



Rubber elastomeric nanocomposites with antimicrobial properties



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ABSTRACT

In this paper we show an elastomeric nanocomposite that exhibits antibacterial and antifungal activity. It comprises a rubber blend matrix and a nanofiller, which is a modified bentonite clay (Nanobent® ZR2). We have developed innovative technology for the nanofiller incorporation into the rubber matrix. This new approach was successfully implemented in pilot production at the Polish chemical manufacturer Spoivo (Spółdzielnia Pracy Chemiczno-Wytworczej 'Spoivo', Radom, Poland). Here we reveal that addition of the functionalised bentonite affects the mechanical and thermal behaviour of elastomers. For example, by adding 1–3% of bentonite nanoparticles we strongly enhanced elongation and tensile stress at break, whereas stiffness remained unchanged. We observed improvement of the thermal properties of the nanocomposites yielded and extension of the temperature usage range (from –29 to 311 °C). As a proof of concept we present the antimicrobial effect of elastomeric nanocomposites verified on a wide range of both pathogenic and opportunistic reference bacteria strains, as well as reference strains of yeasts. The proposed method of hydrophilic nanofiller introduction into the rubber elastomer is economically viable and enables fabrication of elastomeric elements with high added value. Their significant antibacterial and antifungal activity makes them desirable in medicine, biomedical engineering, and the food industry.

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1. Introduction

In the last few decades the engineering of new polymer materials has been focused on products with antimicrobial properties. Some of the most interesting are polymer nanocomposites (PNC) created by the addition of nanosized fillers (i.e. clays, carbon nanotubes, graphene, or nanoparticles) into polymer matrices. Antimicrobial polymers have been used as coatings in many areas such as food processing, biomedical devices, filters, and additives for antifouling paints. Some applications require the use of elastomeric material [1] (e.g. polyurethane [2] or silicone rubber [3,4]), thus there is growing interest [5] and commercial demand for elastomeric nanocomposites (ENs). They are beginning to replace traditional materials due to superior barrier properties, better mechanical and thermal characteristics, [6] and increased electrical conductivity [7–9]. This creates tremendous potential for the packaging industry and for fabrication of personal protective equipment or clothing

[10]. Other important applications of ENs in the medical and food industries are closely related to these materials' antimicrobial activity.

A very important risk factor for the development of environment-associated infections is the use of various elastic devices, both in medicine and in food production. Rubber surfaces may serve as propagators for the growth of microorganisms. Gram-negative and Gram-positive bacteria as well as fungi are causative agents of environment-associated opportunistic infections. In the case of opportunistic microorganisms the main problem is the constantly increasing resistance of bacteria to the variety of antimicrobial agents in use, including widely used chemotherapeutics, antibiotics, and disinfectants [11,12]. Additionally, both pathogenic and opportunistic microorganisms can cause economically significant losses. Other global problems are zoonotic and opportunistic diseases as well as the use of huge amounts of antibiotics. They are applied not only to fight infections and inhibit bacterial growth, but also as growth promoters in farm livestock. Veterinary antibiotics, for example, are widely used to treat disease and to protect the health of animals [13]. The end effect of an increased antibiotic level in the environment and in food or food-producing animals is not completely understood. What we know so far is that the frequent use of antimicrobials raises the antibiotic resistance of bacteria and enables the transmission of

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the resistance genes to other organisms, e.g. to human. Opportunistic bacteria like *Staphylococcus simulans* or *Bacillus* species can be causative agents of diseases in animals [14] and zoonotic infections in man [15]. For these reasons it is appropriate to explore new possibilities and materials effective in the prevention of the above microorganisms' propagation and transmission, or even in their eradication from the environment.

Antimicrobial activity against a spectrum of bacterial and fungal strains inhere in various nanocomposites [16–19]. Cationic polymers, as an example, are applied to reduce bacterial diseases caused by implanted devices, e.g. catheters [20]. Effective control of microbial contaminants in food and in the environment may be achieved e.g. during food processing by the direct addition of antimicrobially active nanocomposite to packaging materials. The literature reports that nanocomposites inhibit the growth of a wide variety of both Gram-positive and Gram-negative bacteria, including major foodborne pathogens like microorganisms (such as *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis*) [20–22].

Several strategies have been attempted to harness the antibacterial properties of the elastomer nanocomposites and polymers in general. Metal nanoparticles are successfully used for this purpose, mostly of silver, gold, or copper. The antibacterial properties of nanoparticles result from their high surface-to-volume ratio. This allows easy ion release and penetration through the biological membranes of microorganisms, causing their necrosis [23]. Metal nanoparticles can be useful for toxin neutralisation [24]. PNC with silver nanoparticles are used in medical and dental equipment, clothing, and prostheses to increase resistance to infection [25], and copper ions have strong fungicidal activity [26,27].

