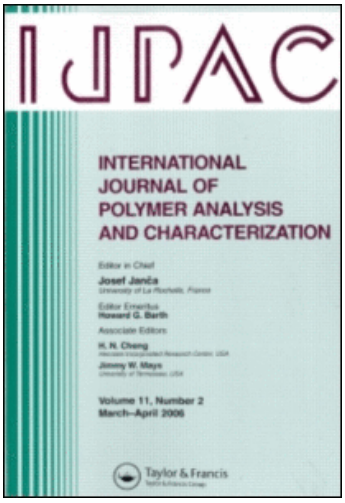

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Characterization of Antibacterial, Mechanical, and Structural Properties of Polyvinyl Chloride/Silver Nitrate Composites Prepared by Thermoplastic Compounding

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CHARACTERIZATION OF ANTIBACTERIAL, MECHANICAL, AND STRUCTURAL PROPERTIES OF POLYVINYL CHLORIDE/SILVER NITRATE COMPOSITES PREPARED BY THERMOPLASTIC COMPOUNDING

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Polyvinyl chloride/silver nitrate composites were prepared by thermoplastic compounding. Antibacterial activity against gram-negative and gram-positive bacteria was determined by agar diffusion test. X-ray diffraction, X-ray photoelectron spectroscopy, and optical microscopy analyses were carried out to determine the effect of polyvinyl chloride modification on structural properties. The mechanical characteristics of prepared films were observed using stress-strain analysis. The results revealed that final composites exhibit sufficient antibacterial properties against tested bacteria, with nonuniform distribution of silver particles in the PVC matrix, which caused a decrease in mechanical properties. X-ray characterization proved the presence of the modifier, mostly in Ag^+ form.

Keywords: Antibacterial activity; Mechanical properties; Polyvinyl chloride; Silver nitrate; Structural properties; Surface characterization; Thermoplastic compounding

INTRODUCTION

Polymers, due to their good mechanical properties, easy high-temperature processability, and low cost, are widely used in the area of biomedical devices and food packaging.[1] However, these materials do not possess either bacteriostatic or bactericidal properties in their bulk state to resist colonization by microorganisms like

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bacteria, molds, and yeasts. This can lead to the formation of biofilms, which are defined as the sessile communities irreversibly attached to a substratum and embedded in a matrix of extracellular polymer substances produced by bacteria themselves.[2–7] In health facilities, biofilms are the source of serious biomedical device–related infections, such as bacterial contaminations in intravascular, urinary, bloodstream catheters, and medical prostheses,[5,8–10] periodontitis,[11] and ventilator-associated pneumonia,[12] among others that cause an increase in morbidity and mortality rate as well as health costs.[13,14]

To avoid biofilm formation in medical devices, several inorganic and organic substances have been applied to the polymer matrix. Concerning inorganic anti-infective agents, silver ions (Ag^+) have been evaluated as a powerful substance for its strong bacteriostatic and bactericidal activity.[4,15–17] In addition, the effectiveness of the silver cations' action and the growing resistance of multi-resistant microbes against antibiotics mean that silver and its compounds are receiving attention for medical use. For instance, one important approach has been to coat the external and internal surfaces of bladder catheters with silver and silver oxide including silver hydrogel, which significantly reduced the rate of catheter-associated bacteria.[2,9,18,23] Likewise, medical devices coated with silver sulfadiazine, silver nitrate, and silver chloride including benzalkonium chloride and/or chlorhexidine have been broadly proved against several pathogens by in vitro studies.[2,5,9,19] Also silver-doped phosphate-based glasses act as a system for delivery of silver ions to help control urinary tract infections in patients needing long-term indwelling catheters and wound dressing.[4]

Among the different methods adopted for the silver incorporation into polymers, melt mixing is convenient as it can provide silver ions on a long term-basis. Thermoplastic polymer composites including silver combine excellent high-temperature processability of the thermoplastics with the inherent antimicrobial property of the silver. Silver-based antimicrobials capture attention not only because of the nontoxicity of the active Ag^+ to human cells but because of their novelty as a long-lasting biocide with high-temperature stability and low volatility.[20] The melt blending technique has been broadly used for preparation of antibacterial polymer materials,[21,22,24] permitting high uniform distribution of the antibacterial agent through the polymeric matrix.

