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Plasma Polymerisation of Maleic Anhydride: Just what are the right deposition conditions?

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Abstract

Maleic anhydride plasma polymers enable amine containing biomolecules and polymers to be covalently coupled to a surface from an aqueous solution without any intermediate chemistry. The challenge in developing these functionally active plasma polymers lies in determining the optimal deposition conditions for producing a stable, highly active film. Unlike many previous studies that explore highly varied pulsed and continuous wave (CW) deposition conditions, this paper focuses on the comparison of films deposited under the same low nominal power conditions (1 W) and compares a range of CW, ms and μ s pulsing parameters that can be used to produce this power condition. The use of attenuated total reflectance – Fourier transform infra red spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) has enabled the quantitative examination of the effects of processing parameters on the chemical functionality of the films. For the first time, the molecular specificity, surface sensitivity and high mass resolution of time-of-flight static secondary ion mass spectrometry (ToF-SSIMS) has been exploited to compare these films and multivariate analysis techniques used to explore the relationships between plasma processing parameters and surface chemistry. The results of the studies clearly demonstrate that a range of conditions can produce maleic anhydride films, with optimal functionality seen under μ s pulsing regimes. Critically, the study demonstrates that the tight control and monitoring of the deposition parameters is critical if these films are to be manufactured with optimal functionality, stability and minimum processing time.

Keywords

Maleic anhydride; plasma polymerisation; pulsed plasma; TOF-SSIMS; plasma characterisation

INTRODUCTION

Polymerisation of maleic anhydride is of particular interest in the biomaterials industry due to the reactive anhydride units in the chemical structure that enable amine containing species such as proteins and peptides need to be surface immobilised under aqueous conditions.^{1–3} Many techniques have been used to polymerise maleic anhydride. Homo-polymerisation has been achieved using γ and UV radiation, free-radical initiators, pyridine bases, and electrochemical initiation.^{4–6} Copolymers of maleic anhydride and its isomeric acids (or ester derivatives) have been formed with a wide variety of monomers, such as styrene,⁷ 8 vinyl chloride,⁹ 10 and acrylic acid.² Often the experimental set-up required to produce conventional maleic anhydride

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homopolymers and copolymers is extremely expensive and requires installation of specialised or high-pressure instruments.¹¹ Copolymerisation is generally the preferred route for production, however this approach suffers from variable yield (anhydride group concentration), long reaction times, excessive use of solvents and the requirement for extensive extraction of the product to remove trapped solvent, monomer fragments and reaction inhibiting agents.¹² Biocompatibility can be a significant issue in copolymerised maleic anhydride, due to the presence of reaction by-products and the choice of co-monomer resulting in toxicity and/or carcinogenicity.^{13, 14}

Plasma polymerisation has been used as a solvent-less deposition technique for producing anhydride functional polymer films for a number of years.^{1, 15–20} The range of properties produced in these films is directly related to the extent of fragmentation that occurs during excitation and deposition of the film. As a result, the retention of reactive or functional species from the monomer can be challenging and is dependent on the reactor system being used. In most instances, the fragmentation processes within the plasma may be controlled via the deposition parameters, namely power, flow rate and temperature. As with all plasma polymers, the retention of chemical functionality competes with the need to create a stable, adherent film. While reducing the power will reduce monomer fragmentation, it also reduces the reactive species available to adhere the film to the substrate and create the cross links that make the coating insoluble. For maleic anhydride, the deposition conditions themselves pose some difficulty. At relatively low input energies it is possible for ring opening of the anhydride groups to occur and the deposited films can contain mostly dissociated products rather than the desired anhydride groups. A number of studies have shown that under pulsed plasma conditions highly functional maleic anhydride thin films could be deposited by minimising the effective power delivered to the system,^{17,21} but this in itself raises a number of issues.

In the pulsing regime, the power is switched *on* and *off* in milli (ms) or micro (μ s) second intervals. The ratio of these times is then used to calculate an effective power delivery in the system or the duty cycle. One of the key issues then becomes that a large number of different t_{on}/t_{off} values can be used to deliver same effective power. A general consensus emerging from the general plasma polymerisation literature is that varying the time domain from a few microseconds to tens of milliseconds has a major effect on the film formation and most importantly the functional group retention.^{1, 17, 22–25} Increasing the t_{off} times has been shown to initially increase film thicknesses, however OFF-times that extend beyond this initial film growth regime have been shown to increase the deposition processing time without improving the chemical functionality or significantly increasing film thickness.²⁶ Longer t_{on} times lead to significant monomer fragmentation and loss of functional groups even though the desirable thickness can be achieved in a short processing time.²² An added complication is that few researchers actually measure the RF modulation trigger pulse and thus, delays in ignition and their resultant effects on the effective power/duty cycle go unmonitored and thus unreported.^{24, 27}

In this study, we have revisited the pulsed plasma polymerisation of maleic anhydride. Unlike many previous studies that explore highly varied pulsed and continuous wave (CW) deposition conditions, this paper focuses on the comparison of films deposited under the same low nominal power conditions (1W). It then compares a range of deposition parameters that can be used to produce this nominal power under CW, ms and μ s pulsing regimes. We have used ATR-FTIR and X-ray photoelectron spectroscopy (XPS) to quantitatively examine the effects of experimental variables, termed 'processing parameters', on the chemical functionality of the films. For the first time, the molecular specificity, surface sensitivity and high mass resolution of time-of-flight static secondary ion mass spectrometry (ToF-SSIMS) has been exploited to compare these films and multivariate analysis techniques used to explore the relationships between plasma processing parameters and surface chemistry. The results of these studies

clearly demonstrate that a range of conditions can produce maleic anhydride films, however the monitoring of the pulsing conditions together with control of the power delivery is essential if these deposition systems are to be optimised to produce films that retain both chemical functionality and can be manufactured with the shortest processing times.

