Pulsed Plasma Polymerization of Maleic Anhydride

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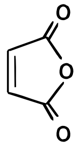
Received August 7, 1995. Revised Manuscript Received November 9, 1995⊗

Plasma polymerization of maleic anhydride has been studied using continuous-wave and pulsed glow discharges. The deposited plasma polymer layers have been characterized by X-ray photoelectron spectroscopy and transmission infrared spectroscopy. Anhydride functionality incorporation into the growing films is found to be greatest during pulsed plasma polymerization with low duty cycles.

Introduction

Maleic anhydride is widely used as an organic reagent which contains two types of reactive site: the anhydride functionality and the >C=C< double bond (structure 1). This molecule can participate in a variety of reactions including: the Diels−Alder reaction[1] (i.e., a [4+2] cycloaddition), attack on allylic hydrogen atoms to form asymmetric carbon centers,[2] photochemical reactions,[3−5] and polymerization. Conventional polymerization,[6] copolymerization,[7−14] and graft polymerization[15] of maleic anhydride have been extensively studied. In general, maleic anhydride functionalized polymers are sought for their improved interfacial adhesion,[16] polymer/polymer compatability,[17] and ability to undergo subsequent surface reactions.[18] Homopolymerization of the monomer can be initiated by a variety of means which include γ-radiation,[19] UV radiation,[20] free radicals,[21] ionic catalysts,[22] or the application of high pressure.[23] In addition, maleic anhydride can participate in condensation polymerization to form unsaturated polyesters.[24] Copolymerization of maleic anhydride with a variety of other monomers can lead to random addition,[7−10] alternating addition,[11−14] and graft copolymers.[25−30]



In the current study, the homopolymerization of maleic anhydride using a radio frequency (RF) glow discharge is investigated using both continuous-wave (CW) and pulsed excitation. This solventless method can be used to deposit polymeric layers with a whole spectrum of chemical and physical properties, depending upon the specific electrical discharge parameters deployed during plasma polymerization (e.g., input power, feed gas composition, monomer pressure, substrate temperature, and substrate position). The number and lifetimes of the various plasma species (ions, radicals, electrons, metastables, and photons) influence which reaction pathways are pursued during glow discharge polymerization. Hence, there is considerable scope for structural and compositional tailoring of growing polymeric films. For instance, average input power is recognized as being a critical parameter, which can be varied either by altering the peak power in a CW electrical discharge or alternatively by pulsing the applied RF voltage. The latter technique has been frequently overlooked in the past, yet it offers scope for the optimization of reactive intermediates as well as access to conventional polymerization reaction pathways during the duty cycle off-period.

Experimental Section

At room temperature maleic anhydride has a vapor pressure of approximately 2.6 × 10^{-1} mbar.[31] Briquettes of maleic

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⊗ Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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anhydride (Aldrich, 99% purity) were ground into a fine powder and loaded into a monomer tube. Plasma polymerization experiments were carried out in an electrodeless cylindrical glass reactor (4.5 cm diameter, 460 cm^3 volume, base pressure of 5.2×10^{-3} mbar, and with a leak rate better than 1.0×10^{-10} kg s^{-1}) enclosed in a Faraday cage.[32] The reactor was fitted with a gas inlet, a thermocouple pressure gauge, a 30 L min^{-1} two-stage rotary pump attached to a liquid nitrogen cold trap, and an externally wound copper coil (4 mm diameter, 9 turns, spanning 8−15 cm from the gas inlet). All joints were grease-free. Gas flow and leak rates were calculated by assuming ideal gas behavior.[33] The substrate was located in the centre of the coil. An L−C matching network was used to match the output impedance of the RF (13.56 MHz) generator to that of the partially ionized gas load; this was achieved by minimizing the standing wave ratio (SWR) of the transmitted power. For the pulsed power experiments, the RF supply was triggered by a signal generator, and a cathode ray oscilloscope was used to monitor the pulse width and amplitude. The pulse rise and fall time was limited by the response of the RF generator to 0.5 μs. The peak power (P_p) delivered to the glow discharge spanned 5−90 W. Pulse on-times (t_{on}) and off-times (t_{off}) could be varied between 20−800 and 20−1200 μs, respectively. The average power $\langle P \rangle$ delivered to the system during pulsing was calculated using the following expression:[34]

$$\langle P \rangle = P_p\{t_{on}/(t_{on} + t_{off})\} \qquad (1)$$

where $t_{on}/(t_{on} + t_{off})$ is defined as the duty cycle.

