

# Rubber composite fibers containing silver nanoparticles prepared by electrospinning and *in-situ* chemical crosslinking

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**Abstract.** Rubber composite fibers containing silver nanoparticles with high morphological stability were prepared through combination of electrospinning and *in-situ* chemical crosslinking. The composite fibers included those of Ag/polybutadiene rubber (BR), Ag/polyisobutylene-isoprene rubber (IIR), and Ag/silicon rubber (SiR). During the study, Ag nanoparticles (Ag NPs) were first generated through reducing the Ag<sup>+</sup> ions in rubber/N,N-dimethylformamide/tetrahydrofuran solutions upon ultraviolet-irradiation; subsequently, rubber composite fibers with uniform diameters from hundreds of nanometers to several micrometers were made by electrospinning the above solutions. The electrospinning was carried out with *in-situ* chemical crosslinking. The results indicated that chemical crosslinking during (and shortly after) electrospinning was able to improve substantially the morphological stability of rubber fibers. As indicated by the results acquired from UV absorption spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscope, Ag nanoparticles with sizes of 10~20 nm were uniformly dispersed in rubber fibers. It was believed that, in addition to the protection of polyvinyl pyrrolidone, a rapid solvent evaporation and limited motion space for a very fine fiber during electrospinning could prevent/mitigate the aggregation of Ag NPs, resulting in a very uniform dispersion. The electrospun Ag NPs/BR composite fibers made of the solution containing very low loading amount (3 wt%) of AgNO<sub>3</sub> demonstrated strong antimicrobial activity.

**Keywords:** rubber, electrospinning, composite fiber, silver nanoparticles, *in-situ* crosslinking

## 1. Introduction

Recently, the incorporation of metal nanoparticles into polymer nanofibers has attracted growing attentions, because this type of nanocomposite nanofibers would combine the unique properties of metal nanoparticles (*e.g.*, magnetic, optical, electronic, catalytic, and antimicrobial properties) with the outstanding characteristics of polymer nanofibers (*e.g.*, the high specific surface area and high interpenetrating capacity in other materials, *etc.*) [1–8]. Among various metal nanoparticles, silver nanoparticles (Ag NPs) have been of particular interest due

to their catalytic property, high electrical conductivity, and antimicrobial activity etc [9–12]. Ag NPs have been synthesized in many different ways including chemical reduction, X-ray irradiation, refluxing and heating methods and bio-reduction [13–15]. Nevertheless, Ag NPs have the tendency to form agglomerates; and thus it has been a technological challenge how to disperse them uniformly in polymeric matrices.

To the best of our knowledge, the polymers that have been electrospun into nanofibers with Ag NPs are mostly thermoplastics such as polyvinyl pyrrolid-

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done (PVP), polyvinyl acetate (PVA), polyacrylonitrile (PAN), *etc.* [17–20]; whereas electrospun Ag NPs/rubber composite fibers have rarely been reported [21]. This is probably due to the reason that rubbers have glass transition temperatures lower than room temperature, and the excellent elasticity might hinder the formation of fibers during electrospinning. Additionally, the macromolecular chains of rubbers are able to move (*i.e.*, rearrange their conformations) in electrospun fibers, such a movement and/or relaxation occurs when the stretching force no longer exists, and is driven by entropy increase. The results often include the breakage and/or conglutination of fibers with prolonging the storage time [22, 23].

