

CHAPTER IX
PLASMA-ASSISTED CONTINUOUS MODIFICATION
OF POLYETHYLENE

9.1 Abstract

The atmospheric pressure plasma dielectric barrier discharge (DBD) device was utilized as an upstream in-line process for continuous melt processing of LLDPE. The active sites on the treated surface resulted from plasma pre-treatment can be another aspect of polymer reactive processing as a source of radicals which performed well to initiate grafting, in melt state, or functionalization. The presence of both oxygen and nitrogen containing functional groups inside the polymeric bulk played a significant role on physical and mechanical properties of the bulk modified linear low density polyethylene. The superior tensile property and oxygen barrier property of film can be obtained by the 8.3 kV plasma-assisted modification of a given polyethylene. In our approach, the plasma-assisted continuous reactive processing technique represented the novel post-reactor modification, the so-called *In-situ* functionalization of polyethylene.

Keywords: Atmospheric pressure plasma treatment, Dielectric barrier discharge, Reactive processing, Polyethylene

9.2 Introduction

In general, a film processing involves uniaxial or biaxial stretching of the extrudate. High melt stretching as well as the least difficulty in production, e.g. by the use of very narrow die for extrusion, are needed to produce a continuous thin film with elevated mechanical properties. The property of molten polymer to indicate a high ability to be drawn or stretched is melt strength. This property can be enhanced in single step during the film production via reactive processing towards the generation of slight crosslinking or grafting structure (Graebing, 2002).

As a source of energetic radicals, the chemical initiators such as benzoyl peroxide and dicumyl peroxide are typically used in reactive processing techniques to modify properties of polymers. Nevertheless, for this work, we propose the physical supply of the radicals for reactive processing via plasma treatment on any particular gas media, especially atmospheric air. This new alternative method is a clean technique since there is no use of any hazardous chemicals. The principle of plasma phenomena and the interaction with the polymer solid surface have been published elsewhere (Fridman *et al.*, 2004). Plasma treatment has attracted more attention as a processing tool for surface modification in plastic industry nowadays. Commercially, plasma application on film production is for finishing purpose, i.e. to improve printability, adhesion, and wettability. The intermediate active species on the plasma treated surface are usually free radicals that readily react to ambient oxygen to form peroxides or other active oxygen-containing species. This brings to the motivating point of generating free radicals attached to the polymer pellets just prior to extrusion. The radical attached pellets are subsequently fed to the extruder, molten and performed as initiators (instead of chemical peroxides) for the continuous reactive extrusion. In this work, polymer pellets were designed to pass through the plasma device before melting in the extruder to stimulate the active surface sites. Therefore plasma technique utilized here can be defined as pre-treatment process. All runs were done in ambient air in order to keep continuous air-to-air process. Besides, the plasma reactive extrusion was carried out in comparison to the ordinary chemical (peroxide) reactive processing. The effect of reactive processing parameters such as

peroxide content in the case of ordinary reactive processing and applied voltage as an external plasma process parameter were investigated.

Characterizations of polyethylene modified with various routes were then done on the twin-screw extrudates.

9.3 Experimental

9.3.1 Materials

Linear low density polyethylene (LLDPE), DOWLEX 2047G, manufactured by The Dow Chemical Company (Thailand) was used. Its melt flow index (MFI), density, and T_m as provided by the supplier were 2.3 g/10 min, 0.917 g/cm³, and 125°C, respectively. The Dicumyl peroxide (DCP) was supplied by Aldrich. It was ground before using. *1,1*-Diphenyl-2-picrylhydrazyl (DPPH) to be used as a radical scavenger for radical measurement was from Fluka. Benzene was used as a medium for colorimetric chemical titration, Xylene with 99% purity was used for Soxhlet extraction, and Iso-propanol (IPA) was from Labscan Asia Co. Ltd. All chemicals were used as received.

9.3.2 Plasma Device and In-line Reactive Processing

The atmospheric plasma processing has been selected instead of low pressure plasma system due to the size independence of materials to be treated by vacuum chamber; thus the continuous process can be carried on. According to the overall process which was the combination of plasma treatment and continuous reactive processing of polymer, the appropriate plasma device to be assembled here was the DBD using ambient air as a process gas. The home-built DBD device was initiated and sustained by high electrical alternating current (AC) voltage with frequency of 500 Hz. The power supply unit and geometry of pellet treatment zone was described in Figures 3.2 and 7.6, respectively. The LLDPE pellets treated with various applied voltages, 8.3 and 9.0 kV were immediately subjected to melt processing using twin screw extruder such that the molten macroradicals can flow and thus the modification or functionalization on the polymeric chains can occur throughout the bulk polymer materials. Inlet port of the plasma treatment compartment was installed with motor-drive feeder allowing pellets to flow into and

out of the treatment chamber vertically through the hopper of twin-screw extruder, Collin[®] co-rotating type model T-20 with screw diameter of 25 mm and L/D=30. Twin-screw speed used was 60 min⁻¹. Temperature profile of the twin-screw extrusion from feed zone through die zone was set as followed: 130, 150, 160, 170, 180, 190°C. The distance between an 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.

Moreover, the low-dose chemical peroxide modification was also performed in order to compare with the plasma-induced radical modification as regarded to the originality of this work. The stock solution of DCP in IPA was used for a final content of 0.02, 0.06, and 0.1 phr to keep crosslink-free in a final product (Tasanatanachai *et al.*, 2008). The solution was then fed into the hopper of resin feed zone using the peristaltic pumping system. In addition, a combination of plasma treatment and peroxide system was investigated as well.

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

9.3.3 Fourier Transform-Infrared Spectroscopy (FTIR)

Infrared absorption analysis was performed using transmission mode of Nicolet NEXUS 670 IR spectroscopy to prove that the functional groups can be formed on the plasma treated surface and consequently could be incorporated into the bulk polymer via melt processing. The sample was prepared as a thin film of approximately 30 µm thick. To obtain the absorbance spectrum, it was normalized to the peak of C-H stretching at 2916 cm⁻¹.

9.3.4 MFI and Rheological Measurement

MFI tester, Zwick 4105, was employed with 2.16 kg at 190°C according to ASTM D1238. At least five runs were done and averaged to obtain the MFI value for each sample. The rheological test was performed using steady-state

capillary rheometer to represent the practical processing conditions. Ceast Rheologic 5000, with maximum load of 40 kN and 15 mm barrel diameter was used with three capillary dies of L/D ratios 5/1, 20/1, and 40/1. The tests were done at 190°C for rheological test. Moreover, melt stretching test which was environmental dependence was performed using die of 5/1 L/D ratio at 190, 200, and 210 °C. The extruded stand diameter was measured using Keyence VG laser analytical device.

9.3.5 Tensile Test

Tensile properties were obtained using Lloyd LRX, universal testing machine according to ASTM D882. The non-orientated sample was prepared using compression machine, Wabash[®] model, with the same procedure of that for 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 ranged 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.

9.3.6 Density Measurement

The density of LLDPE bulk modified with various method were measured using the density kit of Sartorius, model YDK 01 with 4 digits balance. The measurement was done at the temperature of 27°C corresponding to 0.9965 g/cm³ water density. Sixes runs were done for each test, and then averaged.

9.3.7 Gas Permeability Test

The gas permeability tester, Brugger GDP/E, was used to evaluate the oxygen gas permeability through the plastic films in this study. The circular film sample with 110 mm diameter was placed over the volume of 0.4370 cm³ 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 $\text{cm}^3 \cdot \text{mil} / \text{m}^2 \cdot \text{d} \cdot \text{bar}$. The films to be tested were prepared by compression pressing, Wabash[®] model, at 190°C with 20 ton force. Five minutes of preheating period with another 10 min of compression time were applied. The film thickness was then in the range of 70-200 μm .

9.3.8 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were studied using a Dynamic Mechanical Thermal Analyzer NETSCH in the dual cantilever mode. Specimens were of the following dimensions: length 55-60 mm, width 10 mm, and thickness around 3.0 mm. The storage modulus, loss modulus and tan delta were measured using amplitude of 60 μm . The observed temperature range was from -100 to 120°C and the frequency employed was 1 Hz.

9.3.9 Differential Scanning Calorimetry (DSC)

The enthalpic change of a sample was determined using DSC, Mettler 822. DSC calibrated with indium standard prior to use. The samples were first heated from room temperature to 150°C with 20°C/min and held there for 2 min to remove thermal history, then cooled down with 10°C/min to record the crystallization behaviour, and, finally, reheated to 150°C at 10°C/min to trace the melting behaviour. The melting temperature (T_m), and percentage of crystallinity was determined. and calculated from the density measurement of the specimens. 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 quenching 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.

