SiO2 and ZnO Hybrid Nanofillers Modified Natural Rubber Latex: Excellent Tensile Properties and Antibacterial Properties

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Research Article

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SiO_2 and ZnO Hybrid Nanofillers Modified Natural Rubber Latex: Excellent Tensile Properties and Antibacterial Properties

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Abstract

The modification of polymer with nanoparticles has been proved to have good results, but the key of this method is that nanoparticles can maintain uniform dispersion in the polymer. Herein, silica (SiO_2) and zinc oxide (ZnO) hybrid nanofillers were prepared by self-made dispersion equipment to modify natural rubber latex (NRL). The results show that the uniformly dispersed nano-SiO_2 fillers increase the number of entanglements in the molecular chain of NRL, thereby improving the tensile properties. The tensile strength and elongation at break of LZ1S4.2 were increased to 32.61 MPa and 957%, respectively. The increase of the number of entanglements also makes the structure of NRL more compact, and improves the barrier performance and aging resistance. The uniformly dispersed nano-ZnO fillers endow the NRL with excellent antibacterial properties, and the antibacterial rate (For *Escherichia coli* and *Staphylococcus aureus*) is greater than 99.9%. In addition, NRL condoms and gloves incorporating hybrid nanofillers have been proved to have good biocompatibility, and this NRL nanocomposite is expected to be applied to other NRL products.

Keywords Nature rubber latex · Nanoparticles · Tensile properties · Antibacterial

1 Introduction

Natural rubber (NR) is one of the most important biosynthetic elastomers and is used in various fields due to its excellent comprehensive properties [1, 2]. NRL is an aqueous emulsion dispersion of rubber particles in a near-neutral medium. NRL has been widely used in healthcare industry and daily life because of its good elasticity, anti-viral permeability, flexibility, formability, and good human compatibility [3-5]. NRL gloves and condoms are two of its most common products. However, NRL products also face serious problems such as low tensile strength, poor tear resistance, and easy aging, which limit the use of natural latex to a certain extent [6]. In addition, NRL products are also easy to attract bacteria in the environment and cause a large number of bacteria to multiply. The reproduction of a large number of bacteria on the products can not only cause an unpleasant odor, which has a negative impact on human health, but also lead to the degradation of natural rubber latex. This shortcoming is a serious problem that needs to be solved urgently, especially in the application of health care [7]. The continuous development of nanoscience and technology provides an effective way to solve the above problems. Previous studies have shown that nanoparticles can not only enhance the existing properties of polymers, but also endow polymers with new properties, including optical properties [8], electrical properties [9, 10], mechanical properties [11, 12], thermal properties [13], antibacterial properties [14] and other properties.

SiO_2 is an indispensable reinforcing filler in the rubber industry and is widely used to enhance the physical and mechanical properties of vulcanized rubber [15-17]. Conventional silica fillers need to be added in a relatively large amount to achieve the required reinforcing effect. However, studies have shown that when the particle size of SiO_2 particles reaches the nanometer level, the unique nanometer size effect of nanoparticles can not only greatly reduce the content of fillers, but also achieve better reinforcement effects. ZnO is an n-type semiconductor material with many functional properties, such as catalytic properties, electrical properties, optical properties, broad UV absorption, high photostability, thermal stability, and biocompatibility, etc. [18].

ZnO is generally used as a curing activator in the rubber industry [19]. When the size of ZnO reaches the nanoscale, nano-ZnO has photocatalytic antibacterial effect due to the nano-size effect [20]. Therefore, the antibacterial properties of nano-ZnO are the particularly outstanding properties among these functional properties [21, 22].

Despite the outstanding modification effect of nano-scale silica, the agglomeration of nanoparticles and the problem of dispersibility in the polymer matrix are still serious problems [23-25]. Seangyen et al. [26] modified SiO_2 with ammonium laurate surfactant and then mixed it with NRL to prepare a NRL nanocomposite. The test results showed that after adding ammonium laurate surfactant, the silica nanoparticles were not easy to agglomerate, the dispersion in the rubber matrix was improved, and the tensile properties were also improved. Rathnayake et al. [27] found that the NRL incorporating nano-ZnO had superior antibacterial properties compared to the NRL without nano-ZnO. Similarly, the key for nano-ZnO to play its role is that it can be uniformly dispersed in the polymer matrix without agglomeration [28]. Therefore, the surface modification of nano zinc oxide has a great influence. Krainoi et al. [29] prepared a series of nanocomposites by incorporating modified and unmodified nano-zinc oxide into natural rubber by emulsion blending method. The test results showed that the modified nanocomposites Zinc oxide can impart antibacterial properties to natural rubber, but the unmodified nano-oxidative properties not only fail to exert its functional properties, but also have a negative impact on the inherent properties of natural rubber.