Following these developments, in this work medical-grade polyvinyl chloride (PVC) was compounded with silver nitrate in a kneader. The effect of the modification on final antibacterial, mechanical, and structural properties of prepared composites was studied.

MATERIALS AND METHODS

Materials

Medical-grade thermoplastic plasticized polyvinyl chloride RB1 (PVC) with a density of 1.23 g/mL was purchased from Modenplast (Italy). Silver nitrate ($AgNO_3$) was obtained from Penta (Czech Republic). Bacterial strains *Escherichia coli* 3954, *Staphylococcus aureus* 3953, *Klebsiella pneumonie* 4415, and *Pseudomonas aeruginosa* 3955 were supplied by Czech Collection of Microorganisms (Czech Republic).

Methods

Sample preparation. The compounding was performed in a Brabender Plasti-coder kneader at 160°C at the rotor speed of 30 rpm. The volume of the chamber was 50 cm^3. After the complete PVC melting, the addition of silver nitrate followed, and the mixing continued until the attainment of a steady torque. The PVC control sample was prepared through the previous procedure without $AgNO_3$ incorporation. The total mixing time was 10 min. The obtained samples were then compression molded at 160°C for 5 min in a manual press into thin films (1 mm thickness) and subsequently cooled under the pressure of 10 MPa. The compositions and designations of the investigated samples are shown in Table I.

***In vitro* antibacterial activity.** Prepared PVC/Ag composites were cut to round samples (8 mm in diameter). Their antibacterial activity was investigated by an agar diffusion test. Bacteriological solutions of *Escherichia coli* 3954, *Staphylococcus aureus* 3953, *Klebsiella pneumoniae* 4415, and *Pseudomonas aeruginosa* 3955 (concentrations about 1.0×10^8 cfu. mL^{-1}) were prepared and uniformly swabbed onto a nutrient agar plate. PVC/Ag round samples were placed on a petri dish (three samples of each concentration) and incubated at 37°C. After 24 h, the diameters of inhibitions zones in mm were measured around the samples in four directions, from which the average values were calculated.

Mechanical properties. The mechanical properties of prepared PVC/Ag composites were studied on a tensile testing machine T2000 (Alpha Technologies) at 25°C according to the standard ČSN EN 527 1–3. The speed of the moving clamp was 100 $mm.min^{-1}$. Tensile modulus, tensile stress, and tensile strain were determined parameters. Ten specimens (initial length 80 mm, width 15 mm) were tested in each case.

Surface characterization and morphology. The surface properties were analyzed by X-ray photoelectron spectroscopy (XPS) on TFA XPS Physical Electronics equipment by exciting the sample under a reduced pressure 6×10^{-8} Pa with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. Survey-scan spectra were made at the pass energy of 187.85 eV and 0.4 eV energy step. An electron gun was used for surface neutralization. The concentration of elements was determined by using MultiPak v7.3.1 software from Physical Electronics, which was supplied with the spectrometer.

Table I. Designation and compositions of the samples

Sample designation	Concentration of $AgNO_3$ (wt.%)	*Recalculated Ag content (wt.%)*
PVC	0	0
PVC/Ag0.5	0.79	0.5
PVC/Ag1	1.57	1
PVC/Ag2	3.15	2
PVC/Ag3	4.72	3
PVC/Ag4	6.30	4
PVC/Ag5	7.87	5

X-ray diffraction (XRD) measurements were carried out on an X'pert PRO diffractometer equipped with a rotation anode using Cu Kα radiation. Radial scans of intensity versus diffraction angle 2θ were recorded in the range of 20–90° at ambient temperature.

