CHAPTER IV
RESULTS AND DISCUSSION

The results of barrier performance and tensile properties related to structure of LCP/PE blends films are reported in this chapter. The following parts are classified into two major sections. First section is dedicated to a series of studies effects of processing parameters as well as materials influences. For each parameter, results on morphology, tensile and transport properties are discussed. In the second section, the relationships of structure and barrier properties are described, prediction of tensile properties as well as transport properties will be carried out via applying composite theory.

4.1 Effects of Processing Temperature Profiles and Use of Mixing Elements

To study effects of processing temperatures on morphology, six different profiles were used to produce films of neat LDPE and LDPE containing 10 wt% of LCP and 0.5 wt% of compatibilizer. Temperatures of the first and the second zones of extruder, i.e. feed and compression zone, were kept constant at ~180°C and ~200°C , respectively. The temperature of the third zone , metering zone, of the extruder and at the die were varied from 220°C to 300°C, identified as T1-T6 (see Table 3.3 (1), Chapter III). Initial temperature profile setting of T1 was based on the previous work on LCP/PE blend [35], where good fibers with high aspect ratios of 100 or higher and dramatic improvement in films' moduli could be achieved. Further increases in temperature profiles from T2 to T6 were carried out to vary viscosity ratios of the blends and to study their effects on morphology, mechanical and barrier properties. For all studies, screw speed and draw ratio (area of the die lip/ cross-sectional area of the film) were kept constant at 12 RPM and 1.5, respectively.

4.1.1 Film Morphology

Figures 4.1 (a)-(f) are optical micrographs showing the morphologies of 10 wt% LCP blend films produced at different temperature profiles, T1 –T6. In these pictures, LCP dispersed phases can be clearly seen as the bright features dispersed in darker LDPE matrix. It is apparent that LCP fibrillar structure can be formed in the films produced at all six profiles. However, these films contain different amount of LCP fibers with various fiber sizes and aspect ratios. In general, obtained fibers have aspect ratios of higher than 100 giving rise to effective fiber reinforcements. In addition, it can be noticed that fiber diameters increase significantly in the films produced at high processing temperature profiles (T5 and T6). Similar results were also found in the system of LCP/Nylon 6 blends reported by F. P. La Mantia and colleagues [39]. Small droplet can also be observed. Figures 4.2 (a)-(f) are SEM micrographs showing cross sections of 10%LCP/LDPE films fractured in MD. These micrographs reveal that LCP phases are formed into fine fibrous structure in films produced at profiles T1 –T4 and fibers having larger diameters and more or less "ribbon-like" structure are observed in the films produced at profiles T5 and T6. Diameters of fibers existing in the films processed at T1 – T4 are in a range of 1 - 5.5 μm whereas diameters of fibers in films produced at profiles T5 and T6 are approximately 1.5 - 6 μm. The coexisting "ribbon-like" the structure in films of T5 and T6 possess the width of approximately 10 - 20 μm, or about 5-10 times greater than fiber diameters obtained in the film produced at T1-T4. Proportion of ribbon-like structure compared with other morphologies found in film produced at temperature profile T6 is seem to be larger than that of T5. Furthermore, these Figures also show that LCP particles are pulled out from the matrix during the cryogenic fracture, indicating the poor adhesion between the two phases.

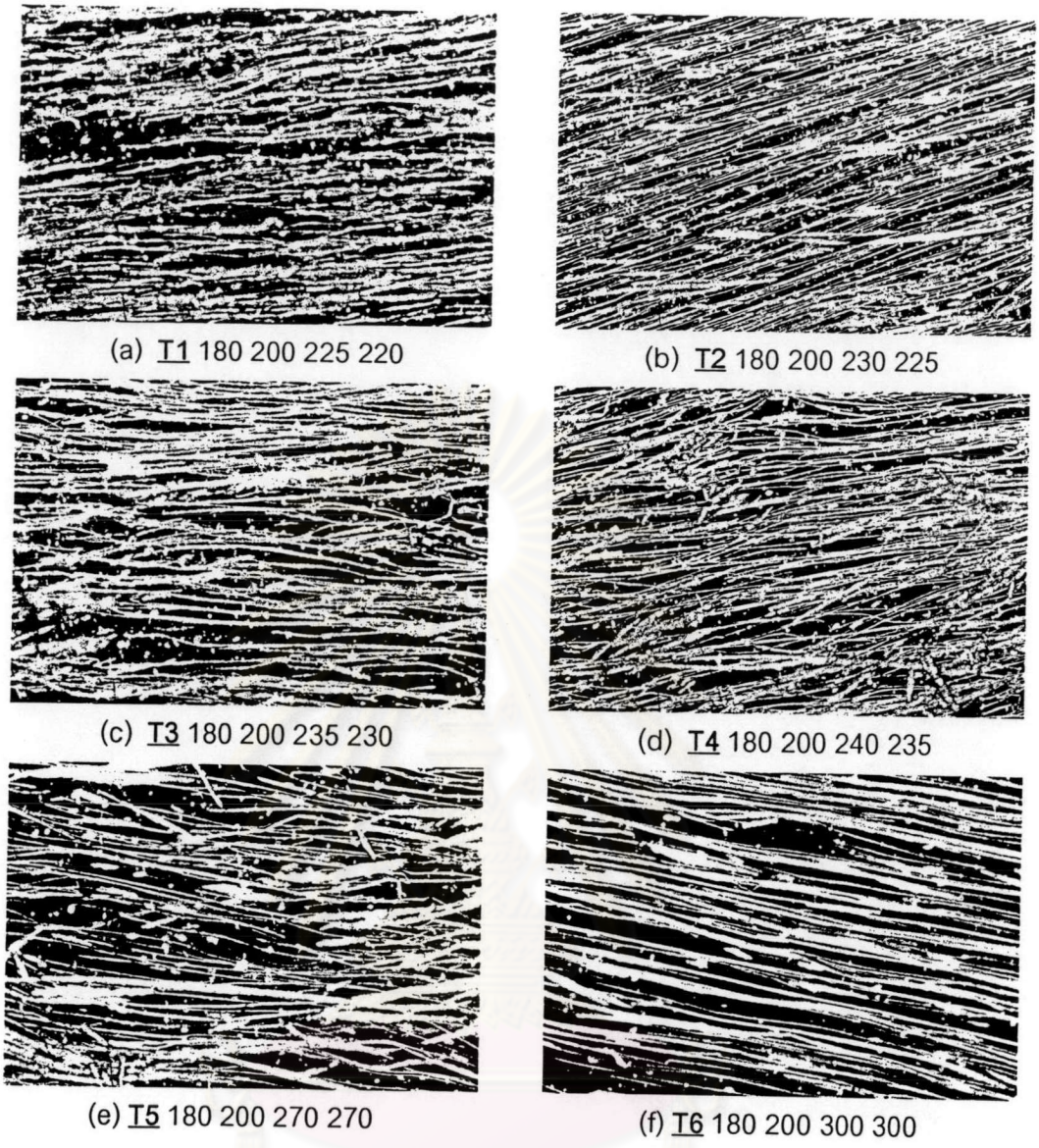
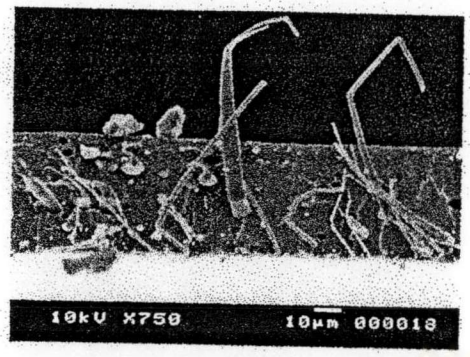


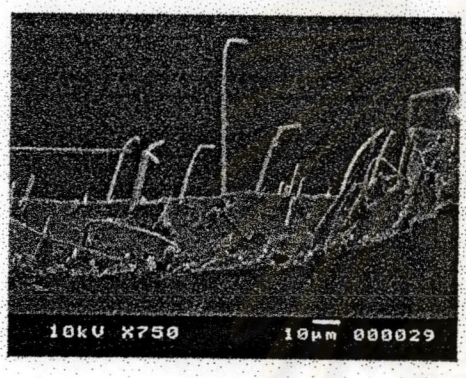
Figure 4.1 Optical micrographs of 10 wt%LCP blend films produced at different temperature profiles T1 –T6 (a-f) (200X magnification) (——100 μm)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

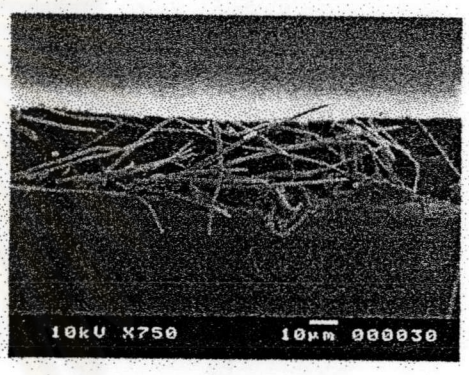


(a) T1 180 200 225 220

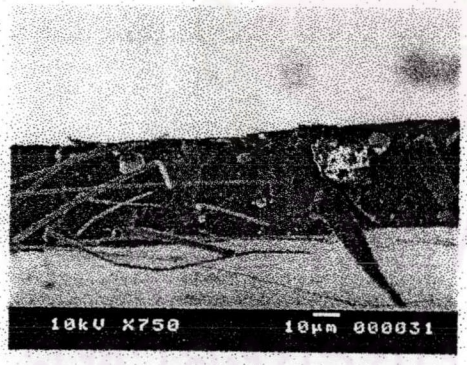
(b) T2 180 200 230 225



(c) T3 180 200 235 230



(d) T4 180 200 240 235



(e) T5 180 200 270 270

(f) T6 180 200 300 300

Figure 4.2 SEM micrographs of 10 wt%LCP blend films produced at different temperature profiles T1 –T6 (a-f) (750X magnification)

Morphology of polymer blends can be affected by various parameters. Viscosity ratio (ratio of viscosity of the minor phase to viscosity of the major phase) has been considered to be one of crucial parameters affecting both size and shape of a disperse phase. In the case of LCP/thermoplastics blends, viscosity of the LCP component must be lower or equivalent to that of the host matrix in order to ensure fiber formation. The similar high aspect ratios of LCP fibers (>100) presented in films produced at T1 to T4 imply that viscosity ratios at these four temperature profiles should satisfy fiber formation requirement. Small diameters of fibers in these all four films should be the results of small initial droplet sizes prior to transformation to fiber. As generally known that finely dispersed LCP phase can be achieved when the matrix viscosity is higher than that of minor phase or viscosity ratio is lower than unity. From preliminary results of rheological study (see Appendix B), viscosity ratios of LCP to LDPE at the temperature range of 225 - 240 ^{o}C (the same range as used at the metering zone of profiles T1 – T4) are approximately lower than unity. Thus, the rheological results tend to support the observed morphologies in the films produced at profiles T1 – T4. The obvious larger fibers or even "ribbon-like" structure obtained in the films produced at T5 and T6 may be attributed to the larger size of initial droplets. In these cases, large initial droplets might be generated because of poor mixing efficiency. At profiles of T5 and T6, high temperatures were used at the metering zone resulting in low viscosity of the matrix. Mixing efficiency, in fact, depends upon shear stress during process and the shear stress is a product of matrix viscosity times shear rate. At a constant low shear rate, the lower matrix viscosities at elevated temperatures (T5 and T6) can cause lower shear stress and correspondingly the poorer mixing ability. As a result, the larger dispersed phase sizes are obtained. In summary, at a very low matrix viscosity, effect of mixing efficiency on the dispersed phase size seems to be very pronounced.

