CHAPTER III
EXPERIMENTAL

3.1 Materials

All materials used for the experiments are shown in Table 3.1. Its specifications and supplier are provided herein. Moreover, the uses of them are described in the table as well.

Table 3.1 Materials used in this contribution

Linear Low Density Polyethylene (LLDPE)

Grade	Specifications (reported by supplier)	Supplier	Remarks
DOWLEX 2045.11	• MFI = 1.0 g/10 min • Density = 0.922 g/cm^3 • Tm = 125°C	DOW Chemical (Thailand)	Used as based resin in chapter IV
DOWLEX 2045	• MFI = 1.0 g/10 min • Density = 0.920 g/cm^3 • Tm = 124°C	DOW Chemical (Canada)	Used as based resin in chapter V and VI
DOWLEX 2047G	• MFI = 2.3 g/10 min • Density = 0.917 g/cm^3 • Tm = 125°C	DOW Chemical (Thailand)	Used as based resin in chapter VII, VIII, and IX

Natural Rubber (NR)

Grade	Specifications	Supplier	Remarks
STR-5L	• Standard Thai Rubber • Packed in blocks	Rayong Bangkok Rubber Co., Ltd (Thailand)	Used as minor phase in chapter IV

Maleic Anhydride (MA)

Grade	Specifications	Supplier	Remarks
MA	• Melting point = 57°C	Acros Company	Used as coagent in chapter IV

Epoxidized Natural Rubber (ENR)

Grade	Specifications	Supplier	Remarks
ENR-50	- 50% Epoxidation	KMUTT Laboratory* (Thailand)	Used as minor phase and coagent in chapter IV

* ENR was kindly supplied by Dr.Nandh Thavarungkul, Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT), Thailand.

Dicumyl Peroxide (DCP)

Grade	Specifications	Supplier	Remarks
DCP	- White flake - 98% peroxide - Melting point = 39°C - 10 h $t_{1/2}$ @ 114°C	Aldrich	Used as chemical initiator in chapter V, VI, and IX

1,1-Diphenyl-2-Picryhydrazyl (DPPH)

Grade	Specifications	Supplier	Remarks
DPPH, Stable radicals	- Purple powder - Melting point = 135°C - ≤ 5% ash	Fluka	Used as radical scavenger in chapter VII, and VIII

Isopropanol (IPA)

Grade	Specification	Supplier	Remarks
IPA, Reagent grade	- Boiling point = 82.2°C	University Store, (UW, Canada)	Used as inert carrier for peroxide solution in chapter V, VI
IPA. Reagent grade	- Boiling point = 82.2°C	Labscan Asia Co.,Ltd.	Used as inert carrier for peroxide solution in chapter IX

Benzene

Grade	Specifications	Supplier	Remarks
Benzene, Analytical grade	• 99.7% purity • Boiling range = 79-81°C	Merck KGaA	Used as solvent for DPPH solution in chapter VII, and IX

Toluene

Grade	Specifications	Supplier	Remarks
Toluene, Analytical grade	• 99.5% purity • Boiling range = 110-111°C	Labscan Asia Co.,Ltd.	Used as solvent for extraction in chapter IV

Xylene

Grade	Specifications	Supplier	Remarks
Xylene, Analytical grade	• 99.8% purity • Boiling range = 137-142°C	Merck KGaA	Used as solvent for Soxhlet extraction in chapter V, VII, and IX

3.2 Methodology

3.2.1 Blending of LLDPE, NR, and ENR with MA and the Agricultural Film Preparations

Melt blending was performed in laboratory internal mixer, Brabender® model W-50. The mixing chamber capacity was 50 cm^3 equipped with thermoplastic mixing head. The mixing temperature and rotor speed were 170°C and 50 rpm (in the unit of min^{-1}), respectively. All runs were done under nitrogen atmosphere to avoid oxidation from atmospheric air. Total volume of blend formulae, excluding MA, was 40 cm^3 which was 80% of chamber capacity. The major phase was 80% w/w of total blend formulae and total rubber content including NR and ENR was 20% w/w, excepted for UV-visible absorbance test which was stated later. The reactive agent used for reactive blending, MA, was loaded only for 3 phr.

