JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 11, No. 10, October 2009, p. 1432 - 1435

Infrared analysis of plasma polymerized hexamethyldisiloxane for biocompatible composites[♣]

E. RADEVA[*], L. PRIMATAROVA, R. DIMITROVA[a], S. POPOVA[a], T. HIKOV, D. FINGAROVA, E. PECHEVA
Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
[a]*Institute Of Organic Chemistry With Centre Of Phytochemistry, Acad. G. Bonchev St., Bl. 9, 1113 Sofia, Bulgaria*

There is an increasing interest in utilizing polymers as matrices for calcium phosphate based composites used in hard tissue implants. Plasma polymerization gives a possibility for obtaining polymers with different compositions and structures from simple monomer molecules, by varying the polymerization conditions. The structure of plasma polymer layers obtained from hexamethyldisiloxane (PPHMDS) was studied by infrared spectroscopy. The analysis of the obtained plasma polymers indicates a long chain polysiloxane structure resulting from the removal of some methyl groups from the monomer molecule. The influence of the plasma polymerization conditions - the monomer flow rate and the current density of the glow discharge on the chemical structure, was studied. The effect of the silica glass substrate on the polymer structure was established. The growth of the hydroxyapatite (HA) layer from a suspension of saturated simulated body fluid (SBF) and detonation nanodiamond (DND) on the polymer film was carried out, and the structure of the obtained layers was investigated. The results emphasize the possibility for tailoring the polymer structure by varying the deposition conditions and the substrate, in order to use them in biocompatible materials.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Biocompatible composites, Thin films, Plasma polymers, Infrared spectroscopy

1. Introduction

Recently, conventional polymers have been widely used in biocompatible composites in human body tissues, bones, cartilages, blood etc [1-3]. Among them, polysiloxanes, remarkable for a number of properties including high mechanical stability, oxygen permeability, transparency etc., have many medical applications [4, 5].

This paper presents results on the structure of plasma polymer films obtained from hexamethyldisiloxane (PPHMDSO) for different plasma parameters on KBr pellet and silica glass (SG) substrates. The growth of a hydroxyapatite (HA) layer on the polymer film, which gives a prerequisite for plasma polymer applications in biocompatible materials, was established.

2. Experimental

The polymer layers were deposited by a plasma polymerization process. The plasma reactor setup which was used for synthesis of the polymer films is described in [6]. In the reactor chamber, the capacitively coupled glow discharge was accomplished between two horizontally aligned electrodes, placed 60 mm from each other. Hexamethyldisiloxane (HMDS) - >99% Merck - was supplied as a monomer. The monomer flow rate was controlled by a regulator for gas consumption (GMR, NOVIS, Bulgaria). The plasma excitation of the monomer gas was achieved at 27.12 MHz using a generator (VEM Inducal Berlin, Germany). The substrates, KBr pellet and silica glass Herasil, were placed on a Teflon plate between the electrodes. The plasma polymerization conditions were controlled by two parameters: the monomer flow rate and the current density of the glow discharge (Table 1).

Fourier transform infrared (FTIR) analysis (BRUKER, VECTOR 22) was used to investigate the bonding structure of PPHMDS in the wave number range 400 to 4000 cm^{-1}. The spectra of the polymer films were typically obtained by averaging 128 scans.

Table 1. PPHMDS *samples obtained under different polymerization conditions.*

[♣] Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

Samples groups	Monomer flow rate [l/h]	Current density [mA/cm^2]	Thickness [nm]
PPHMDS_1	1.0	1.6	107
PPHMDS_2	1.0	0.5	110
PPHMDS_3	2.0	1.6	150
PPHMDS_4	2.0	0.5	220

Further, for the biomimetic growth of the HA layer on polymer film, supersaturated simulated body fluid (SBF) was prepared by dissolving reagent-grade chemicals in double distilled water. The samples (PPHMDS on SG) were immersed in a suspension (10:1 wt.%) prepared from SBF and detonation nanodiamond (DND) for 24 and 48 hours at 37 ^{0}C and pH 7.4. The experiments were carried out in duplicate and reproducible results were obtained. A HA layer growth, after the different treatments, was found from the analysis of the FTIR spectra.

3. Results and discussion

The effects of the plasma polymerization conditions, i.e. the monomer flow rate and the glow discharge current density, on the chemical structures of the PPHMDS obtained on KBr pellets are presented in Fig. 1. For comparison, the spectrum of the monomer (HMDS) is shown.