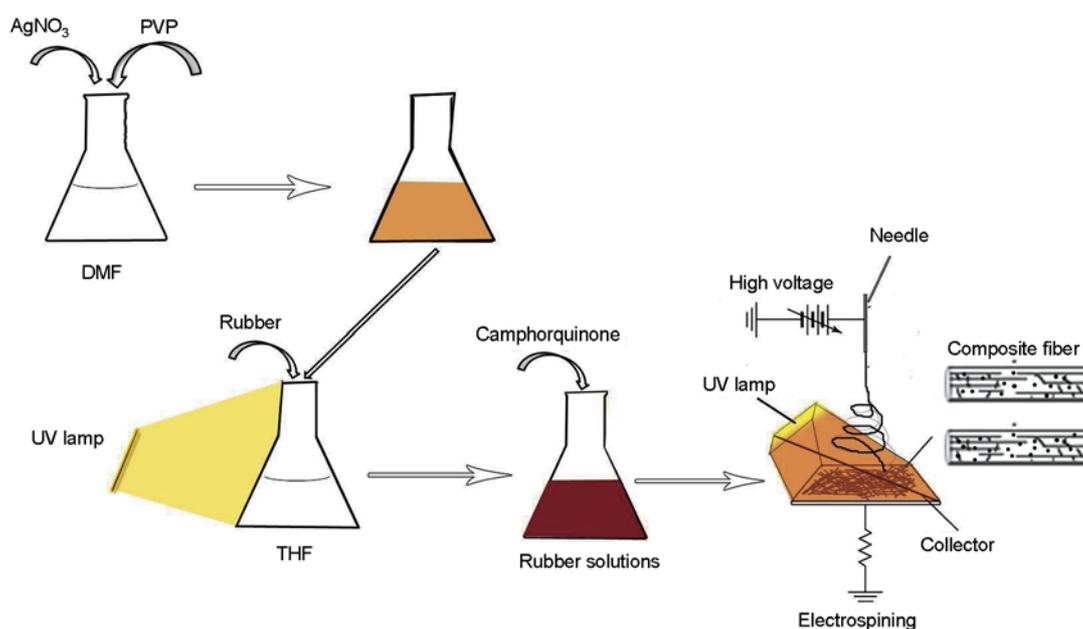
It is expected that the rubber fibers would be important for applications in need of large deformation and elasticity. For example, silicon rubber (SiR) and isobutylene-isoprene rubber (IIR) exhibit excellent biocompatibility and low gas permeability in addition to superior elasticity. Herein, three kinds of rubbers including butadiene rubber (BR), IIR, and SiR were studied. *N,N*-dimethylformamide (DMF) was selected as a co-solvent for three rubbers, as well as the reducing agent for converting  $\text{Ag}^+$  ions into Ag NPs. The resulting solutions containing Ag NPs were directly used for electrospinning. To improve the morphological stability of Ag NPs/rubber composite fibers, the *in-situ* chemical crosslinking was conducted during and shortly after electrospinning; camphorquinone (CQ) was used as the

UV-photo initiator for BR and IIR, whereas a curing agent containing the catalyst of platinum was used for SiR. The addition of PVP into the  $\text{Ag}^+$ /rubber solutions aimed to prevent the Ag NPs from agglomeration, as well as to promote the reduction of  $\text{Ag}^+$  ions into Ag NPs.

## 2. Experimental part

### 2.1. The preparation of Ag NPs/rubber composite fibers

The preparation process is shown in the Figure 1.  $\text{AgNO}_3$  and PVP ( $M=1\,300\,000$ ) (mass ratio of  $\text{AgNO}_3$ /PVP being 1/1, 1 wt% to rubber), supplied by the Beijing Hua-Teng Chemical Reagent Co. (Beijing, China) and Alfa Co. (America), respectively, were dissolved in *N,N*-dimethylformamide (DMF) and the solution was then added to the solvent of tetrahydrofuran (THF) (mass ratio of THF/DMF being 4/1) drop by drop. Polybutadiene rubber (BR), supplied by the Beijing Yan-Shan Petrochemical Co. (Beijing, China), was first kneaded on a two-roll mill at  $\sim 25^\circ\text{C}$  for 10 min. Subsequently, 8 wt% of BR was dissolved in the above THF/DMF solutions. The BR solution was then exposed to ultraviolet irradiation for about 1 h for the reduction of  $\text{Ag}^+$  ions into Ag NPs. Prior to electrospinning, camphorquinone (CQ) was added into the solutions for *in-situ* photo-crosslinking. Finally, the solutions were filled in 30 mL plastic syringes having blunt-end stainless-steel needles with inside diameter of 0.30 mm. The electrospinning setup included an



**Figure 1.** Schematic diagram of experimental process

ES30P high voltage power supply, purchased from the Gamma High Voltage Research, Inc. (Ormond Beach, USA), and a fiber collector of electrically grounded metal plate covered with aluminum foil. The collector was placed at 15~20 cm below the needle and exposed to a 100 W halogen lamp. During electrospinning, a positive high voltage of 10~20 kV was applied to the needle; and the solution feed-rate of 1.5 mL/h was maintained using a syringe pump. Isobutylene-isoprene rubber (IIR), also supplied by the Beijing Yan-Shan Petrochemical Co., had a similar process of electrospinning as BR. Silicon rubber (SiR), supplied by the Dow Corning Co. (USA), also had a similar process of electrospinning as BR except that a curing agent containing the catalyst of platinum (PL-10A: 4%, PL-10B: 6%, SiR: 20%) was chosen for *in-situ* chemical crosslinking.

