Fabrication of surface modified PVA-Silica electrospun mat and its antibacterial activity

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Abstract

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The fabrication of surface modified antibacterial electrospun mat is a promising material for enhanced antibacterial performance. In this study, PVA-Silica (P-S) electrospun mat was fabricated via sol-gel electrospinning and quaternary ammonium silane (QAS) and octadecyltrimethoxy silane (ODS) were applied for the modification of electrospun mat. The chemical bonding and surface elements that fabricated material was represented through analysis of the EDS and IR, and properties of the modified surface was able to be confirmed by

contact angle measurements via water droplets. The surface of ODS modified electrospun mat showed hydrophobic characteristics and QAS modified P-S represented not only hydrophobic property but also positive charge. The antibacterial performance was evaluated using the kinetic test method. Interestingly, the contact time after 150min, gram-negative (*E. coli*) and gram-positive bacteria (*S. aureus*) were shown to be killed by charge-charge interaction with the surface of QAS-P-S electrospun mat. Moreover, the mat maintained the antibacterial performance of more than 99% during recycling. It is expected to be applicable in various fields using antibacterial activity of high-durability, such as membrane, filter, and medical device.

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Chapter 1. Introduction

1.1 Antibacterial field

Bacteria, which is located a major problem of society in infectious diseases, has caused serious problems in the world [1, 2]. The cause of these infections is the growth of bacteria. Bacteria adhering to the surface form biofilms growing up in mediating nutrition. Biofilms indicate a strong resistance about 1000 times greater than a single colony of bacteria, it survives at harsh environment and is difficult to kill even more [3, 4]. Therefore, it is important to research for antibacterial materials for killing and inhibits the growth of bacteria in the initial stage.

In generally, these antibacterial materials can be divided into two types of release and contact. Firstly, Release type to killing bacteria, mainly using metal ion emission, has strong antibacterial activity but not last long [6-8]. Contact type, on the other hand, without the use of metal, has a charge on the surface that direct contact and induce death

of bacteria [9, 10]. However, after the surface have used for a long time, it has the drawback of performance degradation due to bacteria accumulation on the surface of the contact type [11-13].

1.2 Antibacterial nanomaterials

In recent years, nanomaterials have been studied in various fields for unique characteristics of its own. Nanomaterials can be defined as materials having a size 1-100nm, which have special physical and chemical properties depending on the morphology and size of them. Increased high surface-to-volume ratio represents greater reactivity than bulk materials [14].

Using the characteristics, some nanomaterials have already used as antibacterial agents. Nanofibers, which was made polymer having antibacterial property in the backbone, have been studied and nanoparticles using the silver ion have represented excellent antimicrobial activity. In addition, nanoparticles are also used as a template and polymerization on the surface or by treating the surface

with silane having antibacterial activity. Therefore, excellent antibacterial activity using nanomaterials having specific properties was expected [15].

1.3 Synthesis of antibacterial nanomaterials

For preventing the infection of bacteria, various methods for fabrication of the antibacterial materials have been studied and many researches have been promoted in the field of nano [16, 17]. Fabrication of nanomaterials having antibacterial activity can be classified in the method of functionalization using nanomaterials for a template. Another method is to make the antibacterial polymer nanomaterials by polymerization using the monomer, which has functional group in the backbone showing antibacterial activity. In addition, other methods are that metal is used for polymerization that materials also represent antibacterial activity via ion emission.

The method of Surface modification were studied that poly[2-(tertbutylaminoethyl)methacrylate]   (PTBAM),   indicating   the

antibacterial activity because of secondary ammonium group, was polymerized via vapor deposition polymerization (VDP) on the SiO_2 prepared by template. Core/shell nanoparticles represented excellent antibacterial activity and different performance as a function of size [18]. quaternary ammonium silane (QAS), indicating the antibacterial activity, was treated to the SiO_2 nanoparticles having hydroxyl groups through silane coupling reaction and shown antibacterial performance depending on the size [4].

Chemical-oxidation polymerization were studied that the silver nitrate and rhodanine monomer, which possess Ag ion, nitrogen and sulfur indicating the antimicrobial activities, polymerized via oxidation and reduction mechanisms that represent morphology of nanofibers contain Ag nanoparticles [19]. Ferric chloride and rhodanine monomer was used to make core/shell nanoparticles by making simultaneous polymerization of rhodanine and reduction of the iron ions by the chemical-oxidation polymerization to the same concept that was applied to recyclable antibacterial materials [20].

In addition, the composite of cationic cellulose (chitosan), which is known to have antibacterial activity, and polymer were prepared by the method of electrospinning that applied for the surface with an antibacterial performance [21]. Therefore, researches on antibacterial nanomaterials using various synthetic methods have been actively carried out and it is considered based on the potential to be possible to use a variety of antibacterial fields.

1.4 Synthetic method of antibacterial nanomaterials using electrospinning and surface modification

Electrospinning is possible to fabricate the nano-fiber and mat quick and simple and effective. Electrospun materials make suitable to apply the antibacterial nanomaterials, because the materials provide a small pore, large surface and lightly flexible [22-24]. However, Polymer based electrospinning to indicate antibacterial, with a charge of its own, it is rarely reported.

This is because they have two limitations. First, the polymer with a charge their own, surface tension increases, very high electrical force is required. Secondly, particles can be generated by the repulsive force between ionic groups [25, 26]. Therefore, some research has been reported that several of polymers were mixed to reduce the charge of the inside for electrospinning [27-29]. However, mixing the polymer can be reduced antibacterial activity and induced a change in the mechanical properties because of decreasing the electric charge [30, 31].

Surface modification with silane widely used in industrial area because it is an effective and convenient way to give a functional group on the surface [32]. Further, this method has the advantage to achieve high-durability because of chemical bond on the surface by the condensation reaction and hydrolysis, and be used for various applications depending on the functional groups of silane. However, in order to achieve chemical bonding, it has the limitation that substrate possesses a functional group which react with a methoxy or ethoxy group of the silane [33].

