Impedans
PLASMA MEASUREMENT

Continuous-Wave RF Plasma Polymerisation of Furfuryl Methacrylate (FMA) using Octiv ion flux application

INTRODUCTION:

Biocompatible materials, suitable for in vitro and in vivo applications, are of great importance to the healthcare industry. Polymer coatings are used extensively to control and stimulate certain biological responses. The properties of the polymer can be a disadvantage and can be incompatible with certain applications. In that case, surface modification can provide a suitable solution for optimizing compatibility for the biological environment.

The nanometer scale of the surface of a material is important in determining the nature of the chemical interactions occurring at the biological level. The commercially available methods are usually ineligible for cell culture procedures. In that case, surface modification provides an advantage whereby even cell-culture interactions can be monitored and controlled.

There are many possible ways to carry out surface modification. Most of these techniques utilise wet chemistry and can be time consuming and expensive. The plasma processing approach is investigated as it is considered to be a better alternative with high quality surface modification. Plasma processing is used to modify the top surface of a material without disturbing the properties of the bulk material. The main advantage is that the pre-preparation steps can be skipped.

Furthermore, it is also said to be preferred in terms of safety and environmental-friendliness. Although external parameters provide sufficient description of
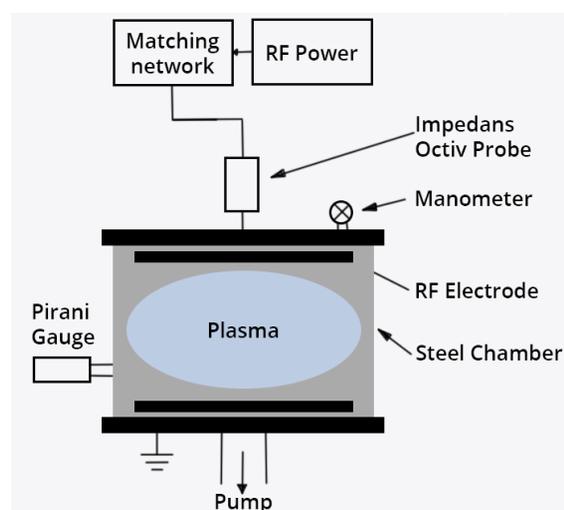

Figure 1. Schematic diagram.

plasma processes in a single system, replication of similar results require trial and error.

Furfuryl methacrylate (FMA) has been used as a precursor to produce polymeric coatings for various applications. In a recent study involving 141 different monomers, FMA was an excellent candidate as a synthetic substrate for human pluripotent stem cell culture and expansion. In addition, it was one of the few potential monomers which had a vapor pressure suitable for plasma polymerization. Studies also mentioned the ability of FMA to provide a furan ring that can be derivatized by Diels–Alder chemistry, making it an excellent candidate for applications in the microelectronics industry such as to immobilize organic molecules onto semiconductor surfaces and in the development of thermally responsive polymer-metal adhesion.

Looking at the fascinating surface properties of FMA-based coatings, this study aims to develop FMA plasma polymer coatings which may be used as substrates for cell attachment and expansion. In this work, the authors have investigated on the plasma phase of furfuryl methacrylate (FMA) and its relationship to the surface chemistry of the generated plasma coatings using mass spectrometry. The plasma produced was also characterized using XPS and ToF-SIMS. Plasma parameters including ion mass spectra, ion flux, and ion energy allowed the calculation of ion mass and ion energy fluxes to the surface. Combined with deposition rate measurements, this revealed the roles of neutrals and ions in the deposition process. The outcomes of this study will contribute to new discoveries of synthetic substrates for cell cultureware.

METHOD:

The authors carried out various methods starting with plasma polymerisation using a stainless steel vacuum chamber which was pumped down by a two-stage rotary pump to reach a base pressure of <0.2Pa. Plasma was then ignited using an RF power generator with a matching network where the silicon wafer substrates were soaked in ethanol before it was dried under a stream of nitrogen. Plasma polymer coatings were deposited at RF power ranging from 2 to 20W for 10mins each. The mass spectrometer was mounted along the reactor mid-line and operated in residual gas analysis (RGA) and positive ion modes to acquire spectra of plasma-phase, neutral species and positive ions. Following this, Static Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses were performed using a nanToF instrument with pulsed liquid metal 79Au+ primary ion gun operating at an energy of 30kV. A mass resolution (m/Δm) of 6500-7000 was typically achieved at normal m/z 27 (C2H3+). The peaks were normalisation to the total counts of the corresponding spectrum.