Materials and Methods

The complete details of the plasma reactor configuration has been described in detail elsewhere.²⁸ Figure 1 shows the schematic diagram of the plasma reactor used in this experiment. Briefly, the reactor consisted of a 15.2 litre stainless steel T-piece vacuum chamber with multiple ports for pressure and temperature measurement, monomer and gas inlets as shown in Figure 1. The RF (13.56 MHz) power generator output was connected to a single powered electrode in the chamber via a manually tuneable impedance matching unit (Coaxial Power Systems, UK). Multiple entry ports provided on each of the three flanges allowed the monitoring of temperature, pressure and plasma characteristics in real time. The pumping system consisted of a BOC Edwards (Model No.RV8) single stage rotary pump connected to the plasma chamber via a throttle Speedivalve®. To prevent corrosion damage of the pump, a cold trap cooled by liquid nitrogen was installed between the throttle valve and pumping port. Thin films were deposited by both continuous and pulsed plasma polymerisation of maleic anhydride precursors (Aldrich, UK, 99%) onto freshly cleaned silicon wafers (Orientation: <100>, Thickness; 525 microns, Compant Technology Ltd, UK). Samples were placed in the centre of reactor vessel on a sample stage for plasma deposition. Prior to plasma polymerisation, the monomer was degassed several times using freeze thaw cycles. The plasma reactor base pressure was then allowed to stabilise below 1×10^{-3} mbar before degassed monomer was allowed to flow into the chamber. Monomer flow rates (Φ) were controlled by a needle valve and estimated by measuring the increase of pressure in the reactor when isolated from the vacuum line. This pressure change was converted to a flow rate using the method described by Yasuda²⁹, which assumes idea gas behavior and gives an estimate of monomer flow rate in $\text{cm}^3 \text{min}^{-1}$ at standard temperature and pressure (STP). A flow rate of monomer vapor of $2.7 \text{ cm}^3_{\text{STP}} \text{min}^{-1}$ was used in all the cases, which corresponded to a operating chamber pressure of ca. 3.2×10^{-2} mbar. Continuous wave depositions were carried out at 1W discharge power (P). For pulsed plasma polymerisation experiments, the RF power supply unit was connected to a TGP 10 MHz pulse generator (Thurlby Thandar Instruments, UK) and the RF waveform was monitored using a TDS3014 digital phosphor oscilloscope (Tektronix Inc., USA). The peak power (P_p) delivered to the glow discharge was set to values of 10 W. The pulse ON-time (t_{on}) and OFF-time (t_{off}) were varied between ms and μs . The nominal power (P_{nom}) delivered to the system during pulsing was calculated using Equation 1:³⁰

$$P_{nom} = P_p [t_{on} / (t_{on} + t_{off})] \quad (\text{Equation 1})$$

The matching unit was set to give optimal matching for continuous wave operation where by the input power was excited and subsequently regulated at 1 W or 10 W (for pulsing of plasma) and power matching was tuned to minimize the reflected values to $\ll 0.05$ W. It is especially important to minimize the reflected power as pulsing of plasma on a poorly matched system can result in significant plasma ignition delay time.³¹

A capacitive probe was used to monitor the plasma breakdown characteristics. The design of capacitive probe has been discussed elsewhere.³² The plasma voltage relative to ground was recorded on the oscilloscope by placing the capacitive probe tip in the glow discharge region. The probe was used to monitor the true ON-time of the plasma which can differ from the trigger signal due to differences in electrical load on RF generator in the absence of plasma i.e. stray

capacitance and inductance, resulting in a delay time. The corrected t_{on} was calculated using Equation 2:

$$t_{on}(true) = t_{on} - \text{delay time} \quad (\text{Equation 2})$$

The nominal power delivered to the system in all three cases was held constant at 1 W. In the pulsed system, (ms and μ s) 1 W nominal power setting was delivered by adjusting the t_{on}/t_{off} ratios to fix a constant duty cycle and effective power. This corresponded to the plasma power-to-monomer flow rate (P_{nom}/Φ) of $0.37 \text{ W/cm}^3_{STP}/\text{min}$ in all the cases.³³ Films were deposited for a total of 20 minutes in all instances.

ToF-SSIMS

ToF-SSIMS analysis was carried out using an IoN-ToF V instrument (IoN-ToF, Münster, Germany) equipped with a Bi cluster liquid metal primary ion source. Positive and negative ion spectra were acquired in a pulsed high current bunched mode, using 50 KeV Bi_3^{2+} . The primary ion beam current was fixed at 0.1 pA and the spectra collected by rastering the beam over a $100 \times 100 \mu\text{m}$ sample area. The primary ion dose was kept below $10^{12} \text{ ions/cm}^2$ to maintain static SIMS condition. Positive mass spectra were calibrated using CH_3^+ (m/z 15.023), C_2H_3^+ (m/z 27.023), C_3H_5^+ (m/z 41.039) and C_7H_7^+ (m/z 91.054) while the negative spectrum was calibrated to CH^- (m/z 13.008), C_2H^- (m/z 25.008), C_3H^- (m/z 37.008) and COOH^- (44.997) peaks. The mass resolution ($m/\Delta m$) at C_3H_5^+ and C_2H^- were above 8000. At least 3 spectra were acquired from each sample in both the polarities.

Multivariate analysis of ToF-SSIMS spectra were performed using MATLAB 7.4 (R2007a, Mathworks Inc, USA), NBScriptGUI and IonToF-Pak (NESAC/BIO, University of Washington, Seattle, USA). The IoN-ToF spectral data (.dat) files were read directly into IonToF-Pak. Initially, a peak list was created by including peaks across the mass range (usually m/z 0–300) that had raw intensities above 100. The integration limits were checked on each peak individually to ensure the correct peak areas were being measured on all the spectra. This IonToF-Pak peak list was then used to create a table for all of the spectra from the samples on which multivariate analysis was required. The results of this preparation were in $n \times m$ matrix format where the rows were samples (spectra) and the column were variables (peaks). The sample data in this new matrix were the normalised to the total intensity of the respective spectra for each sample.

XPS

The XPS spectra were acquired using an Axis Ultra DLD spectrometer (Kratos Analytical, UK). In the spectroscopy mode the samples were irradiated with monochromatic Al K_{α} source ($h\nu = 1486.6 \text{ eV}$, sampling area $300 \mu\text{m} \times 700 \mu\text{m}$). The sample was isolated electrically in order to eliminate vertical differential charging, and a low-energy electron flood source was used for charge compensation. The pressure in the analysis chamber was always maintained below $2 \times 10^{-8} \text{ mbar}$ for data acquisition. Survey spectra were obtained from the surface at 160 eV pass energy, 1 eV step size, from 1200 eV to -5 eV . The data were converted to VAMAS format and processed using CasaXPS, version 2.2.37 and quantified using empirically derived sensitivity factors. High resolution C1s spectra were collected at pass energy of 20 eV and step size of 0.1 eV. High resolution C 1s spectra were fitted with Gaussian-broadened Lorentzian functions (70% Gaussian) after linear background subtraction. Peaks were charge corrected relative to the CHx component at 285.0 eV.

