

Polyurethanes used in the endoprosthesis of joints

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The aim of the studies presented in this paper was the selection of the polyurethanes synthesized from different substrates in order to obtain i) ceramic - biodegradable polymer composite and ii) polyurethane resistant to abrasive wear. The polyurethanes were obtained from the crystalline prepolymers extended by water, because it may have a beneficial effect on the toxicity of the material. The properties of PUs were investigated using infrared spectroscopy, thermogravimetry, differential scanning calorimetry and scanning electron microscopy. In all the tested polyurethanes the peak from the reactive -NCO groups was not observed, which indicates that all the substrates are fully reacted. Such polyurethanes are characterized by interesting properties with the perspective use as components of ceramic-polymer joints endoprosthesis. The designed endoprosthesis should fulfill at least three functions: load bearing function (ceramic core), fastening and stabilizing endoprosthesis to the bone (composite ceramics – biodegradable polymer) and tribologic function allowing mating with parts of the prosthesis (polyurethane layer resistant to abrasive wear).

Keywords: polyurethane, biodegradation, abrasive wear, joint endoprosthesis.

INTRODUCTION

Medicine is an important area of application of advanced materials. Synthetic materials fulfill a major role at the surgery of regeneration of the lost damaged tissues, as well as the reconstruction of the damaged organs. The materials used for the production of prostheses, as the addition to their biocompatibility require also a relatively high strength and adequate tribological characteristics.

The beginnings of endoprosthesis application, in the case of partial or total joint replacement implant, occurred in the mid-twentieth century. The first prosthesis was made from PMMA and Nylon. Because of many restrictions they are not used nowadays¹. A lot of studies have been performed to obtain the best material solution and finally polyethylene (PE) was found as the most suitable material for joint endoprosthesis application². However, during the exploitation the structure of the material changes^{1,3,4}. For this reason, many works have been performed on the modification of the material and construction of the new prosthesis.

Polyurethanes were used in medicine for the first time for bonding of bones¹. Nowadays these materials are used in reconstructive surgery, cardiology, stomatology and many others. They are used primarily as the elements of the artificial heart, vascular grafts, drains, parts of joints endoprosthesis^{4,5,6}. They are characterized by high strength, high wear resistance and the smallest blood clotting of all macromolecular compounds. Moreover, they are well tolerated by the human body^{1,6,7}.

Due to the doctors and patients expectations and demands, new, better materials and prosthesis structure are still being searched. One of the proposed solutions is to produce ceramic – polymer joint endoprosthesis. In such a construction the load-bearing function will be fulfilled by the alumina ceramic core, the function of stabilizing the prosthesis to the bone will be carried out by the composite obtained from the porous alumina ceramic infiltrated by biodegradable polymer. The tribological func-

tion will be fulfilled by polyurethane with increased resistance to abrasive wear and degradation, permanently joined to the ceramic substrate.

The aim of the studies was the selection of the polyurethanes synthesized from different substrates in order to obtain ceramic – the biodegradable polymer composite and polyurethane with increased resistance to abrasive wear and biodegradation. These PUs can find their application in endoprosthesis proposed by the Faculty of Materials Science and Engineering, Warsaw University of Technology and the Institute of Ceramics and Building Materials in Warsaw (Fig.1).

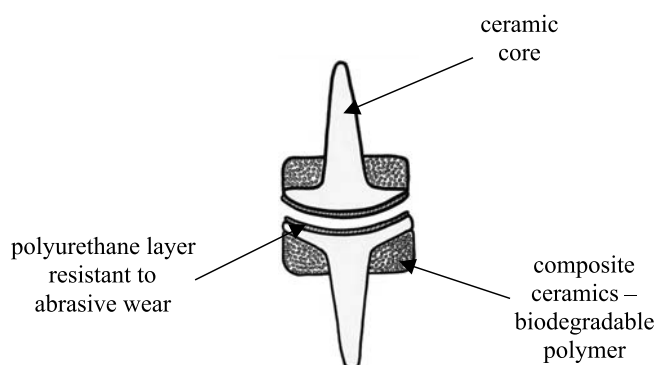


Figure 1. Scheme of the prosthesis

Among many biodegradable polymers⁸ poly(ϵ -caprolactono)diol (PCL) deserves particular interest, because of its biocompatibility and biodegradability, which make it a useful material in resorbable sutures, drug delivery systems, and in bone graft substitutes^{9,10}.