Optical micrographs were taken by an STM microscope and stereoscope in the reflectance mode, equipped with a DCM 310 USB camera set with the software ScopePhoto.

RESULTS AND DISCUSSION

In Vitro Antibacterial Activity

Data related to the diameters of inhibition zones of bacterial growth against *Escherichia coli* 3954, *Staphylococcus aureus* 3953, *Klebsiella pneumoniae* 4415, and *Pseudomonas aeruginosa* 3955 are reported in Figure 1.

Unmodified PVC did not show any inhibition zone. On the other hand, the effectiveness of all prepared samples was observed to be significant against most of the tested bacterial strains even at the lowest Ag concentration (0.5 wt.%). The exception is *Escherichia coli*, which remains resistant up to 2 wt.% of silver. Gram-positive *Staphylococcus aureus*—the most commonly occurring strain in nosocomial infections—was evaluated as the most sensitive because the maximum inhibition zone (about 24 mm) was reached at only 3 wt.% Ag addition. The results published by Galya et al.[16] who evaluated the antibacterial activity of poly(vinyl alcohol) films containing $AgNO_3$, show comparable antibacterial action against both *Escherichia coli* and *Staphylococcus aureus*. This result could be attributed to the difference in the polymeric matrix used as well as the procedure of sample preparation,

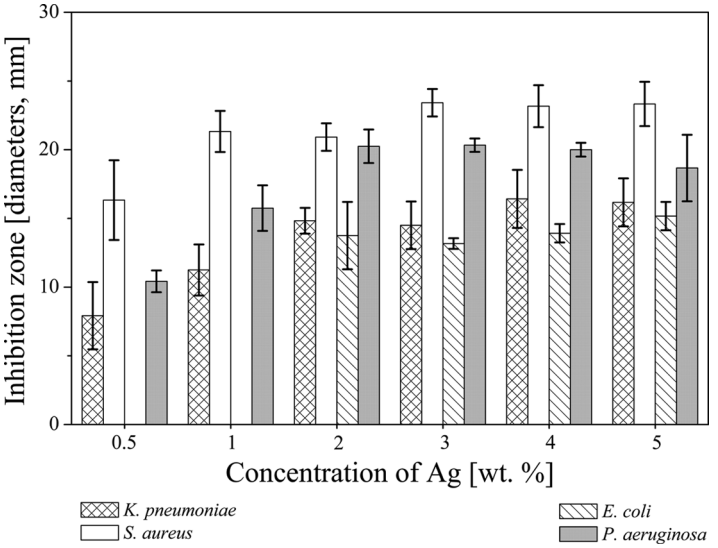

Figure 1. Antibacterial activity of PVC/Ag composites against *Escherichia coli, Staphylococcus aureus, Klebsiella pneumoniae*, and *Pseudomonas aeruginosa*. Error bars represent standard deviations.

which influences the mass of the released antibacterial agent into the surrounding environment significantly. However, in the case of *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*, which are also gram-negative bacteria with various cell wall structure complexities, relevant inhibitory growth also occurred from the lowest tested sample concentration.

Mechanical Properties

E modulus, tensile strain, and tensile stress were measured to characterize the changes in mechanical properties resulting from PVC modification with $AgNO_3$ (Table II). It is clear that $AgNO_3$ addition into the PVC matrix had a significant effect on all the tested tensile parameters when compared to unmodified PVC. The value of E modulus dropped off from 0.98 MPa (measured for pure PVC) to 0.65 MPa for PVC/Ag5 composite, which represents about 34%. A similar trend was observed in tensile strain and tensile stress, when $AgNO_3$ addition caused a decrease in value from 352% to 203% (a decrease of 43%) and from 19.6 to 10.5 MPa (a decrease of 46%), respectively. It can be seen that gradual changes occurred in PVC/Ag composites containing 0.5 to 3 wt.% of the modifier compared to unmodified PVC. After this concentration the values of all tested parameters more or less leveled off. It can be concluded that lower $AgNO_3$ loading results in a more apparent drop of mechanical properties.

