

*BARTŁOMIEJ WAŚNIEWSKI**, *JOANNA RYSZKOWSKA**, *KONSTANTY SKALSKI***,
*MAREK PAWLIKOWSKI***

QUANTITATIVE ANALYSIS OF THE POLYURETHANE COMPOSITES WITH NON-ORGANIC NANOFILLER FOR USE IN IMPLANTS OF INTERVERTEBRAL DISC

The aim of this research was to develop a composite material to be used as an elastomeric core of the artificial intervertebral disc. Two types of polyurethane composites with non-modified SiO₂ and SiO₂ modified NH₂ group were obtained. The composites made of these materials have different filler content. The effect of modifying fillers for the structure and properties of these materials were investigated.

1. Introduction

Artificial intervertebral disc replacement is an alternative to spinal fusion. None of currently available artificial intervertebral discs respect all physiological properties of natural disc. The implanted device should re-establish normal kinematics to the functional spinal unit. The main disadvantage of currently available artificial disc is low ability for damping and unlimited rotational movement by axial rotation [1]. The Bryan disc prosthesis gives similar mechanical properties as the natural intervertebral disc in preventing different mechanical properties of the vertebral column. Its characteristics are the result of polyurethane core [2].

The study on clinical evaluation of the Bryan disc arthroplasty for the treatment of cervical spondylosis started in March 2001. In this study the cervical disc replacement was shown to be reliable and safe for the treatment of patients with cervical spondylosis, producing minimal complications and

* *Warsaw University of Technology, The Faculty of Material Science, 02-507 Warsaw, Woloska 141, Poland; e-mail: bwasniewski@inmat.pw.edu.pl*

** *Warsaw University of Technology, The Faculty of Production Engineering, 02-524 Warsaw, Narbutta 85, Poland*

good surgical results. This is not true in the case of patients with myelopathy [2], therefore studies on new design solutions are needed. Other results of this type of implants [3, 4] suggest that studies are also needed to change the characteristics of polyurethanes, which are an essential element of the construction of the Bryan disc.

Polyurethanes (PURs) have been used for many years to produce various components of the implants [5,6]. Their usefulness is determined by high biocompatibility. They are a very important group of polymers due to their wide range of properties. PURs are used for production of artificial heart valve, stents and other things, thanks to their high biocompatibility with human blood, high resistance to degradation in human body, and high wet angle which is very important to avoid cell growth in implantation region. In the group of commercial biomedical polyurethanes, the following ones: PeletehaneTM, CardiothaneTM, ChronoflexTM, and Estane TM are used in this application. These materials are produced from various groups including polyestrodriols, which are not resistant to hydrolytic degradation [7, 8].

The paper proposes the use of these materials for the manufacturing of polyetherodiols resistant to this type of degradation [9]. Polyurethanes are often synthesized from Aromatic diisocyanates MDI, and the use of these materials provides the polyurethanes with good strength properties [10]. Stiffness is the first of the mechanical properties of intervertebral disc which is very important for the shock absorbing ability of the vertebral column. The other important properties are low permanent strain, high creep resistance, low-friction and high wear-resistance. Combination of these properties of polyurethanes can be obtained through the use of properly selected substrate ratio. A higher modulus will determine, inter alia, the degree of branching of macromolecules [9, 11]. In this work, one proposed the use of ethylene glycol as an extender and glycerin as a cross linking agent. Another way to increase the modulus of elasticity of polyurethanes is the use of a nanofiller. Organic-inorganic nanocomposites, due to their properties, attracted an interest in the recent years. Beneficial properties of these materials are achieved thanks to the connection of matrix (flexibility, elasticity) and nanofiller (high thermal resistance, hardness, stiffness). Nanocomposites exhibit advantageous mechanical and physical properties already at small addition of modifying particles, frequently lower than 5 weight (wt.) in %. Most of nanofillers occur without any surface modification. However, sometimes we need to modify nanoparticles to obtain better dispersion of nanofiller in polymer matrix, for instance. One of such modifications is a chemical one consisting in attaching functional groups i.e. -COOH, -NH₂, -NCO, -OH to nanofiller [12,13]. Polyurethanes are reinforced with different groups of nanofillers, among them there are: nanosilica, nanotubes, montmorillonit, boehmite, et al. [14-18].

In this study, we have developed the two types of polyurethane composites with non-modified SiO₂ and SiO₂ modified NH₂ group. These composites were designed to produce elements of intervertebral disc implant. The effect of modifying fillers for the structure and properties of these materials were investigated.

2. Materials and methods

2.1. Materials

Polyurethane/nanosilica composites were synthesized in bulk with a one-step polymerization method using polyoxytetramethylene glycol (PTMG) of molecular weight ~2023 g/mol (Therathane ® 2000), 4,4' – diphenylmethane diisocyanate (MDI), ethylene glycol (GE) as chain extender and glycerin (G) as bonding agent and silica dioxide (SiO₂) as a nanofiller. Dehydration of the PTMG or mixture PTMG with SiO₂ were dehydrated in temperature of 120°C±5°C under 2-5 hPa pressure. After two hours, the mixture was cooled to 70°C±3°C, with glycol added and glycerin blended for 5min. Then, the mixture was cooled to 60°C±3°C and MDI was added. The samples were obtained by using the free casting method. The heat up process was carried out in the oven in 16 hours.

