Characterization of the surface and mechanical behavior of polyurethane microporous films doped with silver nanoparticles

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Abstract: The aim of this study was to investigate the effects of silver nanoparticles (Ag-NPs) concentration on surface of polyurethane microporous films. The Ag-NPs have a diameter between 1.74-10 nm and were synthesized in the polymer matrix. The effects of Ag-NPs at the surface of polyurethane (PU) microporous films were investigated by means of attenuated total reflection Fourier infrared (ATR-FTIR) spectroscopy, atomic force microscopy (AFM) and contact angle measurements. The mechanical behavior of PU films vs Ag-NPs concentration was also studied. The Ag-NPs induce changes in the PU surface structure, wettability properties, topography and mechanical properties. These phenomena may be due to interactions between Ag-NPs and urethane groups which form new structure urethane-silver-urethane with a specific morphology and the nanostructuring of the surface by means of metallic nanoparticles.

Introduction

Polyurethanes represent a wide class of polymers with multiple applications like foams, rubbers, synthetic leather, coatings, fibers and biomaterials [1-3]. These multiple applications are due to their excellent chemical resistance, good resistance to ozone and oxygen, high tensile, shear strength, high elasticity and flexibility, good biocompatibility. Also, the PU can be made in a variety of forms like film, foam, hydrogel, hydrocolloid and with different properties by varying the type of monomers and adding other compounds.

Silver is one of the non toxic metals used in nanoparticles or ionic form with different materials due to its good antimicrobial properties [4]. Thus silver nanoparticles are used in combination with antibiotics to enhance antibacterial effect [5], in textile fiber to prevent odour or infection with pathogenic bacteria [6,7], to coat PU foams for antibacterial water filter [8] or facemasks to protect against infectious agents [9]. The antibacterial effects of Ag-NPs depend on the total surface area of the nanoparticles. Smaller particles (<10 nm) have a larger surface to volume ratio and are more efficient for antibacterial activity. Also the Ag-NPs have an enhanced antibacterial effect at low concentrations. For example a concentration below 8 μg Ag-NPs/cm² at the surface is sufficient to be completely cytotoxic to *Escherichia coli* [10].

Ag-NPs synthesized in the polymer matrix produce changes in the polymer surface structure and therefore in surface properties. The mechanical behavior of polymer is

also changed [11]. For materials used in biomedical application surface properties are very important because the surface is in contact with the living tissue. For this reason, in this paper we studied the influence of the Ag-NPs over the PU surface structure and properties. Also, we analyzed the mechanical behavior of the PU microporous films vs. Ag-NPs concentration.

Results and discussion

ATR-FTIR spectra

The surface of PU samples with different Ag-NPs concentrations (a control sample without Ag (M) and samples with concentrations of 9.71 (P₁), 44.68 (P₂), 69.11 (P₃) and 97.28 (P₄) ppm Ag-NPs, respectively) was characterized using ATR-FTIR spectroscopy. The characteristic bands for the M and P₁-P₄ samples for the range 3450-700 cm⁻¹, are shown in Figure 1. One may observe from the Figure 1 that there are no new bands, nor some significant displacements of the peaks, due to the nanometric Ag in different concentrations.

Fig. 1. ATR-FTIR spectra of PU sample M, P1 – P4 between 3450-700 cm⁻¹.

However, there are changes of the spectral band surfaces. Thus, the area of the stretch vibration band of the bonded NH group, $\nu(\text{N-H})$, from 3331 cm⁻¹ decreases, while the area of the stretch vibration band $\nu(\text{CH}_2)$, in the range 3010-2820 cm⁻¹, increases with the increase of the Ag-NPs concentration (Figure 2); this phenomenon was also observed in the case of another metal [12]. One may also observe changes in the ratio of the bands specific for the carbonyl group in the range 1770-1640 cm⁻¹. As the Ag-NPs concentration in the PU matrix increases, the stretch band at 1704 cm⁻¹, specific for CO from the urethane groups associated through hydrogen bonds in hard domains, decreases, while band at 1728 cm⁻¹, specific for CO in the free, disordered urethane groups, increases [13-15].

Fig. 2. Modifications of normalized ratio between areas of the stretch vibration bands of CH₂ (2820-3010 cm⁻¹) and NH (3235-3420 cm⁻¹) vs. Ag-NPs concentration.

