

CHAPTER VIII

SURFACE MODIFICATION OF POLYETHYLENE USING ATMOSPHERIC AIR DIELECTRIC BARRIER DISCHARGE

8.1 Abstract

Plasma technique is widely used in the film industry nowadays since it is capable to modify the polarity of topmost layers without affecting the desirable bulk properties of the treated materials. This is reasonably suitable for treating the inert surface of commodity plastics such as polyethylene. The dielectric barrier discharge (DBD) device developed in our laboratory was utilized at atmospheric pressure, thus; the modification procedure was easy in practice. The important plasma process parameters including applied voltage, treatment time, and aging time were investigated. In the range studied, the maximum of generated surface radicals was given by the treatment condition of 30 s and 8.3 kV applied voltage with 10 s of aging time in ambient air. The DBD treatment induced the surfaces with varying roughness and surface feature as observed by SPM and SEM. Since the treatment was operated at ambient pressure by using air as a processing gas, plasma surface treatment of polyethylene primarily resulted in the oxidation of the surface by generation of both nitrogenated and mainly oxygenated functional groups. The O/C ratio was increased significantly for the plasma treated surface. Both physical and chemical changes resulted from plasma treatment led to sharply drop of polyethylene surface contact angle indicating that the interaction of gaseous plasma and solid polyethylene surface altered the surface to be more hydrophilic. Therefore, this DBD can be effective tool in surface modification, especially to enhance the surface hydrophilicity of the hydrophobic polymer.

Keywords: Atmospheric pressure plasma, Dielectric barrier discharge, Surface modification, Polyethylene

8.2 Introduction

In account of the low-cost, relevant mechanical properties, and temperature service range, the inert characteristic of polyethylene (PE) has been often chosen for packaging purpose. However, due to the hydrophobic surface property, it is difficult to adhere PE with other polar materials. Thus, the surface modification is usually involved prior to adhering with other layer materials, coating and printing for finishing purpose (Borcia *et al.*, 2004). There are a few method widely used to modify the surface of PE i.e. chemical etching or chemical modification, flame treatment, and corona discharge treatment.

According to the commercial standpoint, corona discharge technique is the most attractive method nowadays. It is the one of plasma surface modification technique. The principle and the utilization of plasma phenomena have been recognized for, at least, a decade and have been published elsewhere (Fridman *et al.*, 2004). The energetic states of plasma particles cause them to be highly reactive with the surfaces that they contacted. For polymer surface treatment, their energy can crack the organic molecules; consequently create the radicals on the surface. Several subsequent phenomena occur on the plasma-treated surface such as crosslinking, grafting, and functionalization which also affect to the topology. Therefore, plasma surface modification can be utilized as a physico-chemical route to alter only the top-most layer without modification to the bulk property (Chan *et al.*, 1994). It is also an environmental friendly process as no chemicals to be used in the system and no residual solvent on the surface.

Generally, there are two categories of plasma processing which are low-pressure and high- or atmospheric pressure plasma as defined by the condition of gaseous plasma generation. In this work, the atmospheric pressure plasma processing has been selected and the plasma device developed in our laboratory was the dielectric barrier discharge (DBD). It was defined by a pair of parallel plane electrodes of homogeneous geometry with either one or both electrodes are covered by dielectric layer. The DBD always generates non-uniformly random micro-arcs as called silent discharge and, depending on the operating conditions, it can have fairly diffuse appearance. Each micro-discharge is like a miniature reactor.

Regarding to plasma phenomena, the process parameters are highly system-dependent and that developed for one system usually cannot be adopted for others. Therefore it was of interest to investigate the parameters affecting the surface of PE treated with air-plasma using self-designed DBD device. All runs were carried out at atmospheric pressure in order to maintain air-to-air process for further utilization with the continuous plastic production.

8.3 Experimental

8.3.1 Materials

Linear low-density polyethylene (LLDPE), DOWLEX 2047G, was supported by DOW Chemical Company (Thailand). Its melt flow index (MFI) and density as provided by supplier were 2.3 g/10 min and 0.917 g/cm³, respectively. Melting temperature is 125°C. LLDPE film was prepared by pressing at 170°C using Wabash[®] compression machine with 20 ton force. The heating period was 5 min and compression time was another 10 min. The thickness of final film was in the range of 30-50 µm. Sample size for each test was 5 mm x 5 mm.

The *1,1*-Diphenyl-2-picrylhydrazyl (DPPH) used as a radical scavenger for radical measurement was from Fluka. Benzene used as a medium for colorimetric chemical titration was analytical grade supplied by Merck KGaA.

8.3.2 Plasma Surface Modification

The most popular means of plasma generation is through electrical discharges, thus the in-house built DBD was initiated and sustained by high electrical alternating current voltage with frequency of 500 Hz, shown in Figure 3.2. In principle, most of the electrical energy goes into the production of energetic electrons and excitation of processing gases rather than into gas heating. As a result, this plasma is non-thermal and thus provides the mild condition for PE treatment without massive heat damage.

A pair of electrodes was made of stainless steel and both covered by the dielectric material. The electrode dimension was 7 mm x 100 mm and its geometry is illustrated in Figure 7.6. The ionized gas occurred in 7 mm space

between two electrodes, named discharge space or gap distance. Surface modification of LLDPE film was taken place at the middle inside the plasma treatment compartment.