The PUR matrix was made with substrates molar ratio PTMG: MDI: GE: G equal to 40:80:27:24 (1:2:0.679:0.151). The nanofiller was put into the polyurethane matrix in the amount of 0.5; 1; 2 wt. %. The modified silica, and the silica modified with NH₂ groups were used as the nanofiller. Description of the obtained materials is presented in Table 1.

Table 1.

Description of the obtained materials

No.	Sample name	Amount of nanofiller [%] wt.	Modification
1	0	0	–
2	1	0.5	–
3	2	1	–
4	3	2	–
5	1A	0.5	NH ₂
6	2A	1	NH ₂
7	3A	2	NH ₂

Nanofillers in polymeric matrix composites tend to agglomerate if they are introduced directly during polymerization. To avoid such a mechanism in

140 BARTŁOMIEJ WAŚNIEWSKI, JOANNA RYSZKOWSKA, KONSTANTY SKALSKI, MAREK PAWLIKOWSKI

this work, we made a nanosilica – polyetherodiols 20% wt. concentrate. First, the polyetherdiol was melt down in the oven in the temperature of 80°C. Then, nanosilica was put into it and mixed with ultrasonic homogenizer VCX 750 by Sonics during 30min in pulse mode 3/3 (3sec mixing, 3sec stop).

2.2. Methods

For examination of the PU and the composites, we used the methods listed in the following sections.

The presented values are expressed as the mean value with standard deviation.

Contact angle measurements

The water contact angle of selected polyurethane samples was measured at room temperature by the sessile drop method using a contact angel goniometer PGX (Fibro Systems AB).

Tensile strength at break

The strength tests of the PU samples were carried out with the use of an MTS testing machine in accordance with the standard procedure PN-ISO 37:1998. The sample holder travel speed was 500 mm/min (8.3mm/s), and the measurements were taken over the distance of 25mm. The σ_r (MPa) values were calculated with the following formula:

$$\sigma_r = \frac{F_r}{b \cdot d}$$

where F_r is the force recorded at rupture (N), b is the width of the measurement distance (mm), and d is the thickness of the measurement distance (mm), according to the procedure PN-ISO 37:1998.

Permanent set

Permanent distortion of an elastomer after deformation ε_{rt} , (%) was calculated with the following formula:

$$\varepsilon_{rt} = \frac{l'}{l_o}$$

where l' is the measurement distance at rupture after 2min after break (mm) and l_o is the initial measurement distance (mm).

Hardness

A Shore hardness tester from Wilson-Wolpert Durometer (Germany) was employed in accordance with the standard PN-80/C-04238. The Shore A hardness (°) was read directly from the instrument after 15s.

Abrasion resistance

The abrasion resistance of test samples was measured with a Schopper-Schlobach instrument with an APGi circulating roller from Heckert, and the procedure complied with the standard PN-ISO 4649:1999. The test specimens had the form of a roll (16 ± 0.2 in diameter and 2mm high). Standard rubber from (The Institute for Engineering of Polymer Materials and Dyes, Elastomer and Rubber Technology Division in Piastów) was used as the reference material. The abrasion resistance index (ΔV) was calculated with the following formula:

$$\Delta V = \frac{V_s}{V_t}, \quad 100\%$$

where V_s is the loss of volume of the standard rubber (mm^3) and V_t is the loss of volume of the test sample (mm^3).

The density for the test pieces, which were necessary for calculations, were found by the method described in the standard PN-ISO 27811AC1:1996.

Density

The density ρ of PU (g/cm^3) was calculated with the following equation:

$$\rho = \frac{m_1}{m_1 - m_2} \cdot \rho_1$$

where: m_1 is the mass of the test sample in air (g), m_2 is the mass of the test sample in water (g), and ρ_1 is the density of water.

Compression set

Creep tests were performed on the rheological test stand. In the first phase of research on materials on the disc implant, it was assumed that in the design of implants a torus shape polyurethane will be used, and for this reason the samples of this shape have been studied in the work. The study was based on a uniform compression of torus samples made of polyurethane (Fig. 1). Cross section of the sample was about $7,5 \text{ cm}^2$, and its dimensions were similar to the average dimensions of the disks described in the work by D.G.T. Strange et al. [19]

Strain values of the samples for compressive strength were measured with the tensometric extensometer with the range up to 1,5 mm, and the



Fig. 1. Torus sample of polyurethane

accuracy of 0.001 mm. An extensometer was connected to the HMB measuring amplifier with a full-bridge circuit. The amplifier was connected to the computer data logger. The compressive force was 500N and this value was chosen to match the force acting on the L5/S1 level in a human spine while standing. The time of a single measurement was approximately 24h. 24 hours later, the value of the strain in the sample was measured. Those strain values were used as the permanent set (ε_t).

