“ALEXANDRU IOAN CUZA” UNIVERSITY, IASI

FACULTY OF PHYSICS

PHYSICO – CHEMICAL PROCESSES IN PLASMA REACTORS. APPLICATIONS

-Abstract-

Scientific coordinator

Prof. Dr. Nicoleta DUMITRASCU

PhD.

Mihai-Gabriel ASANDULESA

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Plasma polymerization is a physical procedure in witch mostly chemical reactions are involved. Under the influence of plasma energy, organic vapours are activated and fragmented and the new created reactive species are randomly recombined into high branched and crosslinked structures [1, 2]. The final compounds are conventionally called plasma-polymerized films and they contain physical properties that make them unique in all type of polymers. The plasma-polymerized films are adherent to almost all substrate type, could be synthesized from a wide range of precursors, they are thermal stable. [3, 4] Plasma polymerization offers some important applications such as permselective membranes, electrical insulators, protective coatings etc.

In order to obtain polymerized films with controllable properties, the mechanism of plasma polymerization reactions should be understood. Plasma polymerization refers to dissociation reactions of the chemical compounds, the recombination and reactivation reactions of the radicals on the substrates in contact with plasma. The conventional analysis techniques hardly offer informations about the intermediary compounds and these physico-chemical reactions are, therefore, difficult to achieve.

The aim of this thesis is the study of plasma polymerization reactions at atmospheric pressure. The organic precursors used in this work are benzaldehyde, styrene, benzyl alcohol and benzyl chloride. The plasma polymerization mechanism of aromatic compounds combines the intermediary reactions in polymer forming.

This thesis is structured into five chapters. The first chapter, **Physico-chemical processes in plasma reactors,** describes the polymerization reactions of macromolecular compounds from a chemical point a view and the conventional analysis methods. Also, they are presented general aspects concerning plasma polymerization reactions, mechanisms of plasma polymerization and operational parameters that control the plasma processes in polymer films formation.

Plasma includes reactive species that are able to initiate physico-chemical reactions from organic molecules. [1] These physico-chemical reactions are: excitations and ionizations of atoms and molecules, atomic implantation, etching, activations and dissociations of molecules, oxidation of reactive sites, reactivations of units, recombination of radicals etc. [2] The plasma polymerization reactions occur through free radicals and the mechanism is a radical polymerization process. [3, 4]

In the Chapter 2, **Atmospheric pressure discharge for plasma polymerization reactions,** it is described the experimental set-up of the dielectric barrier discharge, the chemical compounds of aromatic type used in this work, the characterization techniques for plasma-polymerized films and the operational parameters that control the plasma polymerization reactions.

The polymerization reactions are generated in a dielectric barrier discharge in helium, working at atmospheric pressure. The stainless steel chamber contains two plane parallel glass dielectrics covered with copper dielectrics with 60 mm diameter. The gap length is fixed at 5 mm and the deposition time is 10 min.

Gas flow rates are constantly kept by two flowmeters: the first flowmeter is used to control the helium flow rate and the second flowmeter control the organic vapours flow rate of the aromatic compounds. The helium flow rate is fixed at 2.5 L/min and the precursor flow rate is maintained at 4 μL/min.

The discharge is driven by 6 kV amplitude high-voltage pulse, 2 kHz frequency and 50% duty cycle. High voltage pulses are applied with a digital waveform generator and a high voltage amplifier. The applied voltage and the discharge current are collected by a digital oscilloscope. The emission spectrum of the plasma was recorded by a monochromator with an optical fiber attached.

In the Chapter 3, **Analysis of plasma-polymerized films,** presents the physico-chemical analysis of final compounds, using the Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and proton nuclear magnetic resonance (^{1}H NMR). Taking into consideration the results of these spectroscopic techniques, it was identified the intermediary compounds obtained by plasma polymerization reactions.