Substances having a functional group are mostly inorganic, which show low flexibility. Therefore, substances are necessary that form composite of polymer/inorganic and represent hydroxyl group on the surface. PVA-Silica is that forms a cross-linking between the internal elements via sol-gel method and electrospun fiber using the sol-gel solution represent flexibility. Hydroxyl group at the electrospun mat is possible that coupling reaction with silane agent [34, 35].

1.5 Objective of this study

Therefore, non-soluble PVA-Silica (P-S) electrospun mat was fabricated in water using sol-gel method. Quaternary ammonium silane (QAS) which has quaternary amine and long alkyl group was successfully treated at the surface of P-S, which represented not only hydrophobic property but also positive charge. In addition, octadecyltrimethoxy silane (ODS) having an alkyl group of the same length was treated for comparison of the antibacterial activity with QAS.

QAS-PVA-Silica (QAS-P-S) represented the antibacterial superior performance to kill 99.9% after a contact time of 150min against gram-negative *E. coli* (*Escherichia coli*) and grams positive *S. aureus* (*Staphylococcus aureus*). It was also possible to maintaining the performance of the 99% to recycling five times. In addition to, It is demonstrated the potential to be used in various fields, such as heavy metal adsorption and sensor, when treating a silane having a functional group [36-38].

Chapter 2. Experimental

2.1 Materials

Tetraethyl orthosilicate (TEOS, 98%) was obtained from Aldrich. Poly (vinyl alcohol) (PVA, 87-89% hydrolyzed, MW 85,000–124,000 g/mol), absolute ethanol and Dimethyloctadecyl [3-(trimethoxysilyl) propyl] ammonium chloride (QAS, 72%), octadecyltrimethoxy (ODS, 90%) silane were also provided by Aldrich. Hydrochloric acid (HCl, 36.5-38%, Aldrich) was used to preparing cross-linking and silane modification for catalyst. Deionized (DI) water was used in the whole experiment.

2.2 Preparation of PVA-Silica gel solution

A silica sol-gel, with the molar ratio (Ethanol : H_2O : TEOS : HCl = 1 : 0.7 : 0.125 : 0.05) was prepared by hydrolysis and condensation reaction. First, 2.08 g TEOS was dissolved in 3.69 g ethanol and 122 µL hydrochloric acid (1 mol/L) was slowly added into the solution

stirred for 1 h at 60 ℃. Second, 6.0 g of 5 wt% PVA solution was prepared in water for the same conditions. Then PVA solution was dropped slowly into the solution and a viscous gel of P-S gel was obtained for 1 h at 60 ℃. Additionally, adjusting until 4% to 5% concentration of PVA, from 5% to 15% adjust the concentration of TEOS, it was confirmed electrospun fiber each.

2.3 Preparation of electrospun mat

The above fabricated P-S solution was injected into a syringe. 27G (0.1 mm) was used as the electrospinning needle, which was connected to the high voltage electrode. Electrical potential was kept from 15 to 16 KV and solution in the syringe was provided by the syringe pump at flow rate of 4 μL/ml. The distance between the collector and the nozzle was 15 cm, after receiving about 2 h, a dense web of fibers was collected on paper and pull off that mat.

2.4 Surface Modification of PVA-Silica electrospun mat

First, the P-S electrospun mat was fixed in 150 ml of water–ethanol mixture solution (3:7, v/v) and injected 150 µL of HCl by using acid catalyst for hydrolysis and condensation between silane and electrospun mat. ODS and QAS of 3 ml, which was silane coupling agents, was injected into solution and the mixture was mildly stirred at room temperature, 3 h. After the coupling reaction with the hydroxyl group of the mat and the methoxy group of Silane is linked, washed about 2-3 times in water and dried at room temperature for 24 h.

2.5 Antibacterial tests of modified PVA-Silica electrospun mats

For the test of antibacterial activity on the surface, 3 cm x 5 cm size of P-S, ODS- and QAS-P-S electrospun mat were prepared. Aqueous suspension of *E. coli* and *S. aureus* ($10^6 \sim 10^7$ CFU/mL) was sprayed on the coated at the 2 times. LB broth was added to mats and hardens at the room temperature. The mats were incubated at 37 ℃ for 24 h and

the bacterial colonies were investigated [39].

Kinetic test was progressed to determine the degree of antibacterial versus contact time. Electrospun mat, which was used to kinetic test, was a P-S, ODS- and QAS-P-S, each samples were prepared in 3 cm x 5 cm size. The mats were put in a liquid medium which is being classified according to the type of bacteria, and allowed to stabilize for 5 min at 37 ℃. Then, 20 µL of *E. coli* and *S. aureus* (10^6~10^7 CFU/mL), which is inoculated, mat and bacteria were in contact thoroughly with 290 rpm. In each tube, 50 µL volumes were taken as a function of contact time at 30 min interval until 150 min and cultured in LB agar plates. The plates were cultured for 24 h at 37 ℃ in incubator and reduction % were calculated by counting the colony grew up [40].

2.6 Characterization

SEM image was used to determine the morphology of the electrospun mat, before and after surface treatment. JEOL 6700 was used to record at magnifications of 10,000 and 30,000. In order to

confirm the internal chemical bonding of composite mat, using FT-IR (Bomem, MB 100 spectroscope), sample of all scan until 600 to 3600 cm^{-1} of wavenumber in the absorption mode. Using a TGA (Perkin-Elmer, Pyris 6) to confirm the weight % of composite mat was performed from room temperature to 600 ℃ at a heating rate of 10 ℃/min in a nitrogen environment.