A decrease in strength and toughness with the higher filler loading was also reported by Radheskumar and Münstedt,[25] who tested the composites of polyamide and elementary silver powder. The decrease in elongation and toughness with increasing modifier concentration shows the existence of weak structure in the composite. On the other hand, in systems of polyvinyl alcohol and $AgNO_3$, prepared by Galya et al.[16] the trend in the same tested parameters did not have such an unanimous character. Although the values of tensile modulus and strength decreased (after the first short increase up to 1 wt.% of modifier), the increasing trend of tensile strain was revealed with the higher $AgNO_3$ concentration in the system. The physicochemical character (hydrophobicity or hydrophilicity) of the polymer matrix (PVC) and the modifier ($AgNO_3$) has a significant influence on the final mechanical properties of the modified systems. Generally, in metal-filled polymer composites sharp metal particles tend to create cavities due to the debonding of the polymer from

Table II. Mechanical properties of prepared PVC/Ag composites (mean/standard deviation)

Sample	E modulus [MPa]	Tensile strain [%]	*Tensile stress [MPa]*
PVC	0.98/0.17	352/11	19.6/0.8
PVC/Ag0.5	0.82/0.13	301/8	16.6/1.2
PVC/Ag1	0.75/0.07	266/13	14.1/1.0
PVC/Ag2	0.62/0.10	246/13	12.7/1.5
PVC/Ag3	0.57/0.16	208/7	10.3/2.1
PVC/Ag4	0.59/0.08	205/21	10.5/1.8
PVC/Ag5	0.65/0.09	203/9	10.5/1.7

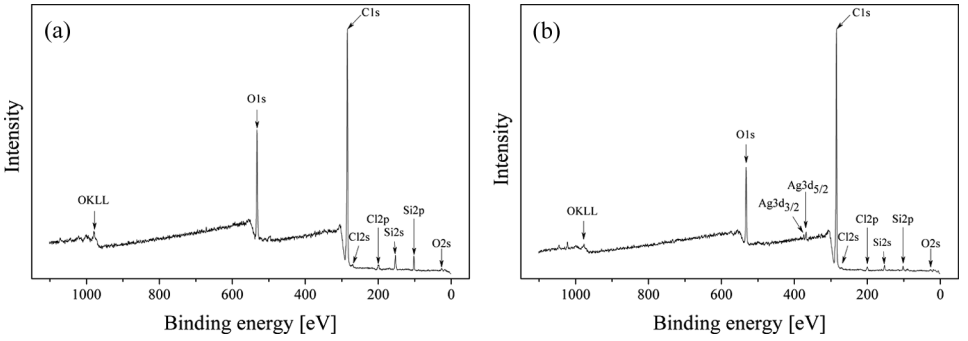

Figure 2. XPS spectra of pure PVC (a) and PVC/Ag5 composite (b).

the modifier surface.[26] This PVC structure disruption caused by $AgNO_3$ modification was also confirmed by the morphological studies discussed below.

Surface Characterization and Morphology

All the prepared PVC/Ag composites (containing 0.5 to 5 wt.% of Ag) were analyzed by X-ray photoelectron spectroscopy to characterize the changes in surface chemistry after the modification with silver. It showed that only the PVC/Ag5 sample proved the presence of silver on its surface. The corresponding spectra and surface composition of the pure PVC and PVC/Ag5 are shown in Figure 2 and Table III, respectively. The obtained XPS spectra are typical for polymeric substrates.[27–29] Besides expected elements occurring in PVC (C, O, Cl), the presence of Si was observed in XPS spectra. This is common in matrixes designed for thermoplastic properties since Si (SiO_2 in low concentrations) has been known to improve processability of the polymers. The detailed XPS spectra of PVC/Ag5 (Figure 3) show two peaks at 374.2 eV and 367.7 eV, corresponding to $3d_{3/2}$ and $3d_{5/2}$ of silver, respectively. The positions reveal a possible occurrence of silver in both Ag^0 and Ag^+ forms. Since the peak at 368.2 has been reported for $3d_{5/2}$ of metallic silver, the negative shift in binding energy can indicate the increasing oxidation state of silver.

