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Surface modification of polyethylene in an argon atmospheric pressure plasma jet

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Abstract

The surface properties of polyethylene can successfully be altered using argon plasmas. In this work, the surface modification of low density polyethylene (LDPE) using an argon atmospheric pressure plasma jet (APPJ) is profoundly investigated. The surface modification is examined using different analysing techniques namely, water contact angle (WCA) measurements for the wettability and X-ray photoelectron spectroscopy (XPS) for the chemical composition. Particular attention is paid to the treatment distance between the plasma jet capillary and the LDPE foil and the applied treatment time. At treatment distances between 5 and 15 mm, the WCA can be reduced with more than 70% within a treatment time of a few ms. XPS measurements reveal that this is due to the incorporation of oxygen containing groups and especially the increased implementation of the O-C=O group has a big influence. At treatment distances above 15 mm, the wettability decreases with increasing treatment distance. The wettability can however be enhanced by increasing the treatment time. Ageing considerations show that the loss in treatment efficiency is restricted to only 25%, meaning that even after 14 days of ageing the WCA reduction upon plasma treatment is still more than 40%. Based on the above mentioned results, the most appropriate parameters can thus be selected to provide an efficient plasma treatment of LDPE using the argon APPJ.

Keywords: Treatment distance; Treatment time; Atmospheric Pressure Plasma Jet; Low Density Polyethylene film; Ageing; Plasma treatment.

1 Introduction

Polyethylene (LDPE) is one of the most widespread polymers used for industrial and medical applications due to its excellent material properties (low density, high flexibility and high chemical resistance) [1]. However, despite these excellent characteristics, LDPE is often unsuitable for use due to its low surface free energy, leading to poor wettability and poor adhesion [2]. In the past, improvements in wettability and adhesion have been obtained using wet chemical processes; however, ecological requirements force the industry to search for alternative environmentally friendly methods. Recently, plasma treatment of polymers has been gaining popularity as a surface modification technique since it does not require the use of water and chemicals. Therefore, it can be considered as an environmentally benign technology. Moreover, it is a versatile technique that only affects the first few atomic layers at the surface without affecting the bulk properties [3, 4]. Plasmas can induce topographical modifications, [5] change the chemical composition [3] of a surface and can also be used for cleaning and deposition purposes. In the preceding works the method has already shown its effectiveness, using different types of non-thermal plasmas operating at low, medium or atmospheric pressure [6-10].

As in all research fields, also in the plasma technology research area, there is a constant evolution of the used techniques. Today, low pressure and atmospheric pressure plasmas have found widespread use for the pre-treatment of polymers in industrial applications. In particular, atmospheric pressure plasma jets (APPJ) have gained a lot of interest in the last few years, because they are easy to integrate into existing production lines and can selectively treat specific parts of a substrate. Also, in contrast to most corona treatments (and dielectric barrier discharges), APPJs are not limited to flat and thin substrates but can also be used for large three-dimensional structures.

Over the last few years, a whole range of papers has been published regarding the effective application of plasma jets for the modification of polymer materials [11-13]. However, a detailed study of the influence of different plasma treatment parameters on LDPE using the plasma jet working at atmospheric pressure in argon has not yet been presented. Therefore, in this work, the influence of plasma jet parameters such as plasma treatment time and treatment distance between the ground electrode and the foil on the surface modification of LDPE will be explored in detail. The effects will be studied for different applied powers at a fixed argon flow rate of 1.25 slm (standard litres per minute). At this flow rate, turbulence will be avoided in the argon flow and the provided afterglow of the plasma is maximal [14]. Finally, the ageing effect of the plasma treated LDPE films will be investigated in detail.

2 Materials and methods

2.1 Polyethylene

The used polyethylene foil is a low density polyethylene (LDPE) film with a thickness of 0.1 mm. This commercially available LDPE foil was purchased from Goodfellow Cambridge Ltd. and has not been subjected to any pre-treatment step prior to plasma modification.

2.2 Atmospheric Pressure Plasma Jet (APPJ)

An atmospheric pressure plasma discharge is generated inside a quartz capillary with an inside and outside diameter of 1.3 and 3.0 mm respectively. Figure 1 shows the used experimental set-up along with an image of the argon APPJ. The high-voltage electrode is a tungsten wire (diameter 1 mm) with a half-sphere-shaped tip and is placed inside the quartz capillary. The ring-shaped ground electrode (length = 10 mm) is placed around the capillary at a distance of 40 mm from the high-voltage electrode and 20 mm away from the edge of the capillary. High purity argon (Air Liquide – Alphagaz 1) is used for the plasma generation with a flow rate of 1.25 slm. At this flow rate, turbulence is avoided in the argon flow, as

turbulence occurs from 1.5 slm on, and the length of the afterglow is maximal [14]. LDPE samples are modified with the plasma jet by scanning the polymer surface with adjustable scanning velocities (0.08 – 4.5 m min⁻¹). The jet is generated by applying an AC voltage (fixed frequency = 60 kHz) to the high-voltage electrode with peak-to-peak values ranging from 7 kV to 14 kV. The voltage applied to the high-voltage electrode is measured using a high voltage probe (Tektronix P6015A), whereas the discharge current is monitored by measuring the voltage over a 50 Ω resistor, which is connected in series between the ring electrode and the ground. The voltage-current waveforms are then recorded using a Tektronix TDS 1002 digital oscilloscope. Using these voltage-current waveforms, the average power P of the discharge is calculated according to the following equation (T = period of the discharge) [15]:

$$P = \frac{1}{T} \int_t^{t+T} I(t)V(t)dt \quad (1)$$

During the LDPE surface modification experiments, the applied plasma power has been varied between 3 and 11 W. To enable an objective comparison between the plasma treatments conducted at different discharge powers, the results will be presented as a function of energy density (J cm⁻²). This value is calculated by multiplying the plasma exposure time with the plasma power and by dividing this value by the cross section of the capillary. The plasma treatment time t can be obtained by dividing the active diameter of the jet (= 1.3 mm) to the plasma scanning velocity.

2.3 Water Contact Angle measurements (WCA)

The wettability of the untreated and plasma treated LDPE films is evaluated using static water contact angle measurements. The static WCA values are obtained at room temperature using a Krüss Easy Drop system. Within minutes after plasma treatment, a 2 µl drop of distilled water is deposited on each sample. Droplets are placed at different positions and images are

captured a few seconds after deposition of each drop. Based on the imaged water drop profile, the static WCA value is obtained using Laplace-Young curve fitting. Every reported WCA value in this work is the average of 10 droplets placed at different positions on one single sample.

2.4 X-ray Photoelectron Spectroscopy (XPS)

Besides contact angle measurements, the chemical composition of the LDPE samples is obtained by XPS. XPS measurements are performed on a PHI Versaprobe II spectrometer employing a monochromatic Al K_{α} X-ray source ($h\nu = 1486.6$ eV). Survey scans and high resolution C1s peaks are recorded at a take-off angle of 45° relative to the sample surface. The XPS survey scans are processed using MultiPak software and from the peak area ratios, the elemental composition of the LDPE samples can be determined. The sensitivity factors to calculate the atomic percentage of C and O are 0.314 and 0.733 respectively. MultiPak is also used to curve-fit the high resolution C1s peak of the LDPE films: the hydrocarbon component of the C1s spectrum (285.0 eV) is used as calibration value for the energy scale. After this calibration step, the C1s peaks are deconvoluted using Gaussian-Lorentzian peak shapes making use of an iterated Shirley background and the full-width at half maximum (FWHM) of each peak is maintained below 1.5 eV.