## 2.2. Characterization of Ag NPs/rubber composite fibers

For morphological characterizations, electrospun BR, IIR and SiR fibers were collected with glass slides on the metal plate; and the fibers were examined with XSJ-2 optical microscope purchased from the Chongqing Optical Instrument Co. (Chongqing, China). UV absorption spectrum of the Ag/BR fiber mat in the 300–700 nm region was obtained by the UV-3150 spectrophotometer purchased from the Shimadzu Co. (Shimadzu, Japan) and a piece of aluminum foil covering with Ag/BR fiber mat was used for UV measurement. A piece of Ag/BR fiber mat was placed on a copper grid to observe the shape and distribution of silver nanoparticles in electrospun Ag NPs/BR composite fiber by H-800 transmission electron microscopy purchased from Hitachi Co. (Japan). XPS measurements were carried out on an ESCALAB 250 purchased from Thermo Electron Corporation (USA) with an Al K $\alpha$  X-ray source at 1486.6 eV photons. The core-level signals were obtained at a photoelectron take off angle of 45° (with respect to the sample surface). The X-ray source was run at a reduced power of 150 W.

## 2.3. Antimicrobial activity test of Ag/BR composite fibers

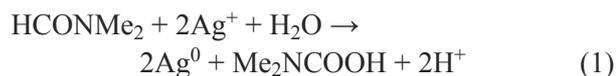
The antimicrobial activity of BR composite fibers with and without Ag NPs was tested against Gram-negative Escherichia coli (E.coli, ATCC 25922) according to Chinese national testing standard of

antimicrobial activity in the ‘Technical Standard For Disinfection’ (2002). For antimicrobial activity characterization, the randomly overlaid fiber mats were obtained by collecting ~1 mg of BR fibers (with and without Ag NPs) with glass slides (25 mm × 25 mm). The agar plates containing test samples and the control (BR fibers without Ag NPs) were incubated at 37°C for 24 h. The reductions of bacteria were calculated according to the equation of ‘Reduction [%] = (B – A)/B · 100’, where A and B are the surviving cells (colony forming unit. mL<sup>-1</sup>) for the plates containing test samples and the control, respectively.

