In-situ green synthesis of silver nanoparticles in natural rubber latex for fabricating rubber composite with antimicrobial property

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Abstract

This work aims to fabricate natural rubber composite with an antimicrobial performance by incorporating silver nanoparticles (AgNPs). The AgNPs were in-situ synthesized by serving $AgNO_3$ precursor in natural rubber latex without reducing agent. The result finds the typical yellowish-brown slurry and shows the surface plasmon resonance (SPR) absorption band between 350-650 nm wavelength, revealing the formation of AgNPs in the natural rubber latex. TEM images display the spherical shape of AgNPs with the size between 5-30 nm. The negative value of zeta potential (-56.7 mV) elucidates more stability of AgNPs suspended in natural rubber latex. The as-prepared natural rubber latex containing AgNPs was utilized to fabricate rubber composite. The tensile test reveals the slight decline in mechanical strength; meanwhile, strain at break of rubber composites containing AgNPs does not significantly changed when compared to rubber composite without AgNPs. The clear inhibition zone suggests an antimicrobial manner of rubber composite containing AgNPs against *E. coli* and *S. aureus* pathogens. This result indicates that AgNPs are the responsible element for rubber composites' antibacterial property. This work substantiates the successful synthesis of AgNPs with a green and cost-effective procedure without utilizing a reducing agent. Moreover, it raises the natural rubber composite with antibacterial performance, which could be widespread end-use applications of natural rubber.

Keywords: Natural rubber; Antibacterial activity; Nanoparticles, Eco-friendly material

Introduction

Over the past decades, metal nanoparticles with diameter less than 100 nm have provided a significant aspect for various medical applications, such as medical devices and diagnostic (Lee and Jun, 2019). Particularly, silver nanoparticles (AgNPs) have attracted enormous attention with a great potential in a widespread range of microbiology applications (Gong et al., 2007; Rai et al., 2009; Shahverdi et al., 2007). This manner is due to its unique biological and physico-chemical performance (Pal et al., 2007). Generally, the AgNPs' properties depend mainly on their size, shape, crystallinity, composition, and preparing method (de Lima et al., 2012; Syafiuddin et al., 2017). Various procedures classified by physic and chemical pathways have been exploited for synthesizing colloidal AgNPs, including conventional chemical reduction by reducing agent such as NaBH4 (Huff et al., 2020), electrochemical reduction (Rodríguez-Sánchez et al., 2000), radiation chemical reduction (Shameli et al., 2010), sonochemical reduction (Elsupikhe et al., 2015). However, the major drawbacks of these approaches are dangerous from toxic chemicals as reducing and capping agents and high cost. Moreover, the metal nanoparticles synthesized from these approaches may cause toxic chemical residue, which limit the utilization of AgNPs in clinical and human applications (Junejo et al., 2014). Consequently, there is a growing interest for the AgNPs's synthe-

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sis protocol with eco-friendly, biocompatible, reliable and low-cost procedure. Various green reducing agents such as microorganism (Saeb et al., 2014), plant extracts (Usha Rani and Rajasekharreddy, 2011; Zhang et al., 2014), ascorbic acid (Qin et al., 2010), chitosan (Zain et al., 2014), and natural rubber (Danna et al., 2016) have been used for synthesis AgNPs.

Natural rubber latex is a milky-white liquid obtained from the tapping bark of Hevea brasiliensis tree. Generally, this complex colloidal suspension contains rubber particles, non-rubber components (lipid, protein, and carbohydrate), and water (D'Auzac, 1989). The main structure of rubber is cis-1,4-polyisoprene (Toki et al., 2002). Several remarkable manners, for instance, high mechanical strength, excellent elasticity, and renewable resource (Smitthipong et al., 2016), consequently, natural rubber both in liquid and solid forms have been extensively exploited in several end-use, ranging from medical devices and health care supplies to automotive and airplane tires (Thomas Kurian and Mathew, 2011). Based on our knowledge, there is scarce literature for the utilization of natural rubber in the synthesis of colloidal AgNPs and preparation of rubber composite with appropriate mechanical properties and antimicrobial performance. Therefore, it is still interesting for this issue.