A typical experimental run comprised initially scrubbing the reactor with detergent, rinsing with isopropyl alcohol, and oven drying; this was followed by a 30 min high-power (50 W) air plasma cleaning treatment. Next, the reactor was evacuated back down to its original base pressure. Subsequently, the monomer vapor was introduced into the reaction chamber at a pressure of approximately 2.6×10^{-1} mbar (which is the vapor pressure of maleic anhydride at room temperature), and at a flow rate[33] of approximately 1.59×10^{-9} kg s^{-1}. Then the plasma was ignited and allowed to run for 10 min to provide sufficient plasma polymer for XPS analysis or 30 min to generate films thick enough for infrared characterization. Upon completion of deposition, the RF generator was switched off, and the system flushed with monomer for 5 min prior to venting up to atmospheric pressure. Each plasma polymer layer was characterized immediately after deposition by X-ray photoelectron spectroscopy or infrared analysis.

A Kratos ES200 electron spectrometer equipped with an unmonochromatized Mg Kα X-ray source (1253.6 eV), and a hemispherical analyzer was used for XPS surface analysis. Photoemitted core level electrons were collected at a takeoff angle of 30° from the substrate normal, with electron detection in the fixed retarding ratio (FRR, 22:1) mode. XPS spectra were accumulated on an interfaced PC computer and curve fitted using a Marquardt minimization algorithm. Instrument performance was calibrated with respect to the gold 4f$_{7/2}$ peak at 83.8 eV with a full width at half-maximum (fwhm) of 1.2 eV. No radiation damage was observed during the typical time scale involved in acquiring the XPS spectra. Instrumentally determined sensitivity factors for unit stoichiometry were taken as being C(1s):O(1s) equals 1.00:0.55. Uniform plasma polymer coverage was assumed by the absence of any Si(2p) XPS signal from the underlying glass substrate.

A FTIR Mattson Polaris instrument was used for transmission infrared analysis of maleic anhydride precursor mixed with potassium bromide, as well as the respective continuous wave and pulsed plasma polymer layers deposited onto pressed potassium bromide discs. Typically, 100 scans were acquired at a resolution of 4 cm^{-1}.

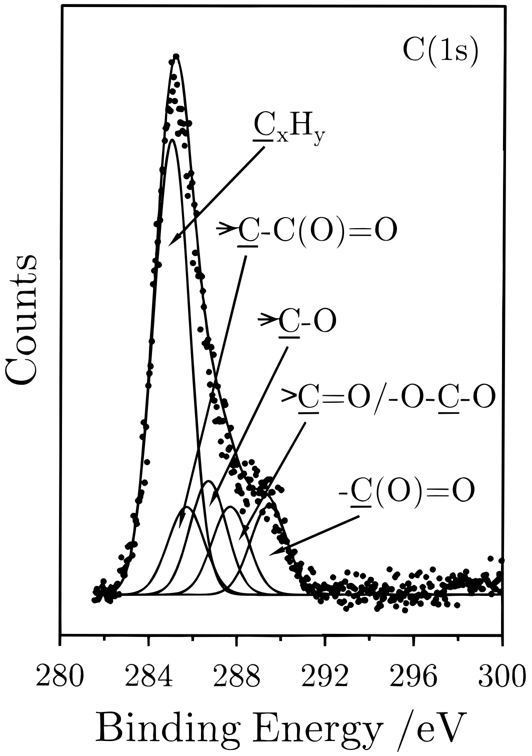

Figure 1. Typical C(1s) XPS peak fit for a 5 W CW maleic anhydride plasma polymer.