The IR bands of the monomer were assigned according to the literature [7, 8]. The formation of PPHMDS was proved by the following features of the spectra (i) an increase in the intensity of the Si–O asymmetric stretching band and the appearance of a doublet (1060 and 1040 cm^{-1}) at higher power of the glow discharge (curve 1 and 3), which was related to the yield of a highly cross linked Si-O-Si network and the contribution from the CH_2 groups from Si-CH_2-Si bonds, formed after hydrogen substraction; (ii) a shift and a decrease in the intensity of the bands due to the CH_3 rocking in Si$(CH_3)_x$ at 600 cm^{-1}, and (iii) the disappearance of the CH_3 groups in the region of 2900 cm^{-1}, undoubtedly showing that some methyl groups were removed from the monomer molecule during the plasma polymerization. Furthermore, the changes in the polymer spectra due to methyl vibrations were an indication of the decrease of Si-$(CH_3)_3$ end groups and methyl groups in the polymer structure as a whole. In addition, the deformation mode of CH_x (x = 1,2,3) groups around 1500 cm^{-1} vibration and the carbonyl functionalities incorporated into the polymer film (peaks in the region 1500-1750 cm^{-1}) were strongly increased, as a result of monomer rearrangement. The band shifts were related to a change in the local environment of Si-O-Si groups, which varies with the polymerization conditions, as the Si-O-C bonds exist together with Si-O-Si ones [9, 10].

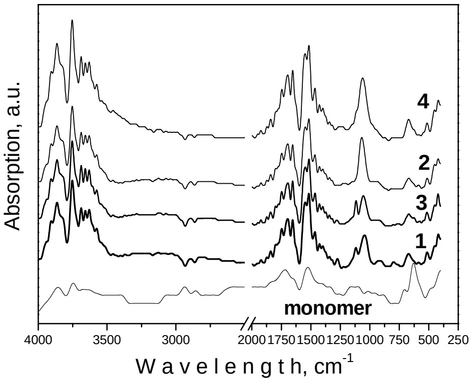

*Fig. 1. FTIR spectra of the monomer and PPHMDS on KBr obtained at:**1** - 1.0 l/h, 1.6 mA/cm^2 ; **2**-1.0 l/h,0.5 mA/cm^2; **3** - 2.0 l/h,1.6 mA/cm^2; **4** - 2.0 l/h,0.5 mA/cm^2.*

Concerning the FTIR spectra of the polymer layers obtained on KBr pellets, the distinctions of the polymer structure depending on the plasma parameters used are as follows:

- The plasma polymer structures obtained at different monomer flow rates and equal plasma current density are very similar. Evidently, the plasma current density is a major parameter influencing the polymer structure.
- An increase in the plasma current density leads to an increase in the energy per unit mass of the monomer, thus changing monomer fragmentation in the plasma field. The power enhancement results mainly in the higher intensity, broadening and splitting of the Si-O stretching vibration at about 1050 cm^{-1}. A well-pronounced shoulder at the long wave number end of the band was observed at higher power levels, too. All changes in the spectra at the higher power point to an elongation of the polymer chain and a higher degree of cross-linking of the branched polymer structure.

The polymerization of HMDS was carried out on SG substrates under the same experimental conditions as on the KBr pellets. In Fig. 2, the spectra of the obtained polymers at different current densities of the glow discharge and equal monomer flow rate are shown. The corresponding spectra of the polymers on KBr pellets are also shown.

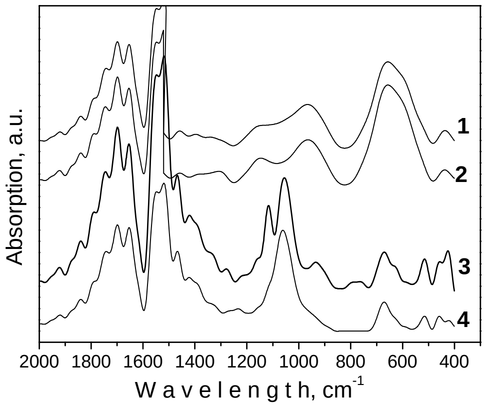

Fig. 2. FTIR spectra of PPHMDS on SG obtained at: ***1*** *- 1.0 l/h, 1.6 mA/cm^2;* ***2*** *- 1.0 l/h, 0.5 mA/cm^2; and FTIR spectra of PPHMDS on KBr:****3*** *- 1.0 l/h, 1.6 mA/cm^2;* ***4*** *- 1.0 l/h, 0.5 mA/cm^2.*