At least three external plasma treatment parameters affected the treated products. They were applied voltage, plasma treatment time, and the interval time prior to the following step (called aging time). According to the limitation of power supply, the applied voltage was varied from minimum that the glow-like discharge can be observed to the maximum voltage before the discharge was unstable. The plasma treatment time was varied as 0.2, 5, 10, 15, 30, and 60 s. The aging time was also varied up to 10 min which was assigned as a steady surface in this work. All runs were done at atmospheric pressure using ambient air as a process gas and the exposure gas during aging period.

8.3.3 Surface Analysis

8.3.3.1 *Total Generated Radical Concentration Measurement*

The conventional method to determine the radicals, intermediate species, left on/near the plasma treated polymer surface was liquid-phase radical trapping method. The evidence of colorimetric chemical titration with 1.0×10^{-4} mol/l benzene solution of DPPH had been employed (Suzuki *et al.*, 1986). After the DBD treatment and aging period, the treated film were then kept in above solution at 70°C for 24 h to decompose the radical formed on/near the treated surface. The amount of DPPH consumed was measured by the difference of UV-visible light absorbance at 521 nm of both pristine and plasma treated film using Shimadzu UV-2550 spectroscopy.

8.3.3.2 *X-Ray Photoemission Spectroscopy (XPS)*

In order to identify the surface elemental composition which affected by atmospheric DBD treatment, the XPS was performed in comparison with untreated LLDPE film. Synchrotron radiation at the National Synchrotron Research Center (NSRC) was utilized as X-ray source. The XPS station was kindly operated below 1.0×10^{-7} mbar. Most of the XP-spectra were recorded using a monochromatic MgK α source. The spot size on the sample was approximately 350 μ m FWHM. The relative atomic concentrations were calculated by VGscientific software.

8.3.3.3 *Fourier Transform-Infrared Spectroscopy (FT-IR)*

Infrared absorption analysis was performed using FT-IR spectroscopy, Nicolet NEXUS 670. Since the DBD treatment of LLDPE film would occur on both surface sides, both transmission mode and Attenuated Total Reflectance (ATR) mode of FT-IR were carried out. To obtain the absorbance spectrum, it was normalized to the peak of C-H stretching at 2916 cm^{-1} .

8.3.3.4 *Contact Angle Measurement*

Static contact angle measurement using Krüss, model DSA-10, was performed to prove the occurrence of polar sites on the air-plasma treated surface. The treated film was then kept in the ambient environment for 15 min. When reached the assigned interval time, the surface contact angle was then measured with $10\text{ }\mu\text{L}$ sessile droplet of deionized water by a micro-syringe.

8.3.3.5 *Scanning Electron Microscopy (SEM)*

SEM, Jeol 5200, was used to investigate the surface morphology of untreated and plasma treated LLDPE films. The sample was then sputter-coated by gold at an argon pressure of 0.1 Torr for 4 min at a current of 10 mA. The micrograph was then captured at the magnification of 10,000.

8.3.3.6 *Scanning Probe Microscopy (SPM) or Atomic Force Microscopy (AFM)*

The topology change was also investigated by AFM using a Scanning Probe Micrometer, Digital Instruments, incorporated with a Nanoscope IV software. Data acquisition was taken in tapping mode. The three-dimensional images were manipulated with the mentioned software. The scan size was $5\text{ }\mu\text{m}$ with scanning rate of 1.489 Hz. The data scale was 200 nm.

8.4 Results and discussion

8.4.1 Effect of External Plasma Process Parameters on Total Radical Concentration Generated on the Treated LLDPE Surface.

Exposure of LLDPE solid to ionized gas can, in principle, create the surface with radicals. Dependence of surface radicals induced via air-DBD treatment on external plasma processing parameters were investigated at 8.3 kV applied to the electrodes. Figure 8.1 showed the plot of generated radicals on the treated surface as a function of plasma treatment time. The dependence of that was not steady but showed the peak at 30 s of treatment with 10 s aged in the ambient air.

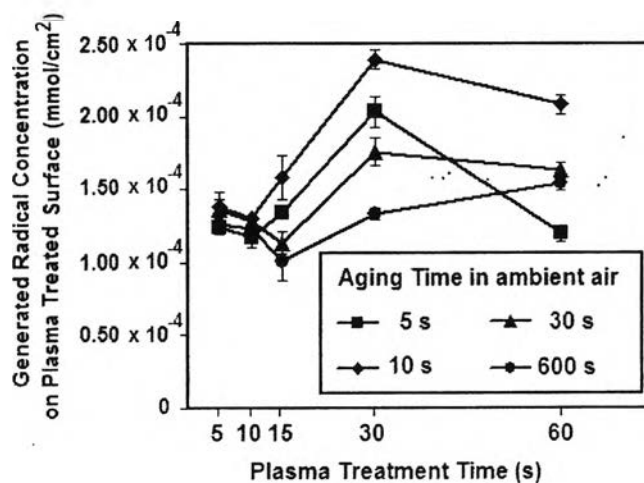


Figure 8.1 Effect of plasma treatment time of 8.3 kV applied voltage on surface radicals with various aging times in ambient air.