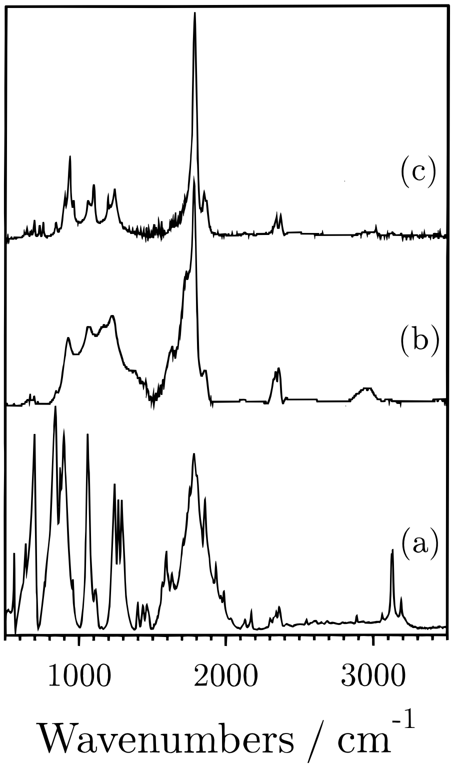

Figure 2. Infrared spectra of (a) maleic anhydride monomer, (b) 5 W CW plasma polymer, and (c) pulsed plasma polymer (on-time = 20 μs, off-time = 1200 μs, and peak power = 5 W).

Results

Continuous Wave Plasma Polymerization. The C(1s) XPS envelope obtained from a low-power (5 W)

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Table 1. Assignment of Infrared Absorbance Bands for Maleic Anhydride Monomer[38]

wavenumber/cm^{-1}	assignment	wavenumber/cm^{-1}	assignment
3190	ν(C−H) (adjacent to CH_2)	1242	δ(C−H)
3131	ν(C−H) (adjacent to CH)	1059	δ(C−H)
1858	νa(C=O)	897	ν(C−C)
1782	νs(C=O)	839	δ(C−H)
1593	ν(C=C)	698	δ(maleic anhydride ring)
1280	ν(C−O)	564	δ(C=O)

[a] ν stretching, δ deformation, a asymmetric, s symmetric.