Formation of LCP fibers can be observed at all temperature profiles implying satisfied conditions for fibrillation. Beside viscosity ratio effect that plays a key role on fiber formation, converging flow is also well known to be another important factor inducing LCP fiber formation in the blends. Converging flow usually takes place at the

die entrance or in the converging die adapter. The previous study [35] reported that the adapter having converging angle of 15° was more effective than the 30° and 90° adapters in both mixing and increasing fiber aspect ratios. In this study, the die adapter having converging angle of 15° was also used. As expected, LCP fibers can be formed at all six temperature profiles used.

It can be seen that processing temperature profiles perform the immense effect on both size and shape of the dispersed phase. However, it was reported that the effects of processing temperature are pronounced only at low shear rate, whereas at the high shear rate, effect of the processing temperature will be diminished [11]. The similar trends are also observed in this study, which will be further discussed in the next section (Effect of screw speed).

Mixing elements were used in this study in order to improve degree of mixing of LCP phase in the PE matrix. Principle of mixing element is to perturb the molten flow in a fashion of promoting mixing between polymer components. When fluid enter a static mixer, it is typically divided by baffles and mixing occurs by splitting and recombining flow streams as shown in Figure 4.3.

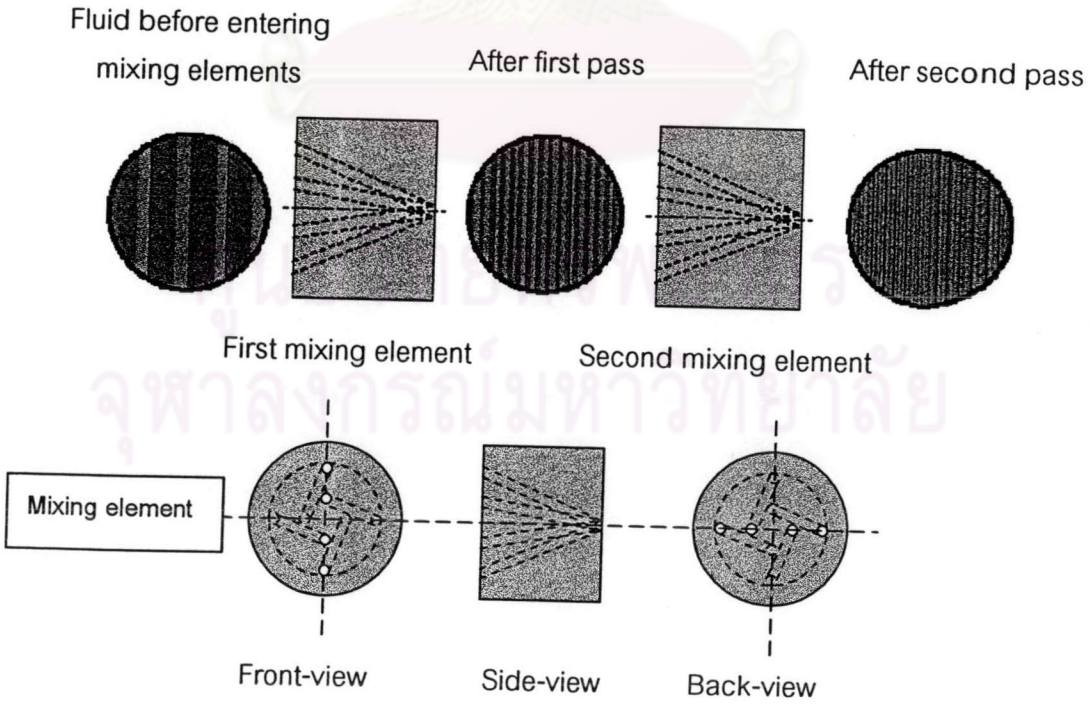
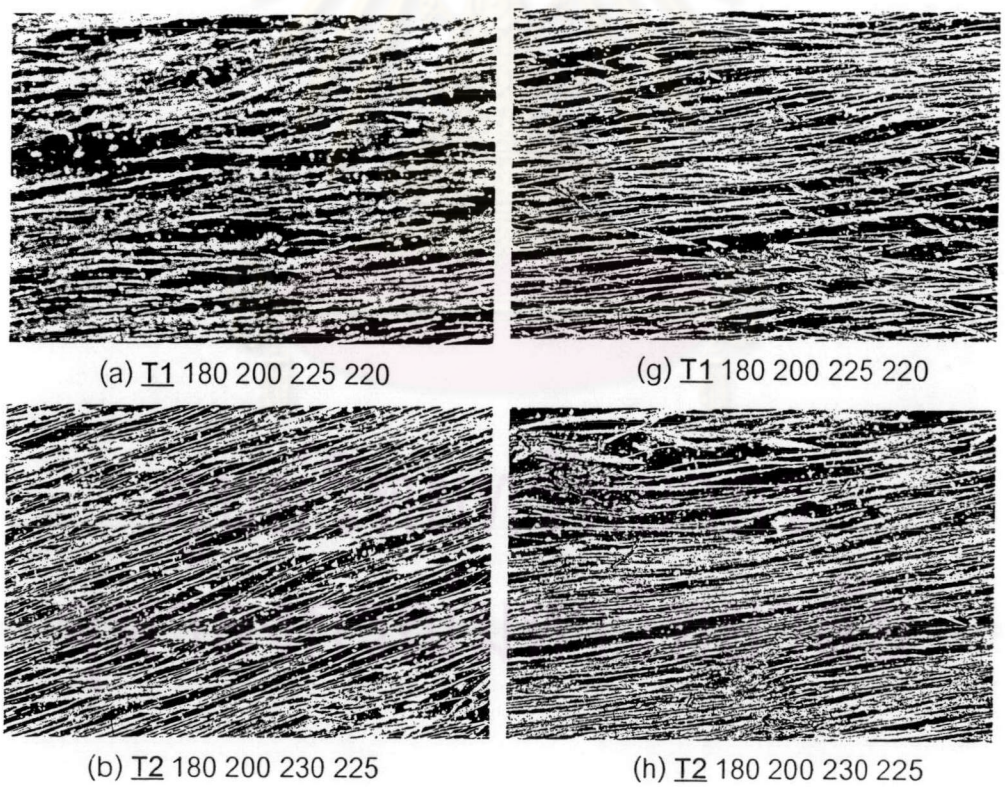


Figure 4.3 Schematic of molten blend flow though mixing elements [35,40]

By examining the films produced using mixing elements, films' physical appearances can be clearly improved. The blend films become more uniform than the films produced without mixing elements. Microstructures of the blend films in Figures 4.4 also show that the more uniform and finer LCP fibers can obtained when blend films were produced by using mixing elements at temperature profiles T1 – T2 (Figures 4.4 (g) – (h)); as compared to blend films produced without mixing elements at the same temperature profiles (Figures 4.4 (a) – (b)). Fibers diameters are approximately 0.5 - 4.5 μm in the film produced at T1- T2 using mixing elements. As previously described, fine fiber is a result of combined effects of small initial droplet and suitable flow field with satisfied viscosity ratio foe fiber formation ($\lambda \leq 1$). This can indicate to the effects of mixing elements on controlling initial droplet size and enhancing dispersion of the LCP phase at these two conditions (T1 and T2).

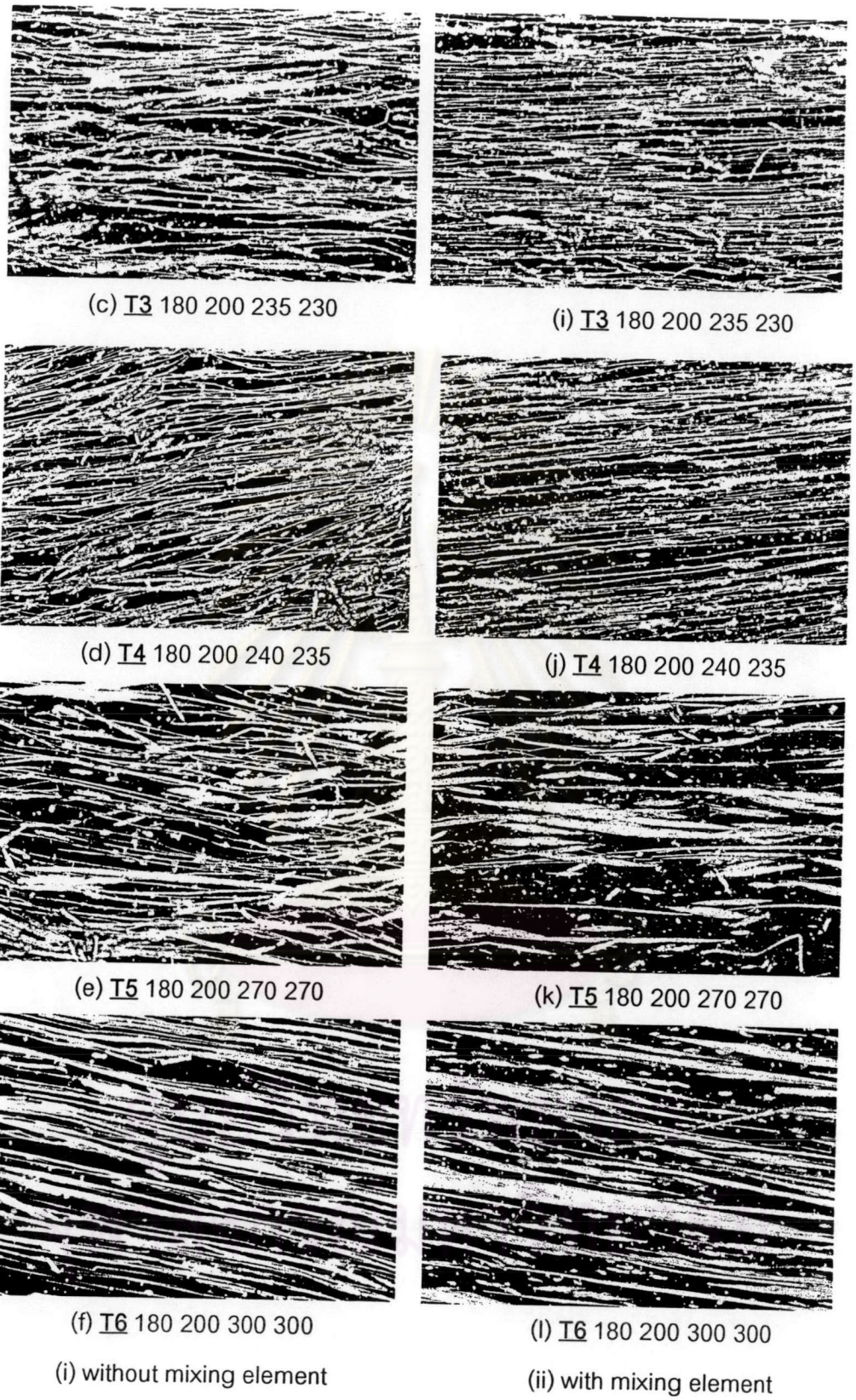


(a) T1 180 200 225 220 (g) T1 180 200 225 220

(b) T2 180 200 230 225 (h) T2 180 200 230 225

Figure 4.4 Optical micrographs showing comparison of film structure when 10 wt%LCP/LDPE blend films were produced without mixing element (a - f) versus with a use of mixing elements (g - l), at temperature profiles T1 – T6 (200X Magnification) (——100 μm)

