Research Article

Antibacterial Nanocomposites Based on Fe$_3$O$_4$–Ag Hybrid Nanoparticles and Natural Rubber-Polyethylene Blends

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For the vulcanized natural rubber (NR), incorporation of silver nanoparticles (AgNPs) into the NR matrix did not exhibit the bactericidal property against *Escherichia coli* (*E. coli*). However, incorporation of AgNPs into polyethylene (PE) matrix showed good antibacterial activities to both Gram-negative and Gram-positive bacteria. In the present work, NR/PE (85/15) blends have been prepared by melt blending with presence of compatibilizer in an internal mixer. To possess antibacterial property, AgNPs (5–10 nm) or Fe$_3$O$_4$–Ag hybrid nanoparticles (FAgNPs, 8 nm/16 nm) were added into PE matrix before its blending with NR component. The tensile test indicated that the presence of compatibilizer in NR/PE blend significantly enhanced the tensile strength and elongation at break (up to 35% and 38% increases, resp.). The antibacterial activity test was performed by monitoring of the bacterial lag-log growth phases with the presence of nanocomposites in the *E. coli* cell culture reactor. The antibacterial test showed that the presence of FAgNPs in NR/PE blend had a better antibacterial activity than that obtained with the lone AgNPs. Two similar reasons were proposed: (i) the faster Ag$^+$ release rate from the Fe$_3$O$_4$–Ag hybrid nanoparticles due to the electron transfer from AgNP to Fe$_3$O$_4$ nanoparticle and (ii) the fact that the ionization of AgNPs in hybrid nanostructure might be accelerated by Fe^{3+} ions.

1. Introduction

Vietnam has been ranked as the fourth largest NR exporter and the fifth largest NR producer after Thailand, Indonesia, and Malaysia. NR was the third commodity after rice and coffee. The government has issued the master plan to reach 800,000 ha of rubber plantations and 1.1 to 1.2 million tons of NR by 2015 or 2020 in the country. The domestic consumption is expected to reach 30% of the NR production by 2030 to develop the end products from natural rubber. NR has excellent mechanical properties but it likes any other polymers which are composed with highly unsaturated chain that is susceptible to oxidative degradation.

Vietnam nowadays is facing the risk of contaminated water and food, especially some highland provinces in the North. Therefore, the antimicrobial performance of housing material appears to be very important in preventing infection from harmful microorganisms. Microorganisms, such as bacteria, algae, and fungi, are commonly found in the ground, water, air, and other living organisms. For example, an infection of *E. coli* can result in food poisoning [1, 2]. One of the most common methods for achieving an antibacterial property for materials is to incorporate an antibacterial agent into them. Antibacterial agents are divided into two groups: inorganic agents and organic agents. The inorganic antibacterial agents, such as ammonium salts, metal salt solutions, antibiotics, and AgNPs, and the organic antibacterial agents, such as alcohol solution applications, are currently the most widely used. Available studies in the literature [3–6] used a

wide range of antibacterial agents in polymers, both thermoplastics and rubbers, to achieve the antibacterial property for these polymers. The antibacterial agents used include AgNPs colloids, silver-substituted zeolite compound, nano-TiO_2, and 2-hydroxypropyl- 3-piperazinyl-quinoline carboxylic acid methacrylate. In this direction, we reported recently the fabrication of antibacterial PE-AgNP nanocomposite for water and food preservation. This PE-AgNP nanocomposite held the antibacterial activity against *E. coli*, *Bacillus subtilis*, and *Salmonella typhimurium* bacteria [7]. However, incorporation of AgNPs into the NR matrix did not give the antibacterial activity for the vulcanized NR against *E. coli* [8]. Recently, new approach to improve the bactericidal property of AgNPs is to combine AgNPs with other oxides, such as silver ferrite nanocomposites [9], Fe_3O_4–Ag core-shell nanoparticles [10, 11], AgNPs containing silica microbeads [12], and Fe_3O_4–Ag hybrid nanoparticles [13]. For Fe_3O_4–Ag core-shell nanoparticles, Chudasama et al. found that their antibacterial activity against the Gram-negative bacteria (including *E. coli*) was better than that of AgNPs [10]. Similarly, for silver ferrite nanocomposites, Kondala et al. [9] reported that their antibacterial activity was higher than those of AgNPs and other antibacterial drugs. Their findings could be attributed to the faster Ag^+ release rate from the silver ferrite nanocomposite.

Polymer blending is an effective way to achieve a desirable combination of properties that are often absent in single component polymers. The NR/PE blends have been studied due to the excellent processing property of PE and the low cost and abundant supply of NR. As the thermoplastic rubber, this blend has both thermoplastic and elastomeric properties. Thus its fabrication is easier than that of thermosetting rubber. This blend can be used in automobile components and other industrial or household applications. The main characteristic of the blends is a two-phase system [14], including the hard polymer phase and the soft rubbery phase. There was a poor adhesion between the interfaces of NR and PE components. Therefore, compatibilizers should be used to enhance the mechanical properties of the NR/PE blend. Pechurai et al. [15] prepared the phenolic-modified polyethylene as the compatibilizer for NR/HDPE blends. They found that the blend with compatibilizer exhibited higher flow and viscosity and mechanical properties. Nakason et al. [16] also reported that NR/LDPE blend with phenolic resin compatibilizers showed higher tensile strength, elongation at break, and tendency to recover from prolonged extension than those of the blend without compatibilizer. Similarly, for the compatibilizer as liquid natural rubber (LNR), Dahlan et al. [17] reported that LNR reduced the interfacial tension within the NR/LDPE blends, thus improving the interaction between the phases, resulting in improved properties. Thus, the incorporation of AgNPs into PE phase of NR/PE blend is expected to enhance its antibacterial activity and mechanical property, as compared to the plain NR.

