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REVIEW

Recent advance in antibacterial activity of nanoparticles contained polyurethane

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ABSTRACT: Polyurethanes (PUs) are among the most widely used polymers with various applications in several industries. Antibacterial activity is an important feature of PU materials used in medical or many other related consumer products. They can, however, be easily colonized by bacteria and fungi, which may cause many problems for human health. It is therefore very important to enhance the antimicrobial properties of PUs, besides improving their chemical and physical properties. The incorporation of some antibacterial materials in the PUs' polymeric matrices is an effective strategy to improve their antibacterial activity. In this regard, the addition of some materials including Ag, Au, ZnO, and TiO_2 nanoparticles, carbon nanotubes and chitosan to the PUs' material structure is reviewed in this article, and their antibacterial mechanisms are discussed. © 2018 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2019**, *136*, 46997.

KEYWORDS: antibacterial activity; nanocomposites; polyurethane

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INTRODUCTION

Polymeric materials are vital compounds in the material world and modern industrial economics. According to their basis of origin, they are classified into three main categories: (1) natural polymers (proteins, polysaccharides, and polyesters), (2) semisynthetic (cellulose nitrate and hydro-halogenated rubber), and (3) synthetic polymers.[1] Polyurethane (PU) is an attractive multifaceted synthetic elastomer[2,3] invented by Profess or Otto Bayer in 1937.[4] PUs are among the most widely used polymers with various applications,[2,5–8] including coatings, adhesives, furniture, paints, additives to automotive oils, medical synthetic materials, food packaging, footwear, construction materials, padding, and so forth.[9–13]

PU composites have many notable applicable properties such as low cost, low density, water insolubility, high abrasion and corrosion resistance, high impact strength, excellent flexibility, controllable hardness, shape memory, damping ability, high elasticity, good processability, biocompatibility and biostability, antiaging, and excellent blood compatibility.[5,10,11,14–16] These properties can be modified for specific applications just by changing the formulation and adjusting the reaction conditions during the preparation procedure[16–18] and, interestingly, their physical and chemical characteristics can be improved through a combination of various additives during the synthesis (polymerization) process.[19] Specifically, the incorporation of nanomaterials (i.e., metal nanoparticles, NPs) could significantly improve the properties of PU materials and their further applicability.[20]

PU materials were first applied in biomedical instruments in the late 1950s[7] and now they are commonly used in medical products, from thermal insulation to medical implants.[4] However, the antibacterial activity is an essential feature of medical or any other related consumer products,[21] but PUs can be easily colonized by bacteria and fungi, which may cause many problems for humans.[22,23] With growing public health awareness, there is an increasing need to develop the antimicrobial properties of PU in addition to improving their chemical and physical properties. Therefore, binding or grafting some active chemicals on the PUs surface is necessary, when polymeric material is in contact with a physiological component.[24] Several materials such as Ag, Au, ZnO, and TiO_2 NPs, carbon nanotubes,[14,25] and chitosan (CS) have been introduced to be

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incorporated into the polymeric matrix of PUs in order to improve their antimicrobial properties. In this regard, much attention has been focused on the combination of NPs as a capable high antibacterial agent, due to their large surface area which provides desirable contact with bacterial cells.[26] Several studies have been done on this, using different NPs as listed in Table I. Many review articles have been written on the application and properties of PUs.[2,13,27–30] Because of the importance of the antibacterial activity of PU materials, for the first time we reviewed the antibacterial performance of these composites and nanocomposites in this study.

Silver Nanoparticles (Ag NPs)

Various metal NPs such as Au, Pt, Ag, and Pd NPs, silver nanoparticles (Ag NPs), and their compounds have been found to be strong antibacterial agents with good antimicrobial efficacy against a broad spectrum of bacterial and other eukaryotic microorganisms.[31–34] The silver ions released from the nanocomposites can interact with amino and thiol groups of proteins, nucleic acid, and cell membranes and disturb the biochemical process of microorganisms.[35,36] However, their mechanism of action is not yet clearly understood,[9] and a suggested mechanism of Ag NPs cytotoxicity toward the bacterial cell is presented in Figure 1.[26] Silver is a noble metal with high biocompatibility,[3] electrical and thermal conductivity, and excellent resistance to oxidation,[37] which gives it various applications such as an antimicrobial filters, medical devices, protective cloths, chemical sensors, and water disinfectants.[20,38,39]

The incorporation of Ag NPs in the polymeric matrix is an effective methodology to modify their properties.[40–42] They have also been embedded in PUs to improve their biocompatibility and the physical features of PUs.[6,33] Likewise, Ag NPs could inhibit the growth of bacteria, even at low concentrations, in/on the PU matrix.[3,43] Dallas *et al.* reviewed the many antimicrobial aspects of polymer silver nanocomposites in terms of the synthetic routes, their advantages, drawbacks, possible improvements, and real applicability in antibacterial and antifungal therapy.[44]

Sheikh *et al.* successfully prepared PU nanofibers contained in Ag NPs (5–20 nm) using an electrospinning technique without the

