TEKSTİL VE KONFEKSİYON

Vol: 31, No: 3

DOI: 10.32710/tekstilvekonfeksiyon.717601

Production and Characterization of N-Halamine Based Polyvinyl Chloride (PVC) Nanowebs

Batuhan ÇOBANOĞLU[1,2] 0000-0002-5508-1739
Fatma Nur PARIN[1*] 0000-0003-2048-2951
Kenan YILDIRIM[1*] 0000-0002-1591-1988

[1]Bursa Technical University / Department of Polymer Materials Engineering / Yildirim, Bursa, Turkey
[2]RB Karesi Textile, Yildirim, Bursa, Turkey

Corresponding Author: Fatma Nur Parın, nur.parin@btu.edu.tr

ABSTRACT

Antibacterial agent N-halamine, 7,7,9,9-tetramethyl-1,3,8-triazaspiro [4.5]-decane-2,4-dione (TTDD), was synthesized, and it was added into the polyvinyl chloride (PVC) nanoweb. A versatile, and relatively simple method, electrospinning, was used to fabricate continuous and uniform nanowebs. 7,7,9,9-tetramethyl-1,3,8-triazaspiro [4.5]-decane-2,4-dione (TTDD) is a cyclic N-halamine that can be chlorinated easily due to three functional groups (imide, amide, and amine). Therefore, TTDD was preferred for PVC regarding having high stability, non-toxic, non-irritant for skin, and renewable. The rechargeable chlorination process was applied to webs using dilute hypochlorite solution. The antibacterial activity of the webs were evaluated using the ASTM 2149 procedure. FTIR, TGA, and SEM were used to investigate the morphology, thermal characteristics, and chemical structures of PVC webs. Scanning electron microscopy (SEM) displayed that the average diameter of the fibers increased with TTDD concentration. The thermal properties of the PVC webs did not changed significantly. All chlorinated webs indicated highly effective antibacterial activities against both *Staphylococcus aureus* and *Escherichia coli* with increased inactivation. Furthermore, the antibacterial efficacy of nanowebs is reformed again by the rechargeable process. The rechargeable chlorination capacity of obtained PVC non-wovens is over > 60% (within 6 hours, in pH 5), for four rechargeable chlorine cycles. The new antibacterial PVC nanowebs have the potential for especially useful in medical applications.

ARTICLE HISTORY
Received: 12.02.2020
Accepted: 03.06.2021

KEYWORDS

Antibacterial efficiency, N-halamine, nanoweb, polyvinylchloride (PVC), electrospinning

1. INTRODUCTION

Microbes are the smallest microorganisms that are a part of daily life and can be found all over the environment and in our bodies [1]. The spread of microorganisms such as bacteria, fungus, algae, and viruses is becoming an increasingly serious problem for healthcare organizations [1, 2]. They are infectious and can cause nosocomial infections in the community if humidity and temperature are optimum [1, 3-5]. Nosocomial infections are usually dangerous to people, and they can be present in everyday products, particularly hospital equipment [6]. Furthermore, washing and disinfection may not be enough to prevent infections, as resistant strains have emerged in recent decades. Antimicrobial agents are being employed in various medical equipment and hospital workers to overcome pathogen-caused hygiene deficiencies [7-10].

In compared to other agents, N-halamines have showed excellent antibacterial activity against Gram-positive and Gram-negative bacteria, fungi, protozoa, and viruses [10-12]. N-halamines can be utilized as biocides due to their long-lasting and rechargeable antibacterial characteristics.

To cite this article: *Çobanoğlu B, Parın FN, Yıldırım K. 2021. Production and characterization of n-halamine based polyvinyl chloride (PVC) nanowebs. Tekstil ve Konfeksiyon, 31(3), 147-155.*

N-halamine structures have one or more nitrogen-halogen covalent bonds and possess unique properties such as high stability over a wide temperature and humidity range, long-term usage, and the ability to be repeatedly regenerated in a chlorine solution [10, 13-19]. As a result, N-halamines could be used in water purification systems, food packaging, coatings, medical devices, the textile industry, hospitals, hygienic products, dental office equipment, and household sanitation.

Electrospinning is regarding a versatile method for fabricating fibrous structures with diameters from micrometers to nanometers [20-24]. Because of the unique properties of electrospun webs like a high specific surface area, high porosity, and low diameter, they need potential use in sterilization applications with fast response behavior [25].

To fabricate protective medical garments, textiles in the form of fibrous structures- non-wovens with antibacterial agents have been widely used for over 20 years [26]. There are several strategies to antibacterial agents such as essential oils, boric acid, chitosan, triclosan, quaternary ammonium salts, and N-halamines addition to non-wovens [21, 27-30]. In this regard, Parın et al. synthesized gelatin nanofibers containing essential orange oil (EOO) and reported antibacterial efficacy against S. aureus bacteria due to the D-limonene component found in orange oil [28]. Chen et al. synthesized and functionalized poly-hexamethylene guanidine (PHMG) using chitosan nanofibers. The resulting nanofibers exhibit a better antibacterial impact against S. aureus and P. aeruginosa bacteria [31]. In another study, Ullah et al. produced fibrous structures by adding silver sulfadiazine (AgSD) to polyacrylonitrile (PAN) [32]. The structures indicated good antibacterial activity against both Escherichia coli and Bacillus. Moreover, Zhang et al. prepared polyurethane/ triclosan coated polylactic acid nonwovens, which were reported to have high antibacterial activity against Staphylococcus aureus and Escherichia coli in a zone test [30]. Zhang et al. reported electrospun PVA fibers modified with quaternary ammonium salt and zwitterionic sulfopropylbetaine showed 99.9% antibacterial efficiency against both gram-positive and gram-negative bacteria [33]. Lv et al. developed antibacterial mats based on AgNPs-loaded starch/PEO nanofibers for medical care. The obtained NFs indicated limited antibacterial activity [34]. So far, studies have revealed that antibacterial agents other than N-halamine compounds have a considerable decrease in bactericidal activity, which is one of the technology's major drawbacks [35].