The contact angle (Krüss, DSA 10) was measured by the angle of the droplet and the surface, in order to determine whether the modification of the surface at ambient temperature. In addition, EDS was used to analyze the elements of the surface, the difference between ODS and QAS silane were determined by atom ratio. EDS was measured using the EDS facility that is connected to a JEOL JSM-6700F microscope.

Chapter 3. Results and discussion

3.1 Fabrication of QAS-PVA-Silica electrospun mat

3.1.1 Synthetic process of QAS-PVA-Silica electrospun mat

Figure 1 show synthetic procedure of cross-linked P-S solution using sol-gel method and electrospinning. The mat was treated ODS, QAS through coupling reaction for hydrophobicity and antibacterial property. P-S solution was reacted hydrolysis and condensation between hydroxyl groups of PVA and ethoxy group TEOS in HCl acid catalyst at 60 ℃ for 1 h.

The resulting P-S solution was injected into a syringe. The needle was connected to the positive terminal of a power supply. The obtained P-S electrospun mat had water-stability, however, hydroxyl groups of surface represented hydrophilic property of $\leq 25°$ (figure 3) [41]. After,

the mat was treated ODS, QAS silane in aqueous solvent, which was water and ethanol solution of volume fraction 3:7 for 3 h at 25 ℃, in order to modification of hydrophobic property [42]. Therefore, modified mats were able to fabricate using silane coupling reaction among silane and P-S mat surface at acid catalyst [43].
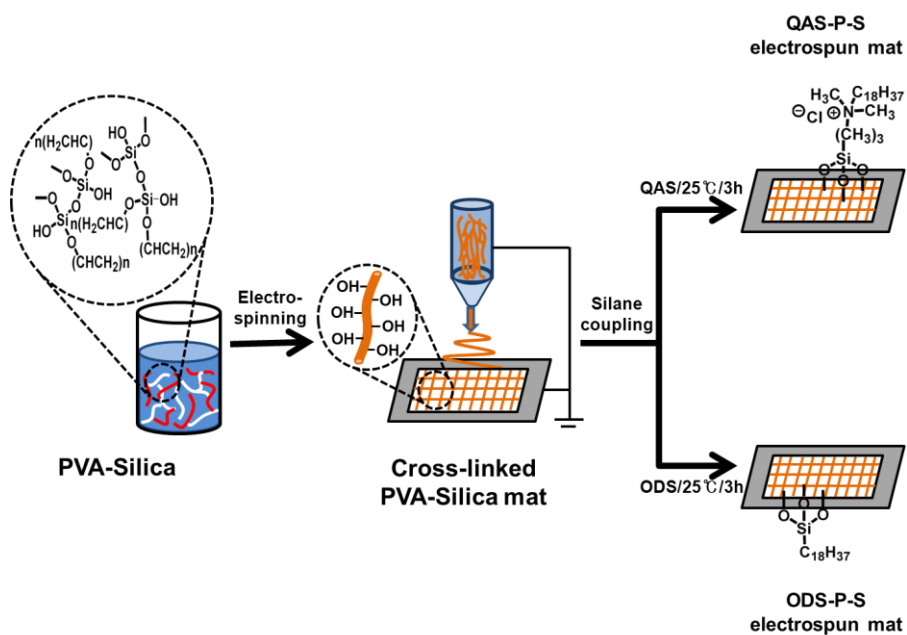
Figure 1. Schematic illustrations of P-S, ODS- and QAS-P-S electrospun mats via electrospinning and silane coupling modification. Inserted photo-images show water-stability as cross-linked P-S electrospun mat. P-S solution was fabricated sol-gel method.

3.1.2 SEM images of PVA-Silica electrospun mats with different concentration ratio

Figure 2 show the morphology of electrospun fiber depending on the concentration of TEOS and PVA. Each mat was prepared by electrospinning of PVA (4, 4.5, 5%) and TEOS (5, 10, 15%), which were total concentration ratio of the solution. When the concentration of TEOS was maintained at 5%, the concentration of PVA increased, images of SEM confirmed that the bead of the inner fiber was decreasing, TEOS of 10 and 15% shown similar tendency. Addition of high molecular weight PVA increased the viscosity of the sol-gel solution and reduced Releigh instability by increasing the conductivity, which was key factor that reducing the bead in the fiber during electrospinning process [2].

The concentration of 5% of PVA and 10% of TEOS, which solution was electrospinning and it was confirmed that the morphology of the fiber having a thickness of ca. 180 nm and no bead. (figure 2h) Electrospun mat added a solution of 15% TEOS was able to confirm

that the non-bead morphology but increased to ca. 220 nm thickness. (figure 2i) When it was the same concentration of PVA, with the increasing of the TEOS, was shown no-bead fiber. Because of cross-linking between PVA and TEOS, the bead reduced in the fiber and the thickness increased [44]. Therefore, there was no bead, and small diameter was considered the optimum condition of electrospun mat at the concentration of 10% TEOS and 5% PVA.

