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Application of microwave/radio frequency and radio frequency/ magnetron sputtering techniques in polyurethane surface modification

W. Kaczorowski*, D. Batory, P. Niedzielski
Institute of Materials Science and Engineering, Technical University of Lodz, ul. Stefanowskiego 1/15, 90-924 Łódź, Poland
* Corresponding author: E-mail address: witold.kaczorowski@gmail.com

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Materials

ABSTRACT

Purpose: The aim of the study is the analysis of the possibilities of application of MW/RF PACVD and RF PACVD/MS systems in polyurethane surface modification.
Design/methodology/approach: As the substrates samples made out of the biocompatibile polyurethane were used. Modifications were performed in MW/RF PACVD and RF PACVD/MS reactors using different gases and process parameters. Topography, thickness and contact angle were measured using Atomic Force Microscopy, Profilometry and Contact Angle Measuring Instrument.
Findings: Optimal plasma parameters ensuring deposition of carbon layers without surface degradation were worked out. Deposited layers were less than 500 nm thick and presented the wetting angle value more than 90º. During the examinations the influence of the gas atmosphere and process parameters used for the preliminary substrates modification were investigated. Obtained results prove the possibility of application of MW/RF PACVD and RF PACVD/MS techniques in deposition of carbon-based coatings on polyurethane substrates used for artificial heart chambers manufacturing.
Research limitations/implications: Modification of polymer surface has to be conducted at low temperatures, up to 100ºC. Unfortunately not all CVD and PVD methods used in this field guarantee the adequate adhesion of manufactured layers deposited in such low temperatures. So far the most promising results were obtained with use of PLD (pulsed laser deposition) techniques. However application of MW (microwave) low temperature plasma source and combination of magnetron sputtering technique with RF (radio frequency) plasma source seems to be equally interesting techniques.
Originality/value: Optimization of carbon layers deposition techniques on polyurethane substrates can be helpful in improvement of modern artificial heart chambers construction. All investigation results obtained in his field attend to work out the new generation of cardiosurgical implants within the confines of multiyear Project „Polish Artificial Hart".
Keywords: Materials; Biomaterials; Polyurethane; DLC; Carbon

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1. Introduction

Artificial substances are very important group of materials used in biomedicine. Special implants for cardiosurgery, orthopedics and ophthalmology are manufactured from polymers. With meaning is their application in laboratories for in vitro investigations (as the laboratory equipment) and in vivo (in biosensors construction). Continuously lasting investigations concerning the refining and improvement of polymer properties for the medical purpose embrace not only designing and manufacturing of new materials, completely different than other but also modifications of well known and practical solutions [1]. Among the most important purposes to attend by the applied polymer modifications are: change of the cell adhesion (e.g. peptides), change of the wetting angle, biocompatibility improvement, surface functionality, friction coefficient reduction, creation of the protection barrier (tissues and structural fluids) [2]. Changes of the polymer properties can be obtained by the physical methods [3] (e.g. Langmuira-Blodgett company), chemical (acid and alkane etching) and physico-chemical [1] (plasma, laser). In presented work modification of polymers surface was conducted with use of plasmo-chemical processes. As the substrate bioconsistent polyurethane was used, material used in artificial heart construction. This polymer is characterized by many very good properties, however application of polyurethane onto elements which have the contact with flowing blood, especially for long-term use implants can bring a risk of degradation and surface damage. In order to improve the wear resistance together with biocompatibility enhancement polyurethane can be subjected to processes of properties changing by both PVD and CVD methods as well. The most important limitation of those methods is the necessity of keeping a low temperature during the modification process. From the other side application of low temperature processes can unfavourably affect the adhesion strength to the substrate surface. Hitherto existing literature data shows that the most promising polyurethane surface modification results were obtained using the PLD (pulsed laser deposition) method [4]. However there are still conducted the investigations with application of other modification techniques. To that purpose in presented work two different devices were used: MW/RF PACVD (microwave and radio frequency plasma assisted chemical vapour deposition) and RF PACVD/MS (radio frequency plasma assisted chemical vapour deposition/magnetron sputtering).

2. Experimental Details

2.1. Samples preparation

Brand name of the polyurethane used in the examinations is *Ellathane.* This polimer is a family of medical-grade thermoplastic polyurethane elastomers. It is characterized by superior resilience, low temperature properties and exceptionally smooth surface. Samples made from Ellethane are clear to slightly yellow in their original state. Polyurethane samples before the modification processes were cleaned in the methanol ultrasonic bath and dried out in compressed air stream.