3 Results and Discussion

3.1 Influence of the distance between the capillary and the foil

The surface modification of LDPE due to plasma treatment using the argon plasma jet is studied in detail at different distances between the capillary and the foil using WCA and XPS. The used plasma jet provides us with a long afterglow propagating in the open air. At a flow rate of 1.25 slm, the afterglow has found to be maximal and the visual length of the afterglow is 41.9 ± 1.0 mm relatively to the ground electrode [14]. Therefore, it could be expected that

the plasma effect drastically diminishes from a distance capillary – foil of 22 mm. The plasma exposure time in this experimental section is kept constant at 78 ms (scan velocity of 1 m min⁻¹). By using this scanning velocity, it is possible to provide consistent results for all plasma powers applied in this work. WCA measurements are carried out on LDPE samples treated at applied powers varying from 3.3 W to 11.1 W. It is also important to point out that plasma treatment should only affect the first few atomic layers without affecting the bulk properties. However, it was observed that from an applied power of 5 W and higher, in particular cases, especially at short distances, the foil melts down and the surface and bulk properties change extremely. It is therefore no longer possible to determine the WCA value under these circumstances. The temperature changes of the LDPE samples before and after plasma treatment at different capillary – foil distances and for different applied powers are measured using an IR thermometer in order to estimate the heating effect of the plasma on the LDPE film. The highest temperature change was 17°C at a 5 mm capillary – foil distance and an applied power of 11 W and the maximum temperature was 44°C. As a result, the observed deformation of the LDPE can be completely attributed to the reaction with the active particles in the plasma and not due to heating effects as the temperature remains much lower than the melting temperature of LDPE (120°C). For most cases, especially the ones used in the WCA and XPS study, the temperature change was less than 5 °C. As the temperature drops within a few minutes back to room temperature, this did not play any role in the treatment results.

WCA measurements on the LDPE film after plasma treatment are thus performed at different distances and different applied powers, giving the results presented in Figure 2. The first trend noticed from Figure 2 is that the applied power has only little influence on the obtained WCA values. Statistical analyses show no significant influence of the applied power on the WCA value within the 95% confidence interval. In contrast to the plasma power, the distance between the capillary and the foil has a large influence on the obtained WCA values. Figure 2 clearly shows that plasma treatment extremely enhances the wettability at short distances. The

effect is maximal at a distance between 5 and 15 mm: the WCA reduces from 103.8° for the untreated LDPE to 28.1° for the plasma treated LDPE, a reduction of 73%. The WCA value is also found to be constant within this treatment distance range. At higher distances, the WCA value gradually increases up to 95° at 45 mm. This value is still beneath the contact angle value of untreated LDPE ($103.8 \pm 0.8^\circ$) suggesting that there still is a small effect of the plasma jet on the LDPE surface even at this large distance. The increase in WCA is rather drastically, starting from a distance of 25 mm. As the visual length of the afterglow is 41.9 ± 1.0 mm [14] relatively from the ground electrode, this means that starting from 22 mm foil – capillary distance the afterglow does not visually reach the foil. This can explain the drastic increase of the WCA.

XPS measurements are performed on LDPE samples after plasma treatment at a power of 3.7 W at different distances. The power has only a small influence on the wettability as can be concluded from the WCA measurements and is therefore not varied. Based on XPS survey scans, the atomic composition of the LDPE samples can be determined and the O/C atomic ratio of the LDPE surface after plasma treatment at different distances is presented in Figure 3. The O/C atomic ratio of the untreated LDPE is 3%. This ratio should be 0% but due to contaminations it is somewhat enhanced. From Figure 3 can be seen that the O/C ratio decreases after plasma treatment with increasing distances. Comparing Figure 2 and Figure 3, a close relation can be found between the O/C atomic ratio and the WCA of the plasma modified LDPE surfaces. The Pearson product-moment correlation coefficient between the WCA and the O/C ratio is -0.97, indicating a strong relation between those 2 parameters. Therefore, the large reduction in WCA values by exposure at close distances can be attributed to the enhanced O/C ratio on the LDPE surface. The observed oxygen incorporation is due to the admixture of air in the plasma effluent. This leads to a higher yield of OH and O in the core of the discharge when the discharge is operating in ambient air [16]. Due to the recombination processes of OH and O with intrusions of nitrogen and oxygen molecules from

the surrounding air, only a low amount of these species will reach the LDPE surface at higher distances, resulting into less hydrophilic surfaces and lower O/C ratios. The WCA values and O/C ratios obtained in this work will be compared with values previously reported in literature in the next paragraph to examine the efficiency of the applied argon plasma jet. Plasma treatment of LDPE in an argon DBD was found to reduce the WCA from 101.8° to 51.9° (50% WCA reduction) and an O/C ratio of 13% was obtained at the surface [17]. In a DC low pressure glow air discharge the WCA was found to decrease from 89.5° to 50.7° (WCA reduction of 43%) and the O/C ratio was increased to 24% [18]. After an oxygen glow discharge treatment, the WCA diminished from 87.4° to 44° (WCA reduction of 50%) due to an increase in O/C ratio up to 18% [1]. Using an atmospheric argon plasma jet makes it possible to reduce the WCA with 61% from 94° to 37° and can result in an O/C ratio up to 33% [19]. This clearly shows that the used APPJ can introduce more O-groups on the LDPE surface which increases the O/C ratio and can more efficiently reduce the WCA especially at low distances between the foil and the capillary.

The C1s peak of the XPS spectra is also investigated in detail to evaluate which oxygen-containing functional groups are incorporated on the LDPE surface by plasma exposure. Figure 4 shows the curve fitting of the high resolution C1s peak of the LDPE foil before treatment and after treatment at a foil – capillary distance of 10, 20 and 30 mm. The C1s envelope of the LDPE samples can be decomposed into 4 distinct peaks: a peak at 285.0 ± 0.1 eV corresponding to C-C and C-H bonds, a peak at 286.5 ± 0.1 eV due to C-O functional groups, a peak at 287.7 ± 0.1 eV attributed to C=O and O-C-O groups and a peak at 289.1 ± 0.1 eV linked to O-C=O groups [20]. As shown in Figure 4, changes in the C1s peaks can be observed. After plasma treatment, the peaks at 286.5 eV, 287.7 eV and 289.1 eV drastically increase especially at low foil – capillary distances. The C1s peaks also change as a function of the different distances: with increasing distances, the peaks at 286.5 eV, 287.7 eV and 289.1 eV decrease. At a distance of 30 mm no difference can be observed between this C1s

peak and the C1s peak of the untreated LDPE. Based on the deconvoluted C1s peaks, the concentration of the different carbon bonds can be calculated and the obtained results are given in Figure 5. The untreated LDPE film contains 96.5% C-C/C-H groups and 3.5% C-O groups, but this value is not presented in Figure 5. From Figure 5, it can be seen that the C-C/C-H concentration increases with increasing distance while the concentration of all oxygen containing groups decreases. At distances up to 15 mm, the concentration of O-C=O groups is higher than the C=O/O-C-O group concentration. This ensures a higher surface energy and a lower WCA value at distances of 15 mm and lower. It has already been noticed in previous work that the strongest correlation can be found between the WCA and the concentration of the O-C=O groups [14]. Apparently, plasma jets are very efficient in producing long-living oxygen species [21, 22] that being carried by the gas flow can reach the surface and interact with it. This may be due to the chain scission mechanisms caused by the active species in the plasma, and the subsequent broken chain reactions with oxygen polar groups on the LDPE surface [23].