9.4 Results and Discussion

9.4.1 Infrared Absorption Analysis

The surface radicals induced by plasma treatment tend to be very active; they can undergo various reactions and subsequently provide some changes on the modified materials as observed in FTIR spectra of plasma modified LLDPE, Figure 9.1.

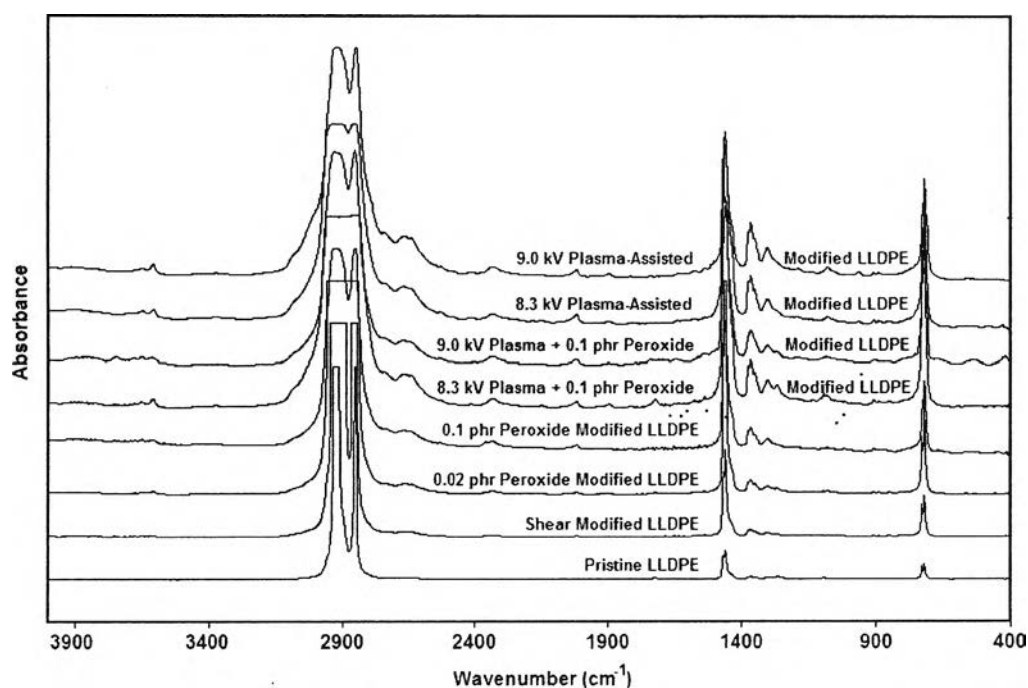


Figure 9.1 FTIR spectra (transmission mode) of pristine LLDPE, shear modified, chemical peroxide modified, plasma modified, and plasma+peroxide modified LLDPE in the range of 400 - 4000 cm^{-1} .

The functional groups which were mainly oxygen based could be formed due to the use of atmospheric ambient air as a process gas. Thus, the species considered regarding to humid air plasma were oxygenated and nitrogenated species (Rajesh *et al.*, 2003). The observed functional groups, such as C=O (carbonyl) in almost species at 1600-1950 cm^{-1} , C-OH (alcohol) at 3300-3500 cm^{-1} , H-C=O (aldehyde) at 2720 cm^{-1} , C-O-C=O (ester) at 1150-1270 cm^{-1} , C-O-O (peroxy) at 3300-3500 cm^{-1} , C-O-C (ether) at 1070-1275 cm^{-1} , H-O-C=O (acid) at 2500-3300 cm^{-1} , and HN-C=O (amide II) at 1475-1650 cm^{-1} were probably generated. In Figure 9.2, additional peaks with some broad bands at approximately 1670-1750 cm^{-1}

corresponding to carbonyl stretching can be clearly seen in plasma modified LLDPE. However, for plasma + peroxide modified ones, the peak corresponding to carbonyl group was insignificant. This was probably due to the tendency in peroxy formation as an evidence of significant absorbance at 3370 cm^{-1} .

Moreover, the characteristic peaks of nitrogenated functional group such as N-H stretching of amide and amine were presented at $3350\text{-}3500\text{ cm}^{-1}$. The peaks at 3370 and 3430 cm^{-1} belonging to O-H stretching in polymer was observed in the insertion of Figure 9.2. The corresponding peaks of O-H stretching were obviously seen at $3600\text{-}3700\text{ cm}^{-1}$ in Figure 9.2 as well.

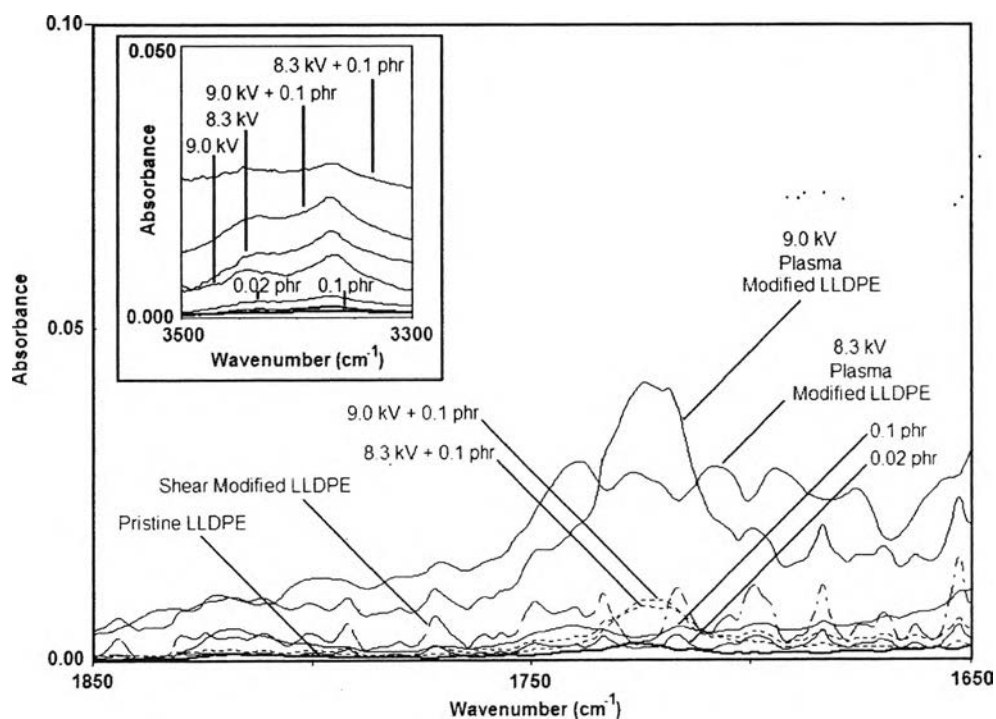


Figure 9.2 FTIR spectra of pristine LLDPE, shear modified, chemical peroxide modified, plasma modified, and plasma+peroxide modified LLDPE in the range of $1650\text{-}1850\text{ cm}^{-1}$ and $3300\text{-}3500\text{ cm}^{-1}$.

Since, the assumption of equals in sample thickness and weight was made, both shear and chemical peroxide modifications showed much less effect on the functional group formation. Therefore, the nitrogenated and mainly oxygenated functional groups observed inside the bulk polymer implies that the pre-plasma

process succeeds in transfer the free radicals to functionalize a polymer (LLDPE) during extrusion. The presence of these functional groups, mostly carbonyl group, provides the advantages for further interactions to other reactive species or becoming reactive sites on PE backbone. This approach is thus a potential clean and easy method to functionalize polyolefins to undergo a wide range of reactions, become compatible with other polymers, or improve specific properties.

9.4.2 Rheological Analysis

Figure 9.3 shows the MFI values of the modified LLDPE. MFI of the pristine LLDPE as measured in our laboratory was 2.13 g/10 min. Plasma treatment strongly influenced on MFI of modified LLDPE since they had lower MFI values than that of shear modified ones (0 phr DCP). When DCP was incorporated, MFI decreased rapidly and, as expected, the value got lower when increasing in DCP content.