In this work, the AgNPs were in situ synthesized in the natural rubber latex by adding $AgNO_3$ precursor without utilizing a chemical reducing agent. The synthesized AgNPs suspended in rubber latex were conducted the color transformation by UV-Vis spectroscopic analysis. The morphology and size of AgNPs were visualized using transmission electron microscopic (TEM) analysis. Zeta potential measurement was utilized for evaluating the stability of AgNPs in latex medium. Furthermore, the mechanical and antibacterial properties of natural rubber composite containing AgNPs were assessed. The rubber composite without AgNPs was also prepared as a control material to study the effect of AgNPs in the desired composite material.

Experimental procedure

Materials

High ammonia natural rubber (HANR) latex with 60% dry rubber content (60%DRC)was acquired from Thai Rubber Latex Co. Ltd., Thailand. Poly(ethylene oxide fatty alcohol) hexadecylether (Terric 16A-16) as a non-ionic surfactant was supplied from East Asiatic Company, Thailand. Silver nitrate ($AgNO_3$) with a purity of more than 99% was purchased from Sigma Aldrich, USA. 50% N-tert-butyl-benzothiazole sulfonamide (TBBS) suspension was utilized as an accelerator. Sulfur (S) suspension was exploited as a vulcanizing agent. 50% Stearic acid and 50% zinc oxide (ZnO) suspensions were employed as the activator. All curing agents were commercial grade and procured by Lucky four Co., Ltd., Thailand.

In situ synthesis of silver nanoparticles suspension in natural rubber latex

50 mL natural rubber latex (60% DRC) was stabilized using 3 phr (0.3 g) terric as a non-ionic surfactant and stirred throughout 24 h. Otherwise, 0.1 M $AgNO_3$ solution was prepared being a raw material for synthesizing Ag nanoparticles (AgNPs). Afterward, as-prepared $AgNO_3$ solution with various content (10, 15, and 20 mL) was added into stabilized natural rubber latex at room temperature. Later the reaction mixture was heated upward 60 °C and stirred throughout 8 h. Eventually, the synthesized Ag nanoparticle suspended in natural rubber latex was received at the end of the reaction. The schematic preparation of Ag nanocolloids suspended in natural rubber latex is illustrated in Figure 1. Various techniques were utilized to assert the natural rubber latex containing Ag nanocolloids.

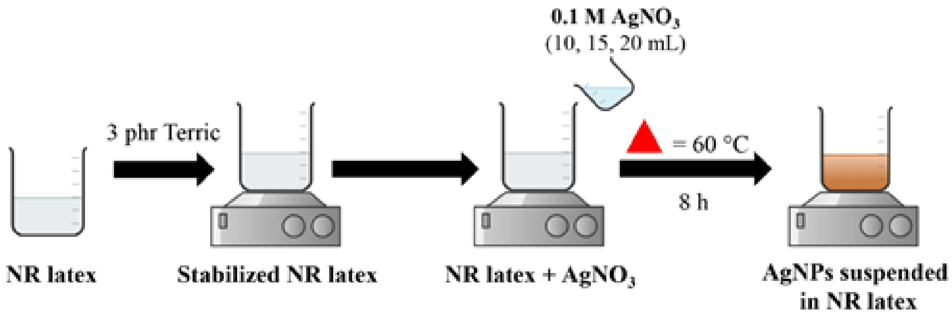

Figure 1. Schematic preparation of silver nanoparticles suspended in natural rubber latex.

Table 1. Rubber/PLA blend compositions.

Entry	Samples	$AgNO_3$ (mL) in NR latex	S (phr)	TBBS (phr)	Stearic acid (phr)	ZnO (phr)
1	NR	-	1.5	1.5	1	5
2	AgNR-1	10	1.5	1.5	1	5
3	AgNR-2	15	1.5	1.5	1	5
4	AgNR-3	20	1.5	1.5	1	5

Natural rubber composite

Natural rubber latex and natural rubber latex containing Ag nanocolliods were mixed with curable agents according to ASTM D1076: 2010. Formulation of latex compound for fabrication of natural rubber composite containing AgNPs is presented in Table 1. Then, natural rubber compounds were poured into the glass plate. Afterward, the natural rubber compound was dried and cured at 50 °C for 24 h in the hot oven before drying and curing again in a vacuum oven at 50 °C for 24 h. Natural rubber composites contained with AgNPs were acquired. Natural rubber composite without AgNPs was also prepared and utilized as a control sample.

Characterizations

The formation of Ag nanocolloids suspended in natural rubber latex was evaluated by using a UV-Vis spectrophotometer (Shimadsu UV-VIS Spectrometer (UV-2600)). UV-Vis spectra of the as-synthesized colloid sample were scanned in the range between 200-700 nm.