This paper aims to demonstrate the antibacterial performance of the NR/PE blend containing Fe_3O_4–Ag hybrid nanoparticles. The tensile property of blend was also investigated to reveal the effect of the compatibilizer. The compatibilizer was prepared by functionalization of NR crepe via photochemical degradation using UV irradiation in the presence of H_2O_2.

2. Materials and Methods

2.1. Materials. Iron (III) acetylacetonate ($Fe(acac)_3$) 99.99%, silver nitrate ($AgNO_3$) $\geq$ 99%, sodium borohydride ($NaBH_4$) $\geq$ 99%, and sodium stearate $\geq$ 99%; solvents, 1-octadecene, dichlorobenzene (DCB, 99%), absolute ethanol, and hexane; and surfactants and reductant, oleic acid (OA) 99%, oleylamine (OLA) 70%, and 1,2-hexadecanediol (HDD) 90% were purchased from Sigma-Aldrich, Ltd.

PE granules type HDPE was purchased from IRPC Public Company Limited (grade G2855, Polimaxx Polene, Thailand).

Nonvulcanized Vietnamese NR used in this study is ribbed smoked sheet NR (type RSS-1, with Mooney viscosity ML = 80) obtained from Haiphong Plastic and Rubber, Ltd., Vietnam. It was compounded with sulfur (3 phr), zinc oxide (5 phr), stearic acid (1 phr), mercaptobenzothiazole (0.9 phr), and tetramethylthiuram disulfide (0.45 phr). For producing the bright color sample, the carbon black was replaced by nanosilica at 5 phr (phr = parts by weight per hundred parts of rubber). As-received nanosilica, purchased from MTI Corporation (USA), was used without any further organic modification. All other chemicals were of analytical grade and were purchased from Haiphong Plastic and Rubber, Ltd., Vietnam. The PE content of 15 phr in blend was chosen from our previous screening investigation on tensile property of NR/PE blend, in which the PE content varied from 5 phr to 20 phr.

Compatibilizer was prepared as follows. An amount of 4 g NR crepe was dissolved in 40 mL toluene in a glass flask with a mechanical stirrer. Hydrogen peroxide solution (30 wt.%, 10 mL) was added and thoroughly mixed with the above solution. The mixture was then poured into the Petri dish. The system was then placed in UV irradiation (Model F300S, Fusion UV Systems, Inc., USA). After 4 times of irradiation (5 m/min), the clear supernatant toluene layer was decanted. Toluene was then removed under reduced pressure of a vacuum pump. The as-prepared product was rinsed with distilled water and then dried at 70°C and kept in the absence of light before use. Table 1 shows the mix design for the 8 types of samples.

2.2. Synthesis of AgNPs and Fe_3O_4–Ag Hybrid Nanoparticles

2.2.1. Synthesis of AgNPs. AgNPs were prepared by the reduction of silver nitrate using sodium borohydride in the presence of sodium stearate. A 20 mL volume of 1.0 mM silver nitrate was added dropwise to 100 mL of 10 mM sodium stearate; then 10 mL of 4.0 mM chilled sodium borohydride solution was added dropwise into the above mixture. The reaction mixture was stirred vigorously during 30 minutes by using the magnetic stir plate and sonicated for another 30 minutes. Afterwards, the AgNPs was extracted with 100 mL xylene at 50°C. The average size of these AgNPs, which were well dispersed in the PE matrix, was about 5–10 nm (as can be seen by TEM image in Figure 1).

TABLE 1: Mix design of neat NR and NR/PE blends samples investigated (phr = parts by weight per hundred parts of NR).

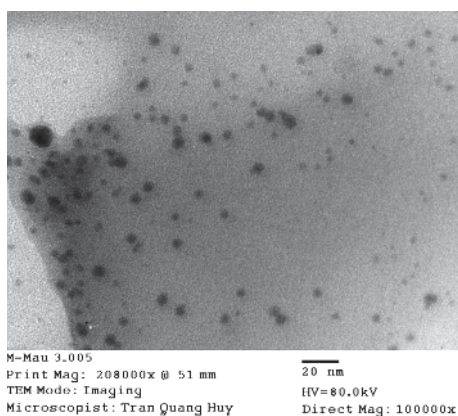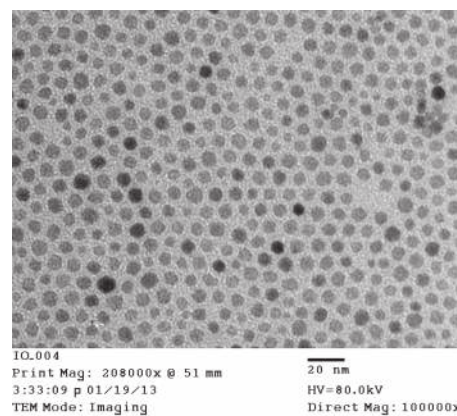| Samples	PE	Neat NR	NR/PE	NR/PE+Cpt	PE-AgNP	NR-AgNP	NR/PE-AgNP	NR/PE-FAgNP
NR		x	x	x		x	x	x
PE (15 phr)	x		x	x	x		x	x
Nano-SiO$_2$		x	x	x		x	x	x
Sulfur		x	x	x		x	x	x
Stearic acid		x	x	x		x	x	x
ZnO		x	x	x		x	x	x
Mercaptobenzothiazole		x	x	x		x	x	x
Tetramethylthiuram disulfide		x	x	x		x	x	x
Compatibilizer (10 phr)				x				
AgNPs (0.1 wt.%)					x	x	x	
FAgNPs (0.1 wt.%)								x

FIGURE 1: TEM image of AgNPs dispersed in PE matrix (at 2 wt.%).