Figure 8.2 shows the plot of generated radicals as a function of plasma treatment time, measured at 5 s of aging time. Using the self-designed DBD device, total radical concentration generated on the plasma treated LLDPE surface increased with the applied voltage and likely decreased with long treatment time. More severe of plasma conditions at the greater applied voltage led to lower amount of net generated radicals as a result of the greater chance for disappearance reactions as well as other terminating reactions e.g. degradation, functionalization and slight surface cross-linking.

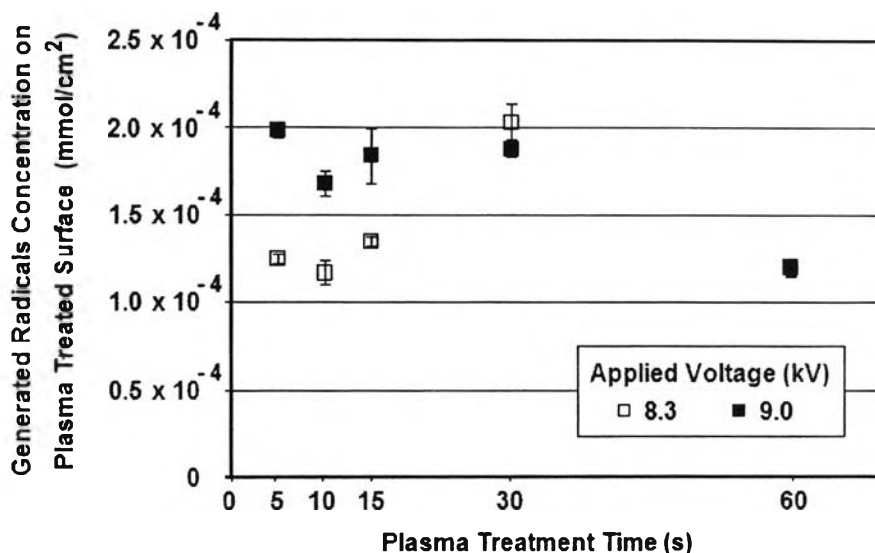


Figure 8.2 Dependence of generated radical on plasma treatment time with 8.3 and 9.0 kV applied voltage at 5 s of aging time in ambient air.

Amount of radicals would appear as a result of co-occurrence of two competing reactions during plasma treatment that were radical formation due to the air-plasma bombardment and radical disappearance which could be the reactions mentioned above (Chan *et al.*, 1994).

8.4.2 XPS Analysis

The XPS-spectra of pristine LLDPE and 8.3 kV air-DBD treated LLDPE are shown in Figure 8.3. High resolution C1s, O1s, and N1s scans provided more precise information about the main elemental compositions expected to be found on the air-plasma treated surface. The XPS-spectrum of pristine LLDPE showed two C1s peaks and a peak of O1s. However; for the plasma treated LLDPE surface, there were several C1s peaks with O1s peak(s) and N1s peak(s). The deconvolution of the core level C1s and O1s peaks is shown in Figure 8.4. Two C1s components at binding energy 285.5 corresponding to C-H, aliphatic C-C and C=C and 288.5 eV corresponding to C-O / C=O were found in the virgin LLDPE. A peak of O1s at 533.5 eV was noticeable on the untreated LLDPE implying to the presence of oxygenated compositions which was generally observed for most PE (Borcia *et al.*, 2003). After plasma treatment, an additional C1s peak at 290 eV and two

additional O1s peaks were observed which were attributed to the generation of C and O bonding such as C-O / C=O / -COO. The bonding of nitrogen and oxygen has to be in account since the several N1s peaks were also found in the air-plasma treated LLDPE. The intensity of 285.5 eV C1s peak changes insignificantly which, however, implies that aliphatic C=C could occur on the treated surface. The C1s was shifted to higher binding energy implying to bonding with nitrogen species as well. However, theoretical predictions can be used as a guide only and are not sufficiently accurate to give unambiguous interpretation of peak shifts caused by different bonding states (Compbell *et al.*, 2000).

In order to extract quantitative information from this observation, the curve fitting software supplied with the instrument was used to calculate the relative contribution of C1s and O1s components and reported as O/C ratio. The spectral peaks from a mixture were approximately the sum of the individual elemental peaks. Oxygenated composition for the plasma treated surface was increased significantly from the 10.88% O/C ratio of the pristine LLDPE, shown in Figure 8.5.

