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Polyurethane coating with thin polymer films produced by plasma polymerization of diglyme

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Abstract. Aqueous-based polyurethane dispersions have been widely utilized as lubricants in textile, shoes, automotive, biomaterial and many other industries because they are less aggressive to surrounding environment. In this work thin films with different thickness were deposited on biocompatible polyurethane by plasma polymerization process using diethylene glycol dimethyl ether (Diglyme) as monomer. Molecular structure of the films was analyzed by Fourier Transform Infrared spectroscopy. The spectra exhibited absorption bands of O-H (3500-3200cm^{-1}), C-H (3000-2900cm^{-1}), C=O (1730-1650cm^{-1}), C-O and C-O-C bonds at 1200-1600cm^{-1}. The samples wettability was evaluated by measurements of contact angle using different liquids such as water, glycerol, poly-ethane and CMC. The polyurethane surface showed hydrophilic behavior after diglyme plasma-deposition with contact angle dropping from 85^0 to 22^0. Scanning Electron Microscopy revealed that diglyme films covered uniformly the polyurethane surfaces ensuring to it a biocompatible characteristic.

1. Introduction

Medical grade Polyurethanes are one of the most biocompatible and blood-compatible materials known up to present days. These materials are extensively used in the development and manufacturing of medical devices ranging from catheters to artificial organs [1,2]. In spite of its usefulness as biomaterial many drawbacks must be addressed for a tailored application as for instance the hydrophobic characteristic and the hydrolytic instability of many medical-grade polyurethanes. Therefore it is of paramount importance the set up of surface treatments in order to improve the coupling of polyurethanes with the living environment. In this scenario low-pressure plasma material processing may play an important role [3-10]. The key feature of such kind of plasmas is that electrons may attain energy in excess of several eV in comparison with the heavy particles present in the discharge. This unusual non-thermal equilibrium situation is very efficient in molecular fragmentation through electron impact giving rise to a very reactive chemistry in a relative cold environment whose kinetics is not easily controlled [3-5]. Therefore it is essential to perform different plasma diagnostics in order to probe the trends of chemical species as well as the electrons behavior for different plasma

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parameters, such as RF power coupled to the plasma chamber, gas pressure, gas flow and so on [3-5,9,10].

In the field of biomaterial science and technology, plasma polymerized polyethylene glycol di-methyl ether has been attracting the attention of the scientific community due to its non-fouling properties [11-15]. If appropriate plasma parameters are set, polymer films can be synthesized keeping quite similar molecular structure to that of polyethylene oxide-like (PEO-like) with the advantage that these films are not soluble in water. The aqueous solubility of PEO makes it inappropriate for many biomaterial applications. In order to retain the monomer structure within the plasma deposited films and consequently its functionality, many different issues have been addressed in recent literature as for instance: film deposition under low mean RF power level by controlling the power supply on/off ratio [16,17], decreasing of monomer residence time and consequently the reduction of its interaction with the plasma environment [17], cooling of substrate with liquid nitrogen [18], energy reduction of the ions reaching the substratum [4,5], and so on.

In order to determine the appropriate experimental parameters that would result in customized hydrophilic transparent film in plasma polymerization of PEO-like coatings this paper deals with plasma polymerization of diglyme at relatively low RF power levels using silicon, quartz plates and medical grade polyurethane rectangular pieces of 2 cm^2 as substrates. Molecular structures of plasma polymerized diglyme and polyurethane were characterized using Fourier transform infrared spectroscopy (FTIR here in).