Size and morphology of the colloidal AgNPs sample in natural rubber latex were observed by a transmission electron microscopic (TEM) (JSM-1400, JEOL). Ag nanocolloids in latex were deposited on copper grid coated with carbon membrane and dried at room temperature for 1 h. The measurement was performed at 200 kV accelerating voltage. Dimension of AgNPs was determined from 100 particles by the Java image tool (ImageJ software).

Stability of AgNPs suspended in natural rubber latex was evaluated from zeta-potential values (ζ) by a zeta potential analyzer (DTS1070, Malvern Instruments). 50 µL of the as-prepared sample was diluted with deionized water at a 1:100 ratio before transferring to a folded capillary cell for measurement.

Uniaxial tensile manner of natural rubber composite with-and-without AgNPs was manipulated by a tensile machine (Instron 5566). The cured rubber composite sheets were cut into tensile specimens conforming to ASTM D412 (elastomer tensile testing). The measurement was proceeded at a 500 mm/min crosshead speed with a constant 1 kN static load cell under room temperature.

The antibacterial property of as-prepared rubber composite with-and-without AgNPs was assessed by considering the clear inhibition zone. The specimen with a diameter of 10 mm was placed on the Muller Hinton agar plates after being spread by 100 mL of

1×108 CFU/mL bacteria suspension on the agar plate. Subsequently, the agar plates containing rubber composites were aerobically incubated for bacterial culture in an incubator at 37 °C for 24 h. A clear zone around samples, providing the material's antimicrobial fashion, was measured in a millimeter unit using the digital vernier caliper. Two types of bacteria, including Escherichia coli ATCC25922 (gram-negative type) and Staphylococcus aureus ATCC25923 (gram-positive type) were provided to evaluate the antimicrobial susceptibility of the fabricated rubber composites.

Results and discussion

Physical appearance observation

$AgNO_3$ solution was added at various amounts into natural rubber latex for in situ generating Ag nanocolloidal particle within the given latex. Generally, it is notable that the reduction of Ag ion (Ag^+) to Ag metal nanoparticles (Ag^0) can basically approve by the color transformation of the raw material from colorless to brown color. The observed transformation can elucidate to the Ag nanocolloids formation (Saeb et al., 2014; Usha Rani and Rajasekharreddy, 2011). The changed-color phenomenon arises from the excitation of surface plasmon resonance (SPR) in the formed metal nanoparticles, electric field of visible light interacted with the confined electron gas within metal particle (Katz and Willner, 2004).

In this work, the color transformation of natural rubber latex after adding $AgNO_3$ as a precursor at various amount was observed as demonstrated in Figure 2. The natural rubber latex is milky-white liquid which generally consists of rubber particles and non-rubber components (protein, liquid, and carbohydrate) dispersed in water medium (Eng and Tanaka, 1993). After adding $AgNO_3$ solution, there is a color transformation of rubber latex from white to yellowish brown, indicating the formation of Ag nanocolloids suspended in the rubber latex. Furthermore, considered an increasing quantity of $AgNO_3$ solution, it is the color change from the typical lighter yellowish-brown (10 mL $AgNO_3$) to stronger yellowish-brown slurry (20 mL $AgNO_3$). As a result, it can be suggested the variation in size, shape, and concentration of the synthesized AgNPs in natural rubber latex (Saeb et al., 2014). As for the reduction process of Ag ion to form AgNPs in natural rubber latex, it could be suggested that the protein fraction as a non-rubber component in rubber latex play a crucial role in the formation of AgNPs. This rationale is consistent with Danna et al (Danna et al., 2016). They explained that the protein fraction in natural rubber can act as reducing agent for the formation of AgNPs, observing from the protein denaturation after rubber film soaked in the $AgNO_3$ solution.

