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Original Article

Facile Construction of Silver Decorated on Carbon Nanotube in Natural Rubber and Polyethylene Blend for Antibacterial Activity

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Abstract: The study described the preparation of composite material through the dispersion of carbon nanotubes (CNTs) decorated with silver nanoparticles (Ag NPs) in the matrix of blending natural rubber (NR) and polyethylene (PE) for use as an antibacterial agent. The FESEM results indicated the uniform and defect-free surface of the synthesized composites. The mechanical properties of synthesized composite improved with a 65% increase in tensile strength, a 38% increase in elongation, and a 40% increase in hardness compared to the original NR/PE blend materials. Although the addition of CNTs-Ag NPs did not considerably affect the thermal stability of the NR/PE blend, it prevented *E. coli* bacterial growth by 35%. This opens up new possibilities for using the composite in various applications, particularly in the field of public health and wellness.

Keywords: NR/PE blend, Natural Rubber, Carbon nanotubes, silver nanoparticles, *E. coli*.

1. Introduction

Natural rubber (NR), a versatile material known for its elasticity, strength, and durability, is a polymer derived from the sap of the rubber tree (Hevea brasiliensis). NR is widely used in various industries due to its excellent physical and mechanical properties, such as high resilience, good tensile strength, and tear resistance [1]. Applications of NR include tire production, molded goods, extruded products, calenderer products, adhesives, and latex-based products such as dipped products, foam products, and binding products [1]. However, one of the disadvantages of NR is that it is vulnerable to environmental factors such as heat, light, and ozone, which can cause it to deteriorate over time [1]. Additionally, NR is a finite resource, and its production is heavily dependent on the rubber tree, making it susceptible to fluctuations in supply and prices. Despite these drawbacks, natural rubber remains a popular and essential

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material in many industries, and research is ongoing to find ways to improve its properties and sustainability.

There are two major approaches to improving the properties of NR: chemical modification of its molecular structure and blending NR with other polymers as well as additives. The chemical modification involves changing the molecular structure of NR to enhance its properties, such as its resistance to environmental factors [1]. Blending NR with other polymers, such as polypropylene (PP) or polyethylene (PE), can overcome the limitations of NR and improve its performance [2, 3]. The combination of NR/PE, consisting of repeating units of CH_2 groups, overcomes the limitations of outdoor use of simple NR due to its high chemical inertness. Additionally, to attain the desired properties with regard to performance and cost-effectiveness, the use of additives is an effective solution. The additives used in polymer blends can be categorized into five groups: fillers, vulcanizing agents, anti-degradants, plasticizers, and others [3, 4]. Among those, Carbon nanotubes (CNTs) are a unique type of additive, as their properties have been widely discussed in various documents [5-8]. These nanotubes are known for reinforcing composites, including polymers, which enhance their physic mechanical properties [9-12]. However, the dispersion and alignment of CNTs can be challenging, as they tend to agglomerate into large particles during the introduction process, causing defects in the material [13, 14]. Many chemists have explored chemical functionalization to promote the alignment of CNTs in polymers [15-18]. Despite these challenges, ongoing research continues to search for ways to improve the properties of NR, making it a valuable and indispensable material in various industries.

On the other hand, there is a growing demand for materials with antibacterial properties in practical applications, and one of the most widely used protocols is the use of silver nanoparticles (Ag NPs). The ability to prevent bacterial growth, such as Gram-positive bacteria (*E. Coli*, *Bacillus subtilis*) and Gram-negative bacteria (*Salmonella typhimurium*), has been demonstrated by various papers [19, 20]. Currently, Ag NPs dispersed on CNTs (Ag NPs/CNTs) are gaining attention from researchers due to their superior antibacterial abilities compared to single Ag NPs [21-25].

Herein, we put our effort to disperse CNTs-Ag NPs within the matrix of NR/PE blend, with the goal of enhancing the mechanical properties such as tensile strength, elongation, and hardness. Moreover, the synthesized composites were also applied for their ability to prevent the growth of *E. coli* bacteria. This study has opened up new possibilities for the use of NR in various applications, including those in the public health and wellness field.