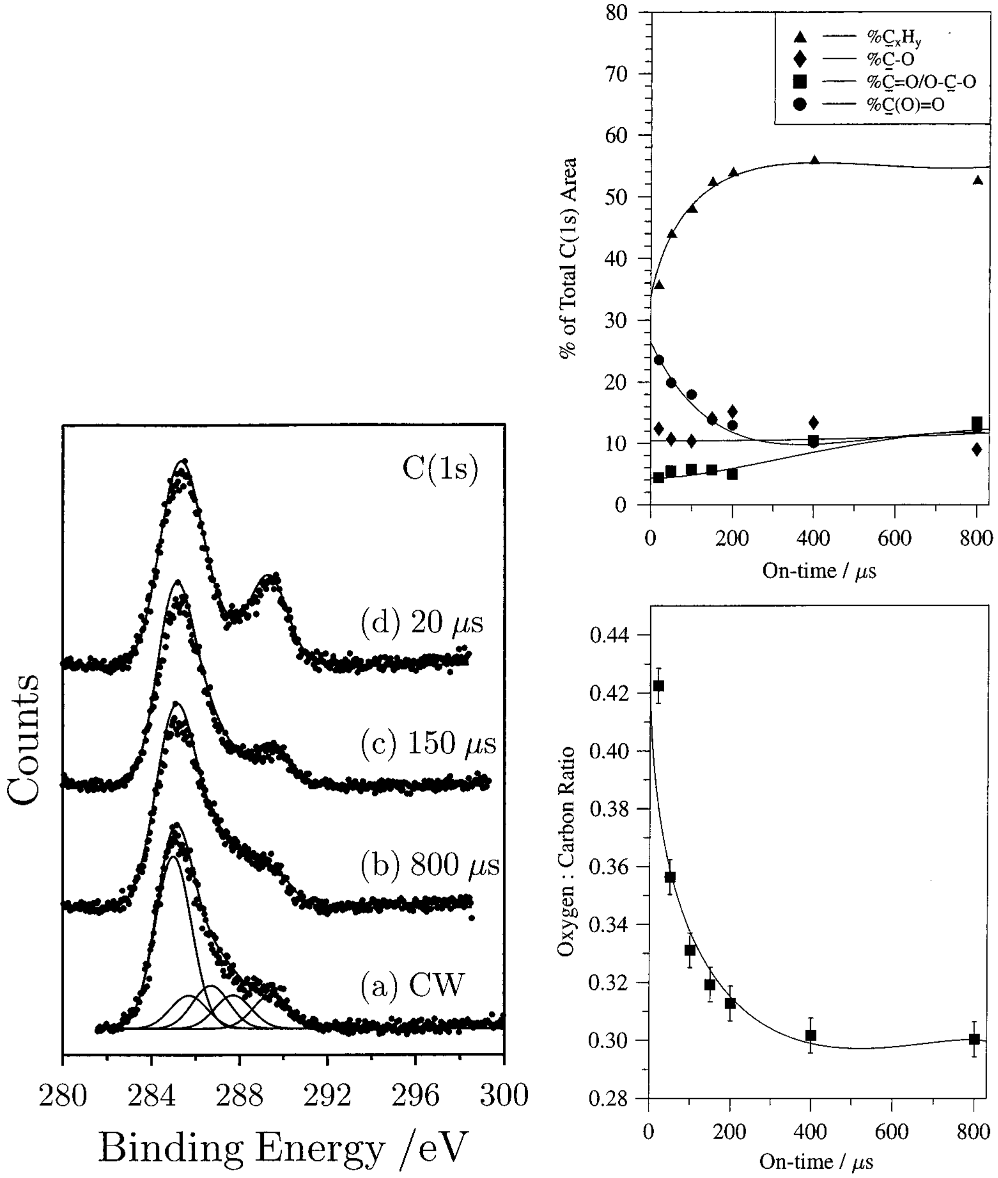

Figure 3. Pulsed plasma polymerization experiments with variable on-time (peak power = 5 W, and off-time = 1200 μs): (left) C(1s) XPS spectra; (top right) variation of C(1s) functionalities; (bottom right) variation of oxygen to carbon ratio.

continuous wave plasma polymerization experiment can be curve fitted with five Mg K$\alpha_{1,2}$ components having equal full widths at half-maximum corresponding to 55% C_xH_y (285.0 eV),[35] 10% >*C*−C(O)=O (285.7 eV),[35] 14% >*C*−O (286.6 eV),[35] 11% >*C*=O/O−*C*−O (287.9 eV),[35] and 10% −C(O)=O (289.4 eV)[36] environments (Figure 1). Hydrocarbon/cross-linked carbon, C_xH_y, is found to be the predominant carbon center in the C(1s) envelope, with smaller amounts of oxygenated functionalities. This is significantly different from the equal contributions expected from just the >*C*−C(O)=O and −*C*(O)=O environments if the monomer had undergone conventional polymerization.