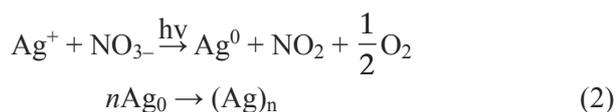
## 3. Results and discussion

### 3.1. In-situ formation of silver nanoparticles

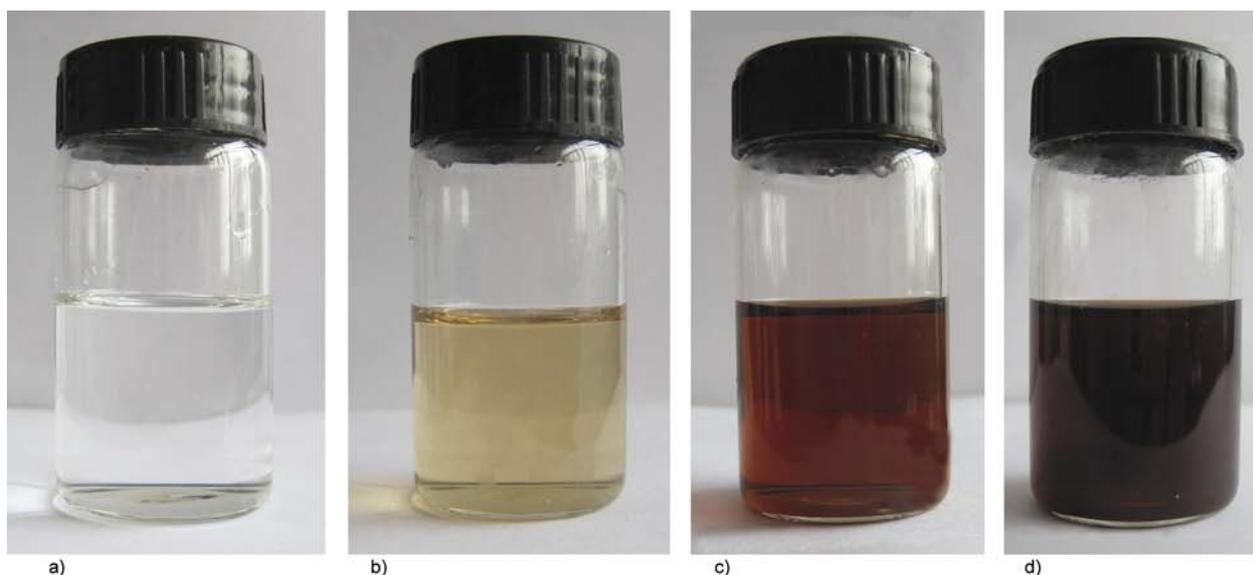
In this study, DMF was used as a reducing agent for converting Ag<sup>+</sup> ions into Ag NPs. During the reactions performed at room temperature, the following reaction according to Equation (1) would occur:



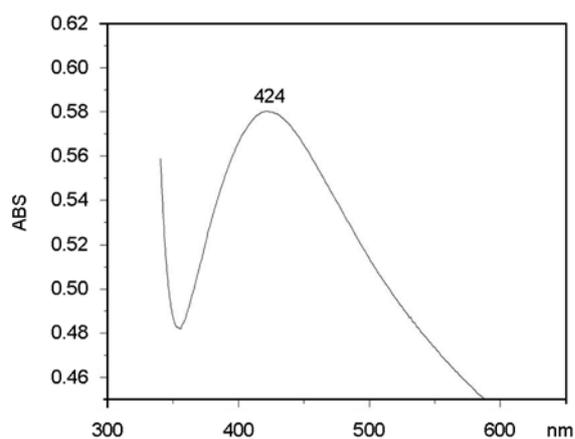
However, the reaction would proceed at a low rate when performed at room temperature. In this study, we obtained the quick *in-situ* synthesis of Ag NPs in the rubber solution with further ultraviolet irradiation. The following reaction given by Equation (2) took place during the ultraviolet irradiation process:



The reduction of Ag<sup>+</sup> ions by DMF could be monitored from the color evolution of the solution. Visual observation showed that, as the reaction proceeded, the color shifted from light yellow, bright yellow, to dark brown after 10, 30, 60 min, respectively, as depicted in Figure 2. In this study, we also introduced PVP into the rubber solution in order to protect the Ag NPs from agglomeration; so that they could be uniformly dispersed in electrospun composite fibers. The fast evaporation of solvent during the process of electrospinning also prevented from Ag NPs self-aggregation in the rubber fibers because of very limited space. The absorption spectrum of Ag/rubber composite fiber mat is shown in Figure 3 and it can be seen that an absorption band with a sharp maximum at about 424 nm arises. Small metal-