Dynamic mechanical analysis

Compression tests by dynamic mechanical analysis (DMA) were carried out on cube-shaped specimens with dimensions of $3 \times 3 \times 3 \text{ mm}^3$. The tests were carried out on a Thermal Instruments dynamic mechanical analyzer (Q800 TA). The frequency-dependant storage modulus was also evaluated with a 4.5–9 Hz frequency sweep at a constant temperature of 37°C with 1.5% strain and 0.01 N static force. Similar parameters were used by Hafeman and co-workers [20]. The storage modulus (E') value was recorded as a function of frequency. Dynamic tests were also carried out in three-point bending mode on specimens with dimensions of $12 \times 2 \times 60 \text{ mm}^3$ the distance between supports was 35mm. The tests were performed with an amplitude of deformation during the bending of $25 \mu\text{m}$ and during compression $10 \mu\text{m}$.

Compressive stiffness

Compression toroidal samples of 1 and 2mm were made in the LfC in Zielona Góra. Before performing measurements on each sample, a grid was plotted in order to facilitate the imaging of emerging strains. The mesh was

applied using a marker. Lines were drawn around the perimeter at 1.5mm, and cross every 5°. An image of the ring with the grid is shown in Fig. 2.

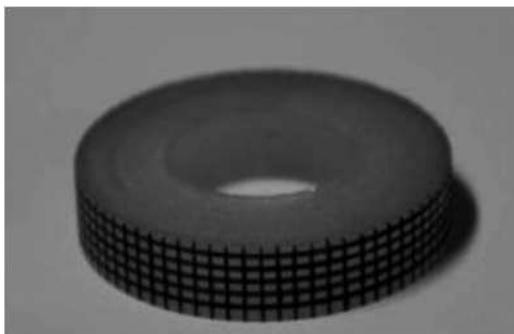


Fig. 2. Torus with additional test grid

The test procedure in the course of compression at 1mm deformation consisted of: preload with a force of 20N, deformation of the torus by 1mm at a rate of 0.017mm/s, with the same speed, and then removing the pre-load. Image samples before and after deformation of 1mm are shown in Fig. 3.

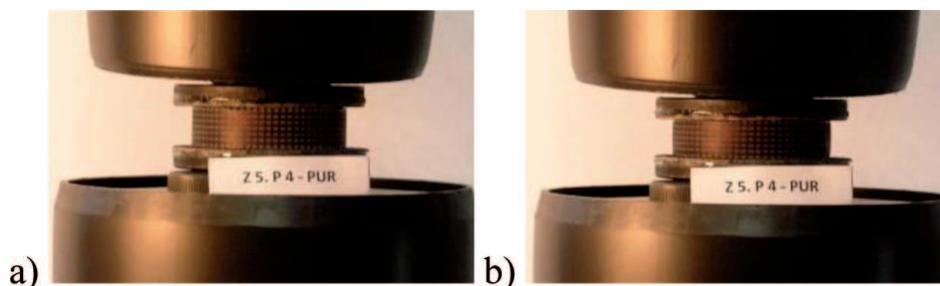


Fig. 3. Toroidal samples of 2A sample before (a) and after compression test (b) at 1mm

The procedures during compression at 2mm displacement were similar. After the preload with 20N, the sample compress at 2mm at a rate of 0.017mm/s. Then, there was a return with the same rate, and then pre-load was taken off.

3. Results

In polymeric materials, the introduction of nanosilica filler causes changes in the density of the developed materials (Table 2). The introduction of the filler changes the polymerization process of the polyurethane matrix, resulting in a decrease in the density of composites 1, 1A and 2A. The introduction of larger amounts of filler results in an increase in density, expected as a result

of the filler with a higher density than the matrix density. The introduction of filler reduces the contact angle of the composite, while a higher filler content causes a decrease in contact angle (Table 2). In result, we obtained materials with hydrophobic characteristics, which can facilitate reduction of cell adhesion to the surface.

Table 2.

Mean values of the density, contact angle and hardness of the PU/nanosilica composites

Sample	$\bar{\rho}$ [g/cm ³]	σ_{ρ} [g/cm ³]	$\bar{\alpha}$ [°]	σ_{α} [°]	\bar{H} ,[°ShA]	σ_H ,[°ShA]
0	1.0452	0.007	102	1.09	62	0.69
1	1.0419	0.006	93	1.08	63	0.53
2	1.0468	0.007	90	1.09	64	0.38
3	1.0476	0.008	87	1.07	65	0.69
1A	1.0418	0.003	88	1.08	64	0.95
2A	1.0429	0.003	85	1.08	54	0.53
3A	1.0467	0.006	85	1.09	28	0.95

where: $\bar{\rho}$ – density, $\bar{\alpha}$ – wet angle, \bar{H} – hardness, σ_x – standard deviation

An important feature of the materials used as implants is the abrasive wear (Fig. 4). Abrasive wear of composites 1, 2, 1A and 2A is about 25% lower than that of the polyurethane matrix.