3.2 Influence of treatment time

Another parameter that influences the effect of the APPJ treatment is the exposure time. In this section, LDPE films are therefore exposed to an argon APPJ for varying treatment times. During these experiments, the argon flow rate is kept constant at 1.25 slm while the capillary-foil distance is maintained at 20 mm based on the results obtained in the previous section. The plasma treatment time can be altered by changing the scanning velocity: by altering the scanning velocity between 4.5 and 0.08 m min⁻¹ the treatment time can be varied between 0 and 1 s. However, since different discharge powers are used, the results will not be represented as a function of treatment time but as a function of energy density (J cm⁻²) to enable an objective comparison. Increasing the exposure time results in a higher temperature of the LDPE surface. However the temperature change was less than 12°C and the maximum

temperature remains less than 40°C, so this did not affect the other results. Figure 6 shows the WCA measurements after APPJ treatment under the above mentioned conditions as a function of energy density. The results presented in this figure state that LDPE plasma treatment increases the wettability of the LDPE film. The WCA decreases from 103.8° to less than 30°, a reduction of more than 70% upon plasma treatment. The WCA values gradually decrease with increasing energy density until saturation is reached and from that point on, the WCA does not significantly change anymore. The reached WCA is then considered as the plateau WCA value. Figure 6 also clearly shows that the applied power influences the WCA results. At a power of 11.1 W, the WCA decreases more slowly than at the other powers as a function of energy density during plasma treatment. This is due to the very short treatment time at energy densities of less than 50 J cm⁻² (less than 50 ms) so the treatment time is too short to incorporate high amounts of oxygen on the LDPE foil.

XPS measurements are also performed on plasma treated LDPE films at an applied power of 3.7 W in order to obtain the evolution of the chemical composition of the LDPE as a function of energy density. Based on the XPS survey scans, the atomic O/C ratio (%) is determined as a function of energy density and the results are presented in Figure 7. This figure clearly indicates that the O/C ratio increases with increasing energy density during plasma treatment. Comparison of Figure 6 and Figure 7 also shows the strong correlation between the measured WCA values and the O/C ratio: the higher LDPE hydrophilicity can be attributed to the incorporation of oxygen containing groups. Curve fitting of the high resolution C1s peak of some XPS spectra at certain energy densities are summarized in Figure 8. The C1s peak of the untreated film has already been depicted in Figure 4. From these figures can be seen that the peak at 285.0 eV decreases and the peaks at 286.5 eV, 287.7 eV and 289.1 eV increase after plasma treatment with increasing energy density. After deconvolution of the C1s peaks, the concentration of the different carbon bonds can be determined and the results are shown in Figure 9. From this figure, it can be concluded that with increasing energy density the

concentration of the C-C/C-H decreases while the concentration of all oxygen containing groups increases. At energy densities above 45 J cm^{-2} , the concentration of the O-C=O group still increases while the concentration of the other oxygen groups remains the same or decreases with increasing energy density, resulting in a higher surface energy and an enhanced wettability [14, 21-23].

3.3 Ageing

Different authors [24-26] have stated that the increase in surface hydrophilicity upon plasma treatment is only temporary: if a polymer surface which has become hydrophilic after plasma treatment is stored under suitable conditions, the surface can regain its original hydrophobicity. This process is referred to as hydrophobic recovery or ageing process. For our experiments, where the purpose is to enhance the wettability of the LDPE, ageing should be avoided as much as possible. Therefore, the ageing behaviour of the plasma treated LDPE films is investigated in this work. For this purpose, LDPE films are placed at 20 mm from the end of the capillary and then exposed at an energy density of 27.3 J cm^{-2} using an applied power of 3.7 W. This treatment condition is selected to provide us with an LDPE surface containing the maximum amount of oxygen groups (a so-called saturated LDPE surface) as can be seen from Figure 6. After plasma treatment, the LDPE samples are stored in ambient air at room temperature for a period of 14 days.

Figure 10 shows the evolution of the WCA as a function of storage time. The WCA of the untreated LDPE is $103.8 \pm 0.8^\circ$ but this value is not included in the figure. As can be seen in Figure 10, the ageing process of the LDPE film is characterized by a quick increase in WCA during the first storage hours. At longer storage times, the WCA increases more slowly and finally reaches a plateau value after 4 days of storage in air. The WCA increases from $43.2 \pm 2.7^\circ$ immediately after treatment to a plateau value of $58.4 \pm 1.0^\circ$. The loss in treatment efficiency L (%) during storage can be calculated using the following equation:

$$L = 100 \frac{\theta_{s1} - \theta_{s2}}{\theta_{s1} - \theta_{untreated}} \quad (2)$$

where θ_{s1} is the saturation value of the WCA after plasma treatment, θ_{s2} is the plateau value of the WCA after storage in air and $\theta_{untreated}$ is the WCA value of the untreated material. Based on this equation, the loss in treatment efficiency during storage is $25 \pm 4\%$. It is also worthwhile to mention that the maximal WCA value is still much lower than the WCA of the untreated LDPE surface, which means that the major part of the surface wettability is kept after plasma treatment. Ageing after an argon DBD plasma treatment results in a loss in treatment efficiency of $50.0 \pm 3.4 \%$ after 2 days of ageing [27] while after an oxygen plasma treatment in a parallel plate reactor the loss in treatment efficiency is even 81% after 2 days of ageing [28]. This means that the ageing of the APPJ treated samples is quite slow since the loss in treatment efficiency is much lower compared to other ageing behaviours previously described in literature.

4 Conclusion

The wettability of LDPE foils can successfully be enhanced using an argon APPJ. Different parameters are considered and special attention is paid to the treatment distance and time. At treatment distances capillary – foil between 5 and 15 mm, the wettability of LDPE drastically increases as the WCA reduces with 73% . This is due to the increased O/C ratio at the LDPE surface. At treatment capillary – foil distances of more than 15 mm, the plasma effect however starts to decrease. The WCA increases and the O/C ratio at the surface decreases. The visual length of the plasma afterglow is 22 mm from the capillary, explaining the drastically reduced wettability from a treatment distance of 25 mm on. A treatment time of less than 100 ms is sufficient to reduce the WCA with more than 70% and to reach a plateau WCA value of less than 30° . The reduced WCA is due to the increased O/C ratio at the LDPE surface. At higher treatment times, especially the concentration of the O-C=O group increases, leaving us with a higher surface energy and an enhanced wettability.

Ageing studies show that after plasma treatment the WCA quickly increases during the first hours of storage. After 4 days of ageing, the WCA reaches a plateau value leading to a loss in treatment efficiency of only 25%. This means that even after a long storage period, the reduction in WCA due to plasma treatment is still more than 44%. All these results provide thus a map for different treatment parameters in applied power, treatment distance and treatment time in order to select the optimal settings for an efficient plasma treatment of LDPE using an argon APPJ.

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Figure 1: Experimental set-up (a) and visual view (b) of the plasma jet.

Figure 2: Influence of the distance on the WCA measurements on LDPE after plasma exposure during 78 ms for different applied powers.

Figure 3: O/C ratio of LDPE as a function of distance after plasma exposure at an applied power of 3.7 W and treatment time of 78 ms.

Figure 4: C1s peaks of untreated LDPE film (a), LDPE film APPJ plasma treated at an applied power of 3.7 W and treatment time of 78 ms at a distance of 10 mm (b), 20 mm (c) and 30 mm (d).

Figure 5: The concentration of C-C/C-H (\blacklozenge), C-O (\blacksquare), C=O/O-C-O (\blacktriangle) and O-C=O (\bullet) bonds as a function of distance for LDPE film APPJ plasma treated at an applied power of 3.7 W and a treatment time of 78 ms.