Table 1 summarizes the infrared assignments for maleic anhydride. A comparison of the infrared spectra for the maleic anhydride precursor, and the 5 W CW plasma polymer shows that the sharp spectral features

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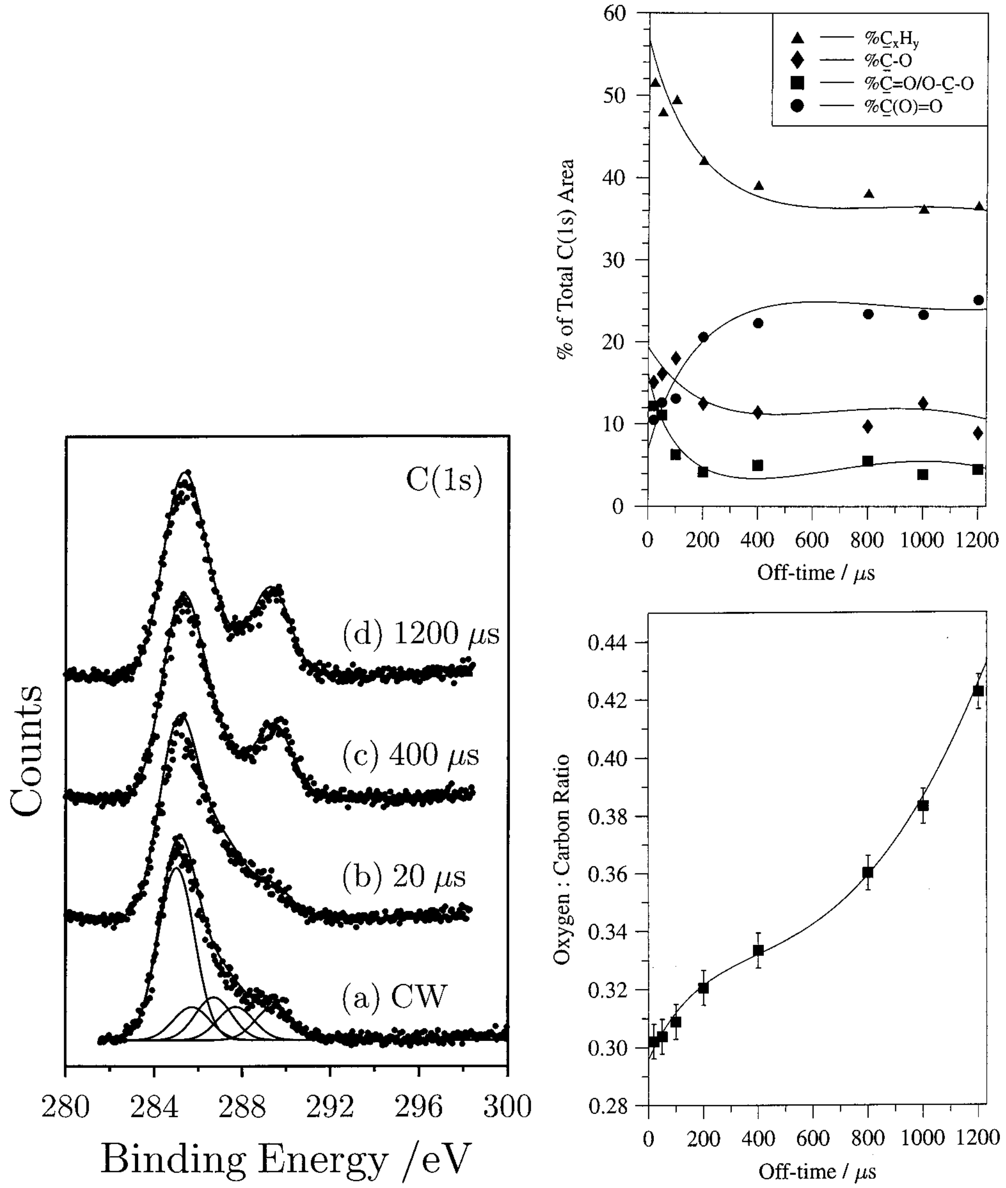

Figure 4. Pulsed plasma polymerization experiments with variable off-time (peak power = 5 W, and on-time = 20 μs): (left) C(1s) XPS spectra; (top right) variation of C(1s) functionalities; (bottom right) variation of oxygen-to-carbon ratio.

characteristic of the monomer are broadened (and in some cases lost), Figure 2. This can be attributed to a high level of cross-linking.[37] Certain bands are still discernible in the CW plasma polymer: 2995 cm^{-1} (C−H stretch), 1860 cm^{-1} (asymmetric C=O stretch), 1780 cm^{-1} (symmetric C=O stretch), 1647 cm^{-1} (C=C stretch), 1240 cm^{-1} (C−O stretch), 1053 cm^{-1} (C−H deformation), and 920 cm^{-1} (C−H out-of-plane bending).