Generally, the very high molecular size of NR, natural macromolecules leading to high melt entanglement could be reduced for ease of processing by the process called mastication. The chunk NR was masticated using two-roll mill machine at ambient temperature with 10 min of mastication time. The roller speed was 30 min^{-1} and the gap distance was adjusted to be 5-10 mm throughout the mastication process. Rubber phase was then cut into small pieces and the reactive agent for reactive blending, MA, was ground before feeding to the mixer to get better dispersion and distribution.

Table 3.2 Blend formulae and melt blending step in batch mixer

Ingredient	**Minute of Addition**	**Binary Blend (LN)**	**Ternary Blend (LEN)**	**Reactive Blend (LMEN)**
1st (major phase)	0	LLDPE	LLDPE	LLDPE
2nd	3rd	NR	ENR	MA
3rd	6th	-	NR	ENR
4th	9th	-	-	NR
Further mixing time		6 min	3 min	3 min
Total mixing time		9 min	9 min	12 min

The blend formulae and step of mixing was concluded in Table 3.2. Blending started with melting of major phase which was the base resin. Certain amount of LLDPE was filled first and allowed to melt for 3 min prior to the addition of second ingredient. The third and fourth ingredient were filled step by step with constant interval addition time, 3 min. NR was the last ingredient for all blends. After that the blend was kept mixing according to the further mixing time for each blend to allow the uniform mixing. Hence, the total melt blending time for binary blending, ternary blending, and reactive blending were 9, 9, and 12 min, respectively.

The mixture was then removed from the batch mixer, placed on stainless steel plate, and cooled down by ambient air. It was then shredded into small pieces by a shredder machine and kept over night in vacuum oven at 110°C before passing through the twin-screw extruder (TWE) to get better homogeneity.

Collin® co-rotating type twin-screw extruder, model T-20 with screw diameter of 25 mm, and 30 of L/D ratio was used. Another process parameter, screw speed was varied as 80 and 90 min^{-1}. Temperature profile of TWE from feed zone through die zone was set as followed: 150, 155, 160, 175, 185, 195°C. The throughput rate was measured during the twin-screw extrusion.

The extrudate was further processed into the thin film by using single screw chill-roll cast film extruder, Collin®. It was equipped with a flat-slit die dimension of 0.8 x 250 mm. The screw speed used for this step was fixed at 40 min^{-1}. The same temperature profile as imposed during the twin-screw process was set. The stretching roll was chilled with 15-20°C of chilled water. As the stretching or draw ratio (DR) was another process parameter in this work, the film was processed with various DR, 7, 10, 15, and 20. Typically, DR was referred to the degree of stretching during the melt solidification resulting to the orientation of film. It was defined by the ratio of rate or speed of stretched film to that of extrudate and expressed, in this work, as the ratio of chill-roll speed and extrudate speed.

$$\text{DR} = \text{Chill-roll speed} / \text{Extrudate speed}$$

Chill-roll speed = $(2\pi r) \times (\text{rpm})$ in the unit of distance/time (i.e. cm/min)

Whereas: r = roller radius

rpm = round per minute of roller (in min^{-1})

Extrudate speed = $Q / (D \times A)$ in the unit of cm/min ($\mathrm{g/min.cm^3/g.1/cm^2}$)

Whereas: Q = throughput rate in g/min

D = density of extrudate in $\mathrm{g/cm^3}$

A = cross-sectional area of slit die

3.2.2 Melt Processing (Batch Process) of Low-Dose Chemical Peroxide Modification

Free-radical modification of LLDPE using the Dicumyl peroxide (DCP) was performed in laboratory internal mixer, Haake Rheomix 90 with 200 cm^3 of chamber volume. However, the material to be filled was only 90% of chamber capacity. Thus, 180 g LLDPE pellet corresponding to $\approx$ 196 cm^3 was filled. The processing variables to be examined in this work were the process temperature (C), chemical peroxide quantity (P), and mixing rotor speed (R). Another important parameter to be in account was the peroxide addition method (M). Moreover, without chemical peroxide feeding, the shear modification of LLDPE was also performed as a controlled sample. Therefore, the reaction temperatures were varied as 170, 185 and 200°C. Amount of DCP was varied as 0 (shear modification), 0.02, 0.06, and 0.1 phr. Rotor speeds were set as 30 and 70 min^{-1}. The peroxide addition was carried out by three different forms of mixing states. The first method (Mi) was the addition of peroxide solution into molten polymer. The stock solution, DCP-dissolved in IPA, was prepared by dissolving given amounts of DCP in 2 cm^3 of IPA. Small droplet of stock solution was then loaded frequently into the molten LLDPE. Special care was taken to minimize its loss during feeding since the solution would volatile easily. The second peroxide addition technique (Mii) was the addition of solid peroxide into the molten LLDPE. The last one (Miii) was the solid peroxide and solid LLDPE were fed and heated simultaneously. After peroxide was added, the reaction had been further continued to reach 10 min of mixing time. Then the sample was removed from the chamber, placed on stainless steel plate and cooled down by atmospheric ambient air. Finally, the modified LLDPE was carefully ground into small pieces using the Willey mill laboratory grinder.