Different nanoparticles have their main functional properties. At present, there are many studies on the modification of polymer matrices filled with a single nanoparticle. At the same time, there are also a small number of literatures showing that the synergistic modification of two nanoparticles can produce unexpected effects [30, 31]. Herein, in order to combine the outstanding functional properties of nano-SiO_2 and nano-ZnO, the high-speed and high-pressure nano-disperser invented by our group was used to process these two nanoparticles, and finally a composite nano-dispersion that can be uniformly dispersed without agglomeration was obtained. Due to the nanometer size of the fillers and its good dispersibility, the nano-SiO_2 in the hybrid nanofiller not only improved the mechanical properties of the NRL, but also improved the aging resistance and barrier properties to a certain extent, while the nano-ZnO endowed the NRL with excellent antibacterial properties. In addition, the NRL condoms and gloves incorporating hybrid nanofillers still had good biocompatibility, so this nanocomposite was expected to be applied to other natural latex products.

2 Materials and Methods

2.1 Materials

SiO_2, analytical pure, was purchased from Xilong Chemical Co., Ltd. (Guangzhou, China). ZnO, analytical pure, average size about 50 nm, was purchased from Xilong Chemical Co., Ltd. (Guangzhou, China). Polycarboxylate sodium salt dispersant 5040, was purchased from Nantong Yongle Chemical Co., Ltd. (Nantong, China). Nature rubber latex, the solid content is 60wt%, was purchased from Thai Rubber Group Co., Ltd. (Thailand). Casein, analytical pure, was purchased from Tianjin Dingshengxin Chemical Co., Ltd. KOH, analytical pure, was purchased from Xilong Chemical Co., Ltd. (Guangzhou, China). Sulfur was purchased from Guangzhou Xintian Chemical Materials Co., Ltd. Accelerator PX was purchased from Shijiazhuang Tuochuang Chemical Products Sales Co., Ltd. Antioxidant 264 was purchased from Guangdong Shunde Lanya Co., Ltd.

2.2 Preparation of Nanocomposites and Products

The composite nano-dispersion was prepared by mixing ZnO and SiO_2. The specific preparation method is as follows: The polycarboxylate sodium salt dispersant 5040 was dissolved in deionized water, then ZnO powder was slowly added under magnetic stirring at 50°C. The mass ratio of ZnO powder to dispersant is 2:1. The mixed liquid was then put into an emulsifying machine for 50 minutes at a speed of 2000 rad/min and sonicated for 30 minutes. Finally, the mixed liquid is dispersed with a high-speed and high-pressure nano-dispersing machine to form a ZnO nano-dispersion liquid. The high-speed and high-pressure nano-disperser used is an invention patent of our group [32]. Then, SiO_2 powder was added to the ZnO nano-dispersion liquid, and the above steps were performed again to finally obtain a uniformly dispersed and stable composite nano-dispersion liquid.

The particle size distribution and average size of the particles in the ZnO and SiO_2 dispersions which were prepared by the above equipment were analyzed by a nanoparticle analyzer (SZ-100Z, HORIBA, Japan), respectively, as shown in Fig. 1. The average particle size of the ZnO nanoparticles is about 78 nm, and the D90 (the particle size at which the cumulative particle size distribution reaches 90%) is 100 nm. The average particle size of SiO_2 nanoparticles is about 65nm, and the D90 is 95nm. These results show that the nanoparticles treated with the above-mentioned equipment are stably and uniformly dispersed in the aqueous solution, and there is no large agglomerate, which is also the premise of its function.