XRD spectra of pure PVC (a) and PVC/Ag5 (b) are shown in Figure 4. No peak of silver has been observed in the nontreated sample (a). The diffraction peaks of PVC/Ag5 composite at 27.9°, 29.5°, 32.3°, 38.1°, 46.3°, 54.9°, 57.6°, 67.4°, 74.6°, 76.8°, and 85.9° correspond to the crystals of silver in Ag^+ form (b). Mostly the peaks typical for AgCl were provided, which might be due to the dechlorination from the PVC during the melt mixing procedure. In addition, the occurrence of Ag_2O, generated during the compounding at the process temperature, and residual

Table III. Surface compositions of pure PVC and PVC/Ag5 (mean/standard deviation)

Sample	C1 s [%]	O1 s [%]	Si2p [%]	Cl2p [%]	*Ag3d [%]*
PVC	79.4/2.0	15.4/1.9	4.3/0.2	0.9/0.1	–
PVC/Ag5	84.0/1.4	13.2/0.8	1.9/0.5	0.8/0.2	0.14/0.07

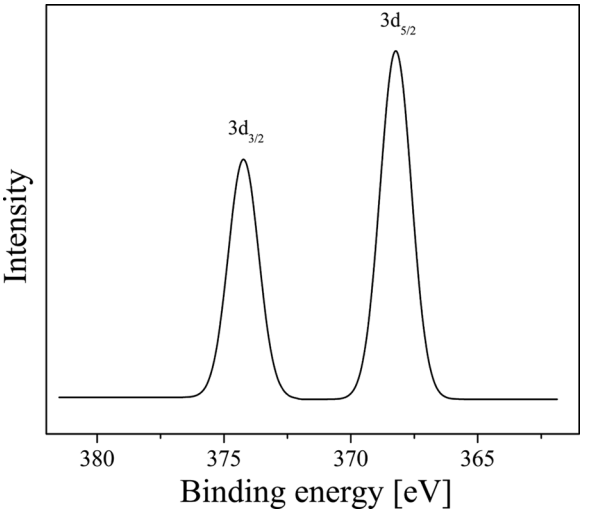

Figure 3. XPS spectra in 3d Ag band of PVC/Ag5 composite.

$AgNO_3$ can be assumed from the obtained results (the peaks at 38.1° and 29.5°, respectively). There is no clear evidence of metallic silver in PVC/Ag5 composite from XRD data.

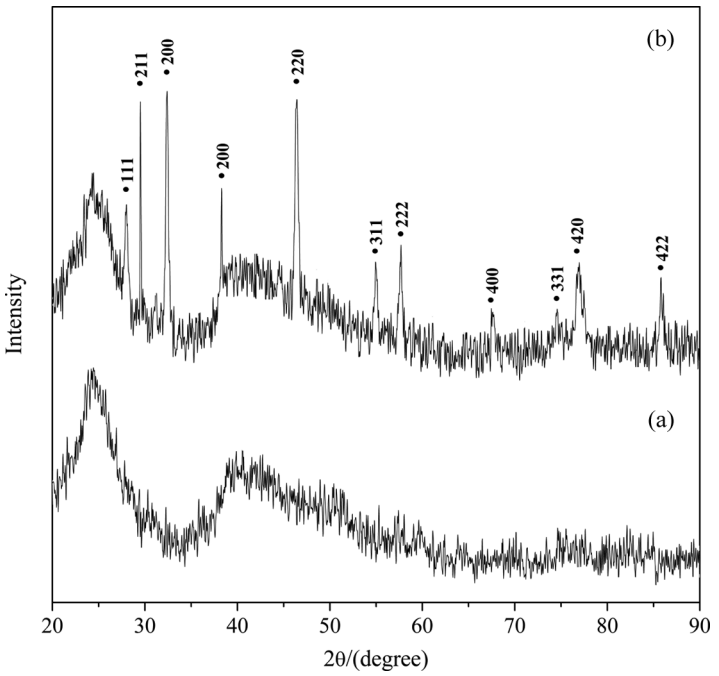

Figure 4. XRD spectra of pure PVC (a) and PVC/Ag5 composite (b).

