



## CHAPTER IV

### BREATHABLE FILM FROM REACTIVE PROCESSING OF LLDPE/NR BLENDS WITH ENR AND MALEIC ANHYDRIDE

#### 4.1 Abstract

The high oxygen permeability film, so-called breathable film, can be produced via reactive blending and processing of linear-low density polyethylene, natural rubber, and epoxidized natural rubber with small content of maleic anhydride as a reactive coagent. The foam-like structure of the produced breathable film was purposed by the reaction between the functional groups during the extrusion. Oxygen permeability of the blended films can be controlled by the blend compositions, screw speed, and draw ratio during the chill-roll casting step. The blended films exhibit not only the good breathability but also the outstanding UV screen-off with small transparency trade-off. These properties are suitable for the films to be used in agricultural applications to enhance the growing and production of fruit trees, flowers, vegetables, and even grains, especially during the growing stage of plants.

**Keywords:** Breathable film, Oxygen permeability, Natural rubber, Polyethylene, Reactive processing

## 4.2 Introduction

Polyethylene (PE) is the most universally used thermoplastic material in the agricultural section, especially in the film form. It is noticeable that many uses of agricultural film are for planting purpose which requires some properties to enhance the growing and production of agriculture products. One example of this function is being a barrier to liquids and insect attack while maintaining the gas permeability through pores. Generally, oxygen is needed because of high respiration rate during the growing stage of baby plants; therefore, the film with high oxygen permeability is a must.

The physical and mechanical merits of the product can be done easily by blending of polymers which results in rapid and simple way to develop new materials with low cost. According to the polymer blending principle, the hydrophobicity of the methyl backbone of PE can be compatible with natural rubber (NR), known chemically as 1,4-*cis*-Polyisoprene. Besides, their low surface tensions are relatively closed. NR is a natural polymer that is very flexible and prone to photodegradation and ozone attack while PE is more weather stability. Adding NR to PE could enhance degradability of the PE film. Many researches have investigated the blending of NR with PE for thermoplastic elastomer in term of stability and mechanical properties. The photo-oxidation stability of the NR/LDPE blend (70/30 wt%) systems was very rapid for the blends without stabilizer under tropical level of laboratory UV exposures (Bhowmick *et al.*, 2001).

Moreover, Ahmad, Sahrim *et al* studied the system of NR and HDPE with use of liquid natural rubber (LNR) as compatibilizing agent (Sahrim *et al.*, 1994) while Abdullah, Ibrahim *et al* (Abdullah *et al.*, 1995), and Dahlan, H.M. *et al* (Dahlan *et al.*, 2002) studied the NR and LLDPE blending system. They proposed that the active terminals of LNR was expected to induce chemical bonding within rubber phase and interfacial interaction between rubber and plastic phases which can significantly improve in physical properties of the blends.

In addition to LNR, the property of epoxidized natural rubber (ENR), epoxide-modified NR, was investigated in NR blending systems. The transport behavior, mechanical properties, the permeability of two types of gas which were

oxygen and nitrogen through the NR, ENR, and their blends were considered by T. Johnson *et al* (Johnson *et al.*, 1999; 2000). They had found that pure NR had been the highest oxygen permeable and the permeability of both gases decreased with increasing of the mole percentage of epoxidation. In all blends, the permeability of the blends to oxygen and nitrogen decreased with increasing ENR content. In the same manner, the solvent uptake decreased with increasing in epoxidation whereas no epoxidation or pure NR had the highest uptake. For the mechanical properties, ENR showed the good oil resistance, low nitrogen and oxygen gas permeability, strain crystallizing. Moreover, the reaction between epoxide group of ENR chain and acid group such as ethylene-acrylic acid was utilized as compatibilizing path to improve the miscibility in the blends (Sanjoy *et al.*, 1993). Therefore, ENR can be potential material to bring the excellent properties to the blend.

In this work, the blending of LLDPE and NR was carried out with high LLDPE content (80-90 wt%) and maleic anhydride (MA) was used as reactive agent to functionalize LLDPE and subsequently performed as the compatibilizer in the LLDPE/NR blending system. Moreover, ENR was used as a coagent or compatibilizing agent in this system due to the reactive epoxide group. Our approach is to make the breathable film via reactive processing of MA functionalized LLDPE and ENR in the rubber phase to give rigid crosslinked points that were hard to deform upon stretching. These rigid points were distributed in the melt extrudate and the by-product moisture added pressure to blow the film slightly and thus made the film foamed with structure of melt tearing opening the pores for oxygen permeability. The effects of processing parameter which were the blend compositions, screw speed, and draw ratio on film structure and permeability were investigated. Moreover, UV absorption of the blended films was determined as well.

### **4.3 Materials and Method**

#### **4.3.1 Materials**

Natural rubber, STR-5L grade, used as dispersed phase in the blends was obtained by Rayong Bangkok Rubber Co., Ltd. Epoxidized natural rubber with 50% epoxidization was kindly supplied from laboratory by KMUTT. For polymer

matrix, linear low-density polyethylene (LLDPE) of commercial film grade (DOWLEX 2045.11G) was supplied by Dow Chemical Company (Thailand). Its properties are also supplied from the manufacturer as followed: MFI = 1.0 g/10 min, density = 0.922 g/cm<sup>3</sup>, T<sub>m</sub> = 125°C. Maleic anhydride with melting point of 57°C was purchased from Acros company. All chemicals were used without further purification.

#### 4.3.2 Blends Preparation

For ease to process, NR was masticated on two-roll mill at ambient temperature before further used. The mastication time was 10 min and roller speed of 30 min<sup>-1</sup> was set with adjustable gap distance in the range of 5-10 mm.

