eXPRESS Polymer Letters Vol.15, No.9 (2021) 853–864
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2021.68

Antimicrobial effect of silver nanoparticles plated natural zeolite in polyurethane foam

Gy. Czél[1], *L. Vanyorek*[2], *A. Sycheva*[3], *F. Kerekes*[4], *E. Szőri-Dorogházi*[2,5], *D. Janovszky*[3*]

[1]Institute of Ceramic and Polymer Engineering, University of Miskolc, H-3515 Miskolc-Egyetemváros, Hungary
[2]Department of Chemistry, University of Miskolc, H-3515 Miskolc-Egyetemváros, Hungary
[3]MTA-ME Materials Science Research Group, ELKH, University of Miskolc, H-3515 Miskolc-Egyetemváros, Hungary
[4]Elastico Ltd., H-3525 Miskolc, Hungary
[5]Higher Education and Industry Cooperation Center of Advanced Materials and Intelligent Technologies, University of Miskolc, H-3515 Miskolc-Egyetemváros, Hungary

Received 7 January 2021; accepted in revised form 12 March 2021

Abstract. In the present study, a new method for the synthesis of the open-cell soft polyurethane foam (PUF) is developed. Silver nanoparticles are synthesized on the surface of ultrafine grain (100–500 nm) natural zeolite particles and this zeolite is than placed as a filler in the polyurethane. The Ag content of natural zeolite and PUF is about 5 wt%, and 1500 ppm, respectively. Most of the zeolite particles are partially or fully covered in the polyurethane cell wall which is favorable for long-term storage. However, as soon as the foam comes into contact with water or human sweat, the montmorillonite content of the zeolite swells and breaking through the cell wall of the foam structure. Indeed, particles of the zeolite protrude from the polyurethane matrix with the nano-silver particles showing a favourable biocide effect. The antibacterial effect of the natural zeolite containing Ag nanoparticles was examined against *Escherichia coli* (Gram-negative), and *Micrococcus luteus* (Gram-positive) strains in a 24 and 72 h interval. The results show that the natural zeolite containing Ag nanoparticles filler has an antibacterial effect, especially against Gram-positive bacteria.

Keywords: *polymer composites, antibacterial material, polyurethane foam, montmorillonite natural filler, natural zeolite filler*

1. Introduction

Synthetic polymers are appearing in increasing amounts in our daily lives [1]. The development of technical plastics puts a great responsibility not only on industrial partners, but also on materials scientists as well. PUR foam (PUF) is a poorly recyclable synthetic polymer. Every scientific activity towards the ‘greening’ PUF is an important challenge. Extending the life cycle of products ameliorates the difficulty connected with the obligation to recycle.

Polyurethanes have many applications that include: construction, vehicle parts, footwear, automotive, packaging, bedding, flooring, medical devices, insulation, coating, as an outstanding substrate for oils, and for organic solvents absorption [2–6]. The biological use of polyurethane foams is increasing owing to the biocompatible property of polyurethane [7]. However, polyurethane foams in humid and oxygen-rich environments allow the appearance and growth of aerobic bacteria, thus destroying the colour, odour, and elastic properties of the foams. The growing amount of polyurethane justifies extending their use to a preferred field of application where the antibacterial activity is also important. Infections are known to cause serious public health problems [8], and therefore, in all fields of application, the prevention of bacterial adhesion and/or proliferation is extremely important.

[*]Corresponding author, e-mail: fekjd@uni-miskolc.hu

Polyurethane foam with antibacterial properties has so far been achieved in two ways. On the one hand, composites have been created by using an antibacterial, naturally occurring filler. Until now, several different natural fillers have been investigated: nutmeg [9], curcumin [10], chitosan [11], cloves [12]. The application of the fillers obtained from natural sources has attracted much more attention because natural-fillers improve the environmentally friendly character of PU foams. On the other hand, metal and a metal oxide, sulphide nanoparticles (NPs) have been introduced into the structure or surface of the polyurethane foam, specifically Ag [13–17], Cu, Zn and its oxides [18–20], CdS [21]. Of this, Ag nanoparticles are the most commonly used as soldering raw material and in medical applications, as the presence of silver poses a low threat of toxicity toward humans and animals. However, silver presents significant toxicity to over 600 hundred species of bacteria, fungi, and viruses.

Fillers as zeolites are natural or synthetic compounds, having hydrated alumina-silica structures of alkaline and alkaline-earth metals [22, 23]. The structure of natural zeolites allows for metallic ion charging or, due to their high specific surface area, they are suitable for carrying metallic nanoparticles on zeolite particles. Okuyama *et al*. [24] developed a process for producing antibacterial flexible polyurethane foam containing Ag ion-charged synthetic zeolite. Synthetic zeolites include Ag ion-charged zeolites [25], but the metal ion content of naturally occurring natural zeolites is negligible and has no antibacterial effect. Natural zeolite always contains other minerals, so it is mainly used as an adsorbent [26, 27], feed additive [28, 29] and soil improver [30]. Natural zeolites contain not only water-absorbing aluminosilicates but also swellable smectite and its constituent natural montmorillonite. The property of swelling is important for our research.

Our goal is to improve the usability and life cycle of PUF via a biocidal additive using silver doped PUF in a bacterial environment. This article is a part of the development of PUF, a synthetic raw material with an antibacterial effect that has been found especially important today. With the help of nanotechnological processes, we designed polyurethane foam that can be made a simple by a procedure, and which has an effective bactericidal property. In addition, it exerts its bactericidal effect only after human activation. Our special goal is to adopt a montmorillonite additive in order to reach the delayed applicability of zeolite added PUFs.

2. Experimental section

2.1. Materials

The natural zeolite was commercially available from Geoproduct Ltd. and originated from Mád (Tokaj region, Hungary). Its mineral composition based on X-ray analysis, is presented in Table 1. The main component is the smectite group (45.8 wt%) from which montmorillonite, a clay mineral, plays an important role due to its swelling properties. Montmorillonite content was 30 wt% for the present research. Natural zeolite also contains other crystalline minerals, such as clinoptilolite, quartz, cristoballite, sanidine, in smaller amounts. The particle size range was between 1.5 and 260 μm.

Silver nitrate, $AgNO_3$ (Alfa Aesar Ltd.) as silver precursor, and ethanol (VWR Ltd., USA), as reducing material were used for the decomposition of the silver nanoparticles onto the zeolite surface. Polyethylene glycol (PEG400, Sigma-Aldrich Ltd., USA) colloid stabilizing agent was applied for dispersing the silver-coated zeolite particles. The polyol component contained a triol named Lupranol 2009 (BASF Ltd., Germany), butanediol, PEG400 deionized water, tin catalyst and TEGOSTAB catalyst (Evonik Ltd., Germany). The isocyanate component

Table 1. Mineral composition of the natural zeolite used in the experiments (in a dry basis).

Phase name	Rietveld [wt%]	Empirical formula
Smectite group	45.8	$M_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2{}^*$
Clinoptilolite	33.5	$Ca_{1.9}Na_{1.76}K_{1.05}Mg_{0.17}Al_{6.72}Si_{29.2}O_{72}\cdot 23.7(H_2O)$
Cristobalite	8.8	SiO_2
Sanidine	2.6	$K_{0.75}Na_{0.25}AlSi_3O_8$
Quartz	2.3	SiO_2
Amorphous	7.0	–

$^*M = Ca^{2+}$ or Mg^{2+}

was diphenyl methylene diisocyanate (BorsodChem Zrt., Hungary).