UV-visible spectroscopic analysis

The formation of AgNPs in natural rubber latex was also investigated by UV-Visible spectroscopic analy-

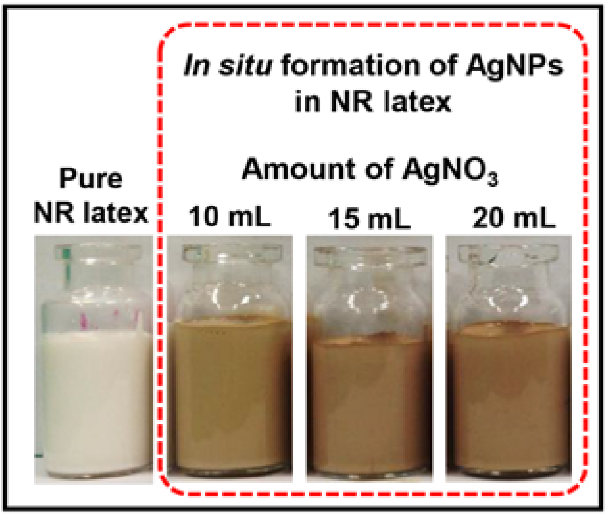

Figure 2. Physical appearance of pure natural rubber latex and AgNPs suspended in natural rubber latex by adding various amount of 0.1 M $AgNO_3$ solution.

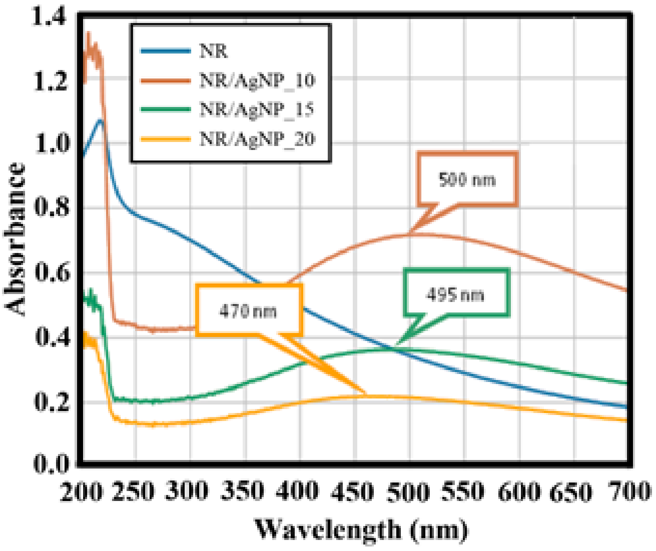

Figure 3. Figure 3. UV-Vis absorption spectra of natural rubber latex with-and-without AgNPs prepared at various amount of $AgNO_3$ precursor (10, 15, and 20 mL $AgNO_3$).

sis. Generally, AgNPs exhibit the absorption peak in UV-Vis technique because of the SPR phenomenon (Kelly et al., 2003). Electrons of metal nanoparticle can easily move between valence band and conduction band and these electrons provide a SPR absorption band in this spectroscopic technique (Balan et al., 2007).

Figure 3 shows the UV-Vis absorption spectra scanned with wavelength between 200-700 nm of the as-synthesized samples prepared at various amount of $AgNO_3$ precursor. As a result, the natural rubber latex without Ag nanocolloids does not provide the absorption peak of the synthesized metal nanoparticles. When $AgNO_3$ precursor were added into rubber latex, there is a notable detection of broad absorption peak in the range between 350-650 nm centered at 500 nm (10 mL $AgNO_3$), 495 nm (15 mL $AgNO_3$), and 470 nm (20 mL $AgNO_3$). It can assert the formation of AgNPs in the natural rubber latex (Sastry et al., 1998). Furthermore, there is no absorption band observed at more than 500 nm, revealing that most of the synthesized Ag nanocolloids in rubber latex have small size and similar morphology (Kelly et al., 2003). It has been explained that larger metal-nanocolloidal dispersions can suggest the absorption spectra with broad or additional bands because of higher multipole plasmon excitation (Kamat et al., 1998). This rationale can exploit to elucidate why an increment of $AgNO_3$ precursor from 10 mL to 20 mL changed absorption peak of AgNPs suspension from high intense to broad and less intense. The size and morphology of synthesized AgNPs was further visualized by TEM analysis.

TEM analysis

The morphology and size of colloidal AgNPs suspended in natural rubber latex prepared at different amounts of $AgNO_3$ precursor (10 and 20 mL $AgNO_3$) were observed as illustrated in the typical TEM images (Figure 4).