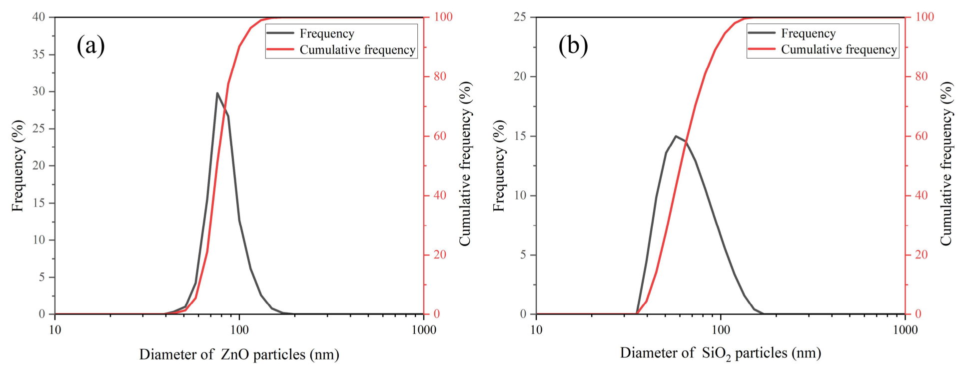

Fig. 1 Size distribution diagram of (a) ZnO particles and (b) SiO_2 particles

All preparation procedures were strictly in accordance with the production steps of industrial products. The formula of the compounding agent is shown in Table 1, and its preparation method is as follows: KOH and casein were completely dissolved in deionized water, respectively. Then the prepared casein, KOH, sulfur, accelerator PX and anti-aging agent 264 were added to natural latex (The solid content is 60wt%), stirring was continued until it was completely dissolved, and finally an appropriate amount of distilled water was added to make the emulsion viscosity suitable.

The natural rubber latex, the composite nano-dispersion and the compounding agent were mixed evenly, and the glove and condom samples were prepared by the dipping method. The specific process was as follows: Firstly, the cleaned and dried molds (glove glass mold and condom glass mold) were dipped for 5 s, then dried at 85 °C for 20 min, and then leached in water at 75 °C for 30 seconds after drying. Next, hemming was performed, followed by drying at 120°C for 40 minutes. After demolding, they were put into a drum dryer and vulcanized at 120°C for 20 minutes. Finally, experimental samples of gloves and condoms were obtained, which were used in different tests.

Table 1 Formula of the compounding agent

Raw materials	content (phr)
NRL	166.67
Casein	0.017
KOH	0.021
sulfur	0.667
Accelerator	0.667
antioxidant	0.667

All samples were coded. Zx in the code L-ZxSy represents the mass fraction of oxidative nanoparticles, and Sy represents the mass fraction of silica nanoparticles, as shown in Table 2, that is, each component is expressed in different proportions quality.

Table 2 Component content corresponding to each code

Sample code	Nature rubber latex (phr)	ZnO (phr)	SiO_2 (phr)
LZ0S0	100	0	0
LZ1S0	100	1	0
LZ1S3	100	1	3
LZ1S3.4	100	1	3.4
LZ1S3.8	100	1	3.8
LZ1S4.2	100	1	4.2
LZ1S4.6	100	1	4.6
LZ1.5S4.2	100	1.5	4.2

2.3 Tensile Properties

The tensile properties of the specimens were measured at room temperature using a universal precision tensile machine (Universal WD-E type, Guangzhou Guangcai Experimental Instrument Co., Ltd.). The sample is annular, and the test speed is 500mm/min, according to the Chinese National Standard GB/T528-2009 *Determination of Tensile Stress-Strain Properties of Vulcanized Rubber or Thermoplastic Rubber*. At least five tests were performed for each sample with different filler content to calculate the average value. Then a batch of samples were prepared and aged at 70°C for 168h in an aging test chamber (401A, Qidong Shuangleng Testing Equipment Factory). Other conditions were carried out in accordance with the Chinese National Standard GB/T 3512-2014 *Vulcanized Rubber or Thermoplastic Rubber Hot Air Accelerated Aging and Heat Resistance Test Standard*. The tensile properties were tested after aging to study the effect of composite fillers on the aging resistance of NRL. The condom samples prepared by LZ1S4.2 were used for the blasting performance test, which was determined according to the ISO 4074:2014 *Nature rubber latex male condoms-Requirements and test methods standard*.

2.4 Scanning Electron Microscope (SEM)

The morphologies of the different samples were investigated with Merlin scanning electron microscopy (Zeiss). The samples were cryogenically fractured in liquid nitrogen. And for easy viewing, all surfaces of the samples were sputter-coated with gold prior to scanning. The fractured samples were observed on a scanning electron microscope instrument using an accelerating voltage of 20 kV to obtain microscopic morphologies of different samples.

2.5 Antibacterial Tests

The Guangdong Provincial Microbiological Testing Center of China was commissioned to test the antibacterial properties of the NRL gloves and condoms prepared in this study. *Escherichia coli* (ATCC 8739) and *Staphylococcus aureus* (ATCC 6538P) [33] were selected as the strains for this test, according to the current Chinese national standard GB/T 21866-2008 *Antibacterial coating* (*paint film*) *antibacterial activity determination method and antibacterial effect test*. Before testing,