Fig. 3. The steric conformation change for the urethane groups at the PU surface, due to their interaction with Ag⁰.

The same phenomenon is observed in the bands ν_{sim} (C-O-C), associated with the urethane structure placed upon the ester ones, where the absorption band at 1134 cm^{-1} increases, while that band at 1169 cm^{-1} decreases with the increase of the Ag-NPs concentration. The weak band at 1018 cm^{-1} , characteristic for ν_{sim} (C-O-C), associated with the ester structure, becomes a very weak shoulder for the samples P₃ and P₄ (Figure 1).

The above mentioned phenomena might be explained if we consider that the urethane group has four different steric conformations: *cis-cis*, *trans-trans*, *cis-trans* and *trans-cis* [16]. Thus, at the surface of the polyurethane matrix, one may have these conformations in different molar ratios. By introducing the nanometric silver into PU, new urethane-Ag-urethane structures will be formed at its surface, which modify the molar ratio and the steric conformation of the urethane structures (Figure 3).

This might be possible because the zero valence Ag may react with the p electrons of the nitrogen and oxygen from the urethane structure (-HN-CO-O-) as one has observed in the case of the polyvinyl pyrrolidone where Ag⁰ forms associations with the p electrons of the =N-CO- structure [17].

AFM Studies

The topography and roughness of the PU surface were studied by AFM. The AFM $z(x,y)$ images were used in order to estimate the root mean square roughness, R_{rms} . The root mean square roughness of the surface was calculated according to the formula:

$$R_{\text{rms}} = \sqrt{\frac{\sum_{n=1}^N (z_n - \mu)^2}{N}} \quad (1)$$

where: N - the number of data points of the image; z_n - height data of the n-th point; μ - average height.

The root mean square roughness of the PU surface, R_{rms} , decreases with the increase of the concentration of Ag-NPs, which shows that the Ag-NPs presence into the polymer matrix has the effect of smoothing the PU samples surface (Table 1). The roughness reduction according to the increase of the Ag-NPs concentration is attributed to the modification of the urethane clusters morphology, passing from the cylindrical and spherical geometry [14] to plane structures, where the urethane groups react with the Ag-NPs, leading to plane organized forms [13].

Tab. 1. The root mean square roughness, R_{rms} , of the PU samples.

Sample	M	P ₁	P ₂	P ₃	P ₄
R_{rms} (nm)	104.65	103.65	85.70	75.21	62.36

Ag⁰ has a contribution to the modification of the surface topography. This phenomenon is very well emphasized from the AFM images in the surface topography (Figure 4). One may also notice the micropores at the PU surface, for all the samples in Figure 4.

Fig. 4. AFM images of microporous surface PU: a) M; b) P₁; c) P₂; d) P₃; e) P₄.

Static contact angle and surface energy of PU

The PU surface wettability was evaluated by measuring the static contact angle (sessile drop method) of the bidistilled and deionized water on the surface. As liquids for the calculation of the PU surface energy, we used bidistilled and deionized water and pure ethylene glycol. The surface energetic characteristics of the liquids used for measurement are presented in Table 2. The relation between the contact angle and the interfacial tension solid-liquid γ_{SL} , liquid-vapors γ_{LV} and solid-vapors γ_{SV} , is given by Young equation [18]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (2)$$

One may separate γ_{LV} and γ_{SV} into two interaction components: a disperse one, γ_{LV}^d , γ_{SV}^d representing the van der Waals interactions, and the polar one, γ_{LV}^p , γ_{SV}^p , representing the polar interactions between the dipoles of the molecules of the two mediums in contact. The interfacial solid-liquid tension may be obtained from the equation [19]:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\left(\sqrt{\gamma_{SV}^p \gamma_{LV}^p} + \sqrt{\gamma_{SV}^d \gamma_{LV}^d}\right) \quad (3)$$

From the equations (2) and (3) results:

$$\gamma_{LV}(1 + \cos \theta) = 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p} + 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} \quad (4)$$

The surface energy is sum of its components:

$$\gamma_{SV} = \gamma_{SV}^p + \gamma_{SV}^d \quad (5)$$

The PU surface energy γ_{SV} and its components (polar γ_{SV}^p and disperse γ_{SV}^d) have been determined from the equations (4) and (5), using the values of the contact angle measured for two different liquids.

