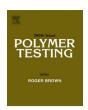
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Material performance

Synthesis and characterization of nano silver based natural rubber latex foam for imparting antibacterial and anti-fungal properties

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ABSTRACT

Synthesis and characterization of nanosilver based antimicrobial natural rubber latex foam (NRLF) is described. Silver nanoparticles were synthesized by reducing silver nitrate by trisodium citrate in an aqueous medium. UV–Vis spectrophotometer analysis, particle size analysis and transmission electron image analysis proved that the resultant silver nanocolloid was an aqueous dispersion consisting of stable nanometer size silver particles. Antibacterial activities were tested against Gram-positive Staphylococcus aureus and Gramnegative Escherichia coli (E. coli) bacteria, whereas antifungal activities were tested against Aspergilles niger (A. niger). It was found that the resultant NRLF samples inhibit the growth of the these bacteria and fungus in a very strong manner.

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1. Introduction

Metallic silver and silver based compounds have been investigated by several researchers as an antibacterial and antifungal agent over several decades [1–5]. In recent years, development of consumer goods using nano-sized silver and its derivatives has attracted great attention due to the strong antimicrobial activities compared to bulk silver materials. Antimicrobial activities of silver nanoparticles against different kinds of microorganisms have been reported by several researchers [1,2,5-8]. Silver nanoparticles against different kinds of fungus have been reported by a lesser number of researchers. Kim et al. [9] reported the antifungal activities and the mode of action of silver nanoparticles against the fungus Candida albicans. They have suggested that silver nanoparticles could disrupt the structure of the cell membarane of the fungi and cause inhibition of its budding process, hence nano sized silver has a significant antifungal activity against Candida albicans. Panacek et al. [10] reported the antifungal activity of silver nanoparticles on the same fungus species. Furthermore, they have found that the minimum inhibitory concentration (MIC) of nano sized silver was lower than the cytotoxicity level of tested human cells. It was reported that silver nanoparticles could inhibit fungi in low concentrations and those levels did not have any toxic effect on human cells.

Mirzajani and co-workers [11] recently investigated the possible mechanism of inhibition of Gram-positive S.aureus by silver nanoparticles. They concluded that the bactericidal effect of SNP on Gram-positive bacteria mainly came from the destruction of cell membrane by pit formation. They also reported that SNP inhibits Gram-positive bacteria more than that of Gram-negative bacteria due to a thick peptidoglycan (PGN) layer in the bacteria cell wall. Morones et al. [2] have reported the possibility of killing Gram-negative bacteria by SNP. In their studies they suggested three main killing mechanisms. The first mechanism is SNP attached to the cell membrane and disturbing the permeability of the cell wall, respiration and the proper functions of the cell wall. The second mechanism they proposed was SNP penetrating through the cell wall and damaging the DNA of the bacteria. The third mechanism

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was silver ions released by SNP interacting with thiol groups in protein and inactivating the bacteria protein, as reported by Feng et al. [12].

Syntheses of antimicrobial products with silver nanoparticles have been reported by many researchers. Li and coworkers [3] found that surgical masks coated with silver oxide nanoparticles do not cause skin allergy on the users. Son et al. [4] reported that the antimicrobial polymer nanofiber (cellulose acetate) could be synthesized by treating silver nanoparticles on the surface by UV irradiation. Maneerung et al. [13] reported that the impregnation of freeze-dried silver nanoparticles into bacterial cellulose showed good antimicrobial activity against Gram-negative Escherichia coil (E.coli) and Gram-positive Staphylococcus aureus (S.aureus). Roe et al. [14] have found a method of making antimicrobial plastic catheters by silver nanoparticles on standard PE-BAX polyamide 20 gauge catheters.