$5 \times 5 \times 4$ mm³ templates were cut from gloves and condoms. Prepare at least 3 pieces of each antibacterial sample, and at least 6 pieces of blank samples (3 blank samples are used to detect the number of viable bacteria immediately after inoculation, and the other 3 blank samples are used to detect the number of viable bacteria 24 hours after inoculation). For testing, a sterile loop of bacteria (pre-cultured) was transferred to a small amount of nutrient broth (obtained by dissolving 3 g beef extract, 10 g peptone and 5 g sodium chloride in 1 L deionized water, and then diluting 500 times the volume), the bacterial concentration was maintained between 2.5 × 105 CFU/ml ~ 10 × 105 CFU/ml. In a sterile petri dish, 0.4 ml of inoculum was dropped on the surface of each sample and then the inoculum was covered with a 40×40 mm^2 film. The film was then pressed down so that the bacterial solution was spread evenly under the entire film. After inoculation, it was incubated at 35°C for 24 hours. All samples were recovered immediately after: 10 ml of SCDLP broth(4.2.3.6, It is composed by 17 g casein peptone, 3 g soy peptone, 5 g sodium chloride, 2.5 g disodium hydrogen phosphate, 2.5 g glucose, 1 g lecithin, and 1 L deionized water.) was added to the petri dish, then the samples were rinsed thoroughly and colonies were counted.

After inoculation on the template, the number of bacteria produced immediately per square centimeter of the blank template is denoted by U0. The number of bacteria per square centimeter in the blank template and antibacterial sample plate after culturing for 24 h was denoted by Ut and At, respectively. The formula for calculating the antibacterial activity value (R) and the antibacterial rate is as follows:

$$R = (\lg Ut - \lg U0) - (\lg At - \lg U0) = \lg Ut - \lg At \quad (1)$$

$$\text{The antibacterial rate} = \frac{(Ut - At)}{Ut} \times 100\% \quad (2)$$

2.6 Skin Irritation Tests

According to the different uses and parts of NRL gloves and condoms, a skin allergy test and a vaginal irritation test were performed on condoms, and a skin irritation and sensitization test, one broken skin irritation test, and an intact skin irritation test were performed on gloves. All test methods were tested with reference to the Chinese National Standard GB 15979-2002 *Hygiene Standard for Disposable Sanitary Products*.

3 Results and Discussion

3.1 Tensile Properties

In order to combine the functional properties of nano-SiO_2 and nano-ZnO, the two nanoparticles were prepared into a composite dispersion and blended with NRL to prepare a series of nanocomposites with different contents. As shown in Fig. 2, the tensile strength and elongation at break of LZ0S0 and LZ1S0 were almost the same. This shows that 1 phr of ZnO particles have little effect on the tensile properties. Firstly, the tensile strength of NRL nanocomposites increased with the increase of nano-SiO_2 content, indicating that the addition of rigid silica particles can improve the rigidity of natural latex. Besides, before the content of nano-SiO_2 reached 4.2 phr, the elongation at break of NRL nanocomposites increased as a whole with the increase of nano-SiO_2 content. This is because the 4.2 phr nano-SiO_2 particles can be uniformly dispersed in the NRL, and less agglomerates are formed, which will be confirmed in the SEM images in later chapters. But when its content reached 4.6 phr, the elongation at break of the NRL nanocomposites suddenly decreased, this is because many larger agglomerates can be formed easily when the contents of SiO_2 were 4.6 phr, which form serious defects in the matrix, resulting in a decrease in elongation at break. This is similar to the result obtained by Xu et al. [34]. Considering the changes of tensile strength and elongation at break, LZ1S4.2 has the best tensile properties, and its tensile strength and elongation at break are increased to 32.61MPa and 957%, respectively.

