Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

16: 1 (2016) 42-46

COMPOSITES THEORY AND PRACTICE

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Received (Otrzymano) 08.02.2016

STUDY OF MECHANICAL PROPERTIES OF POLYMER COMPOSITES CONTAINING SILVER NANOPARTICLES FOR MIDDLE EAR PROSTHESES

The aim of this study is to investigate the mechanical properties of polymeric composites prepared by means of extrusion and injection moulding. Three stable thermoplastic polymers (high density polyethylene, polysulphone and polyamide) were used as composite matrices. Antibacterial silver nanoparticles nAg were used as the modifying phase. The mechanical properties of the tested materials were determined during uniaxial stretching. Such parameters as Young's modulus *E*, tensile strength *Rm* and elongation at maximum force *εFmax* were measured. The results show that neither the preparation technology nor the amount of modifier impair the mechanical properties of the tested composites. The addition of silver nanoparticles does not cause a loss of strength, while it increases the Young's modulus of the materials.

Keywords: thermoplastic polymer, nanocomposites, nanosilver, mechanical properties.

BADANIA WŁAŚCIWOŚCI MECHANICZNYCH KOMPOZYTÓW POLIMEROWYCH ZAWIERAJĄCYCH NANOCZĄSTKI SREBRA PRZEZNACZONYCH NA PROTEZY UCHA ŚRODKOWEGO

Głównym celem pracy jest badanie właściwości mechanicznych kompozytów polimerowych otrzymanych w procesie wytłaczania i wtrysku. Do badań użyto trzech stabilnych polimerów termoplastycznych (polietylen o wysokiej gęstości, polisulfon i poliamid). Jako fazę modyfikującą zastosowano antybakteryjne nanocząstki srebra nAg. Właściwości mechaniczne materiałów zostały wyznaczone w próbie jednoosiowego rozciągania. Wyznaczono moduł Younga *E*, wytrzymałość na rozciąganie *Rm* i wydłużenie przy maksymalnej sile *εFmax*. Na podstawie otrzymanych wyników stwierdzono, że zaproponowana w pracy technologia otrzymywania materiałów, jak również ilość użytego modyfikatora nie pogarszają właściwości mechanicznych kompozytów. Dodatek nanosrebra nie powoduje obniżenia wytrzymałości, natomiast podnosi moduł Younga materiałów.

Słowa kluczowe: polimery termoplastyczne, nanokompozyty, nanosrebro, właściwości mechaniczne

INTRODUCTION

The key requirement of modern materials used for middle ear prostheses is optimal sound transmission that is influenced by numerous biological, acoustic and mechanical factors. High frequency sound transmission is affected by various parameters of the implant, such as its surface, stiffness, Young's modulus, Kirchhoff modulus, friction, density and weight [1-3]. The lightness of the structure depends partly on the type and size of the implant, but - first of all - on the material it is made of. The higher the specific gravity of the implant, the lower its high frequency sensitivity. Thus, in order to provide optimal high frequency transmission, middle ear implants should be as lightweight as possible [4].

Taking into account biological factors, the prosthesis material ought to be antibacterial and stable in the environment, especially in the case of chronic middle ear inflammation. Moreover, bacterial infections have profound consequences with respect to the patient's comfort and the costs of medicinal drugs. Research on the potential antibacterial properties and interaction between the material and bacterial walls has therefore become increasingly relevant [5]. Currently it is extremely important to apply an implant which is capable of fulfilling the assigned functions in the human body. Such a kind of implant should be safe, biocompatible and must not be toxic, mutagenic or cancerogenic. It is often expected that the material should be bioactive, bacteriostatic or even bactericidal. However, such medical devices may lead to postoperative complications like bacterial infections and biofilm formation, which may not always be eradicated by antibiotics [6, 7]. As increasing antibiotic resistance is a major medical issue, silver nanoparticles may be used due to their broad antimicrobial activity toward multiple species of microbes including multidrug-resistant bacteria and fungi. This makes them an invaluable alternative for traditional antibiotic treatment [8, 9].

As far as the mechanical properties are concerned, the middle ear implant should retain its shape and stable measurements for a prolonged period of time, along with tensile strength and rigidity. The materials used for middle ear prostheses ought to be resistant to live load and fatigue conditions. Additionally, middle ear implants have to enable micro-movements between the tympanic membrane and the middle ear. The presented work investigates how silver nanoparticles (nAg) affect the mechanical properties of various polymer composites.