3.2.3 Plasma Surface Treatment

3.2.3.1 Treatment of LLDPE Pellets

There were two types of atmospheric pressure plasma device utilized for LLDPE pellet treatment in this contribution. The first one was APPJ. Both jet nozzle and power supply was kindly supported by JE Plasma Consult GmbH, Germany. Another one was the DBD which was developed in our laboratory. The treatment compartment was designed for the application of each system. Both plasma apparatuses were operated at atmospheric pressure to keep continuous air-to-air process.

3.2.3.1.1 Using APPJ

The APPJ and 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. To generate and sustain the plasma, a sinusoidal high voltage (kV-range) with a frequency of typical 10 kHz (mid-range) was supplied to the system. The working or processing gas was pure nitrogen (≥98% purity) and the LLDPE pellets were exposed to the plasma in a glass tube shown in Figure 3.1.

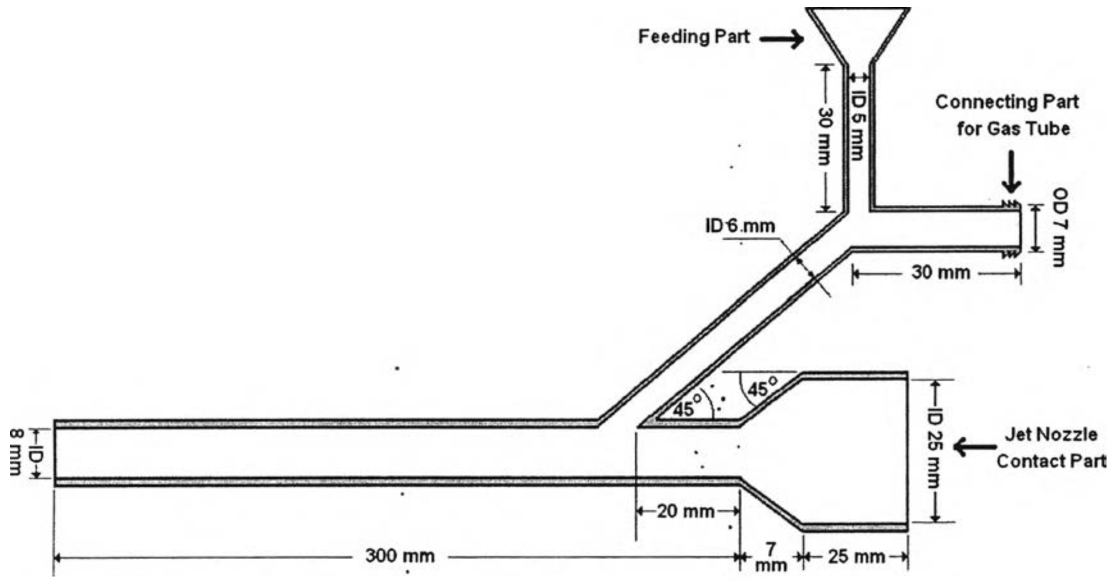


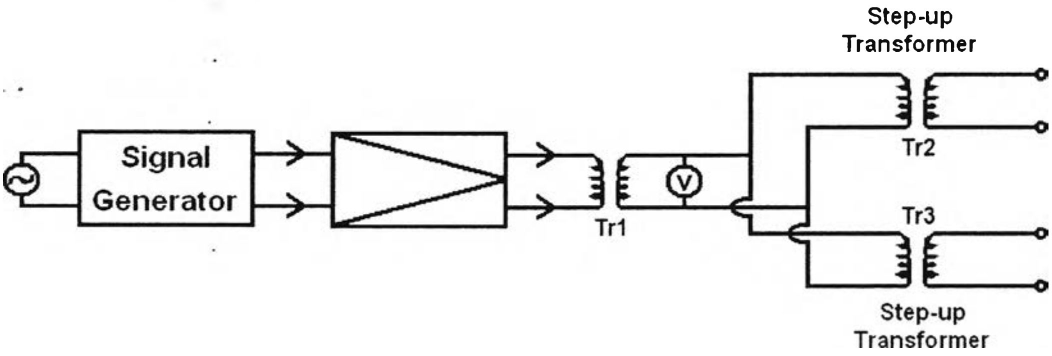
Figure 3.1 Glass tube reactor geometry for APPJ treatment of polymer pellets.