Research work on producing silver nanoparticles has been extensive [15–18] and Balan et al. [19] have summarized some of the methods of making silver nanoparticles as follows:

- I. Chemical reduction of silver ions generally in the presence of stabilizing agents
- II. Thermal decomposition in organic solvents
- III. Reversed micelle processes
- IV. Photo reduction
- V. Ultrasonic radiation
- VI. 60 Co- γ -irradiation
- VII. Microwave irradiation

Among the above mentioned methods, chemical reduction is a well established method to produce SNP with reproducible results and smaller particles sizes. Also, the chemical reduction method is very easy to carry out in a laboratory and it is a cost effective way of producing SNP. Moreover, using chemical reduction, SNP can easily be produced on a large scale. At the same time, the bottom up approach of producing nanoparticles offers very small nanoparticles as compared to that of a top down strategy (physical method) [20]. The citrate reduction method in aqueous medium is the most suitable method of making an alkaline solution of the nanocolloids [21–23].

The objective of this study was to produce a novel latex foam material that has antimicrobial properties against two main groups of bacteria and fungi. The antibacterial and antifungal properties of resultant NRL foam samples were evaluated for antibacterial activities by agar diffusion against *E. coli*, a Gram-negative bacterium, and *S. aureus*, a Gram-positive bacterium. Anti fungal activities of the resultant NRL foam pieces were investigated by parallel streak against *Aspergillus niger* as the fungus.

Based on the existing literature data found in many international journals and websites, none of the published evidence has studied the antimicrobial properties of natural rubber latex foam. Also, none of the published research work has synthesized SNP incorporated antimicrobial NRLF foam. Therefore, this research work will be very useful to be considered by future researchers in the related field.

2. Materials and method

Natural rubber latex (Low Ammonia (LATZ) type) and other rubber chemicals for making NRLF were supplied by Zarm Scientific & Supplies Sdn Bhd, Malaysia. Chemicals for synthesis of silver nano-particles were obtained from Merck KGaA, Germany and Sigma Aldrich Chemicals, USA.

2.1. Synthesis of nano silver based NRLF

2.1.1. Synthesis of silver nanocolloids

The silver nanocolloid used in this work was synthesized 90 days in advance according to the method reported by Monteiro et al. [24] and stored in an amber glass bottle to evaluate its stability.

2.1.2. Compounding and production of nano silver based NRLF
The formulation used to make the silver nanocolloid incorporated NRLF is shown in Table 1. First, LATZ type NRL was mixed with sulphur, antioxidant, previously prepared silver nanocolloid and potassium oleate soap and stirred at 10 rpm. After 2 h, zinc 2-mercaptobenzhiozolate (ZMBT) and zinc diethyldithiocarbamate (ZDEC) were slowly added to the mixture. Then, the compounded NRLF compound was matured for 8 h at room temperature with continuous stirring at 10 rpm.

After maturation, the NRLF compound was vigorously beaten using a stand mixer (KENWOOD, kMix) to make a fine foam until the volume was increased up to three times (beating time about 5 min). After that, 3.00 pphr of ZnO together with 0.30 pphr of diphenylguanidine (DPG) were added as the primary gelling agent to the foam and beating was continued for another 90 s. Then, secondary gelling agent, 1.00 pphr of sodium silicofluoride (SSF) was quickly added and the foam was beaten for another 90 s. Finally, the un-gelled foam was immediately poured into an aluminum mould and allowed to gel for 2 min at ambient temperature. Gelled foam was then cured in a hot air oven at 100 °C for 2 h. Next, the cured foam was stripped from the mould and thoroughly washed with de-ionized water to remove soap and non-reacted elements. After washing, the cured NRLF was dried in a hot air oven at 80 °C for 8 h. The resultant foam was off-white in color. The same

Table 1Formulation for latex compound for synthesis of antimicrobial natural rubber latex foam samples (phr).

Ingredients	Dry parts per hundred rubber (pphr)
60% LATZ type NR Latex	100.00
20% Potassium oleate Soap	2.00
Silver Nanocolloids	6.99×10^{-7}
50% Sulphur	2.50
50% Phenolic type Anti oxidant (vulkan ox SKF)	1.00
50% ZMBT	1.00
50% ZDEC	1.00
40% ZnO	3.00
40% DPG	0.30
25% SSF	1.00

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