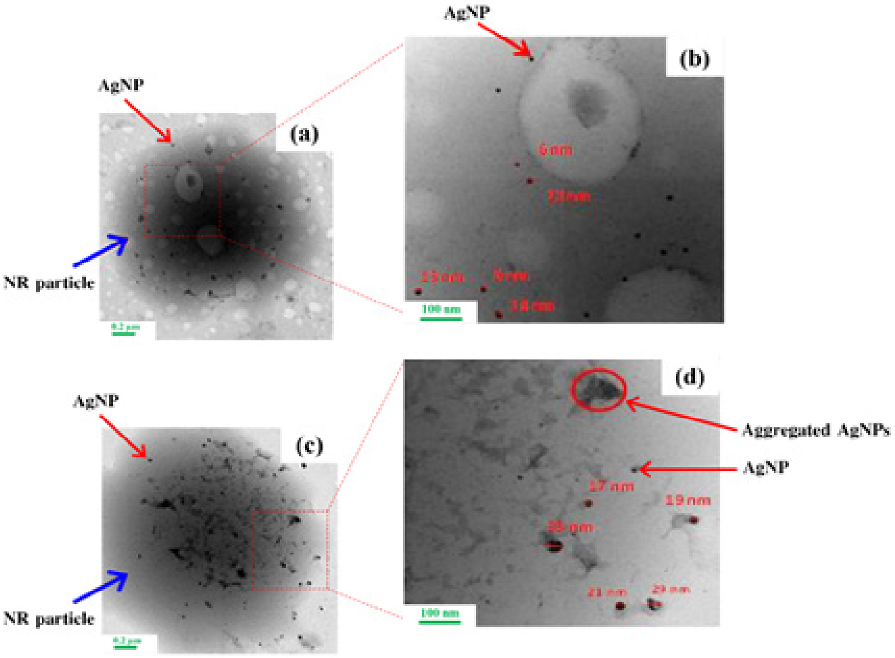

Figure 4. TEM images of AgNPs suspended in natural rubber latex: (a and b) AgNPs prepared at 10 mL $AgNO_3$ and (c and d) AgNPs prepared at 20 mL $AgNO_3$

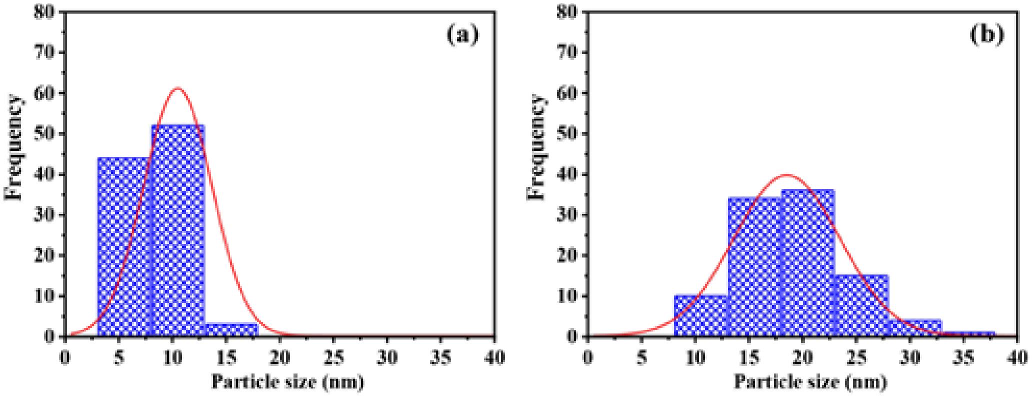

Figure 5. Morphology and average AgNPs suspended in natural rubber latex: (a) AgNPs prepared at 10 mL $AgNO_3$ and (b) AgNPs prepared at 20 mL $AgNO_3$

As a result, it can be clearly seen that the morphology of colloidal AgNPs is a mostly spherical shape. AgNPs prepared by 10-mL $AgNO_3$ precursor provide the metal nanoparticle with an average size of 11.52±5.39 nm and narrow size distribution (Figure 5a). However, the addition of 20-mL $AgNO_3$ precursor receive the AgNPs with larger size (21.84±5.15) and broader size distribution (Figure 5b) when compared to those of the smaller-content precursor. Moreover, it finds the aggregation of AgNPs (Figure 4d). This result can describe that an escalating quantity of $AgNO_3$ precursor provides an increment in Ag ion concentration in latex medium, relating to the increased amount of Ag nanoparticles in the system as well. Therefore, it is mostly possible that the neighboring metal nanoparticle can aggregate together to form the large-sized metal nanoparticles (Usha Rani and Rajasekharreddy, 2011).