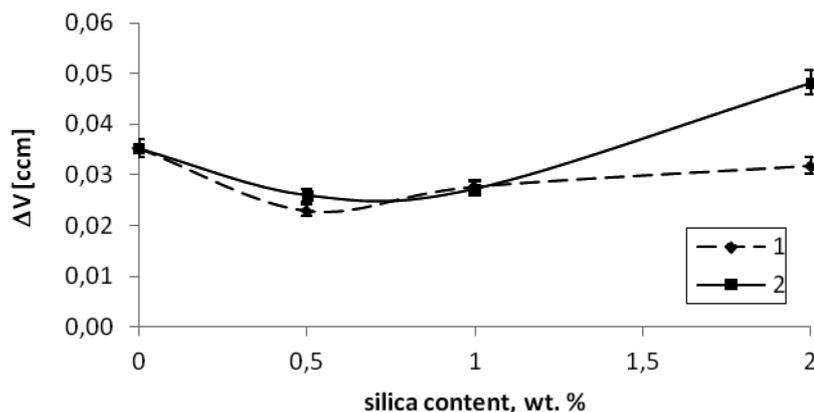


Fig. 4. Abrasive wear expressed as the mean value of six measurement with standard deviation of the PU and PU/SiO₂ composites with: 1) non-modified silica, 2) silica modified by –NH₂ groups

In the case of elastomers, one of the basic goals of research is to study hardness. In the result of the analysis performed, it was found that the hardness of materials ranges from 0 to 4, and 1A is approximately 63° Sh A (Table 3). A clear decrease was observed in the hardness of the composites

2A and 3A, indicating a substantial modification of the filler influence on the process of synthesis of these materials. Considering tensile principal characteristics of the produced materials, we have found that the breaking strength of these materials (R_m) clearly decreases after the introduction of higher amount of the nanofiller, but with a significant drop in positive permanent deformations of these materials (Table 3). The Young's modulus shows that a higher value was achieved for composite with 2% non-modified nanosilica. The decrease in the Young's modulus for modified nanosilica indicates a different mechanism of built-in polyurethane matrix.

Table 3.
Mean values of strength characteristic of the PU/nanosilica composites from static tension test

Sample	\bar{R}_m , [MPa]	σ_{Rm} , [MPa]	\bar{E} , [MPa]	σ_E , [MPa]	$\bar{\epsilon}_r$, [%]	$\sigma_{\epsilon r}$, [%]	$\bar{\epsilon}_{rt}$, [%]	$\sigma_{\epsilon rt}$, [%]
0	6.2	0.21	3.84	0.23	282	6	1.4	0.02
1	5.3	0.20	3.64	0.24	193	11	0.38	0.01
2	4.8	0.19	3.58	0.22	187	9	0.55	0.01
3	4.3	0.23	3.88	0.23	131	8	0.65	0.02
1A	5.2	0.13	3.68	0.07	185	8	0.42	0.01
2A	4.8	0.21	3.61	0.18	153	7	0.58	0.01
3A	4.4	0.21	3.42	0.26	131	9	0.8	0.02

where: \bar{R}_m – tensile strength, \bar{E} – Young modulus, $\bar{\epsilon}_r$ – elongation to break, $\bar{\epsilon}_{rt}$ – permanent deformation, σ_x – standard deviations of the measurements

The endurance tests were evaluated for susceptibility of the tested materials to creep. Sample curves describing the deformation of composites are shown in Fig. 5, after an initial increase in strain is passed in the plateau region.

The results of the analysis indicated a permanent deformation during tension and compression tests of the polyurethane matrix and composites, which is summarized in Fig. 6. Stuffing both composites with modified and unmodified nanofiller decreases the ability to creep. Lower creep was observed in the composites with unmodified nanosilica, the reason for this difference in the mechanism is different incorporation of the filler in the structure of the polyurethane matrix. An increase in the filler content decreases the final strains of the produced nanocomposites. Mobility restrictions of the macromolecules in the polyurethane matrix by nanoparticles result in an increase in the creep resistance of these materials. The introduction of 2% of the unmodified filler causes a drop in permanent deformation by more than 90%.