Matrix of blend formulae was kept constant at 80 wt% of LLDPE and total rubber content including NR and ENR was 20 wt%, otherwise was stated. Small amount of MA used as reactive agent was 3 phr. Rubber phase was cut into small pieces and MA was ground before feeding to the mixer for ease of dispersion and distribution. All melt blending were prepared in 50 cm<sup>3</sup> of chamber volume of laboratory internal mixer, Brabender<sup>®</sup> W-50 with thermoplastic mixing head, with rotor speed of 50 min<sup>-1</sup>. The blending steps started with melting of a certain amount of LLDPE at 170°C for 3 min. MA was then added at 3<sup>rd</sup> minute before ENR was added by 6<sup>th</sup> minute and the blend had been further mixed for 3 min before the last ingredient which was NR was added at 9<sup>th</sup> minute. After that the blend was kept mixing for another 3 min to allow the uniform mixing. Therefore, the total mixing time was 12 min for reactive blending (LMEN). For binary and ternary blends which are non-reactive blending the mixing step was shifted up by keep interval time constant for each step resulting in 9 min of the total blending time. All runs were done under nitrogen atmosphere to avoid oxidation from atmospheric air. The blend then was removed from the batch mixer and placed on stainless steel plate with cooling down by ambient air.

#### 4.3.3 Twin-Screw Extrusion

To obtain better homogeneous mixing, the blend given by internal mixer was shredded into small pieces and kept over night in vacuum oven at 110°C

before passing through the Collin<sup>®</sup> co-rotating type twin-screw extruder, model T-20 with screw diameter of 25 mm. Two screw speeds, 80 and 90 min<sup>-1</sup>, were carried out. Temperature profile of twin-screw extrusion from feed zone through die zone was set as followed: 150, 155, 160, 175, 185, 195°C.

#### 4.3.4 Chill-Roll Cast Film Processing

The extrudate was further processed into the thin film by using single screw chill-roll cast film extruder, Collin<sup>®</sup>. It was equipped with a flat-slit die dimension of 0.8 x 250 mm. The screw speed used for this step was 40 min<sup>-1</sup>. The same temperature profile as imposed during the twin-screw process was used. The film was processed with various draw ratios that were 7, 10, 15, and 20.

#### 4.3.5 FT-IR Spectroscopy

Infrared analysis was performed with Nicolet NEXUS 670 IR spectroscopy to confirm the occurring of LLDPE-g-MA obtained by reactive blending. The range observed was 400-4000 cm<sup>-1</sup> with 32 scans.

#### 4.3.6 Scanning Electron Microscopy (SEM) and Polarizing Optical Microscopy (POM)

SEM Jeol 5200 were used and SEM micrographs were taken from cryogenically fractured surface of the blend processed by twin-screw extruder to investigate the morphology of binary, ternary, and reactive blends. According to the SEM principle, and non-conductive property of both LLDPE and NR phases, they were needed to be differentiated otherwise the phase difference cannot be observed. For that reason, the extraction of rubber phase was selected. The detail of rubber-phase extraction is as followed. The blend extrudate was kept in liquid nitrogen and then fractured immediately to avoid the phase change during the breaking process. Then they were kept 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 before sputter-coating with gold at an argon pressure of 0.1 Torr for 4 min at a current of 10 mA. as the final step for SEM sample preparation.

Moreover, the SEM was the method to confirm the foam-like structure of the cross-section of reactive blend extrudate. For this purpose, to observe the voids inside the blend, the rubber phase was not needed to be extracted. Furthermore, the appearance of breathable film was made out by POM, Leica DM RXP with magnification of 20.

#### 4.3.7 Density Measurement

Solid density of the films of LLDPE, binary blend, ternary blend, and reactive blend were evaluated according to ASTM D792 at 27 °C using the density kit, Sartorius, model YDK 01 with 4 digits balance. At least six runs were measured and then averaged to obtain the reported density.

#### 4.3.8 Gas Permeability Test

A 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 cm<sup>3</sup> 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 method for this test and the gas permeability was reported in the unit of cm<sup>3</sup>.mil/m<sup>2</sup>.d.bar.

#### 4.3.9 UV-Visible Light Spectroscopy

UV-visible light spectrometer, Perkin Elmer model lambda-10, in range of 200-800 nm was used to measure the absorbance of radiation in the visible light and UV regions. Samples were prepared as thin films. Moreover, to study the effect of NR content on the UV and visible light radiation absorption, the blend formulation of 90 wt% LLDPE and 10 wt% NR was prepared as well.

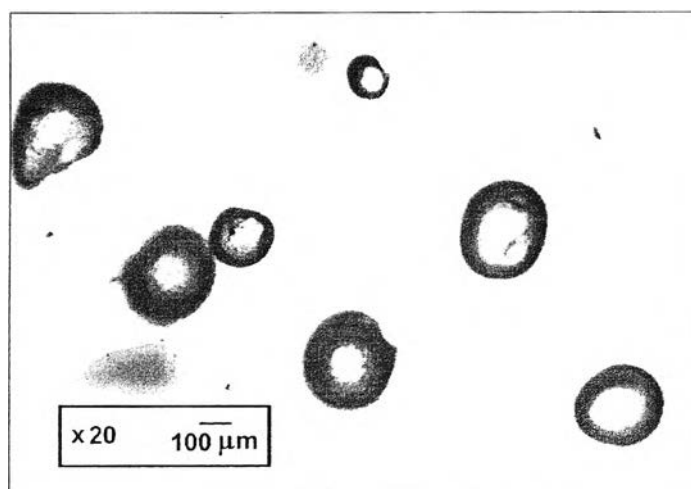
### 4.4 Results and Discussion

To understand easily, the sample with blend formulations and preparations will be symbolized by "LMEN s/d". The meaning of each are as followed: L =