ATR-FTIR

ATR-FTIR measurements were performed on a Perkin Elmer Spectrum One Fourier Transformation Infrared (FTIR) spectrophotometer, with a Specac Silver Gate Essential Single Reflection ATR System, consisting on a Germanium crystal at a fixed angle of 45°. Plasma polymer coated Si wafer were placed face down such that the polymer film was in contact with the germanium crystal. Pressure was applied to wafer using a mechanical plunger to ensure there was intimate contact between the plasma polymer coated Si wafer and crystal. 100 scans with a nominal resolution of 4 cm⁻¹ were collected for each sample.

A background spectrum of air was collected prior to sample analysis and this was subtracted from the results before reporting them.

Derivatization and Hydrolysis Studies

0.2 mM solution of trifluoroethylamine ($\geq 99.5\%$ Aldrich, UK) in methanol was allowed to react with freshly prepared maleic anhydride plasma polymer films (CW and pulsed). The reaction was allowed to proceed for 2 hours at room temperature. On completion of this time, the samples were washed several times with methanol, dried under a stream of nitrogen and were immediately used for XPS characterisation.

In a second study, freshly prepared pulsed ppMA films were also immersed in a solution of ethylenediamine ($\geq 99.5\%$ GC, Sigma Aldrich, UK, 100 mM) in isopropanol alcohol (IPA) and the reaction was allowed to proceed for 2 hours at room temperature. The samples were rinsed in fresh IPA and dried under a stream of nitrogen. The samples were used immediately for ATR-FTIR analysis.

To monitor the hydrolysis of the films, freshly deposited maleic anhydride plasma polymer samples were soaked in a mixture of de-ionized water (DI water) and hydrochloric acid (pH 2.0, ~ 0.3 mM) held at 90 °C. The progression of the hydrolysis reaction was monitored by ATR-FTIR analysis and a reaction time of 4 hours was found to be sufficient to open the anhydride ring structure and generate the diacid (M-ACIDpp) (data not shown). On completion of the hydrolysis reaction, the samples were washed several times with DI water and dried under a stream of nitrogen. The samples were used as negative controls for amine-anhydride derivatisation reactions.

RESULTS

Measurement of the pulsing cycle times ($t_{on/off}$) and investigation of plasma breakdown characteristics in both CW and pulsed conditions for MA polymerisation were performed by recording the oscillograms of RF discharge voltage waveforms using a RF probe.³² The nominal power delivered to the system in both continuous and pulse plasma polymerisation system was maintained at 1 W. As shown in Figure 2 (a) – (d), the use of ms and μ s ON and OFF times show differences in the discharge waveform characteristics with a noticeable delay from the applied RF ON-trigger pulse. As shown in Figure 2 (b), a delay of 2 ms in plasma ignition was observed, hence the ON-time was set to 12 ms in order to achieve the desirable 10 ms ON-time which was required to deliver a nominal power input of 1 W over the cycle. Similarly in μ s pulsed time regimes, a delay time of 20 μ s was detected under these pulsing conditions, as has been shown in Figure 2 (d). Hence to achieve 80 μ s pulse ON-time, the ON-trigger was set to 100 μ s. The ON and OFF times reported in this work have been corrected for delay time in plasma ignition.

ATR-FTIR Analysis

Infrared spectroscopy was used to probe the molecular structure of the plasma polymer coatings immediately after deposition. Comparison between MA plasma polymer films shown in Figure 3 and spectra from the monomer (see Supplementary Figure S1a) confirmed the presence of anhydride functional groups and ring structures after plasma polymerisation, although their relative intensities varied. Figure 3 (a) compares the ATR-FTIR spectra from 1W CW and pulsed ppMA films. All three spectra have peaks typical of an anhydride ring structure at wavelengths of 1780 and 1860 cm^{-1} . It is interesting to note that there was no detectable contribution from carboxylic groups (1730 cm^{-1}) deposited at nominal powers of 1 W. However, films prepared at higher continuous wave discharge powers of 10 W show a strong presence of carboxylic groups at wavelengths of 1730 cm^{-1} along with concurrent loss of peaks associated with anhydride moieties (see Supplementary Figure S1 b) agreeing with the results of previous ppMA studies.^{1, 17} Normalised spectral overlays from the anhydride-associated regions located at 1780 cm^{-1} and 1860 cm^{-1} in Figure 3 (b) and (c) show increases in the areas of these peaks when the film was deposited under μs pulsing conditions. CW and ms films show very similar ATR-FTIR spectra.

XPS Analysis

XPS analysis of freshly deposited ppMA coatings indicated the deposition of a film rich in carbon and oxygen. Complete attenuation of the substrate (Si wafer) and elemental quantification from multi-point XPS analysis indicated that the plasma polymer films were homogeneous and greater than 10 nm thick. Using ellipsometry, the thickness of the CW plasma polymerised maleic anhydride film was measured to be 22 ± 1 nm, while the thicknesses of ms and μs pulsed plasma polymerised films were 17 ± 0.7 nm and 12 ± 1 nm respectively. Table 1 shows the elemental atomic compositions determined by XPS survey spectra and various carbon chemical environments determined by high resolution C1s scans. Contributions from various functional groups determined by curve fitting of the C 1s spectra are shown in Figure 4. The C 1s envelope obtained from all three plasma deposition conditions were fitted with five components corresponding to C-C (285 eV), C-C(O)=O (285.7 eV), C-O (286.6 eV), C=O/O-C-O (287.9 eV) and C(O)=O (289.4 eV) binding environments³⁴. As shown in Figure 4, the hydrocarbon environment was found to be the prominent carbon centre in the C 1s envelope for all of the ppMA films.

To study the retention of anhydride functionality in the ppMA films, changes in C(O)=O anhydride group component at 289.4 eV were monitored. With the nominal power held constant at 1W, increases in the -C(O)=O contribution to the C1s spectra were observed with shorter ON-time and longer OFF-times (i.e. μs pulsing), together with a parallel increase in the O/C ratios (see Figure 4 and Table 1). As this binding energy shift is associated with ester and acid as well as anhydride functionality, from this data alone it is difficult to determine the exact relationship between deposition power and the chemical functionality of the coating.