Zeta potential observation

Zeta potential can be utilized to investigate the net surface charge of the metal nanoparticles. The colloidal particle in the solution can repel each other, preventing the tendency of particle agglomeration. Consequently, this analysis reveals insight information about the potential stability of metal nanocolloids in the medium (Mohammed J. Haider and Mehdi, 2014). Generally, it has been referred that metal nanoparticles are stable when the value of zeta potential is higher positive than +30 mV or lower negative than -30 mV

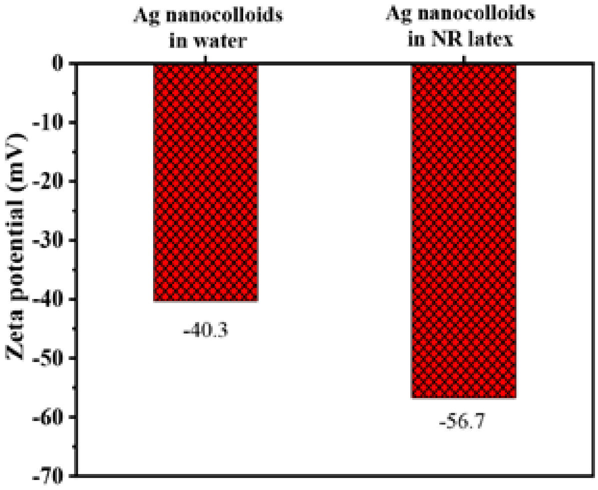

Figure 6. Zeta potential of AgNPs suspended in natural rubber latex compared with AgNPs suspended in water.

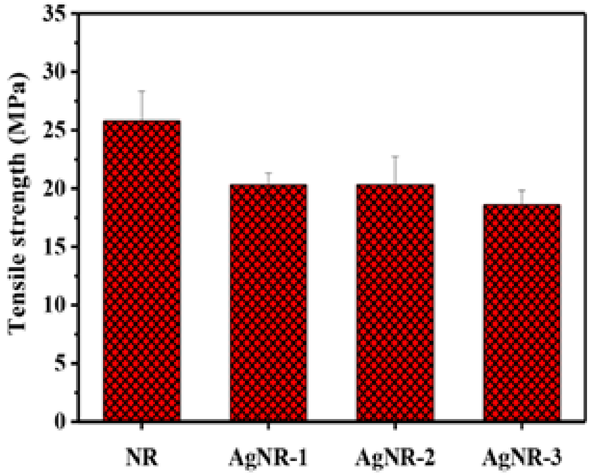

Figure 7. Tensile strength of natural rubber composite.

(Meléndrez et al., 2010). Herein, the zeta potential value of Ag nanocolloids suspended in the natural rubber latex was assessed and compared with AgNPs suspended in water, as demonstrated in Figure 6. As a result, AgNPs in water reveal the negative value (-40.3 mV) of zeta potential, meanwhile, AgNPs suspended in natural rubber latex also suggest the negative value (-56.7 mV). This manner could demonstrate that the synthesized Ag nanocolloids is stable in natural rubber latex, having strong electrostatic charges on the particles to prevent particle agglomeration.

Mechanical properties of rubber composites

Natural rubber latex and natural rubber latex containing AgNPs were mixed with curing agents to fabricate rubber composites as following the formulation in Table 1. The cured rubber sheet was cut into tensile specimen and determined the tensile properties as shown in Figure 7-8. As a result, there is a slight decrement in tensile strength of rubber composite containing with AgNPs compared with that of NR composite without AgNPs (Figure7). The tensile strength value reduces from 25.78 MPa (NR composite without AgNPs) down to 20.30 MPa (AgNR-1), 20.32 MPa (AgNR-2), and 18.58 MPa (AgNR-3). The slight decrement in tensile strength could indicate the poor compatibility of natural rubber matrix and AgNPs as an inorganic filler. Moreover, it is probably that there is the aggregation of AgNPs in the rubber matrix, resulting in the reducing mechanical strength.