Polyurethanes developed for the purpose of the endoprosthesis are fabricated from the crystalline prepolymers extended by water. This method has been developed at the Faculty of Materials Science and Engineering, Warsaw University of Technology¹¹. Using water as a chain extender may advantageously contribute to the lower toxicity of degradation products of the polyurethanes.

EXPERIMENTAL

Materials

Two types of polyurethanes: biodegradable and also with increased resistance to abrasive wear and degradation were studied.

Biodegradable polyurethanes were obtained from the following substrates:

- poly(ϵ -caprolactono)diol (PCL) with the average molecular weight of 2000 g/mol, supplied by Sigma-Aldrich,
- 4,4'-methylenebis(cyclohexyl)isocyanate (H_{12} MDI), supplied by Sigma-Aldrich,
- ethylene glycol (EG), supplied by POCH Gliwice,
- distilled water (w).

Selection of polyurethane with increased resistance to abrasive wear and degradation was carried out by synthesizing different polyurethanes from the following substrates:

- oligodiols:
 - poly(tetramethylene ether) glycol (PTMEG) with the average molecular weight of 2000 g/mol, supplied by Du Pont,
 - oligo(ethylene adipate) (OAE) with the average molecular weight of 1940 g/mol, supplied by Alfaster,
- isocyanates:
 - 4,4'-methylenebis(cyclohexyl)isocyanate (H_{12} MDI), supplied by Sigma-Aldrich,
 - 4,4'-methylenebis(phenyl isocyanate) (MDI), supplied by Sigma-Aldrich,
- distilled water (w).

Polyurethanes were obtained by the prepolymer method. The prepolymer samples were synthesized with the molar ratio of isocyanate to oligodiol equal to 2.00. Extension of prepolymer chains was carried out using polyaddition reaction with glycol as a chain extender or polycondensation reaction with water as a chain extender. As a result of the polycondensation reaction of isocyanate groups with water a CO_2 by-product is formed. Therefore, to limit the formation of bubbles of CO_2 in the bulk of polyurethane, polycondensation reaction was carried out not with a liquid but with the prepolymer solidified by the crystallization. In order to produce biodegradable polyurethane crystallization of prepolymer was performed at three different temperatures (7°C, 22°C and 30°C), while the polyurethanes with increased resistance to abrasive wear were produced from prepolymer crystallised at 7°C.

Table 1. Samples of biodegradable polyurethanes

Sample codes (type of PU)	Type of the chain extender	Crystallization temperature of the prepolymer
PU/EG	ethylene glycol (EG)	–
PU/w7	distilled water (w)	7°C
PU/w22	distilled water (w)	22°C
PU/w30	distilled water (w)	30°C

Table 2. Samples of polyurethanes with increased resistance to abrasive wear and degradation

Sample codes (type of PU)	Type of oligodiol	Type of isocyanate
PTMEG/MDI	poly(tetramethylene ether) glycol (PTMEG)	4,4'-methylenebis(phenyl isocyanate) (MDI)
PTMEG/ H_{12} MDI	poly(tetramethylene ether) glycol (PTMEG)	4,4'-methylenebis(cyclohexyl)isocyanate (H_{12} MDI)
OAE/MDI	oligo(ethylene adipate) (OAE)	4,4'-methylenebis(phenyl isocyanate) (MDI)
OAE/ H_{12} MDI	oligo(ethylene adipate) (OAE)	4,4'-methylenebis(cyclohexyl)isocyanate (H_{12} MDI)

Wear resistant polyurethanes were made from two oligodiols (PTMEG and OAE) and two isocyanates (H_{12} MDI and MDI) to select the polyurethane with the most advantageous properties.