2. Experimental setup

Diglyme ($CH_3O(CH_2CH_2O)_2CH_3$) plasmas were excited by a RF power supply operating in 13.56 MHz whose output power could be adjusted from 0 to 300 W (Tokyo HY-Power model RF-300^{TM}). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300^{TM}) that allows minimizing the reflected RF power. All experiments were run with the RF output kept fixed on 5 W in diglyme atmospheres in the pressure of 20 Pa (150 mTorr) within a stainless steel cylindrical, 210 mm of internal diameter and 225 mm long, parallel plate electrodes plasma reactor. This reactor is provided with eight lateral entrances, positioned at the mid plane between the electrodes, which can be used for setting optical, electrical and mass diagnostics and the low (mechanical pump) and high (turbo-molecular pump) vacuum systems. The vacuum inside the plasma chamber is monitored by pirani^{TM} (thermocouple) and penning^{TM} (inverse magnetrom) gauges. The turbo-molecular pump is connected to the chamber through a gate valve and is used for cleaning purposes. The pressure is pumped down to 1.33 x 10^{-4} Pa (10^{-6} Torr), and the chamber is purged with argon several times before each experiment. The inner side of the plasma chamber was polished up to the optical quality (roughness of 0.5 microns or less) in order to minimize the retention of impurities and facilitate the cleaning process. The plasma chamber walls were heated with a temperature-controlled belt in order to minimize the monomer's condensation as well as the humidity. Diglyme from a stainless steel bottle was fed into the plasma chamber through a needle valve. The mass spectrometry was realized using a mass spectrometer and energy analyzer (Hiden Analytical model EQP-300^{TM}), operating in the mass and energy range from 1 to 300 amu and from 0 to 100 eV, respectively. The background mass spectra with the plasma turned off were carried out at the same pressure condition of diglyme plasma polymerization processes. These spectra were used to control the number of chemical species resulting from the fragmentation within the mass spectrometer and also to detect the presence of contaminants resulting from the plasma chamber cleaning process. The block diagram and the photograph of the experimental setup are presented in figures 1 and 2, respectively.

Diglyme films were deposited on medical grade polyurethane samples, silicon and quartz substrates for one hour. Film thickness was determined through step meter technique using an Alpha Step Tencor-100^{TM}. Typical polymer film thickness was 50 nm. Diglyme and polyurethane structures were studied through infrared spectra obtained with a Perkin Elmer Lambda-9^{TM} spectrometer. The hydrophobic/hydrophilic characteristics of plasma-polymerized Diglyme were investigated through

contact-angle measurements using de-ionized water as probe liquid and a Ramé-Hart goniometer model 100^{TM}.

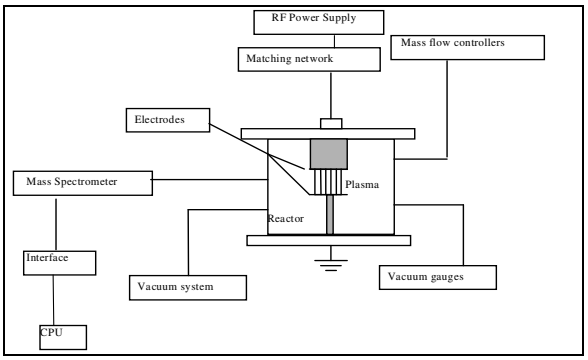


Figure 1. Block diagram of the experimental setup used in plasma polymerization of diglyme films.

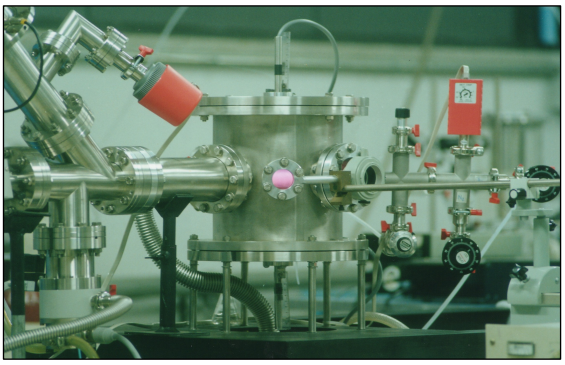


Figure 2. Photograph of the experimental arrangement.

