CHAPTER VII
ATMOSPHERIC PRESSURE PLASMA DEVICE AS AN EFFECTIVE TOOL FOR SURFACE MODIFICATION

7.1 Abstract

Plasma techniques are widely utilized as a processing tool in industrial application nowadays. Surface treatment via plasma has been extensively investigated and operated at both low pressure (vacuum) and high pressure (atmospheric pressure) conditions. The plasma device to be employed for each intended application is in need of its plasma process parameter optimization as well as other parameters relevant to the production. The atmospheric pressure plasma operation is currently raising attention since the production or the treatment can be done without a vacuum system; consequently a continuous treatment process can be performed. Two types of atmospheric pressure plasma apparatuses, which were the Atmospheric Pressure Plasma Jet (APPJ) and the Dielectric Barrier Discharge (DBD), were introduced for polymer surface treatment. Both performed well to initiate the surface radicals even with a short plasma treatment period, thus they can be effective for either pre- or post-surface treatment of polymers.

Keywords: Polymer surface modification, Atmospheric pressure plasma jet, Dielectric barrier discharge

7.2 Introduction

Manmade plasma is very useful for diverse applications. The development of plasma devices to suit the functions of intended applications has been done for a long time. One such application is for material surface treatment, especially for polymer materials (Hollander *et al.*, 1999; Chan *et al.*, 2004).

To create and keep the plasma going, ionization of the gases is accomplished by applying energy to strip electrons from atoms using either electric or magnetic fields (Fridman *et al.*, 2004).

The plasmas considered in this contribution are initiated and sustained by electric fields which are produced by alternating current (AC) power supply. In the conception of this plasma, most of the electrical energy flows into the production of energetic electrons and excitation of process gases rather than into gas heating. As a result, this plasma contains hot electrons which are a few to tens of eV and at or near the ambient temperature of the ions and neutral species (John, 2005). These plasmas are non-thermal, and are also referred to as electric discharges, gaseous discharges, or glow discharges.

Two categories of plasma processing, as defined by the conditions of generation, are low-pressure and high- or atmospheric-pressure plasma. For low-pressure plasma, the discharge can be initiated easily but the operating system is quite expensive, and the material to be treated is extremely dependent on the size of the vacuum chamber (Fridman *et al.*, 2004). To overcome the unsatisfactory conditions and to carry on with the continuous process in this work, atmospheric pressure plasma processing has been selected instead. There are several types of atmospheric pressure plasma apparatuses used for the purpose of surface modification, such as corona discharge, jet, and dielectric barrier discharge. Corona discharge is characterized by bright filaments extending from a sharp high voltage electrode towards the substrate where the corona discharge produces non-uniformity of low plasma density. It is currently used practically in the film industry. Another type is the atmospheric pressure plasma jet (APPJ) which is like a continuous nonthermal arc that creates a stable, homogenous, and uniform discharge. The last one is dielectric barrier discharge (DBD) as defined by a pair of parallel plane electrodes of homogeneous geometry with either one or both of the electrodes covered by a dielectric layer. Principally, the intermediate species on the plasma-treated surface that are free radicals have the potential to undergo several termination reactions such as crosslinking, grafting, and functionalization (Lehocky *et al.*, 2003). Therefore, the use of generated radicals or further peroxides formed on the polymer surface via plasma surface treatment as initiators, instead of chemical peroxide, was studied in this research. The atmospheric pressure plasma apparatus chosen is DBD using atmospheric air as a process gas and APPJ using nitrogen gas as a process gas. Differences in the aim from the ordinary use of plasma surface modification are the form of substrate treated and the order of the plasma treating step in the overall process. Polymer pellets will be passed through the plasma apparatus, not film, to generate the free radicals or peroxides on the pellet surface before being further processed in the extruder and shaped by chill-roll casting to make the film. Therefore the plasma technique used here can be defined as a pre-treatment process.

For this research, our motivation was to create an intermediate active species, i.e. induced radicals, on the polymeric surface, by two atmospheric pressure plasma devices, APPJ and DBD. Such a plasma technique provides a chemically mild, environmentally friendly and mechanically non-destructive means of free radical generation. APP non-thermal non-equilibrium plasma represents a current trend in novel atmospheric pressure plasma processing because of its potential for large-volume 2D/3D "cold" plasma processing (Andreas *et al.*, 1998). Another approach was dielectric barrier discharge (DBD), which always generates non-uniform random micro-arcs, so-called silent discharge. However, the type of dielectric barrier materials influences the discharge characteristic since the dielectric barriers are often used to control the formation of the microdischarges or streamer by quenching the charging of the dielectric before an arc can be formed. To avoid uneven treatments such as pitting or pinholes, the glow discharge is preferred. Technically, a uniform glow discharge at atmospheric pressure can be generated under the conditions of some specific requirements:

- To initiate plasma, the applied voltage should be greater than the breakdown voltage for the process gases. As long as the applied or gap voltage is smaller than the breakdown or ignition voltage, there is no discharge activity and the device will behave like a series combination of two capacitances. The breakdown voltage is significantly dependent on the product of the pressure and the gap distance. For plane parallel electrodes, the breakdown voltage needed to be applied for air is shown in Figure 7.1.