	PVA 4%	PVA 4.5%	PVA 5%
TEOS 5%	a)	b)	c)
TEOS 10%	d)	e)	h)
TEOS 15%	g)	h)	i)
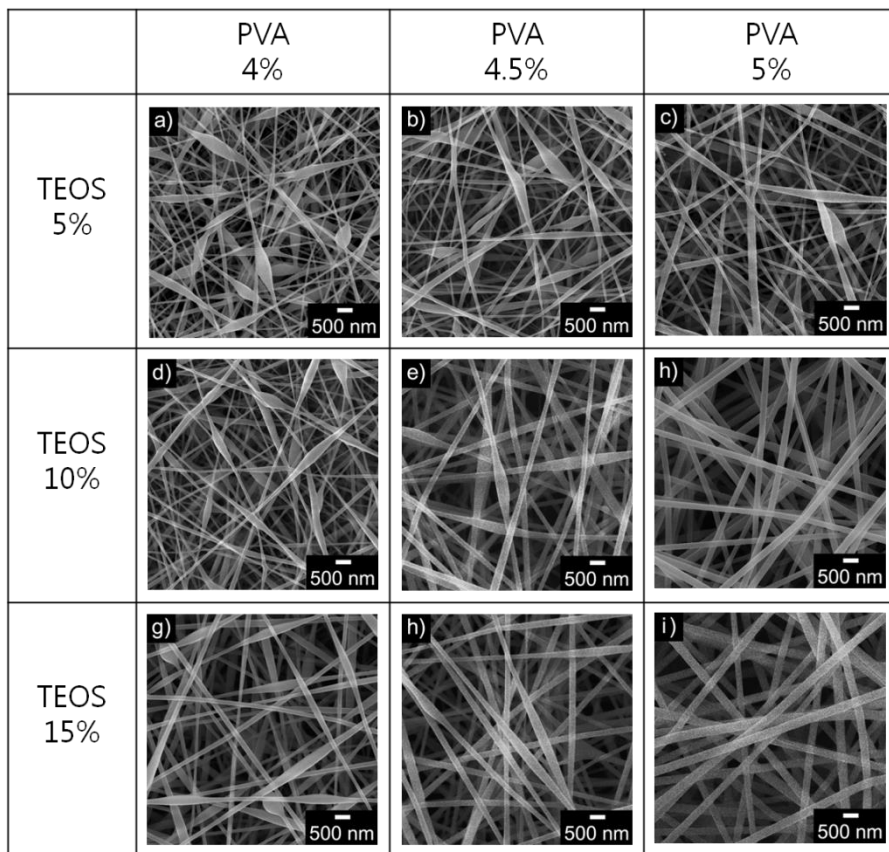
Figure 2. FE-SEM images of electrospun mats from solution containing TEOS 5% and a) PVA 4%, b) PVA 4.5%, c) PVA 5%. TEOS 10% added to d) PVA 4%, e) PVA 4.5% and h) PVA 5%. g) PVA 4%, h) PVA 4.5% and i) PVA 5% contained in TEOS 15%

3.1.3 SEM images of PVA, PVA-Silica and silane modified PVA-Silica electrospun mats

Figure 3 represent field-emission scanning electron microscopy images of the bead-free PVA, P-S and modified electrospun mat with ODS, QAS silane. As shown in the images, as-spun PVA of 5% size was ca. 160±5 nm (figure 3a) and inner fiber size of P-S electrospun mat, which added 10 % TEOS, was ca. 180±7 nm. (figure 3b) The concentration of TEOS was optimum for bead-free, small size and narrow distribution (figure 2h) [45]. Increased size in cross-linked mat was confirmed that TEOS of Silica precursor was reacted with PVA and Silica which were exist in fiber [46].

ODS and QAS modified P-S electrospun mats were shown thicker fiber, each of them was ca. 210±5 nm, 220±3 nm, than pristine as-spun mat (figure 3c, d). Morphology of fiber was not changed after water-medium post-treatment for silanization that was another proof of cross-linking because of water solubility of PVA [47]. However, swelling phenomena was present. Increased size was affected swelling of fiber

and silane coating. Taking these facts into account, cross-linking between PVA and TEOS was successfully reacted by hydrolysis and condensation reaction and silanization in water-medium was possible that provided simple modification for multi-functional properties of surface.
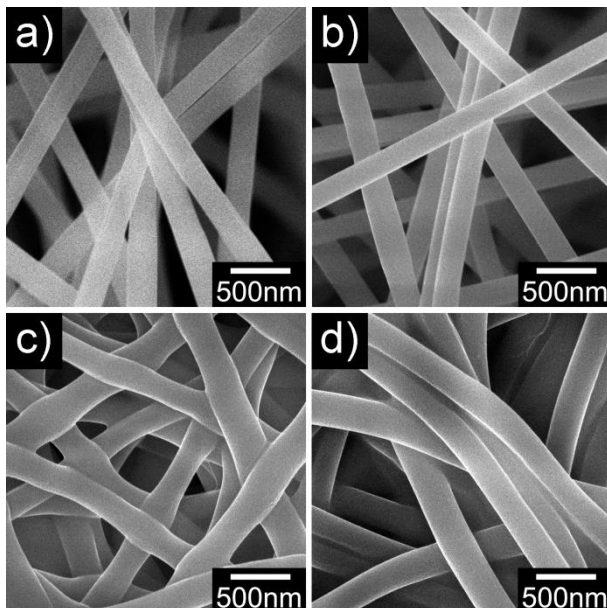
Figure 3. Representative FE-SEM images of a) pristine PVA, b) cross-linked P-S electrospun mats and c) ODS- and d) QAS-P-S electrospun mats. Silane modification was progressed in aqueous solvent (water:ethanol)

3.2 Characterization of QAS-PVA-Silica electrospun mat

3.2.1 Surface energy analysis of silane modified PVA-Silica electrospun mats

Water-contact angle was performed to confirm hydrophobicity of surface [48]. Hydrophobic property via long alkyl groups was expected prohibits adhesion of bacteria because of low surface energy between bacteria and surface. P-S represented hydrophilic surface of ca. $\leq 25°$ (table 1, figure 4a). Therefore, non-modified electrospun mat indicated property of hydrophilicity and water permeated the surface [49].

ODS-P-S only has long alkyl groups that represented hydrophobic properties and reacted with hydroxyl groups of surface via hydrolysis and condensation [50]. The mat represented higher angle than ca. $141\pm3°$ that proved transition of surface from hydrophilic to hydrophobicity (table 1, figure 4b) [4].