To prevent metastable quenching by oxygen that causes reduced jet lengths, the pellet must be purged by nitrogen gas and then fed to the treatment zone. The processing gas flow rate was varied as 7, 8, 9, 10, 15, 20 L/min. For feeding zone, the gas flow rate was varied toward 10 L/min. With 5.5 kV ignition-voltage, the applied jet-voltage amplitude was varied from 6.6, 7.7, 8.8 to 9.9 kV. At 9.9 kV a maximum power of 58 W was delivered to the plasma jet as measured via Tektronix TDS 7254 oscilloscope equipped with high voltage probe. The length of nitrogen plasma jet was verified as pictures captured by commercial CCD camera.

Sampling method of LLDPE pellet to be treated was controlled to be almost the same spherical shape and size (by weight), therefore; asymmetrical shape of pellet was ignored. The pellets were fed one by one at the pellet feeding part in Figure 3.1, then was purged and pushed by nitrogen gas. The assumption of zero initial pellet-velocity, no friction between the moving pellets and the tube surface was made. To define the plasma treatment time, the pellet velocity and the jet length was measured. Using projectile motion of the pellets come out of the glass tube, the pellet velocity could be calculated backward via the distance measurement as constant jet velocity throughout the plasma-jet volume was applied.

3.2.3.1.2 Using DBD

The DBD used in this research was developed in our laboratory. The electrode and the plasma treatment zone were designed accordingly to achieve the requirement of the treating process and the uniformly discharge. It was constructed regarding to surface modification application at atmospheric pressure using ambient air as a process gas. This plasma unit utilized a variable voltage control to be a power supply which consisted of the sinusoidal high voltage of 500 Hz as limited by step-up transformer used. With adjustable input voltage, it was able to control the output or voltage applied to the DBD. The ionized gas occurred in the space between two electrodes named discharge space where the treatment of pellets was. A schematic diagram of the power supply unit was shown in Figure 3.2.



Tr1 : Step-up transformer, V_{in} = 0-70 V, V_{out} = 0-220 V, 50 Hz

Tr2 : Step-up transformer, V_{in} = 0-230 V, V_{out} = 0-15 kV, 50 Hz

Tr3 : Step-up transformer, V_{in} = 0-230 V, V_{out} = 0-15 kV, 50 Hz

Figure 3.2 Schematic of high voltage power supply unit for DBD.

For treatment of LLDPE pellets, the pellets to be treated were assigned to flow through the plasma treatment zone by the gravity. Thus the treatment compartment was designed for vertically pellet feeding in and out the plasma treatment zone. Electrode geometry consists of a pair of plane parallel electrodes made of stainless steel with the dimension W x L was 7 x 100 mm. The gap distance between the electrodes was 7 mm to allow flowing of a normal commercial pellet. The dielectric material used as dielectric barrier was Polymethyl methacrylate (PMMA) sheet with 1 mm thickness. The dielectric barrier was placed adjacent to outer surface of both electrodes. The specific detail of DBD geometry for pellet treatment was shown in Figure 3.3.

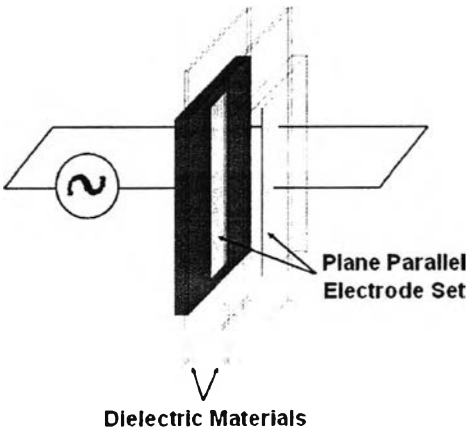


Figure 3.3 Electrode arrangement of DBD for pellet treatment.