Pulsed Plasma Polymerization. Both pulsed and continuous-wave plasma polymerization of maleic anhydride produced films with excellent adhesion characteristics to glass, KBr, and PTFE substrates. The variation in anhydride group retention during pulsing was investigated as a function of duty cycle parameters (on-time, off-time), and peak power. A fixed duty cycle off-period of 1200 μs, and peak power of 5 W produced a significant enhancement of the $-C(O){=}O$ anhydride group C(1s) component at 289.4 eV at the expense of cross-linked carbon/hydrocarbon (C_xH_y) species with decreasing on-times down to 20 μs, below which incomplete coverage of the glass substrate was observed (Figure 3a). Curve fitting of the C(1s) envelope also shows that there is an insignificant variation in the amount of $>C{-}O$ groups, while the $>C{=}O/O{-}C{-}O$ concentration is reduced at shorter on-periods (Figure 3b). This is accompanied by an increase in the total oxygen:carbon ratio (Figure 3c).

Similarly, for a constant duty cycle on-time (20 μs) and peak power (5 W), the $-C(O){=}O$ anhydride group concentration rises with longer off-times at the expense of C_xH_y and $>C{=}O/O{-}C{-}O$ centers, together with a parallel increase in oxygen to carbon ratio (Figure 4).

It can be concluded that anhydride functionality incorporation is favored by short on-times and long off-times. In both cases, this amounts to a lower average power input; therefore, a further study was undertaken in which the on- and off-times were kept fixed (see ref 1) while the peak power was varied (Figure 5). The $-C(O){=}O$ anhydride group feature at 289.4 eV in the C(1s) spectrum diminishes at higher peak powers. This