Plasma Polymer Reactivity – XPS and ATR-FTIR Analysis

As the reactivity of maleic anhydride plasma polymers (i.e. amide linkage formation) is a key component of their functionality, the effect of plasma deposition parameters on reactivity of the films was investigated via a wet chemical derivatization reaction with subsequent analysis via XPS and ATR-FTIR.

Tri-fluorinated derivatizing agents are commonly used in XPS analysis because of the high detection sensitivity of fluorine and the readily distinguishable chemical shift in the C1s spectra associated with the introduction of CF_3 groups to the surface ($\sim +7.9$ eV relative to C-C charge corrected to 285.0 eV). In this case, trifluoroethylamine was reacted with the plasma polymer films to qualitatively compare the effects of the plasma polymerisation conditions on the

reactivity of the resulting films. A schematic of the reaction of anhydride groups with amine groups is shown in Figure 5, with the elemental composition determined by survey and high resolution C 1s scans shown in Table 2.

Increases in the fluorine and nitrogen content of the surfaces after exposure to the trifluoroethylamine indicated that the films deposited under μ s pulsing conditions had the highest level of anhydride groups available for nucleophilic attack by trifluoroethylamine (see Table 2). By considering N 1s signal as reference marker, our XPS data suggests that $\sim 37\%$ of oxygen present in anhydride environment on freshly deposited μ s pulsed plasma polymerised maleic anhydride reacted with TFEA derivatizing agent. While only $\sim 16\%$ and $\sim 14\%$ oxygen in anhydride environment were available for derivatization reaction in case of films deposited by CW and ms plasma conditions respectively (Calculations included in supplementary data S1c). In order to confirm that the TFEA was reacting with the anhydride groups on the sample and not by electrostatic interactions, samples were hydrolysed by soaking them in a 0.1 mM HCl + Water (pH 1.9) solution for 2 hours at 90 °C and then exposing them to the same derivatisation reaction. These samples acted as a negative control. As shown in Figure 6, there were significant changes in the coating chemistry evident from the XPS analysis of these hydrolysed films, but reaction of these films with the derivatizing agent did not result in the introduction of any nitrogen or fluorine on the surfaces and there is no evidence of a shift in the C 1s spectra associated with the addition of CF₃ groups (~ 292.9 eV). Further XPS data has been included in supplement section where survey and high resolution elemental scans of μ s pulsed plasma polymerised maleic anhydride has been shown after reaction with TFEA derivatizing agent (Supplement Figure S1d). The C 1s data (Supplementary Figure S1d (ii)) shows the presence of CF₃ groups introduced on the surface after reaction with TFEA derivatizing agent. N 1s data suggests presence of amide linkage formed between amine groups present on TFEA and anhydride groups from maleic anhydride plasma polymer. Hydrolysed films of μ s pulsed plasma polymerised maleic anhydride have been shown not to react with TFEA by XPS survey scans (Supplementary Figure S1e (i)). Further C 1s and N 1s high resolution XPS scans confirm that no CF₃ groups or amide linkages were present on the hydrolysed maleic anhydride plasma polymer sample (Supplementary Figure S1e (ii)). Absence of CF₃ groups and N 1s signal after reaction of hydrolysed maleic anhydride samples with TFEA would also indicate that contributions from electrostatic interaction between derivatizing agent and carboxylic groups present on the surface are negligible.

In a separate experiment, surfaces were also exposed to ethylenediamine and monitored using ATR-FTIR analysis. The reaction results in the opening of the anhydride ring structure (i.e. loss of anhydride symmetric stretching 1780 cm^{-1}) leading to the simultaneous formation of an amide linkage (i.e. appearance of amide symmetric stretching 1680 cm^{-1}) and carboxylic acid groups (i.e. appearance of carboxylic symmetric stretch 1700 cm^{-1}). The reaction chemistry is shown in Figure 7. Figure 8 shows the infrared spectral overlays before and after reaction with ethylenediamine (Figure 8 a and b respectively). The ATR-FTIR spectral comparison clearly shows that intense anhydride indicative peaks present at wavenumbers 1850 , 1780 and 1280 cm^{-1} on freshly deposited polymer films were replaced by peaks at 1700 and 1680 cm^{-1} indicating the presence of carboxylic and amide groups respectively after reaction with ethylenediamine. Again, hydrolysis of the plasma polymer samples prior to exposure to the ethylenediamine prevented the formation of amide linkage and clearly demonstrated the reaction was due to the presence of the anhydride groups.

ToF-SSIMS Analysis

Both positive and negative ToF-SSIMS spectra of ppMA films displayed peaks that could be assigned to the maleic anhydride monomer. However, the negative ion spectrums from ppMA were found to provide more useful molecular and structural information. The chemical

composition of each peak was identified from the m/z ratios. The final structure of each peak was determined based on the MA monomer structures. Figure 9 (a) – (e) shows negative ion ToF-SSIMS spectra obtained for a typical ppMA films deposited by μ s pulsed plasma polymerisation. Figure 10 shows the molecular structures assigned to some of these intense fragments. A notable series of ions in the negative ions SIMS of plasma polymerised maleic anhydride appears at m/z 97, 99 assigned to $[M - H]^-$ and $[M + H]^-$ and in a further a series at 111, 121, 145 and 169 which has been assigned to $[M + C_xH_y]^-$ where $x = 1, 2, 4$ and 6 and $y = 0$ and 1 respectively. High mass peaks $[nM + C_xH_y]^-$ were also observed for all plasma polymer films (CW, ms and μ s), although the relative ion intensities differed as a function of the plasma processing condition.

The selection of secondary ion fragments derived from the parent MA monomer and the assignment of chemical structures incorporated in polymer films shown above is not an exhaustive dataset. Moreover, due to the complex relationship between plasma deposition parameters and resultant surface chemical properties a multivariate analysis approach was chosen to examine the differences among ToF-SSIMS spectra as a function of changing plasma deposition parameters.