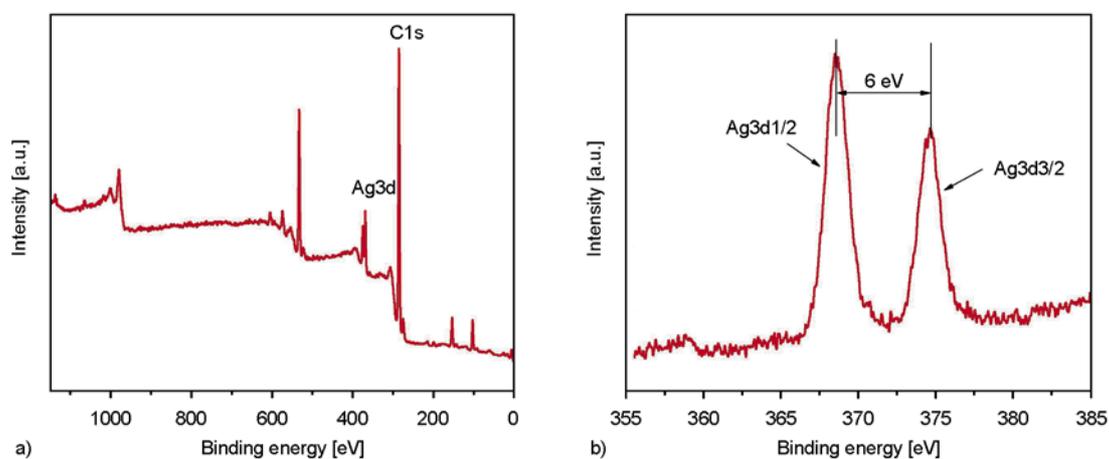


**Figure 2.** Color evolution of  $\text{AgNO}_3/\text{DMF}$  solution with ultraviolet irradiation for varied time periods of (a) 0 min, (b) 10 min, (c) 30 min, and (d) 60 min



**Figure 3.** UV spectrum of Ag NPs/BR composite fiber mat prepared from the solution containing 3 wt%  $\text{AgNO}_3$

lic particles exhibit a high optical absorbance due to the existence of discrete energy levels of electron and particularly of specific states. Ag NPs with diameters below 5 nm have a rather high absorbance band with a maximum at about 400 nm and with diameters of  $\sim 10$  nm exhibit absorption bands at 410–450 nm depending on their chemical environment. Based on the maximal absorbance at 424 nm caused by Ag/rubber fiber mat, small spherical particles of silver with diameters of 10 nm or less were formed. Figure 4 showed the spectrum in the Ag 3d region of the Ag/rubber composite fibers. It was evident from the spectrum that two peaks occurred at 368.1 and 374.1 eV, corresponding to Ag 3d<sub>1/2</sub> and 3d<sub>3/2</sub> binding energies, respectively. The result further confirmed the existence of Ag(0) in the Ag/rubber composite fiber mat [24, 25].



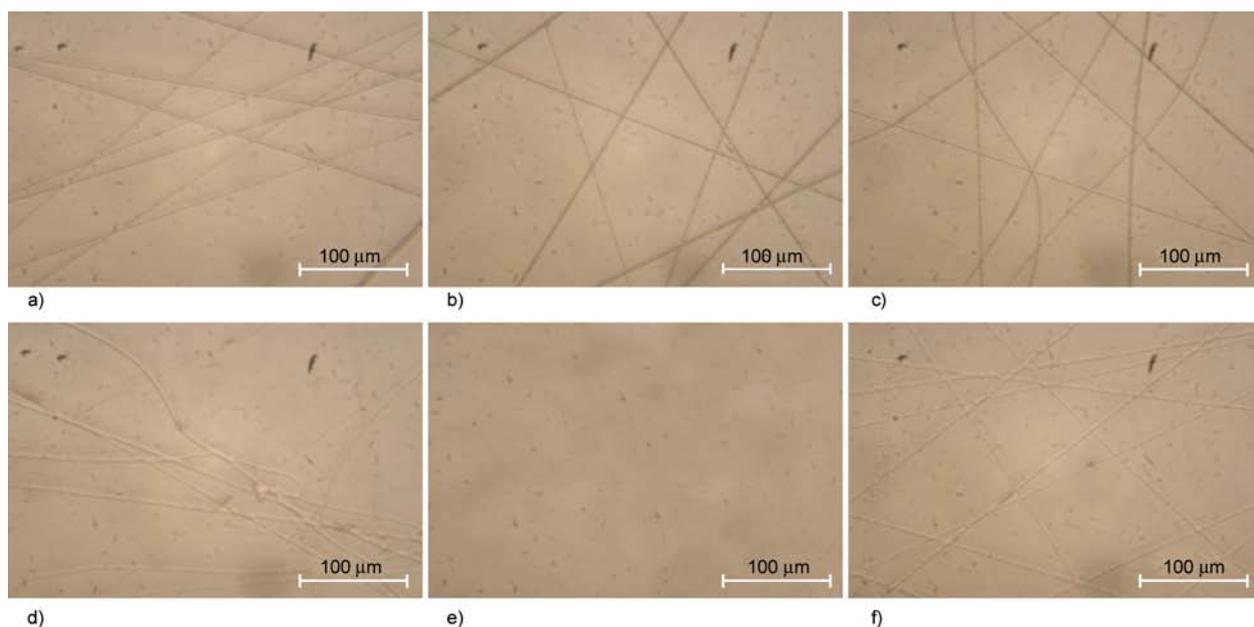
**Figure 4.** Wide-scan and Ag3d XPS spectra for electrospun Ag NPs/BR composite fiber mat prepared from the solution containing 3 wt%  $\text{AgNO}_3$ : (a) wide-scan, (b) Ag3d