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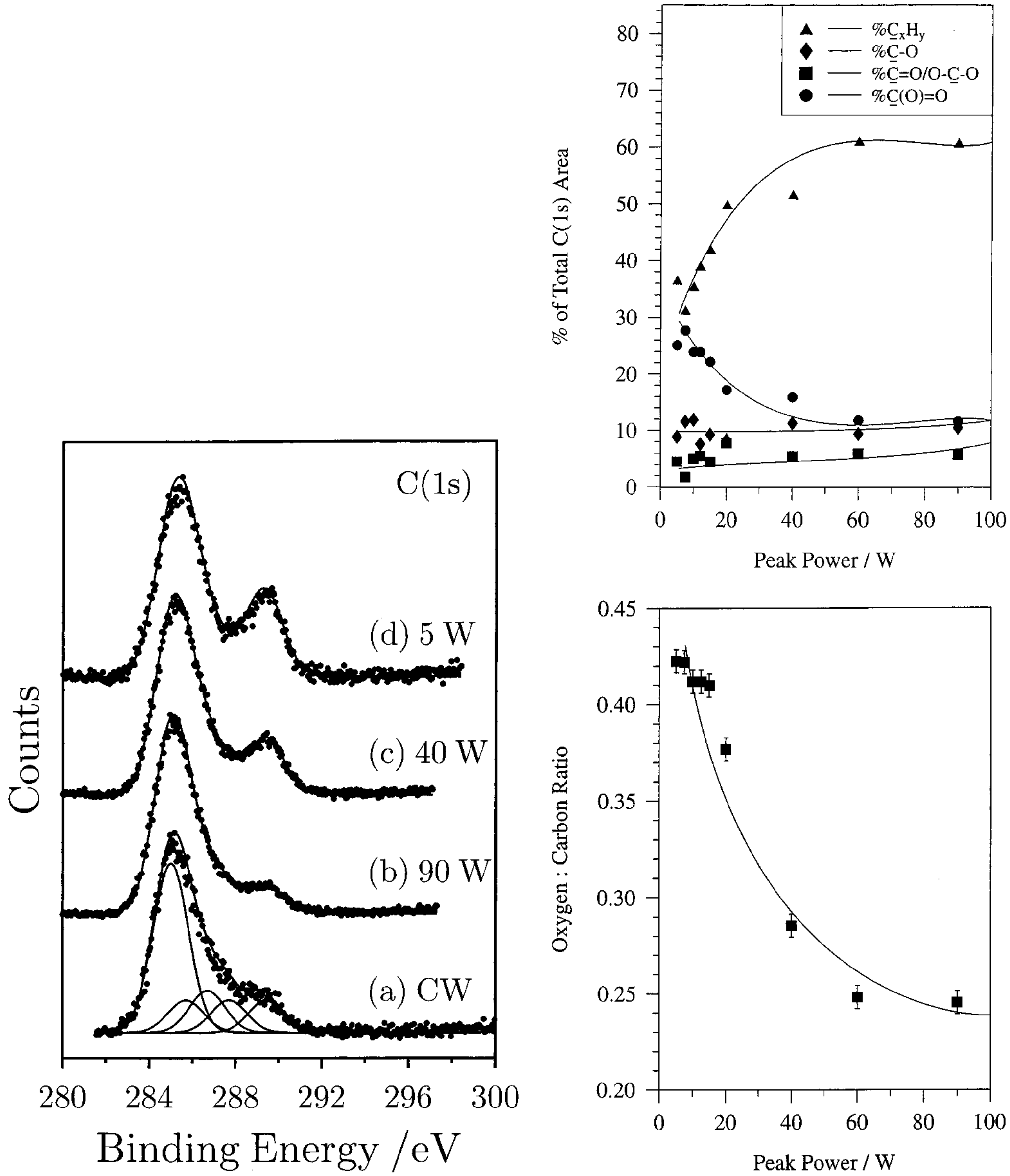

Figure 5. Pulsed plasma polymerization experiments with variable peak power (off-time = 1200 μs, and on-time = 20 μs): (left) C(1s) XPS spectra; (top right) variation of C(1s) functionalities; (bottom right) variation of oxygen-to-carbon ratio.

suggests that retention of the anhydride functionality depends on the average power as well as the duty cycle parameters (t_{on} and t_{off}).

Infrared analysis of the pulsed plasma polymer layers unveils a closer resemblance to the maleic anhydride monomer absorption spectrum compared to the CW plasma polymer (Figure 2): bands in the 600–1300 cm^{-1} region are better resolved, indicating less cross-linking. The >C=C< stretch seen at 1647 cm^{-1} for the CW plasma polymer is absent. Hydrolysis of the anhydride functionality by air can be ruled out in the plasma polymer films because of the lack of any infrared absorbance due to C=O acid stretching[38] at 1708 cm^{-1}.

Discussion

Continuous wave glow discharge polymerization of maleic anhydride yields a material which is predominantly a hydrocarbon network with a small level of oxygenation. This is in agreement with other studies, which have shown that oxygen-containing organic precursors generally tend to form plasma polymers with a low oxygen content.[37] For instance, this has been found for plasma-polymerized maleic anhydride using a CW microwave energy source.[38]

Pulsed plasma polymerization can lead to greater functional group retention,[39,40] as we have also found in the present study where anhydride group incorporation into the plasma polymer is governed by the duty cycle parameters, with greater chemical selectivity being attained at short on-periods and long off-times. Electron impact, ion bombardment, and VUV irradiation by the electrical discharge will result in the formation of free radical centers at the growing film surface and in the vapor phase.[41] These can subsequently act as

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(40) Rinsch, C. L.; Panchalingam, V.; Savage, C. R.; Wang, J. H.; Eberhart, R. E.; Timmons, R. B. *ACS Polym. Prepr.* **1995**, *36*, 95.