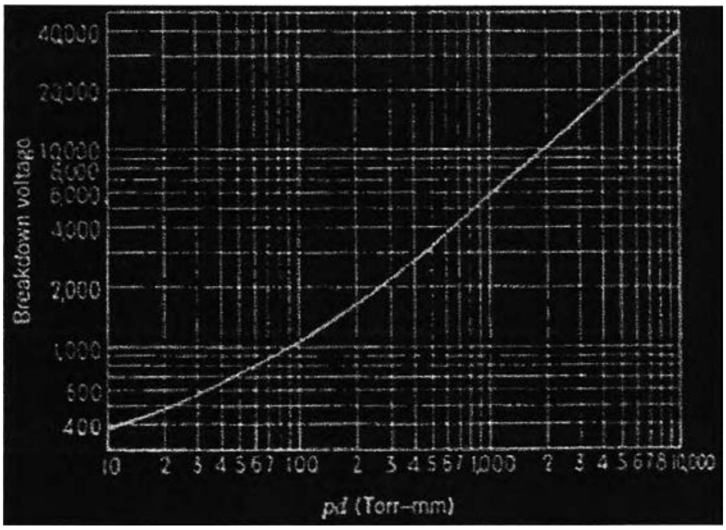


Figure 7.1 Breakdown voltage for plane parallel electrodes at 20°C as a function of pressure and gap distance for air as a process gas (*pd*) (Lieberman *et al.*, 1994).

- To get a stable atmospheric glow discharge, an AC voltage at a frequency of at least a half to several kilohertz is required. Nevertheless, there is a range of frequency for stable glow discharge which depends on the specific gas and the material used as the dielectric barrier, in the case of DBD.

The continuous air-to-air process and an effective reduction of unwanted polymer degradation typical for our APPJ and DBD renders this approach very attractive for the plastics industry for both downstream (Masayuki *et al.*, 2007; Wang *et al.*, 2007) and upstream applications as employed in this work. According to the plasma generation and process, such an innovation can be referred to as a physico-chemical technique for the reactive plasma-processing of polymers.

The utilization of both plasma devices to induce the radicals on polymer pellet surfaces was investigated in this work. The induced radicals were referred as the physical initiators for subsequent use as the reaction-driving species. In other words, the upstream plasma-treatment process was in focus and, hence, there are some important parameters different from those found for ordinary applications described above, e.g. the substrate geometry to be treated and the subsequent plasma process. Polymer pellets, and not a continuous thin film, are being passed through an APPJ and DBD for surface treatment prior to the following inventory process. All plasma runs were done using nitrogen gas (for APPJ) and ambient air (for DBD) at atmospheric pressure in order to maintain the continuous air-to-air process for the next step processing, such as extrusion and injection molding.

Part I Atmospheric Pressure Plasma Jet (APPJ)

7.3 Experimental

7.3.1 Materials

The LLDPE pellets used in this study represent commercially available film grade 2047G material, supplied by DOW Chemical Company (Thailand). Its melt flow index (MFI), according to ASTM D1238, is 2.3 g/10 min. The density of the pellet is 0.917 g/cm^3, as reported by the supplier.

The *1,1*-diphenyl-*2*-picryhydrazyl (DPPH), a radical scavenger, was purchased from Fluka. Benzene UV-spectroscopy grade with ≥ 99.5% purity, supplied by Merck KGaA., was used as the solvent for radical measurement. All chemicals were used as received.

7.3.2 Atmospheric Pressure Plasma Jet (APPJ)

7.3.2.1 Nitrogen-Plasma Jet Observations

Both APPJ and the power supply system used in this work were jointly developed by JE Plasma Consult GmbH and Reinhausen GmbH, Germany. The jet nozzle diameter was 8 mm. Nitrogen was selected to be the process gas; consequently this could be defined as a nitrogen atmospheric pressure plasma jet (NAPPJ). The sinusoidal high voltage with a mid-range frequency of typical 10 kHz was supplied to the system. The treatment of the LLDPE pellet was done in a glass tube (shown in Figure 3.1). The pellet must be fed by nitrogen gas to prevent meta-stable quenching by oxygen that causes reduced jet lengths. The processing gas flow rate was varied as 7, 8, 9, 10, 15, and 20 L/min. For the feeding zone, the gas flow rate was varied toward 10 L/min. Due to the 5.5 kV ignition voltage, the applied jet voltage was from 6.6, 7.7, 8.8, to 9.9 kV. The power delivered to the plasma jet was measured using a Tektronix TDS 7254 oscilloscope equipped with a high voltage probe.

7.3.2.2 Nitrogen APPJ Treatment of LLDPE Pellets

The represented LLDPE pellets to be treated were qualified by an almost spherical shape and same size (by weight); therefore, asymmetrical shaped pellets were assumedly ignored. The pellets were fed one by one at the pellet feeding section and were flushed by nitrogen gas. For this reason, a zero initial pellet velocity was assumed. In addition, to simplify the analysis, no friction between the moving pellets and the tube surface was assumed. Thus, a constant jet velocity throughout the plasma-jet volume was applied. The pellet velocity was measured backward via the distance measurement of the projectile motion of the pellets coming out of the glass tube.