2. Experimental Section

2.1. Materials

Silver nitrate ($AgNO_3$), ammonia solution (NH_4OH), Glucose ($C_6H_{12}O_6$), Zinc oxide (ZnO), stearic acid (n-$C_{17}H_{35}COOH$), mercaptobenzothiazole ($C_7H_5NS_2$), and tetraethyl thiuram disulfide were purchased from Sigma-Aldrich. Carbon nanotubes (MWNTS - 4060, nanotube length: 5.103 - 15.103 nm, purification: 95% - 98%, surface area: 40 - 300 m^2/g) were purchased from Shenzhen Nanotech Prot Co.Ltd, China. High-density polyethylene (HDPE) with high crystallinity of 75-85%, melting temperature 130-150 ^oC, and density of 0.941- 0.965 g/cm^3 was purchased from IRPC Public Company Limited, Polimaxx Polene, Thailand. Natural rubber (RSS-1) with 80 Mooney viscosity was purchased from Haiphong Plastic and Rubber, Ltd., Vietnam. All the chemicals were used as received and without further processing.

2.2. Synthesis of CNTs-Ag

Firstly, CNTs were modified by using HNO_3 concentrate following the previous report. 5 g CNTs were mixed with 200 ml HNO_3 63% in 2 neck flasks and refluxed for

24 h. Then, the mixture was filtrated and washed with Deion water until pH = 7. The material was dried at 100 ºC for 4 h before being decorated by the Ag mirror. The Ag mirror was prepared via Tollens' reaction as follows 1 ml NH_3 0.4% was added dropwise into a two-neck flask containing 50 ml $AgNO_3$ 10^{-3} M and 15 ml anhydrous EtOH at room temperature. Then 0.5 g PVA was added and continuously stirred for 1 h at room temperature to make silver complex. Glucose (0.1 g) was added slowly, and the solution became yellow. The solution was mixed with 1 g of modified CNTs and transferred to an autoclave. This mixture was kept at 150 ºC for 24 h, and then the materials were filtrated and washed with Deion water until pH 7. The successful dispersion of Ag nanoparticles on the CNTs (CNTs-Ag) was evidenced by the FESEM and EDX (Figure S1).

2.3. Fabrication of NR/PE Blend Containing CNTs-Ag Composite

The NR/PE/CNTs-Ag blend composite (85/15/1) was created following a previous report. PE was placed in an internal mixer, followed by the addition of composite additives and antibacterial CNTs-Ag, which was mixed for 2 minutes to obtain a homogeneous mixture of PE/CNTs-Ag. NR was then added with the best ratio of NR: PE being 85:15 in volume and mixed for an additional 3 minutes. Finally, compatible and cured additives were added, and the mixture was mixed for 4 minutes (table S1). The mixture was then taken to a press and formed into the NR/PE/CNTs-Ag composite at 175 ℃ for 20 minutes.

2.4. Characterization

All mechanical properties- tensile strength, elongation, and module elasticity were measured by the ASTM D638 standard on Zwick Z.2.5 in Germany. The hardness of materials was measured on ASTM D2240 following the norm. The Differential scanning calorimetry (DSC) was performed on NETZSCH DSC 204F1. The thermal gravimetric analysis (TGA) is performed on NETZSCH TG209F1. Samples are heated from room temperature to 700 ºC with a 10 ºC/min heating speed in an inert atmosphere. The morphology of all models was observed by Field Emission Scanning Electron Microscope (FESEM), S4800, Hitachi, Japan.

2.5. Antibacterial Tests

The antibacterial properties were tested using the Beckman Coulter DU-730 in the USA. The cell density during culture was assessed by measuring the optical density (OD 600) of the *E. coli* cell culture. The OD600 value corresponds to the cell density or number of cells in each volume of *E. coli*. The test for bacterial growth was conducted following the ASTM E2149-10 procedure.

3. Results and Discussion

3.1. Characterization of Synthesized Composite

FESEM images were used to study the effect of morphology on the mechanical properties of synthesized composites. Figure 1 reveals a uniform and defect-free surface of the synthesized composites. Figure 1a demonstrates a strong connection between the NR and PE phases without any signs of phase separation. In contrast, Figures 1b and 1c provide the even dispersion of CNTs-Ag in the NR and PE phases, resulting in a material free of clumping. In addition, in Figure 1d, CNTs-Ag is regularly interwoven to create a composite network that enhances the properties of the composites by forming a tight bond.

The influence of CNTs-Ag NPs content on the material processing process was evaluated using the melting torque of three samples with the same CNTs and CNTs-Ag NPs content (1%) at 170 ℃, as shown in Figure 2. The melting characteristics of these samples were found to be the same according to the data recorded by the soft Haake Polylab. The torque initially increases rapidly to a maximum value when the mixing chamber is closed, then decreases slowly due to the formation of a stable material flow under the action of the two

screws. Upon heating and contact with the surface of the mixing chamber, the material starts to melt at the surface of the CNTs and CNTs-Ag NPs, causing the torque to decrease and reach a stable value gradually.