2.2. Grinding

Grinding experiments of natural zeolite were carried out in a unit designed horizontal-axis ceramic stirred media mill. This milling machine is designed for the production of small quantities (50–120 g) of ultrafine grinds in both dry and wet environments. The zeolite powder was ground at room temperature using an alumina lined crucible. The diameter of the alumina balls was 2 mm. The filling ratio of the grinding media in the milling chamber was 70 V/V%. Isopropanol was used as a process control agent. Samples were taken after 30 and 60 min experiment times.

As-received, natural zeolite powder sample was first dried and divided below 63 µm particle size by sieving. Zeolite powder smaller than 63 µm particle size is hereinafter referred to as raw zeolite. To increase the specific surface area, the zeolite powder was ground. A rapid decrease in zeolite fineness was already observed after 30 min (Table 2). After 30 min grinding time, the particle size distribution by LPSA of zeolite became bimodal, there were two modes x_{m1} = 0.252 µm, and x_{m2} = 1.282 µm. (D_X diameter corresponds to X% fineness of the particle size volume distribution in Table 2.)

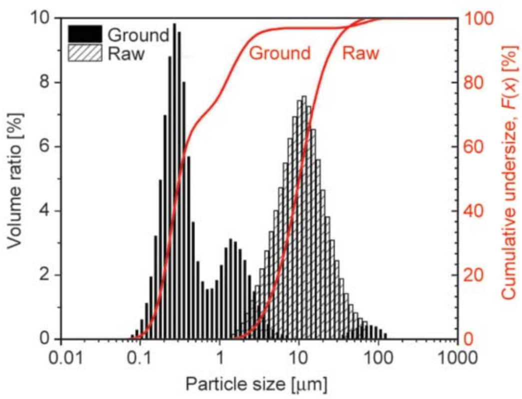


Figure 1. Particle size distributions of the raw zeolite (feed) and ground products (grinding time:60 min).

In Figure 1 it can be seen that the bimodal nature of the histogram of the zeolite remains after 60 min of grinding time. The particle sizes were not decreased but increased slightly, the agglomeration of particles took place. Figure 1 shows the particle size distribution before the grinding process and after 60 min of grinding. The mode value of zeolite is significantly shifted to the submicronic and ultrafine-grained size range.

2.3. Synthesis of the polyol based silver nanoparticles as an additive for antibacterial PUR

The manufacturing process can be divided into three major parts (additive manufacturing, foaming, activation). The first step is to process is the synthesis of Ag particles on the surface of the ground nanoparticulate natural zeolite. In which, 0.394 g silver nitrate was dissolved in 100 ml ethanol. After 4.70 g zeolite was added to the silver nitrate solution, which was sonicated by a highly efficient ultrasonic homogenizer (Hielscher UIP 1000 hdt.) at 20 kHz for 10 min. The silver content of the zeolite support was ~5.00 wt% (1 kg of zeolite contains ~50 g of Ag particles). Such high-intensity ultrasound treatment leads to the formation of vapour microbubbles that can be induced in an alcohol based solution containing silver ions. Then, these microbubbles will collapse, resulting in intense local heating (~5000 K) and high pressure (~1000 atm); these micro volumes are the so-called 'hot spots'. The energy released in these 'hot spots' was enough lead to the reduction of Ag-ions to silver nanoparticles, in the presence of ethanol as a reducing agent, based on the Equation (1):

$$2AgNO_3 + C_2H_5OH \rightarrow 2Ag^0 + C_2H_4O + 2HNO_3 \quad (1)$$

Table 2. The characteristic cumulative particle size distribution of raw and ground zeolite.

Cumulative percentage [V/V%]	Particle size of the raw zeolite [µm]	Particle size after 30 min of milling time [µm]	Particle size after 60 min of milling time [µm]
D 10	3.9714	0.1617	0.1580
D 50	10.5077	0.3094	0.3475
D 60	12.6166	0.3784	0.3766
D 70	15.4918	0.6387	0.6643
D 80	20.3477	1.1985	1.2218
D 90	32.7738	1.9293	1.3744
D 95	64.2960	2.9825	2.9760

In addition to Ag^0 particles, acetaldehyde and nitric acid are formed in the ethanolic phase. The ethanolic phase was evaporated overnight by a rotary vacuum evaporator, after the Ag/zeolite additive had been dried at 105 °C,. This powder that contained silver is well suited for antibacterial polyurethane production, and therefore this was also tested as a solid additive. For our practical application, we named this additive nano-Ag-ZEO.

In the case of PU additives, fast dispersibility and compatibility are very important, and thus polyethylene-glycol was used as a dispersant. In the next step, the Ag/zeolite additive (3.00 g) was dispersed in 12.00 g PEG400 using an ultrasonic homogenizer in order to enhance dispersibility in the polyol component of the PUF. The silver content of the PEG400 based dispersion is 1.00 wt%. This additive can be used immediately or stored for later use in an airtight container. The schematic procedure of the synthesis of polyurethane foam is presented in Figure 2.

Production of antibacterial agent

After vacuum evaporation, the solid and liquid-free powdered antibacterial additive was ready to use in the foaming process. This additive can be used immediately or stored for later use in an airtight container. There were two ways to implement the active biocide zeolite agent into the polyol phase of the later developed PUF. In one case antibacterial agent was suspended in a polyol (PEG400), and this suspension was used to make the antibacterial polyurethane foam. In the other case, the pure zeolite powder with Ag particles was added to the production of polyurethane foam directly into the Lupranol (BASF) triol component. Especially this second, dry powder application was dedicated to supporting the large-scale industrial production of antibacterial open-cell foams.

Production of open cell polyurethane foam and activation

In the foam production phase, 2.9 wt% zeolite with Ag content, 50.3 wt% polyol and 46.8 wt% isocyanate components were mixed. After stirring, the reaction mixture was foamed into a block in an open die with free foam rise. The basic reaction of Polyurethane Formation (Simplified) is given in Equation (2):

$$\text{OCN–R–NCO} + \text{HO–R–OH} \rightarrow \rightarrow \text{OCN–R–NH–CO–R–OH} \quad (2)$$

The blowing agent was carbon dioxide generated by the reaction of water and diisocyanate as Equation (3):

$$\text{2OCN–R–NCO} + \text{HOH} \rightarrow \rightarrow CO_2 + \text{OCN–R–HN–CO–NH–R–OH} \quad (3)$$

Theoretical research has shown that the bactericidal ability of silver in the ionic state is strong, but the bactericidal effect is lost when the ion source is depleted [31, 32]. Although the bactericidal effect of metallic silver is weaker than that of ionic silver, its mechanism of action persists until metallic silver is