FIGURE 2: TEM image of Fe$_3$O$_4$ NP dispersed in DCB.

2.2.2. Synthesis of Fe$_3$O$_4$–Ag Hybrid Nanoparticles. At first, Fe$_3$O$_4$ nanoparticles (Fe$_3$O$_4$ NPs) were prepared. In a typical synthesis, acetylacetonate (0.162 g, 0.63 mmol), Fe (III) acetylacetonate (0.6 g, 1.9 mmol), and hexadecanediol (0.58 g, 1.5 mmol) were charged into 100 mL three-neck flask. At the same time, 3.6 mL OA, 3.6 mL OLA, and 30 mL of 1-octadecene solvent were added to the above mixture. The concentrations of Fe(acac)$_3$, OA, OLA, and HDD in the reaction solution are equal to 63 mM, 372 mM, 372 mM, and 75 mM, respectively. The reaction mixture was magnetically stirred and degassed at room temperature for at least 30 min before heating to 100°C and remained at this temperature for 30 min in order to remove water. Temperature continued to be increased to 200°C and remained at this temperature for another 30 min. Then, reaction solution was ramped to 295°C with a heating rate of 5–7°C/min and maintained for 30 min before cooling to room temperature. The as-synthesized Fe$_3$O$_4$ NPs were purified from free excess ligands before doing the synthesis of Fe$_3$O$_4$–Ag hybrid nanoparticles. In typical purification, 20 mL of the Fe$_3$O$_4$ NPs solution was mixed with 20 mL of ethanol. The Fe$_3$O$_4$ NPs were then collected using a magnetic bar and the supernatant was discarded. The Fe$_3$O$_4$ NPs were thereafter dispersed in

5 mL hexane and precipitated by adding 5 mL of ethanol. The precipitation-redispersion procedure was repeated two more times and the Fe$_3$O$_4$ NPs were finally dispersed in DCB. The average size of these Fe$_3$O$_4$ NPs was about 8 nm (as can be seen by TEM image in Figure 2).

Fe$_3$O$_4$–Ag hybrid nanoparticles were prepared using seeding growth method. 5 mL of DCB solution containing 500 mg AgNO$_3$ and 3 mL OLA was added dropwise into 20 mL DCB containing 100 mg purified Fe$_3$O$_4$ NPs (at 170°C). The mixture was maintained at this temperature for 60 min before cooling down to room temperature. The TEM image of these Fe$_3$O$_4$–Ag hybrid nanoparticles was presented in Figure 3 with the larger ones being AgNP nanoparticles ($d \approx$ 16 nm) and the smaller ones being Fe$_3$O$_4$ NPs ($d \approx 8$ nm)

2.3. Fabrication of NR/PE (85/15) Blends Containing AgNPs or Fe$_3$O$_4$–Ag NPs

2.3.1. Fabrication of PE Nanocomposite Containing AgNPs or Fe$_3$O$_4$–Ag NPs. The PE nanocomposites with high concentration of nanoparticles (2 wt.%) were prepared by solution blending method. PE granules were firstly dissolved in xylene solvent (10 wt.%, stirring at 90°C). Thereafter nanoparticles were added to this solution under sonication for 1 hour.
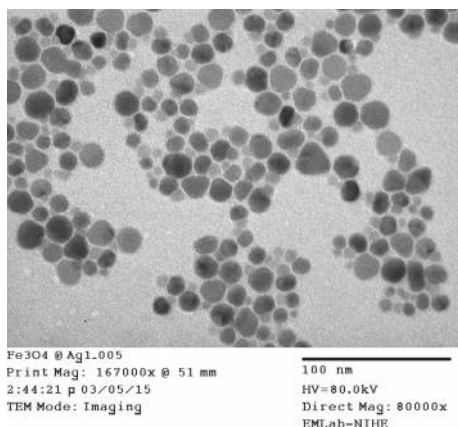
FIGURE 3: TEM image of Fe_3O_4–Ag hybrid nanoparticles dispersed in DCB.

Xylene was then removed at high temperature (120°C) under reduced pressure.

To fabricate the final PE nanocomposites, the above as-prepared nanocomposites were mixed with PE granules and then blended in an internal mixer at 50 rpm and 170°C for 8 min to extrude the final PE nanocomposites with the content of AgNPs at 0.1 wt.%.

2.3.2. Fabrication of NR/PE Blends Containing AgNPs or Fe_3O_4–Ag NPs.

To fabricate the final (NR/PE-AgNP or NR/PE-FAgNP) nanocomposites (with AgNPs at 0.1 wt.%.), the above as-prepared PE nanocomposites were mixed with NR crepe and its ingredients by the internal mixer (150°C, 9 minutes, 50 rpm). The melt mixture was then quickly transferred and molded by a hot pressed instrument (Toyoseky, Japan) at 160°C for 20 minutes.

2.3.3. Fabrication of NR Nanocomposite Containing AgNPs or Fe_3O_4–Ag NPs.

The NR nanocomposites with high concentration of nanoparticles (2 wt.%) were prepared by solution blending method. NR crepe was firstly dissolved in toluene solvent. Thereafter nanoparticles were added to this solution under sonication for 1 hour. Toluene was then removed under reduced pressure at 70°C.