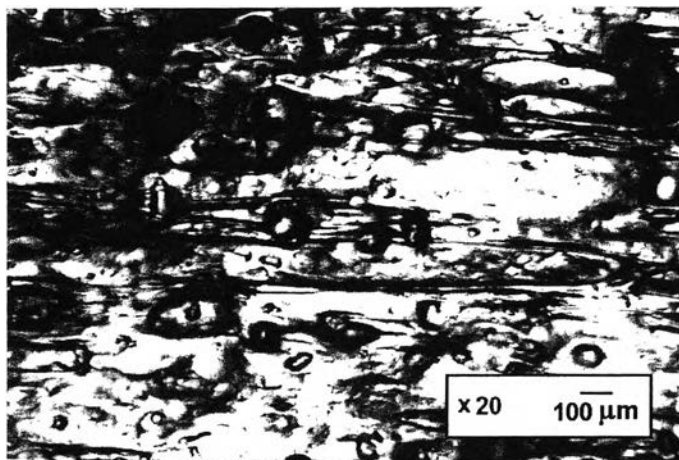
LLDPE, M = Maleic Anhydride, E = ENR, N = NR. Moreover, the order of the capital letters can notify the step of adding and mixing in the Brabender<sup>®</sup> internal mixer. The small letter “s” represents the twin-screw speed in the unit of  $\text{min}^{-1}$  and “d” represents the draw ratio of chill-roll casting step.

#### 4.4.1 Appearance of Film Products

The film products of basic binary blend were yellow, depending on rubber content, and the film containing ENR got a darker yellow. The films of LL (pure LLDPE), binary, and ternary blend sample types were solid homogeneous films but not for reactive blend film. The reactive blend film showed foamed structure (many voids inside, as seen by POM) with rather rough surface as shown in Figure 4.1. The film thickness was shown in Table 4.1. These average values were used to evaluate the gas permeability as well. According to the chill-roll casting procedure, the tension force is applied to process the extrudate into the film form. Therefore, the air bubbles or voids developed in the reactive blend extrudate were more clearly seen during the stretching process since the void expansion was occurred and the film thickness was reduced (Figure 4.1). The bubbles are well distributed, even though not uniform size, on the film making the rough path and so this interior structure is thought to be good for agricultural application such as wrapping the baby fruits or flowers to protect them from insect attack because of the voids and the rough path of the film may delay or lock up the intrusion of the insects.



(A) POM micrograph of LMEN before stretching.



(B) POM micrograph of LMEN stretching film.

**Figure 4.1** POM micrographs of the reactive blend before and after stretching.

**Table 4.1** Average thickness of the film products

Sample Type	Average Thickness ( $\mu\text{m}$ )	
	Draw Ratio = 15	Draw Ratio = 20
LLDPE	$92.50 \pm 0.79$	$85.00 \pm 0.35$
LN 80	$91.00 \pm 0.50$	$87.00 \pm 0.50$
LN 90	$79.00 \pm 0.35$	$74.00 \pm 0.35$
LEN 80	$81.50 \pm 0.35$	$70.00 \pm 0.00$
LEN 90	$78.50 \pm 0.50$	$72.50 \pm 0.50$
LMEN 80	$270.00 \pm 5.00$	$237.50 \pm 0.35$
LMEN 90	$270.00 \pm 0.35$	$200.00 \pm 0.35$

Density of uniaxial drawn films produced with two draw ratios are shown in Table 4.2. Since the films of LLDPE, binary, and ternary blends were solid homogeneous films, the density, as expected, increased with draw ratio. This was due to high stretching level during the chill-roll casting, which consequently facilitated the molecular chain packing. Moreover, increasing twin-screw speed also



affected the chain orientation because of more homogeneous blend can be obtained at higher shear rate. On the other hands, the voids inside the films of reactive blend significantly reduced the solid density. Use of high draw ratio during the production of reactive blend film decreased the density of the films because of the void expansions, hence; more empty spaces were inside the films. By comparison the density of a foamed film (LMEN) and a ternary blend film (LEN), the percentage of voids was then evaluated. The reactive blend films produced by both twin-screw speeds and both draw ratios had approximately the same percentage of voids which was 4% void inside the films.

**Table 4.2** Average density of the film products

Sample Type	Average Density (g/cm <sup>3</sup> )	
	Draw Ratio = 15	Draw Ratio = 20
LLDPE	0.920 ± 0.001	0.921 ± 0.001
LN 80	0.914 ± 0.002	0.916 ± 0.001
LN 90	0.916 ± 0.003	0.919 ± 0.002
LEN 80	0.914 ± 0.002	0.916 ± 0.001
LEN 90	0.915 ± 0.001	0.918 ± 0.001
LMEN 80	0.882 ± 0.003	0.880 ± 0.002
LMEN 90	0.879 ± 0.003	0.878 ± 0.002

#### 4.4.2 Throughput Rate

The output rates of the blend extrudate were determined at the processing time coming out of twin-screw extruder. The average value was calculated from at least 10 sampling. The extrusion output rate of binary (LN), ternary (LEN), and reactive blends (LMEN) are shown in Table 4.3. It was true that increasing in screw speed leads to increase in throughput rate; however, the different value of the throughput rate between two speeds of reactive blend was the least. This indicated that the reactive blend has its melt strength being improved significantly