N-halamine modified electrospun poly(vinyl alcohol) (PVA) membranes for food packaging applications were investigated by Liu et al. The antibacterial activity of the resulting surfaces has been found to be 99.99 percent [36]. In a similar study reported by Tian et al. that PS/PU modified with 5, 5-dimethyl hydantoin which is a N-halamine compound and their study showed high antibacterial efficiency (99.77%) against both E. coli and S. aureus [37]. Ma et al. also developed rechargeable N-halamine based nanofibrous sulfonated-polyethyleneimine (PEI-S) surfaces that exhibited almost 100 % biocidal activity and high disinfection efficiency with 99.9% [38]. 7,7,9,9-tetramethyl-1,3,8-triazaspiro [4.5]-decane-2,4-dione (TTDD) is a cyclic N-halamine. Song mentioned in his PhD thesis that cyclic N-halamines are very efficient, which can last relatively long. Besides, N-halamines with imide functionality exhibit higher biocidal activity than those with amines (imide > amide > amine) [39]. TTDD structure includes these three functional groups. Due to TTDD properties of rechargeable bactericidal action, rapid inactivation rate, and environmental safety, and high durability, TTDD which is synthesized by the halogenation of nitrogen–hydrogen (N–H) bonds-containing precursors, has a lot of potential in the medical field as an antibacterial material [40].

PVC is one of the leading polymers which are commercially important thermoplastic [41]. PVC-based materials have competed with metals, ceramics, glass, and other polymeric materials due to high mechanical strength, excellent physical and chemical durability, low-cost properties [42]. Various studies have been performed on PVC including various antibacterial agents such as zinc oxide (ZnO) [43,44], silver [45], silver zeolite (SZ) [46], and modified silver nanoparticles [46], titanium dioxide (TiO_2) [47]. These agents were introduced to the polymer by various methods of production. Lala et al. fabricated electrospun PVC/$AgNO_3$ fibers [49]. Zampino et al. investigated PVC-silver zeolite composite to produce antibacterial biomedical products [46]. In this study, PVC was incorporated with silver zeolite in various ratios between 2 and 20 wt %. Antibacterial tests were performed at 6 h, 24 h, and 7, 14, and 30 days. The test results indicated that PVC with 20 wt % of silver zeolite had a maximum antibacterial effect. According to the zone inhibition test, the fibers showed antibacterial protection against *E.coli* bacteria. Moreover, there has just one study about N-halamine containing PVC material via an extrusion and injection molding process in literature. Chylinska et al. produced PVC composites with N-chlorinated poly(3-(4'-vinyl benzyl)-7,8-benzo-1,3-diazaspiro[4.5] decane-2,4-dione) (MPS TET-Cl) [50]. The antibacterial test results showed strong antibacterial activity against *S. aureus* and *E. coli.*

Previous studies have mostly focused on PVC fibers with various antibacterial agents. However, the antibacterial agents-loaded PVC fibers have demonstrated limited antibacterial effectiveness since these antibacterial agents have no rechargable effect. In addition, TTDD has been chosen as an antibacterial agent owing to functional groups in cyclic TTDD. TTDD includes imide, amide, and amine

functionalities. When all of the above compounds were chlorinated, N-halamine compounds were formed, which worked as good biocides. [51]. To the best our knowledge, there is no study on PVC non-woven surfaces with rechargeable antibacterial properties by using electrospinning method. In the current study, we tried for the first time to introduce of TTDD into PVC nanowebs as an antibacterial compound and investigate antibacterial effect of this compound. By varying TTDD concentration, the properties of PVC nanowebs were investigated in terms of microstructure, thermal, and chemical properties. Furthermore, rechargeable chlorination capability was observed and antibacterial efficiencies were evaluated against *S. aureus* and *E. coli* bacteria.

2. MATERIAL AND METHOD

2.1 Material

The polyvinyl chloride powder (PVC, Mw=43,000 g/mol), N, N-Dimethylformamide (DMF) and potassium iodide (KI), Hydrochloric acid (HCl) with 36.5-38% purity, tetrahydrofuran (THF), sodiumthiosulfate pentahydrate ($Na_2S_2O_3.5\ H_2O$), ethanol (99.5% purity), Triton X-100 (laboratory grade) were used. All chemicals were purchased from Sigma-Aldrich Chemical Company. ACE® brand NaOCl (P&G, Belgium) household bleach was used for chlorination. All the reagents were used without purification. Antibacterial testing was performed by Muller-Hinton II agar culture media.

2.2 Synthesis of TTDD

The TTDD was prepared according to a general procedure carried out previously [21]. TTDD was synthesized by reacting 2,2,4,4-tetramethyl-4-piperidone, potassium cyanide, and ammonium carbonate in a mole ratio of 1 : 2 : 6 in 100 mL of water/ethanol (1: 1 v/v) solution for 48 hours at room temperature. Then the reaction mixture was filtered and TTDD was produced. Afterwards, TTDD was washed with hot water, and dried TTDD was vacuumed for 24 hours in ambient conditions. TTDD synthesis is shown in Figure 1.

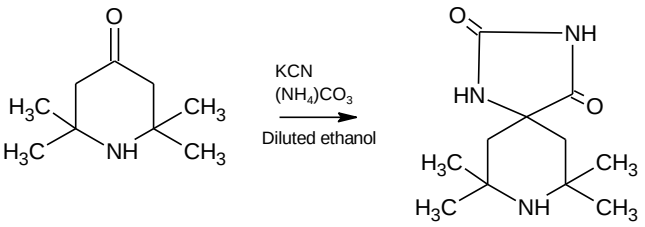

Figure 1. Synthesis of 7,7,9,9-tetramethyl-1,3,8-triazaspiro [4.5]-decane-2,4-dione (TTDD) [21].

2.3. Preparation of Antibacterial Nanowebs

The polymer solutions were electrospun using a laboratory machine called an electrospinning device (INOVENSO Nanospinner 24, Turkey). PVC was dissolved in DMF and THF binary-solvent systems (67.5:17.5, v/v) solution to obtain a 15% (w/v) PVC solution for the electrospinning process. The PVC solutions were put in a magnetic stirrer at room temperature till a homogeneous solution was obtained. Subsequently, different concentrations (1, 3 and 5 wt%) of TTDD were added to the PVC solutions concerning the total polymer solutions. After TTDD had dissolved in PVC solution, the mixture was transferred into a plastic syringe (20 mL) and attached to a stainless steel nozzle.