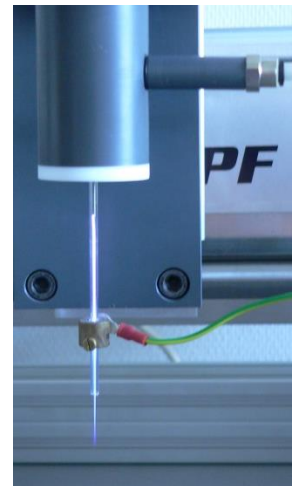
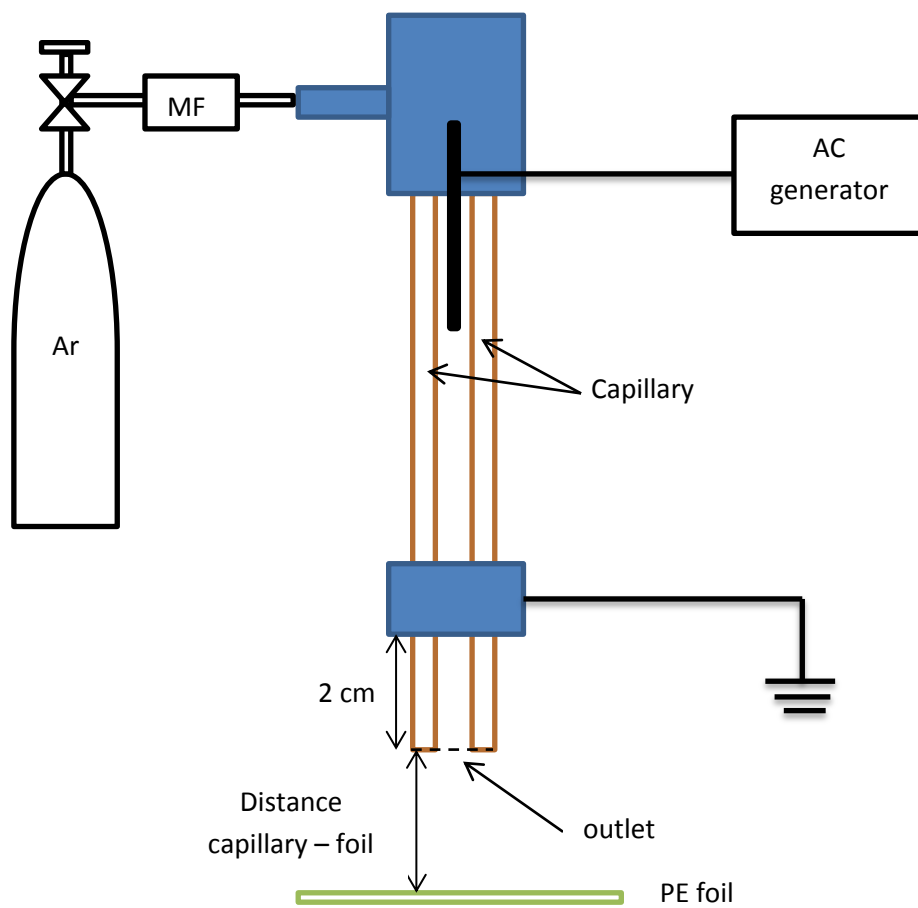
Figure 6: Contact angle of the LDPE film as a function of energy density for an APPJ exposure at a capillary – foil distance of 20 mm.

Figure 7: O/C ratio of LDPE as a function of energy density for an APPJ exposure at an applied power of 3.7 W and a capillary – foil distance of 20 mm.

Figure 8: C1s peaks of LDPE film APPJ plasma treated at a distance of 20 mm for an applied power of 3.7 W at an energy density of 7.3 J cm^{-2} (a), 21.8 J cm^{-2} (b) and 43.6 J cm^{-2} (c).

Figure 9: The concentration of C-C/C-H (\blacklozenge), C-O (\blacksquare), C=O/O-C-O (\blacktriangle) and O-C=O (\bullet) bonds as a function of energy density for LDPE film APPJ plasma treated at a capillary – foil distance of 20 mm with an applied power of 3.7 W.

Figure 10: Evolution of WCA of the plasma-treated LDPE films as a function of storage time.



(a)

(b)

Figure 1

Black and white version (in print)