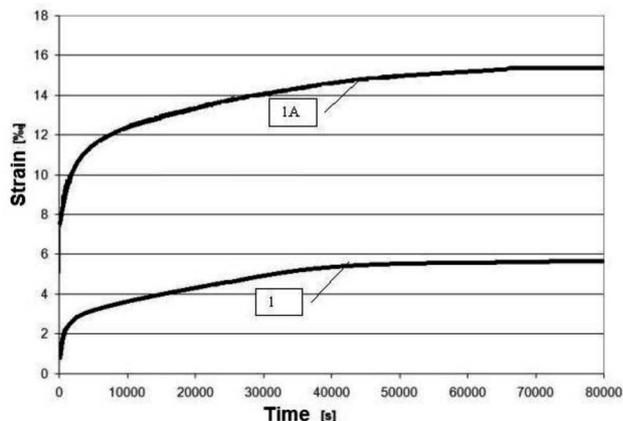


Fig. 5. Deformation process of the nanocomposites 1 and 1A

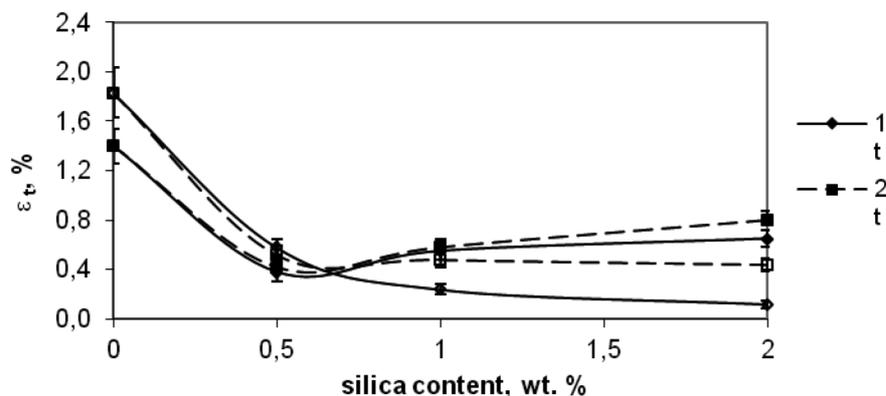


Fig. 6. Comparison of susceptibility to creep of the PU and PU/SiO₂ composites determined in tensile tests with: 1t) silica, 2t) silica modified by –NH₂ groups and determined in compressions tests with: 1c) silica, 2c) silica modified by –NH₂ groups

The results of analysis of polyurethane matrix and composites subjected to cyclic strain in bending and compression tests are shown in Fig. 7 and Fig. 8. They contain DMA curves for both bending and compression tests.

Tables 4 and 5 summarize the results obtained from DMA materials determined during the three-point bending and the compression tests. Both measurements were performed with varying frequency at a constant strain amplitude, which makes it possible to evaluate changes in dynamic elasticity. The analysis of DMA have shown that, after the introduction of 0.5% wt. of unmodified and modified nanosilica-NH₂ groups, the storage modulus determined at the bend decreases more than 10 times, in comparison with

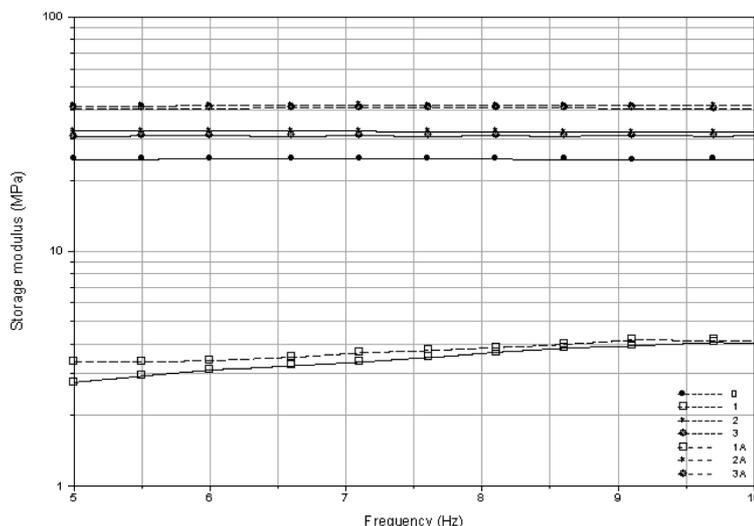


Fig. 7. Storage modulus during bending of the PU and PU/SiO₂ composites

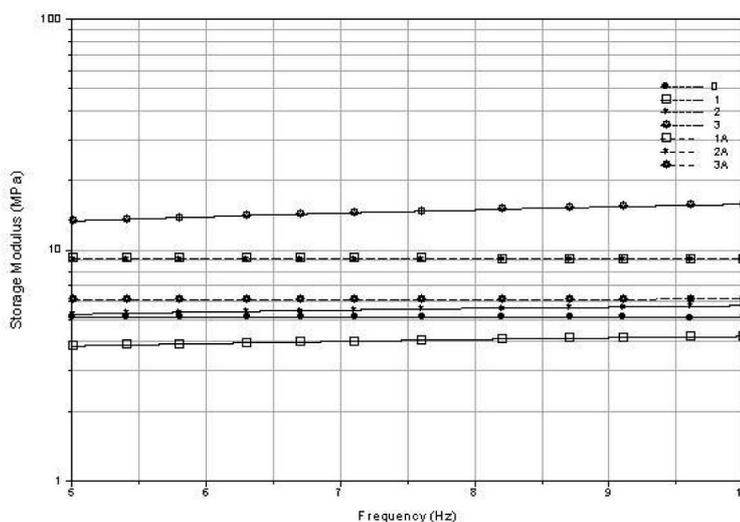


Fig. 8. Storage modulus during compression of the PU and PU/SiO₂ composites

the storage modulus of the PU matrix. The introduction of a slightly greater amount of a filler causes an increase in the module by approximately 25% compared with the matrix material.

The introduction of a filler also causes changes in the second set of parameters, $\tan \delta$ – the tangent of the phase angle. This property is an indicator of how efficiently the material loses energy due to molecular rearrangements and internal friction. It is the ratio of the loss to storage modulus and therefore is independent of geometry effects. Polyurethanes are fairly elastic, so $\tan \delta$

Table 4.