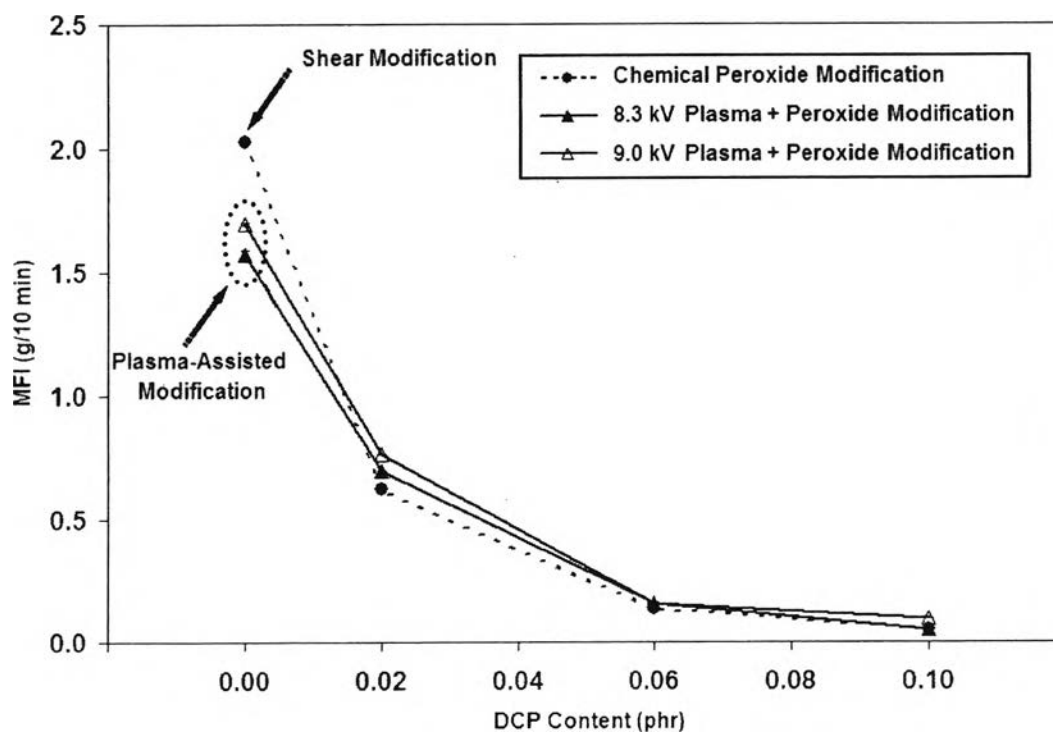


Figure 9.3 MFI of LLDPE modified with various methods as a function of chemical peroxide content.

However, at high DCP content, the effect of plasma treatment in the plasma+peroxide modified LLDPE did not play a significant role since the influence of chemical peroxide dominated. There was no gel formation or crosslinking occurred at all conditions used since nothing was left after Soxhlet extraction by refluxing xylene for 24 h. Thus, reducing in MFI was due to the strong entanglement caused by increase in branching and molecular weight, as evidenced by increasing flow activation energy, shown in Table 9.1.

It was recognized that the long chain branches (LCB) had an effect on shear flow which was a temperature dependence variable. Therefore, the correlation between $1/T$ of absolute temperature and the natural log of viscosity was illustrated in Figure 9.4. At fixed shear rate, $\ln \eta$ increased with $1/T$ by the non-linear relationship according to Arrhenius equation.

$$\eta = A \exp (E_a/RT)$$

Where A is the coefficient related to the melt viscosity and R is the universal gas constant, 8.314 J/mol K . The slopes of these plots would provide the activation energy for flow, E_a , as reported in Table 9.1. Increasing DCP content led to a large change in viscous flow activation energy for chemical modification. The higher activation energy derived in this results implied that the more LCB was presented, and hence, the appearance of branched structures restricted the flow (Dealy *et al.*, 1990). However, shear modification (0 phr of DCP) could not promote the detectable long-chain branched since the values was not significantly greater than the activation energy of based resin which, in this study, was 29.73 kJ/mol .

This was not really true for plasma assisted modification and plasma + peroxide modification. Both 8.3 kV and 9.0 kV plasma pretreatment (0 phr of DCP) could promote the change in molecular structure since the E_a were greater than that of based resin.

Table 9.1 Flow activation energy of bulk modified LLDPE measured at shear rate of 50 s^{-1}

Reactive Processing Parameters		Activation Energy of Flow
DBD (kV)	DCP (phr)	at Apparent Shear Rate of 50 s^{-1} (kJ/mol)
0	0	29.73
0	0	31.13
0	0.02	36.26
0	0.06	52.02
0	0.10	73.06
8.3	0.02	36.72
8.3	0.06	34.72
8.3	0.10	33.35
9.0	0.02	35.12
9.0	0.06	50.43
9.0	0.10	31.47
8.3	0	44.21
9.0	0	42.96

However, the values were fluctuated and tended to get slightly lower at high DCP content. The flow activation energy was the important molecular parameter to insight into the structure of polymers. Nevertheless, since LLDPE was modified with various methods, many different side-chain lengths and/or chemical molecular characteristic would be obtained. The plasma + peroxide modified LLDPE showed moderate structure heterogeneity due to the molecular structure changing with small chemical structure alteration. More heterogeneity was found for peroxide modified LLDPE as high E_a observed.

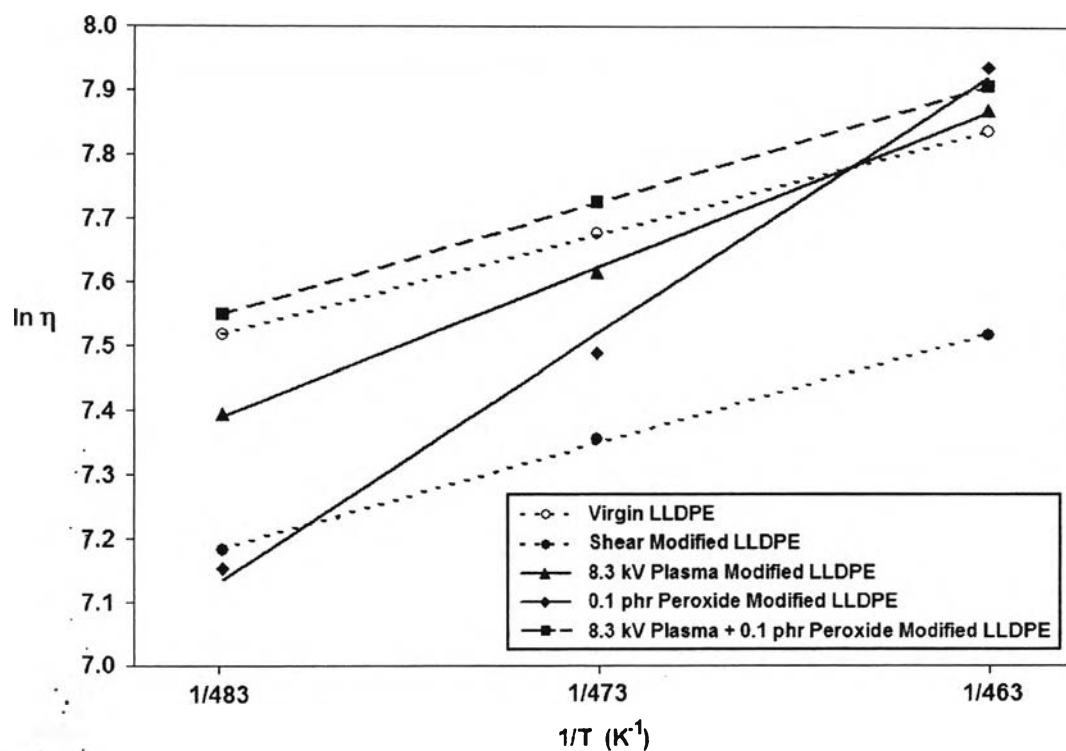


Figure 9.4 Arrhenius plot of bulk modified LLDPE.

Elongational viscosity plotted with elongational rate is shown in Figure 9.5. The higher in elongational viscosity could be attributed to grafting or slight crosslinked structure that was formed after plasma treatment (Bocok *et al.*, 2005). The elongational viscosity of 8.3 kV plasma modified LLDPE was comparable with 0.1 phr DCP modified one. Of course, both chemical and physico-chemical reactive extrusions showed greater elongational viscosity than that of shear modified and pristine LLDPE. The highest elongational viscosity occurred with the plasma+peroxide modified LLDPE.

In addition to grafting formation, it possibly attributes to the interaction among the functional groups induced via plasma treatment prior to melt mixing. This was confirmed by FT-IR spectra (Wu *et al.*, 2006).