Samples of polyurethanes produced and their codes are listed in Table 1 and Table 2.

Methods

Infrared spectroscopy was performed using Nicolet 6700 spectrometer in the range of wave number from 4000 to 400 cm^{-1} .

Thermal degradation was carried out with the thermogravimeter model TGA Q500 TA Instruments by heating up to 600°C under a nitrogen atmosphere.

Thermal analysis was performed with differential scanning calorimeter model DSC Q1000 TA Instruments, equipped with a liquid nitrogen cooling unit. All measurements were carried out from -100 to 250°C with a heating rate of 10°C/min.

Surface morphology of the fractured samples was observed with scanning electron microscope (SEM) Hitachi S-3500N. The fractured surfaces were obtained by breaking the samples at the liquid nitrogen temperature.

Abrasive wear was measured according to Schopper-Schlobbach method (PN-ISO 4649:2007 standard).

RESULTS AND DISCUSSION

Biodegradable polyurethanes

New polyurethanes made of crystalline prepolymer based on poly(ϵ -caprolactono)diol extended with water are characterized by the better mechanical properties than the polyurethanes extended with ethylene glycol (Table 3). Young's modulus of polyurethanes obtained from crystalline prepolymers decreases with the increase of prepolymer crystallization temperature.

Table 3. Comparison of hardness (H) and Young's modulus (E) of biodegradable polyurethanes

Type of polyurethanes	H [°Sh D]	E [MPa]
PU/EG	38	12.0
PU/w7	57	15.7
PU/w22	57	14.7
PU/w30	58	13.9

In all the tested biodegradable polyurethanes the peak from the reactive -NCO groups.

(2260 cm^{-1}) was not observed, which indicates that all substrates are fully reacted (Fig. 2).

Polyurethanes extended by water are characterized by higher thermal degradation temperature than the PU extended by glycol. They exhibit higher temperature of the mass loss at 5% (Table 4).

All the tested polyurethanes have similar glass transition temperature (T_g) (about -45°C). The PU extended by