Comparing the spectra of PPHMDS obtained on KBr and SG substrates leads to the observation of differences which can be pointed out. The Si–O-Si stretching vibrations (around 1000 cm^{-1}) are highly diminished and shifted. This could give evidence for the interaction between the growing polymer and the SG surface. The strong unresolved peak in the region 500-750 cm^{-1} (lines 1 and 2) is most probably due to the existence of various arrangements of the CH$_x$ (x = 1,2,3) groups around the silicon atoms. Moreover, despite the different experimental conditions, the polymers formed on an SG surface had almost the same Si-O-Si network. Therefore, in our case the synthesis of plasma polymers strongly depends on the substrate surface structure. As is known, the SG surface possesses an acidic character due to the large amount of silanol groups (Si-OH) (Fig. 3), so an interaction between the latter with monomer fragments could be expected. Probably, the monomer degradation begins by removing some methyl groups as well as by fragmentation of the monomer's Si–C and C–H bonds [11, 12]. When SG is used as a substrate, the precursors obtained after monomer fragmentation, especially at higher a plasma power level, could react and form covalent bonds with SG silanol groups, as for example O-C bonds (peaks in the region 1500-1750 cm^{-1}) (Fig. 2), or react with other Si-O-Si bonds to create a branched siloxane network (the peaks observed in the region 900 to 1100 cm^{-1}) (Fig. 2). The growth of the hydroxyapatite (HA) layer on the polymer film on SG was investigated by FTIR. In order to estimate the grown layer properties, the spectrum of the support (PPHMDS on SG) was substracted from the corresponding spectra.

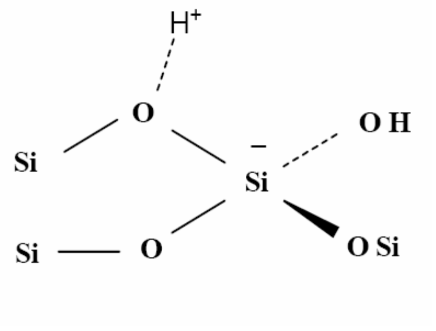

Fig. 3. Schematic presentation of the silica glass surface and silanol groups.

In Fig. 4, the resultant spectra are presented with the example of the PPHMDS_3 sample after its immersion for 48 hours (line 1), and 24 hours (line 2) in the suspension (10:1). For comparison, the spectrum of DND (line 3) and the spectrum of PPHMDS on an SG substrate (line 4) are also given.

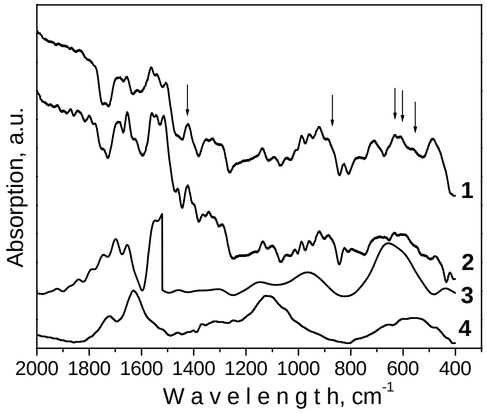

*Fig. 4. The resultant FTIR spectra obtained after 48 hours (****1****) and 24 hours (****2****) of growth, the spectrum of PPHMDS obtained on SG at 2.0 l/h and 1.6 mA/cm^2 (****3****) and the DND spectrum (****4****).*

As seen from Fig. 4 - lines 1 and 2, no distinct HA layer was observed. However, an absorbance band of acid phosphate at 870 cm^{-1} and the triply degenerate asymmetric P-O bending vibration of the phosphate groups (PO_4^{3-} at 570, 602, and 632 cm^{-1}) as well as some carbonate bands (at 870 and 1420 cm^{-1}) were registered, with intensities increasing with the time of immersion. The best results were established for polymers obtained at 1.6 mA/cm^2 current density and 2.0 l/h monomer flow rate.