Principal Component Analysis of ToF-SSIMS spectra

PCA was used to analyze the negative ion ToF-SSIMS spectra of ppMA films deposited under continuous wave and pulsed conditions. Figure 11 (a) shows the score on the first PC as a function of the plasma processing condition, which captured 93% of the variation in the entire dataset. Figure 11 (b) presents the loadings for the first PC, giving the relationship between the peaks in the spectra and the corresponding PC score. The results clearly separate the negatively loaded continuous wave coatings from the positively loaded pulsed films. Analysis of the loadings plot shows that the differences between the continuous wave and pulsed plasma polymers films can be attributed to changes in the intensity of the secondary ion fragments between spectra rather than the introduction of new fragments to the spectra (further verified by univariate analysis). The loading plot suggests that the fragmented monomer species like C^- , O^- , OH^- and C_2^- correlated with films deposited by continuous wave plasma polymerisation. This would suggest higher fragmentation and incorporation of these fragments in film during CW deposition. This is supported by the presence of increases in the intensities of the hydrocarbon fragments C_2H^- , C_4H^- and C_6H^- at m/z 25, 49 and 73 respectively indicative of monomer fragmentation under CW conditions.

Positive loading of secondary ion fragments correlate with the pulsed plasma films and are dominated oxygen-rich fragments, but also contain intact monomer units. There are high positive scores on secondary ions at m/z 41, 82, 99 and 111 which can be assigned to C_2HO^- , $C_4H_2O_2^-$, $[M+H]^-$ and $[M+CH]^-$ respectively (see Figure 10 for molecular structures) suggesting that a monomer-like surface chemistry has been obtained by pulsed plasma polymerisation. Comparison of datasets for films deposited by pulsed plasma polymerisation enables us to separate the samples on the scores plot (Figure 12 a), and indicated that the microsecond films contained more intense monomer related species than the millisecond films.

Varying Plasma OFF-time

General consensus in literature on organic pulsed plasma polymerisation system is that, relatively short ON-time is favourable to deposit highly functional polymer films. The current study is in agreement with the literature, as we have successfully shown that the μ s pulsing regime results in films with a higher level of functional group retention as compared to films deposited under ms and CW conditions. Recent developments in mass-spectral sampling technique have brought forward new evidence on the role of negative ions and cluster formation in pulsed plasma polymerisation systems^{22, 35, 36}. These investigations have clearly shown the

presence of cluster ions ranging up to multiple monomer mass units generated by ion-neutral chemistry in gas phase predominantly occurring in the plasma off-period^{35, 36}. In light of these reports, we extended the study to explore the effects of varying the OFF-time in an attempt to explore the optimal t_{on}/t_{off} ratios to maximise the functional group retention for maleic anhydride plasma polymers.

To investigate this, plasma ON-time (t_{on}) were held constant at 80 μ s while t_{off} was varied from 800 μ s, 600 μ s, 400 μ s, 200 μ s and 50 μ s. This had the effect of slowly increasing the total power delivered to the films from 0.9 W to 1.2 W, 1.7 W, 2.9 W and 6.1 W respectively. The resulting surface chemistry was investigated using ToF-SSIMS and results interpreted using multivariate analysis.

Figure 13 shows the score and loading plot respectively, with PC1 captured 82% of the variance in the dataset. The scores on PC1 (Figure 13 a) clearly separated ppMA films as a function of the OFF-times. It is clear from the scores plot that $t_{off} = 50$ μ s is classed as an independent sample set with little resemblance to other two sample groups. Analysis of the loadings plot (Figure 13 b) indicates that differences between the coatings are attributed to changes in the intensity of the secondary ion fragments rather than the loss or addition of specific peaks in the spectra with changing plasma deposition parameters. Positively loaded peaks correlate with samples deposited at t_{off} 200 and 400 μ s and are dominated by a hydrocarbon molecular series represented by C_xH^- , where $x = 2, 4, 6, 8, 10$ and 12 . Low m/z molecular fragments at 12 (C^-), 13 (CH^-), 16 (O^-), 17 (OH^-) and 24 (C_2^-) were also found to have positive loading. The ions loading negatively correlated with samples deposited at longer OFF-times of 600 and 800 μ s, and were predominantly monomer fragments which included C_2HO^- (m/z 41), C_3HO^- (m/z 53), $C_3H_2O_2^-$ (m/z 70), $C_4H_2O_2^-$ (m/z 82), $[M + H]^-$ (m/z 99) and $[M + CH]^-$ (m/z 111).

It is interesting to note that on the scores plot (Figure 13 a) there is a transition in the score values occurring between t_{off} 400 μ s and t_{off} 600 μ s. The data suggests that for the selection of OFF-times investigated in the experiment, the relative surface chemistry of the film switches from one containing more hydrocarbons fragments to one with more monomer fragments between OFF-times of 400 and 600 μ s, ie total power changing from 1.2W to 1.7W. It is also interesting to note the presence of positively loading secondary ion fragments at m/z 97 (C_8H^-), 121 ($C_{10}H^-$) and 145 ($C_{12}H^-$). Though these secondary ions were noticed on each individual negative ion maleic anhydride ToF-SSIMS spectra, changes in their intensity with the deposition conditions means that they load with samples prepared at t_{off} 200 and 400 μ s (Figure 13 (b)).

The scores on the second PC of the negative ion spectra (capturing 17% of the variance in the dataset) separates t_{off} 50 μ s sample from the t_{off} 200–800 μ s sample (see 13a and b). At an effective power of 6 W (t_{off} 50 μ s), there is evidence of monomer fragmentation and ring opening seen from the loading of m/z 41, 43, 65 and 73 ions assigned to C_2HO^- , $C_2H_3O^-$, $C_5H_5^-$ and C_6H^- respectively. Strong positive loading of secondary ion fragment at m/z 45 assigned to $COOH^-$ confirms that the monomer has undergone ring opening process before being incorporated into the films as carboxylic groups. It is also interesting to note that there is a higher intensity of OH^- fragment when compared to O^- secondary ion fragment, correlating with samples deposited under very short OFF-times ($t_{on} = 50$ μ s). This observation suggests that either more polymer chains terminate with OH groups, possibly due to cleavage of carbonyl double bond or due to a higher yield of OH groups from the fragmentation of $-COOH$ containing species present on the surface. Negative loading of peaks associated with samples prepared at t_{off} 200–800 μ s contained both hydrocarbon and monomer fragments. The presence of some negative loading hydrocarbon fragments along with monomer fragments at m/z 25 (C_2H^-), m/z 27 ($C_2H_3^-$) and 53 ($C_4H_5^-$) is due to the fact that this PC groups the spectra from the t_{off} 200 and 400 μ s samples as well as 600 μ s and 800 μ s samples (see Figure 14 a).

