials* 2022; 5: 718–728. DOI: 10.1021/acsaenm.1e03448.
6. Łoczechin A, Séron K, Barras A, et al. Functional carbon quantum dots as medical countermeasures to human coronavirus. *ACS Appl Mater Interfaces* 2019; 11: 42964–42974.
7. Agrawal N, Mishra P, Ranjan R, et al. Nano-cubes over nano-spheres: shape dependent study of silver nanomaterial for biological applications. *Bulletin of Materials Science* 2021; 44: 44. DOI: 10.1007/s12034-021-02487-2.

8. Choudhary S, Kumar R, Dalal U, et al. Green synthesis of nanometal impregnated biomass-antiviral potential. *Mater Sci Eng C* 2020; 112: 110934.

9. Galdiero S, Falanga A, Vitiello M, et al. Silver nanoparticles as potential antiviral agents. *Molecules* 2011; 16: 8894–8918.

10. Hamza R, Gobouri A, Al-Yasi H, et al. A new sterilization strategy using TiO$_2$ Nanotubes for production of free radicals that eliminate viruses and application of a treatment strategy to combat infections caused by emerging SARS-CoV-2 during the COVID-19 pandemic. *Coatings* 2021; 11: 680.

11. Jeremiah S, Miyakawa K, Morita T, et al. Potent antiviral effect of silver nanoparticles on SARS-CoV-2. *Biochem Biophys Res Commun* 2020; 533: 195–200.

12. Salleh A, Naomi R, Utami N, et al. The potential of silver nanoparticles for antiviral and antibacterial applications: a mechanism of action. *Nanomaterials* 2020; 10: 1566.

13. Talebian S, Wallace G, Schroeder A, et al. Nanotechnology-based disinfectants and sensors for SARS-CoV-2. *Nat Nanotechnol* 2020; 15: 618–621.

14. Teirumnieks E, Balchev I, Ghalot R, et al. Antibacterial and anti-viral effects of silver nanoparticles in medicine against COVID-19-a review. *Laser Phys* 2021; 31: 013001.

15. Tong Y, Shi G, Hu G, et al. Photo-catalyzed TiO$_2$ inactivates pathogenic viruses by attacking viral genome. *Chem Eng J* 2021; 414: 128788.

16. Zhou J, Hu Z, Zabihi F, et al. Progress and perspective of antiviral protective material. *Advanced Fiber Materials* 2020; 2: 123–139.

17. Panáček A, Kvítek L, Smékalová M, et al. Bacterial resistance to silver nanoparticles and how to overcome it. *Nat Nanotechnol* 2018; 13: 65–71.

18. Silver S, Phung L and Silver G. Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds. *J Ind Microbiol Biotechnol* 2006; 33: 627–634.

19. Chitichotpanya P, Inprasit T and Chitichotpanya C. In vitro assessment of antibacterial potential and mechanical properties of Ag-TiO$_2$/WPU on medical cotton optimized with response surface methodology. *J Nat Fibers* 2017; 16: 1408520.

20. Khwanmuang P, Rotjanapan P, Phuphuakrat A, et al. In vitro assessment of Ag-TiO$_2$/polyurethane nanocomposites for infection control using response surface methodology. *React Funct Polym* 2017; 117: 120–130.

21. Moongraksathum B, Chien M and Chen Y. Antiviral and antibacterial effects of silver-doped TiO2 prepared by the peroxy Sol-Gel method. *J Nanosci Nanotechnol* 2019; 19: 7356–7362.

22. Liga MV, Bryant EL, Colvin VL, et al. Virus inactivation by silver doped titanium dioxide nanoparticles for drinking water treatment. *Water Res* 2011; 45: 535–544. DOI: 10.1016/j.watres.2010.09.012.

23. Ma J, Guo X, Zhang Y, et al. Catalytic performance of TiO$_2$@Ag composite prepared by modified photodeposition method. *Chem Eng J* 2014; 258: 247–253.

24. Noreen A, Zia K, Zuber M, et al. Recent trends in environmentally friendly water-borne polyurethane coatings: A review. *Korean J Chem Eng* 2016; 33: 388–400.

25. De Smet D, Wéry M, Uyttendaele W, et al. Bio-Based Waterborne PU for Durable Textile Coatings. *Polymers* 2021; 13: 4229. DOI: 10.3390/polym13234229.
26. Jengarn J, Wongthida P, Wanasen N, et al. Genetic manipulation of porcine epidemic diarrhoea virus recovered from a full-length infectious cDNA clone. *J Gen Virol* 2015; 96: 2206–2218.

27. Wanitchang A, Saenboonrueng J, Kaewborisuth C, et al. A single V672F substitution in the spike protein of field-isolated PEDV promotes cell fusion and replication in VeroE6 cells. *Viruses* 2019; 11: 282.

28. Qin Y, Ji X, Jing J, et al. Size control over spherical silver nanoparticles by ascorbic acid reduction. *Colloids Surf A Physicochem Eng Asp* 2010; 372: 172–176.

29. Dehnavi A, Aroujalian A, Raisi A, et al. Preparation and characterization of polyethylene/silver nanocomposite films with antibacterial activity. *J Appl Polym Sci* 2013; 127: 1180–1190.

30. Miyagi T, Kamei M, Misuhashi T, et al. Charge separation at the rutile/anatase interface: a domain factor of photocatalytic activity. *Chem Phys Lett* 2004; 390: 399–402.

31. Akhavan O and Ghaderi E. Self-accumulated Ag nanoparticles on mesoporous TiO₂ thin film with high bactericidal activities. *Surf Coat Tech* 2010; 204: 3676–3683.

32. Jaiswal S, McHale P and Duffy B. Preparation and rapid analysis of antibacterial silver, copper and zinc doped sol–gel surfaces. *Colloids Surf B Biointerfaces* 2012; 94: 170–176.

33. Qu R, Gao J, Tang B, et al. Preparation and property of polyurethane/nanosilver complex fibers. *Appl Surf Sci* 2014; 294: 81–88.

34. Wattanodorn Y, Jenkan R, Atornjitjawat N, et al. Antibacterial anionic waterborne polyurethanes/Ag nanocomposites with enhanced mechanical properties. *Polym Test* 2014; 40: 163–169.

35. Hong SM, Kim JW, Knowles JC, et al. Facile preparation of antibacterial, highly elastic silvered polyurethane nanofiber fabrics using silver carbamate and their dermal wound healing properties. *J Biomater Appl* 2017; 31: 1026–1038.

36. Chen J, Wang Q, Luan M, et al. Polydopamine as reinforcement in the coating of nano-silver on polyurethane surface: Performance and mechanisms. *Prog Org Coat* 2019; 137: 105288. DOI: 10.1016/j.porgcoat.2019.105288.