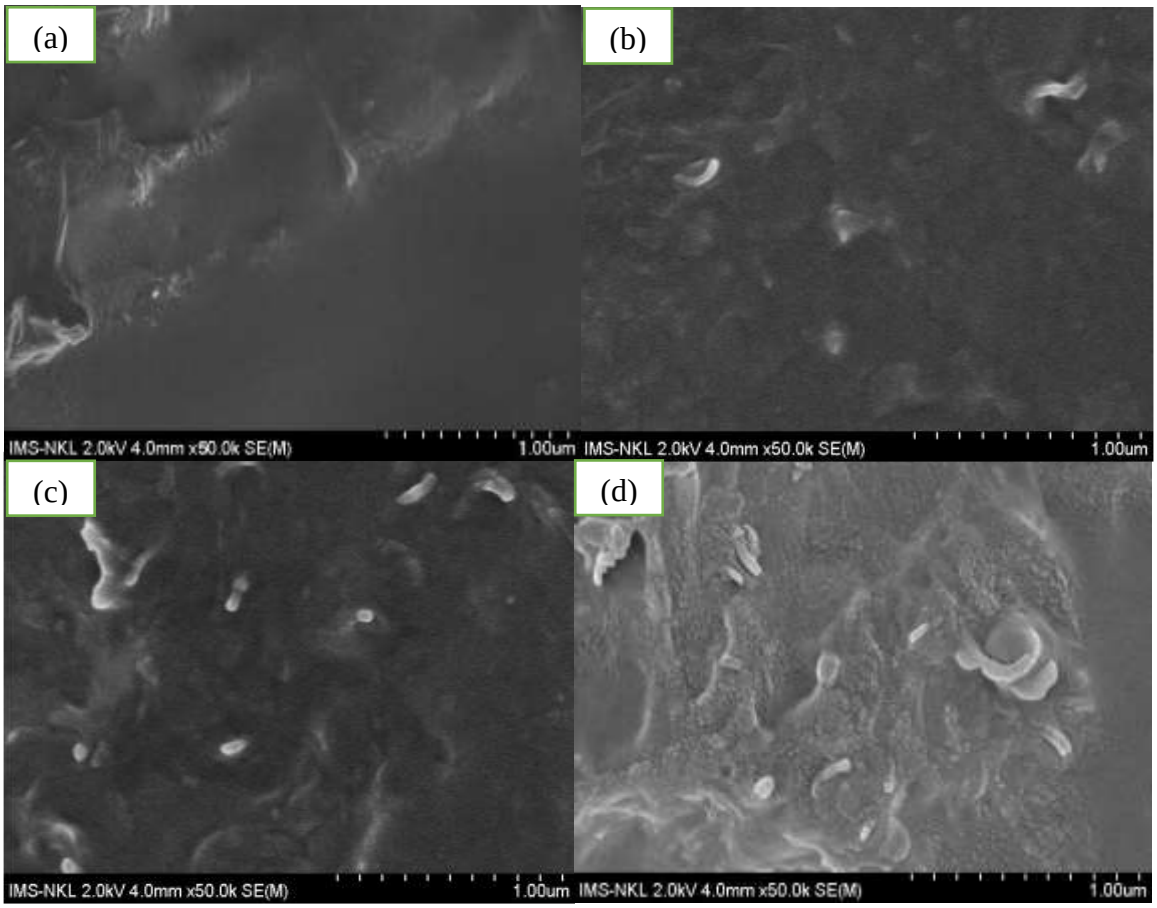

Figure 1. FESEM image of (a) NR/PE; (b) NR/CNTs-Ag; (c) PE/CNTs-Ag; (d) NR/PE/CNTs-Ag.

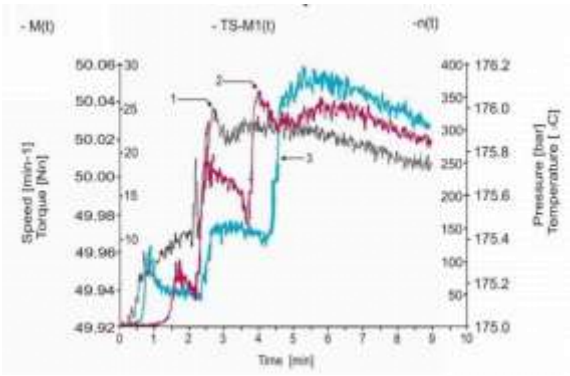

Figure 2. The melting torque diagram of (1) NR/PE, (2) NR/PE/CNTs, (3) NR/PE CNTs-Ag.