(Continue on next page)



(c) T3 180 200 235 230

(i) T3 180 200 235 230

(d) T4 180 200 240 235

(j) T4 180 200 240 235

(e) T5 180 200 270 270

(k) T5 180 200 270 270

(f) T6 180 200 300 300

(l) T6 180 200 300 300

(i) without mixing element

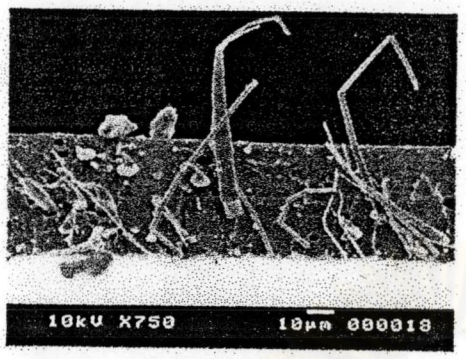
(ii) with mixing element

Figure 4.4 Optical micrographs showing comparison of film structure when 10 wt%LCP/LDPE blend films were produced without mixing element (a-f) versus with a use of mixing elements (g-l), at temperature profiles T1 – T6 (200X Magnification) (——100 μm)

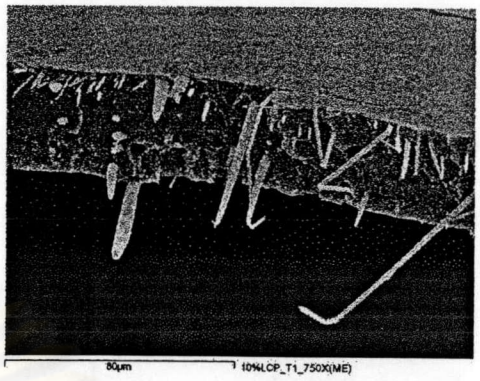
However, effects of mixing elements on morphology at higher temperature profiles, T3 - T6, are not similar to the two lower temperature profiles of T1 and T2. Although structures of very fine fiber can be observed in films produced at temperature profiles T3 and T4, the larger fibers having diameter of approximately 5 -10 μm are also present. These can be clearer seen in SEM micrographs in Figures 4.5. The greatest diameter fibers of 15 - 20 micron are observed in blend film of T5. It is also noticeable that, large fibers in film of T5 may have small aspect ratios because fiber/ribbon-like structure breaking is observed (see Figure 4.4 (k)). The findings of fiber size increasing in the films produced at high temperature profiles of T3 – T5 imply to effect of mixing elements reduced in mixing and dispersing the LCP dispersed phase at the high temperature conditions of T3 –T5. It is presumably because temperature settings at zone 3 of these profiles are fairly far above the melting point of LCP and LDPE, viscosity of both matrix and dispersed phases may be too low to obtain further improvement in mixing efficiency. Low viscosities of LCP and LDPE can even cause the instability of the flow. Further increasing of fiber diameters and generation of LCP ribbon structure may be the result of less effective mixing when the matrix viscosity is low along with instable of droplets.

"Ribbon-like" structures of LCP still can be observed in films produced at profile T6 by using mixing elements. However, the proportion of ribbons remaining in the films produced at profile T6 is decreased compared to LCP ribbon structure presented in film LCP/LDPE produced without mixing elements at the same profile of T6. "Ribbon-like" structures in film produced at T6 is replaced by thin and long fibers when using mixing elements. The ribbon widths of 15 - 20 μm and the fiber diameters of 3-5 μm are observed. Development of high aspect ratio fibers seem to be the result of decreasing of initial droplet size in blend film produced using mixing elements compared to the film produced at the same profile without mixing elements. This indicates that there should be a suitable range of viscosity ratios where mixing elements can well perform its role in producing critical initial droplet size through effective mixing and dispersion. This optimal droplet size can then transform into fine fibers under a

proper flow field. The high aspect ratio fibers obtaining in the blend films of T6 should give rise to enhanced mechanical properties.

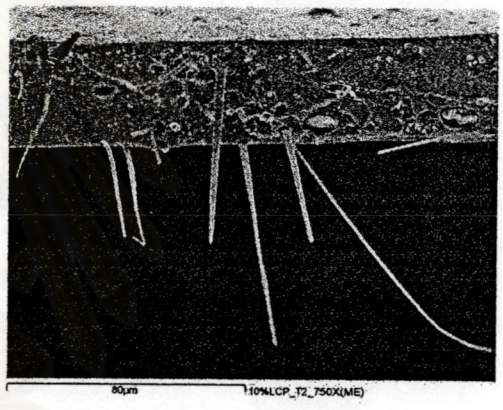


(a) T1 180 200 225 220

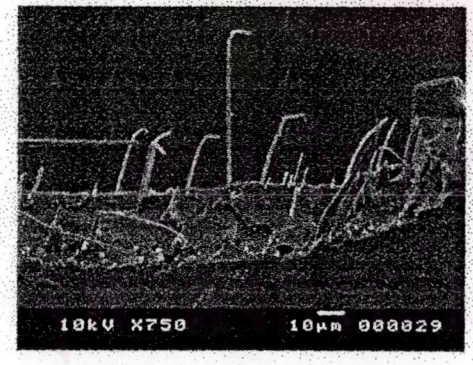


(g) T1 180 200 225 220

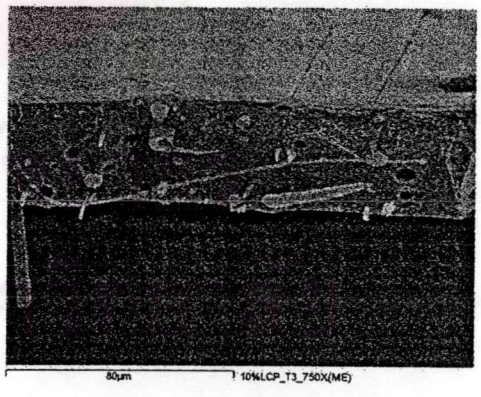
(b) T2 180 200 230 225



(h) T2 180 200 230 225



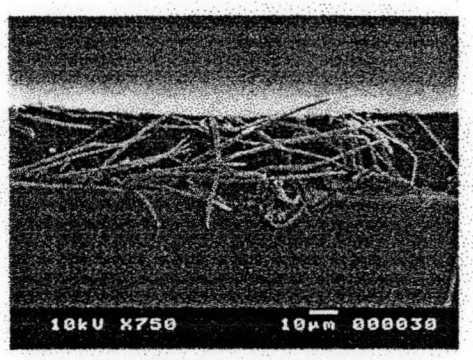
(c) T3 180 200 235 230



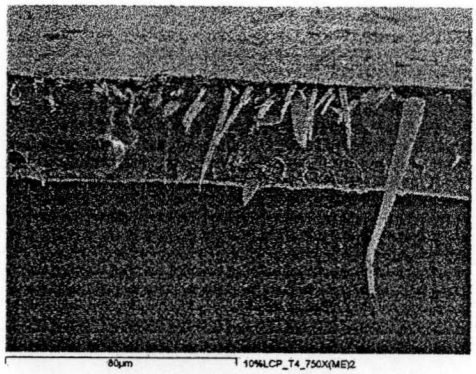
(i) T3 180 200 235 230

Figure 4.5 SEM micrographs showing comparison of film structure when 10 wt%LCP/LDPE blend films were without mixing element (a-f) versus with a use of mixing elements (g-l), at temperature profiles T1 – T6 (750X Magnification)

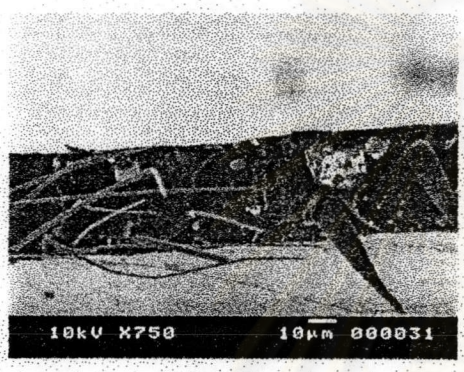
(Continue on next page)



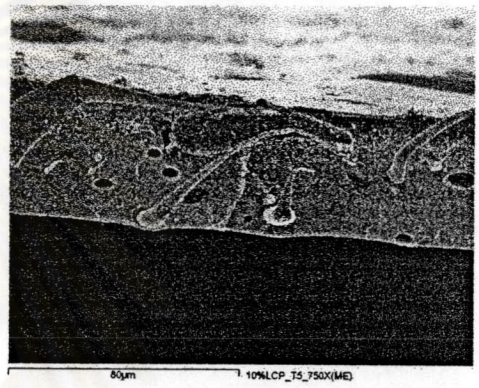
(d) T4 180 200 240 235



(j) T4 180 200 240 235

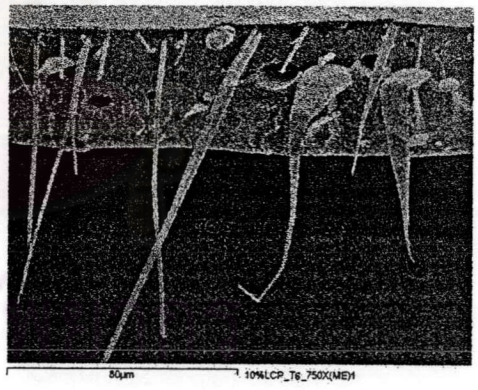


(e) T5 180 200 270 270



(k) T5 180 200 270 270

(f) T6 180 200 300 300



(l) T6 180 200 300 300

Figure 4.5 SEM micrographs showing comparison of film structure when 10 wt%LCP/LDPE blend films were without mixing element (a-f) versus with a use of mixing elements (g-l), at temperature profiles T1 – T6 (750X Magnification)

4.1.2 Tensile Properties

4.1.2.1 Tensile Properties as a Function of Processing Temperature

Effect of processing temperature on tensile properties of LDPE films and 10%LCP/LDPE films are reported in this section and displayed in Figures 4.6 and 4.7. LDPE films were produced at six different temperature profiles of T1 - T6 in order to study influences of processing temperature on the neat matrix. Moduli of LDPE films in machine direction (MD) and transverse direction (TD) in Figure 4.6 show that different processing temperature profiles have no considerable effect on LDPE films in both directions. Indeed, tensile properties in both directions, MD and TD, of all LDPE films prepared under studied conditions have almost the same properties (see Figures 4.5). This is indicative of a more or less isotropic LDPE films due to a relatively low take-up speed during film formation; there appears no effect of preferred orientation.