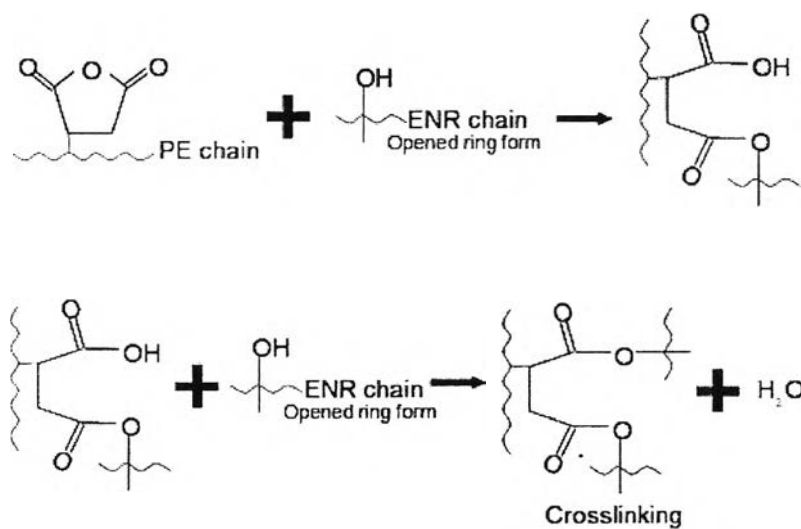
due to the occurring of slight crosslinking or grafting that makes some rigid junctions which are hard to break in the melt.

**Table 4.3** Average throughput rate determined at the processing time coming out of twin-screw extruder

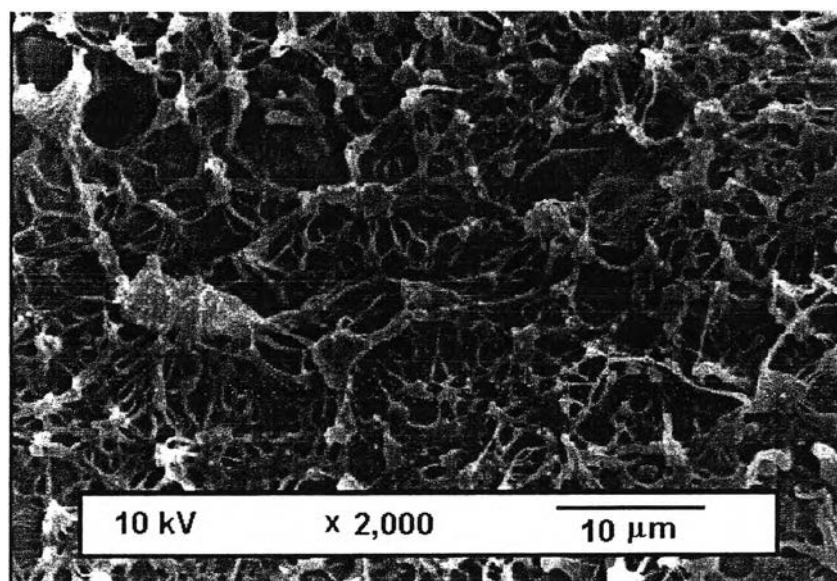
Sample Type	Average Throughput Rate (g/min)	
	Screw Speed = 80 min <sup>-1</sup>	Screw Speed = 90 min <sup>-1</sup>
LN	8.34 ± 0.07	9.95 ± 0.04
LEN	7.56 ± 0.06	8.25 ± 0.05
LMEN	7.23 ± 0.03	7.60 ± 0.04

Grafting of dispersed phase to the thermoplastic matrix (LLDPE) could promote interfacial adhesion and thus improved mechanical properties compared with mechanical blending without reaction. In this case, MA can attack to unsaturated bond of both PE chain and NR but it is more reactive to NR than LLDPE due to the nature of double bond available for the reaction; therefore, the initiating sites either at the LLDPE chain end or at the middle of LLDPE chain could further react with double bond of maleic anhydride. In our mixing step, hence, MA was allowed to react with melted LLDPE first to form LLDPE-g-MA. However, high shear rate under severe conditions, also known as shear modification, can break the polymer chain providing the macroradicals consequently to be the hydrogen abstracting species. therefore, maleic anhydride addition can occur along the polymer chain as well. MA grafted on LLDPE chain was then obtained and prompt to react with ENR. The remaining MA could react finally with NR and form the grafted polymer e.g. NR-g-MA (which also become compatible with ENR). As no initiator or peroxide added in the system, the possible reaction might not cooperate with the succinic route. The Diels-Alder reaction would be the key route for this addition reaction. The '*in situ*' LLDPE-g-MA, ENR-g-MA were expected to occur and ultimately '*in situ*' LLDPE-g-MA-ENR by reaction between maleic anhydride and epoxide group was generated and could react further to form crosslink junctions,

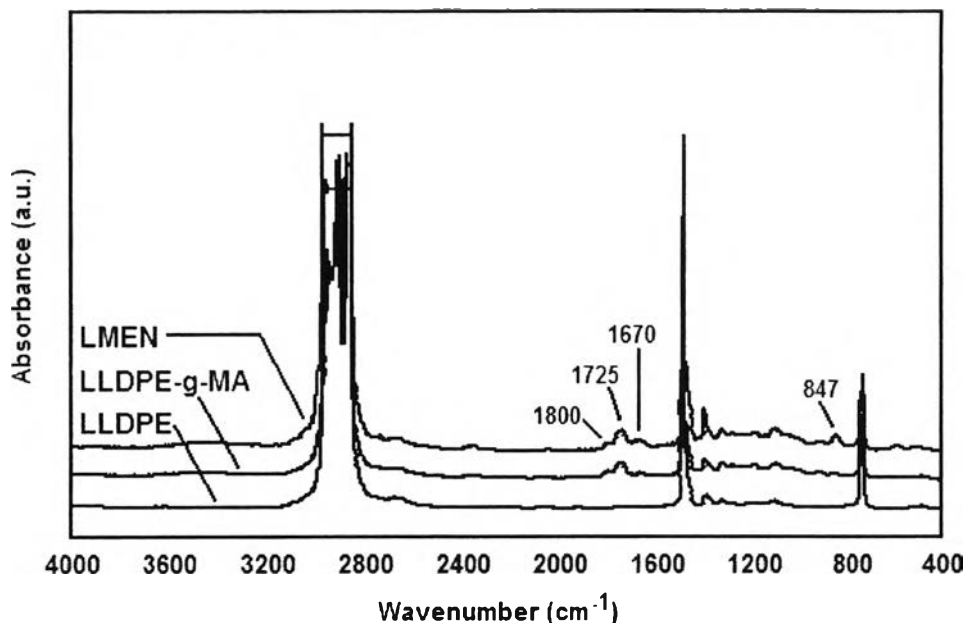
together with water as a by-product that was released out as demonstrated in Figure 4.2. The reaction can move forward as water was removed. As a result, upon stretching (drawing) the melt was broken but not the rigid crosslink junctions, see Figure 4.3.