To fabricate the final NR nanocomposites (with AgNPs at 0.1 wt.%.), the above as-prepared nanocomposites were mixed with NR crepe and other ingredients and then blended in an internal mixer (120°C, 9 minutes, 50 rpm). The melt mixture was also then quickly transferred and molded by a hot pressed instrument (Toyoseky, Japan) at 160°C for 20 minutes.

2.4. Mechanical Study.

The tensile test was conducted by using Zwick z2.5 tensile tester (Germany) according to the ASTM D638 standard. Average data were obtained by measuring each sample piece 3 times. All tests were performed at room temperature.

A hardness durometer (Shore A) was used for hardness evaluation of vulcanized NR (neat NR) and NR/PE blends, in accordance with ASTM D2240. All reported data were averaged from at least 3 specimens made from the same batch.

2.5. FTIR, UV-Vis, and DSC Tests.

Infrared and UV-Vis spectra were obtained by using the FTIR NEXUS 670 (Nicolet, USA) and the UV-Vis spectrophotometer (GBC, CINTRA 40, USA). Differential Scanning Calorimeter (DSC) was obtained by using NETZSCH DSC 204F1 Phoenix instrument. About seven milligrams of the sample was put into an aluminum pan with a cover. The samples were heated from room temperature to 280°C at a rate of 10°C min^{-1}. DSC experiments were conducted in the nitrogen atmosphere with flow rate of 20 cm^3·min^{-1}.

2.6. Antibacterial Growth Test.

E. coli DH5α was purchased from Invitrogen (USA). Luria-Broth medium was provided by Merck (Germany). To evaluate the cell density during culture, the instrument Beckman Coulter DU-730 (USA) was used. In this test, the optical density OD_{600} measures the light absorbance of an E. coli cell culture sample. The OD_{600} value corresponds to the cell density or cell number in a given E. coli culture volume. Different cell strains may have different cell numbers at a given OD_{600} value, but $OD_{600} = 1$ usually means there are about 1×10^9 cells per mL culture.

Bacterial precultures were prepared with the aim of generating the subcultures of bacterial populations in a large scale in the lag phase so that the number of bacterial cells was constant before the log phase or exponential growth phase [18]. By this means, the growth rate of the bacterial cultures due to the presence of nanocomposites was evaluated over time. The OD_{600} values in the range of 0.1–2.0 for cell densities of E. coli culture indicated the bacterial growth rates.

Precultures of Bacteria. A volume of 100 μL of stock culture in glycerol of E. coli was pipetted into 3 mL of medium in a 15 mL test tube and shaken overnight at 200 rpm and 37°C. Afterwards, a 500 μL aliquot of preculture was inoculated into 100 mL of medium in a 500 mL Erlenmeyer flask and shaken at 200 rpm and 37°C until the OD_{600} absorbance value reached 0.3. These precultures were used promptly for bacterial growth rate testing.

Preparation of Nanocomposites Testing Samples. The as-prepared nanocomposites were cut into square pieces with dimensions of 1×1 cm^2, washed with acetone to remove all impurities on the surface, and autoclaved at 120°C for 20 min before use.

Monitoring of the Bacterial Lag-Log Growth Phases in the Presence of the Nanocomposites. The monitoring test for the evaluation of the bacterial growth was adapted from the procedure in ASTM E 2149-10. Ten square pieces of autoclaved nanocomposites were placed into each 100 mL bacterial preculture in a 500 mL Erlenmeyer flask (as described previously) in which OD_{600} had reached 0.3, and shaking was continued at 200 rpm and 37°C. From this time forward, the OD_{600} value of each bacterial culture was monitored every 30 min until it reached 2.0. The obtained data were

the average of three cultures. The relative OD_{600} values were then standardized to evaluate the influence of the nanocomposites on the growth rate of the bacteria. The pure bacterial cultures were used as controls.

3. Results and Discussion

3.1. Mechanical Test. Depending on the type and content of nanofiller, the presence of nanoparticles in the NR or its blends may enhance the tensile property. In this study, nano-SiO_2 was used as nanofiller/nanoreinforcer (as shown in Table 1). In comparison with carbon black (traditional filler), the tensile test indicated that the addition of nano-SiO_2 (5 phr) in NR matrix significantly increased tensile strength and elongation at break (up to 43% and 88% increases, resp.). By using the combination of FE-SEM with a tensile test for nano-SiO_2 filled NR, Urushihara et al. [19] found that the formation of nano-SiO_2 aggregates with high elastic modulus in the NR matrix. On the other hand, during the melting mixture of NR/PE blend, nano-SiO_2 not only was dispersed into NR matrix but also can be incorporated into the PE matrix. In this direction, Hongling et al. [20] reported that the incorporation of nano-SiO_2 in LDPE increases the tensile force and elongation at break, which reached the maximum value when the nano-SiO_2 content was 6 wt.%. Arunava et al. [21] reported the variations of specific heat in NR filled with nano-SiO_2. They found that the specific heat values increase with the increase of nano-SiO_2 concentrations. In their nanocomposite, nano-SiO_2 could make cross-link with NR chains causing an increase in the molecular weight of NR as well as the specific heat values.

To possess the antibacterial property, AgNPs or FAgNPs were added to the NR and its blends (at 0.1 wt.%). This very low content of nanoparticles might not change the tensile property of the material. In the previous work [7], for PE-AgNP nanocomposites, we did not observe the change in tensile and thermal properties, as compared to the plain PE. In this study, similar results were obtained for the tensile strength of PE-AgNP and NR-AgNP with the low concentration of AgNPs. Thus, the presence of AgNPs in both of PE matrix and NR matrix did not change the tensile strength.

