

## Structure of Thin Plasma Polymer Films on the Base of Hexamethyldisiloxane\*

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**Abstract.** Plasma polymers and composites based on hexamethyldisiloxane (PPHMDSO) were synthesized and studied by FTIR. By varying plasma polymerization parameters, fillers with various nanodiamond particles (DNDs) and post ammonia plasma modification the changes in the structure were achieved. At higher current density an elongation of the polymer chain and high cross-linking were observed. The decrease of the monomer flow rate led to a long-chain and branched polysiloxane network. The structure of the composites contained DND particles distributed in the polymer matrix. The ammonia modification led to a higher degree of cross-linking due to the additional decrease of hydrocarbon groups. This work demonstrates the possibility to produce composites with controlled chemical structure by changing plasma parameters, DND nanofillers and post treatment in ammonia plasma.

PACS codes: 68.65.-k

### 1 Introduction

Plasma polymerization is an attractive method for obtaining thin films with substantially different structure and properties compared to the conventional polymers. This is due to the mechanism of the plasma polymerization process where the monomer subjected to the successful fragmentation and recombination forms a polymer. Therefore, the chemical structure of the plasma polymers depends not only on the used monomer, but also on the plasma polymerization conditions. By varying different parameters, films with desired chemical structure and properties could be obtained. There is an interest to use plasma polymers and especially organosilicon ones as protective coatings, sensitive films in sensors, electroluminescent displays etc [1-5]. Moreover plasma polymerization process allows using modifiers and fillers to produce new composites. Therefore, there is a possibility to expand areas of application by obtaining materials with controlled structure and properties. Synthesis of biocompatible thin films is another attractive example of plasma polymers application [6].

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\*Talk given at the Second Bulgarian National Congress in Physics, Sofia, September 2013.

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The paper presents results on the effect of the main plasma parameters, ammonia plasma modification and detonation nanodiamond (DND) fillers, modified with silicon or silver, on the chemical structure of plasma polymers obtained from hexamethyldisiloxane (HMDSO).

## **2 Experimental**

### **2.1 Synthesis of Plasma Polymerized HMDSO Films (PPHMDSO) and Composites**

The plasma polymerization process was performed in a vacuum system described previously [7]. HMDSO (Merck 99%) is used as a monomer. Information about the process of obtaining the polymer films is given in [8]. The composites deposition was carried out in the same plasma polymerization equipment. Nanodiamond particles used in the experiments were obtained by a detonation of carbon-containing explosives (DND) and modified with silicon (Si-DND) and silver (Ag-DND). The mixture of DND powders and HMDSO was shaken for 15 min in an ultrasonic apparatus; further the container with the mixture was stirred (275 r.p.m) continuously at room temperature. The subsequent modification by ammonia plasma was at 0.17 dm<sup>3</sup>/min NH<sub>3</sub> flow rate and 0.16 mA/cm<sup>2</sup> current for 5 minutes [6].

### **2.2 FTIR Spectra**

FTIR absorbance spectra of the PPHMDSO films were recorded by a Bruker spectrometer in the 4000–600 cm<sup>-1</sup> spectral region with a resolution of 2 cm<sup>-1</sup>.

## **3 Results and Discussion**

The FTIR spectra of the PPHMDSO obtained at diminishing monomer flow rate are displayed in Figure 1(a,b,c).

The reduction of the monomer flow rate leads to more pronounced intensity increase of the Si-CH<sub>3</sub> stretching absorption at 799 cm<sup>-1</sup> [Si-(CH<sub>3</sub>)<sub>2</sub> and Si-CH<sub>3</sub> groups], in comparison to 846 cm<sup>-1</sup> absorption [Si-(CH<sub>3</sub>)<sub>3</sub> end groups]. This certifies that more CH<sub>3</sub> groups have been removed at lesser monomer flow rate. It suggested that the decrease of the monomer flow rate leads to elongated and more branched polysiloxane chain at the expense of predominantly Si-O-Si bridges.