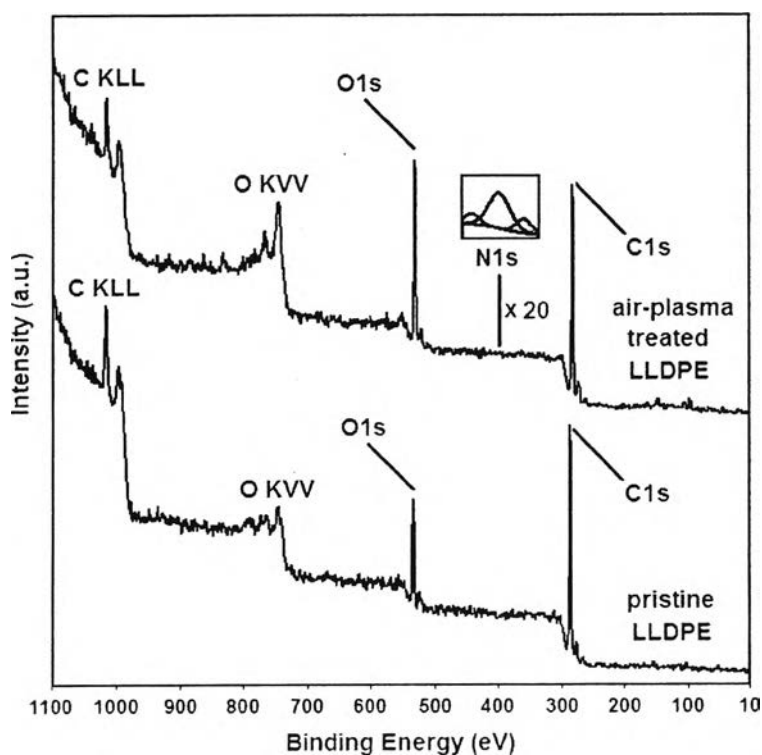
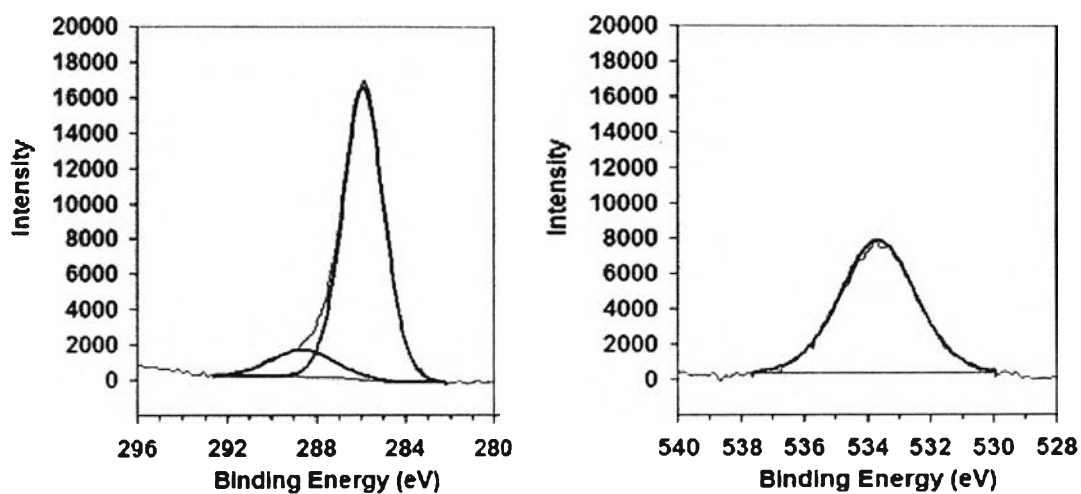


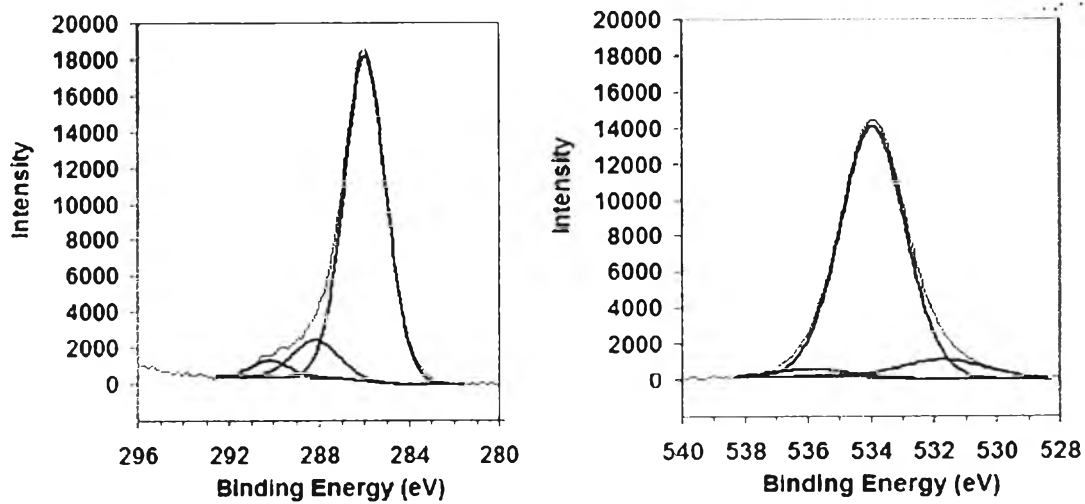
Figure 8.3 XP-spectra of virgin LLDPE and LLDPE treated with 8.3 kV for 15 s.



C1s

O1s

(a) Pristine LLDPE.



C1s

O1s

(b) LLDPE treated with 8.3 kV for 15 s.

Figure 8.4 Deconvolution of XPS core level C1s and O1s spectra.