Similar to QAS has also same alkyl groups that were treated on P-S mat [51]. QAS modified electrospun mat show ca. 129±1° (figure 4c, table 1). However, lower angle represented than ODS modified mat, because ammonium ion represent positive charge that enhance binding energy between water [52]. In addition to fiber shape of the modified mats was not transformed [1]. Hence, hydrophilic PVA-Silica surface effectively modified using ODS, QAS silane from hydrophilic to hydrophobic property which was proved water contact angle.
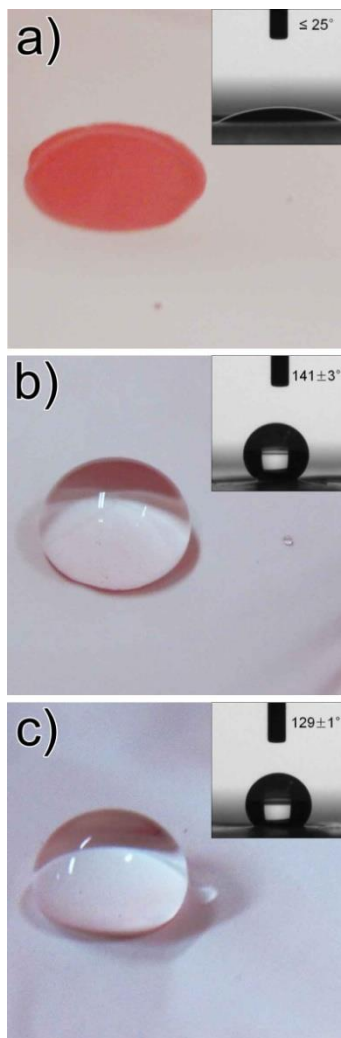
Figure 4. The photo-images of water-adhesion of a) P-S, b) ODS- and c) QAS-modified P-S electrospun mat. (Inset: water droplet images and numerical contact angle values) Contact-angle was measured via drop shape method.

Table 1. Contact angle between water droplet and surface of electrospun mats.

Substrate	Contact angle($\theta°$)
P-S	22.1±2
ODS-P-S	141±3
QAS-P-S	129±1

[a] These values were measured contact angle (DSA 10)

3.2.2 FT-IR and EDS analysis of modified electrospun mats

FTIR and EDS spectra of as-spun fibers also indicated that PVA and TEOS cross-linking were formed and whether surface modification was treated or not [36]. FT-IR represented Silica had asymmetric, symmetric stretching and bending vibration of Si-O-Si bond at 1045 cm^{-1} and Si-OH peak at 960 cm^{-1} (figure 5) [53]. PVA represented a very high intensity of the C-OH at 1094 cm^{-1} and EDS was shown ca. 69.3, 30.7 atomic % of C, O element (figure 6, table 2) [30, 44].

Cross-linked P-S represented a broad peak at 1100-1250 cm^{-1}, this proved the binding of Si-O-C (figure 5). This represented that transferred to a slightly higher wavenumber by the over-lapping between Si-O-Si and C-OH, the broad peak was caused by the C-O stretching movement of PVA and Si-O-Si asymmetric stretching [32, 36, 43]. EDS spectra were seen that element of Si was shown ca. 11.9 atomic % and increased O element compared pristine PVA because of cross-linking (figure 6, table 2).