The jet length captured by commercial CCD camera and the velocity of the pellets coming out of the glass tube outlet were calculated simultaneously to obtain the plasma treatment time.

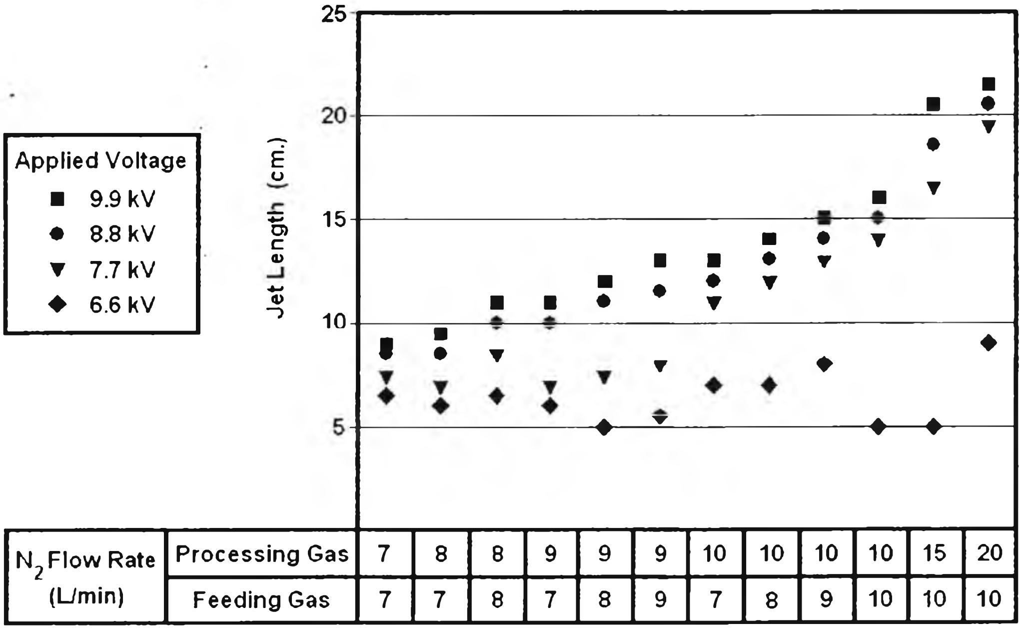
Another important factor for the radical generation is the latency time, the time-interval between the plasma treatment and the beginning of the next production step (i.e. extrusion). In this work, the defined interval time was named ‘latency time’ or ‘aging time’. During latency time, the plasma-treated pellets were exposed to ambient air to allow for the interaction of the initiating sites and environmental atmospheric air. By setting the vertical distance (S_y) between the glass tube outlet and the pellet collector as 30 and 122 cm, the latency times were then varied depending on the velocity of the pellets coming out of the glass tube. Therefore, these values were set to study the effect of latency time on the amount of generated radicals on the pellet surfaces.

As the radicals were expected to generate on the pellet surfaces, it was necessary to determine the total concentration of these species. The conventional method applied popularly to determine the radical concentration on the surface is liquid-phase radical trapping with DPPH, a radical scavenger, in a benzene solution, as used by Suzuki (Suzuki *et al.*, 1986). The evidence of radicals was then obtained by colorimetric chemical titration with the above reagent. The plasma treated pellets were kept in a 1.0 x 10^{-4} mol/l benzene solution of DPPH at 70°C for 24 h to decompose the radicals on and near the pellet surfaces. The amount of DPPH consumed was measured by the difference of UV-Visible light absorbance at 520.5 nm between the pristine and plasma-treated pellets, determined by UV-Visible light spectroscopy (Varian V-550).

7.4 Results and Discussion

7.4.1 Jet Observations

Without any specific instruments to verify the plasma state, one can commonly define the plasma region as the visible light generated by the plasma source. Figure 7.2 shows the dependence of jet length on various nitrogen gas flow rates for both processing and feeding gases at various applied voltages. It is clear that an increasing gas flow rate for both parts results in longer jet lengths, especially for 8.8 and 9.9 kV applied voltage.



N_2 Flow Rate (L/min)													
	Processing Gas	7	8	8	9	9	9	10	10	10	10	15	20
	Feeding Gas	7	7	8	7	8	9	7	8	9	10	10	10

Figure 7.2 Dependence of the plasma-jet length on various N_2 flow rates for both process and feed gases at various applied voltages.

The flow of nitrogen gas through the jet nozzle and the supplying of high electrical energy generated visible light, which was defined, in this work, as the reaction region. This was a basis of the passive method of emission plasma spectroscopy (Fantz *et al.*, 2005). From the mentioned basis, jet length (as captured by CCD camera) was varied depending on both gas flow rate and supplied energy. These are proposed as concurrent factors. Increasing the applied voltage can generate more energetic species while a high flow rate can expand the volume of the plasma jet. Therefore, the jet length is not only dependent on the gas flow rate, but also on the voltage supplied to the jet nozzle. Since the flow rates of feed gas were varied to not faster than the process gas, the equality of the processing and feeding gas flow rates provides the longest jet for each flow rate due to the relatively fast total gas velocity, the so-called jet velocity. This consequently provided better prevention of meta-stable quenching, hence, allowing a longer jet extent. Therefore, from the jet length observed, the main factor in providing a long nitrogen-plasma jet is the process gas flow rate, followed by the feed gas and applied voltage, respectively.