The authors also used X-Ray Photoelectron Spectroscopy (XPS) to determine the chemical composition of he surface. It was operated at 10kV and 20mA and the elements in the plasma layer were identified the

energy range 0-1100 eV at a pass energy of 100 eV and a step size of 0.5 eV. CasaXPS software was used to determine the line shape which was assumed to be Gaussian-Lorentzian components. A Quartz Crystal Microbalance (QCM) was used to measure the deposition rate during the plasma polymer film deposition. The silicon wafer substrates were placed as close as practicable to the QCM during plasma polymerisation experiments.

Finally, the authors measure the ion flux to the RF electrode using the Impedans Octiv VI probe placed in series between the matching network and the RF electrode. The ion flux for a collision-less sheath is given by the Bohm flux,

$$J_i = \exp\left(-\frac{1}{2}\right) n_i \sqrt{\frac{kT_e}{m_i}}$$ (1)

The authors noticed that the ion flux was constant to all surfaces in contact with the plasma and the ion flux was measured as it was connected to the RF electrode.

FINDINGS:

This paper provides detailed experimental analysis on the plasma using mass spectroscopy, Static Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), X-Ray Photoelectron Spectroscopy (XPS), Quartz Crystal Microbalance (QCM) and Ion Flux measurements.

The plasma phase of FMA monomer was probed by in situ mass spectrometry as a function of RF power. In EI MS, in the absence of plasma (Figure 2), the dominant peaks in the MS were at m/z 69 C4H5O+, 81 C5H5O+, 121 C7H5O+, and 166 C9H10O+. In addition to these dominant peaks, other peaks with lower intensities also appeared in the MS including m/z 18 H2O+, 28 CO+, 41 C3H5+, 57 C3H5O+, 95 C5H3O+, 136 C8H8O+, and 148 C9H8O+.

Given that the most intense peak in the mass spectrum represents the furanylmethyl fragment ion (81 m/z) (denoted FM in the spectra), this indicates that this fragment ion has a high level of stability. Proposed
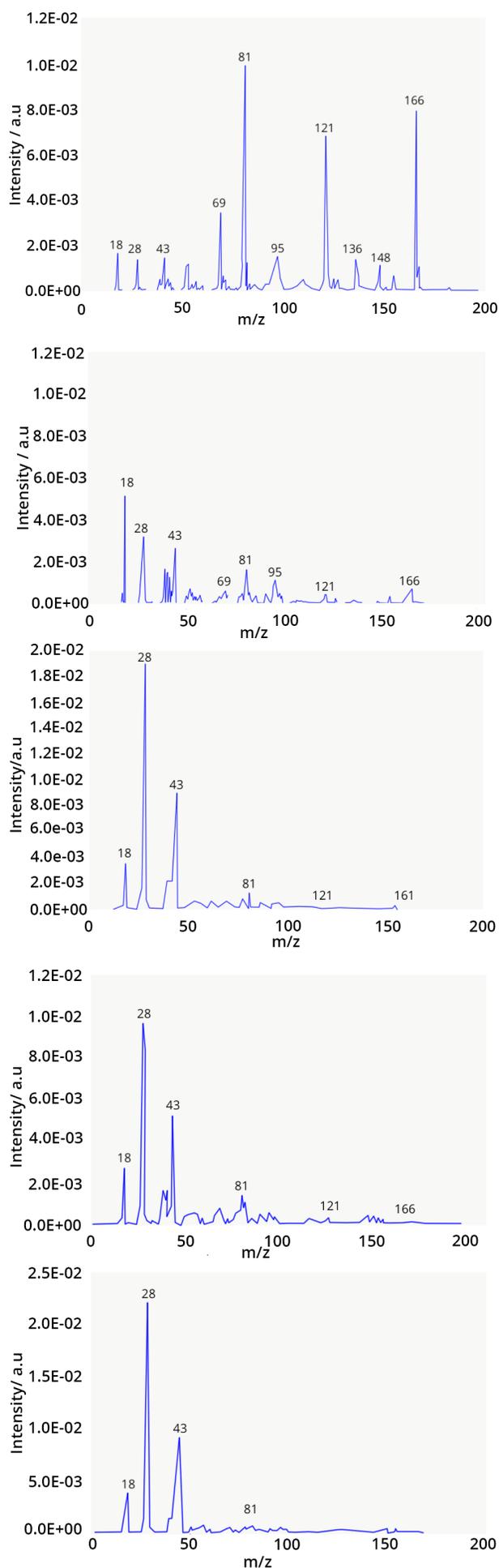
Figure 2: Mass spectra of the neutral species at 4.6 Pa.

fragmentation patterns used for the assignment of m/z fragment peaks in the EI mass spectra.