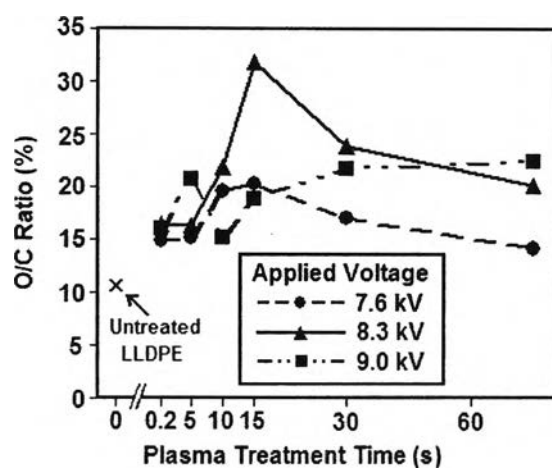


Figure 8.5 O/C ratio of plasma treated LLDPE surface with various voltages applied to DBD.

Oxygen increased even very short treatment time, 0.2 s, until peaked at 31.92 % O/C ratio with 15 s of plasma treatment time before drop down. Compared with radical concentration measurement, the similar trend was found even if the exactly treatment time that provided the maximum generated surface radicals and that of O/C ratio were not the same. However, the results of O/C ratio could, relatively, support the surface radical generation results. The conclusion that total of oxygen incorporated in polymer surface depended on the amount of generated surface radicals seemed to be allowed. At 15 s treatment time of 8.3 kV applied voltage performed the highest O/C ratio while, at this condition, the generated radicals on treated surface was the lowest at longest aging time. This may imply that the reactive radical sites initiated by this plasma treatment condition had been incorporated with surrounding molecules to be the oxygenated functional groups. Moreover, the presence of nitrogenated species on the treated surface confirmed that the surface free radical sites induced by DBD treatment could react with atmospheric nitrogen in ambient air.

8.4.3 FT-IR Analysis

Because of the unpaired electrons left on the DBD treated surface, they are very active which can undergo various further reactions. One of those is coupling

with surrounding species, therefore the processing gas and/or the environmental matter is another factor to be concerned. In this work, the nitrogen and oxygen based functional groups could be formed as a result of air-plasma (Rajesh *et al.*, 2003). In fact, the ATR-FTIR was suitable to analyze the surface of material, it was not shown here and the transmission mode was presented as related to both surface side of plasma treatment. However, in our case, the IR spectra given from both was not different significantly. FTIR spectra of the pristine LLDPE and plasma treated LLDPE films were shown in Figures 8.6 – 8.8. With 7.6 kV, the significant difference with the untreated LLDPE was not observed but the spectra of very short treatment time (0.2 s) of 8.3 kV and 9.0 kV showed additional peaks at 1300 cm^{-1} and 1370 cm^{-1} corresponding to symmetric stretching of nitro compounds $-\text{N}-\text{OO}$. A lot of small peaks at $1600 - 1950\text{ cm}^{-1}$ were found as the characteristic peaks of carbonyl group. Moreover, the peaks belonging to N-H stretching in amines and amides were presented at $3350-3500\text{ cm}^{-1}$. The corresponding peaks of O-H stretching were obviously seen at $3550-3800\text{ cm}^{-1}$ as well.

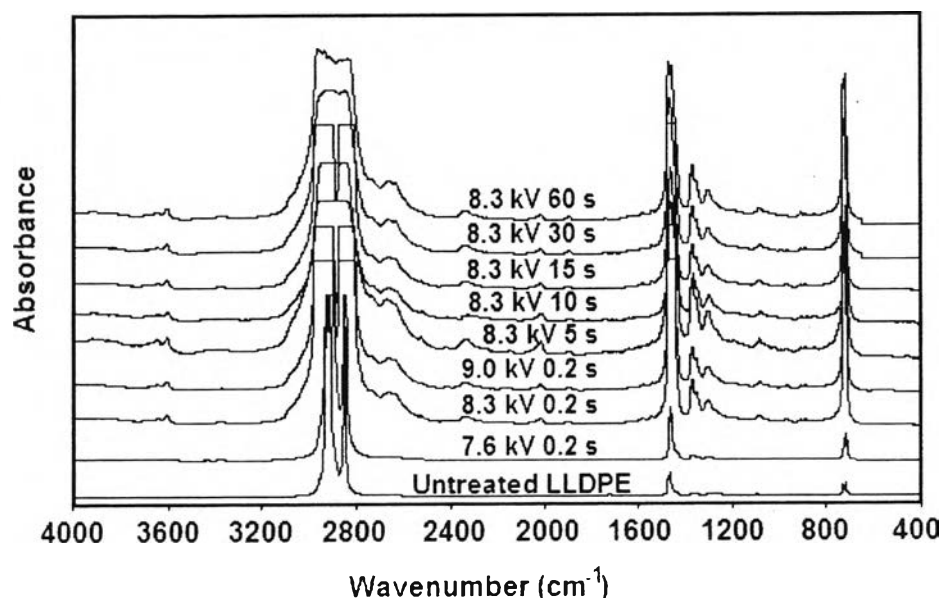


Figure 8.6 Infrared absorbance spectra (transmission mode) of pristine LLDPE, and 8.3 kV plasma treated LLDPE with various treatment time.