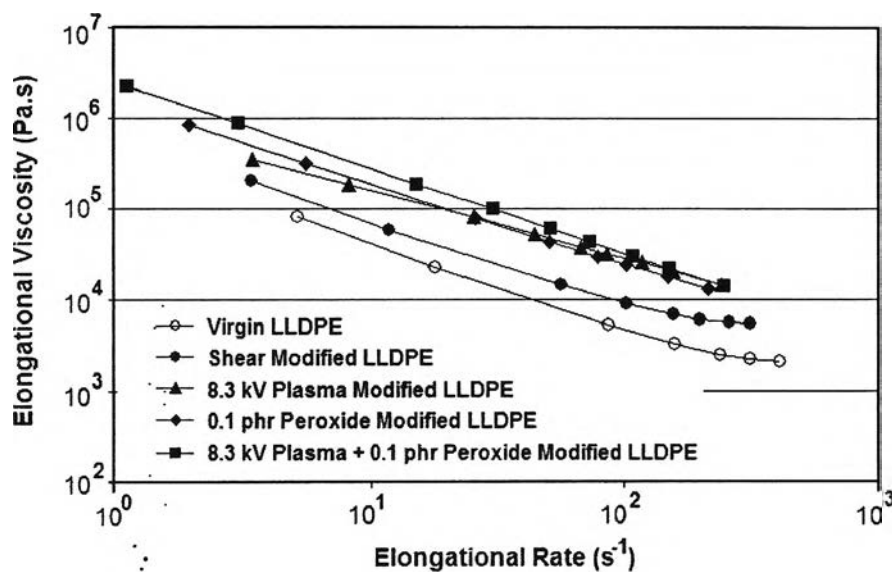


Figure 9.5 Elongational viscosity of virgin LLDPE and LLDPE extrudate modified with various methods. Condition for capillary rheometer: 40/1 L/D ratio of round flat-entrance die at 190°C.

Moreover, the melt strength were measured and reported as the melt stress at break according to three different temperatures, shown in Figure 9.6. In general, when increasing temperature, the molecular distance increases consequently reduces the molecular force and weakens the melt strength (Wong *et al.*, 1997). The experimental results indicated that, the melt strength increased with temperature. This was not as expected; however, it could happen depending on the conditions used. The initial values of the velocity and acceleration conditions were very important factors for the melt stretching measurement. The present results were obtained at the condition before the starting of melt fracture. The optimum condition for melt stretching measurement was the extrusion speed of 12.50 mm/s corresponding to 0.0555 g/min of apparent output flow at shear rate of 100 s⁻¹. The pulley start speed was 20 mm/s with 20 mm/s² acceleration. Since the tested

condition was fast, the diameter of extrudate stand was very little and it was solidified quickly. Thus, higher die temperature could keep longer fluid state of the extrudate. Moreover, increasing temperature reduced the melt viscosity and increased the melt coming out of the capillary die as the extrudate diameter slightly increased at comparable tension speed. The melt still flowed easily prior to solidification by environmental air, consequently provided the strain hardening due to the polymer chain orientation. On the other hands, this was explained as the pressure effects on the melt strength. Decreasing pressure as temperature increased can cause the melt strength to increase.

The LLDPE bulk modified with 8.3 kV air-plasma had the highest melt strength. This showed the contrary with elongational viscosity results since the melt stress at break of plasma+peroxide modified LLDPE was as low as peroxide modified LLDPE. This would be explained in term of the difference in molecular chain orientation of extentional flowing field and the shearing flowing field without extentional tensile stress (Rohn, 1995). Melt strength was the measurement of force applied to the extrudate during stretching under uniaxial stress until the melt broken up; hence, strain hardening had an effect on this result as well.

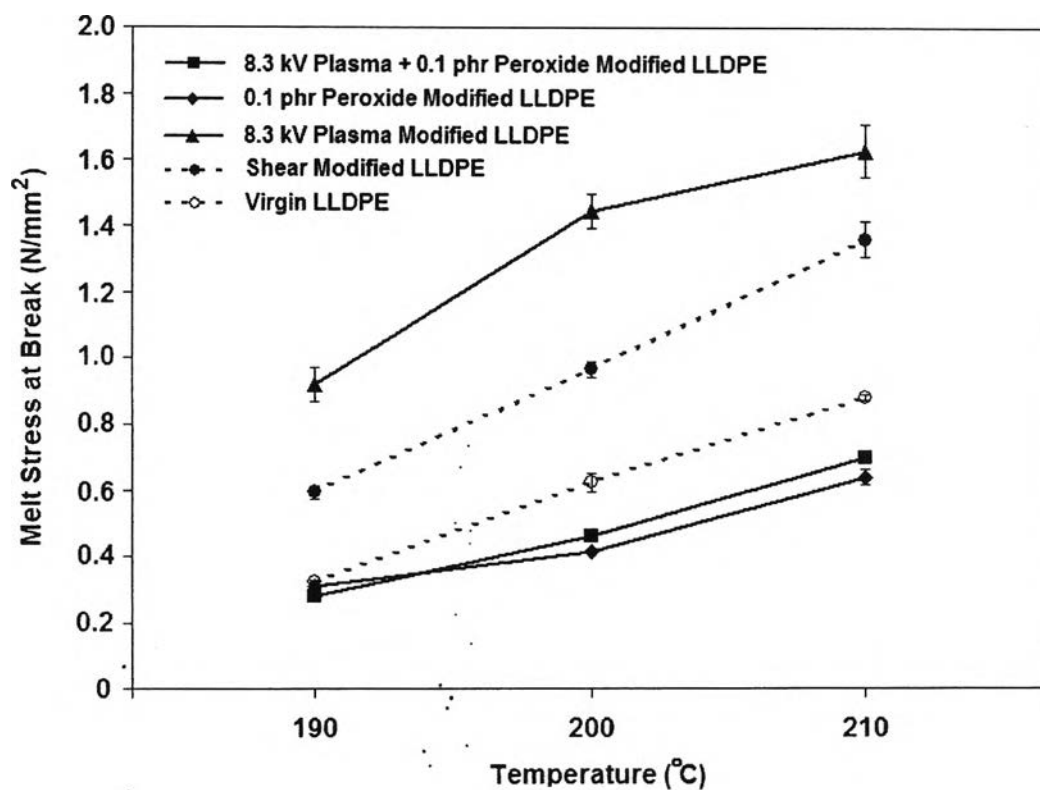


Figure 9.6 Melt stress of LLDPE modified with various methods. (Measurements were done using die of 5/1 L/D ratio at different temperature, 190, 200, and 210°C.)

Another viscoelastic property measured in this work was the extrudate die swell which was shown as percentage change in extrudate swell, Figure 9.7. Unsurprisingly, the swell ratio increased with real shear stress. The sample of LLDPE bulk modified with 8.3 kV plasma performed the highest of die swell at low shear rate implying to the highest elastic recovery among the sample group.

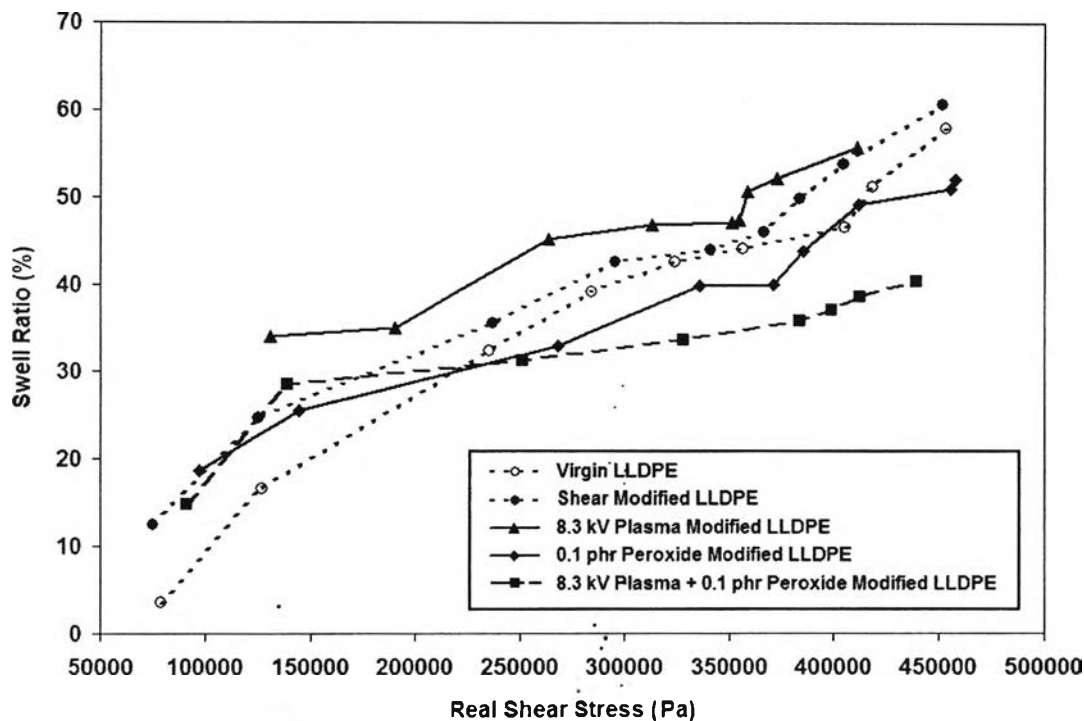


Figure 9.7 Extrudate swell ratio vs. real shear rate coming out of 40/1 L/D ratio at 190°C.

For the plasma + peroxide modified LLDPE, the dependence of die swell on high shear stress was less corresponding to the low elastic recovery. This was possibly due to some chemical interaction occurred with short chain branches under the shear field. Moreover, a greater number of branching obstructs swelling of the extrudates (Legendijk *et al.*, 2001).