DISCUSSION

The glow discharge deposition process involved in the plasma polymerisation process gives rise to a large number of simultaneous molecular cleavage and recombination events at any given time. Numerous studies have shown that by controlling the physical variables of the deposition process (pressure, temperature, power, flow rate, etc.) it is possible to have significant control and selectivity over the mechanism of bond dissociation, thus offering a greater control on the chemical and physical properties of the plasma polymer film.²⁹ In this study, a range of surface analysis techniques were combined to investigate the relationship between plasma discharge conditions and functional group retention of maleic anhydride plasma polymers all deposited under the same nominal power conditions.

Comparison of ATR-FTIR spectral intensities acquired from continuous and pulsed MA films reveals a higher peak area corresponding to anhydride ring structures when films were prepared under short (μ s) pulse regimes. The changes in absorption spectral band intensities at 1250 cm^{-1} assigned to cyclic anhydride also suggests that more maleic anhydride ring structures were conserved during the deposition. It is interesting to note that CW and ms films show similar infrared spectral intensities, and have very similar anhydride indicative peak areas at 1860 cm^{-1} , 1780 cm^{-1} , and 1250 cm^{-1} . It is also notable that in all the three discharge regimes, there is no evidence of any carboxylic acid absorbance spectral band at 1700 cm^{-1} . The absence of carboxylic group signals in these ATR-FTIR spectra suggests that nominal power of 1 W (delivered by continuous or pulsed polymerisation technique) is insufficient to ring open the maleic anhydride molecule; a factor that is required for the formation of carboxylic acid groups on the surface.

One complexity in the analysis of the ATR-FTIR data is that the absence of a carboxylic acid infrared absorbance spectral band may be due to limitations in the sensitivity offered by the technique. XPS offers higher surface sensitivity than ATR-FTIR analysis. XPS analysis of the surfaces indicated noticeable differences between the C–H (285.0 eV) contribution for films deposited under continuous wave (CW), ms and μ s conditions. The CW coatings had approximately 20% higher C–H component compared with films that were deposited under μ s pulse regime. This suggests that CW plasma deposition leads to higher fragmentation of monomer relative to the two pulse films investigated in this study. There is also a two-fold increase in the –COO component when the film is deposited using μ s pulsing regimes. However, a limitation of the XPS analysis lies in the fact that both anhydride and carboxylic groups have binding energy shifts of $\sim +4.1\text{ eV}$ relative to C–C at 285.0 eV .

The use of chemical derivatisation enabled differentiation of the anhydride and acid contributions to the surface chemistry using both XPS and FTIR. The results clearly demonstrated that the reactivity of the coatings and thus the film chemistry were strongly dependent on t_{on}/t_{off} ratios, and that differences in chemical properties of plasma polymer films were evident even when deposition is carried out under same nominal powers. Of course XPS and FTIR data sample different depths within the film, with the FTIR data including information well beyond the 10 nm sampling depth of XPS. This may account for the significant changes in O/C ratios detected by XPS that were not evident in the FTIR data as atmospheric aging may be making a more significant contribution to the XPS data.

ToF-SSIMS analysis provided a unique opportunity to investigate the surface chemistry and derive molecular level information about the films. Principal component analysis of negative ion MA plasma polymer films gives insight into the molecular properties as well as into the influence of pulse plasma discharge conditions on polymer formation. The data clearly suggests that a decrease in t_{on} time is necessary to enhance the anhydride groups on the plasma-polymerised surface. Low m/z secondary ion molecular fragments (e.g. C^- , O^- , OH^- , C_2^- ,

etc.) were found to load and correlated with films deposited at relatively long t_{on} times (ms and CW), suggesting that the monomer has undergone relatively higher and undesirable fragmentation (compared to film deposited under μ s pulsed regime). In contrast, samples deposited at relatively short ON-times (μ s) were always found to contain relatively high m/z secondary ion molecular fragments, which were indicative of intact monomer [M] structures. Comparison of ToF-SSIMS data further emphasises that the use of a shorter t_{on} time helps to conserve the monomer structural integrity incorporated in the film.

The physics of plasma dictates that the plasma gas phase at any given instance comprises of positive, negative and neutral species, which contribute to the process of film growth at the plasma reactor wall and substrate³⁶. The ON-time is dominated by the reaction of positive ions with positive, negative or neutral species present in the gas phase. Recombination of charged species in the gas phase leads to the formation of oligomeric structures that are accelerated towards the reactor wall or substrate due to the presence of plasma sheath^{22, 24}. The sheath potential itself inhibits the negative ions present in the plasma to approach any surface thus its concentration steadily increases in the bulk gas phase during plasma ON-time. The collapse of these potentials during the plasma pulse OFF-time allows a flux of negative ions to diffuse to the surfaces. Negative ions in both organic²² and inorganic³⁵ plasma deposit systems have been shown to form large oligomeric structures suspended in the gas phase during ON-time and subsequently diffuse to reactor wall and substrate during OFF-times. It is thus obvious to conclude that during the t_{on} period, positive ions dominates the deposition process while the negative species present in the gas phase contribute to the film growth in the t_{off} period.

Numerous studies have concluded that the precise role of charged species in the gas phase (and their contribution to film growth) is strongly dependent on various experimental and operational parameters (eg. t_{on} , t_{off} , discharge power, flow rate, current density etc.). One of the real challenges in investigating the role of t_{off} parameters lies in the fact that to hold P_{ave} constant, you need to simultaneously vary t_{on} , a factor that further complicates the interpretation of any data. In our preliminary studies shown here, we chose to allow the P_{ave} to vary. This in effect enabled us to probe the effects of relatively small changes in the P_{ave} (0.9–6W), while exploring a wide range of OFF-times. Although our experimental design is not optimal to address all these issues, it does enable us to establish a critical balance between total deposition time and film functionality which is critical for the manufacturing of these films. The ToF-SSIMS results from this initial study clearly indicated that there are distinct regions in the deposition chemistry that can be related to the combined effects of power and off time.