7.4.2 Effect of External Plasma Process Parameters on the Total Radical Concentration Generated on Treated LLDPE Surfaces

Generally, there are (at least) two factors that control the radical concentration–plasma treatment and latency time–for further uses. For the APP-Jet used in this work, the total quantity of radicals generated on the plasma-treated pellet surface was studied by varying *(i)* the feeding and processing gas flow rates, *(ii)* the applied voltage amplitude, and *(iii)* the latency time.

In terms of maximized total radical concentration, an extended jet length corresponding to a larger plasma-peller interaction volume is preferred. In Figure 7.3, the total measured radical concentration on the LLDPE pellet surfaces is plotted against the applied voltage amplitude. Parameters are the 1:1 ratio gas flow, and the latency time. From these data it is obvious that the higher the gas flow rate is, the more radicals there are found on the pellet surfaces. There is only a weak dependence on the applied voltage amplitude in the range from 6.6 to 8.8 kV. However, a slight maximum is found at 7.7 kV. Hence, again, the gas flow rate had a stronger influence on the induced-radical concentration than the voltage applied to APPJ.

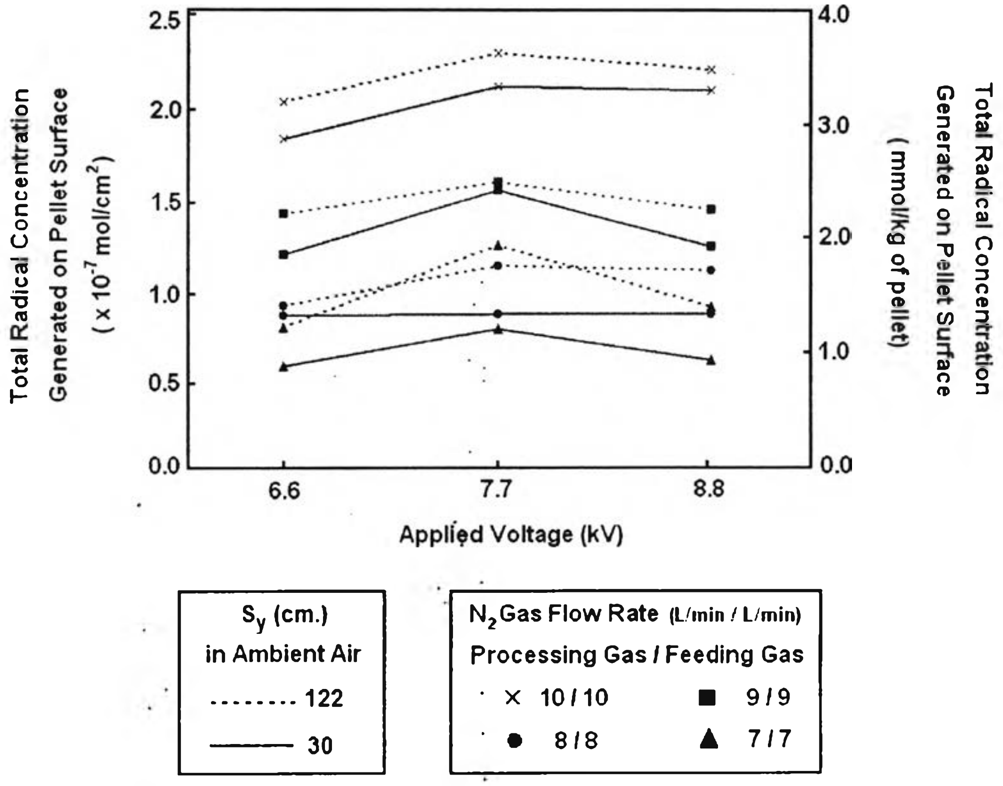


Figure 7.3 Dependence of the total radical concentration on the applied voltage amplitude at 1:1 ratio of process and feed gas flow rates.

To study the effect of different feed and process gas ratios on the radical concentration, the process gas flow rate was kept constant while varying the feed gas flow rate. The result shown in Figure 7.4 implies that the feed gas flow rate reduces the level of contaminating oxygen and drastically affects the surface radical concentration.