2.2. Film preparation

Views of the devices using MW/RF PACVD and RF PACVD/MS methods are presented on Figs. 1 and 2. MW/RF apparatus is equipped with two independent plasma inducing sources [5,6]. First one – radio frequency 13.56 MHz energy source is connected through the matchbox with the electrode, where on the specially designed specimen holder, were fixed modified samples. Second one – 2.45 GHz frequency energy source is connected through the circulator with the resonance chamber mounted opposite to the electrode in upper side of the apparatus.

Fig. 1. View of PACVD/MS system

Fig. 2. View of MW/RF PACVD system

RF PACVD/MS device is equipped similarly as the first one with the radio frequency energy source, whereas in the top chamber cover is fixed the magnetron with all necessary systems [7-9].

Samples in this apparatus were mounted on the water cooled RF electrode.

In presented examinations following gases and their mixtures were used: methane CH_4, Argon Ar, Nitrogen N_2, and Oxygen O_2. During the polymer modifications performed with use of the plasma, according to In – Hung description four types of processes can occur: cross-linking, etching (degradation), layers synthesis and surface functionality. Each of those processes is depended on applied plasmo-chemical process parameters. In case of presented investigations the surface modification was grounded on preliminary modification in inert gases and subsequent deposition of carbon based layers. In dependence on applied modification method directly on the polyurethane substrates was manufactured either carbon layer (MW/RF method) or gradient Ti based carbon layer (RF/MS method). Carbon-based layers have already found the application in many fields of biomedicine [10,11], and properties which are distinguished [11,12] can constitute a great alternative to other layers used as the polyurethane cover. Basic ranges of the parameters applied during conducted processes are presented in Table 1.

2.3. Characterization

Polyurethane use on present examinations is a material with smooth hydrophobic surface. Conducted investigations are an attempt to work out the technology assuring as small as possible surface expansion while keeping its hydrophobic properties. The most important aspect of the examinations was to ensure the process temperature at the level which will not result in substrate degradation (Fig. 3). This parameter in performed deposition processes was strongly depended on the negative self bias generated on the RF electrode and on the gas mixture. Taking into consideration different construction of used devices and methods of samples fixation inside the reaction chambers the maximum parameters determining the "safe" self bias voltage were worked out. For MW/RF method safe self bias was about 350 [V], whereas for the RF PACVD/MS method it was in the range of 550 [V]. The differences in negative self bias values appear as the result of the method of the heat transfer from modified sample. In firstly described method samples were placed on the specially designed sample holder about 40 mm below the upper edge of the reactor. In second reactor polyurethane samples were placed on the water cooled radio frequency electrode (see Fig. 4).

Fig. 3. View of the polymer substrates after the modification process performed at too high self bias potential (left side) and optimal parameters (right side)

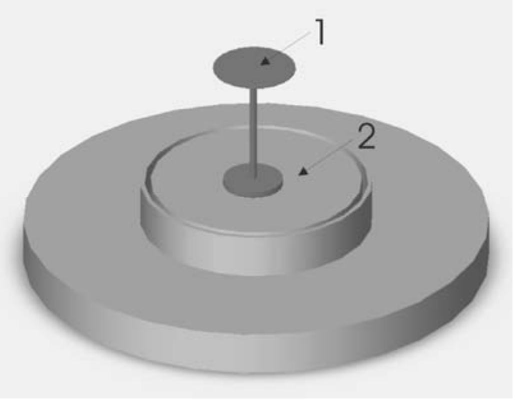

Fig. 4. Samples arrangement in the reaction chamber of devices: 1 -MW/RF system, 2 – RF/MS system

Table 1.
Plasma processes parameters

RF PACVD/MS		
Stage of process	Modification	Deposition
Pressure [Pa]	1	1→20
Self bias [V]	500	300→500
Sputtering current [A]	-	5→4
Gases flow [sccm]	Ar – 10 O_2 – 10	Ar - 10→0 CH_4 – 1→30
Time [s]	600	600
MW/RF PACVD		
Pressure [Pa]	10	100
Radio frequency power [W]	70	70→ 50
Microwave power [W]	300	300→150
Gases flow [sccm]	Ar, N_2, O_2 – 10	Ar- 20→0 CH_4 – 20
Time [s]	200	900

Next task taken into consideration during the examinations was the analysis of the influence of the chemical composition of the atmosphere inside the reaction chamber on the adhesion and expansion of the modified surface. Performed investigations made it possible to find the correlation between the gases (amount and mixture) and the polymer surface topography change. Thanks to those examinations it was also possible to match the polyurethane modification processes parameters. On Fig. 5 is presented the change in the surface topography in dependence on different gases (argon, oxygen, nitrogen) used in the substrates modification processes in MW/RF method. In this case the same energetic parameters were kept during the primary modification process and carbon-based layers deposition. The only parameter which was changed during the modification process was a type of the gas introduced onto the reaction chamber. It was noticed that the smallest surface expansion was obtained when using argon. Those relations were also confirmed at different process energetic parameters. On the basis of obtained examination results argon was typed as the most suitable gas for further optimization processes. During the investigation using the MW/RF method no significant problems with adhesion of the layers to the polymer substrates were observed.