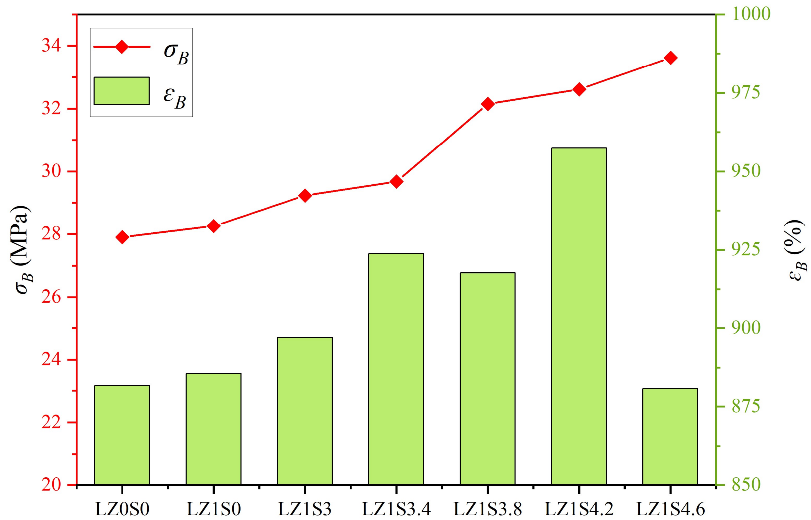

Fig. 2 Diagram of tensile strength and elongation at break of NRL nanocomposites

As can be seen from the previous article, LZ1S4.2 has the best tensile properties. For practical applications, it is most meaningful to study the effect of the optimal content on the performance of the product. Therefore, Fig. 3(a) and Fig. 3(b) showed the changes in tensile strength and elongation at break of LZ0S0 and LZ1S4.2 before and after aging, respectively. Fig. 3(a) showed that the tensile strengths of LZ0S0 were 27.16 MPa and 16.40 MPa before and after aging, and the properties decreased by about 40%. However, the tensile strengths of LZ1S4.2 before and after aging were 29.70MPa and 20.63MPa, respectively, and the performance was only reduced by 30%. Fig. 3(b) showed the elongation at break of LZ0S and LZ1S4.2 before and after aging, both of which showed a decrease in performance of about 12%. The experimental results show that the incorporation of nano-SiO_2 can increase the aging resistance of NRL to a certain extent, especially for the tensile strength. Of course, the improvement in aging resistance is attributed to the good dispersion of SiO_2.

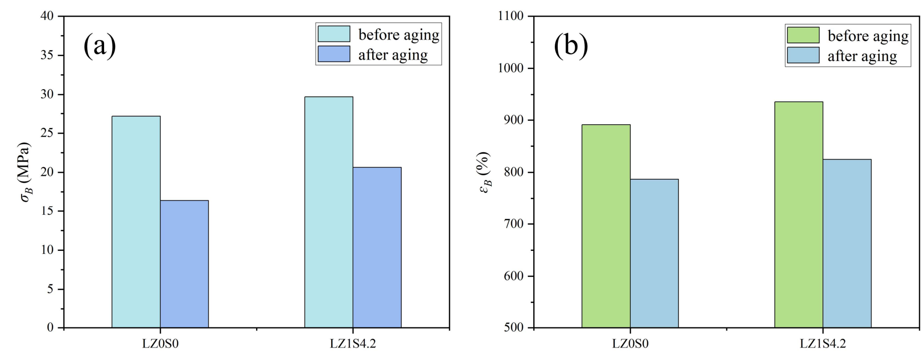

Fig. 3 Diagram of (a) tensile strength and (b)elongation at break before and after aging of LZ0S0 and LZ1S4.2

A key test that NRL gloves and condoms need to pass before they are officially put into use is the blasting performance test. Especially for condoms, condoms with poor blasting performance are very easy to be damaged, resulting in contraceptive failure. Therefore, good blasting performance is the key to the function of condoms. In the previous tensile test, we obtained the best addition content of nano-SiO_2 and nano-ZnO. However, whether it will affect the bursting performance of condoms is also an aspect that needs to be studied. Therefore, in this paper, we chose the condoms prepared with LZ1S4.2 and the qualified conventional condoms on the market to test the blasting performance. It could be found from Fig. 4 that the condoms prepared in this study had higher blasting pressure and blasting capacity than conventional condoms, which indicates that this condom has better mechanical properties. This is a great help in preventing condoms from breaking. The increase in blasting pressure and blasting capacity is due to the improvement in tensile properties. In addition, under the same volume change, the pressure changes of the condom prepared with LZ1S4.2 were smaller than that of the conventional condom, which indicated that the condom was softer after adding nanoparticles. And this was expected to improve the user experience.

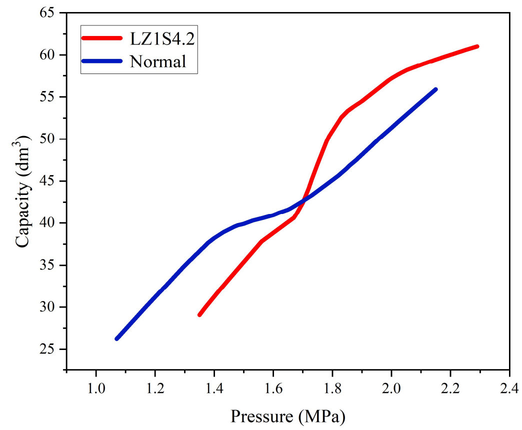

Fig. 4 Diagram of blasting properties of NRL condom with nano-fillers and normal NRL condom