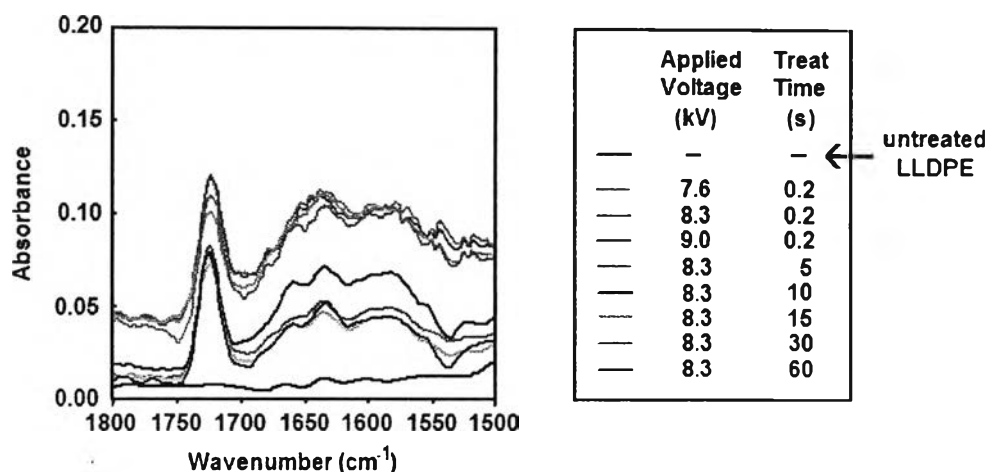


Figure 8.7 HATR-FTIR spectra of virgin LLDPE and plasma treated LLDPE surface: the observation range of 1500 – 1800 cm^{-1} .

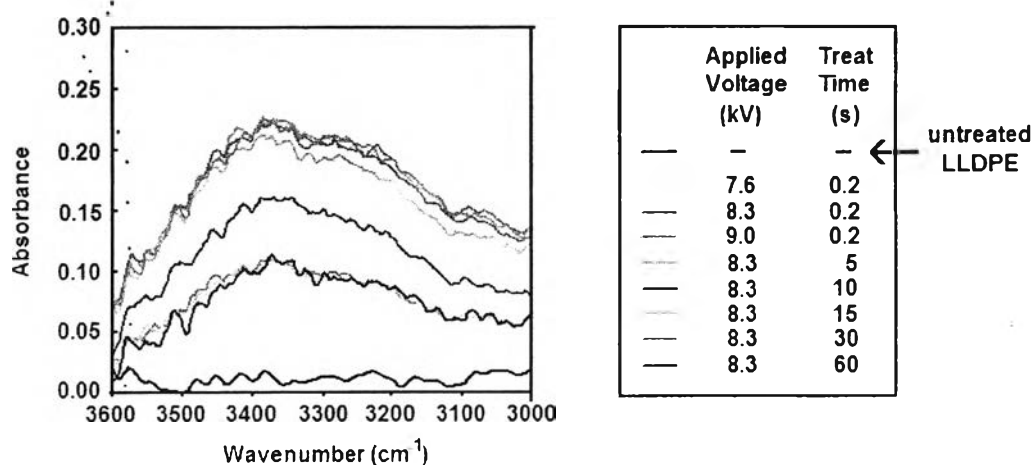


Figure 8.8 HATR-FTIR spectra of virgin LLDPE and plasma treated LLDPE surface: the observation range of 3000 – 3600 cm^{-1} .

Since the nature of oxygen was more reactive than that of nitrogen, oxygen strongly affected the plasma treatment of polymers as also supported by XPS analysis. The decomposition of the surface peroxides promoted polar group formation such as carbonyl, carboxyl, and hydroxyl groups. The modification of chemical component which probably generated during air-plasma treatment and after treatment period as the coupling of environmental species at the reactive radical sites would influence on the hydrophilicity of the plasma treated surface.

8.4.4 Contact Angle Measurement

The contact angle was measured before and after DBD treatment of LLDPE surface. As short as 0.2 s of treatment time, slight decrease of contact angle was noticeable. With longer plasma treatment time, the surface was provided with more polar groups as drastically drop of contact angle from 88.7 degree (based LLDPE) to below 65 degree, as shown in Figure 8.9. The contact angle of LLDPE surface treated with 8.3 and 9.0 kV was not significantly different at long plasma-treat period. On the other hand, they tended to level-off at long period of DBD treatment time. The formation of functional groups was reasonable to provide the hydrophilic property on the treated surface. Nevertheless, the influence of topology had to be in account as a physical effect on the contact angle (Cui *et al.*, 2002; Liu *et al.*, 2004; Sanchis *et al.*, 2006).