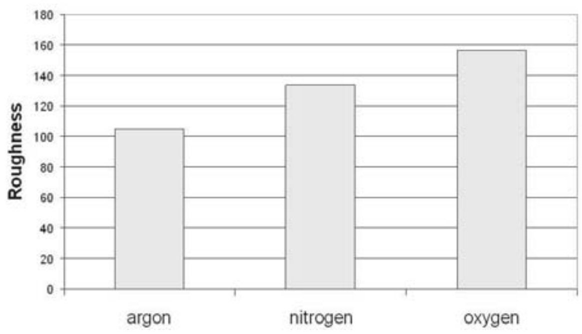

Fig. 5. Changes in roughness of modified surfaces by the carbon-based layers vs different gases introduced into the reaction chamber during preliminary modification processes

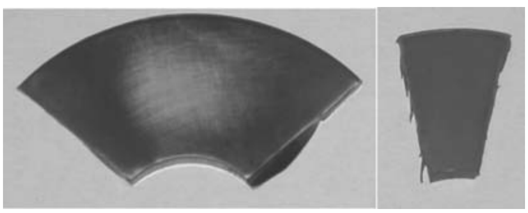

Fig. 6. View of the polymer substrates after the modification processes using RF PACVD/MS technique and application of argon (left side) and mixture of argon and oxygen (right side) for the primary modification processes

In case of RF/MS technique application of pure gases (argon, nitrogen) didn't bring expected results. Only then, when the mixture of oxygen and argon was introduced into the reaction chamber it made it possible to manufacture carbon-based layer with good adhesion (see Fig. 6). Attempts performed in purpose to decrease the surface expansion embraced in this case analysis of the influence of the negative autopolarisation potential on the surface topography, described in one of the next paragraph.

During the investigations processes of deposition of carbon layers conducted using two different gas mixtures (methane or methane with argon) were analyzed. Obtained results presented on Fig. 7 indicates that addition of argon to the methane atmosphere during the whole deposition process can disadvantageously influence on the surface expansion of modified polyurethane surfaces. As it is presented on Fig. 6 application of the mixture CH_4/Ar, mentioned above, results in increased number of surface irregularities in the microscopic view.

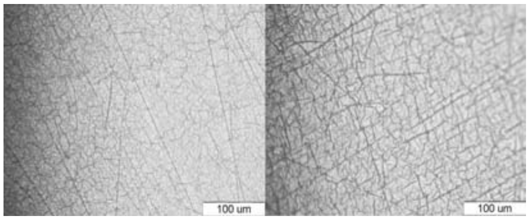

Fig. 7. View of the surfaces of modified polyurethane substrates after the modification processes where during the carbon-based layer deposition pure methane (left side) or methane and argon mixture (right side) was applied

Numerous attempts performed to manufacture carbon layers onto previously plasma modified samples made it possible to work out the parameters making it possible to synthesize carbon layers 500 nm thick. This parameter was analyzed by the measurement of the offset profile occurred as the result of the carbon layers deposition onto partially covered polyurethane surface. A model profile obtained during the thickness measurement of carbon-based layer using the profilometer is presented on Fig. 8.

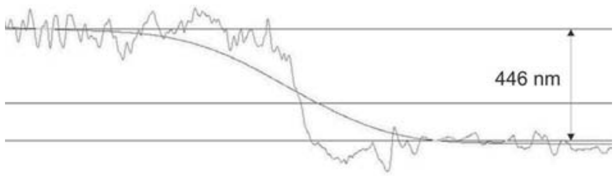

Fig. 8. A model profile obtained during the thickness measurement of obtained carbon-based layer

Taking into consideration assumed goal of performed examinations which is the modification of the polyurethane surface using presented carbon-based layers for the needs of artificial heart it can be expected that the lower will be the thickness of deposited layers the lower stress will be generated in the film. Thus deposited layers will affect the higher durability of the ready heart chamber. Investigations concerning this problem are now in the examination phase. Research direction focused on thickness limitation seems to be correct, especially in case of carbon layers. However in case of gradient carbon layers it is not necessary, because as the research results prove, their construction itself supports the lowering of internal stress of the composite as a whole. Modified polyurethane substrates presents hydrophobic properties. Thus the investigations concerning the influence of applied modifications on the wetting angle were performed using the *Kruss* Nanodrop device. It was noticed that both applied methods MW/RF PACVD and RF PACVD/MS make it possible to manufacture carbon-based layers characterized by the lower wetting angle than its values obtained for a non modified substrate. Neverthless even the modified substrates were still characterized by the hydrophobic properties. Some of the modifications especially using the low energetic MW/RF plasma resulted in drop of the wetting angle to minimal value of 68^0.