The electrical power supply to the nozzle of the syringe was 25 kV with a 1 mL/h flow rate (Figure 2). The distance between a collector and a needle was 15 cm. During electrospinning, the PVC nanowebs were collected on a rotating drum at 100 rpm. In the course of electrospinning, the solvent was evaporated and only nanowebs attached to the aluminum foil forming nanoweb membranes remained. Pure PVC nanowebs were prepared as a control.

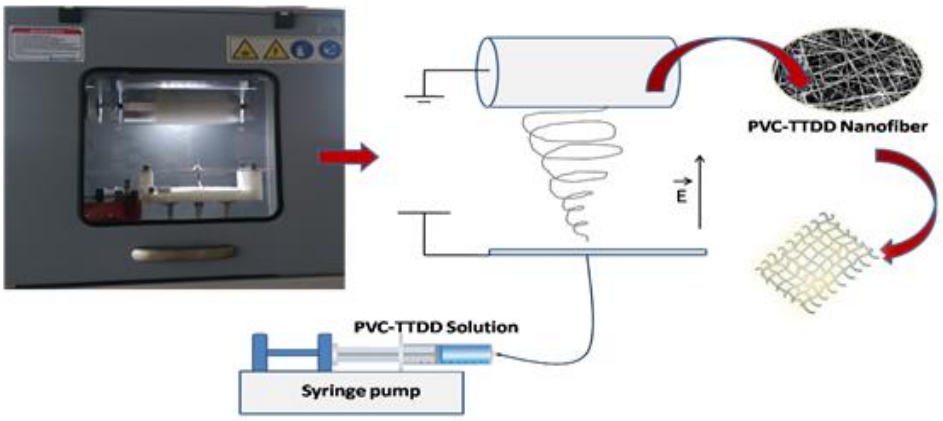

Figure 2. Schematic illustration of the electrospinning process.

2.4 Chlorination and Analytic Titration of the Nanowebs

Many prior studies on the effects of titration and chlorination have been reported [8,10,21,49]. The PVC nanowebs containing 1, 3, 5 % TTDD were chlorinated in pH 7 and pH 5 for 1, 6, and 12 h by soaking, the samples in 10, 20, and 40 % commercial aqueous sodium hypochlorite solution (NaOCl) at room temperature without stirring. Afterward, 0.15 g of the non-ionic surfactant Triton-X was added to each solution. The chlorinated nanowebs were robustly washed with distilled water, then dried in an oven at 50°C for an hour. The amount of chlorine loaded in the structure was calculated by the iodometric/thiosulfate method [52,53] according to the following formula.

$$Cl^{+}\,\% = \left(\frac{35{,}45 \times N \times V}{W \times 2}\right) \times 10 \qquad (1)$$

In this equation, N is the normality of thiosulfate solution, V is the volume of the consumed thiosulfate solution, and W is the weight of the sample titrated. Figure 3 shows the chlorination process of the TTDD.

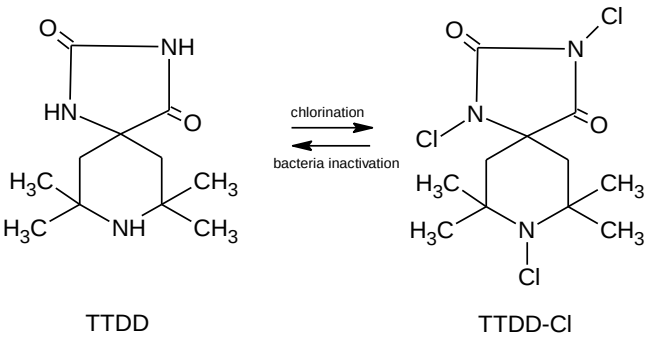

Figure 3. Chlorination process of the TTDD [8,21].

2.5 Rechargeable Chlorination Process

All nanowebs containing 1%, 3% and 5% TTDD was chlorinated again in 30% sodium hypochlorite solution for pH 5 for 6 h. Then, 0.15 g of non-ionic surfactant, Triton-X, was dripped into the solutions.

Afterward, the chlorinated PVC samples was washed with distilled water and dried at 50°C for 1 h to remove free chlorine from the surface of all PVC nanowebs [54].

2.6 Antibacterial Efficacy Test

The antibacterial efficacy of electrospun nanowebs was studied using ASTM 2149 method. The test method was performed with *S. aureus* (ATCC 6538) and *E. coli* (ATCC 35218). Both pure nanoweb (PVC0) and chlorinated nanoweb samples (PVC1, PVC3, and PVC5) were challenged with approximately 10 mL of known concentration of bacteria suspension. The logcfu values of the bacteria on the control samples were *9.67 for S. aureus* and 5.76 for *E. coli*. The nanowebs were divided into three pieces and then put into a sterilized glass jar. The samples were challenged to the bacteria for two different contact times (3 h and 24 h) without rinsing. After, serial dilutions were prepared with phosphate buffer solution (PBS) and placed into Muller-Hilton II agar culture media. The plates were put in an incubator at 37˚C for 24 h. The bacteria colonies were counted and the logarithmic bacterial reduction was determined.

2.7 Characterization of Nanowebs

Thermogravimetric analyses of nanowebs were performed by TA Instrument DSC-Q2000 and Perkin Elmer STA 6000 TGA under 20 mL/min nitrogen flow with a heating rate of 20°C/min in room temperature to 600°C temperature range and under 20 mL oxygen flow in 600-900°C. FTIR data were obtained with a Thermo Nicolet iS50 FTIR spectrometer with a Pike ATR (Attenuated Total Reflectance) adapter, in the range of 4000-400 cm^{-1} recorded with 16 scans at 4 cm^{-1} resolution.Hitachi TM3030 plus187 Scanning Electron Microscope (SEM) (Hitachi Ltd., Tokyo, Japan) was used to characterize the surface morphology and composition of nanowebs with an accelerating voltage of 10 kV. The average fiber diameters were measured by using Image J, version 1.520 software.