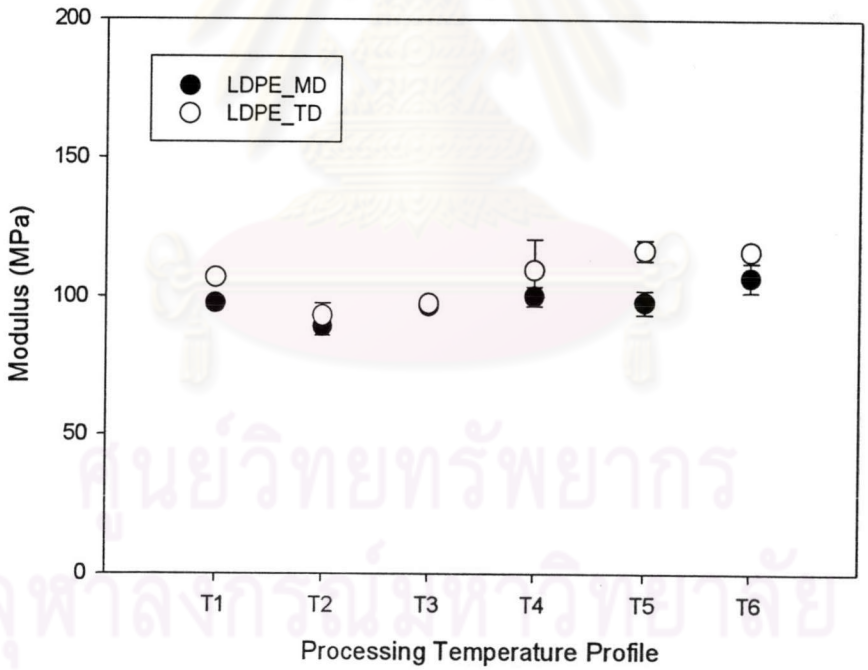
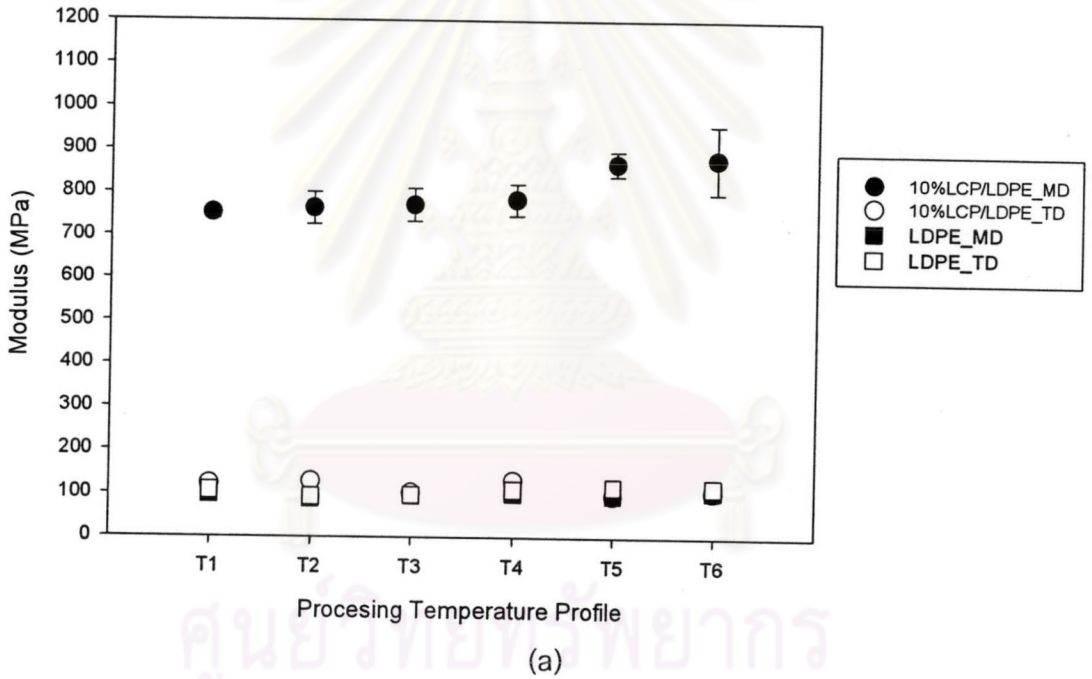


Figure 4.6 Modulus in MD and TD of LDPE films produced at different processing temperature profiles (T1-T6)

Incorporation of 10 %LCP by weight into LDPE films show a great improvement on moduli in machine direction, while the moduli in transverse direction are essentially unaffected as compared to the neat LDPE films produced at the same

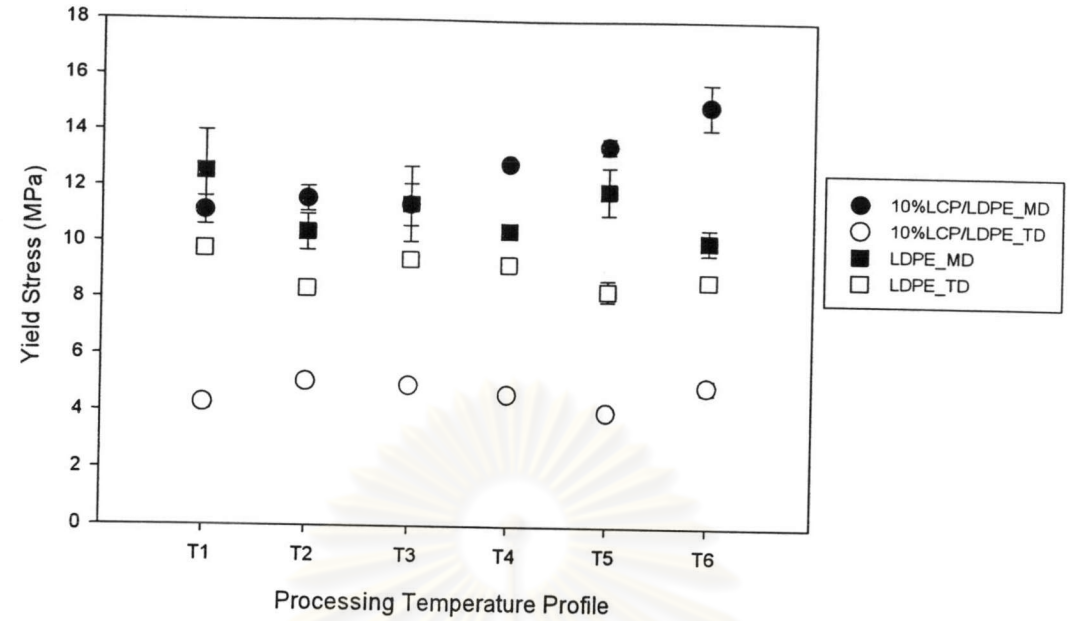
conditions (see Figure 4.7). MD moduli of 10 wt%LCP/LDPE blend films are approximately 600-800% greater than that of pure LDPE films. MD Yield strengths of blend films are slightly increased from approximately 11 to 15 MPa, but TD yield strengths of all blend films fall below TD yield strength of the neat LDPE films. The increase in modulus and yield strength of these films can be explained by self-reinforcement effects of the LCP fibers formed during the extrusion process. The preferential orientation of LCP fibers in the flow direction results in anisotropic properties of the blend films and thus the films show superior tensile properties in machine direction. Decreasing in TD yield strengths of the blend films could be due to weak interaction between LCP fiber and matrix interface.



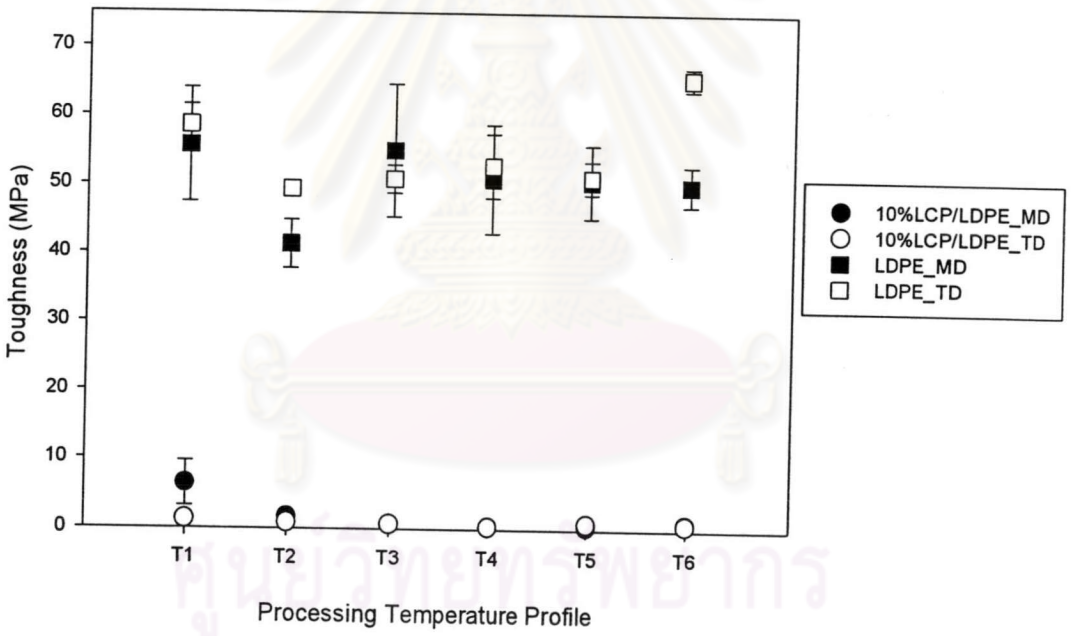
(a)

Figure 4.7 Tensile properties of LDPE and 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) : (a) modulus, (b) yield strength and (c) toughness

(Continue on next page)



(b)



(c)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Figure 4.7 Tensile properties of LDPE and 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) : (a) modulus, (b) yield strength and (c) toughness

When considering the effects of processing temperatures on tensile properties of blend films in Figures 4.7 (a) - (c), slight increasing of films' moduli and yield strengths in machine direction are observed as temperatures at zone 3 and die increase from T1 to T4. It is, however, interesting that upon further increase of zone 3 and die temperatures to 270 °C and 300°C for the profiles of T5 and T6, noticeable improvements in both moduli and yield strength are present, as compared to those for LCP/LDPE films produced at T1 –T4. Increase of tensile properties of the blend films with processing temperature may be attributed to different morphologies of LCP present in the blend films. It has been well realized that properties of immiscible blend can be influenced by many factors, i.e. blend composition, interfacial tension, dispersion and distribution as well as size and shape of the dispersed phase. In this study, LCP fibrillar structures with effective aspect ratios ($L/D \geq 100$) are mainly obtained in all six profiles. These are in good agreement in tensile properties improvement. Increment of tensile properties when processing temperatures rise may be attributed to increasing number of effective fibers in the blend films. By a closer examination, a higher improvement in tensile properties can be observed in the films produced with high processing temperatures at T5 and T6. These are possibly due to the effect of increasing surface area of LCP phase [41]; when the LCP phase become "ribbon-like" structures, the ratio of surface area to volume may increase as compared to LCP fiber structure with similar effective lengths of ~100 μm or higher. Under loading, the greater surface area is better in load transferring. In other words, increasing ratio of surface area to volume can lead to improvement of reinforcement effectiveness.