The values of the contact angle of the water with the PU surface and the PU surface energy are shown in Table 3.

Tab. 2. Components of the surface energy of the liquids used for testing the polymer surface and interface properties [20].

Liquid	γ_{LV}^p (mN/m)	γ_{LV}^d (mN/m)	γ_{LV} (mN/m)
Water	51	21.8	72.8
Ethylene glycol	19	29	48

Tab. 3. Water contact angle θ and surface energy γ_{SV} (polar component γ_{SV}^p , disperse component γ_{SV}^d) of PU.

Sample	θ (°)	γ_{SV}^p (mN/m)	γ_{SV}^d (mN/m)	γ_{SV} (mN/m)
M	71.61	25.56	6.39	31.95
P ₁	70.75	22.95	9.28	32.23
P ₂	54.61	42.06	5.75	47.81
P ₃	73.50	24.17	6.23	30.40
P ₄	84.40	19.72	21.32	41.04

From Table 3 one may notice that the water contact angle decreases at M, P₁ and P₂, while it begins to grow with P₃, arriving at P₄ to be almost 13° bigger than M. Thus, for the samples M, P₁ and P₂ the surface wettability increases, while for the samples P₃, P₄ it decreases with the increasing of Ag-NPs concentration. This might be explained considering that Ag-NPs, for concentrations below 45 ppm, is reacting first with urethane structures bonded to the ester chain, which are not organized in clusters. Generally, these are forming hydrogen bonds with –COO– groups from the ester chain and may react easier with Ag-NPs, forming urethane-Ag structures, which enrich the PU surface with C=O groups, capable to form hydrogen bonds with the water. As the Ag-NPs concentration grows, the –NHCOO– groups start to consume in

the arranged clusters urethane-urethane, forming the urethane-Ag-urethane structures; these structures lead to the reduction of the molar concentration of the polar C=O groups on the PU surface, together with the increase of its hydrophobic behavior and thus, the increase of the contact angle with the water.

The surface energy γ_{SV} is generally bigger for the P₁-P₄ samples, in comparison with M. Thus, for the P₂ and P₄ samples, the surface energy is 15.86, 10.09 mN/m respectively bigger than for M. Meanwhile, the dispersed surface energy compound γ_{SV}^d , given by the Van der Waals forces and the induced dipoles, increases at P₄ with 14.93 mN/m in comparison with M, and it overtakes the polar compound γ_{SV}^p with 1.6 mN/m. These results might suggest that Ag-NPs increase the surface energy of the polyurethane, while the urethane-Ag-urethane structures are more hydrophobic, and easily form induced dipoles.

Mechanical analysis

By analyzing the stress-strain curves (σ - ε) in the elastic domain (0.1 – 2 % elongation) for the M and P₁-P₄ samples, one may notice a change of these, according to the Ag-NPs concentration in the PU matrix. Thus, the PU material's capacity of absorbing internal work in the volume unity in the elastic domain (elastic resilience U_e) decreases when Ag-NPs concentration increase (with 68% at the P₄ than M). Also, as the Ag-NPs concentration grows, the PU material becomes softer, the initial elasticity module (E_i) decreases becoming 68% low at the P₄ than M (Table 4). These results suggest that Ag-NPs interact with the PU macromolecules to form new structures, with weaker inter- and intramolecular bonds.

The initial elasticity module (E_i) was obtained from the equation [21]:

$$E_i = \frac{\sigma_e}{\varepsilon} \quad (6)$$

where: σ_e – stress; ε - strain.

The elastic resilience (U_e) was obtained from the equation:

$$U_e = \sigma_e \cdot \ln(1 + \varepsilon) \quad (7)$$

Tab. 4. Elastic resilience (U_e) and initial elasticity module (E_i) of the PU films.

Sample	Elastic resilience (U_e), MPa	Initial elasticity module (E_i), MPa
M	1.50	23.79
P ₁	1.10	16.83
P ₂	1.04	9.76
P ₃	0.74	9.00
P ₄	0.64	7.63

Conclusions

The Ag-NPs have a dramatic action upon the polyurethane structure, as they interact with the –NHCOO- groups bonded to the ester chain, and from the regular urethane-urethane clusters, forming new structures Ag-urethane and urethane-Ag-urethane,

thus modifying the morphology, wettability, surface energy and the topography of the polyurethane matrix surface.