QAS ODS treated electrospun mat that were confirmed by the peak

-CH$_2$, -CH$_3$ peak at 2975 cm^{-1} and 2900 cm^{-1} that caused by the alkyl

groups of the surface (figure 5) [37, 38]. EDS spectra also represented

that QAS had N, Cl on modified surface (figure 6, table 2) [3]. Intensity

of –OH, C-O and Si-O-Si were represented that peaks decreased

compared to P-S and EDS table indicated decreasing atomic ratio % of

Si and O. It proved that the reaction with the ethoxy group of silane and

hydroxyl group of P-S surface occurred. Taking these facts into account,

silane treatment and cross-linking were successful though analysis of

the EDS and FT-IR.
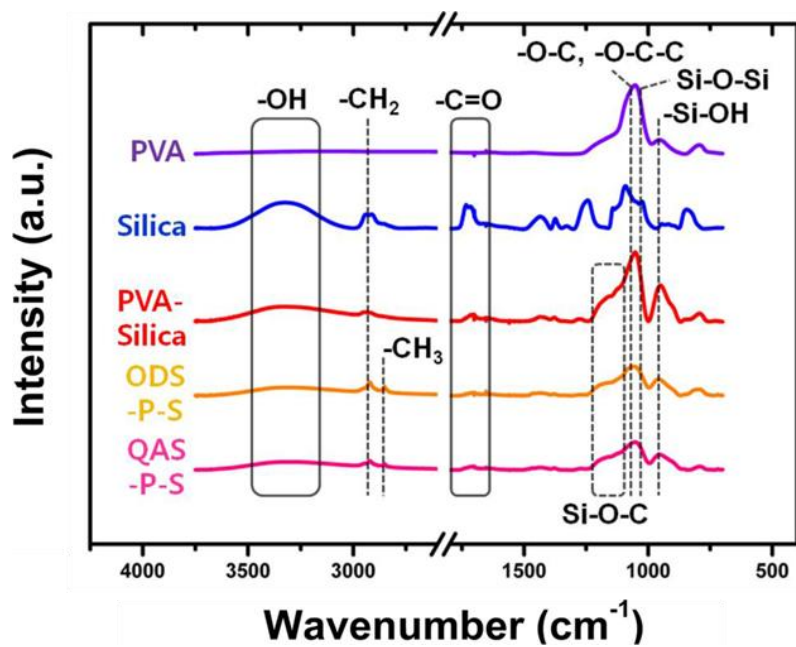
Figure 5. FT-IR spectra of PVA, Silica, P-S, ODS- and QAS-P-S
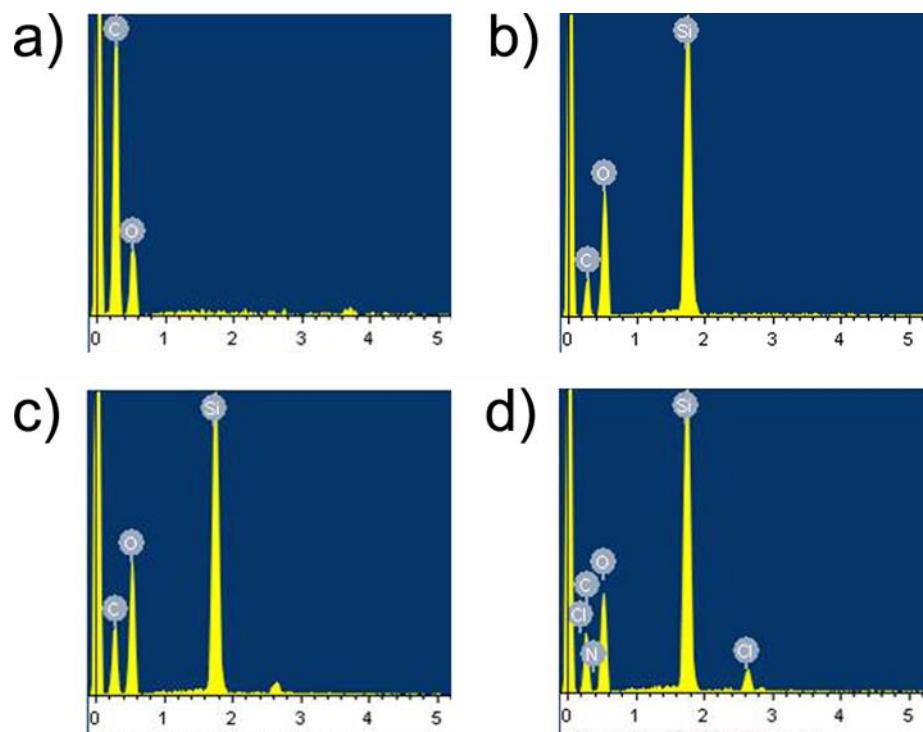
Figure 6. EDS analysis of a) PVA, b) P-S, c) ODS- and d) QAS-P-S

Table 2. Elemental analysis (C, O, Si, Cl and N) of PVA, P-S, ODS- and QAS-P-S electrospun mats.

Element	Atomic ratio (%)			
	PVA	P-S	ODS-P-S	QAS-P-S
C	69.29	37.95	48.39	46.66
O	30.71	50.20	42.99	39.35
Si		11.85	8.62	8.99
Cl	-	-	-	0.75
N	-	-	-	4.25

[a] These values were obtained by elemental analyzer (EDS).

3.2.3 Thermal analysis of modified electrospun mats using TGA

TGA thermogram was compared to determine different PVA:TEOS ratio of cross-linked electrospun mats (figure 7) [48]. TEOS solution ranging from 5, 10, 15 wt% of total solution were made by dissolving in ethanol and deionized water. PVA concentration was maintained 5% of total solution that was optimum in the condition, which the fiber represented the lowest diameter (180±5 nm) and not beads (figure 2).

When added TEOS of 5% into the each solution, thermogram of fibers with different ratios of PVA:TEOS represented that the increase of TEOS content in the electrospun solution resulted in the decrease of weight loss. These results were possible that cross-linked silica in PVA possessed lower fiber degradation at higher temperature. However, diameter of electrospun nano-fiber also increased than low concentration of TEOS. Therefore, TEOS and PVA ratio was determined diameter and morphology by SEM, which TEOS solutions 10 wt% of total solution was optimum for narrow diameter (figure 2).
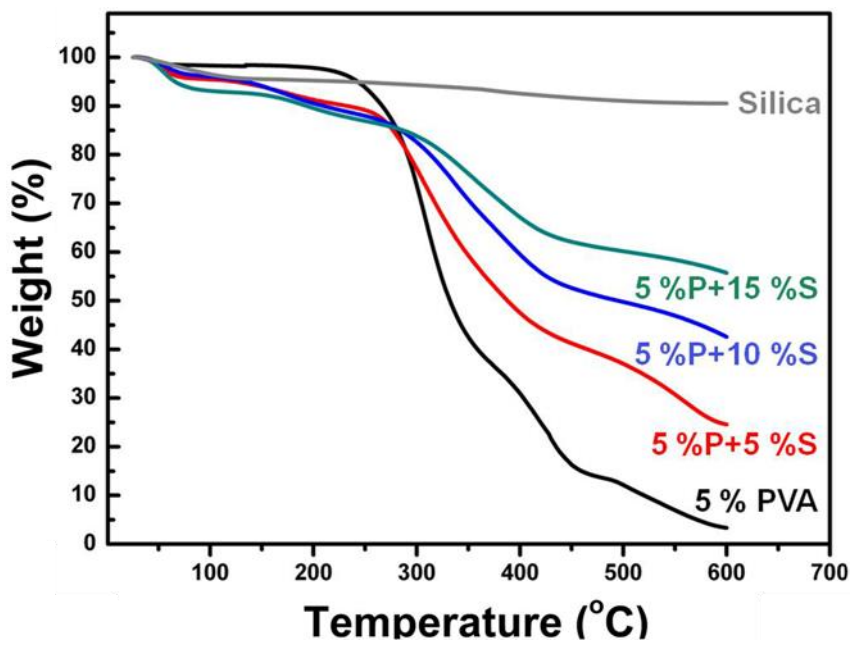
Figure 7. Thermogram of P-S with various PVA:TEOS concentration.