Table I. Antibacterial Activity of PU Composites

Matrix	NPs	Size (nm)	Modification	Antibacterial activity	Antibacterial test	Ref
PU membrane		80	COS[a], DOPA[b]	*E. coli, S. aureus*	Agar plate	126
PU membrane			citric acid, chitosan	*P. aeruginosa*	Spread plate	125
Halloysite nanotubes/WPU				*A. hydrophila* *P. putida* *L. monocytogenes S. aureus*	Agar diffusion	127
Chitosan-PU films			chitosan	*P. putida, S. aureus*	Colony counting	10
WPU/Ag-halloysite nanotube nanocomposites films	Ag	10–30	AEAPTMS[c], chitosan	*E. coli, S. aureus*	Plate counting	33
PU nanofiber	Ag	80–90		*E. coli, S. aureus*	Spread plate	38
PU foams doped with stable Ag NPs	Ag	6–10		*E. coli*	Well diffusion	20
PU/keratin/AgNP	Ag		Iodoacetic acid	*E. coli* *S. aureus*	Disc diffusion	23
Anionic WPU nanocomposites	Ag	5–30		*E. coli* *S. aureus*		36
PU/nanosilver complex fiber	Ag	9–35		*E. coli* *S. aureus*	Spread plate	6
PU films	Ag			*P. putida*		47
Tourmaline NPs/PU hybrid mat	Ag	20		*E. coli*	Inhibition	25
2 K WPU coating	Ag	50		*E. coli* *S. aureus*	Agar-well diffusion	14
PU nanofibrous	Ag	6–10		*E. coli*	Zone inhibition	128
WPU nanocomposites	Ag	5		*E. coli* *B. subtilis*	Agar dish	3
PU nanofibers	Ag	20		*E. coli* *S. aureus*	Spread plate	15
PU foams	Ag	6–12		*E. coli* *B. subtilis*	Colony Count Test	46
PU foam	Ag	10–15		*E. coli*	Pour plate	45
PU nanofibrous	Ag	20–30		*S. aureus*	Agar diffusion	49
Embedded PU sheets with MB, TB and Au NPs	Au	2		*S. aureus*	Agar plate	64
PU foams			Cu NPs	*E. coli* *S. aureus* *K. marxianus*	Agar plate	129
PU acrylate nanocomposites	Ag/TiO_2	30 and 6		*E. coli*	Shaking flask	32
Silver-doped TiO_2/PU Nanocomposites	TiO_2			*E. coli* *S. aureus*	Agar diffusion	9
Acrylic PU coating		40	Rutile TiO_2 NPs	*E. coli*	Instrument Beckman Coulter	73
PU nanocomposite coating films		20	ZnO NPs	*E. coli* *B. subtilis*	Well diffusion	97
PU hybrid materials	ZnO	30–60		*E. coli*	Agar plate	98
PU based nanocomposite	ZnO	60		*E. coli, S. aureus, P. putida*	Pour plate	99
WPU nanowhiskers	ZnO			*E. coli, S. aureus*	Agar plate	53
PU coatings	ZnO	27		*E. coli, B. subtilis*	Agar dilution	100
PU nanocomposites fibers	Tourmaline	50		*E. coli* *Enterococci*	Zone inhibition	128

[a] Chitooligosaccharide.
[b] Dopamine.
[c] 3-(2-Aminoethylamino)propyldimethoxymethylsilane.

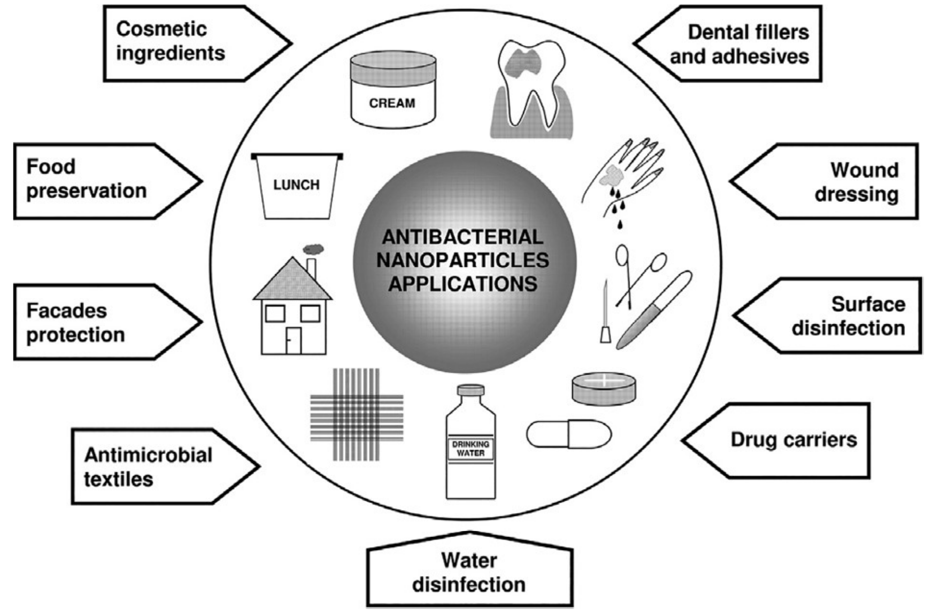


Figure 1. Proposed mechanism for Ag NPs antibacterial activity. (Reproduced with permission from Ref. [26], copyright 2018, with permission from Elsevier, License number: 4377810845605.)

addition of any foreign reducing agent.[15] Their results confirmed the good stability of the prepared nanofiber mats, and their mechanical properties improved by increasing the content of Ag NPs. The antimicrobial tests against *Escherichia coli* and *Salmonella typhimurium*, as two organisms, indicated that these nanofiber mats can be considered as effective and reliable trustable antibacterial agents. Jain and Pradeep also coated the commercial PU foams with Ag NPs through exposure of the foams to NPs solutions (as shown in Figure 2).[45] Their antibacterial tests against *E. coli* showed that no bacterium was detected on the surface of nanocomposite.

In another work, Phong *et al.* prepared the Ag NP (6–12 nm)-coated PU foams to use as a bacterial filter for contaminated drinking water.[46] The microbiological tests were carried out on PU/Ag NP foams with the Coliforms, *E. coli* and *Bacillus subtilis*, which demonstrated the total killing of bacteria with an antibacterial efficiency of 100%.

Saez *et al.* employed a light assisted approach for the fabrication of a nanocomposite, in which Ag NPs were embedded and stabilized within a PU matrix.[47] Their results showed improved antibacterial and antibiofilm activity against *Pseudomonas aeruginosa* with negligible toxicity for human primary skin cells and erythrocytes. Recently, Savelyev *et al.*[48] showed that the biologically active PU materials containing Ag and Cu NPs exhibited good bactericidal properties against both Gram-negative and Gram-positive bacteria, and yeast-like fungi. It was demonstrated that the nanostructured Ag/Cu polyurethanes have a strain-dependent fungicidal effect against *Alternaria alternata*, *Aspergillus niger*, and *Penicillium* spp.

Hong *et al.* fabricated the polycarbonate diol/isosorbide-based antibacterial PU nanofibers containing Ag NPs, using the electrospinning process (as shown in Scheme 1).[49] Figures 3 and 4 show the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of PU/Ag NPs nanofibers containing different Ag NPs content, respectively. The antibacterial activity of the treated PU/Ag NPs fabrics against *Staphylococcus aureus* and methicillin-resistant *S. aureus* (MRSA) was found to be excellent. As can be seen in Figure 5, PU/Ag fabrics placed on the agar medium killed the bacteria around the fabrics. The average diameters of the inhibition zone were measures at 20.41 and 18.24 mm for *S. aureus* and MRSA, respectively. By increasing the Ag NP content applied to the agar medium, the average zones of inhibition were increased, whereas the neat PU did not show any antimicrobial activity. Ag NPs also distinctly improved the thermal, mechanical, and biological properties of PU nanofibers.