The current density increase caused an intensity raising and broadening of the Si-O absorption from 1030 to 1200 cm<sup>-1</sup> (Figure 2). A well-pronounced shoulder at the long wave number end of this band is observed at higher current density. It is obvious that the band contains more than one peak hidden under the broadband

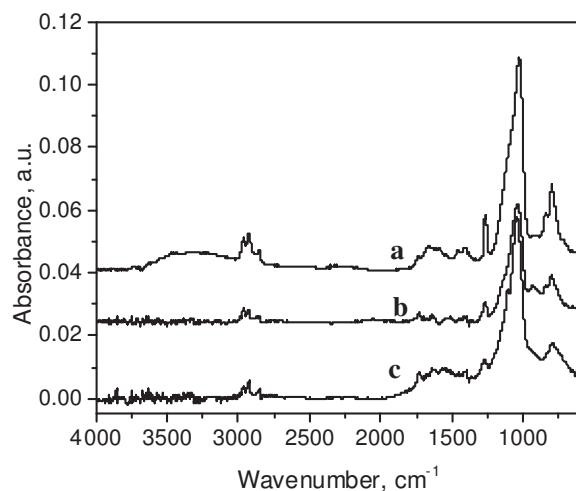


Figure 1: FTIR spectra of PPHMDSO obtained at current density of 0.32 mA/cm<sup>2</sup> and monomer flow rate of: a – 0.17 dm<sup>3</sup>/min; b – 0.08 dm<sup>3</sup>/min; c – 0.03 dm<sup>3</sup>/min.

contour due to different environment in the polymer network where also Si-CH<sub>2</sub>-Si fragments are involved [7]. The enhanced intensity and broadening of the peak at higher current density pointed to an elongation of the main chain as well as to a higher degree of cross-linking mainly due to oxygen atoms in Si-O-Si

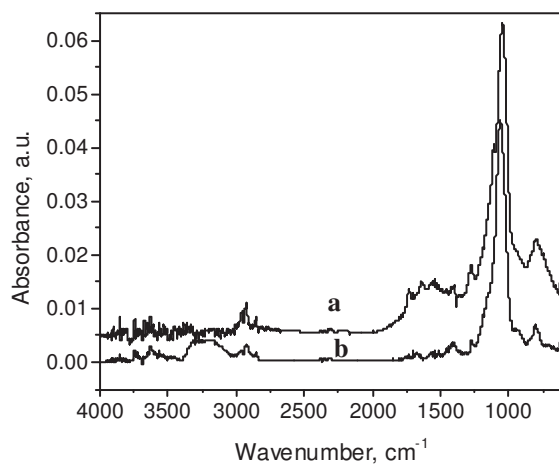


Figure 2: FTIR spectra of PPHMDSO obtained at monomer flow rate of 0.17 dm<sup>3</sup>/min and current density of: a – 0.32 mA/cm<sup>2</sup>; b – 0.16 mA/cm<sup>2</sup>.

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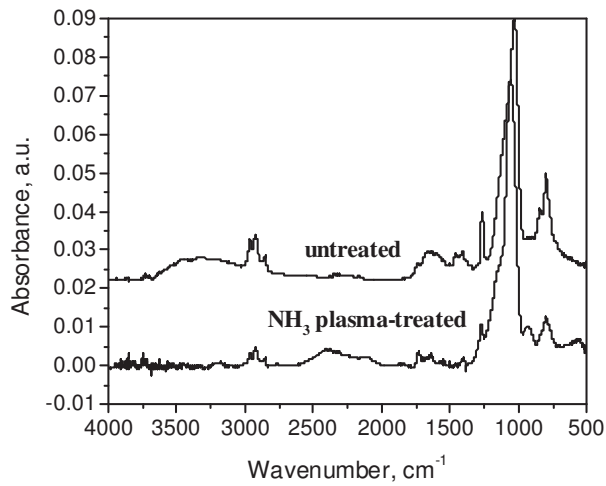


Figure 3: FTIR spectra of NH<sub>3</sub> modified and unmodified PPHMDSO.

groups.

At first glance the FTIR spectra of treated and untreated PPHMDSO films do not differ significantly (Figure 3). Closer inspection of the modified polymer spectrum revealed noticeable decrease of the amplitude of some bands concerning CH<sub>x</sub> groups at 2960 cm<sup>-1</sup> and 2918 cm<sup>-1</sup>, and also the bands of 837 cm<sup>-1</sup> and 800 cm<sup>-1</sup>. This is a clear indication that the ammonia plasma cleaved additional hydrocarbon fragments from the polymer surface. It could be difficult to claim