3. RESULT AND DISCUSSION

3.1 Morphology of Nanofibers

The diameter of fibrous structures was measured using Image J (version 1.520 software) by randomly selecting the diameters of 100 individual fibers for each sample. According to the analysis results, the fiber diameters changed depending on the TTDD concentration. Increased TTDD concentration caused an increase in fiber diameter. As seen in SEM images, the fiber diameters are nonhomogenous [Figure 5 (A1-D1)]. Irıbarren et al. prepared relatively uniform PVC-ZnO composite fibers and they measured the average fiber diameters of obtained fibers as 720 nm. [55]. Lala et al. fabricated PVC with 5 wt% of $AgNO_3$ nanofiber. The fiber showed straighter and good fiber morphology with 509 nm [49]. The fiber diameters of electrospun PVC0, PVC1, PVC3, and PVC5 samples were measured to be 126.8 ± 42.6 nm, 157.2 ± 63 nm, 161.2 ± 65, and 169.7 ± 53 nm, respectively, and the distribution curve as shown in Figure 5 (A2-D2). Moreover, all PVC electrospun webs containing TTDD (PVC1, PVC3, and PVC5) exhibits a web of randomly oriented fiber with a broad distribution from 35 to 411 nm. PVC1 and PVC3 webs showed a bead-like web structure. Figure 5D1 indicated 3D network structure in PVC5 began to form. In a similar study, Akgül and Aykut (2019) observed PVC/$Zn(NO_3)_2$ nanofibers with these structures [56].

3.2 FT-IR Analysis

The FTIR analysis of the electrospun pure PVC web (PVC0), TTDD, and TTDD-loaded PVC webs is given in

Figure 4. The pure PVC webs showed their characteristic bands. The PVC0 webs exhibited peaks at 2911 cm^{-1} (-CH bond stretching), 1333 cm^{-1} (-CH_2 groups deformation), 1254 cm^{-1} (CH-rocking), 959 cm^{-1} (-CH wagging) which were in accordance with the literature [42,51,54,55]. Furthermore, the characteristic peaks of TTDD bands at 3400 cm^{-1} was related to -NH stretching, at 2853 cm^{-1} was due to -CH_3 stretching, at 1781 cm^{-1} and 1733 cm^{-1} was attributed to imide group, and also 1720 cm^{-1} was attributed to ester (-C=O) peak, at 1467 cm^{-1} was related to -CH_3 bending vibrations, as well [57]. The FTIR spectrum showed characteristic peaks of PVC nanoweb at 681 cm^{-1} and 604 cm^{-1} due to the C-Cl stretching mode [58,59]. The characteristic bands of both PVC0 and TTDD loaded webs were all maintained in the resulting webs. However, decreased peak intensity were detected on the spectra of TTDD loaded webs.

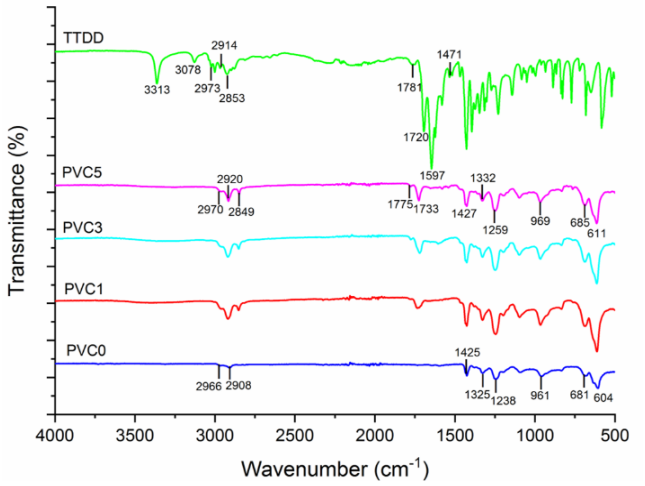

Figure 4. FTIR spectrum of PVC0, PVC1, PVC3, PVC5 nanowebs and TTDD.

3.3 Thermal Analysis

TGA thermograms of pure PVC nanowebs and TTDD-loaded PVC nanowebs in nitrogen at a rate of 20°C/min are shown in Figure 6. Moreover, all of the webs are thermally stable in nitrogen gas below 200°C and mainly displayed three-stage thermal degradation above this temperature, as well [60]. The initial stage of degradation (between 210 and 360°C) was rapid and overlapped with PVC dechlorination [61], with the formation and stoichiometric elimination of HCl and a few chlorinated hydrocarbons. The formation of aromatic compounds via cyclization of conjugated polyene [49] occurred primarily in the second stage (between 360 and 470°C). In the last stage, the degradation of PVC increased to 471°C, and the degradation was completed at 700°C, due to the degradation of complex structures induced by aromatization and pyrolysis of PVC [63,64]. The degradation starting temperature of TTDD loaded nanowebs with decreased as the concentration of TTDD increased. When N-halamine was added to the polymer, the degradation behavior of PVC changed, indeed.