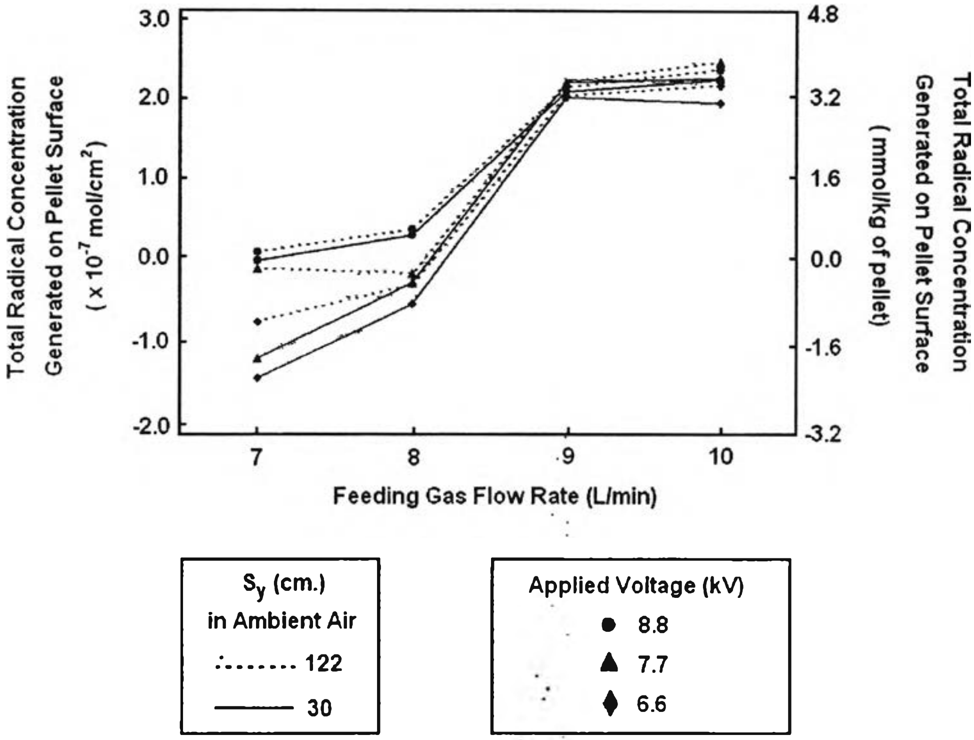


Figure 7.4 Dependence of the total radical concentration on the feed gas flow rate. Parameter: 10 L/min of process gas flow rate.

At flow-rates below 9 L/min, there is a significant contribution of quenching oxygen from the ambient air in the jet itself. It is speculated that this oxygen contamination contributes to the reduction of active plasma species for interacting with the polymer chain and subsequently lessens radicals at the pellet surfaces. Above 9 L/min feed gas flow rate, the detrimental oxygen effect is strongly reduced, yielding significantly higher radical concentrations.

In another set of experiments, whose results are shown in Figure 7.5, the ratio of process and feed gas flow rate was varied from 1:1; 1.5:1; and 2:1 for a fixed feed-gas flow-rate of 10 L/min. It can be seen that at a 1:1 flow-rate ratio, the maximum quantity of generated radicals on the surfaces was still maintained (despite the smallest jet length) supporting the effect of highest plasma treatment dosage (0.84 J/cm^3) as the longest treatment time. However, a 2:1 flow-rate ratio, which has the smallest plasma dosage (0.42 J/cm^3), does not render the lowest amount of radicals. This suggests that two opposite effects may occur simultaneously. At this condition, the residence time is the shortest due to the relatively fast process gas flow. On the other hand, the length or volume of energetic species is the largest, which leads to a greater volume of high density plasma species to modify the pellet surface. At a 1.5:1 flow-rate ratio, plasma was generated moderately, about 0.62 J/cm^3, but the region of high energetic species was shorter than that of the 2:1 flow-rate ratio. These effects may counteract each other to give a minimum of net radicals on the treated surface.

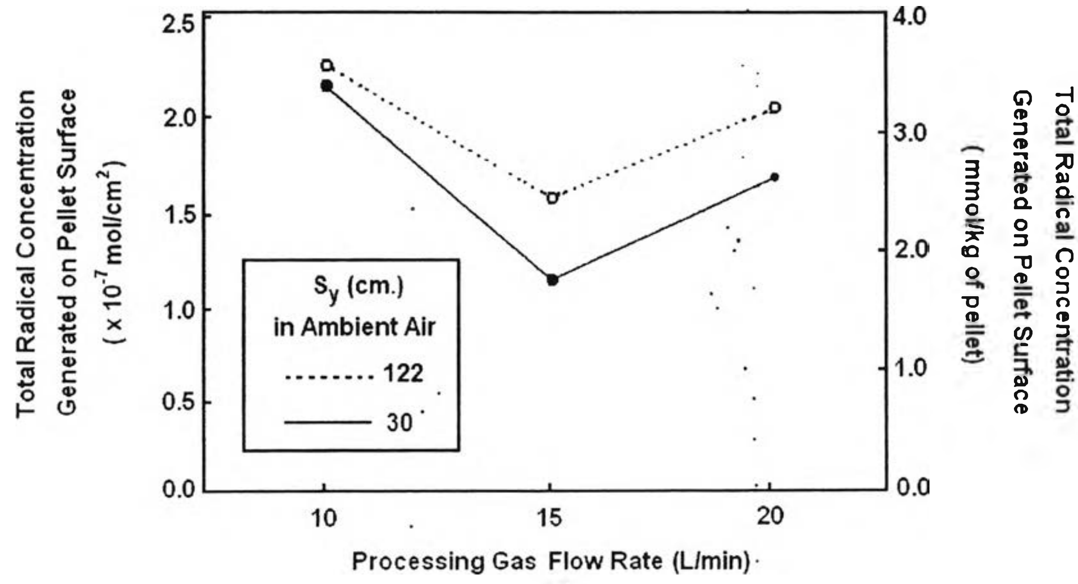


Figure 7.5 Total radical concentration vs. process gas flow-rate.
Parameter: - 10 L/min feed gas flow-rate
- 8.8 kV applied voltage amplitude