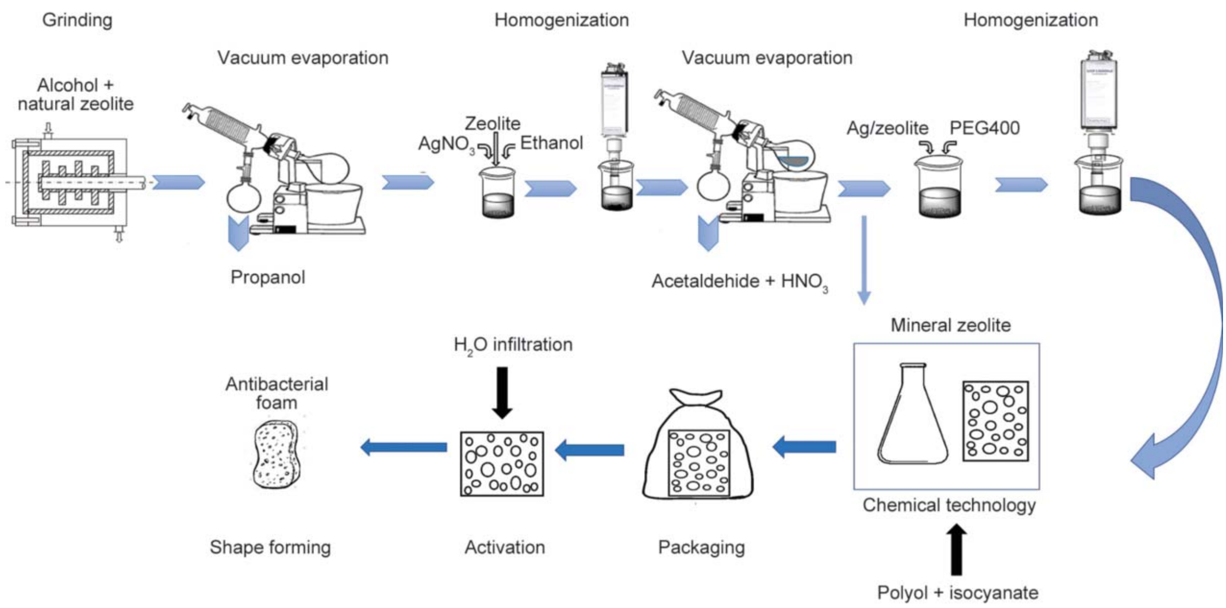


Figure 2. Representative scheme of the procedure.

completely dissolved in the normally acidic liquid present in a bacterial environment. The effect of elemental metals can therefore be extended for a longer period.

2.4. Antibacterial properties

Escherichia coli (DH5α [33], Gram-negative) and *Micrococcus luteus* (Gram-positive) strains as model organisms were used for evaluating the antibacterial activity of Ag-treated natural zeolite and polyurethane foam in antibacterial tests. Conventional LB (Luria-Bertani) broth (tryptone 10.0 g, yeast extract 5.0 g, NaCl 10.0 g, agar 20.0 g, distilled water 1000.0 ml, pH adjusted to 7.0) was inoculated with a single bacterial colony and then cultivated at 37 °C for 24 h with continuous shaking.

2.4.1. Antibacterial test of Ag nanoparticles on natural zeolite, additives and solvents used in the manufacture of foam

For inhibition zone tests, *E. coli* and *M. luteus* suspensions with the same optical density at 600 nm (OD_{600} = 0.4) were prepared by adding sterile LB medium to the starter bacterial suspensions. The living cell concentration of these diluted bacterial suspensions (colony forming units per ml of the bacterial suspension [cfu/ml]) was determined using the plate count method ($3.7\cdot10^8$ cfu/ml for *E. coli* and $1\cdot10^8$ cfu/ml for *M. luteus*). For each test, 100 µl suspension was spread evenly on top of the LB agar plates and then 5 µl from the tested samples was put on the top of the spread layer. In Test 1, the plates were inoculated with *E. coli* suspension and incubated at 37 °C for 24 h, while in Test 2 *M. luteus* plates were incubated for 72 h at 30 °C. The size of the inhibition zone can provide information about the antimicrobial effect and diffusion efficiency of the antibacterial compound released from the surface of the samples investigated.

2.4.2. Antibacterial assays of non activated and activated polyurethane foam

Each non-sterile foam was placed in a separate 100 ml glass flask filled with 30 ml sterile, clear LB medium. The dimension of the used polyurethane foams was 10×10×10 mm. Since the preparation of nano-Ag-ZEO containing foams took place in non-sterile conditions, therefore the microorganisms from the environment (*e.g.* from human skin normal flora) are already on the foam before the antibacterial tests. Therefore the antibacterial property of the activated and non-activated foams were investigated against microorganisms already existed on the surface of the foam. After incubation (37 °C, 24 h in Test 1 and 72 h, 30 °C in Test 2) the antibacterial effect of the tested foams was determined by measuring the turbidity of the LB medium. Ideally, if the activated foam has an outstanding antibacterial effect, then the LB medium will stay clear after incubation, otherwise, the LB medium becomes cloudy.

2.5. Characterisation technics

The particle size distribution (PSD) of the raw material and the ground samples was determined by a Horiba LA-950V2 laser particle size analyser (LPSA) in distilled water, using ultrasonic dispersing for 1 min. Furthermore, the 'outer' (geometric) specific surface area (SSA) of the ground samples was calculated by the same LPSA using shape factor 1.0 (Heywood factor). The micrographs of the powders and the cylindrical samples were acquired by a Hitachi S4800 scanning electron microscope (SEM, Hitachi Ltd, Tokyo, Japan) equipped with a BRUKER AXS type energy dispersive X-ray spectrometer (EDS, Bruker GmbH, Berlin, Germany). The samples were examined by a Bruker D8 Advance diffractometer (XRD) using Cu Kα radiation (40 kV, 40 mA), in parallel beam geometry obtained with Göbel mirror, equipped with a Vantec-1 position sensitive detector (1° window opening), measured in the 2–100° (2θ) angular range, with 0.007° (2θ)/29 s speed. The obtain data from the whole surface and to reduce in-plane preferred orientation effects, the specimen was rotated in the sample plane during the measurement. The crystalline fraction was determined by XRD analysis using peak area determination in TOPAS4 (amorphous hump method). Quantitative results were obtained by the combined use of Rietveld refinement and peak area calculation. The structure of the zeolite with the Ag particles was investigated by an FEI Tecnai G2 transmission electron microscope (TEM) equipped with a LaB6 cathode. The acceleration voltage was 200 kV.

3. Results and discussion

3.1. Characterisation of zeolite with Ag nanoparticles

TEM investigation was performed to confirm the presence and size distribution of Ag particles on the zeolite surface. Figure 3 clearly shows a well-dispersed Ag particle structure on the surface. Considering the measurement possibilities, the value of the measured diameter was between 0–20 nm. The diameter of the silver particles followed the normal distribution. The white dots are Ag particles that were also confirmed by STEM-EDX selected area elemental mapping (Figure 3).

High-resolution TEM images were used to determine the particle size distribution of the Ag particles on the zeolite surface (Figure 4a). The mean diameter of the Ag particles is 4.61 nm; that is, nano-Ag particles were successfully deposited on the zeolite (Figure 4b). The Ag content of natural zeolite is 5±1.2 wt% determined by STEM-SEDX measurements.