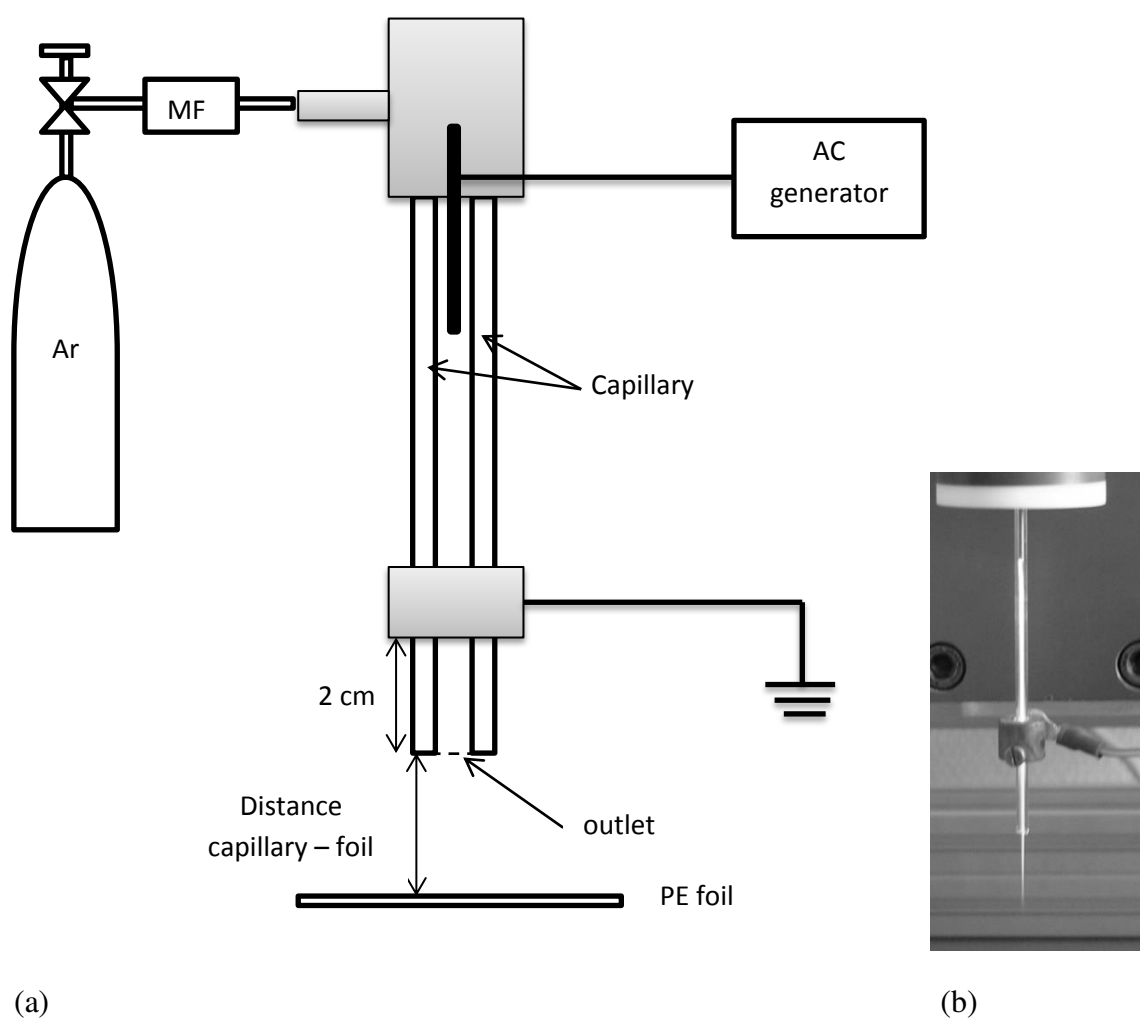


Figure 1

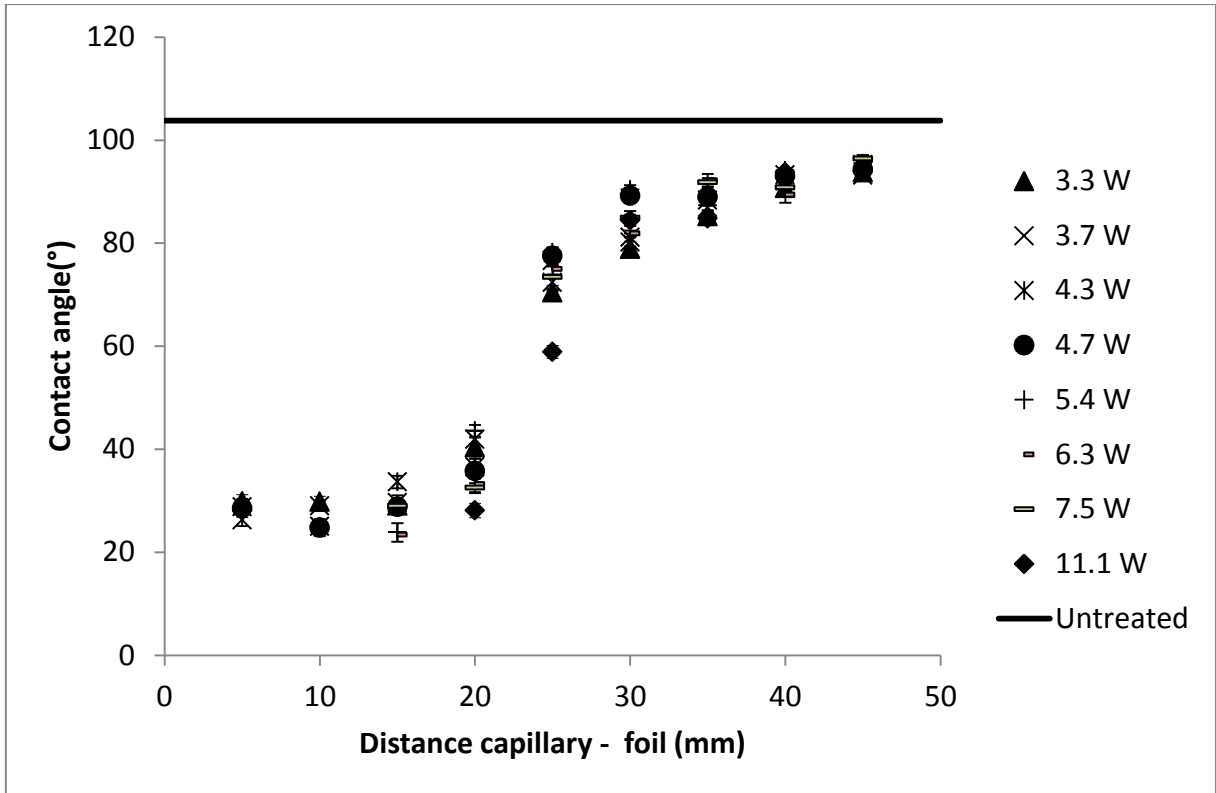


Figure 2

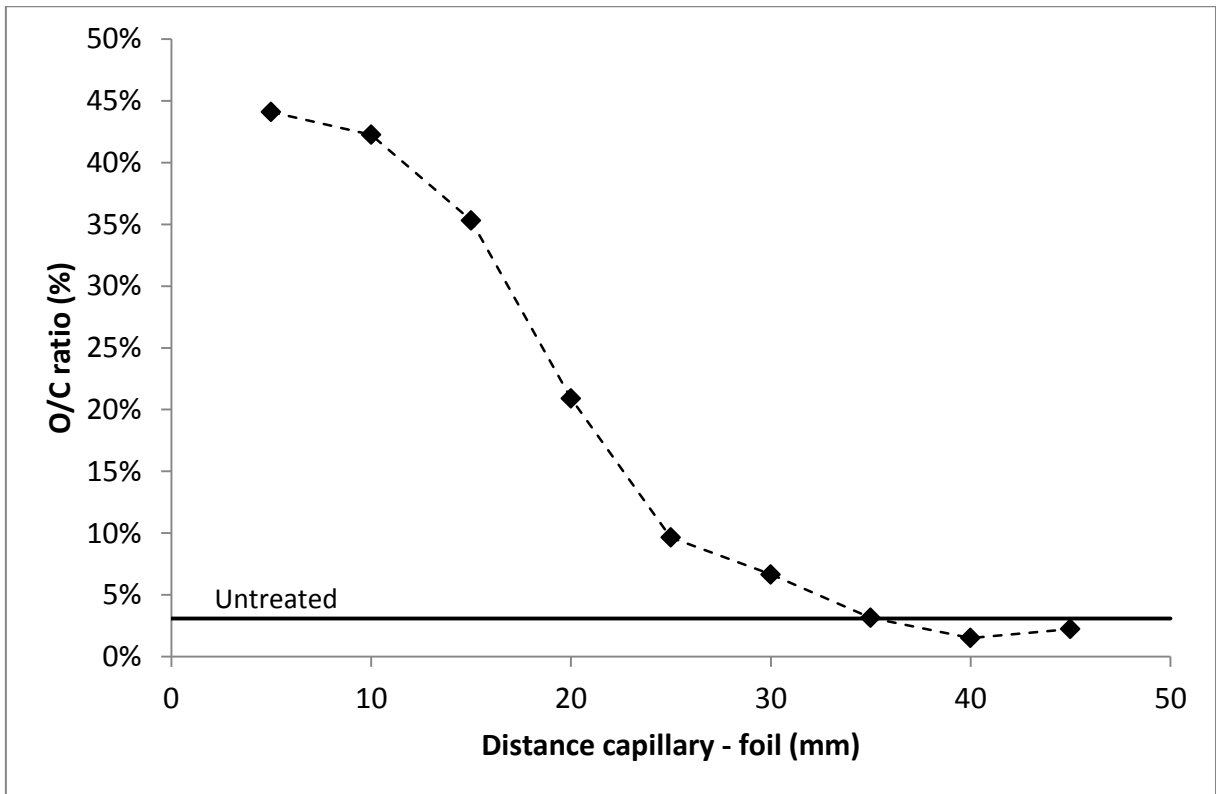


Figure 3