MATERIALS AND METHODS

Polymeric materials and composites were obtained in the process of extrusion and injection moulding. Pure high density polyethylene HDPE (Basell Polyolefins), polysulphone PSU (Sigma-Aldrich) and polyamide PA (Basf) were used as the polymer matrices. Silver nanoparticles nAg (NanoAmor company) with a purity of 99.9%, 80 nm particle size and density of 10.49 g/cm^3 were applied as the modifying additive. The silver participation in the various compositions was respectively 1, 1.5 and 2% by weight. To ensure the optimal process conditions of the material fabrication, polymer granules were dried for two hours at 80°C. Then, using a vertical injection moulding machine with three heating zones (Multiplas), composite blends were prepared and homogenized. The process of homogenization was carried out in a dual cycle, in which the compositions were melted twice. The injection parameters were selected according to the manufacturer's recommendations and tailored to each composition.

The mechanical parameters were established during uniaxial stretching using the universal testing machine Zwick 1435 and intelligent testing software TestXpert 8.1. The tested samples were made of PSU, PA, HDPE polymers and the silver-modified composites and shaped as paddles. Six samples from each group of materials were tested. Their measurements are compliant with the PN-EN ISO 527-1 norm [10]. In order to perform the tensile strength test, the paddles were placed in the grips of the testing machine and tensile force F was applied. The measuring speed of the upper grip of the machine was 50 mm/minute and the measuring length of the paddles was 30 mm. The measuring accuracy of elongation was 0.01 mm, and of the force - 0.5 N with the nominal range of the cylinder - 5000 N. The obtained force-deformation graph made it possible to establish such parameters as Young's modulus E, tensile strength σ and elongation at maximum $\varepsilon Fmax$ force.

RESULTS AND DISCUSSION

Thanks to the static tensile tests, the following parameters were established: tensile strength Rm, Young's modulus E, elongation at maximum force $\varepsilon Fmax$, breaking force RB and elongation at breaking point $\varepsilon Break$. In accordance with Hooke's law, at the beginning of the strain-deformation test the extension of the material was proportional to the force. Then, starting from the yield point on, the samples underwent permanent deformation as a result of further loading. The conducted mechanical tests proved that the force-elongation curves were similar for both groups of materials - the pure polymers and the composites. Such results suggest that the proposed technology of obtaining polymeric paddles by means of extrusion and injection moulding does not impoverish the mechanical properties of the tested materials. All the mechanical parameters are displayed in Table 1.

TABLE 1. **Mechanical characteristics of polymers and composites modified with nanosilver**
TABELA 1. **Parametry mechaniczne polimerów i kompozytów modyfikowanych nanosrebrem**

Material	*Rm* [MPa]	*εFmax* [mm]	*E* [MPa]	*RB* [N]	*εBreak* [mm]
Polysulphone PSU and its composites PSU/Ag					
PSU	73.4 ±4.5	4.0 ±0.1	1206.7 ±352.5	531.1 ±75.8	8.2 ±6.5
PSU/ 1 wt.% Ag	75.0 ±2.5	2.7 ±0.2	1515.7 ±31.3	567.5 ±78.3	3.9 ±1.4
PSU/ 1.5 wt.% Ag	77.4 ±1.4	2.9 ±0.1	1536.9 ±48.0	525.9 ±17.9	5.1 ±1.4
PSU/2 wt.% Ag	76.4 ±1.6	2.9 ±0.1	1537.6 ±28.1	553.0 ±33.3	6.5 ±3.0
Polyamide PA and its composites PA/Ag					
PA	37.9 ±0.7	84.9 ±8.9	521.3 ±18.5	350.9 ±8.6	85.6 ±8.8
PA/1 wt.% Ag	29.3 ±3.2	14.9 ±3.8	463.1 ±38.2	257.8 ±29.2	15.5 ±3.9
PA/1.5 wt.% Ag	33.4 ±1.4	32.0 ±11.2	453,3 ±32.9	264.4 ±100.4	33.6 ±11.1
PA/2 wt.% Ag	31.5 ±1.5	15.5 ±6.6	471.7 ±12.9	268.2 ±35.0	16.4 ±6.6
Polyethylene HDPE and its composites HDPE/Ag					
HDPE	26.6 ±0.5	4.7 ±0.1	679.7 ±16.3	107.3 ±23.8	20.8 ±4.3
HDPE/1 wt.% Ag	28.3 ±0.9	4.7 ±0.3	930.6 ±92.1	76.2 ±25.9	17.8 ±3.4
HDPE/1.5 wt.% Ag	28.1 ±2.3	5.3 ±0.5	680.4 ±27.4	88.9 ±31.0	22.5 ±3.9
HDPE/2 wt.% Ag	28.0 ±0.6	5.5 ±0.6	842.3 ±75.3	69.2 ±14.5	21.3 ±3.3