3.2. Characterisation of open cell polyurethane foam

The new enhanced antibacterial polyurethane foam consists of a cell wall and nearly spherical air cells, as well as an antibacterial additive embedded in the cell wall polyurethane matrix. The presence of openings between the air cells results in an open cell foam structure and the absence of openings results in a closed cell foam structure. The air cells of our

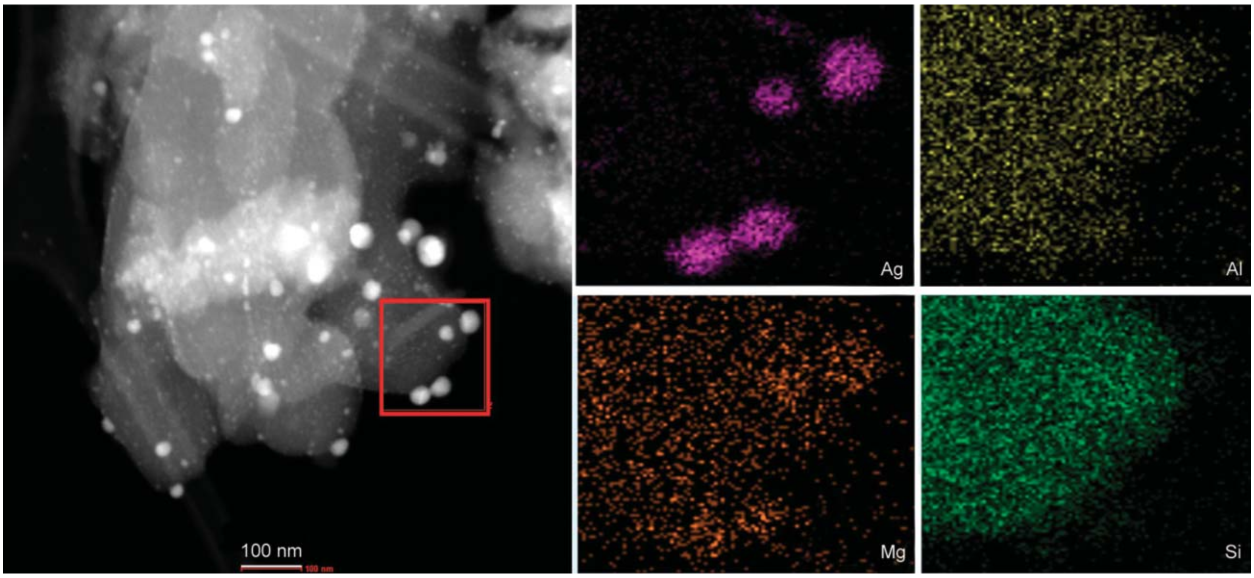


Figure 3. Bright-field TEM (BF TEM) image of the nano-Ag-ZEO and elemental mapping (STEM-EDX) analysis from the area marked with a red square.

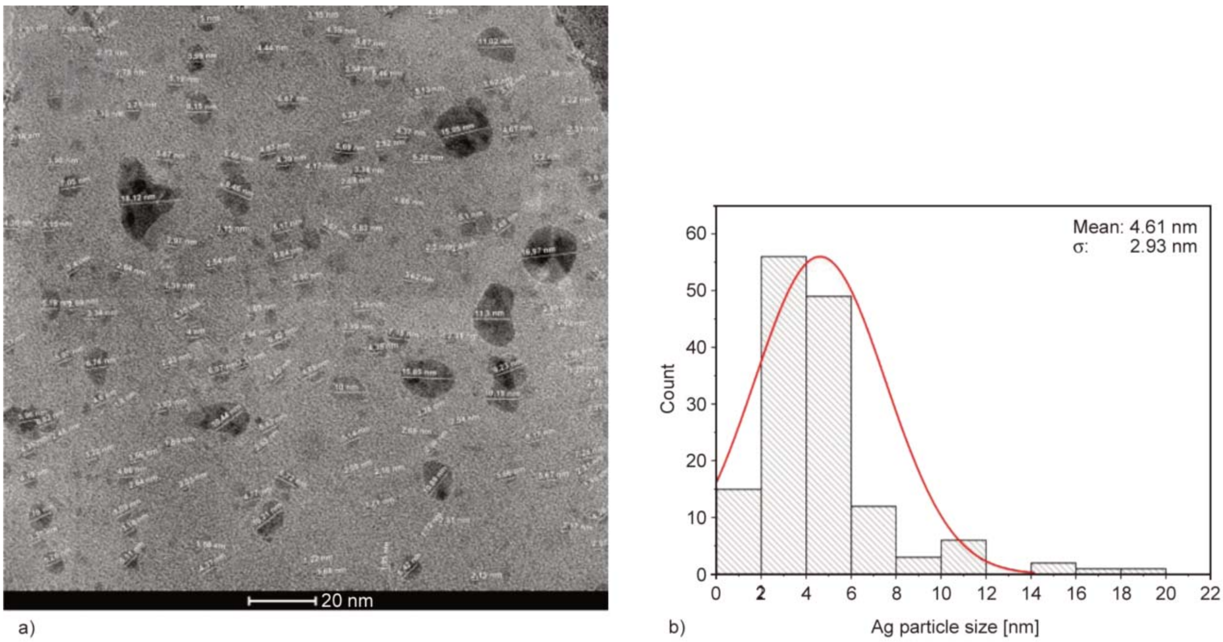


Figure 4. High-resolution TEM image of zeolite surface with Ag nanoparticles (a), and the particle size distribution of Ag nanoparticles (b).

antibacterial polyurethane foam usually have an opening, that is, have an open cell structure, so their water absorption capacity is high. The cell size distribution of polyurethane foam was statistically analysed using ImageJ software from the cross-section SEM images (Figure 5). The mean cell size distribution was 121.68 μm, which is a fine open cell structure.

During foaming, most of the zeolite particles are partially or fully covered in the polyurethane cell wall as can be seen in the cross-section of the polyurethane foam (Figure 6). Unfortunately, due to the presence of oxidation, Ag, Cu, and Zn metal-containing materials in an elemental form are difficult to store, oxidize rapidly in the presence of oxygen, and thus lose or greatly reduce the bactericidal ability that underlies their mechanism of action. Often these materials are placed in airtight and light-proof packaging. The natural zeolite particle coverage of Ag is therefore particularly advantageous, in that it does not lose its bactericidal ability until use. The Ag content of polyurethane foam is about 0.14 wt%.

Water or water-based liquid activation is required to create and/or increase the antibacterial effect. This activating substance may be water or human sweat, because the water-sensitive smectite part and the swellable montmorillonite in it swell into the polyurethane structure, breaking through the cell wall of the foam structure, during which time the parts of the zeolite protrude from the polyurethane matrix with the nano-silver particles (Figure 7). Thus Ag nanoparticles come into direct contact with the bacteria living in the liquid, human sweat, or water soaking the polyurethane foam, releasing the nanosilver particles in an intensified manner. In our case, activation was effective, when the zeolite contains 35 wt% of the montmorillonite clay mineral.