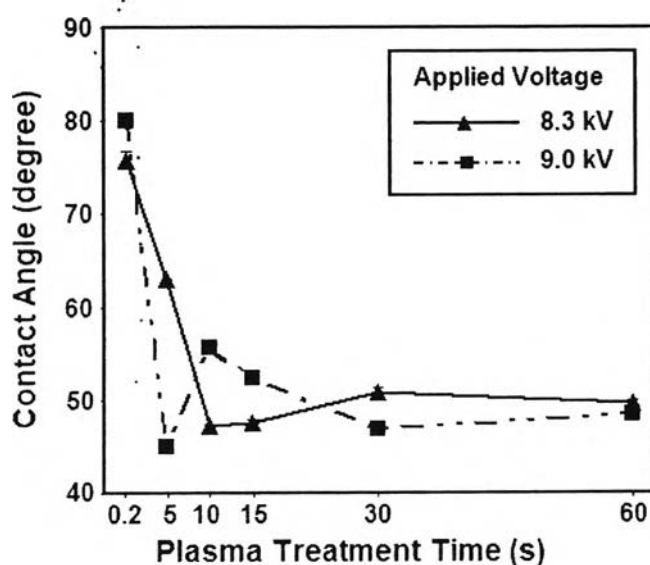
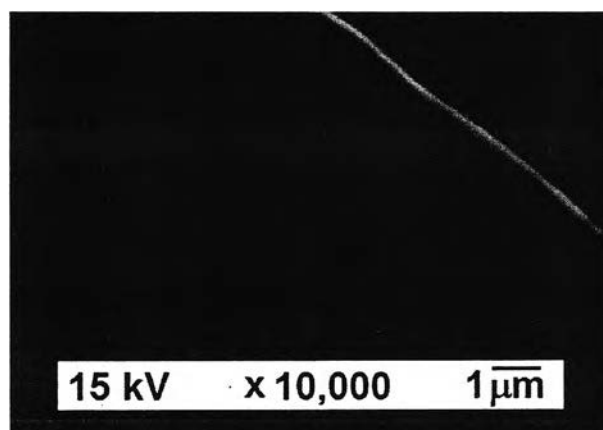


Figure 8.9 Contact angle as a function of plasma treatment time with 8.3 and 9.0 kV applied voltages.

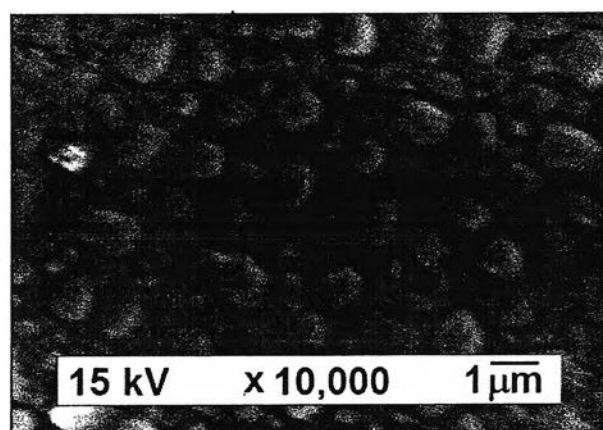
8.4.5 Scanning Electron Micrographs

In addition to the chemical examination, the alteration of surface morphology, so-called physical change, was observed. The surface micrographs of virgin LLDPE and LLDPE treated with 8.3 kV for 30 s were shown in Figure 8.10 (a) and (b), respectively. The rather rough surface was caused by the interaction with

gaseous plasma. This irregularity (domain size less than 1 micron) observed could be referred as etching effect of plasma treatment. Moreover, the high energetic species in plasma restructured the LLDPE surface as the smooth surface disappeared.



(A) Pristine LLDPE.



(B) LLDPE Treated with 8.3 kV applied voltage for 15 s.

Figure 8.10 Scanning electron micrographs of LLDPE surface.

8.4.6 Scanning Probe Micrographs

As expected, it was found that the DBD treatment induced the surfaces with varying surface feature as observed in Figures 8.11-8.12. With greater strength of plasma treatment meaning that higher applied voltage provided rougher surface at short treating period. At longer plasma treatment time, the surface turned

to fuse to be a larger irregular domain. This was probably due to the thermal effect of plasma accumulating at the treated surface which led to melting of outer-most layer of polymer.

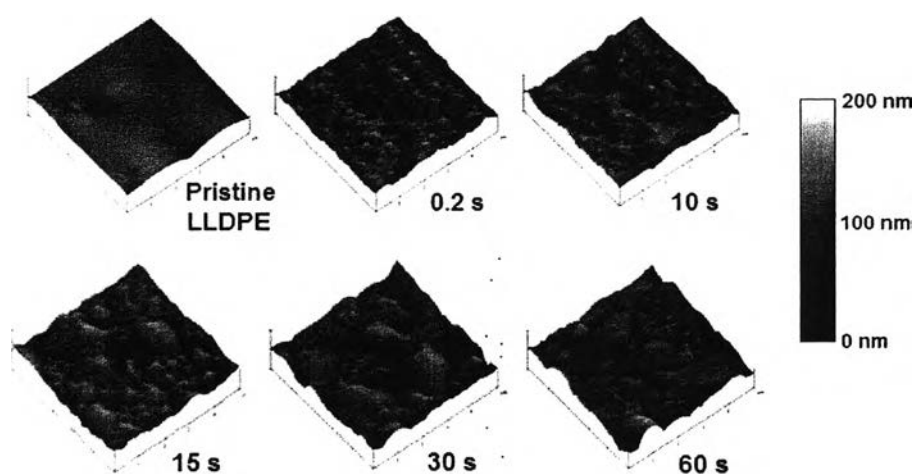


Figure 8.11 Scanning probe micrographs, as obtained by 8.3 kV plasma treatment voltages (scanning area: $5\ \mu\text{m} \times 5\ \mu\text{m}$).