Mean values of results of dynamic three-point bending of the PU and PU/SiO₂ composites

Sample	$\bar{E}'_{5\text{Hz}}$ [MPa]	$\sigma_{E'5}$ [MPa]	$\bar{E}'_{10\text{Hz}}$ [MPa]	$\sigma_{E'10}$ [MPa]	$\overline{\text{Tan}\delta}_{5\text{Hz}}$	$\sigma_{\text{tan}\delta 5}$	$\overline{\text{Tan}\delta}_{10\text{Hz}}$	$\sigma_{\text{tan}\delta 10}$
0	24.59	0,38	24.63	0,34	0.05	0,03	0.08	0,02
1	2.75	0,06	4.05	0,04	0.34	0,03	0.08	0,03
2	32.55	0,43	32.16	0,44	0.07	0,02	0.02	0,03
3	30.78	0,29	30.99	0,34	0.04	0,03	0.02	0,03
1A	3.37	0,04	4.15	0,01	0.24	0,04	0.08	0,04
2A	40.56	0,25	40.49	0,17	0.03	0,02	0.02	0,03
3A	41.57	0,23	40.51	0,18	0.04	0,03	0.02	0,03

Table 5.

Mean values of results of the dynamic compression tests of the PU and PU/SiO₂ composites

Sample	$\bar{E}'_{5\text{Hz}}$ [MPa]	$\sigma_{E'5}$ [MPa]	$\bar{E}'_{10\text{Hz}}$ [MPa]	$\sigma_{E'10}$ [MPa]	$\overline{\text{Tan}\delta}_{5\text{Hz}}$	$\sigma_{\text{tan}\delta 5}$	$\overline{\text{Tan}\delta}_{10\text{Hz}}$	$\sigma_{\text{tan}\delta 10}$
0	5,12	0,31	5,11	0,30	0,02	0,01	0,02	0,01
1	6,08	0,07	6,12	0,06	0,02	0,01	0,02	0,01
2	9,14	0,33	9,14	0,21	0,02	0,01	0,02	0,01
3	9,18	0,22	9,15	0,37	0,02	0,01	0,02	0,01
1A	4,70	0,07	4,96	0,05	0,02	0,01	0,02	0,01
2A	7,57	0,22	7,56	0,27	0,03	0,01	0,03	0,01
3A	7,77	0,35	7,67	0,35	0,02	0,01	0,02	0,01

where: \bar{E}' – storage modulus, $\overline{\text{Tan}\delta}$ – tangent of the phase angle,
 σ_x – standard deviations of the measurements

values lie generally between 0.01 and 1.0. All of the ultra-high performance polyurethanes have similar, very low values of $\text{tan}\delta$.

During bending, $\text{tan}\delta$ changes according to the quantity and type of the filler and has the values in the range from 0.02 for composites 2, 2A, 3, 3A to 0.34 for the first composite. In the case of compression tests, positive minor changes of $\text{tan}\delta$ were observed between different materials and the tangent value of about 0.02 was obtained. The low value of the tangent indicates that the amount of energy dissipated during the deformation of these materials in the processes of reorganization of the macromolecules and the internal friction of the material is small. (The energy loss is due to the molecular rearrangements and internal friction). The natural disk is deformed during the compression by about 0.7mm, at a pressure equal to the strength of 1000 N [19]. Therefore, specified forces were evaluated for the tested materials; these forces are needed to cause a 1 and 2 mm compression of the torus.

For compression tests, we used one sample of each type. The results of these studies are summarized in Table 6.

Table 6.

Results of compression test at 1 and 2 mm, respectively

Material	Compressive stiffness by 1 mm deformation, [N/mm]	Compressive stiffness by 2 mm deformation, [N/mm]
0	695	964
2	715	1002
2A	680	922

4. Discussion

In this work, we examined in detail polyurethanes and composites of these materials containing unmodified silica and nanosilica modified with -NH₂ groups. These materials are of hydrophobic nature. In this type of materials, there usually occurs a limited growth of tissue on the surface [21], which is a favorable property when the materials are used for the manufacturing of intervertebral disc implants.

The standard wear test [22] is recommended for examination of the materials in the implants constructions in which the end plates are not merged with artificial IVD. This method can not be used for examination of implants where the artificial IVD is merged with the end plates. For that reason, in the latter ones a traditional method for polymers of abrasive wear was used. In the group of examined materials, high resistance is exhibited by nanocomposites with 0.5 and 1% wt. of nanosilica. In comparison with other elastomers, these composites were characterized by high wear resistance [23]. The biological disc of functional spine units makes approximately 5,500 motions per day [24], including axial compressing, flexion-extension, torsional twisting, and lateral bending, without taking into account the slight movement and insignificant load that accompany breathing, which is estimated to reach up to 6 million movements a year.

Due to the diversity of the burden which disks are subjected to, the materials to be used for their preparation were subjected to various tests endurance in which the material deformed at a rate ranging from 0.017 to 8.3 mm/s.

Strength properties were determined with tensile test. A drop in elasticity modulus after the introduction of the mentioned amount of the filler (sample 1) confirms the observations obtained basing on the determination of density of produced materials. Most probably, the filler introduced in lower quantities resulted in the formation of matrix of a different structure, e.g. with shorter

hard segments. Hard segments are known to act as filler in polyurethanes, and a change in their structure may effect the lowering of their elasticity modulus.

An increased modulus for nanocomposite 3 (2% unmodified silica) is the result of matrix strengthening caused by the introduction of a greater number of nanoparticles.