Additionally, by this explanation, the negative value radical quantity on the treated surface, especially at an applied voltage below 7.7 kV with low feeding gas flow rate, in Figure 7.4, would be analyzed in terms of the clearing out as-existing free-radicals on the pellet surface. Therefore, these radicals could be flushed out by low energetic plasma species whose energies are not enough to break the covalent bond of the polymeric molecules and, rather, clean the weak-binding species on the treated surface. Generally, free radicals are active species that are randomly dispersed in the atmosphere, and consequently naturally attach on the material surface. Hence, the as-existing free radicals on the untreated LLDPE surface was also evaluated as a control experiment (blank) and then subtracted out of the measured radical concentration to obtain the plasma-induced radicals originating from the covalent bond breaking.

7.4.3 The Effect of Latency Time in Ambient Air

From Figures 7.3 – 7.5, it is quite clear that the amount of radicals generated on the treated pellet surfaces for each fixed parameter obtained at 122 cm of S_y was higher than that of 30 cm. Increasing the latency time is effective enough to increase the total radical concentration. This may reasonably imply that the active sites on the treated surface can further react with oxygen in ambient air atmosphere to become peroxides after moving out of the nitrogen plasma regime. This reaction can cause the rearrangement of radicals or electron-enriched species in different ways, resulting in different products on the treated surface.

Part II Dielectric Barrier Discharge (DBD)

7.3 Experimental

7.3.1 Materials

The same grade of LLDPE and all chemicals as imposed in the APPJ experiment were employed for the DBD experiment.

7.3.2 DBD plasma device

7.3.2.1 DBD Characteristics and Electronic Plasma Diagnosis

In this research, the electrode set and the plasma treatment zone were designed to achieve the requirements of the treating process and the uniform discharge while providing the optimum radical concentration forming on the surface of treated materials.

A plasma apparatus was constructed for the purpose of surface modification at atmospheric pressure using ambient air as a process gas. It was composed of metal electrodes covered by a dielectric material. This unit utilized a variable voltage control as a power supply. With adjustable input voltage, it was able to control the output or processing voltage. The ionized gas is produced in the space between the two electrodes, named the discharge space, where the treatment of pellets occurs. A schematic of the plasma treatment unit is shown in Figure 7.6.

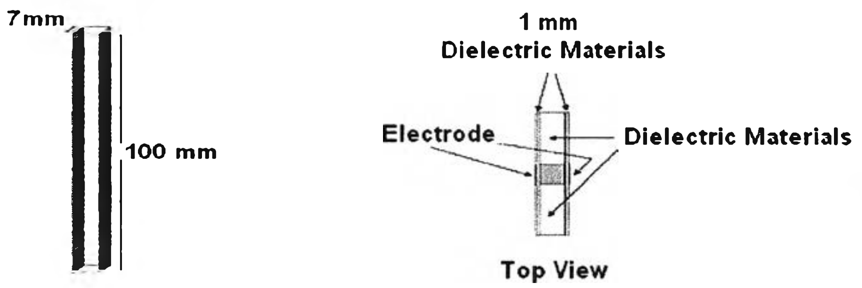


Figure 7.6 DBD treatment chamber geometry for LLDPE treatment.

The plasma treatment chamber was designed with an inlet and outlet for the vertical flow of pellets to be treated (gravity-induced motion). The housing case was made of either a PVC tube or heat resistance glass. The specific details of this set-up can be described as follows:

- The power supply unit consisted of the sinusoidal high voltage of 500 Hz, as limited by a step-up transformer.
- Electrode geometry, as can be classified by the type of plasma apparatus, consists of a pair of plane parallel electrodes made of stainless steel with the W x L dimension of 7 x 100 mm. Two electrode pairs were arrayed in the vertical direction, which results in the gravity flow of the pellets to be treated.
- The gap distance between the electrodes was 7 mm to allow the flow of a normal plastic resin.
- The dielectric material used as the dielectric barrier and reactor case is a Polymethyl methacrylate (PMMA) sheet with 1 mm thickness. The dielectric barrier was placed adjacent to the outer surface of both electrodes.

Electronic plasma diagnosis was done in order to characterize the discharge behavior. The waveform of both current and voltage was captured using an oscilloscope, LeCroy WaveRunner model 6050A (500 MHz, 5 GSs^{-1}), as a signal detector. The voltage applied to the DBD was measured using a resistance voltage divider (R-divider) with a ratio of 1281.93. At the same time, an electrostatic meter, type 2065, was used to evaluate the output voltage in RMS. Since, in principle, the electrostatic meter had no resistance, the effect of instrument loading could be neglected. Thus, the value given by R-divider and the apparent output voltage can be comparable. The divergence factor of the voltage given by both meters was calculated to generate the reasonable waveform of the output voltage. Moreover, the ohmic conductor, with 115 Ω, was circuited in series to estimate the current supplied to the plasma device.