The polysulphone matrix materials demonstrated the highest tensile strength - ranging 70÷80 MPa, as well as the highest Young's modulus - 1200÷1550 MPa and a breaking strength of 440÷610 N. Polysulphone turned out to be the least deformable polymer, and its graph was typical for tough and brittle materials. Both polysulphone and its nanosilver-modified composites were characterized by similar mechanical parameters. The only differences were noted for elongation at the maximum strength. The nanosilver addition led to an increase in crystallinity and thus weaker deformability. The materials based on high density polyamide and polyethylene matrices were characterized by a similar breaking strength but different Young's modulus and elongation parameter. The Young's modulus for pure polyamide was 100 MPa lower than for pure polyethylene, while in the case of the composites the differences were much bigger. In the group of silver-modified polyethylene composites, all the materials showed a similar tensile strength of 28 MPa, regardless of the amount of applied modifier. In the case of the pure polymer, the tensile strength value was slightly lower - 26 MPa. Therefore, one may state a slight increase in this parameter due to the modifying phase. The nanosilver addition also caused an increase in the Young's modulus and a drop in breaking strength.

The increase in tensile strength and Young's modulus is the result of changes in the composite structure which take place during the extrusion and injection moulding processes, such as chains orientation and formation of the oriented layers. It is also a result of the crystallinization connected with the application of nanosilver particles and the proximity of lamellae along the parallel chains of crystals in the polymer. The higher the orientation degree, the larger the tensile strength and Young's modulus [11]. In the group of polyamide materials the most interesting is the pure polymer whose tensile strength and modulus parameters were higher than the values of the silver composites. A minimal modification with nanosilver particles led to a drop in the toughness parameters. This phenomenon may be explained by the absorption of moisture caused by reorientation of the polymer chains. Introducing nanosilver into the polyamide matrix probably leads to forming small voids on the polymer-particle interface. Those empty spaces are potential sites of water absorption which, having evaporated, causes a decline in tensile strength and elasticity of elongation. Still, the mechanical properties of the polyamide composites are weakened so slightly that, instead of calling this phenomenon deterioration, it may be called halting the parameters at a certain stable level. The presence of the modifying phase (1, 1.5 and 2% by weight) influences the mechanical parameters of the polymer to a smaller or larger extent, depending on its structure, characteristics and homogeneity of the particles in the matrix and the applied stresses. In the composite materials containing nanoparticles, the stresses are transmitted not only by the matrix itself, but by the particles as well. The shape and size of those particles, their ability to deform and also the interaction between the matrix and the particles facilitate strengthening or weakening of the composite mechanical properties. Strengthening of the composites also depends on the amount of nanosilver, its dispersion in the matrix and adhesion in the interphase region. As nanosilver particles have a tendency to agglomerate, which may lower the tensile strength of the material, the homogeneity of the granulates is an essential factor. The tensile tests were also performed after incubating the paddles in the physiological fluid and distilled water. The obtained results were similar for both the environments, that is why the samples were also immersed in Ringer's solution. On the basis of the graphs (Figs. 1 and 2) it may be assumed that polysulphone materials display the stable level of strength parameters during the tests. Polysulphone is an amorphous polymer, whose toughness is determined by the motion of molecules of whole chains or their big fragments.

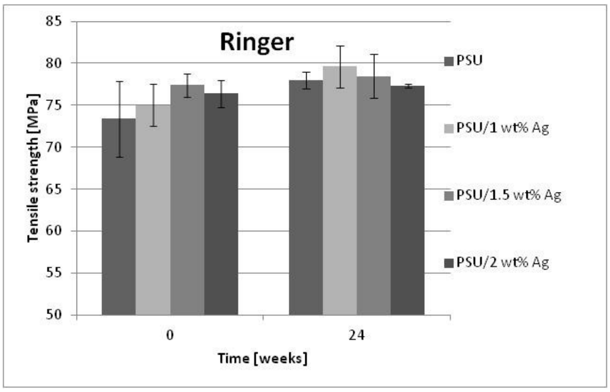

Fig. 1. Tensile strength of polysulphone PSU and its composites modified with silver PSU/Ag during incubation in Ringer

Rys. 1. Wytrzymałość na rozciąganie polisulfonu PSU i jego kompozytów ze srebrem PSU/Ag podczas inkubacji w Ringerze