The melting process showed that the samples using functionalized CNTs (CNTs-Ag) had a stronger equilibrium torque than the simple samples. This confirms that functionalized CNTs serve as a linking agent to help the material system become homogeneous, reducing the material's torque.

Figure 3 depicts the interaction and linking of the mixed NR/PE after 3 minutes of mixing on the HAKKE. The maximum torque (Mmax) is 25 Nn, and the stable torque is 18 Nn. After 9 minutes, the process becomes steady. The interaction and linking of the NR/PE/CNTs after 4.5 minutes result in a new stable phase, with a maximum torque (Mmax) of 27 Nn and a stable torque of 22 Nn. The interaction and linking of the NR/PE/CNTs-Ag after 5.5 minutes also result in a new stable phase, with a maximum torque (Mmax) of 30 Nn and a stable torque of 26 Nn. The results show that the molecules in the NR/PE blend are the most fluctuating, with a less stable bonding. However, the introduction of CNTs and CNTs-Ag creates a tighter network, improving the material's properties.

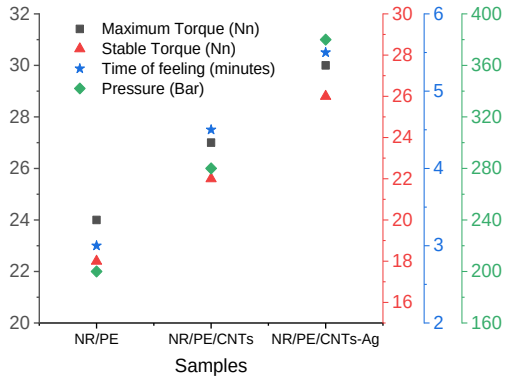

Figure 3. Physical properties of synthesized materials.

In Figure 4, the tensile strength of the NR/PE blends without adding CNTs was 9 ± 0.6 MPa. After the addition of 1% CNTs, the tensile strength increased to 14.2 ± 0.4 MPa, and with the addition of 1% CNTs-Ag, it further increased to 15 ± 0.7 MPa. These results demonstrate a significant increase in the tensile strength of the NR/PE blend material, with the addition of CNTs and CNTs-Ag resulting in a 56% and 65% increase, respectively. This data highlights the potential benefits of incorporating CNTs and CNTs-Ag into the NR/PE blend to enhance its mechanical properties.

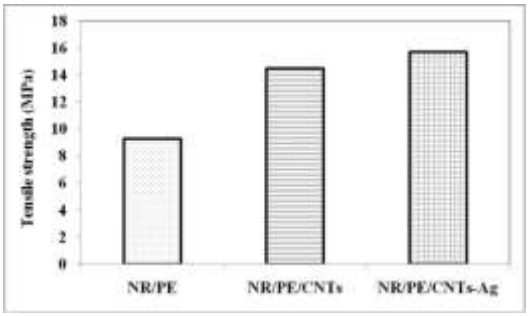

Figure 4. Tensile strength of synthesized materials.

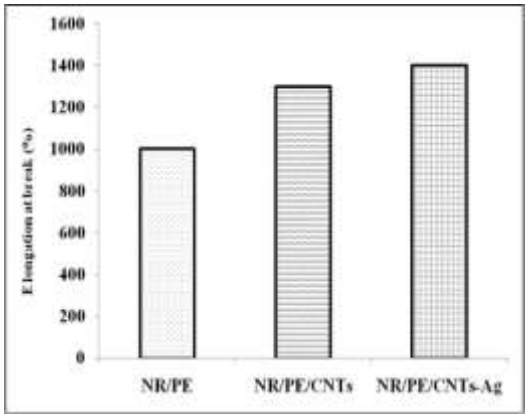

Figure 5. Elongation of synthesized materials.

Figure 5 shows that the NR/PE blend elongates 1000 ± 20%. After the addition of 1% CNTs, the elongation increased to 1320 ± 110%, and with the addition of 1% CNTs-Ag, it further increased to 1380 ± 50%. These results indicate that the presence of CNTs and CNTs-Ag in the NR/PE blend leads to an increase in elongation, with the addition of CNTs resulting in a 32% increase and the addition of CNTs-Ag resulting in a 38% increase. These results further confirmed the effect of incorporating CNTs and CNTs-Ag into the NR/PE blend to enhance its mechanical properties and overall performance.