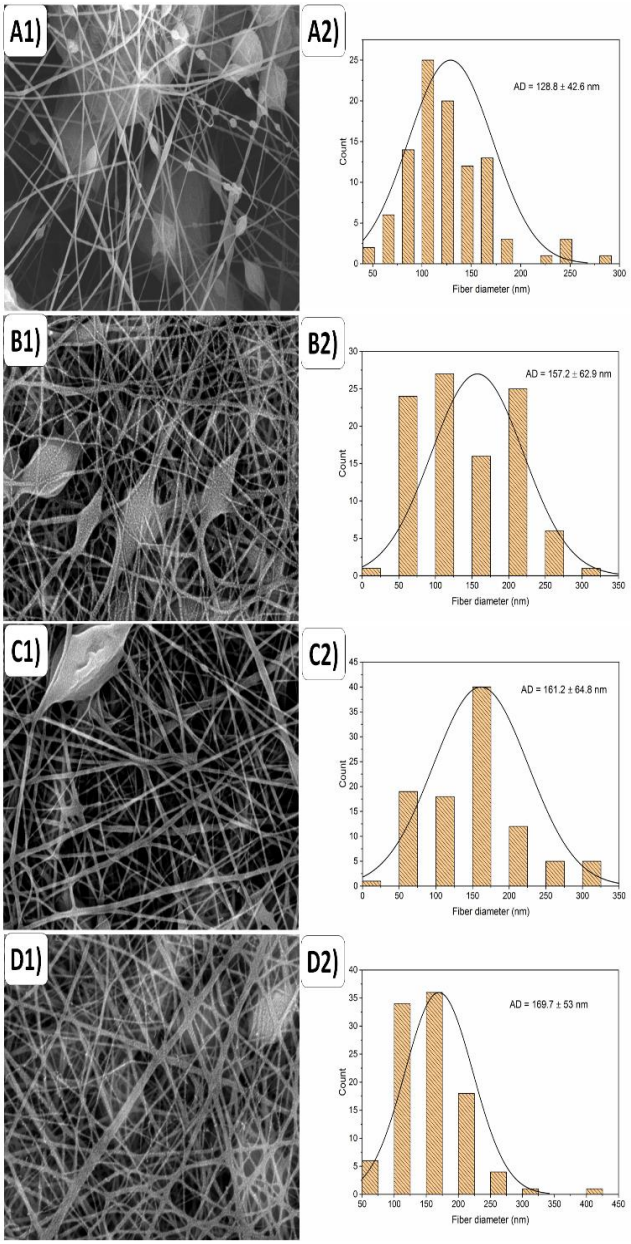

Figure 5. SEM images and fiber diameter distributions of PVC0 (A1&A2), PVC1 (B1&B2), PVC3 (C1&C2), PVC5 (D1&D2

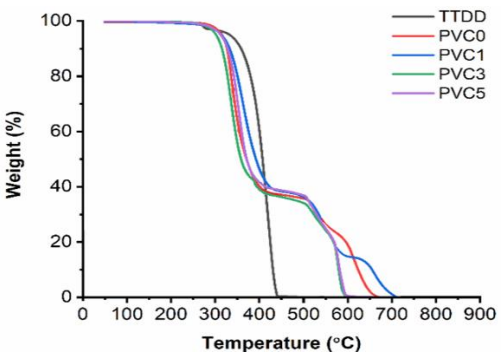

Figure 6. TGA thermograms of PVC nanowebs and TTDD.

3.4 Chlorine Loading and Rechargable Chlorination Process

The amount of chlorine uptake of all chlorinated nanowebs (PVC1, PVC3, and PVC5) increased in pH 5 due to increased NaOCl concentration. In this regard, PVC5 nanoweb samples can be chlorinated up to chlorine loading 1.54, 1.13, and 0.73 % Cl+ for 40% NaOCl solution at 1 h, 6 h, and 12 h, respectively (Table 1). All nanowebs exhibited increased chlorine uptake for the first 6 h. However, chlorine uptake reached saturation nanowebs, except PVC3. Table 2 summarized the chlorine loadings progressively increased with increasing time in pH 7. Furthermore, a high concentration of chlorine reduces interaction with bacteria, causing slower inactivation [37,63,64]. Table 2 summarized the chlorine loadings progressively increased with time in pH 7. The PVC5 nanoweb sample exhibits the highest Cl+ (1.09 percent) uptake value.

Due to amine, amide, and imide functionalities of TTDD, they were analyzed to check if they could recharge antimicrobial TTDD after interaction with NaOCl. Furthermore, even after three recharging cycles, the Cl+ concentration of PVC1 webs remained constant, whereas other TTDD-loaded PVC nanowebs showed high efficiency factors (PVC3 and PVC5). Because the active chlorine concentration of TTDD is critical for its antibacterial activities, the effects of chlorination time and pH on PVC chlorination capability were evaluated. The rechargeable chlorination process is dependent on rising N-halamine concentration, which causes an increase in rechlorination efficiency. It reduced as the procedure time increased. (See Table 3).

Table 1. Chlorination results of PVC nanowebs with N-halamine in pH 5.

Sample ID	NaOCl Concentration			Time
	10%	20%	40%	
PVC1	0.11	0.33	0.71	1h
	0.14	0.29	0.55	6h
	0.10	0.22	0.23	12h
PVC3	0.08	0.34	0.52	1h
	0.13	0.27	0.55	6h
	0.05	0.2	0.58	12h
PVC5	0.17	0.32	1.54	1h
	0.19	0.88	1.13	6h
	0.40	0.60	0.73	12h

Table 2. Chlorination results of PVC nanowebs with N-halamine in pH 7.

Sample ID	NaOCl Concentration			Time
	10%	20%	40%	
PVC1	0.07	0.24	0.42	1h
	0.13	0.26	0.47	6h
	0.21	0.27	0.54	12h
PVC3	0.13	0.34	0.64	1h
	0.19	0.38	0.83	6h
	0.26	0.47	0.87	12h
PVC5	0.26	0.61	0.82	1h
	0.23	0.48	0.98	6h
	0.25	0.47	1.09	12h

Table 3. Rechargable chlorinatonresults of PVC nanowebs with N-halamine for 6 h in pH 5.

Sample ID	Rechargable Chlorination Efficiency (%)			
	1st	2nd	3rd	4th
PVC1	0.11	0.11	0.11	0.07
PVC3	0.55	0.42	0.36	0.33
PVC5	0.95	0.90	0.83	0.75

3.5 Antibacterial Efficacy Testing

A novel antibacterial nanoweb production was aimed in this study. According to chlorination results, they were tested both S. aureus and E. coli with ASTM 2149 standard. As a result, the chlorine uptake of nanowebs in pH 5 was more than in pH 7, and as the amount of chlorine uptake increased, the antibacterial property also increased. The initial bacterial population of PVC0 9.65 and6.04 for S. aureus and E. coli bacteria, respectively, as well as the logcfu values of the control samples, are shown in Table 4. PVC0 nanoweb showed no essential antibacterial activity within 3 and 24 h, respectively. On the other hand, PVC nanowebs with TTDD compound showed complete inactivation of both S. aureus and E. coli bacteria, confirming that the nanowebs had increased antibacterial activities due to the addition of TTDD compound chlorinated nanowebs. PVC1 was challenged with *S. aureus* and *E. coli* while TTDD 88.24% and 71.76% of inactivated bacteria during the tests within the contact time of 24 h. Both PVC3 and PVC5 provided inactivation of 100% within 24 h when challenged with both *S. aureus* and *E. coli* and also the results are summarized in Table 4. The producted nanofibers have unrivaled antibacterial functionalities compared to various kinds of antimicrobial agents containing nanofibers [9].