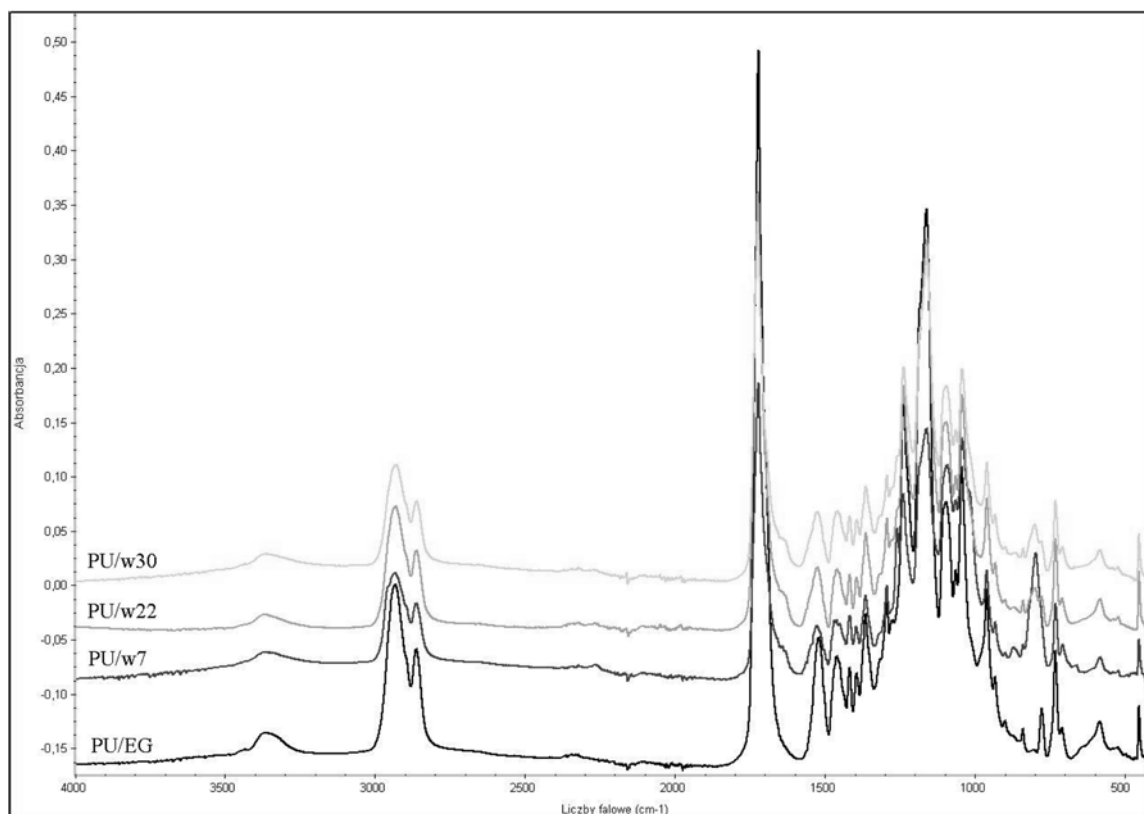


Figure 2. FTIR spectrum of biodegradable polyurethanes

Table 4. TGA results of biodegradable polyurethanes

Type of polyurethanes	Temperature of 5% mass loss [°C]
PU/EG	288.9
PU/w7	295.8
PU/w22	295.8
PU/w30	300.2

glycol exhibits a smaller amount of crystalline phase (lower enthalpy of melting) and it starts to melt earlier than the PU extended by water. It was found that for polymers obtained by the polycondensation reaction of crystalline prepolymers with water, thermal properties depend on the crystallization temperature of the prepolymer (T_k). The higher was the prepolymer crystallization temperature T_k , the lower T_g , ΔH_m and the higher T_m are obtained (Table 5).

The SEM images of the microstructure are shown in Fig. 3. The microstructure of the polymers obtained from the crystalline prepolymers is characterised by spherical