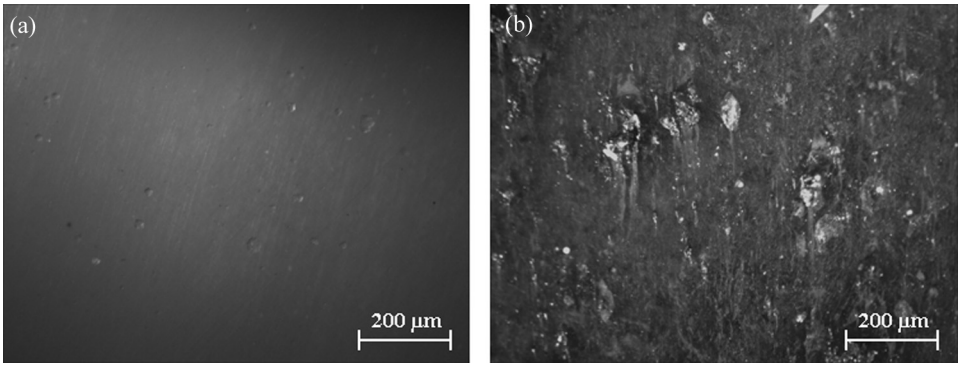

Figure 5. Optical micrographs of pure PVC (a) and PVC/Ag5 composite (b) (surface).

The optical pictures of pure PVC and PVC/Ag5 are depicted in Figure 5 to evaluate the changes in morphology caused by the modification with $AgNO_3$. The films of pure PVC were flat, colorless, and transparent in appearance, compared to the brownish color of prepared PVC/Ag composites, where the irregularly shaped crystals and agglomerates (size up to tens of micrometers) of silver were revealed (Figure 5(b)). A rather random distribution of Ag particles and their clusters was also provided by cross sections of the PVC/Ag5 sample (not shown here). This arrangement can be attributed to the different characters of PVC matrix and modifier with regard to hydrophilicity. It is also in accordance with the results of mechanical testing discussed above, where the decrease of all tested parameters caused by the disrupted structure was observed with increasing silver content in the PVC matrix.

The resulting nonhomogeneous structure of prepared PVC/Ag composites, however, did not negatively influence the antibacterial activity (as it was proved by the agar-diffusion test).

CONCLUSIONS

Composites based on polyvinyl chloride and silver nitrate were prepared by thermoplastic compounding. The aim of the work was to study the effect of modification with silver nitrate on the final antibacterial, mechanical, and structural properties.

The agar-diffusion test proved sufficient activity of PVC/Ag composites against both gram-positive and gram-negative tested bacterial strains. Even the lowest Ag concentration (0.5 wt.%) exhibited antibacterial effect.

The data from mechanical testing revealed a decrease of tensile properties (E modulus, tensile strain, and tensile stress) with increasing modifier concentration. These results were in accordance with the optical micrographs, since the nonuniform structure of silver agglomerates was revealed in prepared PVC/Ag composites.

X-ray observations revealed the presence of silver, mostly in Ag^+ form (chloride, oxide, nitrate). Nevertheless, no concentration of modifier on the surface was detected by XPS in the samples with Ag loading lower than 5 wt.% of recalculated silver content.

It can be concluded that the final mechanical and structural properties of prepared PVC/Ag composites significantly depend on the structure and nature of the polymer matrix and the modifier, as well as on the content and dispersion of silver particles.

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