Nanoparticles modified with NH_2 groups change the polymerization process of polyurethane matrix in a similar way as unmodified nanoparticles introduced in lower quantities.

When nanoparticles do not bond with matrix via chemical bonding, then they act as notch in the obtained composites causing a decrease in their stretching resistance, which was observed in the examined nanocomposites. Few bondings on the surface of the modified nanoparticles being the result of reaction between NH_2 group and NCO groups did not cause an increase in the composites' strength.

As a result of this extreme flexibility, elastomers examined in this project can reversibly extend from 131-289%, depending on the specific material. The materials used as a part of the intervertebral disc structure will be subjected to continued stress. Some changes occur also when elastomers are subjected to continued stress: creep refers to a change in strain when stress is held constant, compression set is creep that occurs when the elastomer has been held in compression, permanent set is deformation remaining after a stress is released.

Permanent set of PU matrix and composites was determined with tensile test and they changed in the range from 1.4 for PU matrix to 0.4 for composite containing 0.5% wt. nanosilica. The permanent set of elastomers are the results of the applied forces. Introducing 0.5 wt. % nanosilica changed the polymerization process of the evaluated PU, thus producing chains facilitating its reconfiguration. Also, changes in the permanent set were evaluated when the elastomer was held in compression. Changes in the permanent set after 24 hours compression (ϵ_t) are similar to the changes in the permanent set after stretching (ϵ_{rt}). All types of the composites show lower permanent set than PU matrix. Differences in ϵ_t between composites containing 0.5, 1% wt. of non-modified nanosilica and composites with nanosilica modified with NH_2 groups depend on mechanism of nanoparticles built in the PU matrix. Introduction of more than 1% wt. of nanosilica brings no differences in the permanent set.

In the result of analysis using the DMA we have found that the storage modulus of the PU matrix during the compression is about 5 MPa and that of the nanocomposite takes the values from 4.5 to 7.8 MPa [25]. Modeling of the implant and the annulus as linear elastic solids showed that the disc

implanted with a nucleus replacement that had an elastic modulus of 3 MPa exhibited biomechanical properties similar to a physiologic model of the IVD. Yao et al. [26] found the ideal elastic modulus of a nucleus replacement to be approximately 7 MPa. The materials examined in this work have similar properties to those used in the work by Meakina and Yao et al. The examined nanocomposites with nanosilica show low ability for losing energy similarly as the ultra-high performance polyurethanes [27]. During the evaluation of compressive stiffness of PU and nanocomposites with 1wt. % of nanosilica, it was found that the forces causing deformation of the samples were almost twice lower than the forces causing deformation of the natural disc [19]. However, elastomeric models with the shape similar to a natural disc charged with a force of 1000 N had strain in the range of 0.5 to 2.2 mm [19]. Torus-shaped model made of the tested materials had compressive stiffness similar to the models of elastomers studied by Strange et al. [19]. The physiologic disc exhibited a clear convex inner and outer annular bulge under loading, both in the anterior and posterior regions. Analysis of the results of this research indicates that the proposed initial model disk made of a nanocomposite containing 1% wt. unmodified nanosilica has the best features among the tested materials.

Acknowledgments

The authors would like to thank the LFC company for enabling the implementation of the compression test in their laboratories. The work has been accomplished under the research project entitled “Development and validation of polyurethane nanocomposite for use as an artificial intervertebral disc” supported by Warsaw University of Technology.

Manuscript received by Editorial Board, September 15, 2011;
final version, May 31, 2012.

REFERENCES

- [1] Bistricic L., Baranovic G., Leskovic M., Govorcin Bajsic E.: Hydrogen bonding and mechanical properties of thin films of polyether-based polyurethane-silica nanocomposites, *European Polymer Journal* 46 (2010) 1975-1987.
- [2] Lafuente J., Casey A. T. H., Petzold A., Brew S.: The Bryan cervical disc prosthesis as an alternative to arthrodesis in the treatment of cervical spondylosis, *The Journal of bone & joint surgery*, 87-B, 4, 2005, 508-512.
- [3] Sasso MR.C., Best N.M.: Cervical Kinematics After Fusion and Bryan Disc Arthroplasty, *J. Spinal Disord Tech*, 2008 21(1), 19-22.
- [4] Anderson P.A., Rouleau J.P., Bryan V.E., Carlson C.S.: Wear Analysis of the Bryan Cervical Disc Prosthesis, *SPINE*, 28, 20S, S186-S194, 2003, Lippincott Williams & Wilkins, Inc.
- [5] Lelah M.D., Cooper S.L.: Polyurethanes in medicine authors, CRC Press, Boca Raton, 1986.