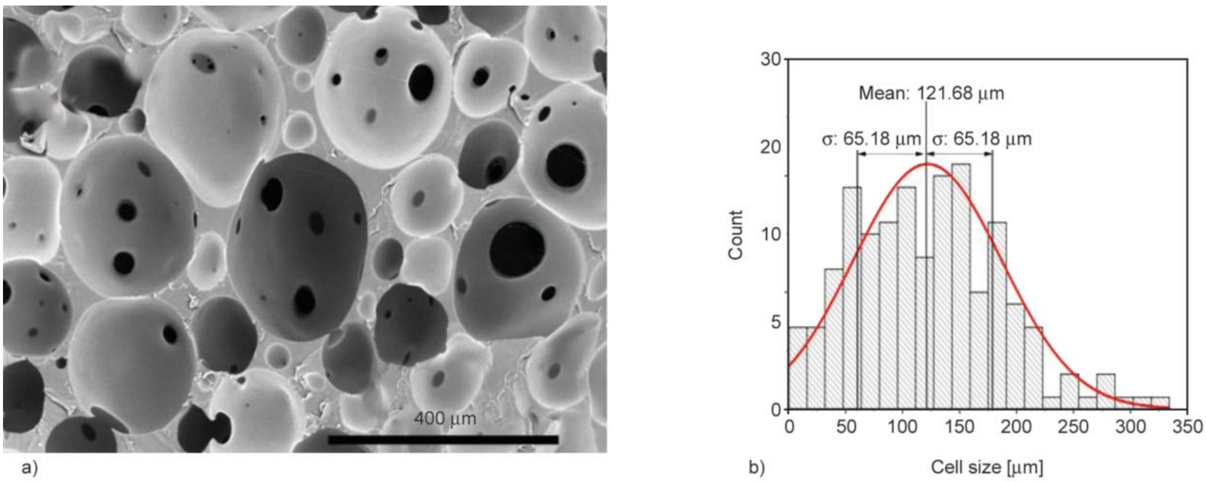


Figure 5. a) Cross-sectional SEM image of polyurethane foam and b) the cell size distribution.

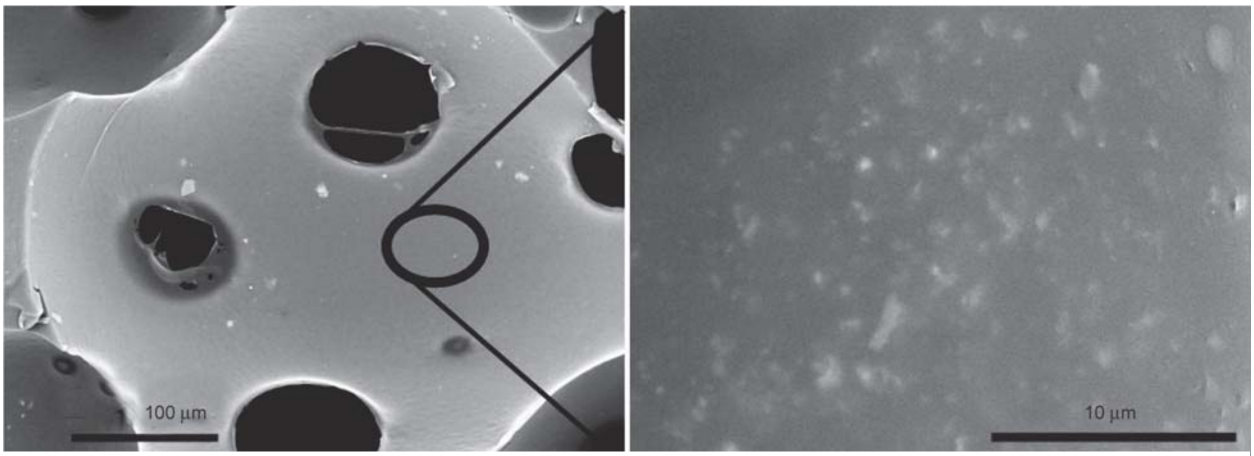


Figure 6. Surface SEM images of polyurethane foam with modified natural zeolite content before activating.

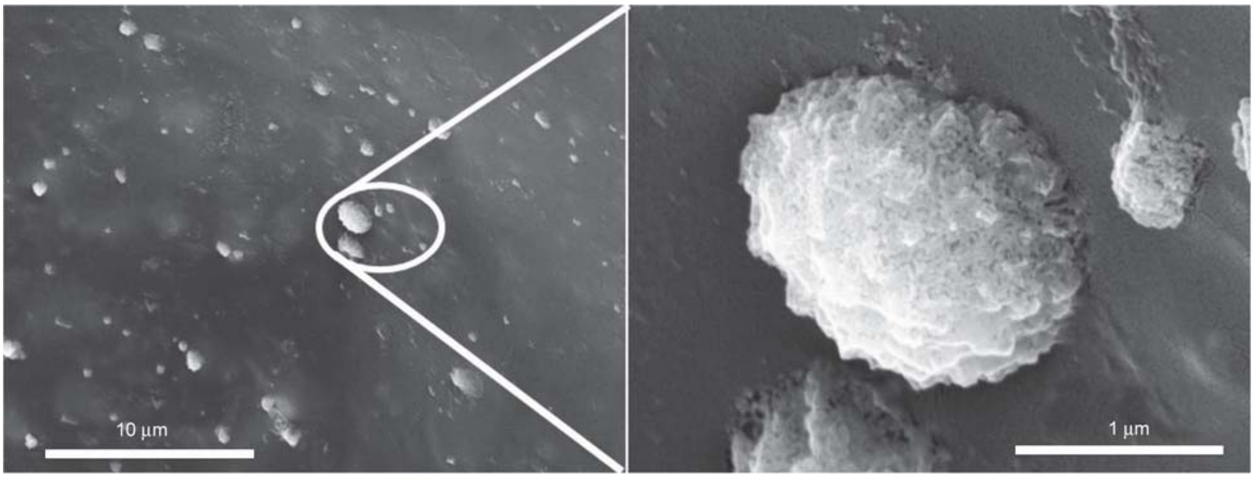


Figure 7. Surface SEM images of activated polyurethane foam with modified natural zeolite content after water activation.

3.3. Antibacterial properties of Ag nanoparticles on natural zeolite, additives and solvents used in the manufacture of foam

To identify the source of the antibacterial effect, the components and solvents used in the polyurethane foam preparation were checked in different combinations in Test 1 and 2. The antibacterial effect was examined for the 20 and 40 wt% of Ag nanoparticles covered natural zeolites (nano-Ag-ZEO) suspensions in water (marked in Figure 8 as 1 and 2, respectively), nano-Ag-ZEO in PEG400 (10 m/m%, in Figure 8 as 3), nano-Ag-ZEO in Lupranol (20 m/m%, in Figure 8 as 4), as well as neat PEG400 (5 in Figure 8) and neat Lupranol (6 in Figure 8).