3. Results and Discussion

Figure 3 shows typical infrared spectra of diglyme plasma polymers deposited on polyurethane substrate (top spectrum) and polyurethane substrate (bottom spectrum). The absorption band centered in 2897cm^{-1} is associated to C-H stretching modes in CH_3 and CH_2 groups. The absorption band between 1730 cm^{-1} and 1650 cm^{-1} is due to C=O stretching. The absorptions observed in the wavenumber range from 1440 cm^{-1} to 1380 cm^{-1} are due to C-H bending modes. The strong band in the range from 1200 cm^{-1} to 1000 cm^{-1} is associated with C-O and C-O-C stretching modes. The IR spectra of plasma polymerized diglyme films demonstrate the preservation of some functional groups of diglyme monomer's structure, i.e. $CH_3O(CH_2CH_2O)_2CH_3$.

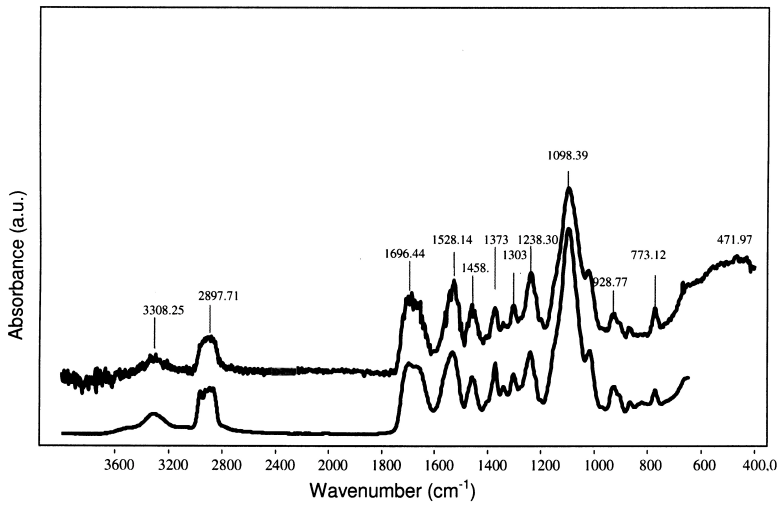


Figure 3. Infrared spectra of plasma polymerized diglyme film deposited on polyurethane surface (top) and polyurethane substrate (bottom).

The accordance between both spectra shows that all IR bands of plasma polymerized diglyme are present in polyurethane spectrum. This means that film thickness was not enough to avoid the appearance of polyurethane bands in diglyme/PUD spectrum. These results allow us to conclude that

for the RF power kept fixed on 5 W the plasma discharges were favorable for the retention of the main monomer's functional groups on plasma polymerized Diglyme films. These results show that the PEO-like characteristics of Diglyme films were preserved for the values of RF power and gas pressure used in the experiment.

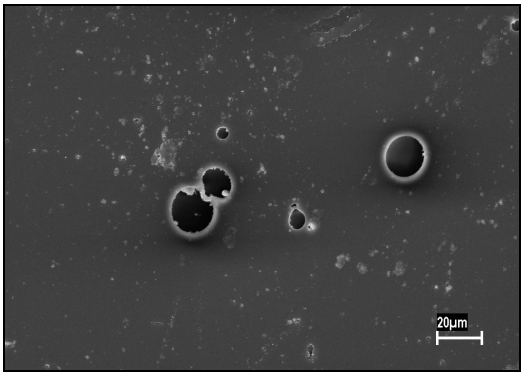


Figure 4. Micrograph 500 times magnified of aqueous-based polyurethane dispersions.