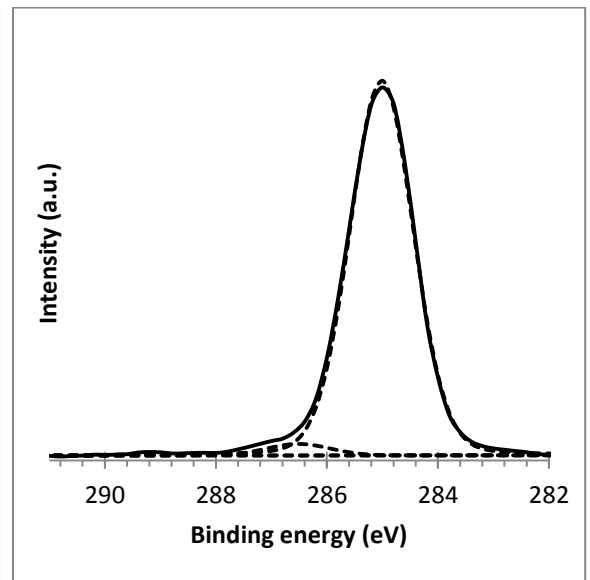
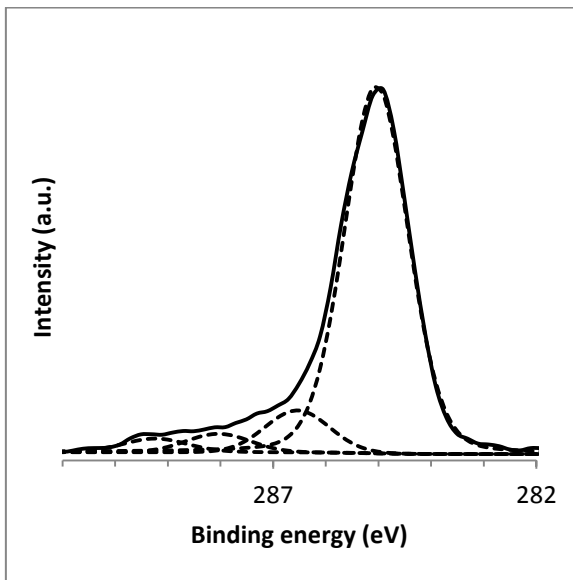
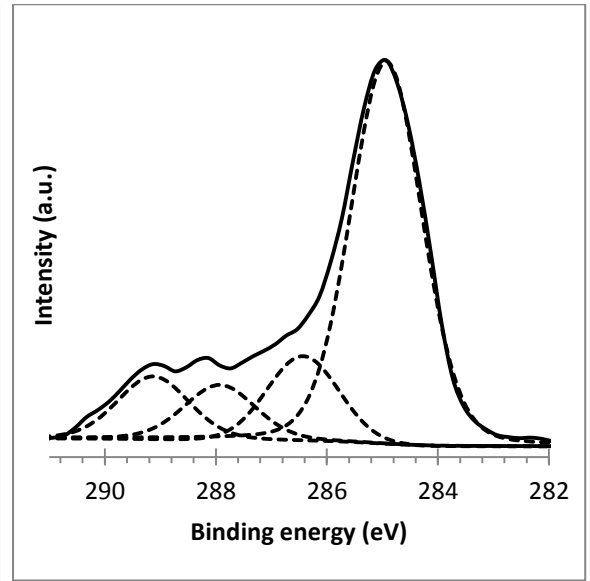
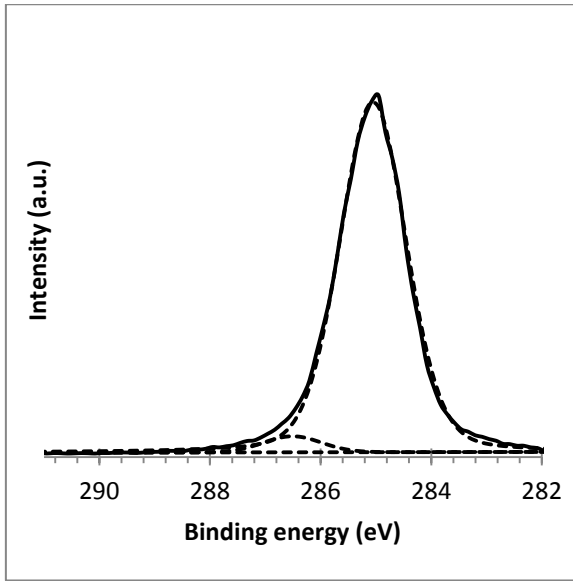