1. Functional Group Retention – P_{ave} 0.9–1.2 W, t_{off} 800 and 600 μ s
2. Functional Group Loss - P_{ave} 1.7–2.9 W, t_{off} 400 and 200 μ s
3. Ring Opening - P_{ave} 2.9–6 W t_{off} ~50 μ s

While these results are preliminary, they serve to highlight that significant insights may be obtained by combining gas phase and surface analytical mass spectrometry techniques in future.

CONCLUSIONS

This study has focused on the deposition of thin polymeric films bearing anhydride groups by plasma polymerisation. The results show that a critical balance of plasma processing parameters is needed to maximise the functional groups retained by these films. The use of capacitive probe in measurement of plasma ON and OFF time has enabled the duty cycle to be set accurately, thus increasing the reliability of reported data. By combining ATR-FTIR and X-ray photoelectron spectroscopy (XPS) the effects of experimental variables on the chemical

functionality of the films were explored and these together with chemical derivatisation experiments clearly demonstrated the changes that occurred in the chemical functionality of the films when they were deposited under the same nominal power, with the μs films demonstrating the highest apparent functionality. .

The molecular specificity, surface sensitivity and high mass resolution of time-of-flight static secondary ion mass spectrometry (ToF-SSIMS) combined with multivariate analysis techniques provided a more detailed insight into the small changes in chemical species present within the films, clearly indicating transitions in the coating chemistry with changes in the deposition parameters. When combined with the XPS and ATR-FTIR data these results gave new insight into the deposition processes that were occurring with slight changes in the hydrocarbon content of the films being the clearest indication of reductions in the film functionality with initial loss of monomer functionality eventually leading to ring opening with increasing power. Interestingly, the subsequent exploration of the effects of changes in both plasma off times and power in the μs pulsing regime demonstrated how small changes in power translated to significant changes in the film composition and thus film functionality. The results clearly demonstrated three distinct deposition regimes that were influenced by the pulsing off time and the resulting small changes in the nominal power delivered to the plasma. This serves to reinforce that monitoring of the pulsing conditions together with control of the power delivery is essential if these deposition systems are to be optimised to produce films that retain both chemical functionality and can be manufactured with the shortest processing times.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Schematic diagram of plasma polymerisation reactor used in this study. Silicon wafers samples for plasma deposition were place in the centre of the plasma reactor on a sample stage equidistant from the monomer inlet and positive electrode.

(a)

(b)

(c)

(d)

Figure 2.

Plasma breakdown characteristics during pulsed plasma polymerisation of maleic anhydride measured by an in-situ capacitive RF probe. Figure (a) shows a series of trigger pulse generated by the pulsing unit and corresponding plasma discharge waveform for each cycle. Figure (b) shows one such trigger pulse and corresponding plasma discharge waveform. Note that the trigger pulse has been set to $t_{on(set)} = 12$ ms, $t_{off(set)} = 90$ ms to achieve an effective $t_{on(measured)} = 10$ ms, $t_{off(measured)} = 92$ ms (i.e. 2 ms delay in plasma ignition). Peak Power for the experiment = 10 W. Figure (c) and (d) shows the trigger pulse and plasma discharge waveforms during μ s pulsing of plasma. Note in Figure (d) $t_{on(set)} = 100$ μ s, $t_{off(set)} = 800$ μ s

to achieve an effective $t_{on(measured)} = 80 \mu\text{s}$, $t_{off(measured)} = 880 \mu\text{s}$ (i.e. 20 μs delay in plasma ignition) Peak Power for the experiment = 10 W.

Figure 3.

ATR-FTIR spectra for maleic anhydride plasma polymers deposited under (a), (i) 1 W Continuous wave (ii) $t_{on} = 10$ ms, $t_{off} = 90$ ms, Peak Power = 10 W (iii) $t_{on} = 80$ μ s, $t_{off} = 800$ μ s, Peak Power = 10 W (b) inset shows the overlay of carbonyl asymmetric and symmetric stretch at 1858 cm^{-1} and 1780 cm^{-1} respectively and (c) inset shows the overlay of cyclic anhydride and ether carbon stretch at 1250 cm^{-1} and 1110 cm^{-1} respectively. (v – Stretching, a – Asymmetric, s – Symmetric)

Figure 4.

XPS C 1s high resolution narrow scans (showing contributions from different carbon environments) presents for maleic anhydride plasma polymers deposited under (a) 1 W continuous wave (b) $t_{on} = 10$ ms, $t_{off} = 90$ ms, Peak Power = 10 W and (c) $t_{on} = 80$ μ s, $t_{off} = 800$ μ s, Peak Power = 10 W.

Figure 5. Simplified reaction schematic of plasma polymerised maleic anhydride films with trifluoroethylamine showing the anhydride ring opening and formation of amide linkage (-CNO) and carboxylic groups (-COOH).

Figure 6.
C (1s) XPS spectra of maleic anhydride plasma polymer deposited by μ s pulse plasma polymerisation compared with hydrolysed sample and its reaction with trifluoroethylamine (TFEA) after hydrolysis.

Figure 7.
Reaction schematic of plasma polymerised maleic anhydride films with ethylenediamine showing the formation of amide linkage

Figure 8.

ATR-FTIR spectra of maleic anhydride plasma polymer (a) $t_{on} = 80\text{ }\mu\text{s}$, $t_{off} = 800\text{ }\mu\text{s}$, Peak Power = 10 W, (b) after reaction of freshly deposited maleic anhydride plasma polymer with ethylenediamine, (c) after reaction of hydrolysed maleic anhydride plasma polymer with ethylenediamine derivatizing agent. Note that the symmetric and asymmetric (C=O) stretch present on the freshly deposited maleic anhydride plasma polymer (peak labelled (2)) has been replaced by symmetric stretch of carboxylic acid groups (peak labelled (3)) after hydrolysis of the sample. (ν – Stretching, *a* – Asymmetric, *s* – Symmetric)

Figure 9.

Negative ion ToF-SIMS mass spectrum of typical maleic anhydride plasma polymer deposited under experimental conditions where peak power has been set to 10 W, $t_{on} = 80 \mu\text{s}$, $t_{off} = 800 \mu\text{s}$, Duty cycle ~ 0.1 . Inset (a) shows some of the intense molecular ion fragments associated with maleic anhydride plasma polymer detected in the mass range of 0–100 m/z. Negative ion molecular fragments indicative of monomeric structure i.e. [M-H]⁻ and [M+H]⁻ were detected at m/z 97 and 99 respectively. Inset (b) – (e) shows some of the most intense maleic anhydride related fragments in 100–200 m/z range.