### 3.2. Morphology of Ag/rubber composite fibers

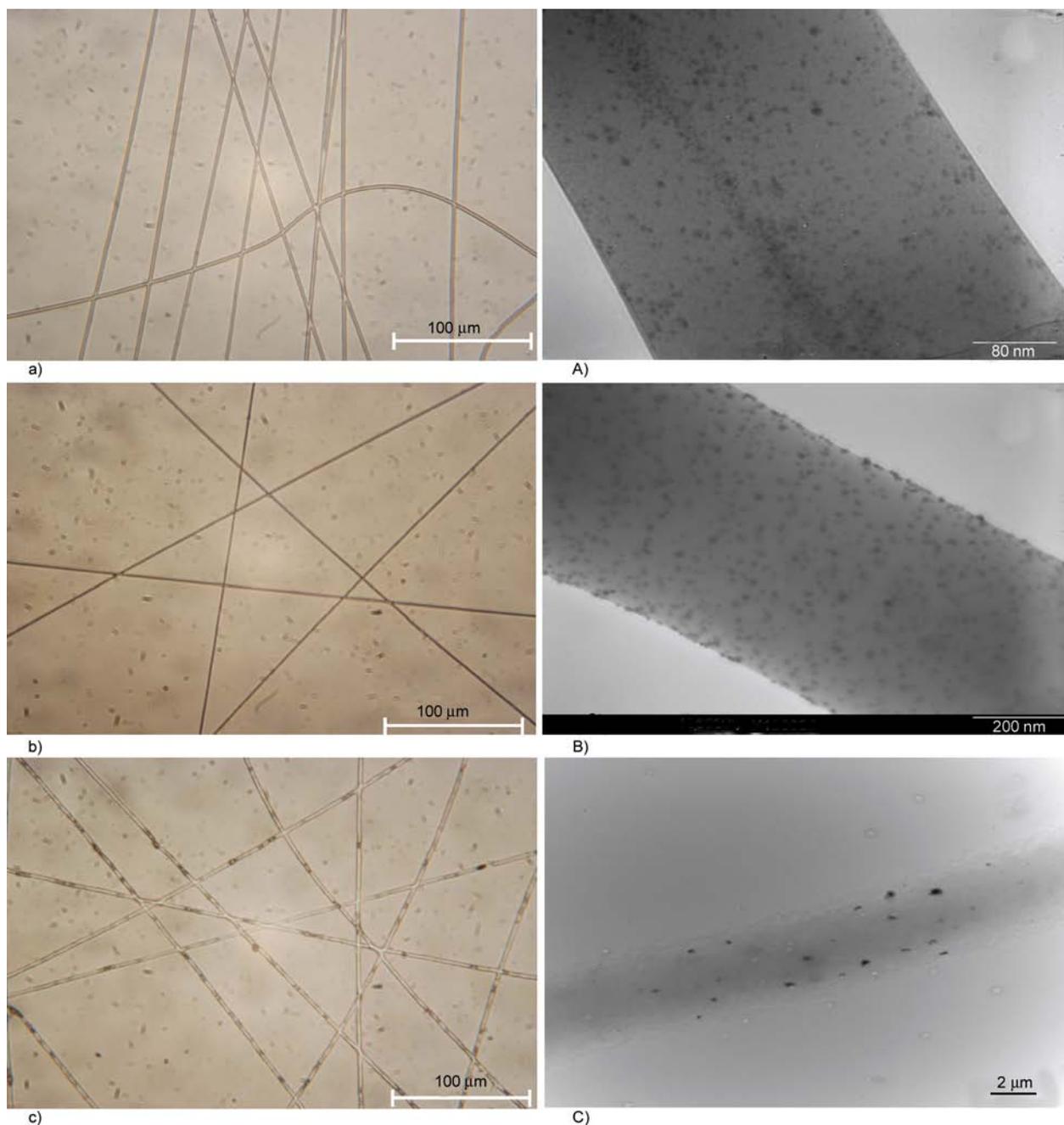
To investigate the morphological stability of electrospun rubber fibers (here only taking BR as an example), the prepared fibers were stored under ambient condition or immersed in THF (a good solvent for BR) (with temperature being  $\sim 25^{\circ}\text{C}$  and relative humidity being  $\sim 50\%$ ) for a period of time  $\sim 20$  h. As shown in Figure 5, the Ag/BR composite fibers immediately after electrospinning possessed the cylindrical morphology, while the morphology was partially lost after storage under ambient condition, further prolonging the storage time led to the conglutination and/or breakage of the fibers for 20 h as seen in Figure 5d. When soaked in THF for 20 h, the electrospun Ag/BR composite fiber were completely dissolved (Figure 5e). Upon a series of experiments, the optimal mass ratio of CQ in BR was identified at 5%, the crosslinked Ag/BR composite fibers still well-retained their morphology even soaked in THF for 20 h; the fibers were merely swollen to a certain degree (Figure 5f). It could be concluded that *in-situ* chemical crosslinking during and shortly after electrospinning was able to substantially improve the morphological stability of electrospun BR fibers. During electrospinning, macromolecular chains in the spinning solution are stretched and/or aligned by electric force; simultaneously, the solvent in the electrospinning jet evaporates rapidly. Unlike thermoplastics, BR has the glass transition temperature ( $T_g$ ) of about  $-105^{\circ}\text{C}$ . The macro-