A large decrease of blend films' toughnesses compared to the neat LDPE films is present in Figure 4.7 (c). Although adding only a small amount of LCP (10 wt%) results in a significant improvement in films' moduli, a dramatic decrease in toughness of about 90 % is obtained. Even though, decreasing in toughness is typical for short-fiber-reinforced polymer composite, such a low toughness is not commonly found in the system of LCP/polyolefin blends reported by other researchers [35-36]. Concerning tensile behavior of this blend illustrated in Figure 4.8. LDPE films show quasi-rubber-like behavior having high elongation while LCP/LDPE film displays a brittle failure characteristic. The lower elongation at break causes lower toughness.

Explanation for these findings could be attributed to poor adhesion between the two phases in the system.

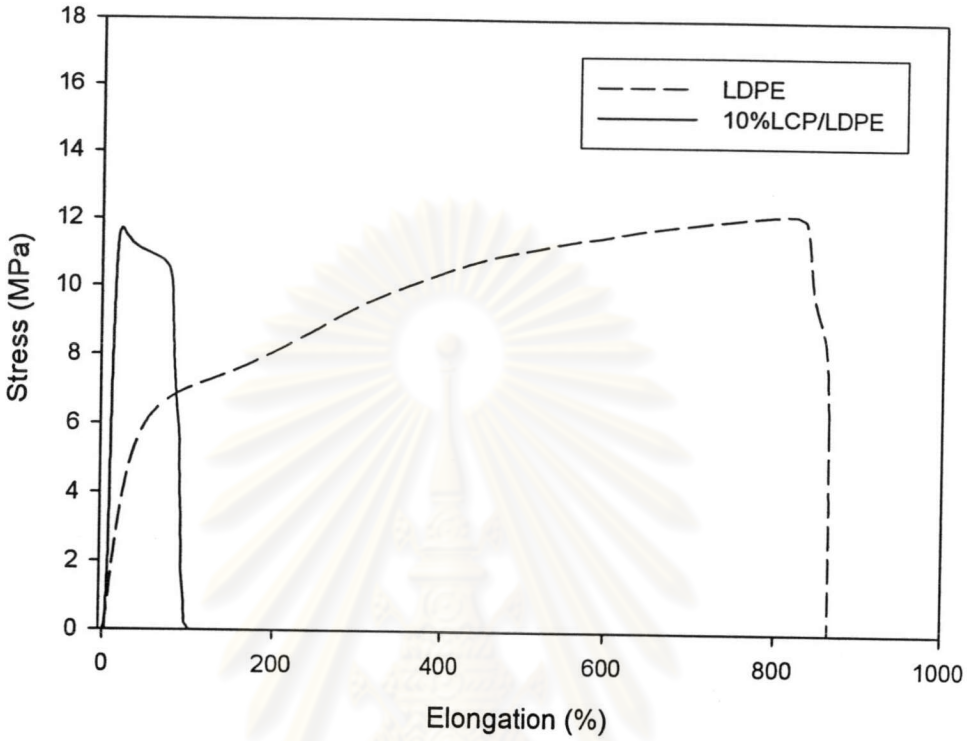
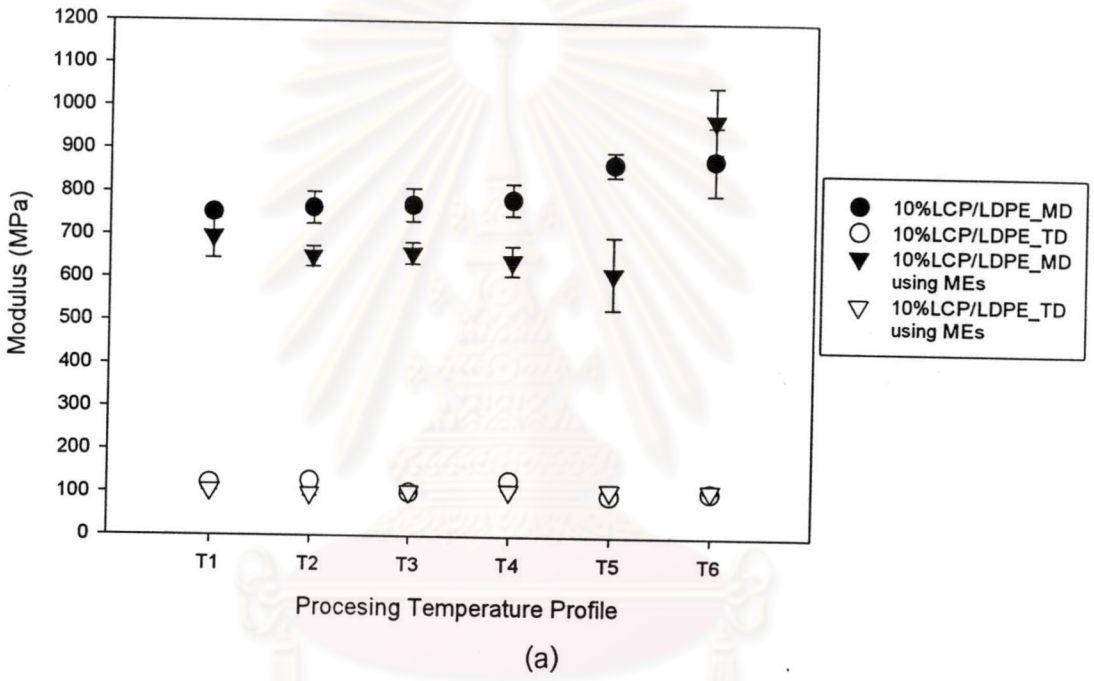


Figure 4.8 Comparison of tensile behavior between LDPE film and 10%LCP/LDPE film

4.1.2.2 Tensile Properties as a Function of Mixing Elements

Comparison of tensile properties of blend films produced by using mixing elements versus blend films produced without mixing elements at six different profiles are shown in Figures 4.9. Tensile properties of blend films produced using mixing elements are generally lower than those of films produced without mixing elements. However, tensile properties of blend films of T6 show an obvious increase. Improvements in modulus and yield strength of films produced at profile T6 with mixing elements are approximately 54% and 40% respectively, as compared to those for blends films produced at profiles T1 –T5. These observation can be related to films' morphology, as previous described. The improvements of tensile properties of blend films produced at profile T6 should be the result of a numerous effective fibers present in the film as earlier mentioned. Decreasing in tensile properties of films produced at

temperature profiles T1 – T5 may be caused by LCP fiber breakage. Although using mixing element can help improve mixing in the LCP/PE blend system, as indicated by fine fibers with high L/D ratios at particular processing conditions i.e., T1 and T2. Mixing elements may also impart possibility of fiber breakage if the LCP dispersed phase has relatively small initial size and fine shape. In the case of films produced at profiles T3 - T5, slight decreases in both moduli and yield strengths could be attributed to decreases of surface to volume ratio when fibers' diameters are increased.



(a)

Figure 4.9 Tensile properties of 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) with a use of mixing elements (MEs) and without mixing elements: (a) modulus, (b) yield strength and (c) toughness

(Continue on next page)

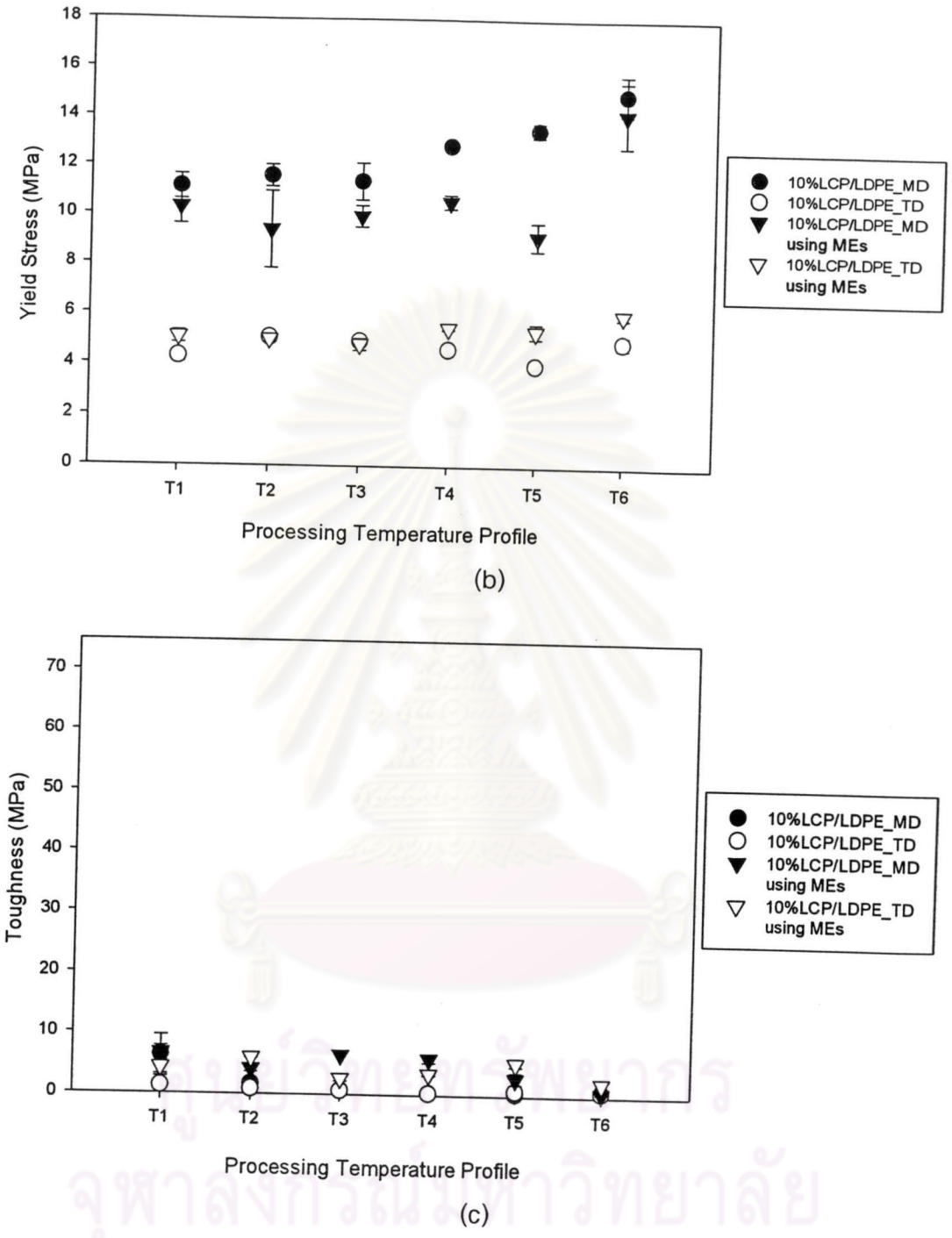


Figure 4.9 Tensile properties of 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) with a use of mixing elements (MEs) and without mixing elements: (a) modulus, (b) yield strength and (c) toughness

4.1.3 Barrier Properties

Oxygen and water vapor transmission rates of 10%LCP/LDPE films processed at different temperatures are illustrated in Figures 4.10 and 4.11. There is no general trends for transmission rates with increasing processing temperatures. Nevertheless, a noticeable decrease in OTR values of 15 % and 40% are observed for films produced at condition T2 and T6, as compared with OTR values of LDPE films at the same thickness of 60 μm.