7.3.2.2 Air-DBD Treatment of LLDPE Pellets

To define the optimum conditions for utilizing the plasma apparatus as a pre-treatment step for reactive processing, it was necessary to study the effect of applied voltage, and also the aging time of treated LLDPE in atmospheric air. According to the limitation of the power supply, the applied voltage was varied from the minimum where the glow-like discharge can be observed, the so-called ignition voltage, to the maximum voltage before the discharge was unstable and then generated the arcs. Therefore, the applied voltage ranged from 6.5 to 9.0 kV. Another important parameter is the latency time of the treated LLDPE pellets in atmospheric air which, in this work, was set as short as 0.2 s.

As the radicals or further peroxides are expected to generate on the pellet surface, the technique used to determine the concentration of these species is the DPPH method. The evidence of radicals was obtained by colorimetric chemical titration with this reagent. The plasma-treated pellets were kept in a 1.0 x 10^{-4} mol/l benzene solution of DPPH at 70°C for 24 h to decompose the radical formed on or near the pellet surface. This temperature, 70°C, is below the α-chain transition of polyethylene; thus, the radical scavenger would interact only at the surface polymer chain. The amount of DPPH consumed was measured by the difference of UV-visible light absorbance spectrum at 521 nm between the pristine and plasma-treated pellets using a Shimadzu UV-2550 spectroscopy.

7.4 Results and Discussion

7.4.1 Electronic Plasma Diagnosis

All data collected for electronic diagnosis of the home-built DBD was presented in RMS. Figure 7.6 is the waveform at the input voltage of 8.3 kV, representing the current and voltage characteristics. There was environmental interference, as a lot of noise was observed. The current and voltage waveforms proved that this plasma device was a type of capacitor, due to the current lead and voltage lag (Wagner *et al.*, 2003). Moreover, there were a significant number of voltage spikes for the current supplied to the electrodes, which was characteristic of micro-arcs that were generated due to the over-breakdown voltage. The process of discharge of a capacitor into a circuit containing a gas gap, containing atmospheric air, between the electrodes, which is sufficiently large, a breakdown occurs in the gap, the gap becomes a conductor, and the capacitor then discharges. In fact, to produce and sustain the glow-like discharge, the frequency of sinusoidal applied voltage should be in kHz. This home-built plasma apparatus cannot operate at more than 500 Hz due to the limitations of the step-up transformer used. However, many filamentary or micro-arcs produced by this DBD can be observed as glow-like or homogeneous discharges as captured by commercial CCD camera, seen in Figure 7.7.

The corrected factor, which was used to transform the value detected by an oscilloscope (R-divider method) to the reasonable voltage, was ≈ 3.7575.

At a frequency of 500 Hz, the ratio of output voltage and input voltage was about 47.63 for the step-up transformer used. The ignition voltage, which is the uniformly distributed micro-discharges over a dielectric surface, was about 6.5 kV. As long as the applied voltage was smaller than 6.5 kV, there was no discharge observed.

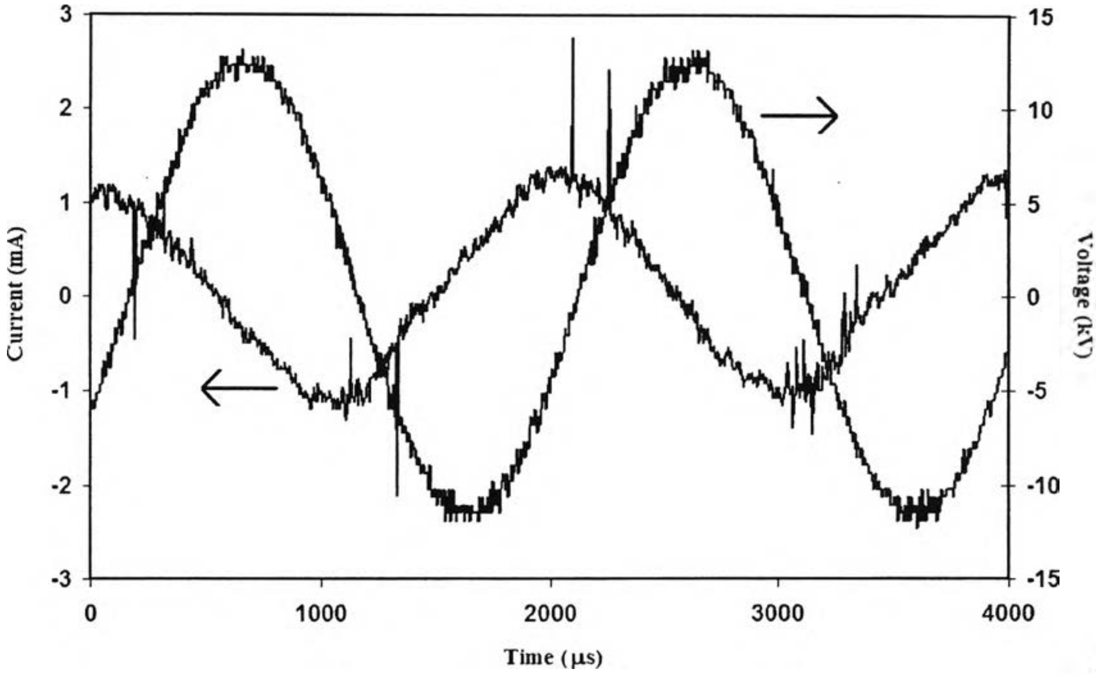


Figure 7.7 Characteristic waveform of the DBD applied voltage and total current.