**Figure 4.2** Possible reaction of LLDPE-g-MA and ENR to obtain H<sub>2</sub>O as a by product.



**Figure 4.3** Cross-sectional SEM micrograph of the LMEN non-extracted extrudate with 90 min<sup>-1</sup> twin-screw speed.



**Figure 4.4** FT-IR spectra of LLDPE film, LLDPE-g-MA, and LMEN.

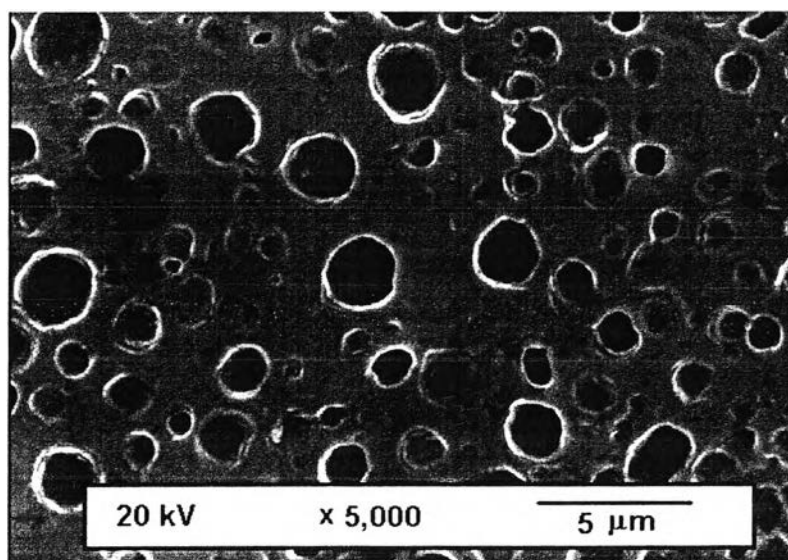
Figure 4.4 shows the FT-IR spectra of LLDPE, LLDPE-g-MA, and LMEN. Comparing with the spectra of LLDPE, the spectra of the MA grafted LLDPE showed characteristic peaks of saturated ring anhydride. The bands at  $1800\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$  were due to symmetrical and asymmetrical stretching of  $\text{C}=\text{O}$ , respectively. For reactive blend film, in addition to the mentioned peaks, the band with medium intensity at  $847\text{ cm}^{-1}$  was observed as it indicated the angular deformation of OH.

The foam-like structure of the extrudate was finally obtained with the LMEN sample as seen in Figure 4. In other words, for the reactive blend containing MA and ENR, the voids or air bubbles inside the blend are expected to generate by (i) water releasing due to the reactions between MA and hydroxyl groups which occur by moisture-sensitive opening of epoxide groups as proposed in Figure 4.2. Since ENR is very sensitive to moisture, moreover, one has to take the bound water molecules into account. The water, or further steam at the process temperature, is rather difficult to vent out of the high viscous polymer matrix. Moreover, the processing equipment used has no the venting port, these steam is still trapped, consequently leaved the voids inside the matrix. (ii) Another possible aspect of void

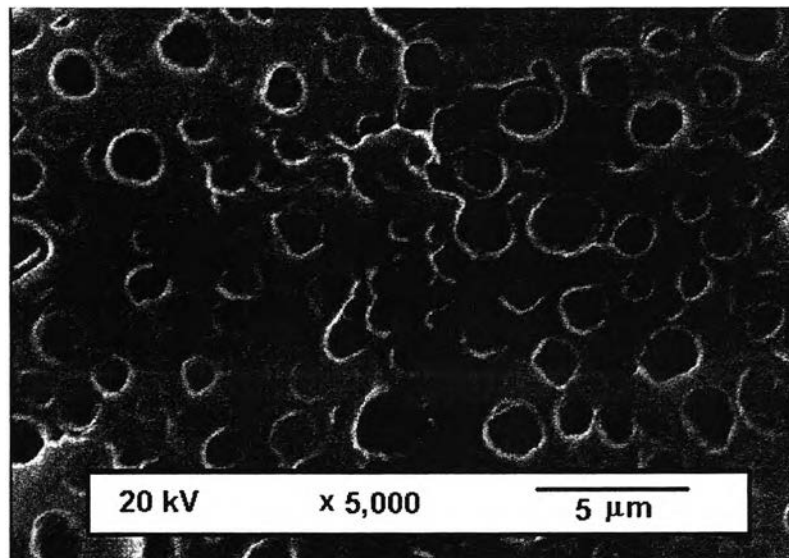
existing is from the effect of difference in physically interaction force during the stretching process. Chemical linkage as grafting or crosslinking and/or physical tie can act as rigid regions. According to tension force contributed during the drawing in chill-roll casting process, the softer regions which were easier to break than the strong ones initiated the empty space first following by void expansion during stretching.