Figure 4

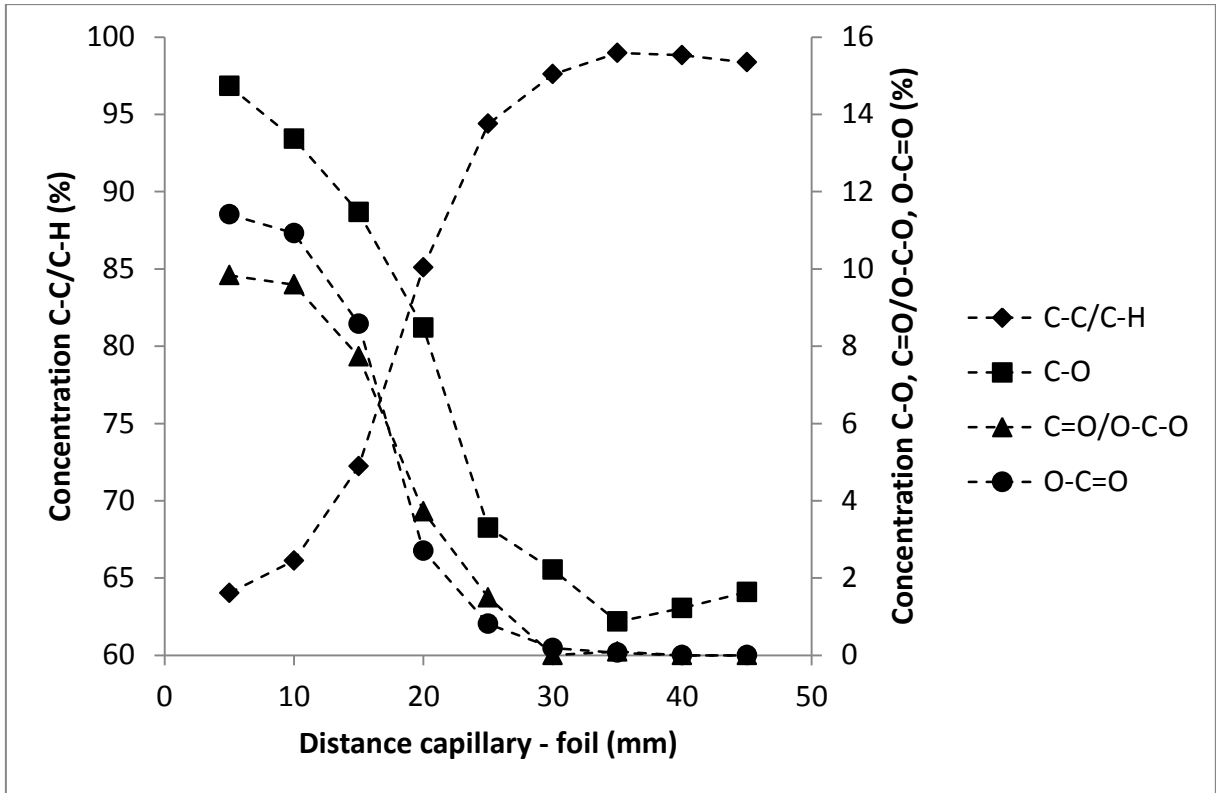


Figure 5

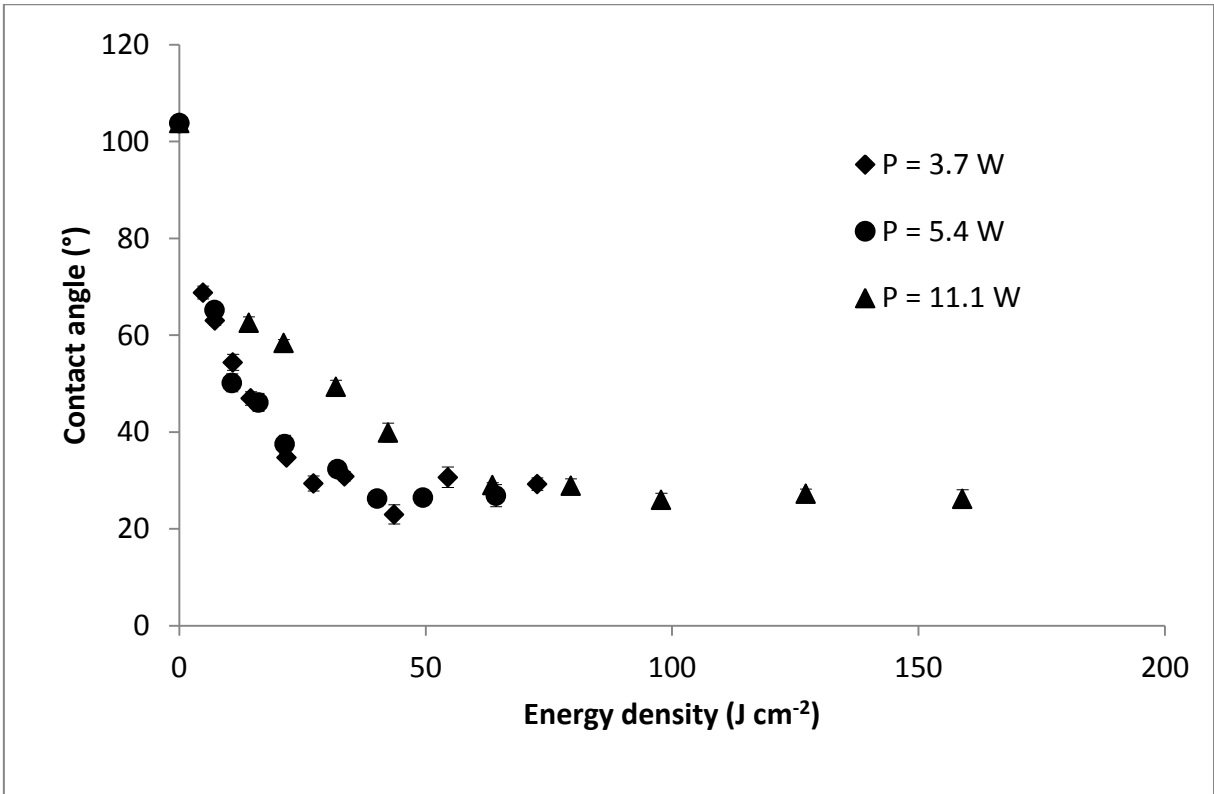


Figure 6

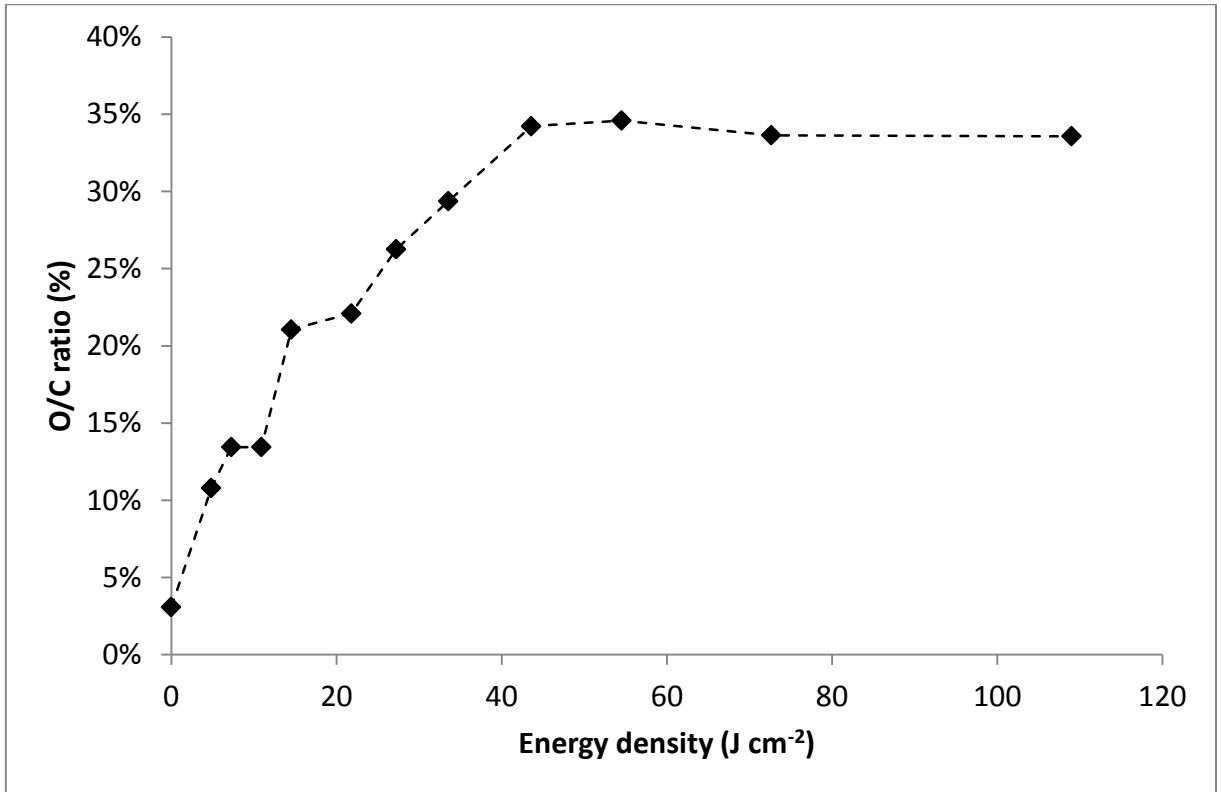
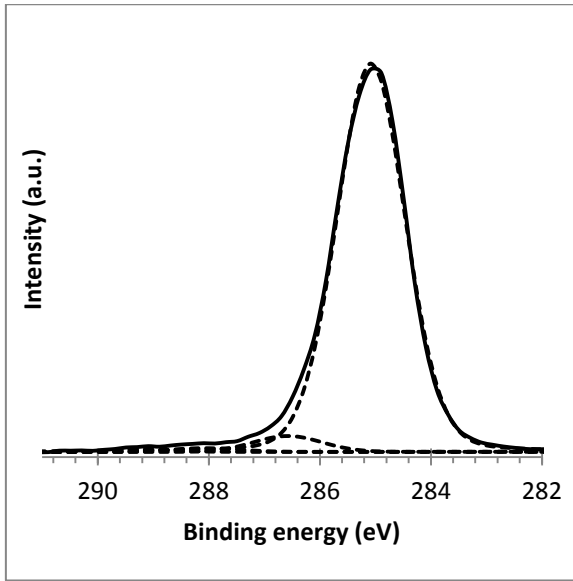
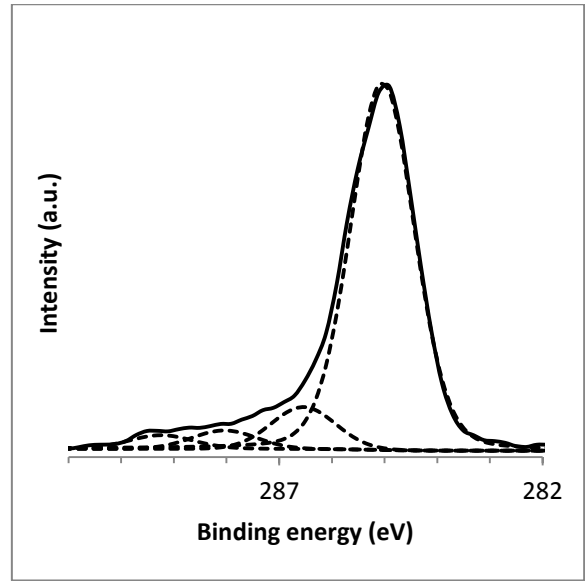