Figure 4 demonstrates tensile strength of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer. As can be seen in this figure, the tensile strength of neat NR was 6.8 ± 0.1 MPa. Addition of the PE component (with the higher tensile strength value of 24.3 ± 0.6 MPa [7]) in the NR matrix caused the higher tensile strength value of 9.2 ± 1.4 MPa (for the NR/PE blend treated with compatibilizer, NR/PE+Cpt). Without compatibilizer, the NR/PE blend had a lower tensile strength (6.3 ± 0.4 MPa) than that of neat NR. Thus, the interactions between the blend components were the main factor in characterizing the tensile properties of the blends.

Figure 5 shows the elongation at break of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer. As shown in this figure, the elongation at break of NR/PE+Cpt was $1009 \pm 96\%$, which was closely related to the values of neat NR ($1158 \pm 73\%$) and neat PE ($1096 \pm 3\%$). Without the compatibilizer, the elongation at break of NR/PE blend was
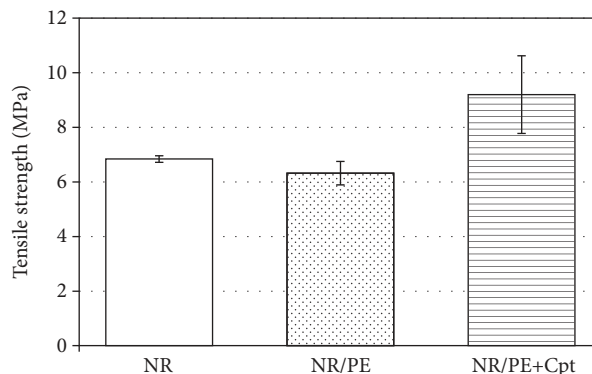

FIGURE 4: Tensile strength of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer.
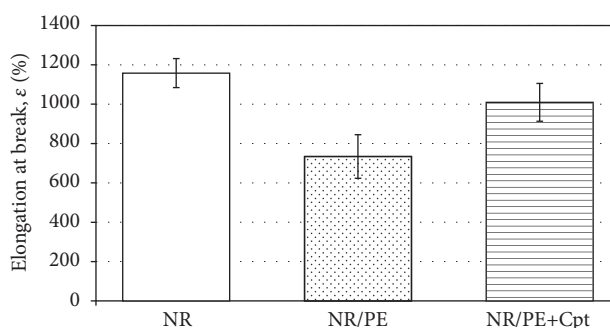

FIGURE 5: Elongation at break of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer.

smaller ($734 \pm 111\%$) due to the poor adhesion between the interfaces of NR and PE components.

The tensile data indicated that the presence of compatibilizer in NR/PE blend increased the tensile strength and elongation at break up to 35% and 38%, respectively. Dahlan et al. [22] reported the lower values obtained for 60/40 blends of NR/LLDPE with LNR. In their work, the blend with LNR had highest tensile and elongation values of 7.3 MPa and 590%, respectively.

Figure 6 presents hardness of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer. The hardness of neat NR was 52.5 ± 1.3 (Shore A). Blending PE in NR matrix resulted in an increase in hardness value (96.8 ± 1.0, for NR/PE+Cpt). This fact could be attributed to the curing of the rubber phases [23]. In this work, the hardness of blend was higher than that reported by Dahlan et al., in which they used LNR as compatibilizer [22].

The FTIR spectra were used to reveal the role of the compatibilizer on the tensile property of NR/PE blend. The NR crepes were examined by using FTIR technique before and after UV/ozone treatment. Figure 7 presents the FTIR spectra of NR crepes (nonvulcanized NR) before and after UV/ozone treatment.

After treatment, some new peaks can be observed such as the peak at 1726 cm^{-1} being assigned to C=O stretching vibration and the peak at 3259 cm^{-1} being assigned to O–H stretching vibration. Thus, after treatment, the modified NR
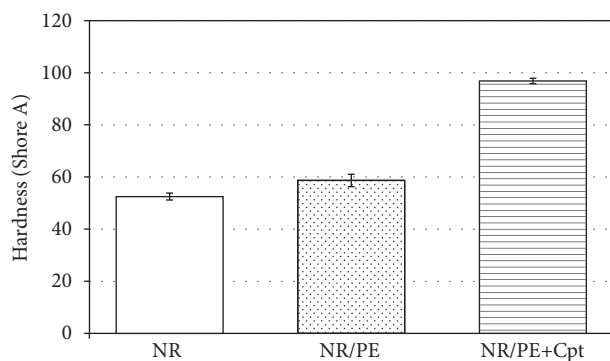
FIGURE 6: Hardness of neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer.
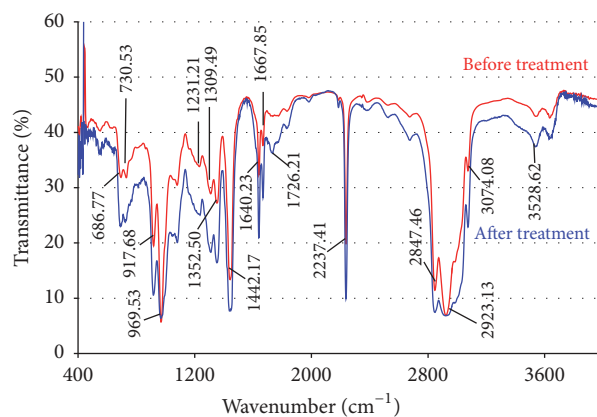