#### 4.4.3 Morphological Examination

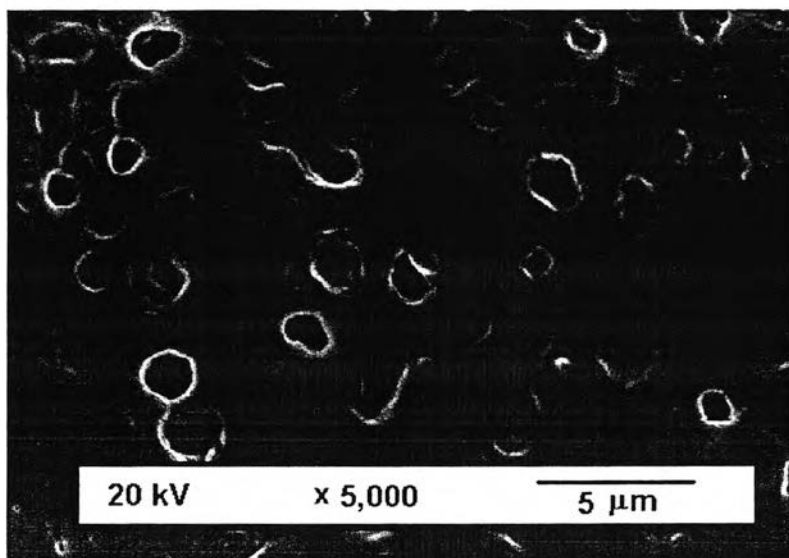
SEM micrographs in Figure 4.5 showed the morphological development of binary, ternary, and reactive blends. It can be seen that the dispersed domain sizes became a little finer and their distribution became narrower. These were due to the '*in situ*' formation of a graft copolymer which acted as a compatibilizer to reduce interfacial tension. The reactive blend micrograph showed the less extraction due to the existing of graft copolymer whose not all molecular chains were extracted out of the matrix. Some segments still appeared implying to occurrence of better adhesion between the blend components. Nevertheless, the empty spaces existing prior to toluene extraction were another aspect of difficult-to-defined boundary.



(A) LN



(B) LLEN



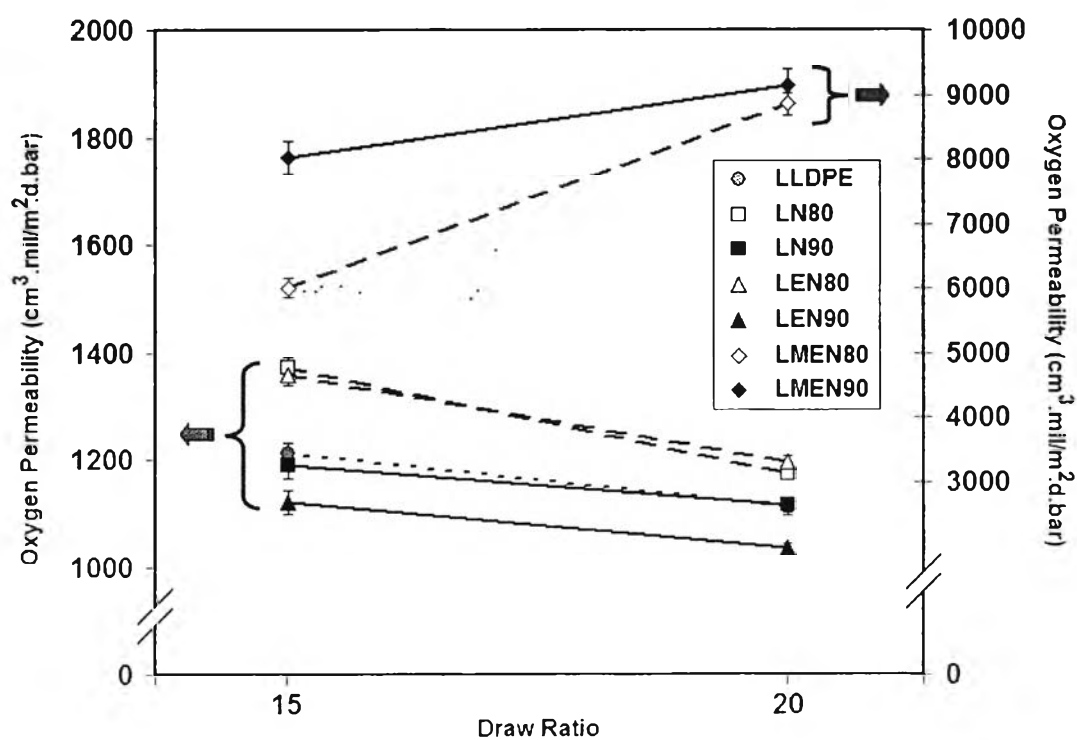
(C) LMEN

**Figure 4.5** SEM micrographs of toluene extracted blends produced by twin-screw speed of  $90 \text{ min}^{-1}$ .

#### 4.4.4 Gas Permeability

The films produced by our process showed that, as seen in Figure 4.6, increasing in screw speed of twin-screw extruder resulted in lower oxygen gas permeability for binary and ternary blend films whereas the reactive blend film performed the opposite trend. This is because more uniform blends were given at higher shear rate. Generally, the permeability of plastic depends on crystallinity,

molecular orientation, molecular chain stiffness, etc. (Feldman *et.al.*, 2001) It is proved principally that higher crystallinity, molecular orientation, molecular chain stiffness leads to lower gas permeability like in this work. The lower in oxygen permeability by the increase in molecular orientation as drawing increase was for solid homogeneous films. In contrast, more bubbles were generated in the reactive blends as increasing screw speed. Once the empty space is formed, these voids can facilitate gas permeability.