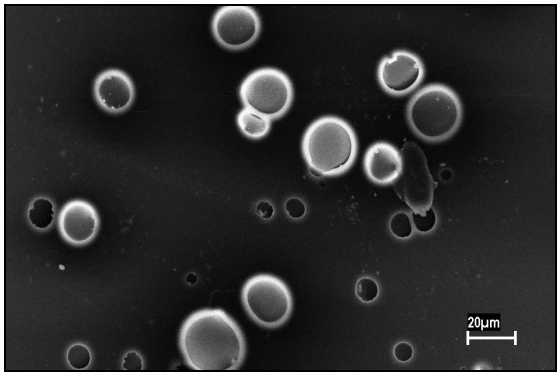


Figure 5. Micrograph 500 times magnified of aqueous-based polyurethane covered with plasma polymerized diglyme films.

Figures 4 and 5 show micrographs of aqueous-based polyurethane dispersions and aqueous-based polyurethane covered with plasma polymerized diglyme films. The pinholes shown in figure 4 are inherently to polyurethane synthesis process. The mean diameter of such pinholes is about tens of microns. It can be seen in figure 5 that plasma polymerized diglyme covers the polyurethane surface as well as the pinholes. The differences on pinholes brightness are due the decreasing of pinhole's depth caused by diglyme deposition. This demonstrates that plasma polymerized diglyme covers uniformly the polyurethane surface. Such features of diglyme films are reinforced if one considers the micrographs shown in figures 6 and 7. It can be seen in figure 7 that diglyme film covers uniformly the smooth glass plate shown in figure 6. Therefore plasma polymerized diglyme may be used as biocompatible protective coating since it is resistant to the aggressive body environment and may be used as a permeable membrane on polyurethane catheter's surface previously embedded with heparin. The contact angle measurements with de-ionized water as a probe liquid revealed a drastic dropping from 85^0 to 22^0 soon after plasma-deposition of diglyme on polyurethane surfaces. This result shows that the experimental condition used in the present work was profitable on the improving of hydrophilic character of polyurethane surface.

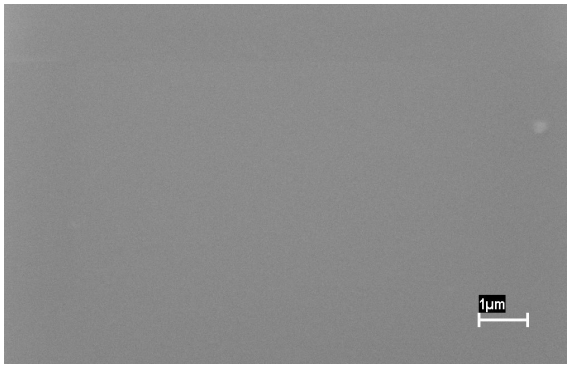


Figure 6. Micrograph 5000 times magnified of glass substrate.

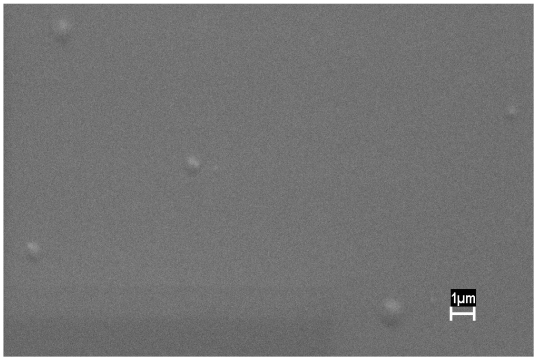


Figure 7. Micrograph 5000 times magnified of plasma polymerized diglyme films deposited over glass substrate.

4. Conclusions

Plasma polymerized diglyme films deposited at monomer pressure of 20 Pa (150 mTorr) and 5 W of RF power coupled to the plasma chamber present a PEO-like characteristic that makes it resistant to body environment and may be used as a permeable-selective coatings for controlled releasing of anticoagulant substances like heparin for instance. The IR analysis of polymeric films revealed that the operation of the plasma chamber at relative low RF power level was successful in producing plasma polymerized diglyme whose structure resembles the monomer's one. Therefore one can conclude that the experimental conditions used in this work resulted in thin plasma polymerized diglyme films with customized biocompatible properties.

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