Moreover, the hardness of these materials was also studied and displayed in Figure 6. According to Figure 6, the hardness of the NR/PE blend is measured at 100 ± 2 ShoreA. The addition of 1% CNTs results in a rise of hardness to 128 ± 50 ShoreA. Additionally, the inclusion of 1% CNTs-Ag leads to another increase in hardness to 138 ± 30 ShoreA. The integration of CNTs and CNTs-Ag composite materials results in a significant hardness improvement by 30% and 40%, respectively. These findings suggest that the dispersal of CNTs-Ag in the NR/PE blend matrix enhances the material properties, resulting in a 65% increase in tensile strength, 38% increase in elongation, and 40% increase in hardness due to improved ion bonding at the surface.

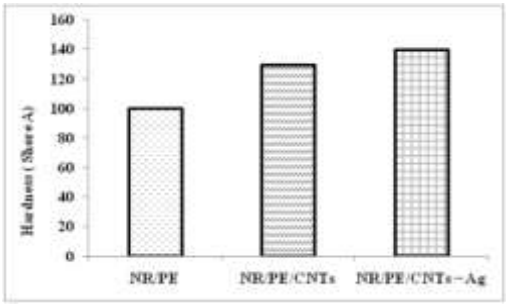

Figure 6. The hardness of synthesized materials.

The thermal stability of synthesized composites has also been studied by thermal gravimetric analysis (TGA) (figure S4, S5) and differential scanning calorimetry (DSC). The results presented in Figure 7 shows that the glass transition temperature (Tg) of the NR/PE blend increased to -56.4 °C (Figure S2), compared to the original Tg of PE (-100 °C) and NR (-70 °C). However, the Tg remained unchanged in the presence of CNTs-Ag Nps in the NR/PE blend matrix. In addition, the results of the study indicated that the melting temperature (Tm) of the NR/PE blend was between the Tm of PE and the Tm of NR. The presence of CNTs-Ag NPs did not cause any significant changes in the Tm of the NR/PE blend (Figure S3). These suggest that the addition of CNTs-Ag NPs did not significantly affect the thermal stability of the NR/PE blend and its melting behavior.

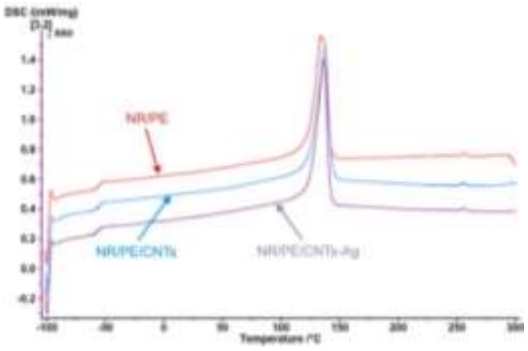

Figure 7. DSC curve of synthesized materials.

3.2. Antibacterial Growth Test

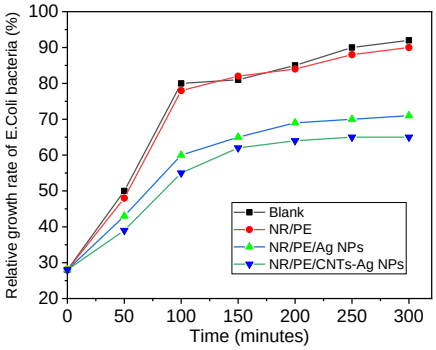

Figure 8. Influence of the synthesized composites on the growth rate of the E. coli bacteria.

The synthesized composites were used for their ability to inhibit the growth of *E. coli* bacteria at room temperature. The results shown in Figure 8 indicate that adding Ag nanoparticles and CNTs-Ag to the matrix of NR/PE composite materials affects the growth rate of *E. coli* bacteria. After 300 minutes, the samples containing NR/PE-Ag were found to inhibit 23% of bacterial growth, while the samples containing NR/PE/CNTs-Ag inhibited 35% of growth. The data suggest that the greater effective surface area and faster release of Ag from the CNTs-Ag nanoparticles contribute to their higher antibacterial activity level than the NR/PE-Ag composite. The high catalytic activity of CNTs-Ag and the large surface area between the bacterial cell

membrane and the hybrid nanoparticles may also inhibit bacterial growth.

4. Conclusion

In an effort to create safer household items for human health, CNTs-Ag were dispersed in the matrix of the NR/PE blend to evaluate its ability to prevent the growth of *E. Coli* bacteria. The resulting composite material displayed improved mechanical properties with a 65% increase in tensile strength, a 38% increase in elongation, and a 40% increase in hardness. Although the addition of CNTs-Ag NPs did not significantly affect the thermal stability of the NR/PE blend, it was found to reduce bacterial growth by 35%. The study suggests that the NR/PE/CNTs-Ag composite is suitable for long-term antibacterial applications due to its excellent mechanical properties and antibacterial effectiveness. This expands the scope of possible uses for the composite, notably in the area of public health and wellbeing.

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