In another work, Wang *et al.* combined the keratin and PU then *in situ* formed Ag NPs to provide PU/keratin/Ag NPs mats with excellent biocompatibility and antibacterial properties.[23] The SEM images of prepared biocomposite mats are shown in Figure 6 for different concentrations of $AgNO_3$ solution which affected the size of Ag NPs. The prepared mats considerably accelerated the wound recovery compared to the conventional gauze sponge dressing.

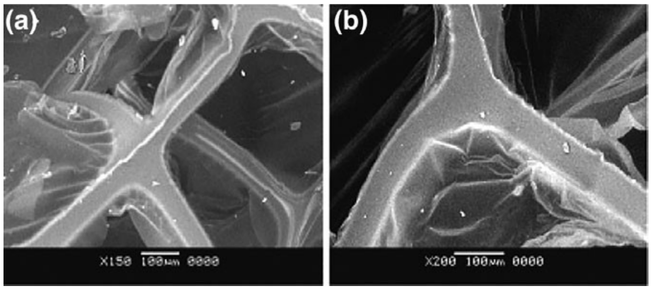
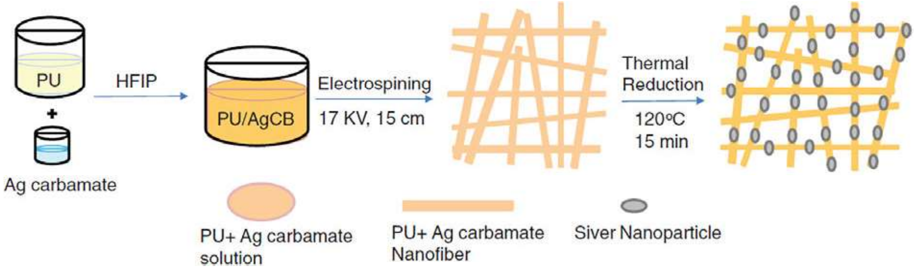


Figure 2. SEM of (a) pure PU, and (b) Ag NPs coated PU. (Reproduced with permission from Ref. [45], copyright 2005, with permission from John Wiley and Sons, License number: 4385440076840.)



Scheme 1. Synthesis procedure of PU/Ag NPs nanofiber fabrics using silver carbamate complex. (Reproduced with permission from Ref. [49], copyright 2017, Reprinted by Permission of SAGE Publications, Ltd.) [Color figure can be viewed at wileyonlinelibrary.com]

Tijing *et al*. incorporated tourmaline (TM) NPs in the PU matrix by electrospinning followed by decorating them with the wire-like Ag NPs using photoreduction under UV light irradiation.[25,50] The prepared highly porous, ultrafine, and nonwoven nanofibers are shown in Figure 7. The incorporation of TM NPs in PU increased the tensile strength and modulus of neat PU with improved hydrophilicity.[50] The prepared TM/PU mats showed high zone inhibition for both *E. coli* and *Enterococci* with increasing efficiency with the increase of TM NP content.[50] On the other hand, the Ag/TM/PU hybrid mat exhibited excellent bactericidal properties depending on the Ag content.[25] In another study, Tijing *et al.* fabricated a bimodal polymeric nanofibrous mat containing PU and Ag NPs (6–90 nm) decorated with poly(ethylene oxide) (PEO),[51] in which the reduction rate of Ag ions in PEO played an important role in the control of Ag NP size. The prepared hybrid nanofibrous mat exhibited strong antibacterial activity, while it was potentially useful as antibacterial tissue scaffolds or for wound-healing applications.

Waterborne PU (WPU) is a safe, eco-friendly, and binary colloidal system in which the PU particles are dispersed in water instead of organic solvents.[27,52] Compared to conventional organic solvent-based PUs, WPU shows the advantages of nontoxicity,[53] low viscosity, and reduction in costs.[3] It was demonstrated that filling the WPU with Ag NPs increases the thermal stability, dynamic mechanical properties, and biostability of polymer, while the stability of nanocomposite was more remarkable over a wider range of Ag contents than that of the Au NPs.[54]

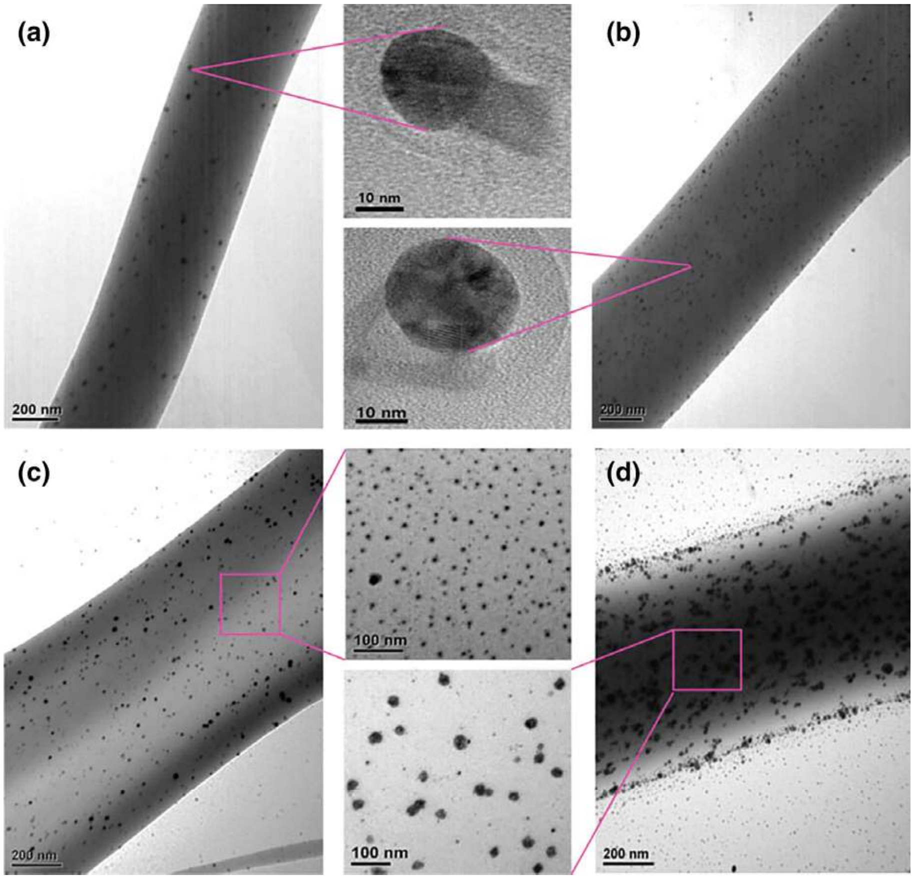


Figure 3. TEM images of PU/Ag nanofibers containing different Ag content of (a) 0.01 wt %, (b) 0.1 wt %, (c) 1 wt %, and (d) 5 wt %. (Reproduced with permission from Ref. [49], copyright © 2017, Reprinted by Permission of SAGE Publications, Ltd.) [Color figure can be viewed at wileyonlinelibrary.com]