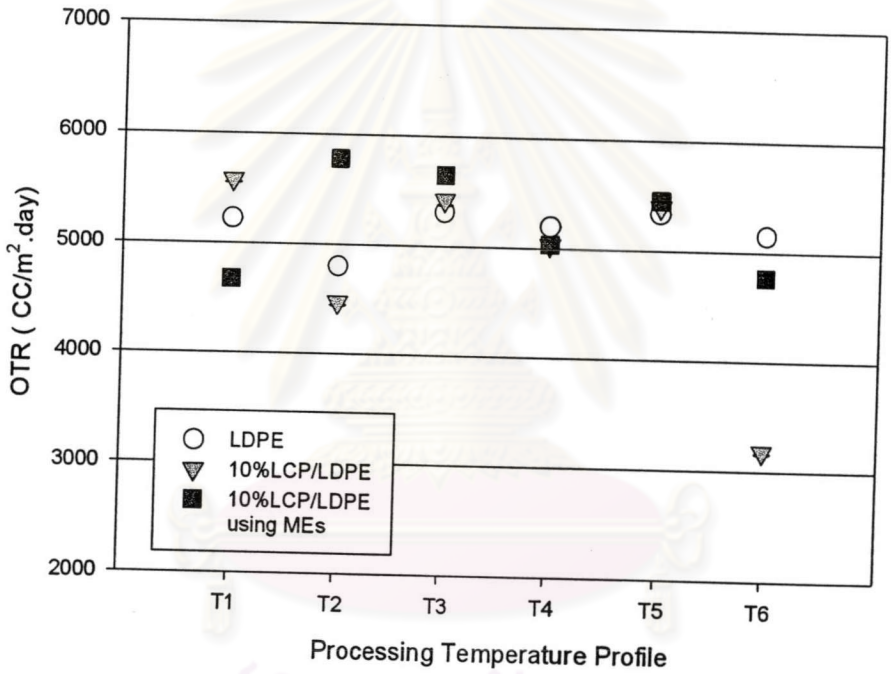


Figure 4.10 Oxygen transmission rate of 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) compare to 10%LCP/LDPE films produced by using of mixing elements and LDPE films

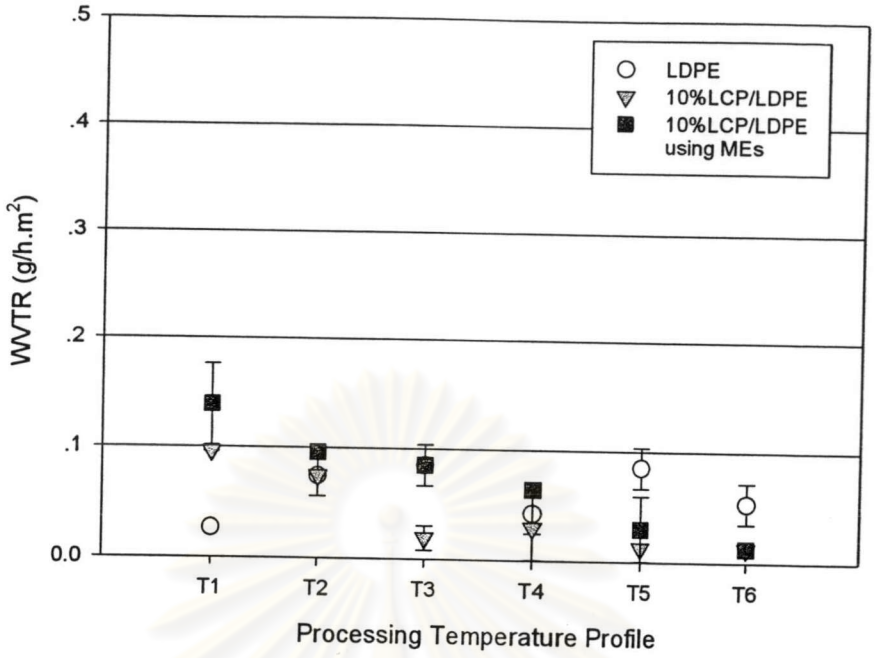


Figure 4.11 Water vapor transmission rate of 10%LCP/LDPE films produced at different processing temperature profiles (T1-T6) compare to 10%LCP/LDPE films produced by using of mixing elements and LDPE films

In general, transport properties polymer blends can be governed by characteristics of both the matrix and the dispersed phase morphology. For this reason, to better understand the controlling mechanisms and contributions from each phase components, studies of crystallinity of PE matrix at various six processing temperature profiles were also carried out. Transport properties of resulting LCP/PE films were then analyzed based on crystallinity of PE and morphology of LCP.

Major factors influencing transmission property of polymers are crystallinity and orientation. Polymer with higher crystallinity is generally better in barrier property [26, 42-43]. Changes in crystallinity of the polymer matrix by an incorporation of LCP were widely reported in many blend systems [30, 43]. In some systems, LCP could enhance crystallinity of the matrix by acting as nucleating sites for spherulites during crystallization process, LCP/PPS, LCP/PBT, LCP/PEN, and LCP/PE for example. In contrast, LCP could reduce crystallinity of the matrix in some systems such as LCP/PEEK and LCP/PBT. In this study, DSC was used for studying crystallinity of the

LCP/PE blends processed at various temperature conditions. Figure 4.12 shows crystallinity changes as a function of temperature profiles. In this figure, slight decreases of crystallinities of approximately 3-6 % are observed in 10%LCP/LDPE films produced at the profiles of T1 to T6 as compared to the neat LDPE films. Crystallinity values of LDPE films and 10%LCP blend films are in a similar fashion at all six profiles, but there is no absolute tendency upon increasing temperatures from T1 –T6. OTR values also show no general trend as a function of temperature profiles. However, the marked low OTR values of PE films containing 10%LCP produced at T6 is observed and a moderate decrease in OTR is also found in film produced at T2. These films posses low OTR of ~ 3000 cc/m^2.day as compared to the higher OTR of ~ 5000 cc/m^2.day for PE films, Produced at the same processing condition of T6. Based on crystallinity of PE and LCP/PE blends, incorporation of 10%LCP into the PE has negligible effects in changing crystallinity of PE matrix. Thus, it is likely that the observed law OTR of LCP/PE films produced at T6 is attributed to the "ribbon-like" structure of the LCP phase obtained at this condition. The larger of surface area of tape or ribbon-like structure perpendicular to the gas traveling direction can give rise to the more effective tortuous pathway for gas traveling across the film thickness.

When mixing elements were used in processing of 10%LCP/LDPE films. Transport properties of these films were almost the same as the films processed without mixing elements. Unfortunately, noticeable low of OTR values of films produced at T6 are absent. This result can be well related to the developed LCP morphology in the form of fine fibers with some fiber breakages, as described in section 4.1.1. There are no ribbon-like structures of LCP, as found in the films produced without mixing elements.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

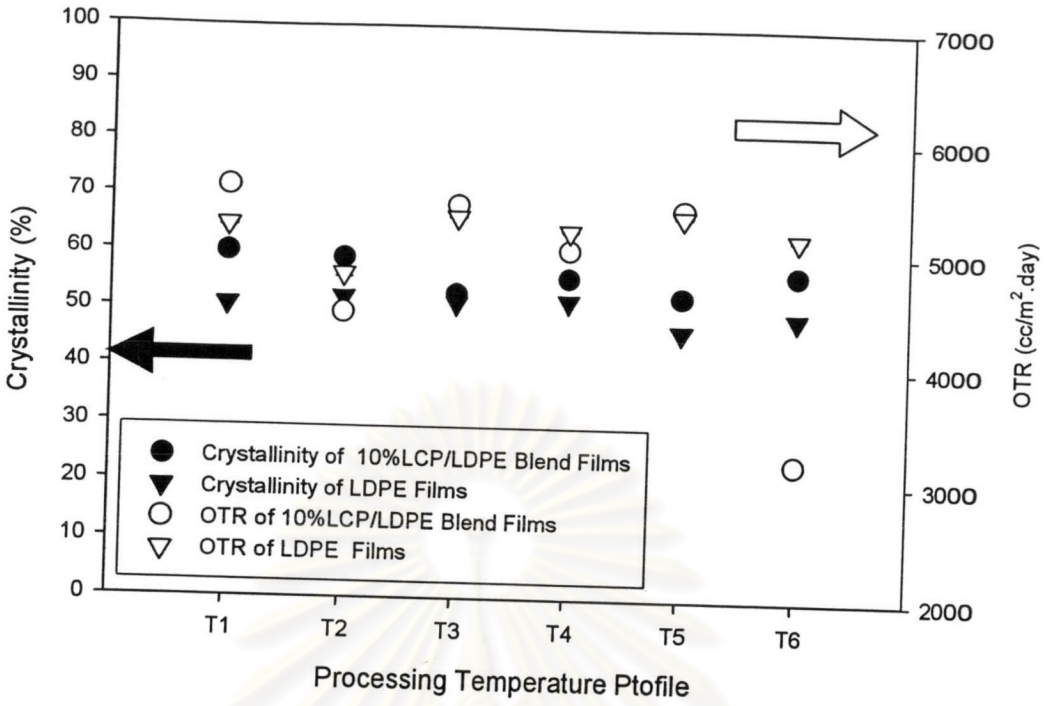


Figure 4.12 Crystallinity and oxygen transmission rate of LDPE films and 10%LCP/LDPE films as a function of processing temperature profiles

In summary, in the studied blend system of 10%LCP/LDPE, the most important factor controlling transport properties of the resulting films is dispersed LCP morphology. Ribbon or tape like structure of LCP with effective lengths seems to play a key role in enhancing oxygen barrier property of the films. Further studies in the following sections involve intensive investigation of how the other parameters affect morphology as well as transport properties of LCP/PE blend films. From the result described, chosen temperature profiles for further studies are T2 and T6 as films produced at these two conditions posses interestingly low of OTR values.