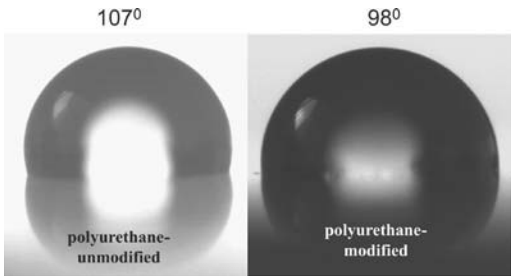

Fig. 9. A model view of the drop on the sample surface obtaiend during the wetting angle investigation

All examinations presented above made it possible to perform the optimization of processes of manufacturing of carbon-based layers on polyurethane substrate. Results of conducted works are presented on Figs. 10 and 11.

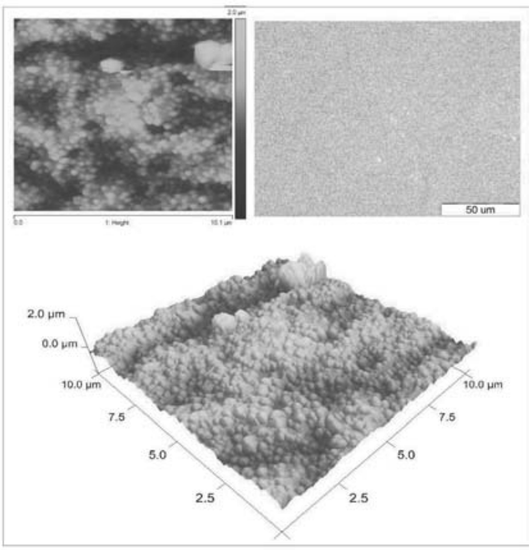

Fig. 10. View of the modified polyurethane surface after the optimization processes performed using the RF PACVD/MS device

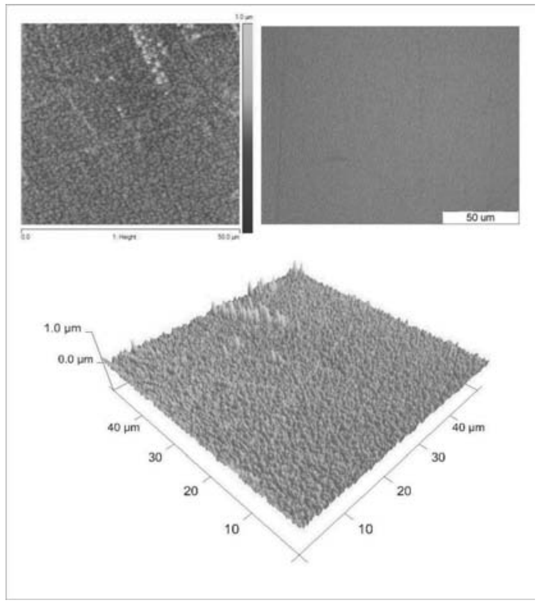

Fig. 11. View of the modified polyurethane surface after the optimization processes performed using the MW/RF PACVD device

As it is presented optimized layers indicate smooth ideal surface with very small granulation. Comparing the surface roughness parameters it can be stated that the smaller surface expansion was obtained by the modification in MW/RF plasma.

3. Conclusions

So far performed processes made it possible to work out MW/RF and RF/MS plasma parameters ensuring deposition of homogeneous and uniform carbon layers onto polyurethane substrates. On the basis of conducted investigations the correlation between the gas mixture introduced into the reaction chamber vs. expansion of obtained surface has been found. For each method separately the influence of a negative self bias voltage onto properties of modified substrate was analyzed. Wetting angle of the substrates before and after modification processes was determined as well as the thickness of deposited layers. Preliminary optimization works made it possible to manufacture layers with a thickness below 500 nm (Fig. 8) characterized by hydrophobic properties (Fig. 9) and surface topography as presented of Figs. 10 and 11. Actually further works concerning optimization processes and characterization of the properties of deposited layers are being conducted.

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