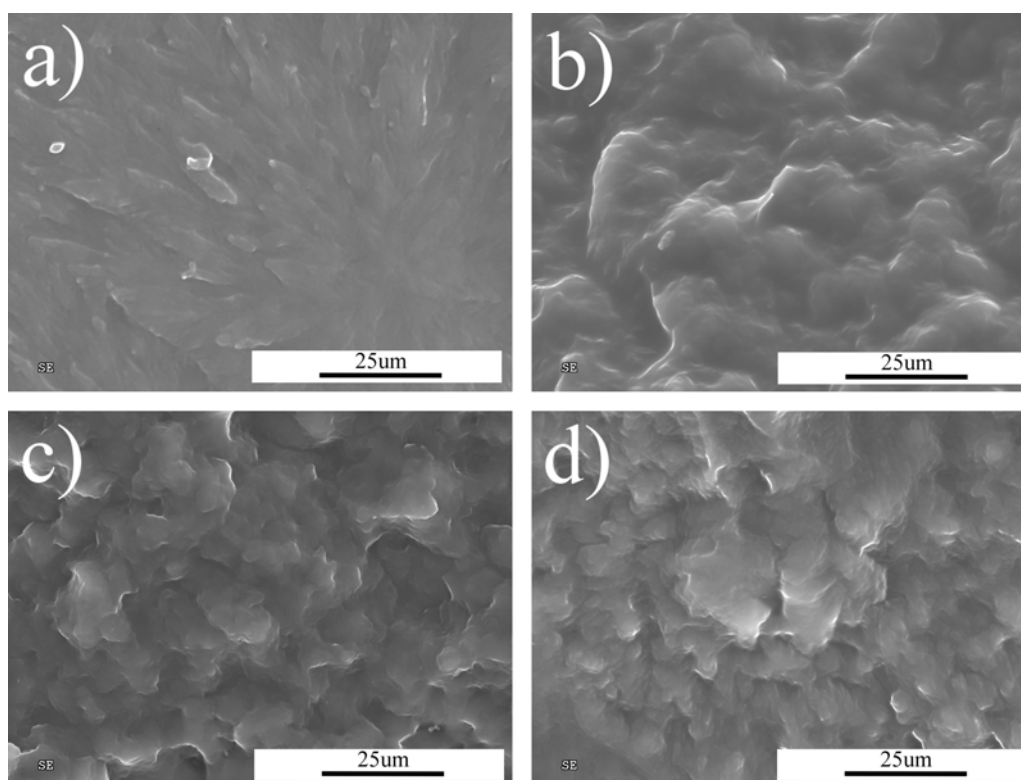


Figure 3. Microstructure of biodegradable polyurethanes a) PU/EG, b) PU/w7, c) PU/w22 and d) PU/w30

Table 5. DSC results of biodegradable polyurethanes

Type of polyurethanes	Glass transition temperature T_g [°C]	Melting temperature T_m [°C]	Melting enthalpy ΔH [J/g]
PU/EG	-44.4	43.4	38.7
PU/w7	-46.2	52.5	43.6
PU/w22	-44.3	54.1	41.4
PU/w30	-43.2	56.0	40.1

shapes of spherulites. The lower the crystallization temperature T_k , the more irregular the spherical shape is, probably due to accelerating of the crystallization process. Polymer obtained by polyaddition reaction with ethylene glycol is characterised by the microstructure of plain spherulites (Fig. 3a).

Polyurethanes resistant to abrasive wear

Polyurethanes from crystalline prepolymers extended by water, based on polytetramethylene ether glycol, are characterized by higher wear resistance and lower density as compared to PU obtain from ethylene oligoadipate (Table 6).

Table 6. Comparison of density (ρ) and abrasive wear (ΔV) of polyurethane resistant to abrasive wear

Type of polyurethanes	ρ [g/cm ³]	ΔV [cm ³]
PTMEG/MDI	1.0833	0.0238
PTMEG/H ₁₂ MDI	1.0556	0.0264
OAE/MDI	1.2502	0.0595
OAE/H ₁₂ MDI	1.2247	0.2353

In Fig. 4 the results of infrared spectroscopy are presented. Also in this case, in all the tested polyurethanes with increased resistance to abrasive wear the peak from reactive -NCO groups was not observed (2260 cm⁻¹). Poly-

urethanes obtained from PTMEG exhibit the very well visible peak from ether bond, while in the case of polyurethanes based on OAE, the peak from ester bond is observed.

Polyurethanes based on PTMEG are characterized by higher temperature of thermal degradation than the polyurethanes based on OAE. Also the influence of the isocyanate type was observed. Polyurethanes based on MDI are characterized by higher temperature of thermal degradation than the polyurethanes based on HMDI. The results of TGA studies are shown in Table 7.

Table 7. TGA results of polyurethane resistant to abrasive wear

Type of polyurethanes	Temperature has for 5% mass loss [°C]
PTMEG/MDI	314.2
PTMEG/H ₁₂ MDI	305.3
OAE/MDI	302.5
OAE/H ₁₂ MDI	299.5

The DSC results for the polyurethane resistant to abrasive wear are shown in Table. 8. In all the tested polyurethanes a clear glass transition temperature T_g is observed. The PU based on PTMEG are characterized by lower T_g than PU based on OAE. The existence of the aromatic rings from MDI raises T_g . PUs based on PTMEG exhibit lower melting temperature of the crystalline phase than the PUs based on OAE.