The surface chemistry of the deposited plasma polymer coatings of FMA was also characterized by XPS and ToF-SIMS. XPS was used to determine the chemical composition of the surface. ToF-SIMS was utilized to analyze the molecular structure of furfuryl methacrylate plasma polymer (FMApp) coatings deposited onto Si wafer substrates at RF power 2–20 W. XPS analysis of FMApp coatings revealed oxygen depletion in the coatings from the expected theoretical value over the range of continuous wave RF power investigated in this study (Table 1).

RF power [W]	Atomic percentage (at%)		O/C
	C	O	
Monomer [Th.]	75.0	25.0	0.33
2	83.9	16.1	0.19
4	83.8	16.2	0.19
10	84.3	15.7	0.19
20	85.8	14.2	0.17

Table 1: Summary of XPS results of FMApp coatings at RF power 2–20 W.

There was no significant change in the oxygen concentration (16.1–15.7 at%) measured in the surface as the RF power increased from 2 to 10 W; given that the O/C ratio remained unchanged (0.19). Nonetheless, increment of RF power to 20 W results in reduction in the oxygen concentration (15.7–14.2 at%) accompanied by an increase in hydrocarbon content. Similarly, the O/C ratio dropped from 0.19 to 0.17. This denotes that the loss of oxygen was due to an increase in the level of fragmentation of FMA molecules at the highest RF power. In addition, at higher RF power the ion assisted etching reactions may also contribute toward the loss of surface oxygen. Similar peaks appeared in the MS as Figure 2 at RF power of 10 W with no significant changes in their relative intensities, however, the intensity of $C_{19}H_{19}O^+$ (m/z 327) fragment dropped to the baseline noise level. Interestingly, at RF of 20 W, fragment ions $C_5H_5O^+$ (m/z 81) and $C_{10}H_9O^+$ (m/z 161) were the only peaks with high relative intensities in the MS, where the remaining peaks declined sharply.

In the EI MS of the neutrals, no fragments with m/z values larger than the one associated with the FMA monomer (m/z 166) were detected. Each signal recorded in the plasma was corrected for fragmentation due to electron impacts in the mass spectrometer by applying the following formula (2):

$$I_c\,(m) = I_m\,(\text{plasma on}) - I_m\,(\text{plasma off})$$
$$\times \frac{I_{\text{monomer}}\,(\text{plasma on})}{I_{\text{monomer}}\,(\text{plasma off})} \tag{2}$$

Overall, increasing RF power leads to a decrease in the peak intensity at m/z 69, 81, 121, and 166 and an increase in peak intensity at m/z 18, 28, and 43. This indicates that the concentration of high molecular weight neutrals, including the intact monomer, become low in the plasma phase due to fragmentation.

To obtain a better understanding of ion contribution to the FMApp coatings, the ion flux across the power range of interest was measured. Combined with the mass spectrometry and ion energy distribution, these measurements allow the ion mass flux, the average ion energy and the surface energy flux to be calculated. The ion mass flux data was then compared to deposition rate measured with QCM. Average ion energy was determined by taking the numerical mean (see Figure S5), and increased from 2.8 to 33.3 eV when the power was increased from 2 to 20 W. Table 2 shows the calculated ion mass flux to the surface versus deposition rate. Effect of power on ion flux, ion mass flux, deposition rate, ion energy, and neutralization energy fluxes to surfaces.

CONCLUSION:

The authors have carried out detailed analysis of the plasma-phase and the surface chemistry of the generated plasma coatings of FMA. It is interesting how the plasma MS results not only show that C5H5O+ fragment has a high stability but also show its potential for oligomerization with itself and other fragments to form high-mass species in the gas-phase and on the surface of the plasma coatings. This means that stable fragments formed in the plasma phase are contributing effectively to the evolvement of the plasma film.

RF power	Ion flux	Ion mass flux	Deposition rate	Ion mass	Average ion energy	Ion energy flux	Neutralisation energy flux
2	0.23	51	290	3	2.8	0.6	1.15
4	0.55	123	320	8	3.4	1.8	2.75
10	0.71	159	450	7	20.6	14.6	3.55
20	0.76	170	286	12	14.6	25.3	3.8

Table 2: Effect of power on ion flux, ion mass flux, deposition rate, ion energy and neutralisation energy fluxes to surfaces.

The correspondence between the plasma-phase and the surface chemistry of the films emphasize the potential of using plasma mass spectrometry to predict the species forming on the surface. The results highlight that comprehensive detailed analysis of the properties of the plasma may be used to modify surfaces for specific applications in future, especially in regards to biomaterials.

REFERENCES:

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