Negative ion molecular fragment	Nominal m/z
C_2H^-	13
O^-	16
$\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}^-$	41
C_4H^-	49
$\begin{array}{c} \text{O}^- \\ \\ \text{O}=\text{C} \\ \\ \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	70
C_6H^-	73
$\begin{array}{c} \text{O}=\text{C} \quad \text{C}=\text{O} \\ \quad \\ \text{C}-\text{C}^- \\ \\ \text{H} \end{array}$	81
$\begin{array}{c} \text{O}=\text{C} \quad \text{C}=\text{O} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	82
$\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{O}=\text{C} \quad \text{C}=\text{O} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	98
$\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{O}=\text{C} \quad \text{C}=\text{O} \\ \quad \\ \text{C}-\text{C}-\text{CH}^- \\ \quad \\ \text{H} \quad \text{H} \end{array}$	111

Figure 10.

Some of the most intense negative ion molecular fragment detected by ToF-SIMS analysis of maleic anhydride plasma polymer deposited under μs pulsed conditions. Probable molecular structures and their nominal mass have been shown in this figure.

Figure 11.

(a) Scores and (b) Loadings for the first principal component from the analysis of negative ion ToF-SIMS spectra of maleic anhydride plasma polymer deposited by continuous wave deposition (1W), millisecond ($t_{on} = 10$ ms, $t_{off} = 90$ ms, Peak Power = 10 W) and microsecond ($t_{on} = 80$ μs, $t_{off} = 800$ μs, Peak Power = 10 W) pulsing conditions. The scores plot legend 1W indicates samples deposited by continuous wave deposition, 10 ms/ 90 ms indicates films deposited by millisecond pulsing of plasma (i.e. $t_{on} = 10$ ms, $t_{off} = 90$ ms, Peak Power = 10 W) and 80 μs/ 800 μs indicates films deposited by microsecond pulsing of plasma (i.e. $t_{on} = 80$ μs, $t_{off} = 800$ μs, Peak Power = 10 W)

Figure 12.

(a) Scores and (b) Loadings plots for the first principal component from the analysis of negative ion ToF-SIMS spectra of maleic anhydride plasma polymers deposited by millisecond (ms) and microsecond (μ s) pulsing of plasma. The scores plot legend 10 ms/ 90 ms indicates films deposited by millisecond pulsing of plasma (i.e. t_{on} = 10 ms, t_{off} = 90 ms, Peak Power = 10 W) and 80 μ s/ 800 μ s indicates films deposited by microsecond pulsing of plasma (i.e. t_{on} = 80 μ s, t_{off} = 800 μ s, Peak Power = 10 W)

Figure 13.

(a) Scores and (b) Loadings plot for the first PC of negative ion ToF-SIMS spectra of maleic anhydride plasma polymer deposited by varying t_{off} times from 50 to 800 μs . The legends on the scores plot indicate the ON and OFF times for each sample. The peak power in each of the 5 sample sets have been fixed at 10W.

Figure 14.

(a) Scores and (b) Loadings plot for the second PC of negative ion ToF-SIMS spectra of maleic anhydride plasma polymer deposited by varying t_{off} times from 50 to 800 μ s. The legends on the scores plot indicate the ON and OFF times for each sample. The peak power in each of the 5 sample sets have been fixed at 10W

XPS elemental composition determined by survey scans and three different carbon environments determined by high resolution C 1s scans of ppMA for different deposition conditions. Where, CW = Continuous Wave deposition, Millisecond (ms) = (t_{on} = 10 ms, t_{off} = 90 ms, Peak Power = 10 W), Microsecond (μ s) = (t_{on} = 80 μ s, t_{off} = 800 μ s, Peak Power = 10 W). (Values in parentheses are standard deviation for each mean, $n = 3$)

Table 1

	Survey Scan			High Resolution C 1s (%)			
	%C ($\pm 1\%$)	%O ($\pm 1\%$)	O/C	C-C	C-C-(O)=O	C-O	C=O/O-C-O
Monomer (theoretical)	57.1	42.9	0.75				
CW	78.2	21.8	0.28	58.8 (2.5)	12.1 (1.7)	11.8 (0.9)	5.3 (0.5)
ms	73.4	26.6	0.36	44.6 (3.1)	19.4 (2.7)	11.1 (1.6)	5.5 (0.7)
μ s	70.1	29.9	0.43	36.7 (2.7)	24.8 (2.1)	8.5 (1.3)	5.3 (0.3)

XPS elemental composition determined from survey scans and six different carbon environments determined by high resolution C 1s scans of MA plasma polymer after reaction with TFEA. Where, CW = Continuous Wave deposition, Millisecond (ms) = (t_{on} = 10 ms, t_{off} = 90 ms, Peak Power = 10 W), Microsecond (μ s) = (t_{on} = 80 μ s, t_{off} = 800 μ s, Peak Power = 10 W). (Values in parentheses are standard deviation for each mean, n = 3)

Table 2

	Survey Scan (%)						High Resolution C 1s (%)					
	C 1s	N 1s	O 1s	F 1s	C-C	C-C-(O)=O/ C-N	C-O/ N-CH ₂ - CF ₃	C=O/O-C-O/ N-C=O	C(O)=O	CF ₃		
CW	73.9 (3.1)	1.3 (0.2)	23.4 (1.2)	1.4 (0.3)	53.3 (1.2)	12.3 (0.6)	14.2 (1.2)	7.1 (1.2)	12.2 (0.6)	0.9 (0.2)		
ms	70.0 (2.1)	1.3 (0.5)	27.1 (1.7)	1.6 (0.6)	47.3 (2.3)	14.3 (2.6)	13.7 (1.4)	9.3 (0.6)	14.3 (2.6)	1.1 (0.4)		
μ s	67.7 (1.7)	2.9 (0.8)	23.3 (2.1)	6.1 (0.5)	43.0 (3.2)	15.8 (1.5)	12.7 (1.7)	9.9 (0.9)	15.8 (1.2)	2.8 (0.5)		