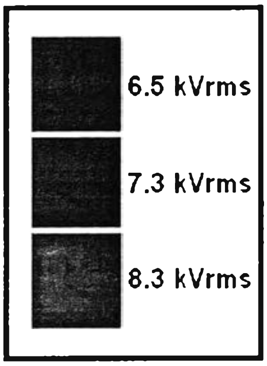


Figure 7.8 Micro-arcs of air-plasma DBD observed as glow-like discharge.

7.4.2 Effect of Applied Voltage on the Total Radical Concentration on the Treated LLDPE Pellet Surface with Very Short Treating and Aging Periods

The short time of plasma surface treatment is quite practically suitable for plastic manufacturing, especially to be used as a pre-treatment procedure. Therefore, the effect of short time of air-plasma exposure and ambient air exposure (latency time) on the radical species left on or near the treated LLDPE pellets was investigated, as shown in Figure 7.9

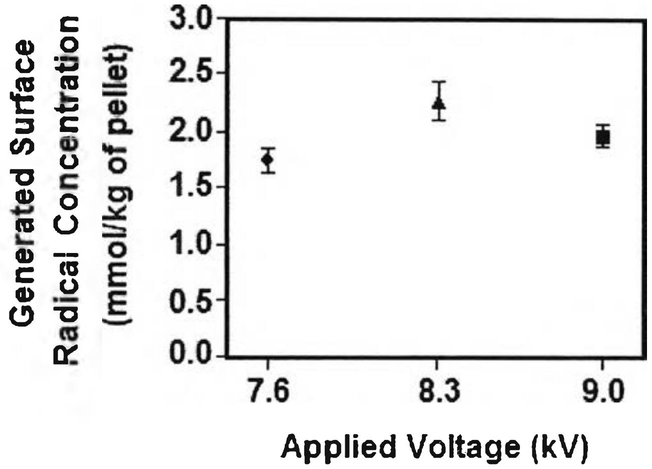


Figure 7.9 Dependence of generated radical concentration on plasma treatment time with various applied voltages at 0.2 s of DBD treatment time and 0.2 s of latency time in ambient air.

The voltage applied to the DBD that provided the maximum radical concentration on the surface was 8.3 kV, not the maximum applied voltage. This is described as an occurrence of both the radical formation and the radical disappearance, its completing phenomena. In general, more severe plasma conditions, which means a greater voltage applied to the plasma device and longer treatment time, can produce a greater number of surface radicals, but these parameters can lead to the disappearance reactions, the same as other terminating reactions such as functionalization, degradation, and also slight surface cross-linking. This is also supported by the total generated radicals on the treated LLDPE surface with fast plasma treatment (0.2 s) and short aging time (0.2 s). The radical concentration was 1.14×10^{-4}, 1.51×10^{-4}, and 1.30×10^{-4} mmol/cm^2 for 7.6, 8.3, and 9.0 kV of applied voltage, respectively.

According to the definition of DBD in which the plasma treatment occurs between a pair of electrodes, the power supplied to the DBD is not so great. This is probably due to the system design and the limitation of the power supply unit as well. However, the amount of surface radicals rendered by DBD was a bit lower than using the APPJ system.

7.5 Conclusions

Nitrogen-APPJ treatment and air-plasma DBD treatment of LLDPE pellets were successfully applied for generating active species like free radicals on the surface of pellets. The plasma jet length is dependent on the applied excitation voltage, which was obvious at a voltage not less than 7.7 kV and a ratio of gas flow rates, which was predominately dependent on processing gas flow rate rather than feeding gas flow rate. The jet length varied from 5 cm to 22 cm. The external plasma process parameters that significantly controlled the amount of generated radicals were applied voltages, feeding and, mainly, processing gas flow rates, and latency time after the treating period, which was represented by the vertical distance of the glass tube outlet and the radical detector, S_y. For the nitrogen-APPJ system studied, the optimum conditions for the maximum total radical concentration left after plasma treatment was at 7.7 kV applied voltage, 10 L/min of both processing and feeding gas flow rates with 122 cm of S_y. For the air-plasma DBD, the use of 8.3 kV applied voltage provided a surface with the maximum radical concentration. This process consumed a very short period of time which was comparable to the LLDPE pellet treatment via APPJ.

Both the nitrogen-APPJ and air-plasma DBD treatments of polymer pellets can be used as an innovative physical method to provide free radicals at the pellet surface, which act as initiating sites for functionalization or reactive processing of the polymer. The large volume of 3D plasma jets was more effective than the random micro-arc DBD; however, this type of atmospheric pressure plasma jet seems to be not the best one for continuous reactive processing due to the nitrogen consumption without a recycling system (at the lab-scale situation). Therefore, the air-plasma DBD was utilized instead.

7.6 Acknowledgements

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