- [6] Lambda N.M.K., Woodhouse K.A., Cooper S.L.: Polyurethanes in Biomedical Applications, CRC Press, 1998.
- [7] Ryszkowska J.L., Auguścik M., Sheikh A., Boccaccini A.R.: Biodegradable polyurethane composite scaffolds containing Bioglass® for bone tissue engineering *Comp. Sci, Technol.*, 70, 13, 2010, 1894-1908.
- [8] Oprea S.: Wpływ struktury na stabilność termiczną usieciowanych poli(estro-uretanów), *Polimery*, 2, 2009, 120-125.
- [9] Hepburn C.: Polyurethane Elastomers, Elsev. Sci. Publ., London 1992.
- [10] Brzeska J., Dacko P., Janeczek H., Kowalczyk M., Janik H., Rutkowska M.: „Wpływ syntetycznego polihydroksymaślanu na wybrane właściwości nowych, otrzymanych z jego udziałem poliuretanów do zastosowań medycznych. Cz. I Poliuretany z aromatycznym diizocyjanianem w segmencie sztywnym”, Cz. II „Poliuretany z cykloalifatycznym diizocyjanianem w segmencie sztywnym”, *Polimery*, 2010, 55, 11-12, 41-46.
- [11] Janik H.: Postępy w badaniach struktur nadcząsteczkowych segmentowych poliuretanów, *Polimery*, 55 (6), 421-430.
- [12] Geceler K.E., Rosenberg E.: Functional Nanomaterials, American Scientific Publishers, North Lewis Way Stevenson Ranch, 2006.
- [13] Mai Y.-W., Yu Z.-Z.: Polymer nanocomposites, CRC Press, Boca Raton, 2006.
- [14] Vega-Baudrita J., Sibaja-Ballesteroa M., Vazquez P., Torregrosa-Maciac R., Martin-Martinez J.M.: Properties of thermoplastic polyurethane adhesives containing nanosilicas with different specific surface area and silanol content, *Int. J. Adhesion & Adhesives* 27 (2007) 469-479.
- [15] Ryszkowska J., Waśniewski B., Pytel A., Zielecka M.: Kompozyty poliuretanowe z nanokrzemionką modyfikowaną grupami izocyjanianowymi, *Polimery*, 2009, 54 (10), 657-666.
- [16] Ryszkowska J., Zawadzak E., Łojkowski W., Opalińska A., Kurzydłowski K.J.: Structure and properties of polyurethane nanocomposites with zirconium oxide including Eu³⁺, *Materials Science and Engineering C* 27, 2007, 994-997.
- [17] Ryszkowska J., Zawadzak E., Hreniak D., Stręk W., Kurzydłowski K.J.: Structure and properties of polyurethane/YAG:Tb³⁺, *Polimery* 52, 2007, 20-24.
- [18] Ryszkowska J., Jurczyk-Kowalska M., Dębowski M., Florjańczyk Z., Kurzydłowski K.J.: Wpływ modyfikacji bemitu na dyspersję w poliuretanowej osnowie, *Inżynieria Materiałowa*, 6 (154), 28, 2006, 1315-1318.
- [19] Strange D.G.T., Fisher S.T., Boughton P.C., Kishen T.J., Diwan A.D.: Restoration of compressive loading properties of lumbar discs with a nucleus implant – a finite element analysis study, *The Spine Journal* 10 (2010) 602-609.
- [20] Hafeman A.E., Li B., Yoshii T., Zienkiewicz K., Davidson J.M., Guelcher S.A.: Injectable biodegradable polyurethane scaffolds with release of platelet-derived growth factor for tissue repair and regeneration. *Pharm Res* 2008; 25, 2387-99.
- [21] Wang S., Lu L., Wang C., Gao C., Wang X.: Polymeric Biomaterials for Tissue Engineering Applications, *Int. J. Polym Sci*, 2010 (2010), Article ID 148513.
- [22] International Organization for Standardization 18192-1:2008. Implants for surgery: wear of total intervertebral spinal disc prostheses – part 1: loading and displacement parameters for wear testing and corresponding environmental conditions for test.
- [23] Król P., Pilch-Pitera B.: Mechanical properties of crosslinked polyurethane elastomers based on well-defined prepolymers, *J. Appl. Polymer Sci*, Vol. 107, 1439-1448 (2008).
- [24] Hallab N., Link H.D., McAfee P.C.: Biomaterial optimization in total disc arthroplasty. *Spine* 2003, 28, S139-52.
- [25] Meakin J.R.: Replacing the nucleus pulposus of the intervertebral disk: prediction of suitable properties of a replacement material using finite element analysis. *J Mater Sci Mater Med* 2001, 12, 207-13.

- [26] Yao J., Turteltaub S.R., Ducheyne P.: A three-dimensional nonlinear finite element analysis of the mechanical behavior of tissue engineered intervertebral discs under complex loads. *Biomaterials* 2006, 27, 377-87.
- [27] Bahattab M.A., Donate-Robles J., Garcia-Pacios V., Martin-Martinez J.M.: Characterization of polyurethane adhesives containing nanosilicas of different particle size, *Int. J. Adhesion & Adhesives* 31 (2011) 97-103.

Ilościowa analiza kompozytów poliuretanowych z nieorganicznym napełniaczem do zastosowań na implanty krążka międzykręgowego

Streszczenie

Celem pracy było opracowanie kompozytu do zastosowań na elastomerowy rdzeń sztucznego krążka międzykręgowego. Wytworzono dwa rodzaje kompozytów poliuretanowych zawierających niemodyfikowany SiO_2 jak również SiO_2 modyfikowany grupami NH_2 . W ramach pracy przeanalizowano wpływ modyfikacji napełniacza na strukturę i właściwości wytworzonych materiałów.