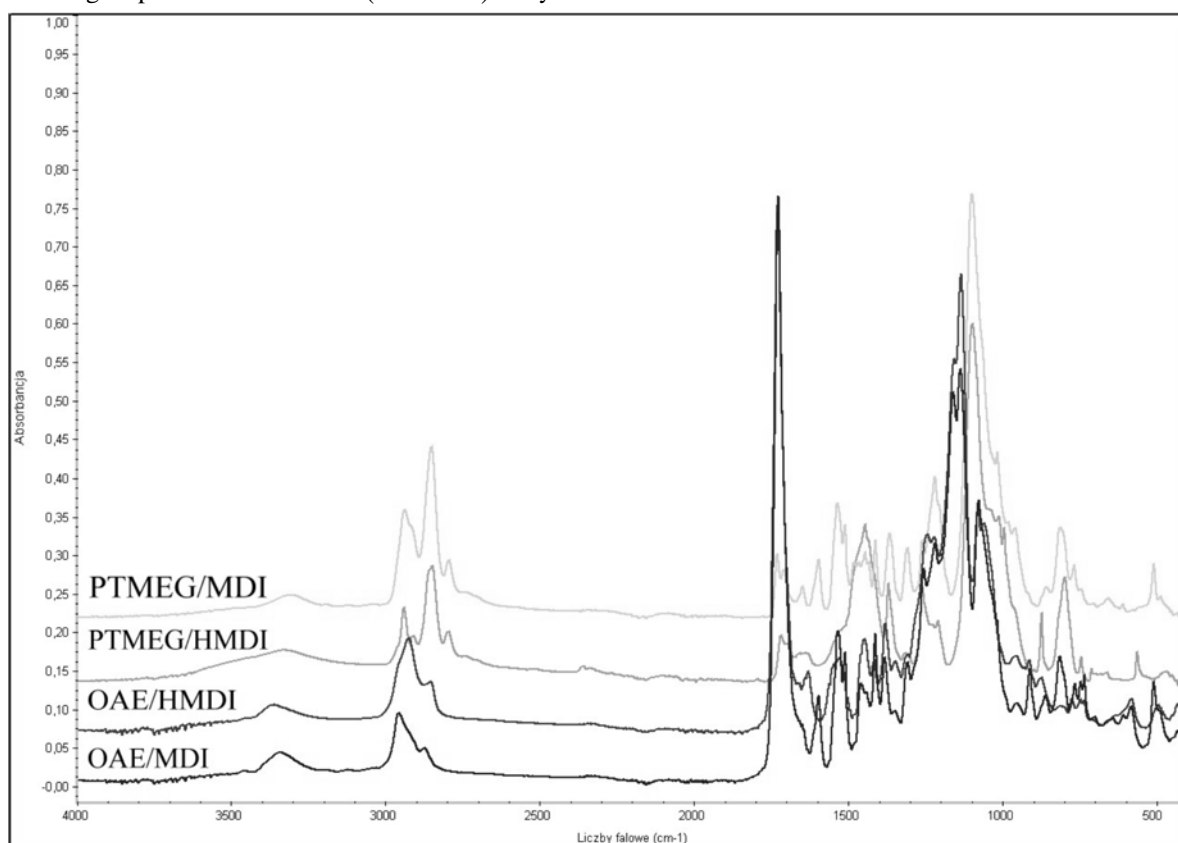
**Figure 4.** FTIR spectrum of polyurethane resistant to abrasive wear

Table 8. DSC results of polyurethane resistant to abrasive wear

Type of polyurethanes	Glass transition temperature T_g [°C]	Melting temperature T_m [°C]	Melting enthalpy ΔH [J/g]
PTMEG/MDI	-69.6	10.1	23.0
PTMEG/H ₁₂ MDI	-75.4	17.9	22.2
OAE/MDI	-32.1	43.0	13.8
OAE/H ₁₂ MDI	-35.8	43.5	14.5

CONCLUSION

Polyurethanes made of crystalline prepolymers extended by water are characterized by interesting properties with the perspective of application as components of ceramic-polymer joints endoprosthesis. Using water as a chain extender may have a beneficial effect on the toxicity of the material. Biodegradable polyurethanes in which water was used as a chain extender are characterized by higher Young's modulus compared to the PUs extended with ethylene glycol. The studies performed also show that poly(tetramethylene ether) glycol (PTMEG) can be used as a substrate to produce polyurethane resistant to abrasive wear. In all the tested polyurethanes peak from -NCO groups was not observed, which means that the substrates are fully reacted.

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