4.2 Effect of Screw Speed

Increasing screw speed leads to increase shear rate in the process and affects rheological properties of materials. In the current study, PE films containing 10%LCP were produced with screw speeds of 12, 20, 40, and 60 RPM at the two different temperature profiles of T2 and T6. Note that, draw ratios were kept constant at 1.5 in order to keep draw ratio constant while increasing the screw speed, take off speed must also be adjust accordingly. It should be noted that cooling method of producing films at very high temperature profiles of T5 and T6 was somewhat different from profiles of T1 to T4. At profiles T5 and T6, molten blend viscosity was quite low leading to consequently low melt strength, therefore air box was adjusted to be at closer position to the die outlet and airflow was decelerated than that of the profiles T1 to T4. However, cooling method for each profile is kept unchanged when increasing screw speed.

4.2.1 Film Morphology

Figures 4.13 (a) to (h) present the effect of screw speed on the morphology of 10 wt%LCP blend films. It can be generally seen that fibrillar structure (in films produced at temperature profile T2) as well as ribbon-like structure (in films produced at temperature profile T6) with high aspect ratios still exist under different shear rates. Both fibers and ribbons in the blends tend to become finer when increasing screw speeds. This can be explained by increases of shear stresses with increasing shear rates. Fiber diameters in the films of T2 decrease from the range of 2.5 - 6.5 μm to 1.5 – 2.5 μm. However, SEM micrographs in Figures 4.14 reveal shorter fibers or tapes at higher screw speed conditions. This may be because of possible combined effects of the high shear rate, high temperature generated in the system and high take-up speed during processing. Therefore, the occurrence of LCP fiber/tape breakage may take place.

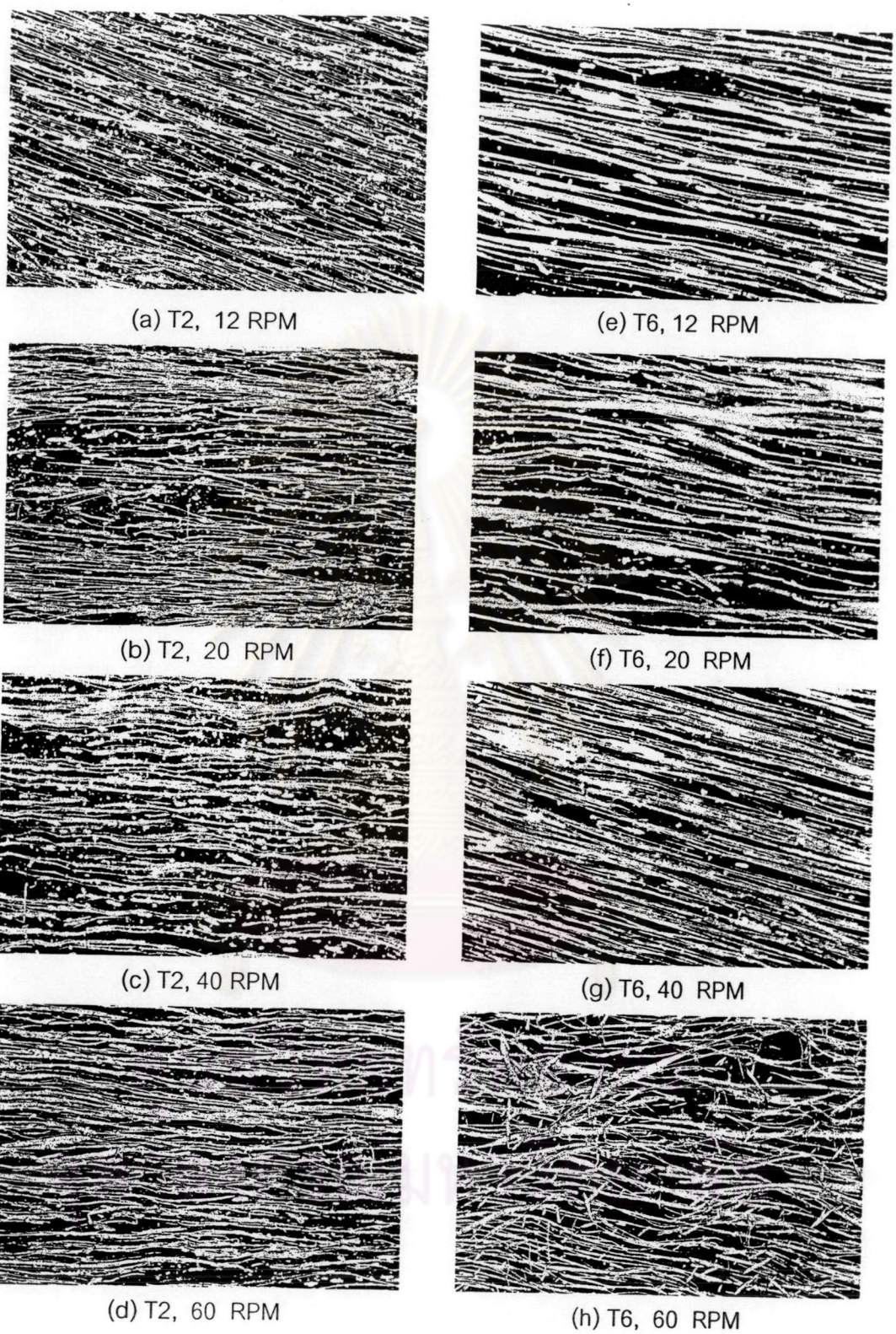


Figure 4.13 Optical micrographs showing effect of screw speed on morphology of 10 wt%LCP/LDPE blend films produced at T2 and T6 (200X magnification) (——100 μm)

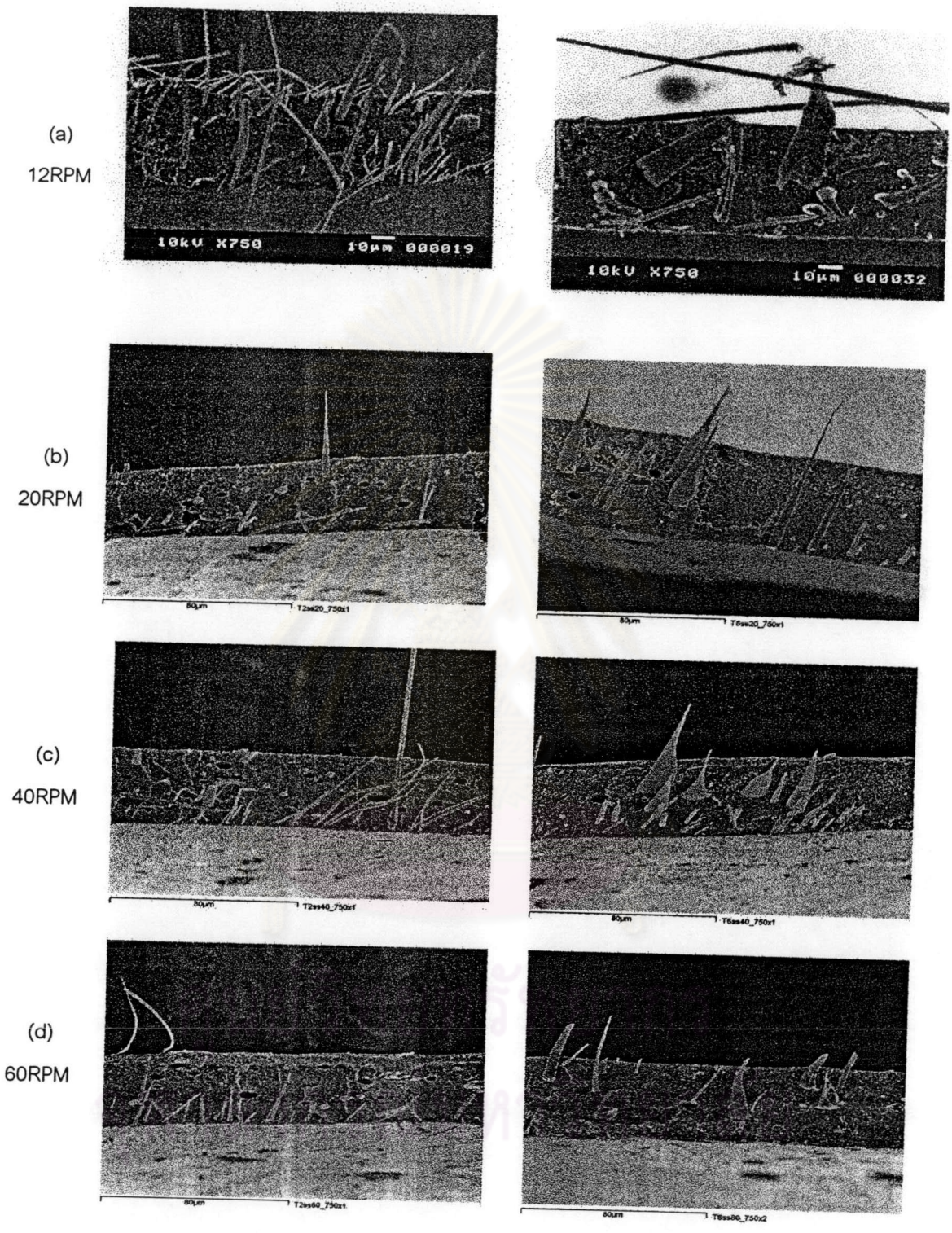


Figure 4.14 SEM micrographs showing effect of screw speed on morphology of 10 wt%LCP/LDPE blend films produced at T2 and T6 (750X magnification) (—10 µm)

4.2.2 Tensile Properties

Results of tensile properties by mean of screw changing speeds are presented in Figures 4.15 (a)-(c). When screw speeds are increased, Films' elastic moduli decrease in both 10%LCP/LDPE films processed at temperature profiles of T2 and T6, whereas LDPE neat films is relatively unaffected. MD modulus of films produced at profile T2 decreases sharply as increasing screw speed from 12 RPM to 20 RPM. Modulus of film T2 produced at screw speed 20 RPM is approximately 20% lower than that of 12 RPM. Further, increases of screw speeds show no significant affects on modulus except a slight increasing tendency at the highest screw speed of 60 RPM. In the case of films produced at profile T6, increasing screw speed from 12 to 20 RPM influences to a slight increase in MD modulus of about 6%. Further increasing screw speeds tend to diminish modulus. The films' moduli at the high screw speed of 60 RPM is about 20% lower than the modulus value obtained at screw speed of 20 RPM. When considering the trends of films' properties produced at two different profiles as a function of screw speeds, it could be possible to predict that modulus of films produced at the two different profiles may meet each other at some point of higher shear rate. This is in agreement with the result reported by W.G. Perkins et al [11] that the effects of processing temperature will be less pronounced or become even obliterated under high shear rate.

Varying screw speeds show no significant effects on yield strength of LCP/PE films (Figure 4.15 (b)), but little improvement of toughness can be achieved (Figure 4.15 (c)). According to the correlation of morphologies and tensile properties, it is comprehensible how increasing of screw speed can affect to blend properties. As previously described, increasing screw speed was followed by increasing take-up speed in order to keep constant draw ratios; the combined effects lead to higher extent of fiber elongation along with fiber breakage. As a result, finer but shorter fibers are obtained with raising screw speed. These LCP morphologies cause unsurprisingly declining trends in tensile properties.