FIGURE 7: FTIR spectra of NR crepes before and after UV/ozone treatment.
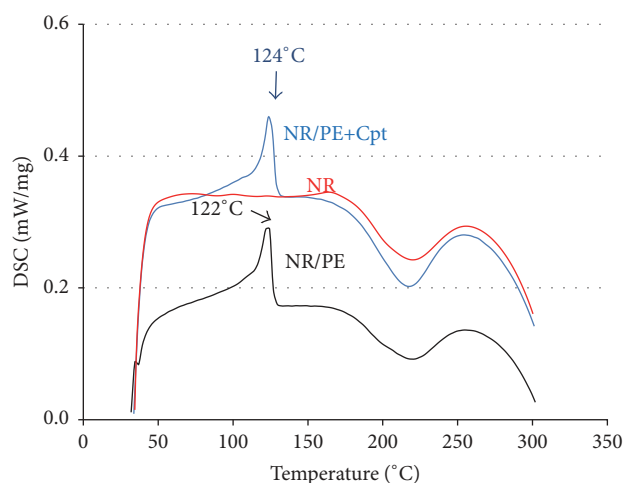

FIGURE 8: DSC plot of heat flow versus temperature for neat NR, NR/PE blend, and NR/PE blend treated with compatibilizer.

with both of hydroxyl terminal and carbonyl terminal groups was obtained.

The appearance of a new band at $1726\,cm^{-1}$ due to C=O groups could be explained by the NR oxidation, which was caused by the metastable species generated by UV radiation and ozone (from atmospheric oxygen). It means the formation of carbonyl groups due to photooxidation at the main NR chain. Similar result was signaled by Moyano and Martín-Martínez [24] with UV/ozone treatment for improving the adhesion of vulcanized rubber. On other hand, the NR with hydroxyl terminal groups (as a result of the photochemical degradation of NR) was initiated by hydroxyl radicals, which might undergo similar mechanism proposed by Ravindran et al. [25].

Similar results could be obtained by chemical degradation of nonvulcanized NR. By oxidative degradation of NR latex using H_2O_2 and $NaNO_2$, Ibrahim et al. [26] found that the LNR had different end groups, depending on the pH of the medium. In an acidic medium, NR with hydroxyl terminal groups was formed. The redox reaction took place in an alkaline medium producing the NR with carbonyl terminal groups.

Therefore, FTIR data indicated that the compatibilizer was a functionalized NR, which has the active groups such as –OH and –C=O in the isoprene chain, which can act as a good agent for improving the interactions between NR and PE components. This fact was confirmed by DSC data of these NR/PE blends with and without compatibilizer (Figure 8). As can be seen in Figure 8, the compatibilizer not only increased the heat flow of NR/PE blend but also increased the melting temperature of PE phase in NR/PE blend.

3.2. Antibacterial Growth Test

3.2.1. Effect of AgNPs in NR and PE on the Growth Rate of the Bacterial Cultures. Figures 9 and 10 show the influence of the PE-AgNP and NR-AgNP nanocomposites on the growth rate of the *E. coli* liquid cultures, respectively. As seen in Figure 9, the growth rates of the pure cultures and mixed cultures with neat PE were almost similar after 2 hours of cultivation. The log phases of the pure cultures and mixed cultures with neat PE were 75% after 2 hours of cultivation,

whereas these were 60% in the cases of mixed cultures with PE/AgNPs. The growth rate of the culture was 70% after 6 hours in the presence of PE/AgNPs. Thus, the *E coli* bacterial growth was strongly restricted by the presence of PE/AgNPs nanocomposite.

In the case of NR-AgNP nanocomposite (Figure 10), the growth rates of the pure cultures and mixed cultures with NR-AgNP were almost similar. The diminished antibacterial property for this NR-AgNP nanocomposite might be attributed to its compounding procedure, including the melting mixture and static vulcanization of NR crepe under pressure at high temperature. This as-prepared method may inhibit the release of Ag^+ ions from the dense cured NR matrix. Rathnayake et al. [8] also found that the presence of AgNPs in NR latex foam matrix did not enhance the antibacterial activity of vulcanized NR latex foam against *E. coli*. In their work, the inherent antibacterial activity of vulcanized NR latex foam might be obtained from ingredients (such as ZnO and diphenyl guanidine).

The data obtained from Figures 9 and 10 suggest the new approach to fabricate the antibacterial NR-based material
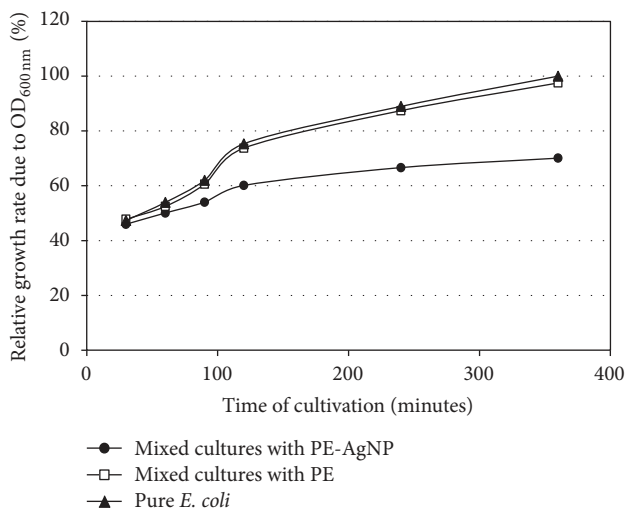
FIGURE 9: Influence of the PE-AgNP nanocomposites on the growth rate of the *E. coli* liquid cultures. The data points represent the means of three cultures (standard deviation < 10%).
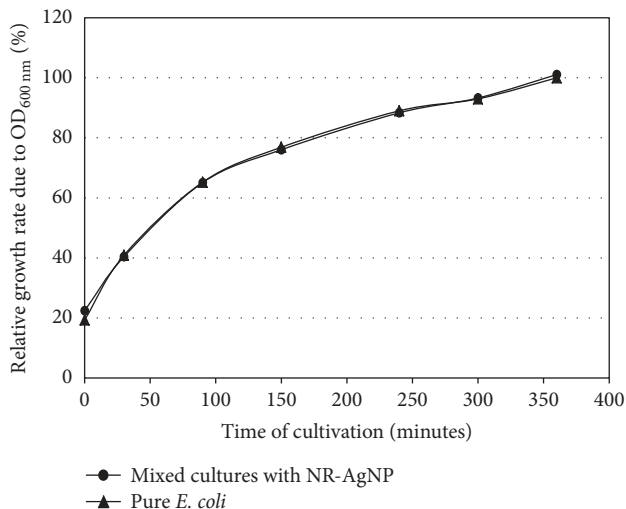