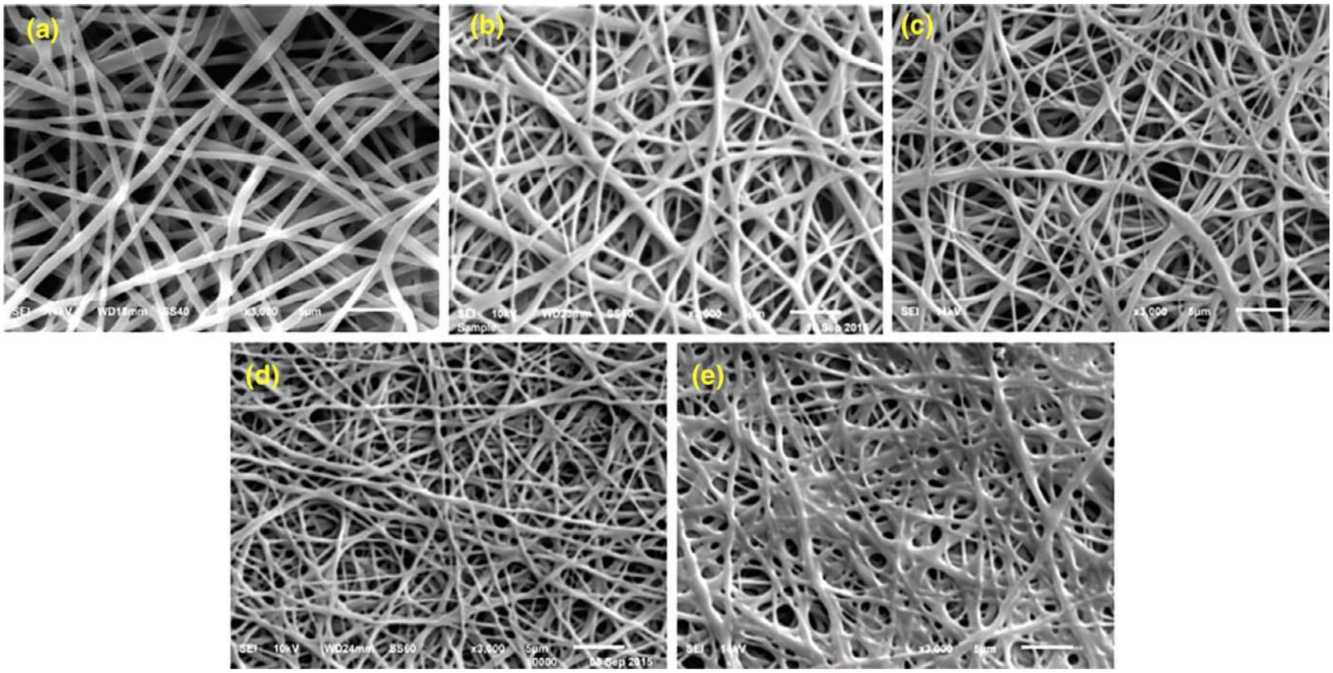


Figure 4. SEM image PU/Ag nanofibers containing different Ag content of (a) 0 wt %, (b) 0.01 wt %, (c) 0.1 wt %, (d) 1 wt %, and (e) 5 wt %. (Reproduced with permission from Ref. [49], copyright 2017, Reprinted by Permission of SAGE Publications, Ltd.) [Color figure can be viewed at wileyonlinelibrary.com]

The biocompatibility and antibacterial properties of WPU/Ag NPs nanocomposites have been studied too. For example, Wattanodorn *et al.* studied the antibacterial properties of anionic WPU by incorporating Ag NPs (5–30 nm) through the *in situ* silver ions reduction.[36] The prepared nanocomposite exhibited a bacterial reduction of 99.99 and 53.97% for *E. coli* and *S. aureus*, respectively. The incorporation of Ag NPs into WPU also enhanced the mechanical properties including tensile strength and Young's modulus, compared to that of the pure WPU. In another work, Hsu *et al.* showed that the Ag NPs (~5 nm) contained in the polyester-type WPU have better biocompatibility than pure WPU.[3] Moreover, the adhesion of *B. subtilis* and *E. coli* on PU/Ag nanocomposites was much lower at all Ag NPs contents, so that the PU containing 30 ppm of Ag NPs exhibited superior physicochemical properties, cellular response, and bacteriostatic effect. Wu *et al.* also showed that the WPU/Ag NPs nanocomposite films prepared by the reduction of Ag ions in the presence of WPU as a stabilizing agent show good antibacterial activity.[37]

Generally, NPs conveniently respond to the surrounding active substances, due to their high surface energy. It causes to both high reactivity and poor stability, which can be resulted to positive and also negative impacts in NP processing.[55] The *in vitro* studies demonstrated that nano-sized particles are more biologically active than equivalent micron-sized particles.[56] The increasing application of commercial nanomaterials may also have potentially negative effects on the ecosystem and human health, because of accumulation, biotransformation, or interaction of NPs in/with plants.[55,57] For example, Ag, Au, ZnO, CuO, and some other compounds exhibiting some degrees of dissolution in soil in the nanoparticulate shape, which can agglomerate and affect the plants ecosystem.[55] Moreover, to straight compromise human health, the nanotoxicity can harmfully affect fetal growth and female reproductivity.[58] The growing use of NPs makes enhancing concerns on their possible environmental impacts within the scientific and regulatory communities.[59]

Ag NPs, as an extensively used antibacterial agent, have been used in wide range of applications and they can be released into the environment by washing, erosion, fracture, and so forth. It was reported that they have negative effects (e.g., toxicity) to human and animals.[60,61] On the other hand, besides the widely usage of Ag NPs, applying the reducing agents can be a potential risk to the health of human and environment.[62] Unfortunately, despite the several studies on the antibacterial activity of Ag NPs-coated PUs composites, their negative effects on the living organisms were overlooked. Due to the application of these composites in the packaging and pharmaceutical industries, it seems that the study of this issue is necessary for human and animal health.