The gas discharge behavior was investigated, without pellet treatment. Waveform of both current and voltage was captured using 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, electrostatic meter, type 2065, was used to evaluate the output voltage in root mean square, 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 could be comparable. The divergence factor of 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.

Intended for the application of treatment during the gravity-induced motion of pellets through the discharged region, it was necessary to study the effect of the voltage applied to the DBD. According to limitation of power supply, the applied voltage was varied from minimum that the glow-like discharge was observed, 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.

3.2.3.2 Treatment of LLDPE Films

The same of both power supply unit (Figure 3.1) and DBD geometry unit (Figure 3.2) as imposed for pellet treatment was utilized for the treatment of LLDPE film as well. Atmospheric ambient air was also used as a processing gas. The different procedure was the form of LLDPE to be treated. The film was fixed on the film holder to obtain the center alignment inside the treatment zone. Therefore, the effect of plasma treatment time was able to be investigated. Generally, 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 latency time or aging time). The applied voltage was varied within the same range as applied for the pellet treatment. 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 time to reach a steady surface in this work.

3.2.4 Continuous Reactive Processing of LLDPE

According to the originality of this work, the modification of LLDPE was purposed to be processed continuously. Therefore, the Collin® co-rotating type TWE model T-20 with screw diameter of 25 mm and L/D=30 was utilized as a continuous melt processing machine. Screw speeds were set at 60 min^{-1}. Temperature profile from feed zone through die zone was set as followed: 130, 150, 160, 170, 180, 190°C.

The low-dose chemical peroxide modification was performed in order to compare with the plasma-induced radical modification. As the chemical peroxide addition method was the important processing parameter, the solution of DCP in IPA was fed to the system when the resin was still solid LLDPE pellet. The volatile of solvent, IPA, provided the fine particle of DCP spraying into the solid LLDPE pellets. Thus the good dispersion and distribution of DCP was given by this peroxide addition method. The stock solution of DCP in IPA was prepared for a final content of 0.02, 0.06, and 0.1 phr to keep crosslink-free in a final product. The solution was then fed into the hopper of resin feed zone using the peristaltic pumping system.

3.2.5 Plasma-Assisted Continuous Reactive Processing of LLDPE

Plasma-assisted continuous modification of LLDPE was accomplished by the combination of plasma pre-treatment and continuous melt processing of polymer. To take the benefit from atmospheric ambient air as a process gas, the DBD device was assembled here as in-line pellet pre-treatment process. Inlet port of the plasma treatment zone was installed with motor-drive feeder allowing pellets to flow into and out of the treatment chamber vertically through the hopper of mentioned TWE. With gravity-induced motion, this electrode geometry provided 0.2 s of plasma treatment time. The distance between the outlet of plasma treatment zone and the screw of the extruder was set at 30 cm, corresponding to 0.2 s of the latency time in atmospheric ambient air which was defined as the interval time between the end of plasma treatment and the starting time of next process. The overall system was shown in Figure 3.4. Treated LLDPE pellet was immediately subjected to the twin screw extruder such that the molten macroradicals could modify throughout the bulk polymer materials. The voltage applied to the DBD was 8.3 and 9.0 kV. Additionally, a combination of plasma treatment and chemical peroxide system was investigated as well.