9.4.3 Tensile Property

Basic mechanical property for a film application is tensile strength; therefore, tensile yield strength, Young's modulus, and % strain at maximum load were evaluated. Yield strength, the stress at which a material begins to deform plastically, of the non-orientated film was ranged from 10 up to 17 MPa as shown in Figure 9.8. The films of 8.3 kV plasma-assisted modified LLDPE performed the best tensile performance which was possibly affected by the relatively high solid density and % crystallinity as shown in Figure 9.12 and Table 9.2, respectively. In general,

the tensile properties, % crystallinity, and density should be in the same trend as they influenced concurrently. However, this conclusion cannot be applied for 9.0 kV plasma-assisted modified LLDPE since its yield strength and stiffness were higher but the density and percentage of crystallinity were lower than those of chemical peroxide modified LLDPE (0 phr DCP). Therefore, changes in molecular structure (branching) with small chemical structure alteration (the presence of functional groups) are not negligible explanation.

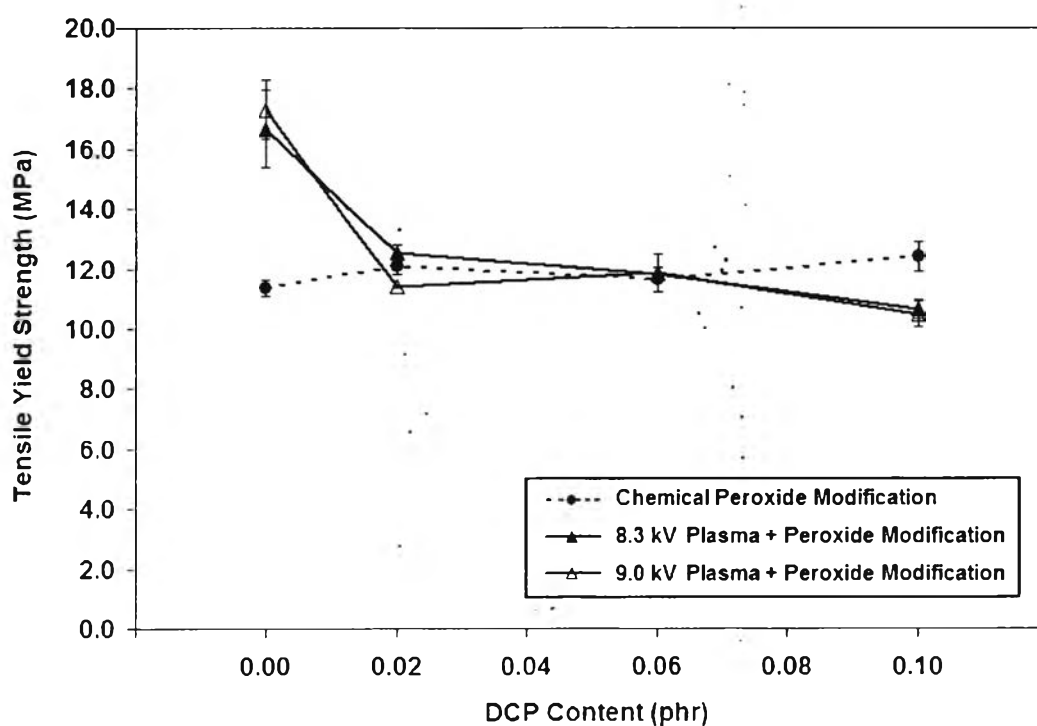


Figure 9.8 Tensile yield strength of bulk modified LLDPE measured according to ASTM D882 with the strain rate of 500 mm/min.

Young's modulus of LLDPE bulk modified with various methods are plotted in Figure 9.9. Modulus of elasticity which is defined as ability to carry stress without changing its dimensions could be referred to the stiffness of a material. It was found that the elastic modulus showed the same trend as that of yield strength. When DCP was incorporated during the modification, the content of chemical peroxide played a significant role on molecular characteristics, particularly at high DCP loaded.

Percentage of strain at a maximum load, shown in Figure 9.10, ranged from 1200 to 2200 %. The fluctuation of the strain is, in general, attributed to the variation of both ordering and disordering parts inside the bulk materials. Long chain branches existing in the LLDPE modified with 0.1 phr DCP, significantly increased the yield strength and stiffness, while decreased the percentage of strain a maximum load due to the entangled chains. Moreover, as the evidence by the increase in slope of the stress-strain curves before failure, in Figure 9.11, the strain hardening behavior or necking occurred with most samples. Since the strain hardening is controlled primarily by the orientation of the amorphous phase of entangled chains and the degree of branching, higher branching results in a higher rate of strain hardening.

As the results of superior tensile strength, modulus and percentage of strain of the films produced in this work, these modified LLDPE could be used in high-load film applications. Nevertheless, the excellence melt strength, as shown in Figure 9.6, and tensile strength of plasma-assisted modified LLDPE allows these given LLDPE to be processed and used as high-strength fiber applications.

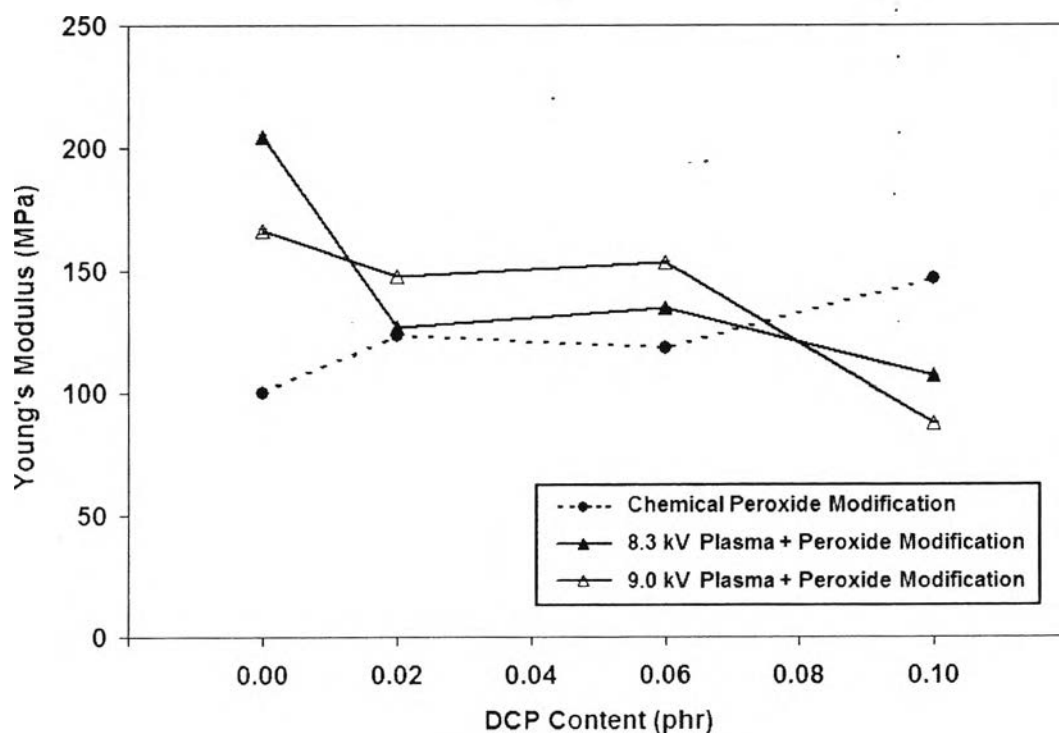


Figure 9.9 Young's modulus of bulk modified LLDPE.