For both Tests 1 and 2, bacteria made an even milky layer on the top of the LB agar plates after incubation. In Test 1, an unambiguous clear zone was observed around the 20 and 40 wt% of nano-Ag-ZEO suspensions droplets (areas indicated in Figure 8 marked as 1 and 2), and a less pronounced inhibition zone was observed for nano-Ag-ZEO in Lupranol (marked as 4). In Test 1, the remaining samples do not show such an inhibitory effect. The results were the same in an antibacterial test with Gram-positive *M. luteus* (Test 2), except that the nano-Ag-ZEO suspended into PEG400 also gave a thin clear zone. Furthermore, the inhibition zone of nano-Ag-ZEO in Lupranol was also wider in Test 2 than in Test 1 (see Figure 8). This allows us to hypothesize that high

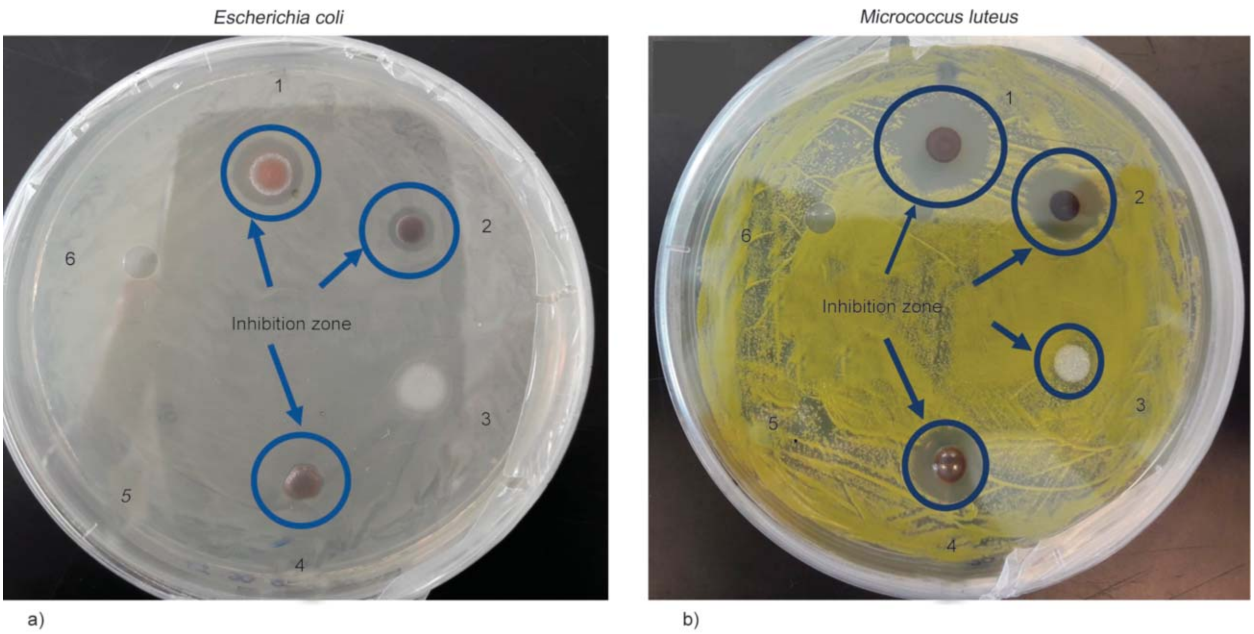


Figure 8. mAgar diffusion tests on *E. coli* (a) and *Micrococcus luteus* (b) bacteria (1 and 2: 20 and 40 wt% of nano-Ag-ZEO suspensions droplets, 3: 10 wt% nano-Ag-ZEO in PEG400, 4: 20 wt% nano-Ag-ZEO in Lupranol, 5: neat PEG400, 6: neat Lupranol).

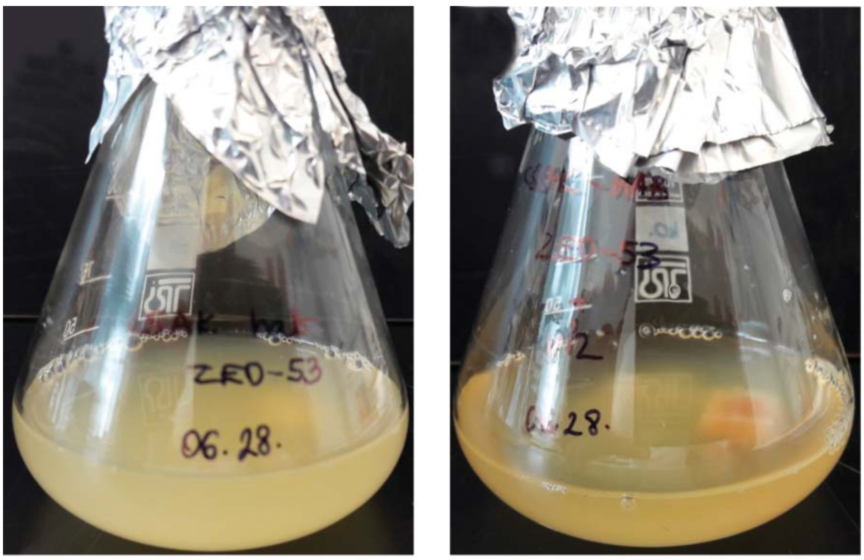
mobility Ag^+ ions can act as antibacterial compounds diffuse far into the texture of the gel and thus discourage the growth of bacterial cells. Both tests provide strong evidence that the nano-Ag-ZEO can be a good candidate for a new antibacterial material, although the qualitative description of this activity is not that straight forward. The suspensions placed on the top of the agar plate could only be normalized to constant volume (5 μl). Therefore the amount of water differed in such a way that the more concentrated suspension contained less water than the diluted one. This can explain the counter-intuitive behaviour of these systems meaning the more diluted suspension was in contact with the LB agar in larger surface and the dissolved Ag ions were able to diffuse more further from the place where the suspension was put on the LB agar plate. As a consequence the antibacterial effect (thus the inhibition zone) was pronounced in case of 20 wt% nano-Ag-ZEO suspension rather than in case of 40 wt% nano-Ag-ZEO suspension. This method was used to decide the question wether the component of the composed PUF have antibacterial effect and not for the quantitative determination of the effective concentration of the nano-Ag-ZEO suspension.

The antibacterial property of non-activated and activated polyurethane foam was investigated in such a way that polyurethane foams with nanoAg-ZEO were immersed in LB solution (Figure 9). As for the antibacterial rate (X), it is calculated according to the Equation (4):

$$X = \frac{OD_{600\mathrm{na}} - OD_{600\mathrm{a}}}{OD_{600\mathrm{na}}} \tag{4}$$

where $OD_{600\mathrm{na}}$ is the optical density at 600 nm in the case of non-activated polyurethane foam and $OD_{600\mathrm{a}}$ is the optical density at 600 nm in the case of activated polyurethane foam. After 72 h, the turbidity of suspensions was measured as OD_{600} by spectrophotometer. The OD_{600} of non-activated and activated foam was 1.42 (Figure 9a) and 0.825 (Figure 9b), respectively. The antibacterial rate is 41.9%, showing that the cell growth inhibitory effect of the activated foam (Figure 9b) was higher compared to the non-activated foam (Figure 9a).

Based on the tests, it can be stated that PU foam containing natural zeolite can have an antibacterial effect even with 0.14 wt% Ag content. Larger amounts of natural zeolite with Ag nanoparticles may further enhance the antibacterial effect. Several studies have been done on this, using Ag NPs as listed in Table 3. It can be clearly seen from the table that, the silver content in PUR is generally much higher, as other researchers have generally provided additives with a complete surface coating or immersion of the foam [15, 16, 34]. In the other cases, when the Ag particles were introduced into the entire cross-section, a larger amount was also used because there were no other additives [35, 36]. According to the solutions reported in the literature, Ag PUF materials exert their beneficial effect only when they are used immediately.



a) b)

Figure 9. Inhibitory effect of the non-activated (a), and activated (b) foam with Ag nanoparticles on the natural zeolite surface.

Table 3. Antibacterial Activity of PU with Ag NP.