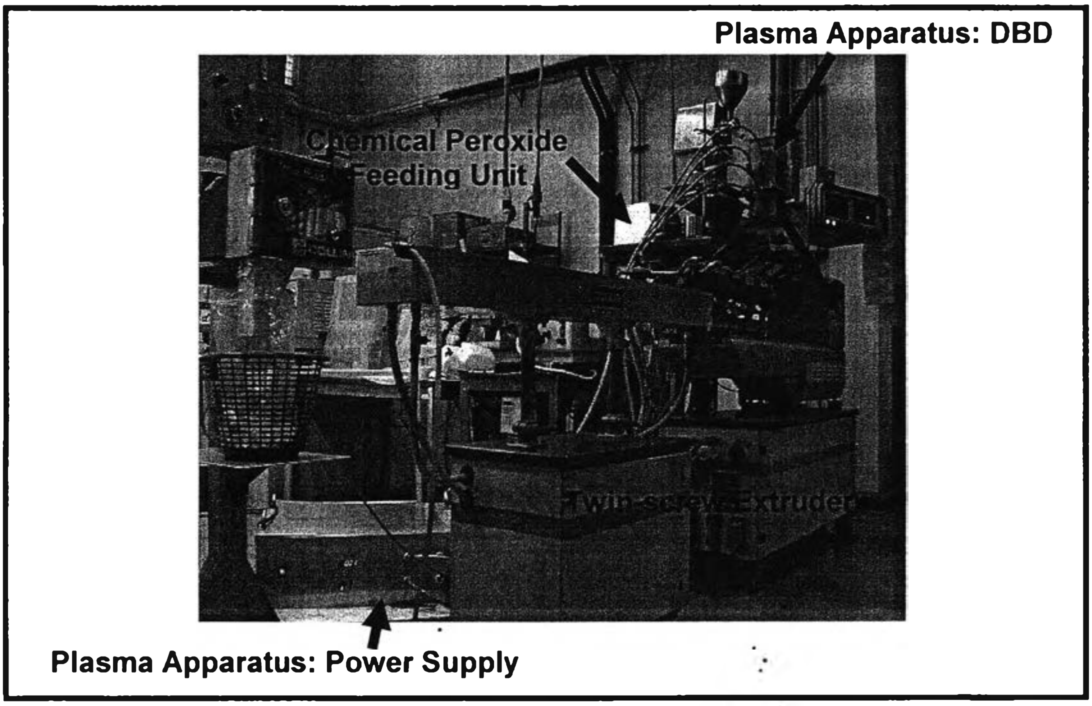


Figure 3.4 The setup of continuous plasma-assisted modification of polymer.

Moreover, the controlled run without any plasma or peroxide treatments was also performed to differentiate the effect of upstream plasma treatment and/or chemical peroxide modification. It was defined as shear modification and the sample was then labeled as shear modified LLDPE in this article.

3.3 Characterizations

3.3.1 Total Radical Concentration Measurement

For plasma surface treatment, the intermediate species revealed on the surface of plasma treated materials which are the radicals or further peroxides were determined in this work using the liquid-phase radical trapping incorporated with chemical titration method. The radical scavenger used was *1,1*-Diphenyl-*2*-picryhydrazyl (DPPH). The solution of DPPH in benzene with the concentration of 1.0 x 10^{-4} mol/l was prepared as a liquid phase radical detector. After plasma treatment and aging period, the plasma treated materials were kept in this solution at

70°C for 24 h to decompose the radical formed on and near the surface. After the radical trapping time, the treated materials were then removed out. The concentration of DPPH solution was measured using UV-visible light spectrometer. 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.

3.3.2 Fourier Transform-Infrared (FT-IR) Spectroscopy

Infrared analysis was performed in order to investigate the vibration and bending of the functional group existing for measured materials. The FT-IR spectrometer, Nicolet model NEXUS 670 IR, was employed for all tests. The range observed was 400-4000 cm^{-1} with 32 scans. Both transmission mode to examine throughout the sample and Attenuated Total Reflection (ATR) mode to examine only the sample surface were performed. The sample film thickness for transmission mode was 20-100 μm. For horizontal ATR-FTIR, the 45° of ZnSe window was used with multiple bounce corresponding to penetration depth of 0.5 – 5 μm. One side of the film surface was needed to be completely flat to the ZnSe window.

3.3.3 UV-Visible Light Spectroscopy

To investigate the absorbance of radiation in the visible light and UV regions of the films produced by blending of LLDPE and rubber, UV-visible light spectrometer, Perkin Elmer model lambda-10, in range of 200-800 nm was used with solid measuring set.

Moreover, other UV-Visible light spectrometers with liquid cell (quartz cell with 1 cm of absorption cell thickness), Shimadzu UV-2550, was used to measure the absorbance at the wavelength of 521 nm in order to evaluate the amount of DPPH consumed for total radical concentration measurement for plasma surface treatment. Another one which was utilized only for APPJ treatment of LLDPE pellets was Varian V-550 spectroscopy.