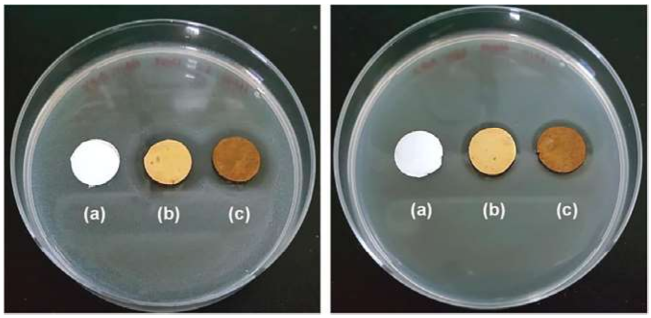


Figure 5. The plate morphology of (a) *S. aureus* and (b) MRSA cells exposed to nanofiber fabrics of (a) PU, (b) PU/Ag NPs (0.01 wt %), and (c) PU/Ag NPs (0.1 wt %). (Reproduced with permission from Ref. [49], copyright 2017, Reprinted by Permission of SAGE Publications, Ltd.) [Color figure can be viewed at wileyonlinelibrary.com]

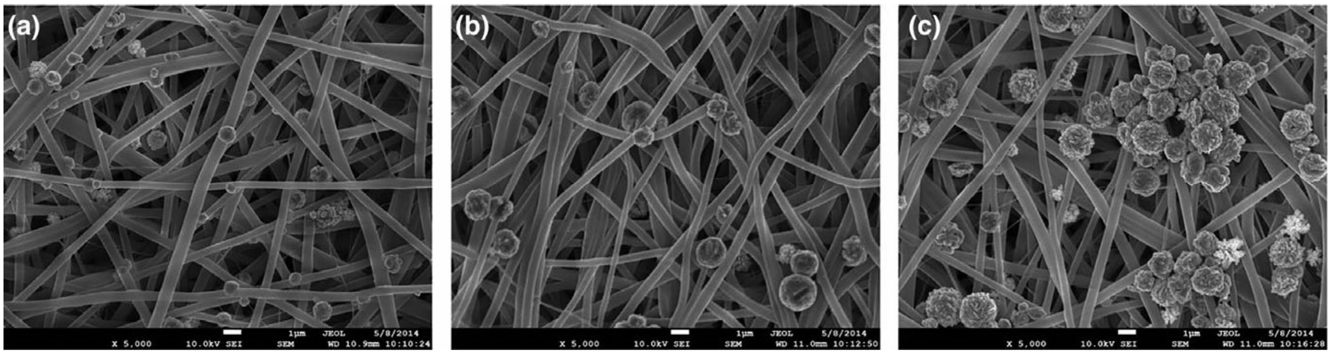


Figure 6. SEM images of PU/keratin mats immersed in different concentrated $AgNO_3$ solution (a) 1%, (b) 2.5%, and (c) 5%. (Reproduced with permission from Ref. [23], copyright (2016) with permission of The Royal Society of Chemistry.)

Gold Nanoparticles

Gold is one of the most important noble metals and has been used, in NP form, in various applications, due to its biocompatibility, nontoxicity, and high stability.[63] Gold nanoparticles (Au NPs) were found to be efficient enhancers of bacterial lethal photosensitization.[64] Unlike Ag NPs, which act as an antimicrobial agent themselves, Au NPs do not kill the bacteria alone.[64] At low concentrations, Au NPs are able to induce PU surface morphological changes and, in the size range ~5 nm, can change the interfacial energy between soft and hard segments, resulting in a change of PU microstructure.[3] There is a limited study on the performance of Au NPs in the antibacterial activity of PU. For example, Naik *et al.* studied the antibacterial activity of embedded PU sheets with methylene blue (MB), toluidine blue (TB), and Au NPs (2 nm).[64] No bacterial killing was observed for the untreated PU, but the dye-impregnated PU has the potential to kill the *S. aureus* bacteria under white light illumination. On the other hand, the addition of Au NPs further enhanced the observed killing to 3.8 $\log_{10}$ (MB) and 4.8 $\log_{10}$ (TB).

It should be noted that the stability of Au NPs in the bio-based tests and their applications is necessary in high ionic strength buffered solutions, whereas their instability was demonstrated in different ionic media.[65] Depend on the solution conditions, the aggregation and collapse of NP or release of Au^{3+} ions can be occurred, which are all undesirable.[65] The chemically synthesis of Au NPs could also lead to the presence of some toxic chemical species on the NPs surface, which may cause adverse effects.[66] In order to avoid such events, specific conditions without using toxic chemicals[67] must be applied for the Au NPs applications, especially in PUs composites, in biological systems.

TiO_2 Nanoparticles

In recent years, TiO_2 semiconductor materials have become increasingly intriguing, owing to their excellent physical and chemical stability, high specific surface area, high reactivity, nontoxicity, and affordable cost.[9,32] Nowadays, TiO_2 NPs is showing a new approach for notable applications as an attractive multifunctional material, especially in photocatalysis, catalysis self-cleaning, UV-protecting agents, and environmental purification.[63,68–71] TiO_2 NPs exhibited a broad spectrum of activity against microorganisms, including positive-bacteria, Gram-negative, and fungi[32,72,73] and also inhibit the growth of pathogens including bacteria, viruses, and cancer cells under mild UV-light irradiation.[9] Its antibacterial activity is attributed to the hydroxyl radicals and reactive oxygen species (ROS) generated on the surface of illuminated TiO_2 and inactivate the microorganism by oxidizing the polyunsaturated phospholipid components of the microbes' cell membrane.[74]

TiO_2 NPs have also been introduced to the polymeric matrix to modify their properties,[75] and several polymeric substrates have been exploited to anchor TiO_2 photocatalyst.[76] Recently, PU/TiO_2 has attracted research attention,[77,78] also exhibiting antibacterial activity in some cases. For instance, Pang *et al.* reported that the dispersion of TiO_2 NPs dominated the acrylic PU surface morphological changes during UV radiation[79] and greatly affected the filled coatings degradation process. In another