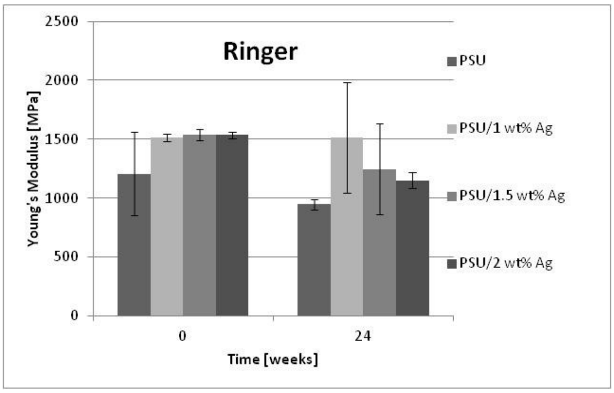

Fig. 2. Young's modulus of polysulphone PSU and its composites modified with silver PSU/Ag during incubation in Ringer

Rys. 2. Moduł Younga polisulfonu PSU i jego kompozytów ze srebrem PSU/Ag podczas inkubacji w Ringerze

The paddles made of semicrystalline polymers, such as high-density polyethylene and polyamide, underwent permanent deformation during the uniform stretching. As a result, local narrowing took place and so-called "micronecks" appeared as visible white areas. The white colour reflects the voids (cavities) in the amorphous phase between crystalline lamellae. The big deformations result from transition from the lamellar into the ordered fibrous structure and from the cavitation process in the material. The cavitation phenomenon - collapsing voids in the polymer - is generated at points where a high local triaxial state of stress is developed. Irrespective of cavitation observed during the deformation above their glass transition temperature, semicrystalline polymers show small changes in volume which are connected with deformation of crystalline regions and breaking of lamellae. The volume changes are attributed to the compressibility of the amorphous phase, especially to the molecules whose mobility depends on the glass transition temperature and the available space inside the crystalline network [12, 13]. In crystalline polymers, above their glass transition temperature, the yield point is determined by the yield point of the crystals, and not of the amorphous phase. Crystals in semicrystalline polymers act as stress concentrators, raising stresses at a local level much above the applied stresses. The presence of crystallites may diminish the material's proneness to multiple breaks and shearing of polymer and, instead, it may promote cavitation at the crystallite level. The formation of voids leads to breaking the chain where the mechanical misfit of lamellae occurs [14]. To put it the easiest way, after the force application, the amorphous phase is deformed, while the crystallite areas may get displaced or undergo interlamellar slips and rotations. Along with the force growth, the plastic deformation of the crystalline phase takes place, which occurs through intralamellar slips and the spherulitic structure changes into the fibrillar structure [15]. To explain the process of the plastic deformation in semicrystalline polymers, such as HDPE or PA, it is worth noting that polyamide is characterized by a relatively high water absorptivity which changes its mechanical properties. Water is a plasticizing factor, thus it influences the plasticity growth in this group of thermoplastics. Entirely dried polyamide becomes brittle, it has low impact resistance but high tensile and bending strength and high modulus of elasticity. The strength of the material decreases after 24 weeks of incubation at 37°C (Fig. 3) as a result of the considerable moisture absorption, which - in turn - is connected with crystallinity of the material (Fig. 4).

Analogical observations were made for Young's modulus (Fig. 4). The polyethylene-based materials (Figs. 5 and 6) showed the increase in the resistance and Young's modulus, which may result from crystallinity growth.

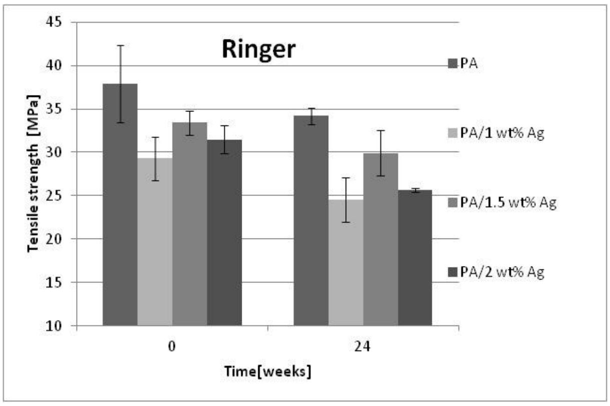

Fig. 3. Tensile strength of polyamide PA and its composites modified with silver PA/Ag during incubation in Ringer

Rys. 3. Wytrzymałość na rozciąganie poliamidu PA i jego kompozytów ze srebrem PA/Ag podczas inkubacji w Ringerze