3.3.4 X-Ray Photoemission Spectroscopy (XPS)

To analyze the chemical elements on the surface, X-ray photoemission spectroscopy (XPS) was employed. The principle of XPS involved the irradiation of the solid in vacuum with monoenergetic soft x-rays such as MgKα and AlKα which the energy was 1.2536 keV and 1.4866 keV, respectively. The emitted electron was detected and sorted by energy. Due to the mean free path of the electrons was very small, the emitted electrons from that limited penetrating power photon originated from only the top few atomic layers. Therefore, XPS would be used to observe the chemical change of the LLDPE surface in this research. The spectral resolution was high enough to analyze such solid surface. The spectrum of each element had unique and the spectral peaks from a mixture were approximately the sum of the elemental peaks from the individual one. Synchrotron radiation at National Synchrotron Research Center, (Siam Photon, NSRC, Thailand) was utilized as X-ray source. The XPS station was kindly supported to examine the surface composition of both pristine and plasma treated LLDPE films.

For LLDPE films, the samples were attached on the sample holder with special care not to touch the sample surface. Most of the spectra were recorded using a monochromatic MgKα source. The spot size on the sample was approximately 350 µm FWHM. The pressure during XPS operation was controlled to be below 1.0 x 10^{-7} mbar. The relative atomic concentrations were calculated by VGscientific software.

3.3.5 Polarizing Optical Microscopy (POM)

Macroscopic morphology of the reactive blend films were observed using Leica DM RXP with magnification of up to 50. The polarized light from the xenon source was used with the reflection mode. The film samples were placed and fixed on the sample holder.

3.3.6 Scanning Electron Microscopy (SEM)

SEM, Jeol 5200, was used to investigate the surface morphology of the sample. In order to observe the phase morphology of the blended extrudates, they were cryogenic broken to avoid the phase change prior to extraction of rubber phase by soaking in toluene at 70°C for 24 h to swell, consequently the rubber phase was dissolved out. The extracted sample was then dried using vacuum oven overnight. However, in case of foam-like structure investigation of reactive blend extrudate, the rubber phase was not needed to be extracted since the structure performed as a composite of the blend matrix and air.

For the surface investigation of LLDPE film and DBD-treated LLDPE films, there was no specific sample preparation.

As non-conductive nature of those samples, they were then sputter-coated prior to the observation by gold at an argon pressure of 0.1 Torr for 4 min at a current of 10 mA. The micrograph was then captured using 10 – 20 kV of filament excitation at the magnification of 2,000 - 10,000.

3.3.7 Atomic Force Microscopy (AFM)

The AFM imaging was carried out using a Scanning Probe Micrometer (SPM), Digital Instruments incorporated with a Nanoscope IV software. Data acquisition was taken in tapping mode that mapped topography by lightly tapping the surface with an oscillating probe tip. The cantilever's oscillation amplitude changed with sample surface topography. The three-dimensional images were manipulated with the mentioned software. The scan size was 5 μm with scanning rate of 1.489 Hz.

3.3.8 Contact Angle Measurement

Static contact angle measurement using Krüss, model DSA 10, was also performed at ambient temperature to prove the occurrence of hydrophilic sites on the plasma treated surface of polymer. The DBD treated film was then kept in the ambient environment for about 15 min to set as a standard for contact angle measurement in this work. When reached the assigned interval time, the surface contact angle was then measured. To perform these studies, 10 μL sessile droplet of de-ionized water was then drop vertically by hand with a micro-syringe onto the film surface. The contact angles were measured five times and then averaged.

3.3.9 Differential Scanning Calorimetry (DSC)

DSC, Mettler 822 was employed to observe the T_m, T_c, heat of fusion of the LLDPE bulk modified with various methods. The sample of 4-8 mg was filled in 40 μL of aluminum pan and sealed with aluminum lid. To delete the thermal history, the sample was scanned as heat-cool-heat by heating from 25 to 150°C at 10°C/min, then was kept at 150°C for 2min to erase the thermal history. The second scan was cooling down to 25°C which T_c was obtained and then reheated to 150°C with 10°C/min. The T_m was given by the last scan. Moreover, the isothermal crystallization was done with the based resin in order to define as 100% crystallinity. The DSC program started with heating to 150°C and then cooling down to 102°C with the heating rate of 10°C/min. It was kept at this temperature for 6 h before quenched to room temperature and then reheated to 150°C. The heat of fusion obtained by this procedure was defined as heat of fusion at 100% crystallinity.

3.3.10 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were studied using a Dynamic Mechanical Thermal Analyzer NETSCH in the three-point bending mode for the analysis of bulk modified LLDPE. The storage modulus, loss modulus and tan delta were measured using amplitude of 60 μm. The frequency employed was 1 Hz. and observed temperature range was from -100 to 120°C for bulk modified LLDPE samples. The sample was prepared using Wabash® compression machine, model V50H-18-CX at 20 ton compression force. Specimens were then cut into the following dimensions: length 55-60 mm, width 10 mm, and thickness 3 mm.