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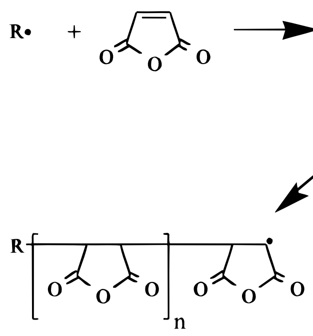
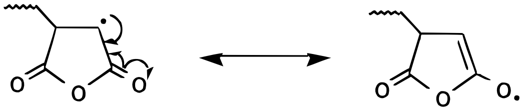
initiation centers for conventional chain growth polymerization during the duty cycle off-time:

On-time: Plasma polymerization →
R$^\bullet$ (incorporated into plasma polymer)

Off-time: radical initiated chain growth:



The maleic anhydride end-group on the growing polymer chain will be stabilized by a resonance effect:[15]



Effectively, the maleic anhydride monomer undergoes plasma initiated graft polymerization during the duty cycle off-period.[18] The lack of any alkene C−H stretching (3200−3100 cm^{-1}) bands[38] in the infrared spectrum of the pulsed plasma polymer materials is consistent with the free radical initiated unzipping of maleic anhydride double bonds during the duty-cycle off-time. On a theoretical basis, one would expect a 50% contribution from the −*C*(O)=O anhydride functionality to the C(1s) envelope if a conventional maleic anhydride polymer had been synthesized. Pulsed plasma polymerization is capable of generating 28% anhydride centres, which is a 167% improvement compared to continuous wave plasma polymerization of maleic anhydride at 5 W. A plot of anhydride concentration versus the average power $\langle P \rangle$, shows that a drop in average power (obtained by any combination of on-time, off-time, and peak power) enhances the anhydride group retention (Figure 6). Previous CW studies using an olefinic carboxylic acid precursor have also demonstrated that there is greater retention of the acid groups at lower powers, which can be attributed to less monomer fragmentation.[42] A drop in plasma sheath potential at lower powers reduces ion bombardment of the growing film,[43] accompanied by less VUV irradiation;[44] both of these effects will help to minimize the occurrence of excessive surface damage during the plasma on-time. Futhermore, any suppression of monomer fragmentation at lower input powers $\langle P \rangle$ will reduce surface etching by atomic oxygen byproducts.[45]

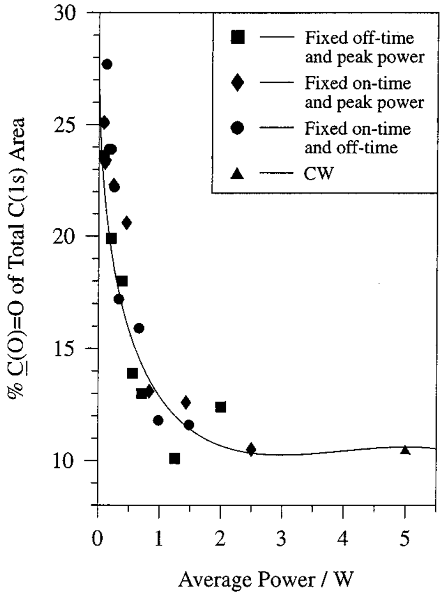


Figure 6. Variation in anhydride selectivity with average power (using different combinations of peak power, off-time, and on-time).

Conclusions

A comparison between continuous-wave and pulsed plasma polymerization of maleic anhydride has shown that there is greater retention of the anhydride functionality originating from the parent monomer during pulsing of the electrical discharge. This can be explained by the fact that lower average power values $\langle P \rangle$ result in less fragmentation of the precursor molecule and in reduced damage of the growing plasma polymer layer during the duty cycle on-time, combined with radical-initiated polymerization of maleic anhydride during the off-period.

Acknowledgment. A.M.H. would like to thank the European Community for financial support during the course of this work.

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