3.3 Application of silane modified PVA-Silica electrospun mats for antibacterial performance

We compared the electrospun mats of PVA, ODS- and QAS-P-S in other to confirm antibacterial activity of the contact type by spray method. *E. coli* and *S. aureus* (10^6~10^7 CFU/mL) was injected into 20 ml of water, which suspension sprayed on the each electrospun mats at 2 times. Autoclaved LB agar broth was poured to the surface and solidified. The mats were incubated at 37 ℃ for 24 h and the bacterial colonies were investigated [39].

As shown in figure 8, on the surface of the P-S and ODS-P-S were confirmed that *E. coli* (figure 8a) and *S. aureus* (figure 8b) grew, however, the surface of QAS-P-S, which represented clear. Unlike the QAS, the ODS without ammonium groups, which confirmed that only alkyl group were not possess antibacterial activity [4]. Therefore, the surface with a quaternary ammonium was able to confirm inducing the death of cells through the contact with the bacteria.

To estimate the degree of antibacterial activity and the degree of

durability, P-S, ODS- and QAS-P-S were compared under the same conditions. Kinetic test was performed to confirm the antibacterial activity, which conditions were that the mats of 3 cm x 5 cm were injected with 20 µL (10^6~10^7 CFU/ml) of gram-negative *E. coli* and gram-positive *S. aureus* solution into the liquid broth [10]. 50 µL of samples were cultured on the LB Plate depending on contact time (min) and counted the surviving colonies after 24 h at 37 ℃.

The QAS-P-S was represented outstanding antibacterial activity against *E. coli* and *S. aureus*. As can be seen from figure 9a, pristine P-S and ODS modified P-S were able to confirm that the bacteria grew. On the other hand, QAS-P-S contact with *E. coli* and *S. aureus* which were killed more than 99.9% after 150 min. The antibacterial activity according to the contact time was confirmed that the colonies of S.aureus was reduced more than 80% when 30min had elapsed, decreased 100% to about 90 min later. In the case of *E. coli*, after 30 min, colonies gradually decreased to ca. 58% and it was confirmed that they had died all after 150 min (figure 9b).

The plot of the contact time (min) vs. reduction (%) graph displayed, which the antibacterial resistance was stronger *E. coli* as compared to *S. aureus* relatively (figure 9b) [51]. These reasons were considered to gram-negative bacteria having structures of multiple layers of peptidoglycan, outer membrane and cytoplasmic membrane compared to gram-positive bacteria, was structurally tight [40, 54]. However, Figure 9a was shown antibacterial properties of 100% against two types of bacteria after sufficient contact time.

According to the researches, which had been proceed, antibacterial properties of QAS was that were represented through the contact mechanism with the bacteria, It was confirmed to be indicative of the presence / absence of antibacterial activity depending on the functional groups of the silane treated surface through the above results [2, 11]. The P-S had not antibacterial property, which it indicated that there was no effect between the surface of bacteria and hydroxyl group [45]. Similarly, ODS modified P-S represented the non-antibacterial, meaning that it was not able to kill bacteria only hydrophobic property.

Meanwhile, QAS had a quaternary amine group possessing a further positive charge while maintaining the alkyl group such as ODS. There was a possibility that achieve a charge-charge interaction for antibacterial activity with the outer membrane / outer wall of the bacteria with a negative charge [4, 55].

Furthermore, QAS-P-S, because of the hydrophobic property via long alkyl groups, accumulated bacteria on the surface were easy removed via just to wash with water [3, 56]. In order to confirm the durability performance of QAS-P-S which was recycled, an experiment was carried out based on 90 min indicating the antibacterial 100% initial and a total of five times at 30 min intervals. As can be shown figure 10, QAS-P-S was shown excellent antibacterial effect of more than 99% in the recycling of 5 times against *S. aureus*. The results described above, the surface of QAS-P-S was dropped easily bacteria and maintained the antibacterial property. This indicated that the QAS and P-S were strong chemical bonding by hydrolysis and condensation mechanism. As a result, it was considered that QAS-P-S presented that

physically / chemically properties were stable, which included having

characteristics very suitable for recycling.
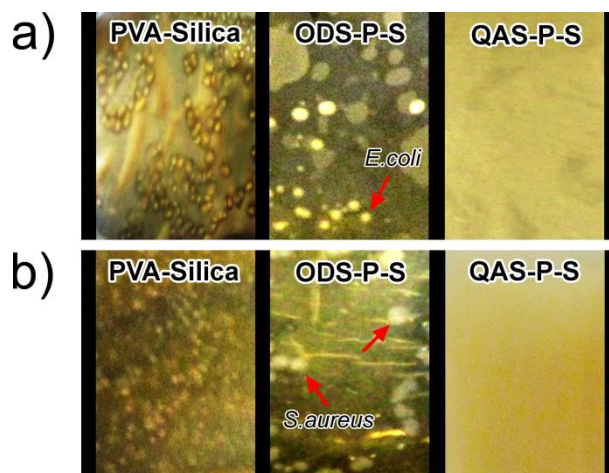
Figure 8. Photograph images of viable colonies on surface of P-S, ODS- and QAS-P-S electrospun mats after spraying bacteria of a) *E. coli*, b) *S. aureus*

Figure 9. Photographs of surviving colonies via a) *S. aureus* (top), *E. coli* (bottom), which bacteria were immersed into LB broth with P-S, ODS- and QAS-P-S for 150 min. b) The plot of reduction % versus contact time between bacteria and QAS-P-S. (Reduction % was calculated (A-B)/A, which A is the number of surviving colonies in the blank and B is the number of surviving colonies in the QAS-P-S)