Disappearance of the smooth surface as replaced by the irregular topology introduces the roughness to the LLDPE surface. Therefore, the concurrently occurrence of chemical modification (functionalization) and physical alteration (surface roughness) caused by air-DBD treatment lead to decrease the water contact angle.

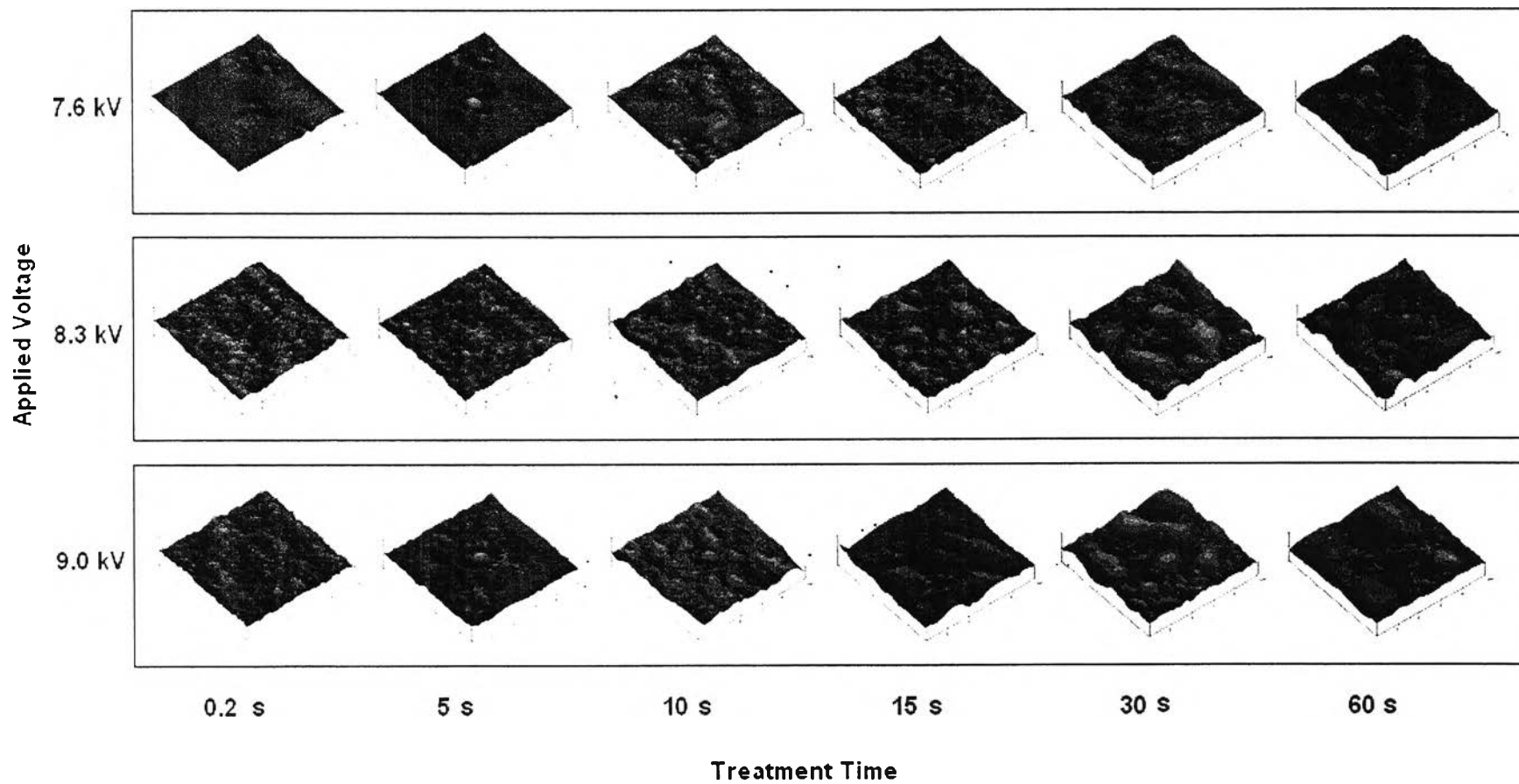


Figure 8.12 Scanning probe micrographs as obtained by different plasma treatment voltage and treatment times. (scanning area: $5\ \mu\text{m} \times 5\ \mu\text{m}$).

8.5 Conclusions

The treatment of LLDPE film with the DBD device using atmospheric air induced the surface radicals which performed well to be initiating sites for nitrogen and mainly oxygen-based functional groups as confirmed by FTIR and XPS analysis. The alteration of hydrophilicity was obtained by the mentioned functionalization. Moreover, the interaction between gaseous air-plasma and LLDPE solid surface created the irregularity on the film surface. The change in surface morphology as well as polar sites formation resulted in the increase in hydrophilic property of the treated surface as the decrease in contact angle was observed. Therefore, the DBD plasma treatment at atmospheric pressure using ambient air as a processing gas can be utilized not only chemical modification but also physical one. The optimum DBD treatment condition was varied depending on the requirement of further processing. For example, surface grafting could do with high amount of surface radicals which was given by 30 s of 8.3 kV applied to the DBD and 10 s of aging time in ambient air. For adhesion with other materials, the elevated functional groups was required, hence the condition of 8.3 kV supplied for 15 s was suitable to be processed.

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