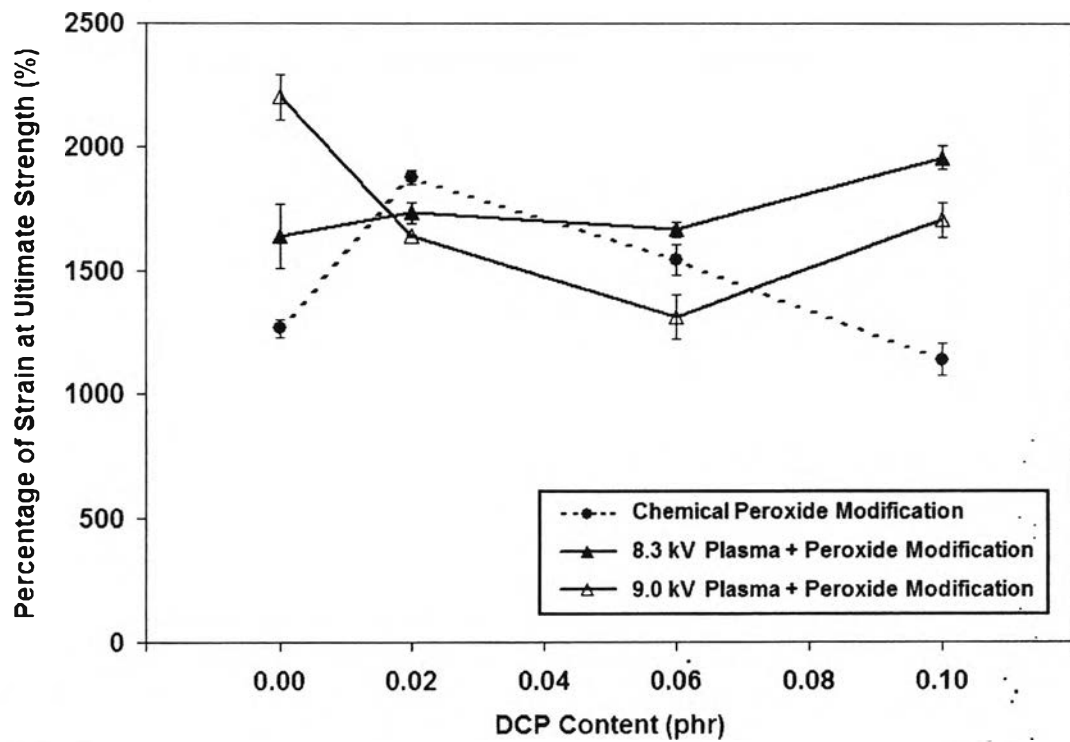


Figure 9.10 Percentage of strain at ultimate tensile stress of bulk modified LLDPE.

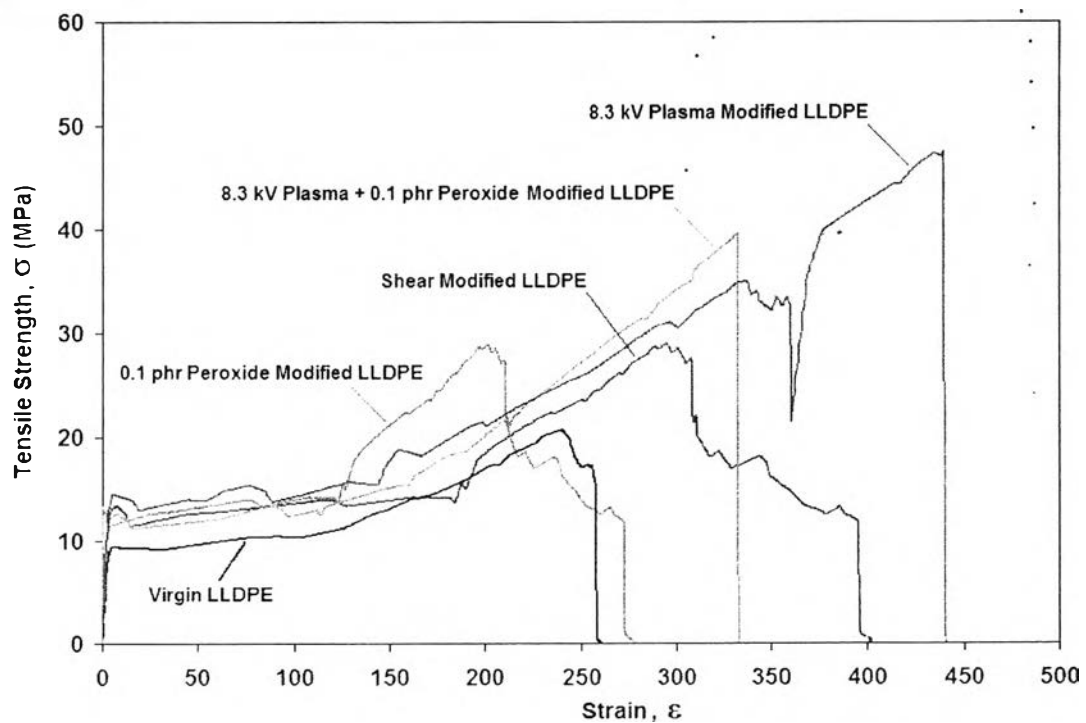


Figure 9.11 Characteristic tensile diagrams of bulk modified LLDPE.

9.4.4 Differential Scanning Calorimetry (DSC) Analysis

Heat of fusion of 100 % crystallinity of the raw resin was measured as 290.49 J/g. The melting temperature (T_m) and crystallization temperature (T_c) were determined, percentage of crystallinity were then calculated as compared to 100% crystallinity of the raw resin, the results were shown in Table 9.2.

The based LLDPE showed, as a certain type, two distinct melting peaks at 118°C and 123°C. This was explained by the presence of polymer fractions that had different degrees of short-chain branching (SCB). The highest melting temperature was due to the ethylene rich or relatively linear molecules crystallizing from the melt first, while the peaks occurring at lower temperature was due to the more branched species which crystallized at later stages (Cran *et al.*, 2005). The bulk modified LLDPE showed single broad endothermic curve with the range of melting peaks around 120°C – 125°C and the peak of crystallization temperature (T_c) ranges from 103°C – 108°C. These were implied that bulk modified LLDPE samples showed significant differences in their molecular structure, particularly in regard to the distribution of chain branching and proportion of polymer in each fraction of LLDPEs as reported by Shanks *et al.* (Shanks *et al.*, 2000). Since single melting peak was obtained in most samples and the lack of the second one (lower melting endotherm) in the bulk modified LLDPE was found, this could be associated with the influence in the crystallization process of the LCB entanglement or amorphous obstructing in the micro-phase segregated melt (Haigh *et al.*, 2000; Munaro *et al.*, 2008).

The highest in T_c of 8.3 kV plasma + 0.1 phr DCP modified LLDPE was, generally, resulted from the ease of crystallization process which probably provided the small crystalline size or ordering part, consequently caused lowest in T_m . This supports the hypothesis that the presence of an amorphous component or chain entanglement can either increase or decrease the tendency to crystallize depending on the branch characteristic such as branch length (Cran *et al.*, 2005). However, the conventional DSC technique demonstrates poor resolution yields curves that may have insufficient detail to enable the identification of an unknown LLDPE (Shanks *et al.*, 2000).

Table 9.2 Data of DSC measurement

Reactive Processing Parameters		DSC Measurement			
DBD (kV)	DCP (phr)	T _m (°C)	T _c (°C)	ΔH (J/g)	Crystallinity (%)
0	0	123	106	183	63
0	0.02	123	106	172	59
0	0.06	125	104	133	46
0	0.10	123	105	86	30
8.3	0	123	104	201	69
8.3	0.02	122	107	110	38
8.3	0.06	123	106	120	41
8.3	0.10	120	108	105	36
9.0	0	122	103	132	45
9.0	0.02	122	106	105	36
9.0	0.06	123	107	117	40
9.0	0.10	121	108	120	41

Increase in total amount of chain branching leads to the lowering of density in final products which is associated with the fact that the SCB is largely excluded from a crystal leading to a disturbance of the regular chain folding. Such disturbance leads not only to decrease in crystallinity, but it also increases the number of tie molecules created upon crystallization. Therefore, the lower % crystallinity is favored by the lower density with increasing total amount of SCB. However, the LCB may play an opposite effects on the crystallinity due to the long range of ordering part. Since the crystallinity of the bulk modified LLDPE were lower than that of virgin LLDPE, it was inferred that the change in crystallinity was dominated by chain entanglement as molecular defects rather than the long side chain effect.

9.4.5 Density

Figure 9.12 shows the solid density at 27°C of modified LLDPE. Generally, the density of semi-crystalline polymeric material depends on both amorphous and crystalline fractions. On the other hands, it is a sensitive probe of the organization of polymer chains within the solid. Interaction alignment of neighboring chains can be induced, consequently forms the crystalline structure (Bocok *et al.*, 2005). When the branches were long, they hinder the crystallization process, resulting in poor packing ability; consequently lower the density of the solid resin. The density of shear modified and plasma modified LLDPE had slightly drop from 0.917 g/cm³ to the range of 0.900 – 0.916 g/cm³. Increasing DCP content decreased the density as the occurrence of branch chains. However, the LLDPEs modified by DCP of 0.06 phr had higher density than expected, especially for the ones cooperating with plasma in-line treatment process.