molecular movement and/or relaxation occur when the stretching force no longer exists, so the BR fibers will collapse, conglutinate, even break. In this study, the method of *in-situ* chemical crosslinking combined with electrospinning was established to obtain electrospun rubber composite fibers with stable morphology. The chemically cross-linked network might restrain the motion of rubber chains and extend molecular relaxation time [26–28], so the substantially improved morphological stability of electrospun rubber composite fibers was achieved.

We also prepared morphologically stable electrospun Ag NPs/IIR and Ag NPs/SiR composite fibers successfully through the combination of electrospinning and *in-situ* chemical crosslinking. Similar to BR, prior to electrospinning, CQ for IIR and platinum-containing curing agent for SiR were added into the solutions for *in-situ* chemical crosslinking. The TEM images in Figure 6 showed the morphologies of crosslinked Ag NPs/IIR and Ag NPs/SiR composite fibers made of 15 min kneaded IIR and as-received SiR. The chemically crosslinked Ag NPs/SiR composite fibers possessed approximately cylindrical morphology with uniform diameters of  $1\sim 2\ \mu\text{m}$ . The diameters of Ag NPs/BR and Ag NPs/IIR composite fibers were  $\sim 400\ \text{nm}$ , which was smaller than the diameters of Ag NPs/SiR composite fiber because SiR is the most elastic rubber. The typical TEM images of the rubber composite fibers containing Ag NPs are shown in Figure 6.



**Figure 5.** Optical microscope images showing the morphological variations of electrospun Ag NPs/BR composite fibers (un-crosslinked: a, b, d, e; crosslinked: c, f; immediately after electrospinning: a–c; kept for 20 h under ambient condition: d; and immersion in THF for 20 h: e, f)