Molecular chains of NRL are easily entangled at the interface between the polymer matrix and nano-SiO_2 [23]. Therefore, For the enhancing mechanism of NRL matrix by nanoparticles, the effect of nano-silica on the entanglement between molecular chains of NRL is given priority. To better illustrate the enhancement mechanism, Fig. 5 was drawn based on the microstructure observed in the SEM images. Fig. 5(a) shows that the molecular chains of pure NRL are entangled with each other. The number of entanglements in pure NRL is relatively small, and the number of molecular chains entangled in different regions is different. The regions with more entangled molecular chains have better mechanical strength, so during the stretching process, the regions with less entangled molecular chains are easily pulled apart. However, as shown in Fig. 5(b), after adding nano-SiO_2, the nanoparticles uniformly dispersed in the NRL act as physical cross-linking points. The molecular chains are more uniformly distributed throughout the polymer matrix, resulting in a more uniform number of entangled molecular chains in each region. Therefore, the NRL nanocomposites have fewer weak points and better tensile properties under external forces. Besides, as the content of nanoparticles increases, the number of entanglements of molecular chains increases, and the tensile strength and elongation at break of NRL also increase. However, when the content of nano-silica reaches a certain value, the excess nanoparticles are very easy to agglomerate together. Such agglomerates not only fail to function as nanoparticles, but also form severe defects in the polymer matrix, leading to a decrease in elongation at break.

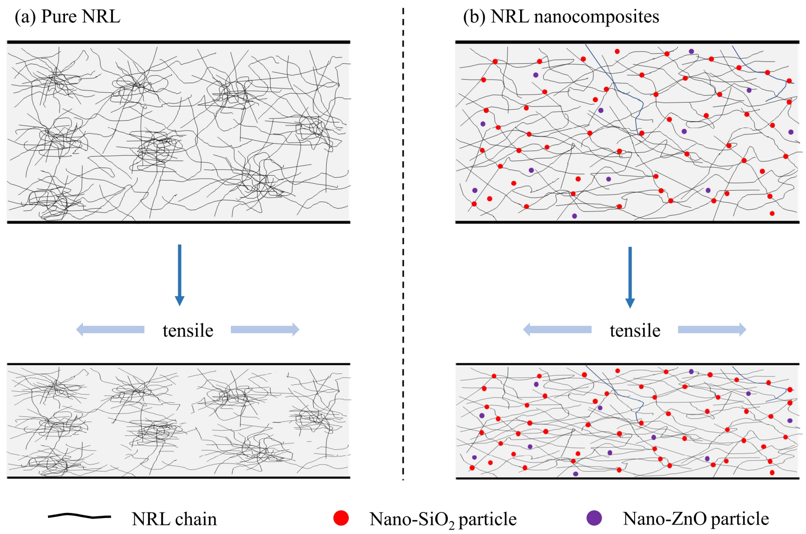

Fig. 5 Schematic diagram of nanoparticles enhancement mechanism

3.2 Scanning Electron Microscope

The properties of polymers largely depend on the microstructure, so scanning electron microscopy was used to study the microscopic morphology of NRL and its nanocomposites. The incorporation ratio of hybrid nanofillers with optimal tensile properties was obtained before, so LZ1S4.2 and LZ0S0 were selected for comparison. Fig. 6(a) and Fig. 6(c) were the SEM images of LZ1S4.2 and LZ0S0, respectively (Fig. 6(b) and Fig. 6(d) are their 10x magnifications, respectively). From Fig. 6(b), it could be found that although two kinds of nanoparticles were added, it was difficult to see the precipitated nanoparticles from the SEM images. This showed that these treated nano-SiO_2 and nano-ZnO had good compatibility with NRL and could be dispersed uniformly in NRL. This was consistent with the results obtained for tensile properties and was also a guarantee of subsequent antimicrobial properties.

In addition, another important information obtained from SEM images was that the barrier properties of natural latex were also enhanced after the incorporation of hybrid nanofillers. Comparing Fig. 6(a) and Fig. 6(c), it could be found that the number and spacing of pores in the NRL were significantly reduced after the incorporation of nanofillers. And the contrast was more obvious in Fig. 6(b) and Fig. 6(d). After statistical analysis of the pore spacing, it was found that the average pore spacing of LZ0S0 was about 92.88 nm, while that of LZ1S4.2 was about 69.15 nm, and the average pore spacing was reduced by about 26%. The reduction in the number of pores and in pore spacing indicated that the barrier properties of the NRL were improved. The improvement of barrier properties can improve the safety of natural rubber latex products during use. As mentioned above, nano-SiO_2 acts as a physical cross-linking point to increase the number of entanglements in the molecular chains of NRL. The improvement of barrier properties is also mainly due to the increased number of entanglements and tighter entanglements of molecular chains, resulting in a denser structure of NRL. Thus, the enhanced barrier properties have great application potential in products.