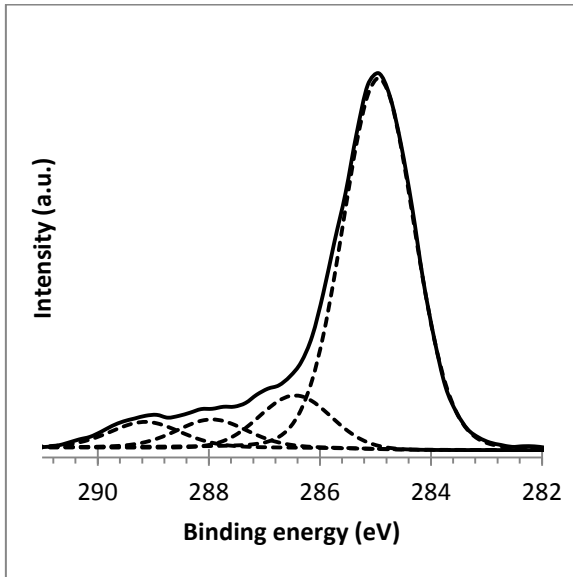
Figure 7



(a)



(b)



(c)

Figure 8

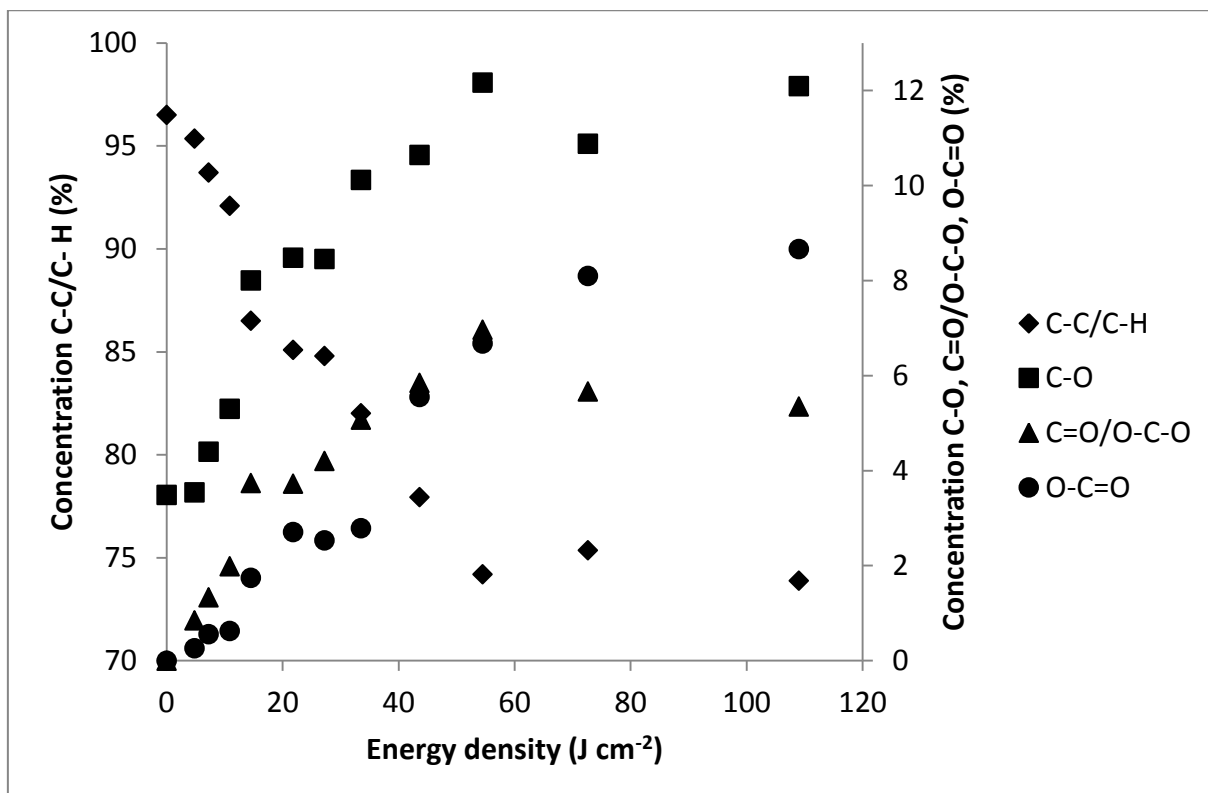


Figure 9

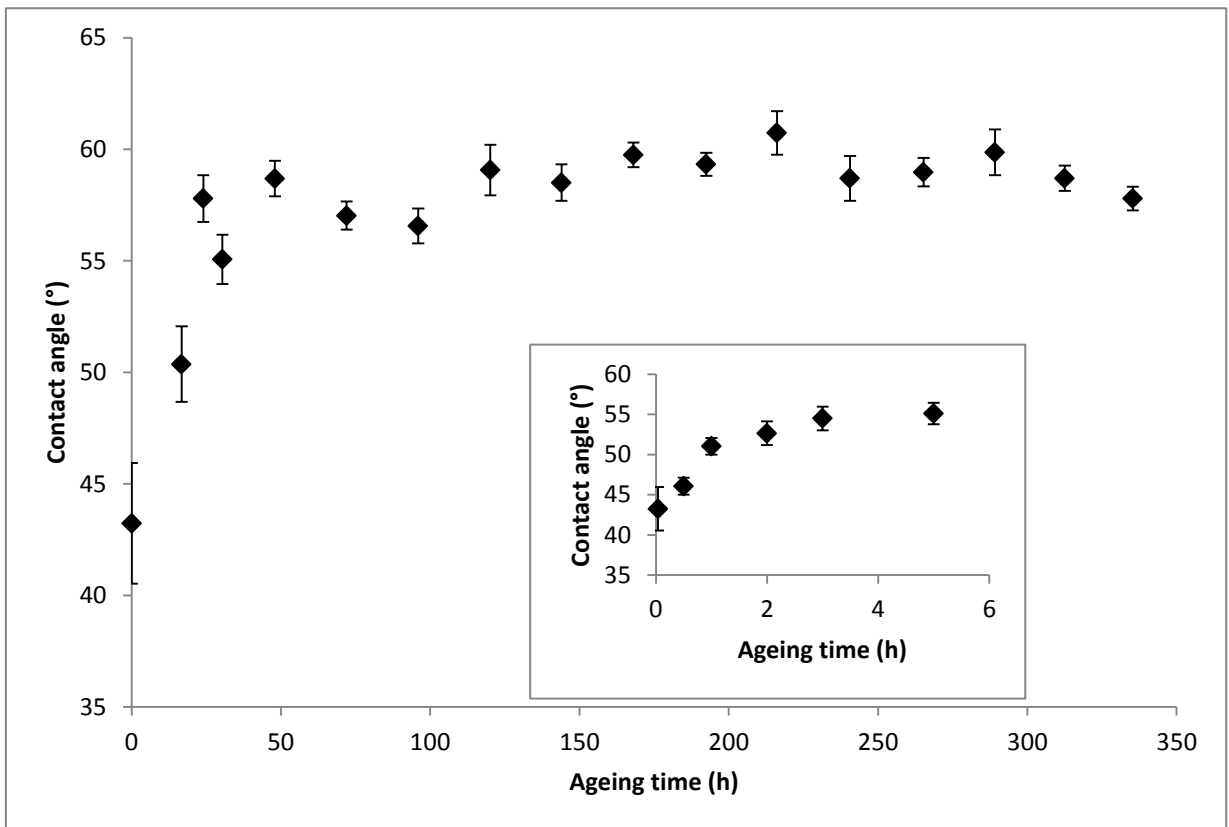


Figure 10