**Figure 4.6** Oxygen permeability of pure LLDPE, binary, tertiary, and reactive blend films.

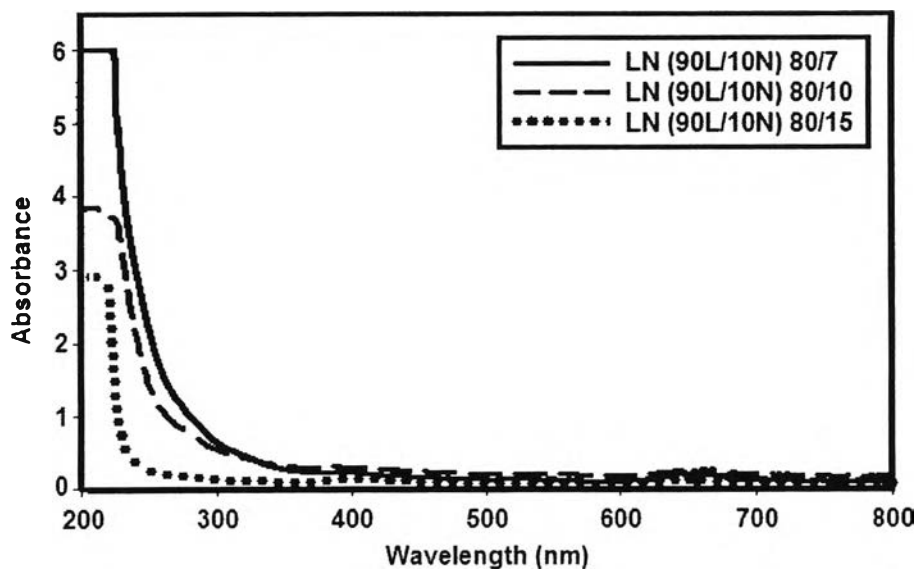
Moreover, increasing in draw ratio leads to void expansion in general and, for the breathable film, this is the advantage from this technique of making reactive blends.

#### 4.4.5 UV-Visible Light Spectroscopy

It can be observed from Figure 4.7 that the blended films with 10 wt% NR were transparency to visible light but when increasing NR content, the

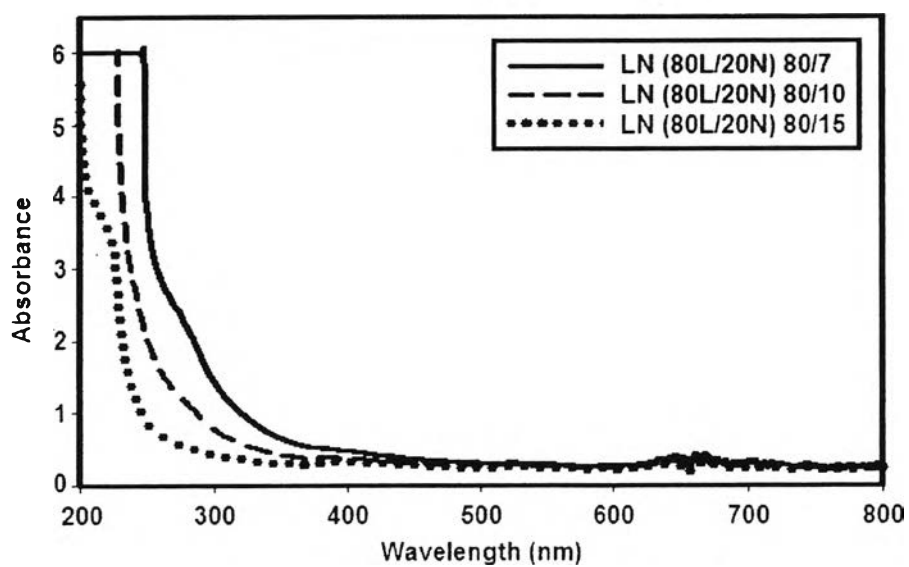
transparency became less which was dependent on draw ratio. The more NR cooperated in the film, the more absorption and the more shift to longer wavelength. When the draw ratio increased, the decreasing in absorbance revealed. This is because smaller size of crystalline structure formed when increasing the draw ratio provides less scattering and then the film is more transparent, especially for blend with low NR. In other words, the higher drawing ratio made the more transparent film and shifting the absorption to higher energy revealing the stronger chain orientation. However, drawing ratios of 7 and 10 were suitable to absorb UVA and UVB. The reactive blend LMEN films made from three draw ratios permitted the similar absorbance of UV light region revealing that increasing drawing had small effect on chain orientation due to the rigidity of crosslink junctions to limit molecular motion. The absorbance increased significantly with the higher rubber content (LN 80 twin-screw speed type). This can confirm that NR was a good UV adsorption material thus the reactive film is possibly easily degraded by UV light or more environmental friendly. Reactive blend film allowed longer wavelength transmission thus reactive blend film can screen-off shortwave UV that is harmful to living organisms. Moreover, the structure of foamed film may lead to scattering of radiation as noticeable is Figure 4.1. This can be so-called physical screen-off which can attenuate a radiation beam after reflection from the sample surface. In addition, the other blend films can be photodegradable materials as the absorbance occurred at the wavelength lower than 300 nm. This suggested that binary, ternary, and reactive blend film products can support growing stage of baby plant.