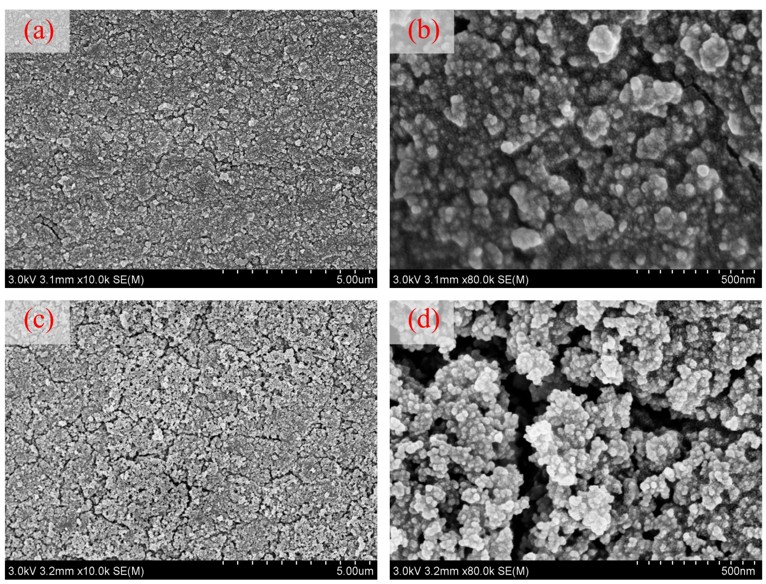

Fig. 6 SEM images of (a)-(b) LZ1S4.2 and (c)-(d) LZ0S0

3.3 Antibacterial Properties

The LZ1S4.2 was made into gloves and condoms for antibacterial performance test, in which nano-zinc oxide is the main component that imparts antibacterial properties to NRL. This is because the band gap energy of ZnO nanoparticles is low, and electrons can easily migrate to different positions on the surface of ZnO nanoparticles under UV light irradiation, thereby forming electron-hole pairs [35]. The holes (h+) generated on the surface of nano- ZnO generate reactive oxygen species (ROS) with water or oxygen in the air, such as hydroxyl radical hydroxyl (-OH), peroxide and other oxidizing substances. And these oxidizing species will be adsorbed on the surface of nanoparticles [36]. Some researchers have found that the main antibacterial mechanism of nano-ZnO particles is the interaction between the generated ROS and cells [37, 38]. In addition, some studies have found that the antibacterial activity does not need to be activated by specific ultraviolet rays, but can be activated by ambient light conditions [39]. This is also a premise that nanoparticles can be added to the polymer matrix to produce antibacterial properties.

During the study, the content of nano-ZnO was found to have a serious impact on the molding process, as shown in Fig. 7(a). In the subsequent molding process of LZ1.5S4.2, discoloration of the finger pads occurred because ZnO had a promoting effect on the vulcanization of natural rubber [40]. The addition of 1.5 phr of nano-zinc oxide resulted in over-vulcanization. However, normal NRL gloves were obtained after adjusting to 1 phr nano-zinc oxide, as shown in Fig. 7(b), which is the reason why only 1 phr nano-zinc oxide was added. Two strains of *Escherichia coli* (ATCC8739) and *Staphylococcus aureus* (ATCC6538P) were mainly detected. The samples to be tested removed from NRL gloves and condoms were carried out in accordance with national standards. Table 3 showed the detailed antimicrobial performance results for NRL gloves and condoms.

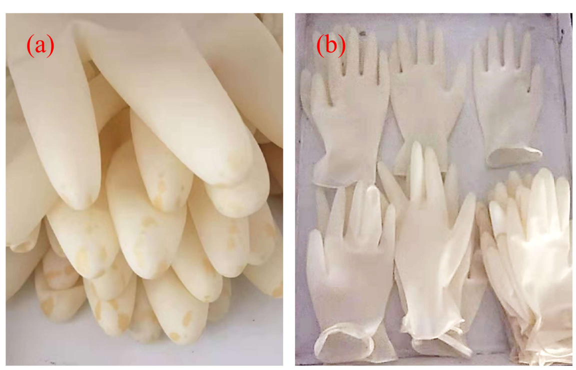

Fig. 7 NRL gloves containing (a) 1.5 phr nano-ZnO and (b) 1 phr nano-ZnO

A higher value of antibacterial activity (*R*) indicates better antibacterial performance, and a value of R greater than 2 indicates passing the antibacterial test. It could be found from Table 3 that the numbers of *Escherichia coli* and *Staphylococcus aureus* both increased by more than 10 times after 24h. From the test results of antibacterial performance, after culturing for 24 hours, there were almost no bacteria on the samples added with nano-ZnO, and the antibacterial rate was more than 99.9%. And the antibacterial activity values (*R*) were all greater than 4.9, exceeding the passing standard of the antibacterial test. It shows that the NRL is endowed with excellent antibacterial properties by 1 phr nano-ZnO fillers. The key to the effect of nano-ZnO is that it can be uniformly dispersed in the polymer matrix and does not agglomerate [28]. Therefore, the excellent antibacterial performance also proves that the ZnO nanoparticles can maintain the nanoscale size and uniformly disperse in the NRL, thereby exerting its unique nanometer effect.