Ag-NPs modify the polyurethane matrix, determining it to absorb a smaller amount of mechanical work. Thus, both the elastic resilience and the initial module becomes smaller, and the polymer becomes softer and less tough.

Experimental part

Materials and samples preparation

The polyurethane (PU) was synthesized from poly(ethylene adipate)diol (PEA) with a molecular mass of 2000 Da, the hydroxyl number 56 mg KOH/g, the acidity number 0.2 mg KOH/g, 4,4'-diisocyanate of diphenyl methane (MDI), freshly distilled, with a concentration in isocyanate of 99.96%, 1,4-buthane diol (BD)> 99% (Sigma-Aldrich) anhydrous and dimethylformamide (DMF)>99.8% anhydrous (Sigma –Aldrich). The synthesis was performed through the prepolymer procedure at 60°C, according to a previous method [22]. The molar ratio between the compounds is PEA:MDI:BG = 1:6:5, the concentration of the solution PU-DMF is 35% dry substance, the viscosity is 80,000 cP at 20°C (by the Brookfield viscosimeter, rotor number 4). The molar mass for PU was 112,000 Da (gel chromatography). Elements analysis: calculated C 60.53%, H 8.49%, N 4.33%; found: C 60.18%, 60.45%; H 8.37%, 8.46%; N 4.55%, 4.61%. The general structure of the PU is shown in Scheme 1.

Molar ratio x:y 1:5 (H – NMR); Moles urethane/1000 g = 3.27.

Scheme 1. The PU molecular structure.

The Ag-NPs were synthesized with sodium borohydrate, in the polymer matrix, according to a known method [23]. The diameter of the nanoparticles was estimated with a Zetasizer device. From the histogram obtained with the Zetasizer device (Figure 5) [13], one can observe that the nanoparticles have a diameter between 1.74-10 nm. The biggest part of the nanoparticles has a diameter between 4-5 nm.

The Ag-NPs concentration in PU was determined by UV-VIS spectroscopy in DMF solution, from a etalon curve. We used a Spectrophotometer of 6505 UV/VIS type (made in England), with computerized data processing.

The microporous films of PU and PU-Ag⁰ were realized through phase inversion in distilled and deionized water at 45 °C, according to the previous data [22, 24].

We realized five types of microporous films: a control sample without Ag (M) and samples with concentrations of 9.71 (P₁), 44.68 (P₂), 69.11 (P₃) and 97.28 (P₄) ppm Ag-NPs, respectively. Ag-NPs concentration is the same in bulk and in the interfacial layer, certified by the ATR FTIR spectra which are the same at surface and in transversal section of PU film.

Fig. 5. Granulometric distribution of Ag-NPs in the PU matrix.

Measurements

ATR-FTIR analysis were done using a **Bruker** Vertex 70 (U.S.) apparatus, having a diamond crystal with 6 mm² of surface. The samples' surface was scanned by an optical radiation in the range of 600-4000 cm⁻¹, under an incidence angle of 45°.

The AFM measurements were carried in the half-contact mode on a SPM Solver PRO-M Russia device, with a cantilever NSG10, at the room temperature 25 °C and at normal atmospheric pressure. The cantilever is rectangular, with a peak height of 10-15 μm, curvature radius of 10 nm and the cone angle $\theta \leq 22^\circ$. The topography and phase were simultaneously registered for each sample on surfaces of 10 μm x 10 μm. The AFM measurements were repeated for different places on the samples, in order to verify the results reproducibility.

The static contact angle measurements were performed through the sessile drop method, with an apparatus KSV CAM 101 (KSV Instruments, Helsinki, Finland). The values of the static contact angle presented were the average of minimum ten measured values obtained on the image of liquid drop profile, for 1±0.1 μl drop size. The maximum error in the contact angle measuring was under 3%.

The mechanical tests were performed on a TIRA test 2161 apparatus (Germany). The sample was strained at the room temperature 25 °C, with a speed of 10 mm/min.

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