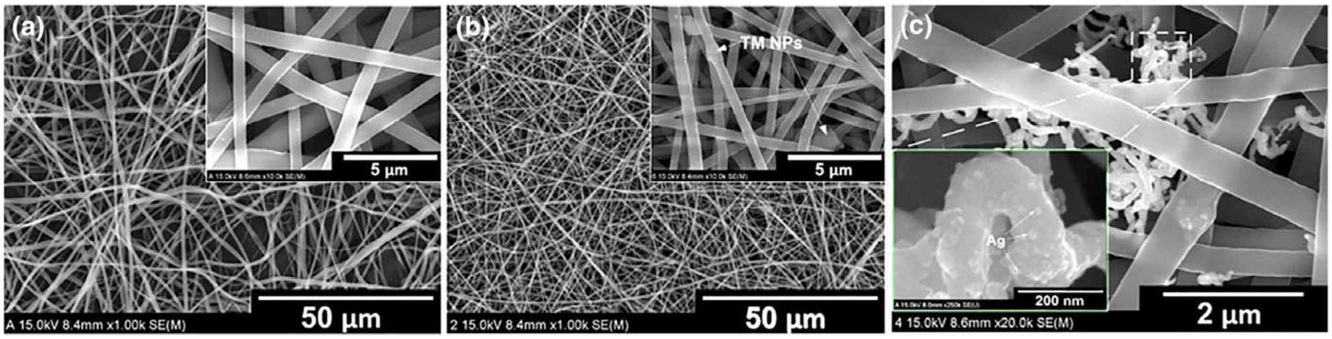


Figure 7. FESEM of (a) neat PU, (b) 3 wt % TM/PU, (c) Ag/TM/PU nanofibrous mat. (Reproduced with permission from Ref. [25], copyright 2018, with permission from Elsevier, License number: 4380650482444.) [Color figure can be viewed at wileyonlinelibrary.com]

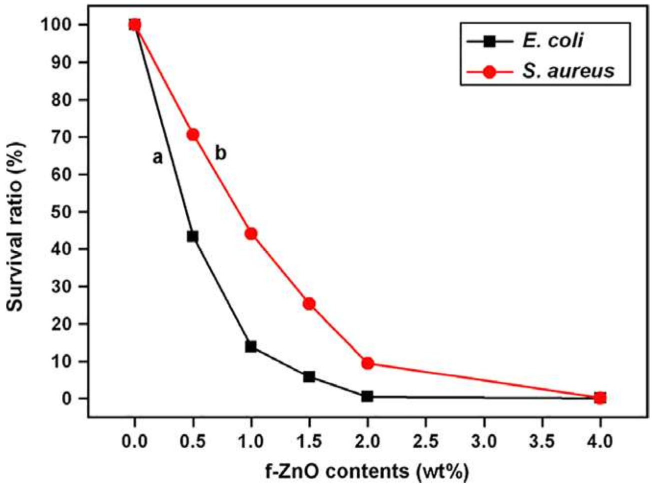


Figure 8. Effects of f-ZnO contents in WPU/f-ZnO composites on the *E. coli* and *S. aureus* survival ratio. (Reproduced with permission from Ref. 53, copyright 2018, with permission from Elsevier, License number: 4380650706875.) [Color figure can be viewed at wileyonlinelibrary.com]

study, however, Nguyen *et al.*[73] indicated that the rutile TiO_2 NPs mitigated the chemical change, weight loss, and mechanical degradation of the styrene acrylic PU coating, but exhibited a photocatalytic effect in the inhibition of *E. coli* bacterial growth.

Saha *et al.* also studied the effects of different NPs, namely TiO_2 (spherical), carbon nanofibers (CNFs, rod-shaped), and nano clay (platelet), on the mechanical and thermal properties of rigid PU (PUR) foam.[80] They showed that the infusion of NPs consistently enhanced the thermal and mechanical properties of the polymer.

The Ag-doped TiO_2 could utilize the antimicrobial properties of both highly antibacterial active Ag and UV-excited TiO_2 NPs.[81–83] On the other hand, due to poor compatibility between organic and inorganic phases, Ag/TiO_2 difficulty dispersed into the polymer matrix homogeneously. Sadu *et al.* successfully synthesized a Ag-doped TiO_2 polyurethane nanocomposite (nAg-TiO_2/PU) emulsion via the methods of solution combustion, step growth, and grafting from polymerization.[9] It exhibited excellent antibacterial activity against both Gram-negative (*E. coli*) and Gram-positive (*Staphylococcus epidermidis*) bacteria.[9]

Although there are several reports on TiO_2/PU coatings with antibacterial capabilities that were fabricated by physical blending, there still remain barriers in antibacterial and antivirus applications, because the agglomeration and uneven distribution of TiO_2, affected the outcome of products.[9]

There are some concerns on the environmental risks of TiO_2 NPs too.[56,59] Although many TiO_2/PU coatings gathered by physical blending with antibacterial capabilities, there still some barriers remain in antibacterial and antivirus applications, due to the agglomeration and uneven diffusion of TiO_2, which affect the outcome of the products.[84]

ZnO Nanoparticles

In the last decade, ZnO semiconductor has received great attention in a wide range of applications, due to its excellent properties, including low cost, high redox potential, nontoxicity,[85,86] and its extraordinary characteristics in electronics, photonics, and optics.[87–90] It showed potential in biomedical applications such as antidiabetic, antifungal, anti-inflammatory, and antioxidant.[91] ZnO NPs possess good thermal stability and biocompatibility and high antimicrobial activity which make it a promising antibacterial agent with excellent activity in a wide spectrum of bacteria.[92,93] Various mechanisms have been evident in their antibacterial activity including photocatalytic ROS generation and Zn^{2+} release, which can destroy the bacterial cytomembrane.[92]

Table II. Inhibitory effects of WPU/NiAl-LDHs/ZnO composites inoculated for 24 h (37 ± 1 °C) [Reproduced from Ref. 52, Copyright 2015, with permission from John Wiley and Sons, License number: 4385520259823][52]

Content of filler	*E. coli* (CFU)	*R* (%)	*S. aureus* (CFU)	*R* (%)
0	7.4×10^4	-	3.4×10^5	-
0.5	4.9×10^3	93.4	8.2×10^4	75.8
1.0	1.9×10^3	97.4	2.1×10^4	93.8
2.0	103	99.9	6.5×10^3	98.1

The incorporation of the high surface area of ZnO NPs in the polymeric matrices has also been studied in order to improve their properties. For example, Chuangqi Guo *et al.* showed that the reaction of hydroxy groups on ZnO NPs with the isocyanate groups of PU could improve the compatibility between these NPs and PU to improve the nanocomposite's thermal and mechanical properties.[94]

The addition of ZnO NPs to the polymer matrices in order to provide antimicrobial activity has received great attention for some applications, such as in the packaging and pharmaceutical industries.[95,96] The high surface area of these NPs creates a strong interaction with bacteria.[97] In a study, El Saeed *et al.* prepared ZnO/PU nanocomposite coating films (ZPN) via uniformly ZnO NPs dispersion (0.1–2.0 wt. %) in PU by ultrasonication.[97] Their results demonstrated an improvement in PU properties, including corrosion and mechanical resistance at lower concentrations, while it was enhanced by increasing the ZnO NPs content. The antimicrobial study was also carried out against Gram-negative (*E. coli* RCMB) and Gram-positive (*B. subtilis*) bacteria. It showed a slowdown in the growth of organisms on the ZPN coating surface. Ambrožič *et al.* fabricated the crosslinked Zn-embedded PU hybrid materials by varying the zinc acetate (ZnAc) which played the roles of both catalyst and source of water molecules.[98] The obtained macroporous nanocomposite (70 wt %) exhibited extremely strong biocidal properties against *E. coli*.