Table 3 Antibacterial test results of NRL gloves and condom

Microorganisms tested	Sample	U0(cfu/cm^2)	Ut(cfu/cm^2)	At(cfu/cm^2)	*R*	Antibacterial rate (%)
Escherichia coli	Gloves	2.1×10^4	2.9×10^5	<0.6	>5.3	>99.9
	Condom	2.0×10^4	3.8×10^5	<0.62	>5.8	>99.9
Staphylococcus aureus	Gloves	2.1×10^4	2.3×10^5	<0.6	>5.2	>99.9
	Condom	2.5×10^4	2.9×10^5	<0.62	>4.9	>99.9

3.4 Skin Irritation Properties

The incorporation of ZnO nanoparticles endowed the NRL with excellent antibacterial properties, at the same time the incorporation of SiO_2 nanoparticles enhanced the tensile properties of the NRL. However, NRL gloves and condoms, as two products that can come into direct contact with human skin, need to have sufficient biocompatibility for their practical application. Therefore, it is necessary to pass the skin irritation performance test to ensure that it will not cause harm to the human body.

Table 4 was the results of the skin irritation test. For different applications of condoms and gloves in real life, skin allergy tests and vaginal irritation tests were performed on condoms, while skin irritation and sensitization tests, one broken skin irritation test and multiple intact skin irritation tests were performed on gloves. As shown in Table 4, this condom with excellent antibacterial properties did not produce skin allergies and did not irritate the vagina. In addition, the gloves were only slightly irritating in the skin irritation and sensitization tests, and did not produce irritating reactions in one broken skin irritation test and multiple intact skin irritation tests. The gloves and condoms prepared with LZ1S4.2 passed the corresponding skin irritation test, indicating that they have good biocompatibility. Therefore, these products are expected to be used safely in daily life and will not cause harm to the human body.

Table 4 Skin irritation test results of NRL gloves and condom

Project	Sample	Animals	Results
Skin allergy test	Condom	guinea pig	No allergy
Vaginal irritation test	Condom	New Zealand rabbit	No irritation response
Skin irritation and sensitization test	Gloves	New Zealand rabbit	Very slight irritation
One broken skin irritation test	Gloves	New Zealand rabbit	No irritation response
Multiple complete skin irritation tests	Gloves	New Zealand rabbit	No irritation response

4 Conclusions

In this paper, NRL/ZnO/SiO_2 nanocomposites with good mechanical properties and antibacterial properties were successfully prepared and applied in products. Thanks to the high-speed and high-pressure nano-dispersing machine, the ZnO and SiO_2 nanoparticles had obtained sufficient surface modification of the dispersant, so that the composite filler was uniformly dispersed in the NRL without agglomeration. The results showed that LZ1S4.2 has the best comprehensive performance. On the one hand, nano-silica acts as a physical cross-linking point, which increases the number of entanglements in the molecular chains of NRL. These increased numbers of entanglements not only improved the tensile properties, resulting in increased tensile strength and elongation at break to 32.61 MPa and 957%, respectively, but also made the structure of the NRL more compact, improving the barrier properties and aging resistance. However, excessive SiO_2 nanoparticles are prone to agglomeration, and the agglomerates will form serious defects in the polymer matrix, resulting in a sudden decrease in elongation at break. On the other hand, nano-ZnO endows the natural latex with excellent antibacterial properties. The antibacterial rates for Escherichia coli and Staphylococcus aureus were both greater than 99.9% and the antibacterial activities were both greater than 4.9. In addition, the irritation and sensitization to the skin of the NRL gloves and condoms prepared with LZ1S4.2 were all within the acceptable range, indicating good biocompatibility. And the blasting performance of this condom was better than that of ordinary condoms. The prepared NRL nanocomposites have been proven to be applied to gloves and condoms, and are also expected to be applied to other NRL products. In addition, this paper can also provide a reference for the research of hybrid fillers-modified polymers.

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Compliance with Ethical Standards

Conflict of interest There is no conflict of interest regarding the publication of this paper.

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