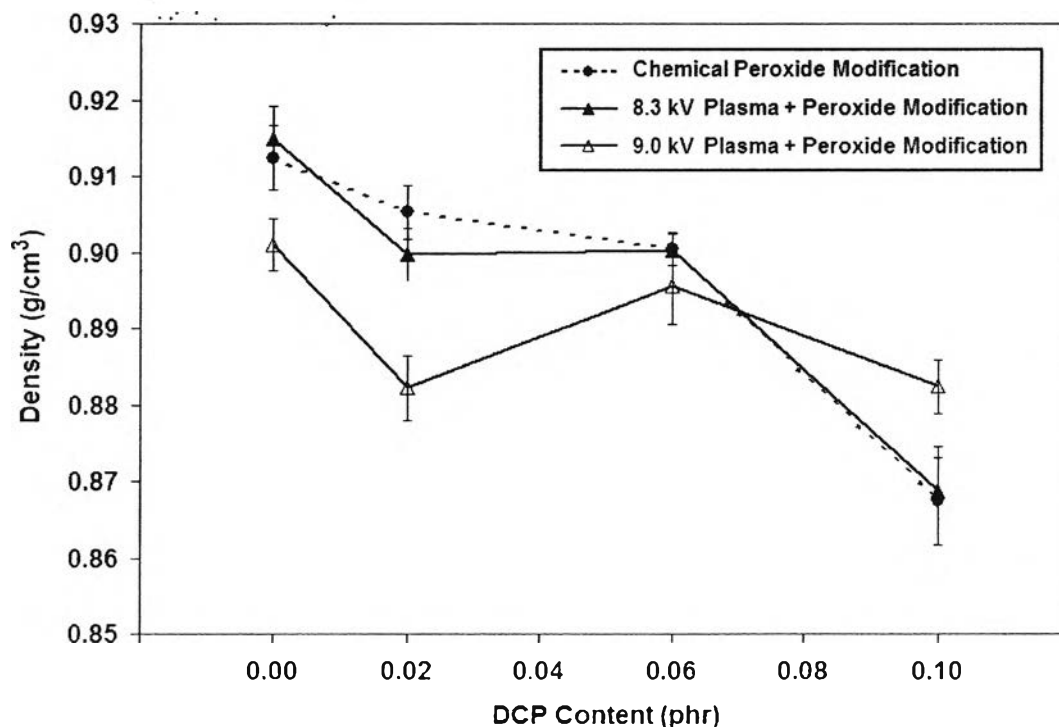


Figure 9.12 Density of LLDPE bulk modified with various methods. Measurements were done at 27°C.

Since the plasma-assisted modified LLDPE had some carbonyl groups, revealed in FT-IR results, these acted as defects on the molecules which discouraged molecular chain packing.

9.4.6 Gas Permeability

Another property that made LLDPE leading commodity plastic worldwide was the good barrier to oxygen gas. In this work, the main application point of view of the final products was packaging film. Therefore, the barrier property of untreated and LLDPE modified with various methods were investigated. The oxygen permeability result was shown in Figure 9.13. The undrawn film of based LLDPE had the gas permeability about $3,233 \text{ cm}^3 \cdot \text{mil}/\text{m}^2 \cdot \text{d} \cdot \text{bar}$. This value was quiet high due to non-orientation of compressed samples. However, both shear modification and chemical peroxide modification allowed larger volume of oxygen gas to pass through the film while the plasma modified LLDPE film showed the opposite trend. LLDPE modified by plasma pre-treatment reduced the oxygen to pass through to film about two times of that of virgin LLDPE. The influence of peroxide concentration fed during the processing on the oxygen permeability was clearly visible for the plasma + peroxide modified LLDPE. The higher amount of DCP was used, the lower oxygen barrier properties of the film were found. However, when plasma-treated LLDPE pellets was processed with low DCP content, 0.2 phr, the oxygen permeability of the film was much lower than that without plasma pre-treatment.

This may be due to the higher in branch density as corresponding to less free volume which obstructed the flow or diffusion of oxygen molecules through the films. On the other hands, more branches led to less free volume for oxygen to pass through. However, it showed opposite trend when the entanglement acted as defects obstructing the molecular ordering (Boersmaa *et al.*, 2003).

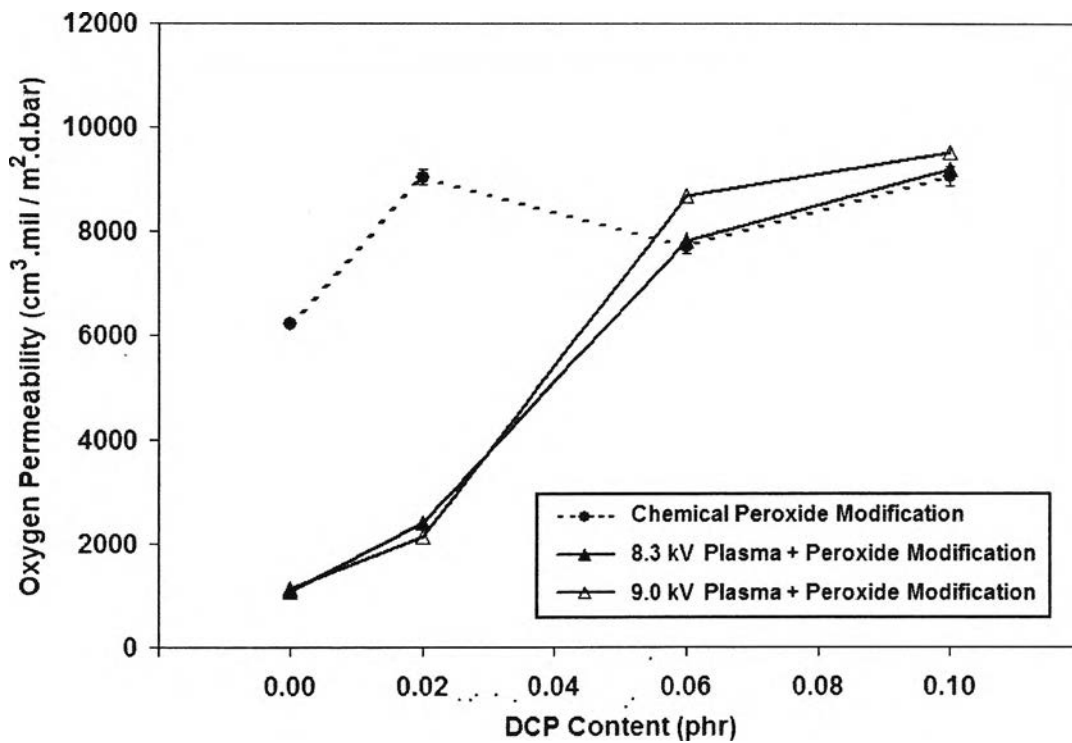


Figure 9.13 Oxygen permeability through undrawn films of LLDPE bulk modified with chemical peroxide or 8.3 kV plasma + peroxide modification.

It becomes clear that the mobility and solubility of the oxygen are very important parameters in the permeability of oxygen through the film. The magnitude of these parameters is governed by polymer–oxygen interactions. In general, the permeability is a function of the diffusion coefficient and the solubility of oxygen. Since the solubility depends on the chemical interactions between polymer and oxygen, it is expected that this parameter plays a significant role when oxygen-containing species are incorporated into the bulk LLDPE films. However, in the films containing some oxygenated functional groups which were the plasma-assisted and plasma + 0.02 phr peroxide modified LLDPEs, oxygen permeability was reduced. This is possibly due to the non-increase in solubility coefficient due to the lack of polar interactions of O_2 with the polar of carbonyl groups inside the bulk polymer (Marais *et al.*, 2002). Moreover, the functional groups generated on the plasma treated surface, as in FT-IR results, plays a significant role in the barrier

property. Such the corresponding peaks of hydroxyl stretching would be attributed to a distribution of intermolecular and/or intramolecular H-bonding, consequently stiffens the polymer chain and, thus, reduces the chain flexibility that makes difficulty for oxygen to diffuse through. However, if the oxy (-O-) bonds are formed, the polymer chains get relatively flexible which allows the gas molecules to diffuse easily.

A high degree of molecular packaging or high % crystallinity, provides the impermeability, so diffusion can only occur in amorphous domains or through structural imperfections. This is not really true for our results since, in addition to the crystallinity, the gas permeability is influenced by other parameters such as the molecular chain stiffness, molecular orientation, and free volume.

9.4.7 Dynamic Mechanical Analysis (DMA)

The dynamic mechanical results were obtained in terms of storage modulus (E'), loss modulus (E''), and $\tan\delta$. Figures 9.14 and 9.15 show the temperature dependence of E' and E'' , respectively. It can be observed that E' of LLDPE modified with 8.3 kV plasma treatment was greater than that of 0.1 phr DCP modified LLDPE and virgin material referring to the high chain stiffness of plasma-assisted modified LLDPE.

Bulk modified LLDPEs had lower E'' than pristine LLDPE at temperature range of -50 to 30 °C. This phenomenon was more pronounced in plasma-assisted modified LLDPE than in chemical peroxide modified LLDPE. All samples exhibited a β -transition in the temperature range of -30 to 0°C. This relaxation temperature has been associated with motions of branched chain units and of the chains contained in the partially ordered crystallite interface. The increase in the intensity and the shift of the location of the β -transition to a higher temperature could mean that the fraction of interfacial chains is increased and its mobility is suppressed. This behavior implies that at room temperature the plasma modified LLDPE performed better oxygen barrier as the chain mobility is less than others.