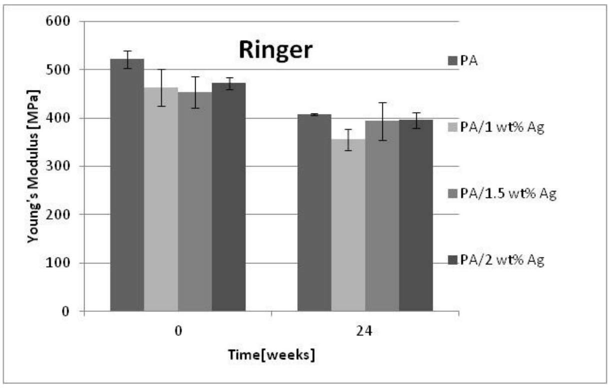

Fig. 4. Young's modulus of polyamide PA and its composites modified with silver PA/Ag during incubation in Ringe

Rys. 4. Moduł Younga poliamidu PA i jego kompozytów ze srebrem PA/Ag podczas inkubacji w Ringerze

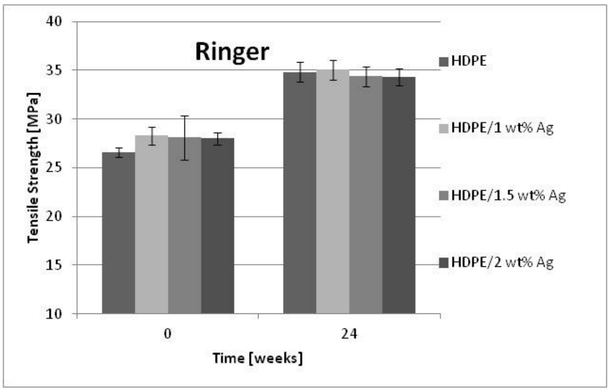

Fig. 5. Tensile strength of polyethylene HDPE and its composites modified with silver HDPE/Ag during incubation in Ringer

Rys. 5. Wytrzymałość na rozciąganie polietylenu HDPE i jego kompozytów ze srebrem HDPE/Ag podczas inkubacji w Ringerze

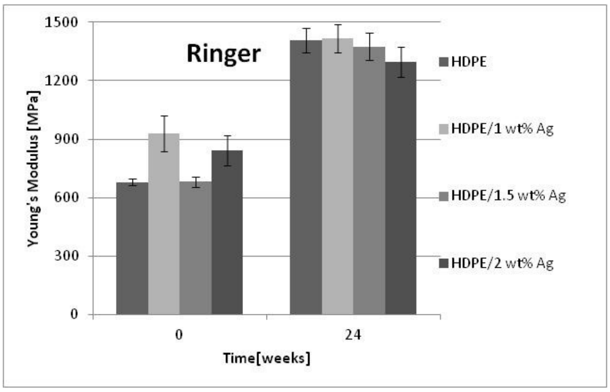

Fig. 6. Young's modulus of polyethylene HDPE and its composites modified with silver HDPE/Ag during incubation in Ringer

Rys. 6. Moduł Younga polietylenu HDPE i jego kompozytów ze srebrem HDPE/Ag podczas inkubacji w Ringerze

CONCLUSIONS

Summing up, the mechanical properties of the materials are extremely important, considering biomechanical functions of the implants they are made of. However, depending on the implantation site, the size of the implant and the manner of manufacturing, it is possible to tailor the material to the specific needs. The materials for middle ear prostheses do not have precise strength requirements. Yet it is common knowledge that the implant material should have such mechanical properties so as to resemble the tissue it is to substitute. Considering the complex structure and the chain of auditory ossicles, as well as the wide spectrum of Young's modulus for particular elements (ligaments, muscles, joint, bones) ranging from 0.049 MPa for ligaments to 14 GPa for bones, it is difficult to design a perfect material [16]. That is why, it may be assumed that all the materials tested in this study perform biomechanical functions and may be used for middle ear implants. Nevertheless, to ensure that the material will meet the medical demands, it is important to study the relation between applied stresses and the transmission of vibration. The long-lasting use of polymers and the stresses they endure may lead to breaking the polymer chains, causing their mechanical degradation, especially the drop of elasticity. Low elasticity may impair the transmission of vibration and, consequently, result in the incorrect sound conduction. The chemical and mechanical degradation are undesirable effects, that is why all the materials for prostheses should be thoroughly tested both under static and dynamic (fatigue) conditions.

Acknowledgements

The work was financially supported by The National Center of Research and Development, No: LIDER/ 154/L-6/14/NCBR/2015.

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