Some of the more common, inexpensive and readily available nanofillers are layered silicates (clays), including montmorillonite (MMT) [7]. MMT is a mineral of volcanic origin with hydrophilic properties. This limits its affinity for polymers. MMT needs to be modified to change its chemical nature to hydrophobic [28]. One of the most commonly used methods is the substitution of the sodium cation by various types of organic cations derived from the alkyl ammonium salts and aliphatic amino acids. Alternatively, substitution by quaternary ammonium salts (QAS) is important for the intercalation of the layered silicates. As a result the surface properties of MMT become organophilic [29,30]. Another approach is silver-exchanged MMT. Its antibacterial and antifungal properties are attributed to electrostatic force upon the cell membranes of fungi (e.g. *Candida* spp.) or bacteria (e.g. *E. coli* or *S. aureus*) [31–35]. The negatively charged membranes of the bacteria are attracted to the surface of the clay, where the positively charged silver ions kill the bacteria or render them unable to replicate.

Techniques for nanoparticle incorporation into rubber are the subject of many studies. Only good compatibility between all components of the mixture results in a nanoelastomer with good utility. Commonly used methods of preparing MMT-based polymer nanocomposites are: in situ polymerisation, preparation of the nanocomposite from the polymer melt using the melt-blend method, the introduction into the rubber solution of toluene-swollen nanofiller, the introduction of an aqueous dispersion of nanofiller for rubber latex, and then coagulation [36–41]. Nadeem et al. provided a new way of introducing nanoparticles into the rubber using a conventional two roll mill [42]. Das et al. used stearic acid mixed with montmorillonite, which facilitated the introduction of nanoparticles to the matrix [43]. Another approach detailed in Polish patent number PL 210522 B1 is based on the mixture of dry ingredient preparation. The premix comprises organophilised MMT, peroxide activator, and maleic anhydride and is added to the rubber together with the other components. Nonetheless, these methods are not practical for nanocomposite fabrication on a larger scale due to the need for major modifications to technology or machinery.

In this publication we demonstrate elastomeric nanocomposites which show an inhibitory effect on both opportunistic and environmental Gram-positive bacteria, bacterial pathogens, and yeasts. We present the influence of Nanobent® ZR2 on the mechanical and thermal

properties of the nanocomposite. Our technology, which is a modified two-mill method, was developed in cooperation with the Spoivo chemical company. The presented method finds practical application in industry and thus can be used for production of elastomeric elements for medical and biomedical engineering and the food industry.

2. Materials and methods

2.1. Materials

Chemicals were used as purchased for the synthesis of elastomer nanocomposites. The first was Nanobent ZR2 from Zebiec in the town of the same name in Poland. Nanobent ZR2 is highly dispersed bentonite modified by quaternary ammonium salt (QAS) of the general formula depicted in Fig. S1 (see ESI).

The other synthesis chemicals included Europrene N 2845, which is a cold polymerized acrylonitrile-butadiene copolymer produced by Versalis S.p.A., San Donato Milanese (MI), Italy. SVR 3L was also utilized, which is a high-quality natural rubber wholly produced from field latex preserved with ammoniac or sodium sulfite, and this was purchased from Dau Tieng Rubber Corporation, Vietnam. Santicizer® 261A plasticiser, which is phthalate alkyl (C7–C9) benzyl produced by Brenntag Poland Sp o.o., Kedzierzyn–Kozle, was also integral, as were zinc white (ZnO) produced by Huta Bedzin, Bedzin, Poland and sulphur from Siarkopol, Tarnobrzeg, Poland. Stearine was purchased from POCH S.A., Gliwice, Poland and factice brown from Kodrewex, Gornice, Poland. Chalk slurry produced by POLCALC, Lodz, Poland was another constituent along with wax (Protector G 35 WP) from Paramelt BV, Heerhugowaard, The Netherlands. The plasticiser (Aflux®), tetramethylthiuram disulphide (Accelerant T), and disulphide benzotriazole (Accelerant DM) were from RADKA Poland, Miekinia-Blonie, Poland.

2.2. Preparation of the nanocomposite

The preparation of elastomer nanocomposites consists of combining the nanofiller Nanobent ZR2 with the rubber during the plasticisation process according to the proprietary Polish patent application P.412842. Mixtures of elastomers were made according to the formulation which is set out in Table 1. The raw elastomeric matrix (0) was supplemented with different amounts of Nanobent ZR2: 1 wt% (sample '1'), 2 wt% (sample '2') and 3 wt% (sample '3') in reference to acrylonitrile-butadiene rubbers.

The preparation flow chart is presented in Fig. 1. The process consists of three main steps: dispersing of the nanofiller in plasticiser, rolling, and vulcanisation. During the first step, nanofiller (Nanobent ZR2)

Table 1
Formulation of elastomers nanocomposites.

Ingredient	Phr (part per hundred of rubber) '0', '1', '2', '3'
Acrylonitrile-butadiene rubbers (Europrene N 2845)	100.0
Natural rubber (SVR-3 L)	16.7
Dispersion:	
NanobentZR2	0%, 1%, 2%, 3%
Santicizer 261A	0, 3.3, 6.7, 10.0
Zinc white	12.5
Stearine	2.5
Santicizer 261A	16.66, 13.33, 10.0, 6.66
Factice brown	25.0
Chalk slurry	66.7
Wax	2.5
Aflux	0.8
Accelerant T	0.67
Accelerant DM	1.67
Sulphur	0.67

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