The chemical structure of plasma-polymerized films was identified by FT-IR technique using a Bomem MB Series 104 spectrometer. The FT-IR spectra were recorded in transmittance mode in the 4000-400 cm^{-1} spectral range and the data were analysed with the GRAMS GALACTIC software. In order to obtain clear FT-IR absorption spectra, the plasma-polymerized films were deposited onto NaCl windows that are transparent in the infrared spectral range. The FT-IR spectra of precursors contains absorption bands corresponding to aromatic ring (aromatic stretching between 3100-3000 cm^{-1}, the CH in-plane deformations between 1330-1000 cm^{-1}, aromatic CH out-of-plane vibrations between 900-650 cm^{-1}, C-C vibrations between 1592-1453 cm^{-1}) and absorption bands specific to the alkyl radical attached. In contrast, the FT-IR spectra of plasma-polymerized films show a broad band around 3300 cm^{-1} corresponding to hydroxyl radicals as the effect of oxidation during plasma polymerization. The CH stretching of aliphatic type is identified between 3000-2900 cm^{-1} and gives informations about initiation reactions of the aromatic precursors. The carbonyl C=O stretching from 1700 cm^{-1} and the C-O type groups located at 1250 cm^{-1} and 1100 cm-1 reveal the presence of oxidation processes. The peaks from 1700-1400 cm^{-1} spectral region, that are specific cu aromatic and aliphatic C-C groups, give informations about the fragmentation reactions. Also, the new peaks from 1200-700 cm^{-1} region are specific to aliphatic CH groups as the effect of alkyl group detachment and aromatic ring opening. [5, 6]

Further informations about the molecular structure of polymerized films could be obtained by ^{1}H NMR technique. The 1H NMR spectra were recorded in the 11-0 ppm range at 400 MHz with a Bruker Avance DRX 400 spectrometer. In order to obtain ^{1}H NMR spectra, the plasma polymerized films were deposited onto glass windows, the solvent used in this study was dimethyl sulfoxide-d_6 (DMSO) and the chemical shift was determined relative to tetramethylsilane (TMS) used as reference. The ^{1}HNMR spectra of aromatic precursors provides strong signals characteristic to aromatic protons and alkyl type protons. Compared to the precursor spectra, the ^{1}H NMR spectra of plasma-polymerized films includes chemical shifting specific to aliphatic protons obtained by ring opening during plasma polymerization. [7, 8]

Complementary informations about the chemical and elemental composition of plasma-polymerized films are obtained by XPS technique. The XPS spectra were recorded with a 5000 VersaProbe spectrometer (physical Electronics), equipped with a monochromatic Al Kα X-ray source ($h\upsilon$ = 1.486 keV). The binding energy was calibrated by the C 1s peak energy, 284.6 eV, used as reference. In order to obtain XPS spectra the plasma-polymerized films were deposited onto glass windows. The XPS spectra of final compounds obtained in plasma environment includes the C 1s and O 1s peaks. The deconvolution of C 1s region reveal the presence of C=C, C-C, C-H at 284.5 eV and oxygen containing groups (such as ether C-O-C linkage type and alcohol C-OH groups at 286 eV, carbonyl C=O type bonds 287.3 eV and -O-C=O units from esters 288.6 eV). The O 1s peak is decomposed in two peaks corresponding to -O- (532.5 eV) and =O at 531.5 eV oxygen type bonds and reveals informations about the oxidation of plasma-polymerized films. [9, 10]

The **Plasma polymerization mechanism** is presented in Chapter 4. The model contains the intermediary reactions: activation and fragmentation reactions of the organic molecules, recombination reactions of the reactive species and oxidation reactions of the plasma polymerized films.

The initiation and fragmentation reactions of the organic molecules lead to radicals generation. Taking into consideration the FT-IR, XPS and ^{1}H NMR spectra of the final compounds it has been observed that the most probable reactions in radical generation are: the pi bond breakage from the aldehyde group of benzaldehyde (FT-IR, C-O at 1068 cm^{-1}; XPS, C-O at 288 eV), the pi bond breakage from the vinyl group of styrene (FT-IR, reduced C=C at 1627 cm^{-1}), hydroxyl detachment from alcohol group of benzyl alcohol (FT-IR, aliphatic CH from 3000-2830 cm^{-1} spectral range; ^{1}H NMR, CH_2 at 4.2 ppm) and chlorine detachment from methylene chloride of benzyl chloride (FT-IR, CH_2-Cl at 1265 cm^{-1}).