Zvekić *et al.* studied the effect of dispersed ZnO NPs in PU varnishes against three bacteria of *S. aureus*, *E. coli*, and *P. aeruginosa* and a strain fungi (*Saccharomyces cerevisiae*) by pour-plate test.[99] However, the pure PU varnishes did not demonstrate antibacterial properties and the presence of ZnO NPs (0.4 and 0.7 wt %) completely inhibited the growth of *S. aureus*, *P. aeruginosa*, and *S. cerevisiae* colonies, but their activity against *E. coli* was found to be questionable suggesting that more detailed research is necessary.

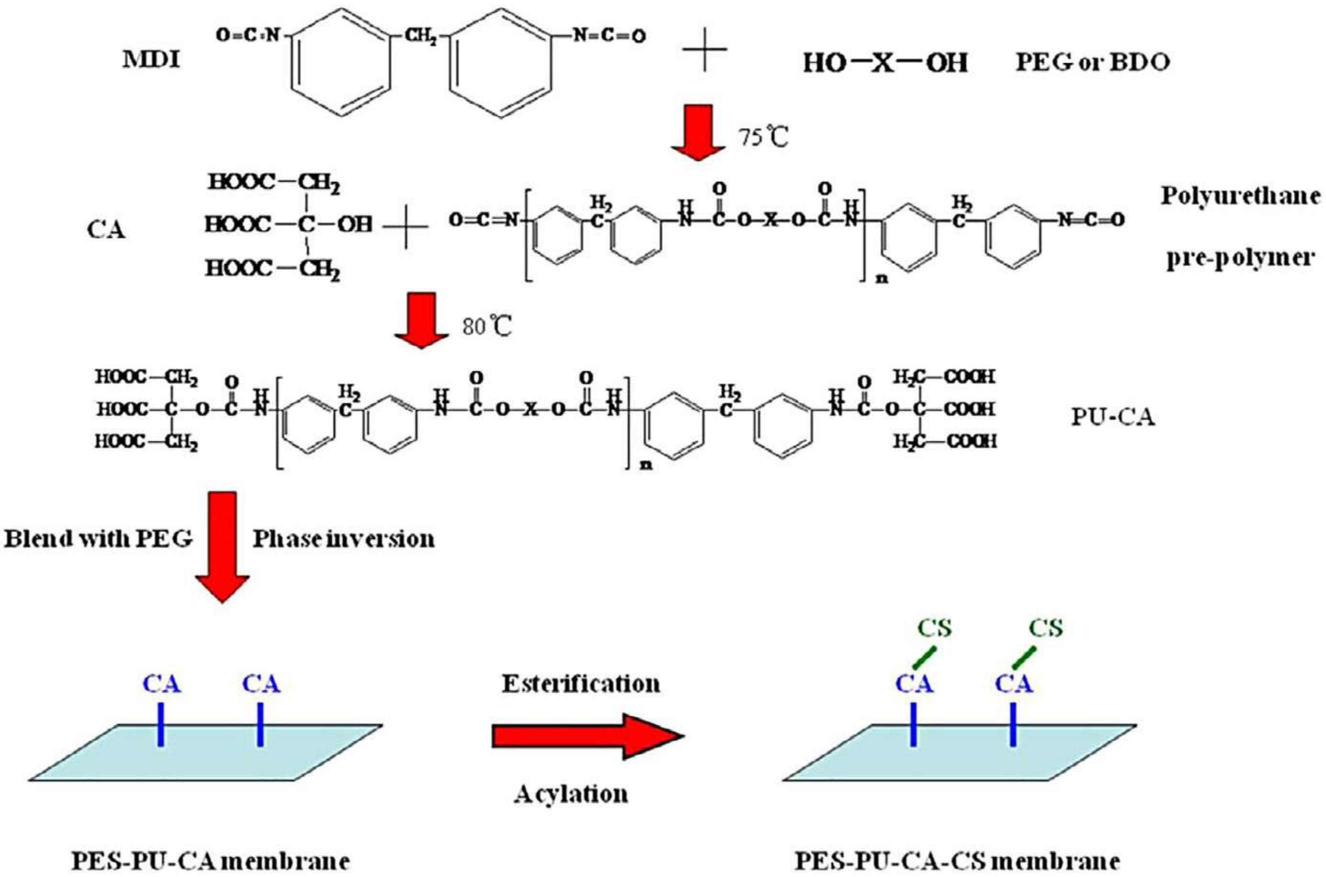


Figure 9. Schematic of PES-PU-CA-CS membrane preparation. (Reproduced with permission from Ref. 125, copyright 2016, with permission of TAYLOR & FRANCIS, License number: 4385511195285.) [Color figure can be viewed at wileyonlinelibrary.com]

Ma *et al.* also reported the preparation of waterborne polyurethane/flower-like ZnO nanowhisker (WPU/f-ZnO) composites.[53] It was demonstrated that appropriate f-ZnO contents with good dispersion in WPU matrix considerably improve the composites performance properties, including their thermal stability, mechanical strength, and water resistance. Their results also revealed that the antibacterial activity of WPU against *E. coli* and *S. aureus* was enhanced at higher f-ZnO content. As can be seen in Figure 8, the survival ratio of *S. aureus* and *E. coli* decreased with an increase in f-ZnO content, whereas the best one was obtained at a loading of 4.0 wt % f-ZnO.

Xiong *et al.* reported the synthesis of WPU/ZnO composites, via *in situ* polymerization, with different NiAl-LDH/ZnO contents.[52] It demonstrated a strong inhibitory effect against *E. coli* and *S. aureus*, even at a low loading level of NiAl/ZnO (0.5 wt %, see Table II). The antibacterial effect of the composites against *E. coli* was stronger than that of *S. aureus.* The ZnO fraction in the films caused the killing of bacteria on contact and prevention of bacterial colonization, but the antibacterial mechanism is not very clear.