FIGURE 10: Influence of the NR-AgNP nanocomposites on the growth rate of the *E. coli* liquid cultures. The data points represent the means of three cultures (standard deviation < 3%).

FIGURE 11: Influence of the NR/PE-AgNP nanocomposites on the growth rate of the *E. coli* liquid cultures. The data points represent the means of three cultures (standard deviation < 3%).

FIGURE 12: Influence of the NR/PE-FAgNP nanocomposites on the growth rate of the *E. coli* liquid cultures. The data points represent the means of three cultures (standard deviation < 5%).

containing AgNPs. In this study, to fabricate NR/PE-AgNP and NR/PE-FAgNP samples, AgNPs were dispersed into PE component (rather than into NR component) before blending.

3.2.2. Effect of AgNPs and FAgNPs in NR/PE Blends on the Growth Rate of the Bacterial Cultures. Figures 11 and 12 present the influence of the NR/PE-AgNP and NR/PE-FAgNP nanocomposites on the growth rate of the *E. coli* liquid cultures, respectively. As seen in Figure 11, the growth rates of the pure cultures and mixed cultures with NR/PE blend were almost identical after 2 hours of cultivation. Their difference of 3% was observed only from the beginning until 2 hours of cultivation. The log phases of the pure cultures and mixed cultures with neat NR/PE blend were
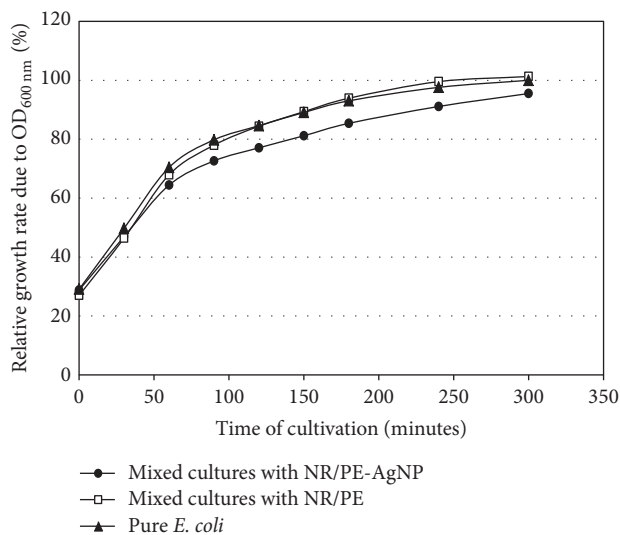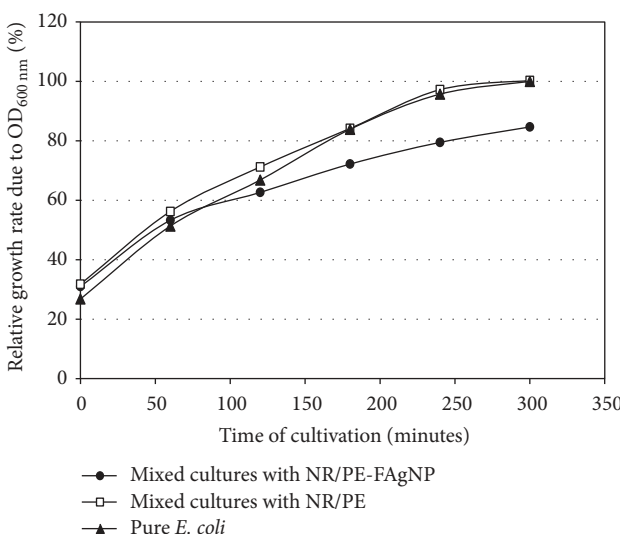
84% after 2 hours of cultivation, whereas these were 77% in the cases of mixed cultures with NR/PE-AgNP. Thus, the *E. coli* bacterial growth was slightly restricted in the presence of NR/PE-AgNP nanocomposite. As compared to PE-AgNP nanocomposite, the antibacterial activity of NR/PE-AgNP was less active; both two nanocomposites had the same concentration of AgNPs (at 0.1 wt.%). This fact could be explained by the larger effective surface area (~7 times) against *E. coli* for PE-AgNP nanocomposite. The NR/PE-AgNP nanocomposite contained a smaller content of PE-AgNP nanocomposite (15 wt.%); thus increasing the content of PE component (>15 phr) should increase the antibacterial activity of NR/PE-AgNP.