Table 4. Antibacterial test results of PVC nanowebs.

Sample ID	Bacteria type	Contact time (h)	log CFU	Bacterial reduction (%)
PVC0 (in pH 5)	*S.aureus*	3	9.65	3.92
		24	9.63	7.84
	E.coli	3	-	-
		24	6.04	88.24
PVC1 (in pH 5)	*S.aureus*	3	9.64	4.90
		24	8.74	88.24
	E.coli	3	-	-
		24	5.21	71.76
PVC3 (in pH 5)	*S.aureus*	3	9.63	7.84
		24	0	100
	E.coli	3	-	-
		24	3.51	100
PVC5 (in pH 5)	*S.aureus*	3	0	100
		24	0	100
	E.coli	3	0	100
		24	-	100

4. CONCLUSION

In this study, organic N-halamin compound (TTDD) compound was added to PVC solution and nanoweb surfaces were successfully produced by electrospinning process. The SEM images revealed the resulting nanowebs possessed relatively non-homogenous average fiber diameters between 35-411 nm and PVC nanowebs have a beaded structure, except PVC5. The amount of TTDD dramatically affected the fiber diameter. The typical FTIR peaks of TTDD were observed in TTDD loaded-PVC and small changes in certain peaks were recorded, owing to physical interactions of TTDD with PVC matrix. According to TGA analysis, the addition of TTDD had no effect on the initial degradation temperature of the PVC. However, the thermal degradation changed after the pyrolysis temperature. The chlorinated nanowebs indicated high antibacterial activity against both *S. aureus* and *E. coli*. Antibacterial activity was found to increase with increasing TTDD amount in 3 h and 24 h. Within 24 hours, PVC5 nanowebs provided 100 % inactivation (approximately 0 logs) of E. coli and S. aureus. Moreover, rechargeable chlorination capabilities were achieved in acidic media with minimum loss during the optimum time (6 h) for all nanowebs. This procedure was carried out four times. The utilization of TTDD bactericidal groups to develop protective electrospun PVC webs with recharged antibacterial efficiency might be a potential application in medical fields.

Acknowledgement

The authors acknowledge Dr. Mehmet Orhan for his help with the antibacterial testing.

REFERENCES

1. Boryo DEA. 2013. The effect of microbes on textile material: a review on the way-out so far. *The International Journal of Engineering and Science (IJES)*, 2(8):9-13.
2. Ramachandran T, Rajendrakumar K, Rajendran R. 2004. Antimicrobial textiles-an overview. *Journal of The Institution of Engineers (India): Series E*, 84(2):42-47.
3. Tshikantwa TS, Ullah MW, He F, Yang G. 2018. Current trends and potential applications of microbial interactions for human welfare. *Frontiers in Microbiology*, 9, 1156.
4. Ducel G, Fabry J, & Nicolle L. 2002. Prevention of hospital acquired infections: a practical guide. *Prevention of hospital acquired infections: a practical guide.* (Ed. 2). Malta.
5. Şimsek EM, Grassie SS, Emre C, 2017. Relationship between environmental conditions and nosocomial infection rates in intensive care unit. *Medical Journal of Islamic World Academy Sciences*, 25, 15-18.
6. Hughes R. 2008. Patient safety and quality: An evidence-based handbook for nurses (Vol. 3). Rockville, MD: Agency for Healthcare Research and Quality.
7. Ji M, Moffett HL, Kunin CM. 1988. Guidelines for improving the use of antimicrobial agents in hospitals: a statement by the Infectious Diseases Society of America. *Journal of Infection Disease*, 157, 869-876.
8. Ren X, Kou L, Kocer HB, Zhu C, Worley SD, Broughton RM, Huang TS. 2008. Antimicrobial coating of an N-halamine biocidal monomer on cotton fibers via admicellar polymerization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 317(1-3):711-716.

9. Aksoy OE, Ates B, Cerkez I. 2017. Antibacterial polyacrylonitrile nanofibers produced by alkaline hydrolysis and chlorination. *Journal of Materials Science*, 52(17):10013-10022.

10. Kocer HB, Akdag A, Ren X, Broughton RM, Worley SD, Huang TS. 2008. Effect of alkyl derivatization on several properties of N-halamine antimicrobial siloxane coatings. *Industrial&Engineering Chemistry Research*, 47(20):7558-7563.

11. Kocer HB. 2012. Residual disinfection with N-halamine based antimicrobial paints. *Progress in Organic Coatings*, 74(1):100-105.

12. Worley SD, Williams DE, Crawford R. 1988. Halamine water disinfectants. *Critical Reviews in Environmental Science and Technology*, 18(2):133-175.

13. Kocer HB, Worley SD, Broughton RM, Huang TS. 2011. A novel N-halamine acrylamide monomer and its copolymers for antimicrobial coatings. *Reactive and Functional Polymers*, 71(5):561-568.

14. Ma Y, Li J, Si Y, Huang K, Nitin N, Sun G. 2019. Rechargeable antibacterial N-halamine films with antifouling function for food packaging applications. *ACS Applied Materials&İnterfaces,* 11(19): 17814-17822.

15. Demir B, Broughton RM, Qiao M, Huang TS, Worley SD. 2017. N-halamine biocidal materials with superior antimicrobial efficacies for wound dressings. *Molecules*, 22(10):1582.

16. Cerkez I, Kocer HB, Worley SD, Broughton RM, Huang TS. 2011. N-halamine biocidal coatings via a layer-by-layer assembly technique. *Langmuir*, 27(7):4091-4097.