In order to shed light on the differences in the surface reactivity of the PPHMDS samples and the SG substrate, we carried out pH measurements. The samples were put in Teflon containers and 20 ml SBF was poured into the container to give an approximate sample concentration of 100 mg/ml. Then the pH was measured in situ at 37°C after 48h. The maximum standard deviation was 0.25 pH units for the SG (from 7.1 to 6.85) and 0.1 pH units for the PPHMDS on the SG. Apparently, on the polymer surface the processes of dissolution and precipitation of the SBF ions and DND particles are not so fast compared to those on the SG substrate. However the change in pH of the solution illustrates the interaction between the polymer and the SBF, which was confirmed by the FTIR spectra of the samples obtained after 24 and 48 hours of immersion.

4. Conclusions

The FTIR study of the structure of the plasma polymer films synthesized from HMDS at 27.12 MHz, on different substrates and under changing plasma conditions, shows the following:

- All polymers obtained have crosslinked and branched Si-O-Si networks, due to the removal of some methyl groups as a result of the monomer fragmentation and the rearrangement of the exited particles during the polymer growth.
- The glow discharge current density strongly influences the structure of the plasma polymer. Increase of the current density leads to an elongation of the polymer chain, as well as to a higher degree of cross-linking of the siloxane network.
- The polymer structure depends on the nature of the substrate. In contrast to KBr, the SG substrate could react by means of SG silanol groups. The polymer film appears to be covalently bonded to the SG via O-C bonds and O-Si-O bonds, thus changing the structure of the polymer film growing on the SG surface compared to those synthesized on KBr. Despite the different experimental conditions, the polymers formed on the SG surface have almost the same Si-O-Si network, but the latter differ from the one obtained on KBr pellets. The ratio of Si-O-Si to Si-$(CH_3)_x$ and the new functional groups of C-O could be modified by changing the experimental parameters.
- After immersion in a suspension of DND and SBF for 24 and 48 hours, the growing structure on the PPHMDS synthesized on SG, shows an existence of phosphate and carbonate groups.

According to all results, the conditions of 1.6 mA/cm^2 current density and 2.0 l/h monomer flow rate are expected to be the most promising for preparing PPHMDS films on SG for growing HA/DND layers. The growth of such materials seems to increase with the time of immersion in a suspension of DND and SBF.

The results emphasize the possibility for tailoring a plasma polymer structure by varying the deposition conditions and substrate, in order to use them in biocompatible materials.

Acknowledgements

This research is supported by a Bulgarian National Scientific Research Fund through Grant TK-X-1708/07 and the European Commission - Research Infrastructure Action under the FP6 "European Integrated Activity of Excellence and Networking for Nano and Micro-Electronics Analysis" - Project number 026134(RI3) ANNA".

References

[1] H.Y. Cheung, K.T. Lan, T.P.Lu, D. Hui, Composites B **38**, 291 (2007).
[2] T. Hoshi, T. Sawaguchi, T. Konno, M. Takai, K. Ishihara, Polymer **48**, 1573 (2007).
[3] S. Lakard, N. Morrand-Villeneuve, E. Lesniewska, B. Lakard, G. Michel, G. Herlem, T. Gharbi, B. Fahys, Electrochimica Acta **53**, 1114 (2007).
[4] L. Lin, H. Sheardown, Biomaterials **26**, 233 (2005).
[5] H. M. L. Tan, H. Fukuda, T. Akadi, T. Ichiki, Thin Solid Films **515**, 5172 (2007).
[6] E. Radeva, D. Tsankov, K. Bobev, L. Spassov, J. Appl. Polym. Sci. **50**, 165 (1993)
[7] J. Schwarz, M. Schmidt, A. Ohl, Surf. Coat. Technol. **98**, 859 (1998).
[8] T. J. Lin, B. H. Chun, H. K. Yasuda, D. J. Yang, J. A. Antonelli, J. Adhes. Sci. Technol. **5(10)**, 893 (1991).
[9] N. Benissad, K. Aumaille, A. Granier, A. Goullet, Thin Solid Films **384**, 230 (2001).
[10] R. A. B. Devine, J. Vac. Sci. Technol. A **6**, 3154 (1988).
[11] A. J. Beck, F. R. Jones, R. D. Short, J. Chem. Soc.,

Faraday Trans. **94(4)**, 559 (1998).
[12] H. Yasuda, T. Hsu, J. Polym. Sci., Polym. Chem. Ed. **15**, 81 (1977).

---

*Corresponding author: eradeva@issp.bas.bg