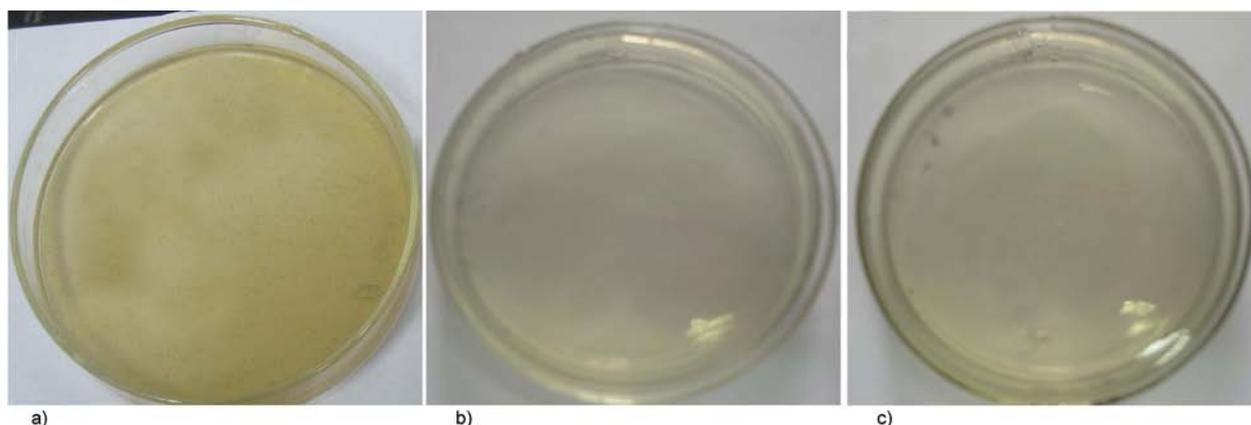
**Figure 6.** Optical microscope images (a–c) and TEM images (A–C) of Ag NPs-containing composite fibers of rubbers including BR (a, A), IIR (b, B), and SiR (c, C)

The Ag NPs were uniformly dispersed/distributed in the composite fibers and the average diameter of Ag NPs was about 10–20 nm, which was consistent with the results acquired from UV absorption spectra. In this study, we used DMF as a reducing agent for converting  $\text{Ag}^+$  ions into Ag NPs at room temperature and UV-irradiation to greatly improve the reaction speed. Different from traditional chemical reduction in solution compounding, besides the protection of PVP, a rapid solvent evaporation and limited motion space in a very fine fiber during

electrospinning could considerably mitigate the agglomeration of the Ag NPs, resulting in a very uniform dispersion and the narrow particle-size distribution as shown in Figure 6.

### 3.3. Antimicrobial performance of Ag NPs/rubber composite fibers

It is likely that the nanoscale sizes of Ag NPs will allow the increase of contact surface with microorganisms, leading to an enhanced antimicrobial performance. In this study, to evaluate the antimicro-



**Figure 7.** Antibacterial activity of Ag/BR composite fiber mats electrospun from the solutions with different  $\text{AgNO}_3$  concentrations of (a) 0 wt% (b) 3 wt% (c) 5 wt% against Gram-negative *Escherichia coli* (*E. coli*, ATCC 25922)

bial activity of Ag NPs/BR composite fibers, the fiber mats were tested against *E. coli* according to the nonwoven fabric attachment method; and the results are shown in Figure 7. Bacteria reductions for the BR fiber mats electrospun from the solutions with the original concentration of  $\text{AgNO}_3$  being 3 and 5 wt% were 99.9% after incubation. It is noteworthy that, if the conversion from  $\text{Ag}^+$  ions to Ag NPs could be 100%, the corresponding Ag NP concentrations in the above fiber mats would be ~1.9 and 3.2 wt%, respectively. This indicated that a small amount of Ag NPs in the composite fibers could introduce very strong antimicrobial activity.

#### 4. Conclusions

The rubber (*i.e.*, BR, IIR, and SiR) composite fibers containing Ag NPs with high morphological stability were prepared through combination of electrospinning and *in-situ* chemical crosslinking. The crosslinked composite fibers could well retain their morphologies whether upon prolonged storage under ambient condition or even upon immersion in THF (a good solvent for BR, IIR, and SiR). The results from UV absorption spectroscopy and TEM revealed that Ag NPs with the average size of 10~20 nm were dispersed uniformly in the electrospun fibers. The results from XPS further confirmed the existence of Ag(0) in the composite fiber mats. This study also demonstrated that the rubber composite fibers containing a very amount of Ag NPs possessed strong antimicrobial activity.

#### Acknowledgements

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