17. Demirci F, Kocer HB. 2019. Preparation of antibacterial polyvinylidene fluoride (PVDF) ultrafiltration membranes with direct addition of N-halamine polymers. *Separation Science and Technology*, 54(5):803-814.

18. Kocer HB, Cerkez I, Worley SD, Broughton RM, Huang TS. 2011. N-halamine copolymers for use in antimicrobial paints. *ACS Applied Materials &İnterfaces,* 3(8):3189-3194.

19. Ren X, Jiang Z, Liu Y, Li L, Fan X. 2016. N-halamines as antimicrobial textile Finishes. G.S. *Antimicrobial Textiles.* USA: Elsevier: Woodhead Publishing.

20. Bhardwaj N, Kundu SC. 2010. Electrospinning: a fascinating fiber fabrication technique. *Biotechnology Advances*, 28(3):325-347.

21. Parin FN, Terzioğlu P, Sicak Y, Yildirim K, Öztürk M. 2020. Pine honey–loaded electrospun poly (vinyl alcohol)/gelatin nanofibers with antioxidant properties. *The Journal of The Textile Institute*, 112(4):628-635.

22. Parın FN, Aydemir Ç, Taner G, Yıldırım K. 2021. Co-electrospun-electrosprayed PVA/folic acid nanofibers for transdermal drug delivery: Preparation, characterization, and in vitro cytocompatibility. *Journal of Industrial Textiles*, Doi:1528083721997185.

23. Parın FN, Yıldırım K. 2021. Preparation and characterisation of vitamin-loaded electrospun nanofibres as promising transdermal patches. *Fibres & Textiles in Eastern Europe*, 1(145):17-25.

24. Ren X, Kocer HB, Worley SD, Broughton RM, Huang T. 2013. Biocidal nanofibers via electrospinning. *Journal of Applied Polymer Science*, 127(4):3192-3197.

25. Fang J, Niu H, Lin T, Wang X. 2008. Applications of electrospun nanofibers. *Chinese Science Bulletin*, 53(15):2265.

26. Goldade V, Vinidiktova N. 2017. Antimicrobial Fibers For Textile Clothing And Medicine: Current State, *ISJ Theoretical & Applied Science,* 3(47):178-194.

27. Parın FN, Yıldırım K, Kavçak Ö, Kalemtaş A, Aydın G. 2020, Eylül. Fabrication of Antibacterial Orange Essential Oil−Loaded Gelatin Fibers. In Y.U. 7. ULPAS Bildiri Kitapçığı (34-38). Bursa, Türkiye.

28. Ahmadi S, Hivechi A, Bahrami SH, Milan PB, Ashraf SS. 2021. Cinnamon extract loaded electrospun chitosan/gelatin membrane with antibacterial activity. *International Journal of Biological Macromolecules*, 173, 580-590.

29. Yina M, Wang Y, Zhang Y, Ren X, Qiu Y, Huang T. 2020. Novel quaternarized N-halamine chitosan and polyvinyl alcohol nanofibrous membranes as hemostatic materials with excellent antibacterial properties. *Carbohydrate Polymers*, 232, 115823.

30. Zhang Y, Li T, Shiu B, Sun F, Ren H, Zhang X, Lou C, Lin J. 2021. Eco-friendly versatile protective polyurethane/triclosan coated polylactic acid nonwovens for medical covers application. *Journal of Cleaner Production*, 282, 124455.

31. Chen S, Li C, Hou T, Cai Y, Liang L, Chen L, Li M. 2019. Polyhexamethylene guanidine functionalized chitosan nanofiber membrane with superior adsorption and antibacterial performances. *Reactive and Functional Polymer*, 145, 104379.

32. Ullah S, Hashmi M, Kharaghani D, Khan MQ, Saito Y, Yamamoto T, Lee J, Kim IS. 2019. Antibacterial properties of in situ and surface functionalized impregnation of silver sulfadiazine in polyacrylonitrile nanofiber mats. *International Journal of Nanomedicine*, 14, 2693-2703.

33. Zhanga T, Gua J, Liua X, Dengshuai W, Huiling Z, Haihua X, Zhuocheng Z, Huali Y, Shiguo C. 2020. Bactericidal and antifouling electrospun PVA nanofibers modified with a quaternary ammonium salt and zwitterionic sulfopropylbetaine. *Materials Science & Engineering C*, 111, 110855.

34. Lv H, Cui S, Yang Q, Song X, Wang D, Hua J, Zhou Y, Liu Y. 2021. AgNPs-incorporated nanofiber mats: Relationship between AgNPs size/ content, silver release, cytotoxicity, and antibacterial activity. *Materials Science & Engineering C*, 118, 111331.

35. Dong A, Wang Y, Gao Y, Gao T, Gao G. 2017. Chemical Insights into Antibacterial N-Halamines. *Chemical Reviews*, 117, 4806-4862.

36. Liu M, Wang F, Liang M, Si Y, Yu J, Ding B. 2020. In situ green synthesis of rechargeable antibacterial N-halamine grafted poly(vinyl alcohol) nanofibrous membranes for food packaging applications. *Composites Communications*, 17, 147-153.

37. Tian C, Wu F, Jiao W, Liu X, Yin X, Si Y, Yu J, Ding B. 2021. Antibacterial and antiviral N-halamine nanofibrous membranes with nanonet structure for bioprotective applications. *Composites Communications*, 24, 100668.

38. Ma Y, Yi J, Pan B, Nitin N, Sun G. 2020.Chlorine Rechargeable Biocidal N-Halamine Nanofibrous Membranes Incorporated with Bifunctional Zwitterionic Polymers for Efficient Water Disinfection Applications. *ACS Applied Materials Interfaces*, 12(45):51057-51068.

39. Liang M, Wang F, Liu M, Yu J, Si Y, Ding B. 2019. N-Halamine Functionalized Electrospun Poly(Vinyl Alcohol-co-Ethylene) Nanofbrous Membranes with Rechargeable Antibacterial Activity for Bioprotective Applications. *Advanced Fiber Materials*, 1, 126-136.