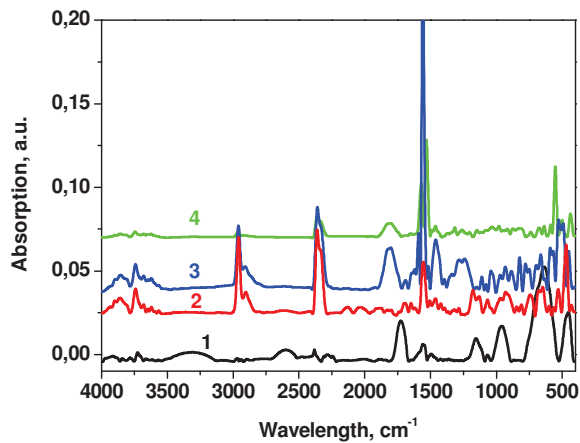


Figure 4: FTIR spectra of PPHMDSO (1), DND/PPHMDSO (2), Si-DND/PPHMDSO (3) and Ag-DND/PPHMDSO (4).

whether some  $\text{NH}_x$  groups are attached to Si or C atoms, because both the corresponding Si-N and C-N band would be hidden under the broadband contour of the Si-O bands. It is evident that additional Si-O-Si bridges have been created which seems to prevail over the Si-N bond formations. Presumably, the  $\text{NH}_3$  plasma treated films have higher degree of cross-linking due to the decrease of hydrocarbon groups.

The different structure of PPHMDSO due to DNDs filler is shown in Figure 4.

There are seen characteristic peaks for  $\text{sp}^3$  bonded carbon at  $1550\text{ cm}^{-1}$  and  $\text{sp}^2$  bonded carbon at  $1160\text{ cm}^{-1}$  of the DND. So, the surface of DNDs/PPHMDSO is characterized with functional groups of the type  $-\text{OH}$ ,  $>\text{C}=\text{O}$ ,  $\text{Si}-\text{O}-\text{Si}$ ,  $\text{Si}-\text{O}-\text{C}$  (Figure 4-2). The formation of new (C-Si-C) bonds and different tetrahedral  $\text{CH}_3$  (the intensive bands in the region  $2800\text{--}3000\text{ cm}^{-1}$ ) proved the existence of both hydrophobic and hydrophilic centers on DND/PPHMDSO surfaces. In the case of Si-DND/PPHMDSO (Figure 4-3), definite peaks at around  $500$ ,  $1200\text{--}1300$ ,  $1470$  and  $1600\text{ cm}^{-1}$  pointed for an increased content of amorphous carbon due to the silanization of DND particles. The appearance of an intensive peak at  $550\text{ cm}^{-1}$  in the spectrum of Ag-DND/PPHMDSO (Figure 4-4), the splitting of the peak at  $1550\text{ cm}^{-1}$  into two peaks and the appearance of a broad band at  $1800\text{ cm}^{-1}$  confirmed the location of Ag ions at the grain boundaries of diamond nanoparticles [16]. A change of polymer characteristic bands is explained by the penetration of DND in the polymer matrix.

The comparison of the spectra of the corresponding  $\text{NH}_3$  plasma treated composites (Figure 5) revealed the surface changes of functional groups after modification. The decrease in intensity of the bands for methyl groups, broadening and intensification of the bands in the region from  $3000$  to  $3440\text{ cm}^{-1}$  was observed.

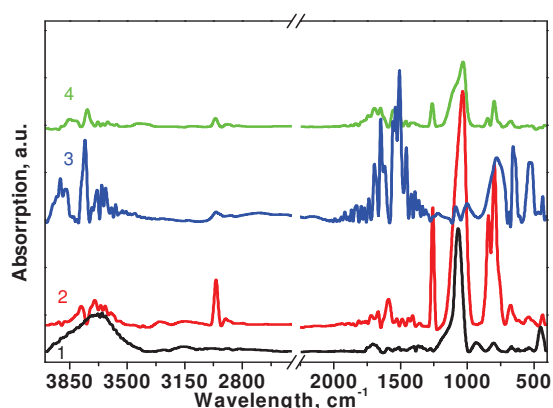


Figure 5: FTIR spectra of PPHMDSO/ $\text{NH}_3$  (1), 6-DND/PPHMDSO/ $\text{NH}_3$  (2), Si-DND/PPHMDSO/ $\text{NH}_3$  (3) and Ag-DND/PPHMDSO/ $\text{NH}_3$  (4).

This is an indication of increased hydrophilic properties of the composites after ammonia modification.

#### **4 Conclusion**

The broad possibilities of the method of plasma polymerization to produce thin composite films from HMDSO and nanodiamond particles were demonstrated. By varying plasma parameters, the type of DND fillers as well as by ammonia plasma modification, changes in the composite structure were achieved. The results indicate the possibility to vary the hydrophilic properties of the obtained composite materials and therefore their bioactivity and biocompatibility.

#### **Acknowledgments**

This research is supported by the Bulgarian National Scientific Research Fund through Grant DFNI\_B01\_18/28.11.12.

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