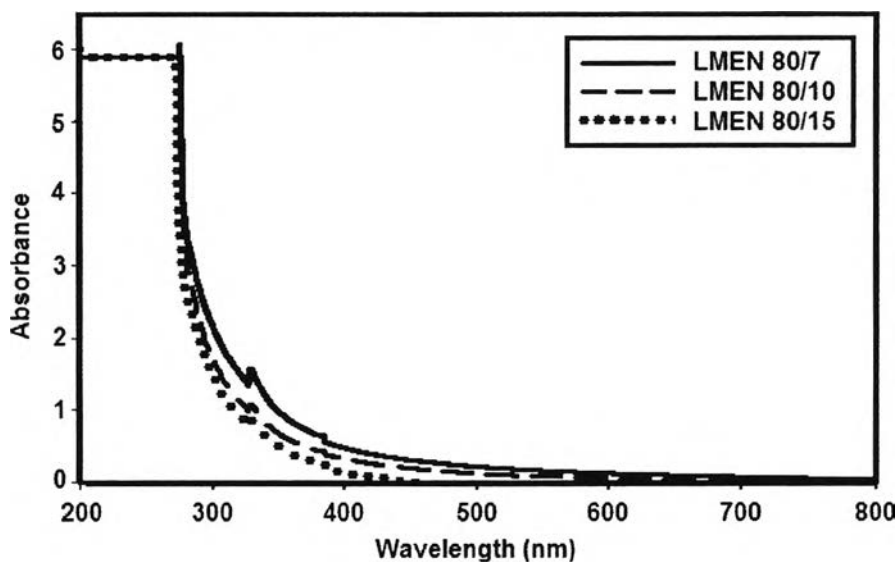
(A)

LN (90 wt% LLDPE + 10 wt% NR) films processed by 80 min<sup>-1</sup> twin-screw speed



(B)

LN (80 wt% LLDPE + 20 wt% NR) films processed by 80 min<sup>-1</sup> twin-screw speed



(C)

LMEN films processed by  $80 \text{ min}^{-1}$  twin-screw speed**Figure 4.7** UV-Visible light absorbance of the film products.

The void size and void distribution seemed not to be well uniform as can be seen in Figure 4.1. Practically, the manufacturing of breathable film which the field of application is hygiene market is the use of mineral fillers, especially  $\text{CaCO}_3$ . In the fabrication process of commercial breathable film, either coated or uncoated mineral filler is compounded cooperated with stretching of the extrudate film. Finally, many micro-pores are presented in the film structure. By both the commercial method and the method carried out in this article, there are three factors that play an important role which are the compounding formulation, the extrusion, and stretching. According to the mixing procedure in our approach, the void size was quite difficult to be controlled due to the technique of void generation was the water-releasing as proposed. Nevertheless, the uniform size and distribution of bubble or void can be prepared if more mixing rate is applied since high shear rate can provide more homogeneous blending that leads to be more possibility of well distributed reaction and by-product releasing as well. Therefore, using high mixing speed in batch and/or continuous processes should be established if the uniformity of the voids is required. However, the proposed applications of the films produced here could be considered

in the agriculture sector, especially for planting. High level of pore size uniformity is not the most important for this application since the respiration of baby plants occurs as a whole cluster. Besides the high oxygen permeability, the reactive blend or breathable film product was translucent, not opaque as commercial micro-pore products. Therefore, these are the advantages of the film produced via our technique which is suitable for agricultural film as supported by all results.

#### **4.5 Conclusions**

The unique breathable film having foam-like structure with crosslink junctions was successfully obtained by grafting and crosslink formation via reactive blending and processing of linear-low density polyethylene (LLDPE), natural rubber (NR) and epoxidized natural rubber (ENR) with small content of maleic anhydride that acts as a reactive coagent. The reactive blended films can provide the UV screen-off and good breathable films while those binary and ternary blended films can provide only UV screen-off. These properties can be controlled by screw speed of extrusion process and draw ratio of cast film process. Highly oxygen permeability found in the foamed film in comparison to pure LLDPE film allows for the use in agricultural applications.

#### **4.6 Acknowledgements**

Thankful acknowledgements are forwarded to Dr.Nandh Thavarungkul (KMUTT) for the support of ENR. Financial support from the Thailand Research Fund (TRF) through the Royal Golden Jubilee Ph.D. Program (RGJ), Grant No. PHD/0228/2545, is acknowledged.

#### **4.7 References**

Abdullah, I., Ahmad, S., and Sulaiman, Ch.S., 'Blending of natural rubber with linear low-density polyethylene', *Journal of Applied Polymer Science*, **58**, p. 1125-1133 (1995)

Bhowmick, A.K., Heslop, J., and White, J.R., 'Effect of stabilizers in photodegradation of thermoplastic elastomeric rubber-polyethylene blends - a preliminary study', *Polymer Degradation and Stability*, **74**, p. 513-521 (2001)

Dahlan, H.M., Zaman, M.D.K., and Ibrahim, A., 'The morphology and thermal properties of liquid natural rubber (LNR) compatibilized 60/40 NR/LLDPE blends', *Polymer Testing*, **21**, p. 905-911 (2002)

Feldman, D., 'Polymer Barrier Films', *Journal of Polymers and the Environment*, **9(2)**, p. 49-55 (2001)

Johnson, T., and Thomas, S., 'Nitrogen/oxygen permeability of natural rubber, epoxidised natural rubber and natural rubber/epoxidised natural rubber blends', *Polymer*, **40**, p. 3223-3228 (1999)

Johnson, T., and Thomas, S., 'Effect of epoxidation on the transport behaviour and mechanical properties of natural rubber', *Polymer*, **41**, p. 7511-7522 (2000)

Sahrim, A., Abdullah, I., Sulaiman, C.S., Kohjiya, S., and Yoon, J.R., 'Natural rubber-HDPE blends with liquid natural rubber as a compatibilizer. I. Thermal and mechanical properties', *Journal of Applied Polymer Science*, **51**, p. 1357-1363 (1994)

Sanjoy, R., Santra, R., Nando, G.B., and Gupta, B.R., 'Studied on reactive blending of epoxidised natural rubber and ethylene-acrylic acid copolymer', *Polymer Plastic Technology and Engineering*, **32(4)**, p. 343-353 (1993)