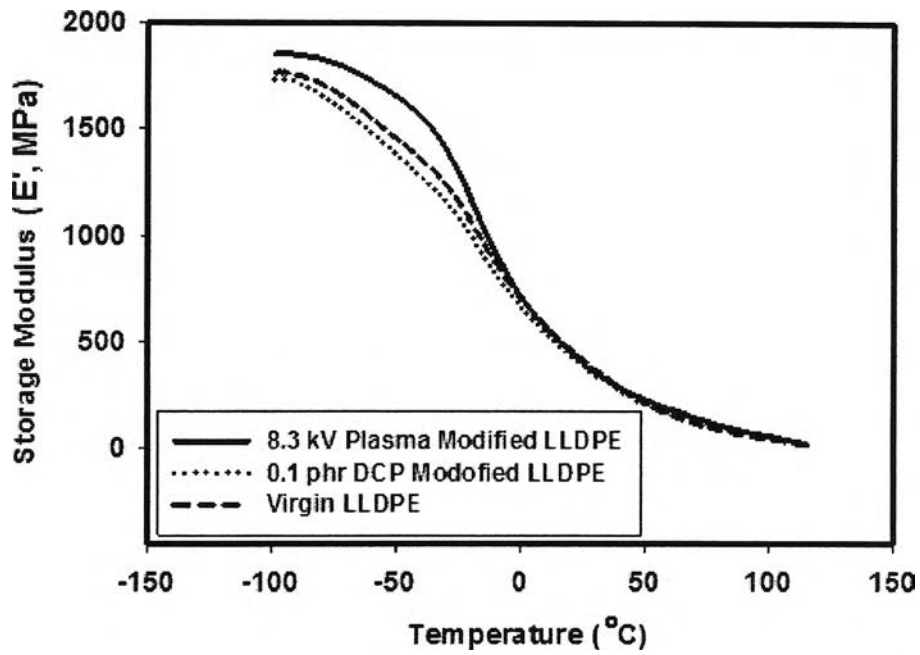


Figure 9.14 Storage modulus of virgin LLDPE, peroxide modified LLDPE, and plasma modified LLDPE.

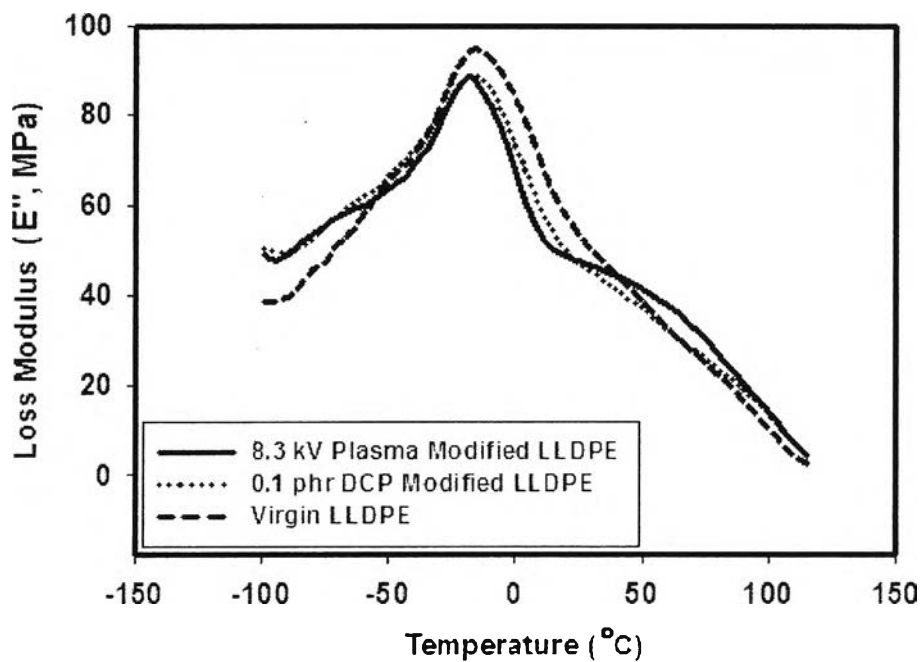


Figure 9.15 Loss modulus of virgin LLDPE, peroxide modified LLDPE, and plasma modified LLDPE.

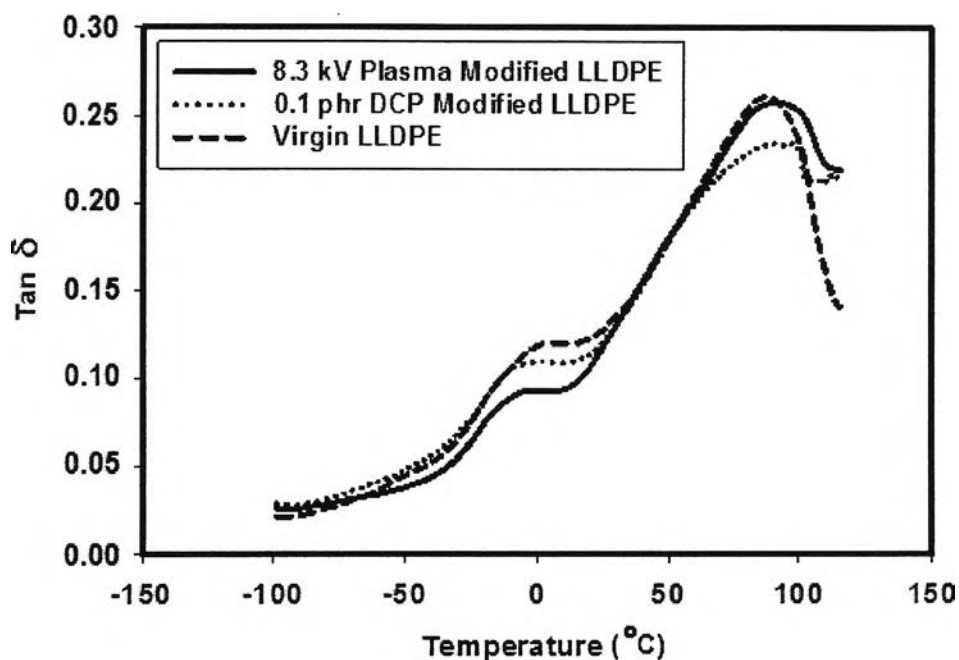


Figure 9.16 Tan δ of virgin LLDPE, peroxide modified LLDPE, and plasma modified LLDPE.

Typically, the stiffness of the materials can be described by either two characteristics (E' , E'') or $\tan\delta$. In Figure 9.16, $\tan\delta$ value at -50 to 40°C of plasma-assisted modified LLDPE was less implying that the molecular chain tended to restrict rather than flow or flex, therefore, allowed less oxygen molecules to pass through the bulk polymer. Another important transition revealing by $\tan\delta$ is α -transition, presented at the temperature range of 80 to 95°C. The α -transition peak of plasma-assisted modified LLDPE shifted to higher temperature which is contributed to the occurrence of difficulty in rotation or partial rotation of short molecular sequences in crystallite. On the other hands, it is primarily dependent on crystalline size and correlates with the degree of crystallinity as observed in Table 9.2.

9.5 Conclusions

The DBD device performed well to initiate grafting, in melt state, or to functionalize oxygen-based species on the polymer chain as confirmed by FT-IR spectra. The greater voltage applied to the DBD, the more content of functional

group was found as evidence of increasing in the absorbance. On the other hands, the chemical peroxide could not provide much of the functional groups inside the bulk modified LLDPE, especially for carbonyl containing groups. MFI values of bulk modified LLDPEs implied that the peroxide modification could alter the physical molecular structure rather than the chemical one which occurred predominantly for plasma-assisted modification. The molecular characteristics of polymer materials, implying from an increase in elongational viscosity and flow activation energy was long chain branching or graft structure which could be occurred during mixing in the presence of radical sites. The maximum of tensile yield strength, Young's modulus, the solid density, percentage of crystallinity, barrier property as well as melt elasticity occurred with the 8.3 kV plasma-assisted modified LLDPE. Moreover, the molecular chain stiffness at the service temperature was enhanced as observed by the DMA analysis. Therefore, the plasma pre-treatment is as good as using chemical peroxide to modify of LLDPE pellets by rendering the improvement in melt-strength as well as increasing in tensile properties. Since the plasma-DBD device developed in our laboratory was operated at atmospheric pressure using an ambient air as a process gas, it can be employed as an in-line continuous plasma-assisted polymer blending or recycling as well.

9.6 Acknowledgements

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