40. Nicholas P. 1997. *Handbook of Engineering Polymeric Materials.* USA: Marcel Dekker Inc.

41. Doble M, Kumar A. 2005. *Biotreatment of Industrial Effluents.* USA: Butterworth-Heinemann, Elsevier.

42. Li X, Xing Y, Jiang Y, Ding Y, Li W. 2009. Antimicrobial activities of ZnO powder-coated PVC film to inactivate food pathogens. *International Journal of Food Science&Technology*, 44(11):2161-2168.

43. Machovsky M, Kuritka I, Bazant P, Vesela D, Saha P. 2014. Antibacterial performance of ZnO-based fillers with mesoscale structured morphology in model medical PVC composites. *Materials Science and Engineering: C*, 41, 70-77.

44. Behboudi A, Jafarzadeh Y, Yegani R. 2018. Incorporation of silica grafted silver nanoparticles into polyvinylchloride/polycarbonate hollow fiber membranes for pharmaceutical wastewater treatment. *Chemical Engineering Research and Design*, 135, 153-165.

45. Zampino D, Ferreri T, Puglisi C, Mancuso M, Zaccone R, Scaffaro R, Bennardo D. 2011. PVC silver zeolite composites with antimicrobial properties. *Journal of Materials Science*, 46(20):6734-6743.

46. Cushen M, Kerry J, Morris M, Cruz-Romero M, Cummins E. 2013. Migration and exposure assessment of silver from a PVC nanocomposite. *Food Chemistry*, 139(1-4):389-397.

47. Lin H, Xu Z, Wang X, Long J, Su W, Fu X, Lin Q. 2008. Photocatalytic and antibacterial properties of medical‐grade PVC material coated with TiO_2 film. *Journal of Biomedical Materials Research Part B:Applied Biomaterials*, 87(2):425-431.

48. Lala NL, Ramaseshan R, Bojun L, Sundarrajan S, Barhate RS, Ying-jun L, Ramakrishna S. 2007. Fabrication of Nanofibers With Antimicrobial Functionality Used as Filters: Protection Against

Bacterial Contaminants. *Biotechnology and Bioengineering*, 97(6): 1357-1365.

49. Chylińska M, Kaczmarek H, Burkowska-But A, Walczak M. 2015. Novel biocidal N-halamine plastic based on poly (vinyl chloride): preparation and characteristics. *Journal of Industrial and Engineering Chemistry*, 28, 124-130.

50. Akdag A, Okur S, McKee ML, Worley SD. 2006. The stabilities of N−Cl bonds in biocidal materials. *Journal of Chemical Theory and Computation*, 2(3):879-884.

51. Ren X, Akdag A, Kocer HB, Worley SD, Broughton RM, Huang TS. 2009. N-Halamine-coated cotton for antimicrobial and detoxification applications. *Carbohydrate Polymers*, 78(2):220-226.

52. Liang J, Chen Y, Barnes K, Wu R, Worley SD, Huang TS. 2006. N-halamine/quat siloxane copolymers for use in biocidal coatings. *Biomaterials*, 27, 2495-2501.

53. Liang J, Wu R, Wang JW, Barnes K, Worley SD, Cho U, Lee J, Broughton RM, Huang TS. 2007. N-halamine biocidal coatings. *Journal of Industrial Microbiology and Biotechnology*, 34, 157-163.

54. Çobanoğlu B, Parın FN, Yıldırım K. 2019, Mayıs. Antibacterial Polyvinyl Chloride (PVC) Nanofibers Containing N-Halamines. In Y.U., 5. ULPAS Bildiri Kitapçığı (79-81). İstanbul, Türkiye.

55. Iribarren A, Rivero PJ, Berlanga C, Larumbe S, Miguel A, Palacio JF, Rodriguez R, 2019. Multifunctional Protective PVC-ZnO Nanocomposite Coatings Deposited on Aluminum Alloys by Electrospinning. *Coatings*, 9(216):2-13.

56. Akgül YI, Aykut Y. 2019. Partially Transformation of Zinc Nitrate to Zinc Compounds on PVC Nanofibers at Low-Temperature Heat Treatment and Investigation of the Products Optical Properties. *Tekstil ve Mühendis,* 26(114):118-124.

57. Zhong Z, Cao Q, Jing B, Wang X, Li X, Deng H. 2012. Electrospun PVDF-PVC nanofibrous polymer electrolytes for polymer lithium-ion batteries. *Materials Science and Engineering: B*, 177(1):86-91.

58. Zhong Z, Cao Q, Jing B, Li S, Wang X. 2012. Novel electrospun PAN–PVC composite fibrous membranes as polymer electrolytes for polymer lithium-ion batteries. *Ionics*, 18(9):853-859.

59. Guo JW, Lin ZY, Huang BR, Lu CH, Chen JK. 2018. Antigen detection with thermosensitive hydrophilicity of poly (N-isopropyl acrylamide)-grafted poly (vinyl chloride) fibrous mats. *Journal of Materials Chemistry B*, 6(21):3486-3496.

60. Cerkez I, Kocer HB, Worley SD, Broughton RM, Huang TS. 2012. Epoxide tethering of polymeric N-halamine moieties. *Cellulose*, 19(3):959-966.

61. Sherif EM, Es-saheb M, El-Zatahry A, Kenawyand E, Alkaraki AS. 2012. Coating electrospun polyvinyl alcohol and polyvinyl chloride fibers as corrosion passivation applications. *International Journal of Electrochemical Science*, 7, 6154-6167.

62. Hussein MA, Kumar M, Drew R, Al-Aqeeli N. 2018. Electrochemical corrosion and in vitro bioactivity of nano-grained biomedical Ti-20Nb-13Zr alloy in a simulated body fluid. *Materials*, 11(1):26.

63. Shnawa HA, Khalaf MN, Jahani Y. 2018. The effects of natural polyphenols and calcium-based thermal stabilizer on the rheological and thermal resistance behaviors of PVC. *International Journal of Plastics Technology*, 22(2):65-385.

64. Nair MR, Thomas GV, Nair MG. 2007. Thermogravimetric analysis of PVC/ELNR blends. Polymer Degradation and Stability, 92(2):189-196.