Matrix	Method	Content [wt%]	Model organism	Antibacterial test	Ref.
PU nanofiber	coating with AgNP solution	0.01–5	*S. aureus*	a) agar diffusion test b) turbidity assay	[15]
PU foam	immersed in silver colloidal solution	10.7	*E. coli*	batch set-up (PU foam disk dipped in bacterial suspension)	[16]
PU foam	AgNP sprayed on the foam	4	*E.coli* *S. aureus*	a) agar diffusion test b) bacterial enumeration test	[13]
PU foam dressing	impregnation with Ag NP	1 mg/cm^2	–	clinical efficacy test	[34]
PU foam	Lignin-Capped AgNP dispersing in the polyol mixture	0.21–0.34	*S.aureus* *P. aeruginosa*	a) direct contact test b) release-killing test	[35]
PU foam	Intermatrix Synthesis inside a PU	1.6–2.1	*E. coli*	a) immersion of cubic PU foam in bacterial suspension b) antibacterial activity of released Ag^+ ions	[36]

Our special montmorillonite additive also allows for the possibility of delayed application, the possibility of timed-delayed use. In our experiments, biocidal activity was detected under circumstances of normal humidity, but it was even greater when we activated the montmorillonite together with water. No method or results performed by other researchers were found for intensified biocidal activity prepared using mineral montmorillonite and exploiting the phenomenon of swelling. The technological implications of our work have been recorded in a patent.

4. Conclusions

Silver nanoparticles were synthesized on a natural zeolite surface. The TEM images showed that the Ag particles were evenly distributed on all components of the natural zeolite. The mean diameter of the Ag particles was 4.61 nm based on the HRTEM images. The Ag content of natural zeolite is about 5 wt%. Open-cell polyurethane foam was produced with Ag nanoparticles plated on the surface of natural zeolite. During foaming, most of the zeolite particles were partially or fully covered in the polyurethane cell wall, and, therefore, the antibacterial effect of Ag nanoparticles was reduced. For later use, this is advantageous because the Ag particles were thus trapped from the oxygen. One of the constituents of natural zeolite is swellable montmorillonite, which swells and breaks through the cell wall of the foam if it comes in contact with water or human sweat. In this way, the Ag nanoparticles are activated against the bacteria. Hence, montmorillonite additive also allows for the possibility of delayed application. Based on our antibacterial studies, the natural zeolite which contains Ag nanoparticles has a strong antibacterial effect which is more pronounced against Gram-positive *M. luteus* bacteria. Natural zeolite is present in large quantities on Earth and can be cost-effectively used for the production of antibacterial polyurethane foam.

Acknowledgements

The work of Anna Sycheva and Dora Janovszky was carried out as part of the GINOP-2.3.2-15-2016-00027 'Sustainable operation of the workshop of excellence for the research and development of crystalline and amorphous nanostructured materials' project implemented in the framework of the Széchenyi 2020 program. The work of György Czél, Lászlo Vanyorek and Emma Szőri-Dorogházi was supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry. The authors are grateful to Mr. Gábor Karacs and Mária Svéda of MTA-ME Materials Science Research Group for the TEM measurement.

References

[1] Rao W-H., Xu H-X., Xu Y-J., Qi M., Liao W., Xu S., Wang Y-Z.: Persistently flame-retardant flexible polyurethane foams by a novel phosphorus-containing polyol. Chemical Engineering Journal, **343**, 198–206 (2018). https://doi.org/10.1016/j.cej.2018.03.013

[2] Akindoyo J. O., Beg M. D. H., Ghazali S., Islam M. R., Jeyaratnam N., Yuvaraj A. R.: Polyurethane types, synthesis and applications – A review. RSC Advances, **6**, 114453–114482 (2016). https://doi.org/10.1039/C6RA14525F

[3] Panda S. S., Panda B. P., Nayak S. K., Mohanty S.: A review on waterborne thermosetting polyurethane coatings based on castor oil: Synthesis, characterization, and application. Polymer-Plastics Technology and Engineering, **57**, 500–522 (2018). https://doi.org/10.1080/03602559.2016.1275681

[4] Naldzhiev D., Mumovic D., Strlic M.: Polyurethane insulation and household products – A systematic review of their impact on indoor environmental quality. Building and Environment, **169**, 106559/1–106559/30 (2020).
https://doi.org/10.1016/j.buildenv.2019.106559

[5] Zhu H., Yang Y., Sheng A., Duan H., Zhao G., Liu Y.: Layered structural design of flexible waterborne polyurethane conductive film for excellent electromagnetic interference shielding and low microwave reflectivity. Applied Surface Science, **469**, 1–9 (2019).
https://doi.org/10.1016/j.apsusc.2018.11.007

[6] Zhao S., Yin L., Zhou Q., Liu C., Zhou K.: *In situ* self-assembly of zeolitic imidazolate frameworks on the surface of flexible polyurethane foam: Towards for highly efficient oil spill cleanup and fire safety. Applied Surface Science, **506**, 144700/1–144700/11 (2020).
https://doi.org/10.1016/j.apsusc.2019.144700

[7] Joseph J., Patel R. M., Wenham A., Smith J. R.: Biomedical applications of polyurethane materials and coatings. Transactions of the IMF, **96**, 121–129 (2018).
https://doi.org/10.1080/00202967.2018.1450209

[8] Defez C., Fabbro-Peray P., Cazaban M., Boudemaghe T., Sotto A., Daurès J. P.: Additional direct medical costs of nosocomial infections: An estimation from a cohort of patients in a French university hospital. Journal of Hospital Infection, **68**, 130–136 (2008).
https://doi.org/10.1016/j.jhin.2007.11.005

[9] Członka S., Strąkowska A., Kairytė A., Kremensas A.: Nutmeg filler as a natural compound for the production of polyurethane composite foams with antibacterial and anti-aging properties. Polymer Testing, **86**, 106479/1–106479/13 (2020).
https://doi.org/10.1016/j.polymertesting.2020.106479

[10] Sienkiewicz N., Członka S., Kairyte A., Vaitkus S.: Curcumin as a natural compound in the synthesis of rigid polyurethane foams with enhanced mechanical, antibacterial and anti-ageing properties. Polymer Testing, **79**, 106046/1–106046/14 (2019).
https://doi.org/10.1016/j.polymertesting.2019.106046

[11] Javaid M. A., Khera R. A., Zia K. M., Saito K., Bhatti I. A., Asghar M.: Synthesis and characterization of chitosan modified polyurethane bio-nanocomposites with biomedical potential. International Journal of Biological Macromolecules, **115**, 375–384 (2018).
https://doi.org/10.1016/j.ijbiomac.2018.04.013

[12] Członka S., Strąkowska A., Strzelec K., Kairytė A., Kremensas A.: Bio-based polyurethane composite foams with improved mechanical, thermal, and antibacterial properties. Materials, **13**, 1108/1–1108/20 (2020).
https://doi.org/10.3390/ma13051108

[13] Picca R. A., Paladini F., Sportelli M. C., Pollini M., Giannossa L. C., Di Franco C., Panico A., Mangone A., Valentini A., Cioffi N.: Combined approach for the development of efficient and safe nanoantimicrobials: The case of nanosilver-modified polyurethane foams. ACS Biomaterials Science and Engineering, **3**, 1417–1425 (2017).
https://doi.org/10.1021/acsbiomaterials.6b00597