In another study, Li *et al.* demonstrated that the ZnO NPs improved the mechanical and antibacterial properties of PU films/coats.[100] The antibacterial activity test via the agar dilution method indicated the excellent performance of prepared PU films doped with ZnO NPs, especially for *E. coli.*

The toxicity of ZnO NPs has been also indicated, dependent on their size, exposure dose, test time, and considered biological model.[57] Despite the current increasing consumption of ZnO NPs and also the enhancing opportunity of their exposure to aquatic organisms, there are many uncertainties regarding the potential toxicity of these NPs.[57,101] However, several studies have focused on the antibacterial effects of ZnO NPs and the affiliated toxicity mechanisms, the similar studies are needed on the ZnO NPs coated PUs, as an important issue.

Chitosan

CS is the second abundant natural biopolymer next to cellulose,[102] obtained from the deacetylation and hydrolysis of chitin, as the component of shells of crustaceans, such as crabs and insects.[103,104] In recent years, CS and its derivatives have received great attraction in a wide range of applications in the pharmaceutical,[105] food,[106] agricultural,[107] and environmental industries,[108–110] due to its special properties such as biodegradability, biocompatible nature, nontoxicity, and ease of modification.[111] It also possesses various biomedical properties, including anti-inflammatory, immuno-enhancing effects, immune-stimulating, antimicrobial activities, and antitumor activities.[112] CS has a fairly good antiseptic activity and a high capacity to suppress or restrict bacterial growth and due to the cationic nature of CS, it is strongly capable to absorb anionic antimicrobial drugs and release them slowly to achieve antimicrobial performance.[113]

The functionalization of synthetic polymers via natural ones, especially polysaccharide such as chitin and CS, is an interesting alternative to improve their antibacterial activities. They provide an unusual flexibility in both mechanical and biological properties in wide range of applications. The presence of $NHCOCH_3$, NH_2, and NHCOO groups in chitin, CS, and PU are convincingly imparts bioactive properties beneficial for biomedical applications.[114] Therefore, several studies have been carried out to addition of CS to the PU composites structure through blending.[115]

Chiu *et al*. demonstrated that CS lamination of thermoplastic PU (TPU) tremendously boosted its antibacterial performance,[116] as well as promoting the tensile, toughness, and laceration strength of the prepared membrane. Interestingly, the antibacterial effect of the membrane had shown an upward tendency, increasing the CS degree of deacetylation. Moreover, it was proven that the antibacterial strength of the laminated membrane was much higher than that of blend membrane. Kara *et al*. examined the antibacterial activity of PU film surface modified with covalent immobilization of CS[10] against the *S. aureus* (as a Gram-positive) and *P. aeruginosa* (as a Gram-negative) bacteria, as the most common microbial pathogens. As a result, the CS surface modification significantly enhanced the antibacterial activity of PU and decreased the number of attached viable bacteria. In another study, Kang *et al*. exhibited the satisfying antibacterial activity of CS/PU blend nanofibers against the *E. coli* bacteria.[117]

Kara *et al*. investigated the antibacterial activity of hexamethylene diisocyanate-based polyurethanes by CS grafting and heparin immobilization, against *P. aeruginosa* and *E. coli* (both Gram-negative) bacteria and *S. aureus* and *S. epidermidis* (both Gram-positive).[118] The bacterial adhesion results indicated a significant reduction in the number of viable bacteria on modified samples. They also assessed the biocompatibilities of the films using L929 fibroblast cells and demonstrated the very high anti-adhesive and antibacterial properties as well as high biocompatibility.[119]

In another study, Lee *et al*. designed a blended CS with polyurethane (CTS/PU) containing silver sulfadiazine (AgSD), as a novel wound dressing, to improve its mechanical strength and antibacterial activity against three types of Gram-negative bacteria: *P. aeruginosa*, Gram-positive *S. aureus*, and Methicillin-resistant *S. aureus*).[120] Their resulted indicated the strong antimicrobial activity of prepared CTS/PU/AgSD fiber sheets by inhibition of bacterial growth, besides the improvement of the mechanical properties of the CTS/PU fiber sheet.

El-Sayed *et al*. applied CS, as chain extender, in the waterborne polyurethane and showed its good antimicrobial activity in acrylic fabrics. It was indicated that its antibacterial activity remained unchanged after 15 washing cycles.[115] Muzaffar *et al*. also developed a series of water dispersible PUs dispersion using CS for textile applications and showed their capabilities to apply for multifunctional finishing of textile materials along with antibacterial properties.[121] In another study, Shih and Huang developed a blended PU and CS polymers for a shrink-proofing and antimicrobial compound finishing process for woolen fabrics.[122] They demonstrated that the addition of CS remarkably increased the shrink-proof and antimicrobial properties of the treated fabric.

Liu *et al*. examined the antibacterial activity of temperature sensitive poly(*N*-isopropylacrylamide)/polyurethane (PNIPAAm/PU) hydrogel-grafted nonwoven fabrics with CS modification and show that the CS modification enhanced the antibacterial activity against *S. aureus* and *E. coli*.[123] In another study, Lin *et al*. immobilized the CS/dextran sulfate onto the surface of TPU membrane after ozone-induced graft polymerization of poly(acrylic acid), and showed that it exhibited higher cell viability than native TPU membrane.[124] Liu *et al*. also immobilized the PU materials by CS and citric acid, and followed the procedure shown in Figure 9, in order to improve its biocompatibility and antibacterial property.[125] The antibacterial activities were evaluated based on an *in vitro* antibacterial test, which confirmed the higher anticoagulant and antibacterial properties of the prepared membrane, compared to the pure PES membrane.

CONCLUSIONS

In this article, the promising antibacterial activity of PU materials resulting in an essential need to use them in a wide range of applications in recent published studies has been reviewed. The incorporation of some materials including Ag, Au, ZnO, and TiO_2 NPs, and CS in the PUs' polymer matrices is an efficient strategy for improving the PUs' antibacterial activity and enhancing their other chemical and physical properties, such as thermal stability, dynamic mechanical properties, and the biostability of polymer. It was also revealed that the antibacterial activity of PUs against a wide range of bacteria is usually enhanced at a higher NP content. Regardless of increasing number of studies on the antibacterial activity of PU materials, more attention is needed on several gaps of study, such as applying other NPs to the antibacterial activity, the effect of different modified NPs, negative effects of NPs addition on environment, and so forth.

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