As shown in Figure 12, the log phase of the pure cultures and mixed cultures with NR/PE blend was 84% after 3 hours of cultivation, whereas this was 72% in the cases of mixed cultures with NR/PE-FAgNPs. Thus, the presence of FAgNPs in NR/PE blend had a better antibacterial activity, as compared to the AgNPs. Tung et al. [13] also found that the FAgNP had a more noticeable bactericidal activity against *Staphylococcus aureus* bacteria than that of AgNPs. They suggested 2 main factors for enhancement in bactericidal activity of FAgNP: (i) high catalytic activity of AgNP with good dispersion and aggregation stability due to the Fe_3O_4 carrier and (ii) large physical surface area between the bacterial cell membrane and the hybrid nanoparticles. Liu et al. [27] and Lubick [28] signaled that a smaller AgNP size should release Ag^+ ion faster. Since the average size of AgNP in FAgNP was bigger than that of the lone AgNPs (Figures 1 and 3), the above-obtained finding could be attributed to the faster Ag^+ release rate from the Fe_3O_4–Ag hybrid nanoparticles. Similar interesting finding was reported by Kondala et al. [9] and Chudasama et al. [10] for Fe_3O_4–Ag core-shell nanoparticles and silver ferrite nanocomposite, respectively. As reported, their nanomaterials had a higher antibacterial activity than that of lone AgNPs. Therefore, we would propose that, in the environment, ionization of AgNPs in hybrid nanostructure might be accelerated by Fe^{3+} ions. Li et al. [29] reported that the cointensification of Ag and Fe^{3+} greatly enhanced the bioleaching efficiency of As-bearing gold ore. In this direction, Takahashi et al. [30] found the electron transfer from Ag core to the FeCo shell in the 15 nm hybrid nanoparticles. Their XPS data indicated that the relative proportions of oxidation states of iron were $Fe^0/Fe^{2+}/Fe^{3+} = 15:56:29$. This electron transfer process (from AgNP to Fe_3O_4 NP in the Fe_3O_4–Ag hybrid nanoparticles) could also be observed by using UV-Vis spectra for the surface plasmon resonance (SPR) wavelength of AgNPs (Figure 13). As seen in Figure 12, the hybridization of AgNPs and Fe_3O_4 NP leads to red shift in SPR and also to the significant broadening of the SPR peak. For the lone AgNPs, the characteristic SPR peak of AgNPs is located at 403 nm [31, 32], whereas it is 418 nm for the Fe_3O_4–Ag hybrid nanoparticles.

4. Conclusion

In this study, the antibacterial NR-based materials were successfully fabricated by using AgNPs and their hybrid nanoparticles. The main detail findings of this investigation include the following.

The NR/PE (85/15) blends were successfully prepared by melt blending with presence of compatibilizer in an internal mixer. The compatibilizer was obtained from the treatment of NR crepe under UV/ozone radiation with presence of H_2O_2. The FTIR data indicated that compatibilizer has the active groups such as –OH and –C=O in the isoprene chain, which can act as a good agent for improving the interactions between NR and PE components. The DSC data indicated that compatibilizer not only increased the heat flow of NR/PE blend but also increased the melting temperature of PE phase in NR/PE blend. The tensile test indicated that NR/PE blend with compatibilizer showed higher tensile strength and
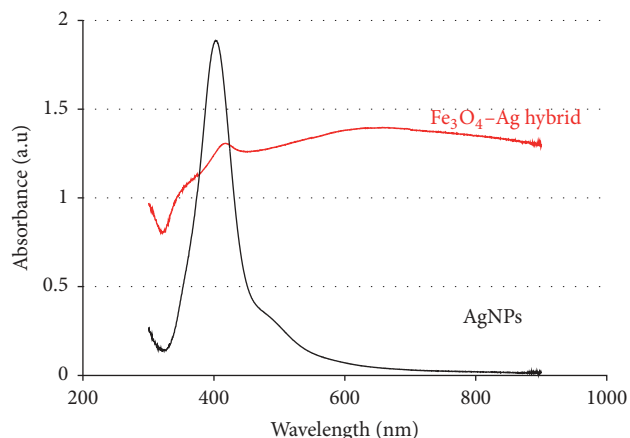

FIGURE 13: UV-visible absorption spectra of AgNPs and Fe_3O_4–Ag hybrid nanoparticles (dispersed in hexane).

elongation at break compared to those of the blend without compatibilizer (up to 35% and 38% increases, resp.).

The antibacterial nanocomposites were successfully prepared from NR, PE, NR/PE blend, and nanoparticles (AgNP: 5–10 nm; FAgNP: 8 nm/16 nm). The antibacterial test against *E. coli* showed that the presence of FAgNPs in NR/PE blend had a better antibacterial activity than that obtained with the lone AgNPs. Two similar reasons were proposed: (i) the faster Ag^+ release rate from the Fe_3O_4–Ag hybrid nanoparticles due to the electron transfer from AgNP to Fe_3O_4 NP and (ii) the fact that the ionization of AgNPs in hybrid nanostructure might be accelerated by Fe^{3+} ions.

From these findings, the application of antibacterial nanocomposites based on Fe_3O_4–Ag hybrid nanoparticles and NR/PE blends appears to be very promising for clean water and food preservation, especially in highland and low-income areas.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.
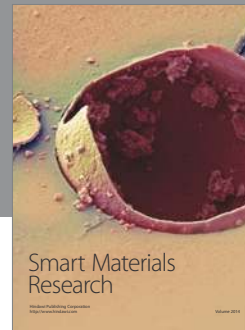
Acknowledgments

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