3.3.11 Rheological Test

3.3.11.1 Oscillatory Rheometer

The viscoelastic characteristics of the polymers in the melt-state were measured with a rotational rheometer operating in the oscillatory mode. TA Instruments model AR2000 with parallel-plate fixture was utilized over the range of 0.01 – 100 s^{-1} of frequency sweeps at a strain level of 2%. Shear rate dependence of the viscoelastic properties such as the complex shear viscosity (η^*), the storage (G') modulus as well as the loss modulus (G'') was performed at 190°C. The sample was prepared using compression press machines with the mold thickness of 1 mm.

The diameter and the distance between these two parallel plates are 25 mm and 0.8 mm, respectively.

3.3.11.2 Capillary Rheometer

Capillary rheometer, Ceast Rheologic 5000, was employed in this work. The cylinder bore diameter was 15 mm. Maximum load was 40 kN. Pressure transducer was placed adjacent to the barrel surface. The test temperatures were 190, 200, and 210°C. The tests were done with 5 min of preheating period. A set of capillary dies with the die diameter of 1 mm was used (L/D ratio = 0.5/1, 5/1, 20/1, and 40/1). All die were flat or $\pi/2$ angle entrance. To obtain the real rheological data, both Rabinowitch and Bagley corrections were applied, consequently, the elongational viscosity was given as well. The extruded stand diameter was measured using Keyence VG laser analytical device comprising of a laser light source and a sensor. Moreover, the melt stretching united was employed at three different temperatures which were 190, 200, and 210°C in order to verify the melt strength using L/D ratio of 5/1. The melt stand distance to the torque measurement was 24 cm with the pulley diameter of 6 cm.

3.3.12 Melt Flow Index (MFI) Measurement

The weight-average molecular weight of a polymer was roughly estimated using MFI value. It was the only specification of melt consistency provided commercially. According to ASTM D1238, for polyethylene, a test temperature and total load were 190°C and 2.16 kg, respectively. The MFI tester, Kayeness Inc. Galaxy V, model 8052 equipped with MFI test set was employed for low-dose peroxide modification of LLDPE in batch process, otherwise using MFI tester, Zwick 4105. At least six runs were done and averaged to obtain the MFI value for each test. The bulky sample coming out of the mixture was ground into small pieces prior to the measurement. Linear regression method was used in order to discuss significance of the change of MFI. Individual data values (averaged) of each test were utilized for the statistical analysis in chapter VI.

3.3.13 Gas Permeability Test

The gas permeability tester, Brugger GDP/E, was used to evaluate the oxygen gas permeability through the plastic films. The circular film sample with 110 mm diameter was placed over the volume of 0.4370 cm^3 of evacuation chamber. The sample to be tested must have at least one smooth side which can be well sealed with the face of the evacuation chamber. The method V of ASTM D1434 was used as a standard for this test and the gas permeability was reported in the unit of $cm^3.mil/m^2.d.bar$. In our cases, the gas observed was oxygen with the mass flow rate of 100 cm^3/min. The films to be tested were prepared by compression pressing, Wabash® model, with 20 ton force at 190°C for LLDPE films. Preheating time was 5 min with another 10 min of compressed time. The film thickness was then in the range of 70-200 μm.

3.3.14 Density Measurement

The density of LLDPE bulk modified with various method were measured according to ASTM D792 at 27 °C using the density kit, Sartorius, model YDK 01 with 4 digits balance. The density of water at the measuring temperature was 0.9965 g/cm^3 as measured during the measurement. At least six runs were measured and then averaged to obtain the reported density.

3.3.15 Tensile Test

Tensile properties were obtained using Lloyd Instrument, LRX, Universal Testing Machine (UTM) according to ASTM D882. The non-orientated sample was prepared using compression machine, Wabash® model, with the same procedure of that of gas permeability measurement. Gauge length of 20 mm was set. Ten specimens were cut to the rectangular shape. The width range was 4.9-5.1 mm and their thickness ranges among 30 – 50 μm. Thickness was taken at three different places on the specimen and averaged for the calculation. Samples were carefully mounted straight and symmetrically in the grips of the machine and then were stressed at a constant strain rate of 500 mm/min until failure.