[14] Farrokhi Z., Ayati A., Kanvisi M., Sillanpää M.: Recent advance in antibacterial activity of nanoparticles contained polyurethane. Journal of Applied Polymer Science, **136**, 46997/1–46997/13 (2019).
https://doi.org/10.1002/app.46997

[15] Hong S-M., Kim J-W., Knowles J. C., Gong M-S.: Facile preparation of antibacterial, highly elastic silvered polyurethane nanofiber fabrics using silver carbamate and their dermal wound healing properties. Journal of Biomaterials Applications, **31**, 1026–1038 (2017).
https://doi.org/10.1177/0885328216687665

[16] Nadafan M., Malekfar R., Izadi-Darbandi A., Dehghani Z.: Microstructural and antibacterial properties of silver nanoparticle-decorated porous polyurethane surface for water purification. Desalination and Water Treatment, **57**, 21286–21293 (2016).
https://doi.org/10.1080/19443994.2015.1123194

[17] Huang Y-H., Chen M. H-C., Lee B-H., Hsieh K-H., Tu Y-K., Lin J-J., Chang C-H.: Evenly distributed thin-film Ag coating on stainless plate by tricomponent Ag/silicate/PU with antimicrobial and biocompatible properties. ACS Applied Materials and Interfaces, **6**, 20324–20333 (2014).
https://doi.org/10.1021/am5057213

[18] Sportelli M., Picca R., Ronco R., Bonerba E., Tantillo G., Pollini M., Sannino A., Valentini A., Cataldi T. R. I., Cioffi N.: Investigation of industrial polyurethane foams modified with antimicrobial copper nanoparticles. Materials, **9**, 544/1–544/13 (2016).
https://doi.org/10.3390/ma9070544

[19] Ashjari H. R., Dorraji M S. S., Fakhrzadeh V., Eslami H., Rasoulifard M. H., Rastgouy-Houjaghan M., Gholizadeh P., Kafil H. S.: Starch-based polyurethane/CuO nanocomposite foam: Antibacterial effects for infection control. International Journal of Biological Macromolecules, **111**, 1076–1082 (2018).
https://doi.org/10.1016/j.ijbiomac.2018.01.137

[20] Kasi G., Viswanathan K., Sadeghi K., Seo J.: Optical, thermal, and structural properties of polyurethane in Mg-doped zinc oxide nanoparticles for antibacterial activity. Progress in Organic Coatings, **133**, 309–315 (2019).
https://doi.org/10.1016/j.porgcoat.2019.04.066

[21] Dorraji M. S. S., Ashjari H. R., Rasoulifard M. H., Rastgouy-Houjaghan M.: Polyurethane foam-cadmium sulfide nanocomposite with open cell structure: Dye removal and antibacterial applications. Korean Journal of Chemical Engineering, **34**, 547–554 (2017).
https://doi.org/10.1007/s11814-016-0261-9

[22] Koohsaryan E., Anbia M.: Nanosized and hierarchical zeolites: A short review. Chinese Journal of Catalysis, **37**, 447–467 (2016).
https://doi.org/10.1016/S1872-2067(15)61038-5

[23] Król M.: Natural *vs*. synthetic zeolites. Crystals, **10**, 622/1–622/8 (2020).
https://doi.org/10.3390/cryst10070622

[24] Okuyama T., Kamimura Y., Yasunaga K.: Process for producing antibacterial flexible polyurethane foam. U.S. Patent 4,937,273, USA (1990).
[25] Wu Z., Goel S., Choi M., Iglesia E.: Hydrothermal synthesis of LTA-encapsulated metal clusters and consequences for catalyst stability, reactivity, and selectivity. Journal of Catalysis, **311**, 458–468 (2014). https://doi.org/10.1016/j.jcat.2013.12.021
[26] Almasoud F. I., Al-Farraj A. S., Al-Wabel M. I., Usman A. R. A., Alanazi Y. J., Ababneh Z. Q.: The potential use of zeolite, montmorillonite, and biochar for the removal of radium-226 from aqueous solutions and contaminated groundwater. Processes, **8**, 1537/1–1537/15 (2020). https://doi.org/10.3390/pr8121537
[27] Chmielewská E.: Natural zeolite: Alternative adsorbent in purification or post-treatment of waters. in 'Modified clay and zeolite nanocomposite materials' (eds.: Mercurio M., Sarkar B., Langella A.) Elsevier, Amsterdam, 87–112 (2019). https://doi.org/10.1016/B978-0-12-814617-0.00012-8
[28] Grigorev M. F., Sidorov A. A., Grigoreva A. I., Sysolyatina V. V: Studying the metabolism of horses when feeding them zeolite-sapropel feed additives in the conditions of Yakutia. IOP Conference Series: Earth and Environmental Science, **548**, 042008/1–042008/6 (2020). https://doi.org/10.1088/1755-1315/548/4/042008
[29] Nadziakiewicza M., Kehoe S., Micek P.: Physico-chemical properties of clay minerals and their use as a health promoting feed additive. Animals, **9**, 714/1–714/15 (2019). https://doi.org/10.3390/ani9100714
[30] Feng N-Q., Peng G-F.: Applications of natural zeolite to construction and building materials in China. Construction and Building Materials, **19**, 579–584 (2005). https://doi.org/10.1016/j.conbuildmat.2005.01.013
[31] Korshed P., Li L., Ngo D-T., Wang T.: Effect of storage conditions on the long-term stability of bactericidal effects for laser generated silver nanoparticles. Nanomaterials, **8**, 218/1–218/12 (2018). https://doi.org/10.3390/nano8040218
[32] Izak-Nau E., Huk A., Reidy B., Uggerud H., Vadset M., Eiden S., Voetz M., Himly M., Duschl A., Dusinska M., Lynch I.: Impact of storage conditions and storage time on silver nanoparticles' physicochemical properties and implications for their biological effects. RSC Advances, **5**, 84172–84185 (2015). https://doi.org/10.1039/C5RA10187E
[33] Blatny J. M., Brautaset T., Winther-Larsen H. C., Haugan K., Valla S.: Construction and use of a versatile set of broad-host-range cloning and expression vectors based on the RK2 replicon. Applied and environmental microbiology, **63**, 370–379 (1997). https://doi.org/10.1128/AEM.63.2.370-379.1997
[34] Namviriyachote N., Muangman P., Chinaroonchai K., Chuntrasakul C., Ritthidej G. C.: Polyurethane-biomacromolecule combined foam dressing containing asiaticoside: Fabrication, characterization and clinical efficacy for traumatic dermal wound treatment. International Journal of Biological Macromolecules, **143**, 510–520 (2020). https://doi.org/10.1016/j.ijbiomac.2019.10.166
[35] Morena A. G., Stefanov I., Ivanova K., Pérez-Rafael S., Sánchez-Soto M., Tzanov T.: Antibacterial polyurethane foams with incorporated lignin-capped silver nanoparticles for chronic wound treatment. Industrial and Engineering Chemistry Research, **59**, 4504–4514 (2020). https://doi.org/10.1021/acs.iecr.9b06362
[36] Domènech B., Ziegler K., Vigués N., Olszewski W., Marini C., Mas J., Muñoz M., Muraviev D. N., Macanás J.: Polyurethane foams doped with stable silver nanoparticles as bactericidal and catalytic materials for the effective treatment of water. New Journal of Chemistry, **40**, 3716–3725 (2016). https://doi.org/10.1039/C5NJ03202D