During plasma exposure, the aromatic ring of the organic molecules could be opened. The FT-IR and ^{1}H NMR spectra of the final compounds contain fragments as the effect of ring breakage. Hence, the FT-IR spectra of plasma-polymerized films reveal that the aromatic/aliphatic CH ratio is reduced. Also, in the fingerprint region, the absorption peaks corresponding to aromatic CH groups are drastically reduced after plasma exposure of the aromatic precursors. The ^{1}H NMR spectra confirm the fragmentation reactions of the aromatic rings: the signals from 1.25 ppm and 0.89 ppm indicate the ring breakage into CH_2 and CH_3 amounts that could be reorganized into aliphatic chains like alkanes.

The spectroscopic techniques used in this work allow us to identify the chemical composition of the final products while the intermediary species are not detected. The addition between two or more reactive species is difficult to predict. The ^{1}H NMR spectra contains signals specific to aliphatic assignable to CH2 and CH3 type groups that could be recombined into aliphatic chains (^{1}H NMR, CH_2 at 4.2 ppm; ^{1}H NMR, CH_2 at 1.25 ppm; ^{1}H NMR, CH_3 at 0.89 ppm).

The radicals created by plasma fragmentations are highly reactive and could be easily oxidized due to atmospheric environment that contains impurities like hydroxyl radicals, nitrogen and oxygen. The XPS spectra reveal the presence of oxygen containing groups in the chemical composition of plasma-polymerized films (ether C-O-C and alcohol R-OH type groups at 286 eV, carbonyl C=O at 287.3 eV and esters O-C=O at 288.6 eV). The FT-IR spectra confirm the presence of oxidation reactions during film growth or after the plasma polymerization process ends. The most probable oxidation reactions are the hydroxyl group attachment to the benzaldehyde and benzyl radicals (FT-IR, OH at 3300 cm^{-1} and XPS, C-OH at 285.5 eV) and, also, the oxygen addition to the styrene radical (FT-IR, C-O at 1097 cm^{-1} and XPS at 285.3 eV).

In the same chapter we included theoretical and experimental results concerning the aromatic ring preservation in the chemical structure of the plasma-polymerized films. It was found that, under plasma influence, the benzaldehyde and styrene vapours can easily create radical by breaking the pi bond from aldehyde and vinyl group, respectively. In this case, the aromatic ring could be easily preserved into the chemical composition of the final compounds. The aromatic ring from benzyl chloride and benzyl alcohol vapours are highly exposed to plasma energy and it could be easily opened. The chemical composition of plasma benzyl alcohol and plasma benzyl chloride films contains aliphatic type groups probably due to aromatic ring breakage.

The Chapter 5, **Applications of atmospheric pressure plasma treatment,** describe experimental results concerning the improvement of wood surface adhesion by plasma treatment.

Finally, the **Conclusion** section summarizes the experimental results that are described in this thesis.

- In this thesis, the dielectric barrier discharge, working in helium, was used to obtain plasma polymerization reactions at atmospheric pressure. The electrical and optical diagnoses show that the discharge is obtained in glow mode.

- Plasma-polymerized films are uniform distributed to the substrates and a good evaluation of the polymer thickness can be obtained. The dependence of the deposition rate function of the composite parameter, W/FM, allowed us to identify the plasma polymerization domains: the monomer sufficient region, the competition region and the monomer deficient region. The discharge power was applied in the range of 3-13.5 W. In this way, it was determined the experimental conditions for plasma polymerization reactions at atmospheric pressure; it was found that the competition region is identified at 3200 MJ/kg which corresponds to a maximum deposition rate of 3.8 nm/s. Also, the plasma polymerization domains were identified by FT-IR absorption spectra and the UV absorption spectra as function of discharge power. The results confirm that the competition region corresponds to the discharge power of 7.5 W.