4 8

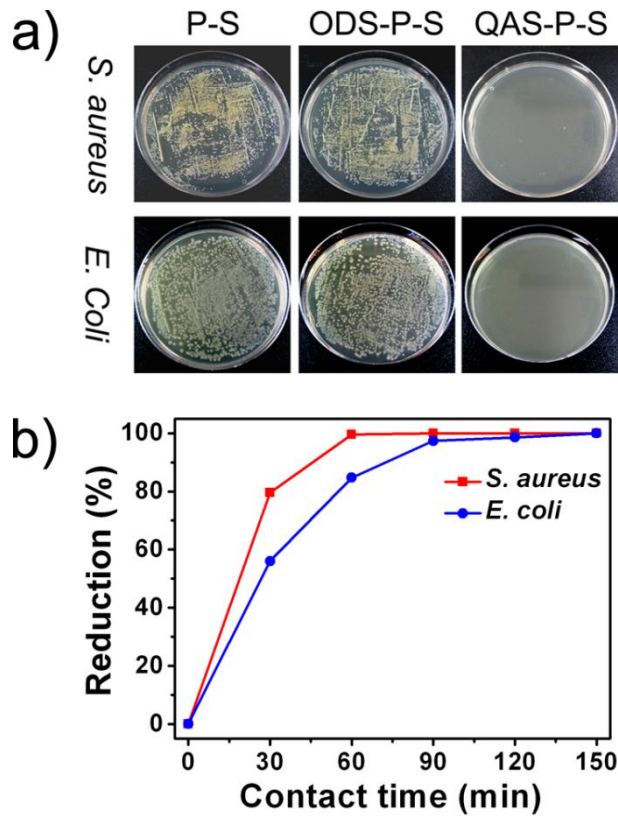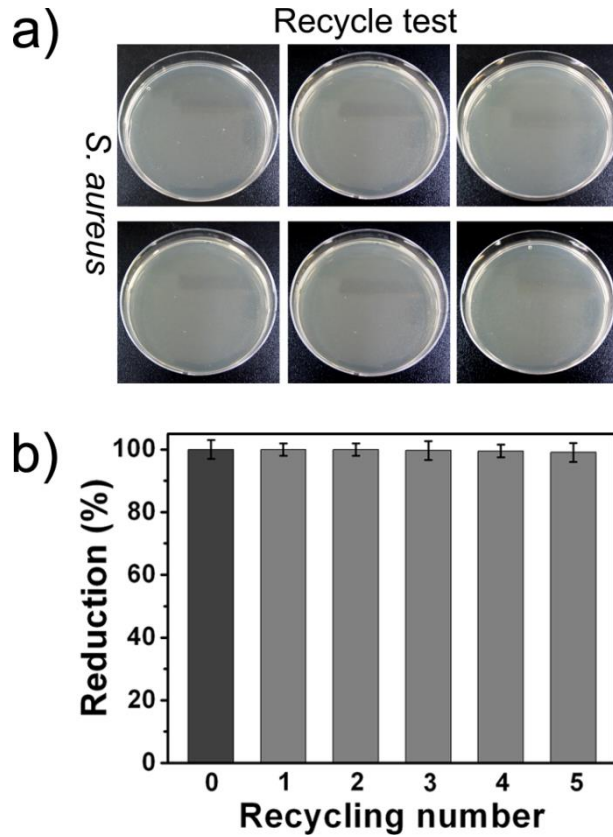**Figure 10**. Photographs of a) antibacterial recycle tests, which progressed at 90 min using *S. aureus* at 5 times. (Recycle tests were arranged in order from the top left), b) as functions of reduction % and recycling numbers. (Reduction % was calculated (A-B)/A, which A is the number of surviving colonies in the blank solution and the B is the number of surviving colonies in the QAS-P-S)

Chapter 4. Conclusion

In conclusion, we successfully fabricated P-S electrospun mat that did not dissolve in water and modified the surface from hydrophilic to hydrophobic by using a coupling reaction between silane and surface of P-S. It had a long alkyl groups and quaternary amine group, QAS silane used in the surface treatment, and furnished hydrophobic characteristics and positive charge on the surface. The peak of the chemical bonding that inside of fabricated material was shown through analysis of the EDS and FT-IR, and properties of the surface modified was able to be confirmed by contact angle measurements of water droplets.

The antibacterial performance was evaluated using the kinetic test that outstanding antibacterial activity of the QAS-P-S was confirmed. The contact time after 150 min, gram-negative and gram-positive bacteria were shown to be killed by charge-charge interaction with the surface. In addition, hydrophobic property via long alkyl group, which facilitated the removal of bacteria on the surface using water washing

after the antibacterial experiment, represneted excellent durability of antibacterial activity of 99% after five recycling test.

As a result, we overcome the limitations of the physical properties via cross-linking of PVA and Silica, the surface was provided positive charge by using simple coupling processing. It was shown excellent antibacterial activity. Further, it represented high-durability via chemical covalent bonding between the surface of P-S and silane and possible to easily remove the accumulation of bacteria on the surface, which represented superior performance for recycling. It is expected to be applicable in many fields, such as practical membrane, filter, and heavy-absorption, in that the surface can be treated with silane having various functional groups.

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초   록

졸-겔 방법에 따라 폴리비닐알코올과 실리카 간의 가교를 이룬 용액을 전기방사를 통해 매트 형태로 제조하고 실란의 종류에 따라 표면을 개질 하여 항균성 표면에 응용하였다. 친수성 매트의 표면은 실란의 알킬기의 도입에 따라 소수성으로 개질되었으며, 더불어 4차 아민을 지닌 실란이 처리된 표면에서는 질소의 양성 전하를 확인 할 수 있었다. 그람 음성인 대장균, 그람 양성인 황색포도상구균과 매트와의 표면 접촉, 시간 그리고 반복 실험을 진행 함으로써 항균성과 내구성을 확인하였다. 이와 같이 제조된 4차 아민-폴리비닐알코올/실리카 전기방사 매트는 150분 동안 균과의 접촉에서 99.9%이상의 우수한 항균성을 확인하였으며, 반복실험에서도 99%이상의 성능을 유지하는 것을 확인 할 수 있었다.