Figure 8 shows stain at break of rubber composites with-and-without AgNPs. Natural composite without AgNPs possesses the stretchability approximately 717%. The natural rubber composites containing AgNPs provide elongation ability at 765% (AgNR-1), 710% (AgNR-2), and 776% (AgNR-3). This result could suggest that the

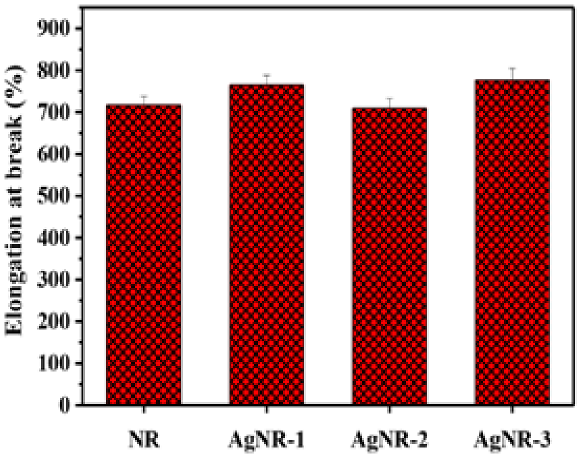

Figure 8. Elongation at break of natural rubber composites.

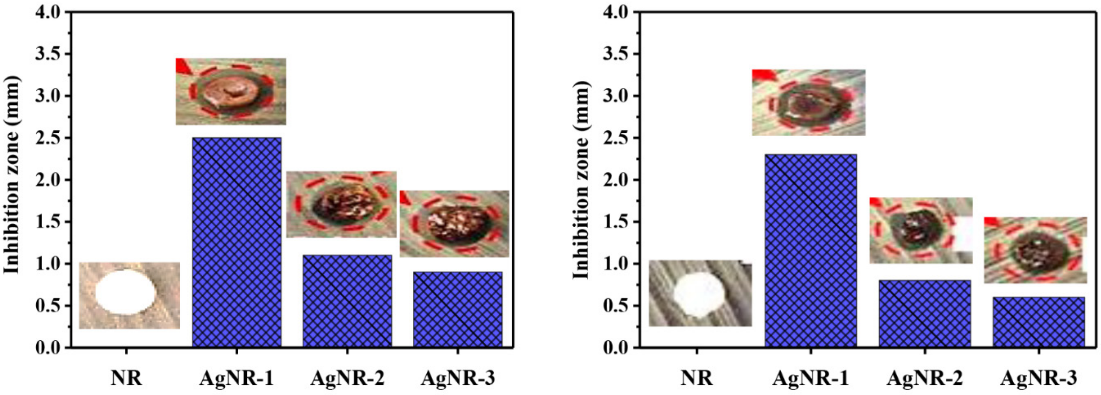

Figure 9. Inhibition zone referred to the antibacterial activity of natural rubber composites against (a) gram-negative *E. coli* and (b) gram-positive *S. aureus* at various types of natural rubber composites.

existence of AgNPs in the rubber composites with the given procedure does not change the elongation ability of the material.

Antimicrobial susceptibility of rubber composites

Figure 9 shows the antibacterial performance of natural rubber composites with-and-without AgNPs. As a result, natural rubber composite without AgNPs does not provide the antimicrobial manner against *E. coli* and *S. aureus*, considering no clear inhibition zone. Whereas natural rubber composites containing AgNPs serve the clear inhibition zone against the given bacterial pathogens, indicating that AgNPs are the responsible element for rubber composites' antibacterial property. AgNR-1 composite demonstrates the largest clear inhibition zone against *E. coli* (2.5 mm) and *S. aureus* (2.3 mm) pathogens. On the contrary, AgNR-2 and AgNR-3 composites are less effective in resisting the tested bacterial pathogens for the agar-disk-diffusion susceptibility test, evaluating from the smaller size of zone inhibition. This phenomenon could elucidate that the AgNPs aggregation may be affected in the diffusion ability of AgNPs out of the material for representing the antimicrobial activity.

Conclusions

AgNPs could be synthesized in natural rubber (NR) latex by adding various amounts of $AgNO_3$ precursor (10, 15, and 20 mL), without any reducing agent. The color of NR latex changed from white to a yellowish-brown color, and the SPR absorption peak of Ag metal was observed, revealing the formation of AgNPs in the natural rubber latex. It can be postulated that the non-rubber components in the NR latex such as proteins play the role of in-situ reducing agent. TEM images suggest the spherical shape of AgNPs with a diameter size of less than 30 nm. Moreover, the Ag nanocolloids are stable in the rubber latex, having a negative value of zeta potential lower than -30 mV. Natural rubber composites containing AgNPs were prepared, and the result found a slight decrement in mechanical strength. The antimicrobial performance of rubber composites was provided when compared to that of rubber composite without AgNPs.

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