- The FT-IR, XPS and 1H NMR spectroscopic techniques allowed us to identify the reactive species and, thus, the plasma polymerization reactions were determined. The infrared spectra contain informations about the activation and fragmentation of the aromatic precursors exposed to plasma energy. The activation reactions of benzaldehyde and styrene molecules are emphasized by double bond breakage from aldehyde and vinyl group, respectively; the activation of the benzyl alcohol could be possible by hydroxyl detachment from the benzyl radical and, also, the activation of benzyl chloride could be possible by the chlorine detachment from the benzyl radical. The ^{1}H NMR spectra of the plasma-polymerized films emphasizes the fragmentation reactions of the aromatic ring. The presence of methylene CH_2 and methyl CH_3 type groups in the final compounds reveal the aromatic ring opening due to plasma exposure. The FT-IR spectra confirmed the fragmentation processes. The XPS spectra revealed the oxidation reactions of the final compounds. The oxidation reactions could appear during film growth (oxidation in the plasma volume) and/or after the polymerization reaction ends (oxidation at the surface).

- The plasma polymerization mechanism of the aromatic compounds contains the physico-chemical reactions during film growth: the activation reactions of organic molecules, the fragmentation reactions of the aromatic ring, the recombination reactions of the reactive species and the oxidation reactions of the polymerized films. This concept is based on plasma-induced radical chain-growth which considers that plasma provides enough energy to activate and dissociate organic molecules followed by recombination of the radicals into three-dimensional structures like polymers.

- The FT-IR and ^{1}H NMR spectra provide informations about the aromatic ring preservation in the chemical composition of the plasma-polymerized films. It was found that the plasma polystyrene films contains the highest percentage of the aromatic rings (the aromatic/aliphatic ratio is 2.3) compared to plasma benzaldehyde films (the aromatic/aliphatic ratio is 1.4), plasma benzyl chloride films (the aromatic/aliphatic ratio is 1.1) and plasma benzyl alcohol films, respectively (the aromatic/aliphatic ratio is 0.4). The thickness measurements confirm the mentioned hierarchy.

The atmospheric pressure plasma treatment of the oak and beech tree samples is an adequate technique to modify the wood surface properties. The plasma treatment effects were indicated by water drops evolution on the wood samples. The treated wood surfaces became more hydrophilic and the adhesion work is improved without modifying the wood surface aspect and the bulk properties.

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List of Publications

Articles

1. **M. Asandulesa,** I. Topala, V. Pohoata, Y. M. Legrand, M. Dobromir, M. Totolin, and N. Dumitrascu, Chemically polymerization mechanism of aromatic compounds under atmospheric pressure plasma conditions, accepted for publication in *Plasma Processes and Polymers,* May 2012.

   Impact Factor: 2,468

   Article Influence Score: 0.721

2. J. G. Vazquez, **M. Asandulesa,** I. Topala, and N. Dumitrascu, Fast imaging study of polymerization plasmas at atmospheric pressure, *IEEE Transactions on Plasma Science,* 39(11), 2170-2171, 2011.

   Impact Factor: 1.174

   Article Influence Score: 0.423

3. **M. Asandulesa,** I. Topala, V. Pohoata, and N. Dumitrascu, Influence of operational parameters on plasma polymerization process at atmospheric pressure, *Journal of Applied Physics,* 108, 093310, 2010.

   Cited by 1 related article

   Impact Factor: 2.079

   Article Influence Score: 0.875

4. R. Schrittwieser, C. Ionita, A. Murawski, C. Maszl, **M. Asandulesa,** A. Nastuta, G. Rusu, C. Douat, S. B. Olenici, I. Vojvodic, M. Dobromir, D. Luca, S. Jaksch, and P. Scheier, Cavity-hollow cathode-sputtering source for titanium films, *Journal of Plasma Physics,* 76, 655-664, 2010.

   Impact Factor: 1.070

   Article Influence Score: 0.305

5. **M. Asandulesa,** I. Topala, and N. Dumitrascu, Effect of helium DBD plasma treatment on the surface of wood samples, *Holzforschung,* 64, 223-227, 2010.

   Cited by 5 related articles

   Impact Factor: 1.307

   Article Influence Score: 0.404

Participation to national and international conferences

Oral presentations: 4

Posters: 3