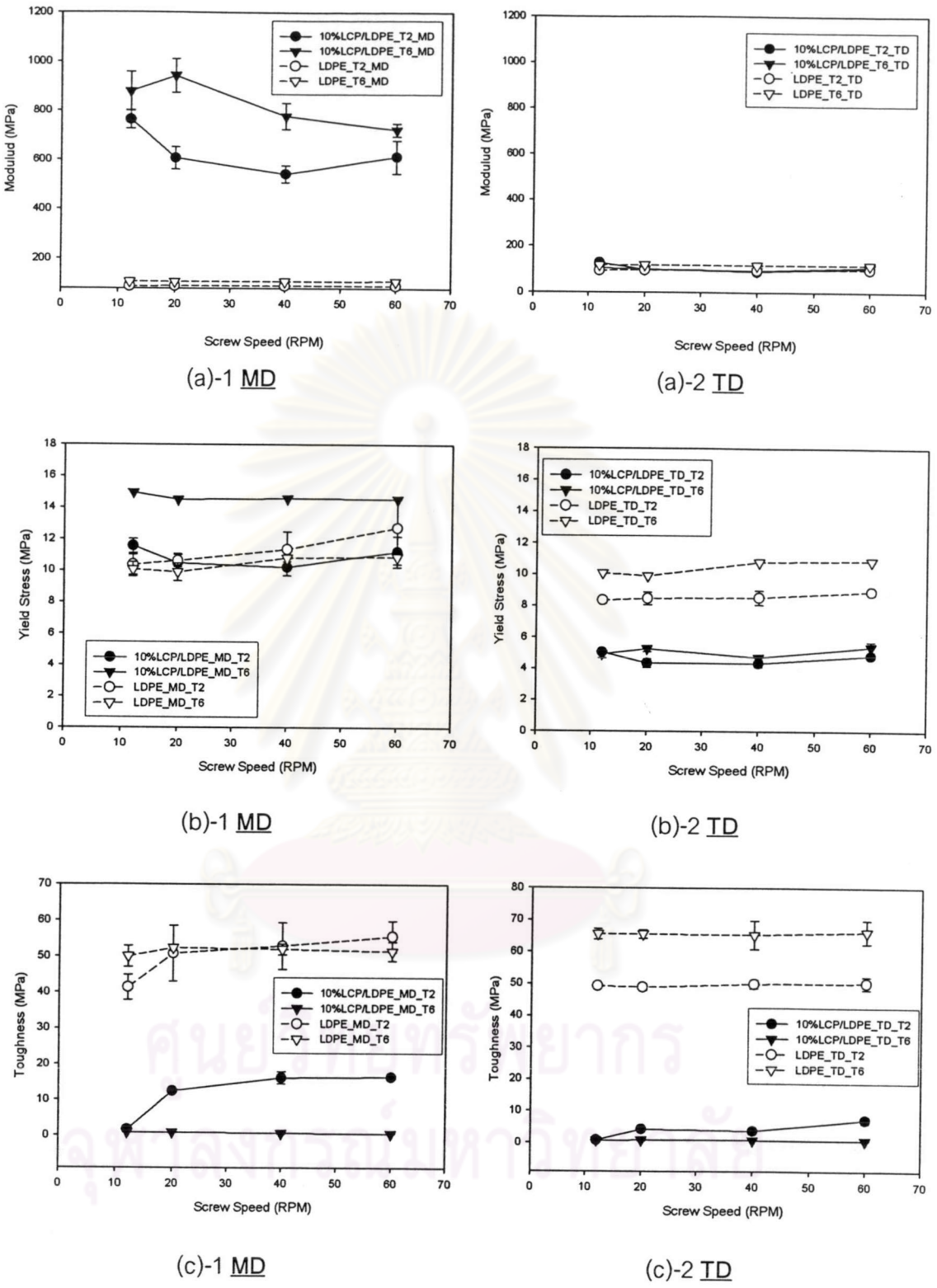


Figure 4.15 Effect of screw speed on tensile properties in MD and TD of 10%LCP/LDPE films produced at temperature profile T2 and T6 as compared to LDPE films: (a) modulus, (b) yield strength, and (c) toughness

4.2.3 Barrier Properties

The influence of screw speed on oxygen transport properties of LDPE film containing 10% weight of LCP are illustrated in Figure 4.16. It can be seen that among all films product, the lowest of oxygen transmission rate value is obtained for films produced at a low screw speed of 12 RPM. Increasing screw speed from 12 to 20 RPM results in higher OTR values. Further increases of screw speed show no dramatic affects on transport properties of both PE films and PE films containing LCP. WVTR values in Figure of 4.17 are also unaffected by screw speeds.

As earlier described, increasing screw speed and take-up speeds caused the reduction of aspect ratios of LCP fibers and ribbons. Increase of OTR values could then be the result of such LCP morphologies in the films produced at T2 and T6; these can possibly create less effective tortuous pathway for gas. In short, of all 10%LCP/PE films produced at various screw speeds, the highest possible tensile properties with the best possible oxygen barrier characteristics can be achieved at the screw speed of 12 RPM. Thus, the following studies of the effects of compatibilizers and LCP contents on the films' tensile and barrier performances will be carrier out at the processing conditions of T2 and T6 and screw speed of 12 RPM.

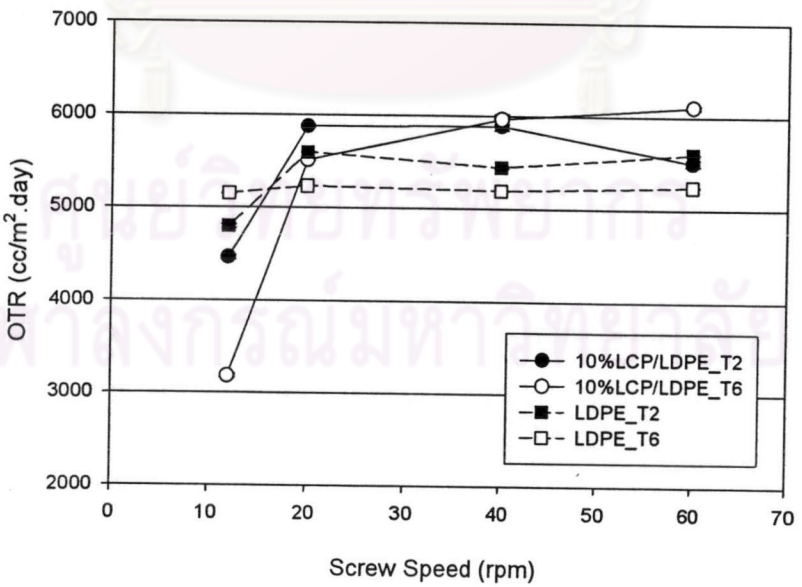


Figure 4.16 Effect of screw speed on oxygen transmission rate of 10%LCP/LDPE films produced at temperature profile T2 and T6 as compared to LDPE films

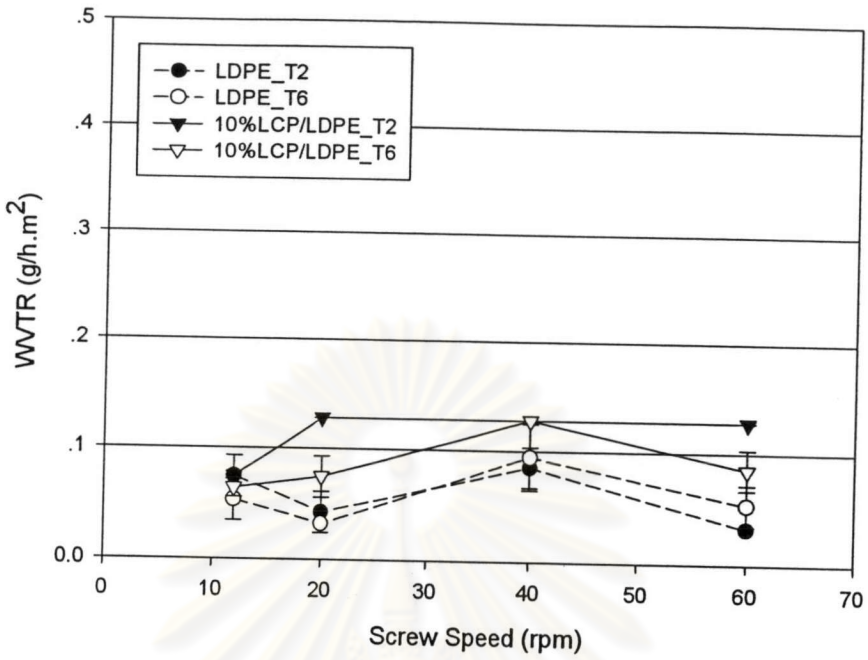


Figure 4.17 Effect of screw speed on water vapor transmission rate of 10%LCP/LDPE films produced at temperature profile T2 and T6 as compared to LDPE films

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.3 Effect of Compatibilizer

Compatibility of the blend components is one of the key factors controlling blend's properties. Incorporation of compatibilizer is widely used to enhance compatibility of blend. In the present work, an ethylene-methacrylic acid copolymer having 9% of methacrylic acid namely Nucrel 0903 was use as a compatibilizer for the blend system of LCP and LDPE. Studying effects of compatibilizer and its content, has been performed by comparing films of 10%LCP/LDPE containing various amount of compatibilizer from 0 to 10.0 % by weight. Note that, all films were produced of the same temperature condition of profile T2, screw speed of 12 RPM, and a draw ratio of ~1.5.

4.3.1 Film Morphology

Effects of compatibilizer content on morphology are illustrated in Figures 4.18 and 4.19. It can be noticed that blend film without compatibilizer seem to have very fine fiber of ~1-2 μm diameters, with very high aspect ratios of >100. Increasing compatibilizer content can result in increasing diameter of the LCP fibers as well as the amount of ellipsoids and droplet. Macosko also reported the similar result [30]. Explanation of such observed LCP morphology in droplet or ellipsoid forms should be due to instability of fiber or thread of dispersed phase. Although compatibility is needed in the blend to induced good dispersive mixing and droplet formation too much compatibilizer may cause fiber breaking by enhancing instability of thread or fiber. Breaking then occurs by thread breakup mechanism.

SEM micrographs in Figures 4.19 (a) evidently show the pullout of LCP fibers in the blend film without compatibilizer. Long and thin fibers can be pulled out without any breaking. This indicates that the two components, LCP and LDPE, are incompatible and have very poor interfacial adhesion. Blend films having some of compatibilizer reveal some of fiber breaking together with fiber pullout. Increasing content of compatibilizer shows no tendency of fiber breaking. This can be thought that compatibilizer used in this study, Nucrel, can modestly improve compatibility for LDPE and LCP in this system. However, there should be some appropriate amount of this

compatibilizer to be used for the particular blends of LCP and LDPE which needs further investigations.

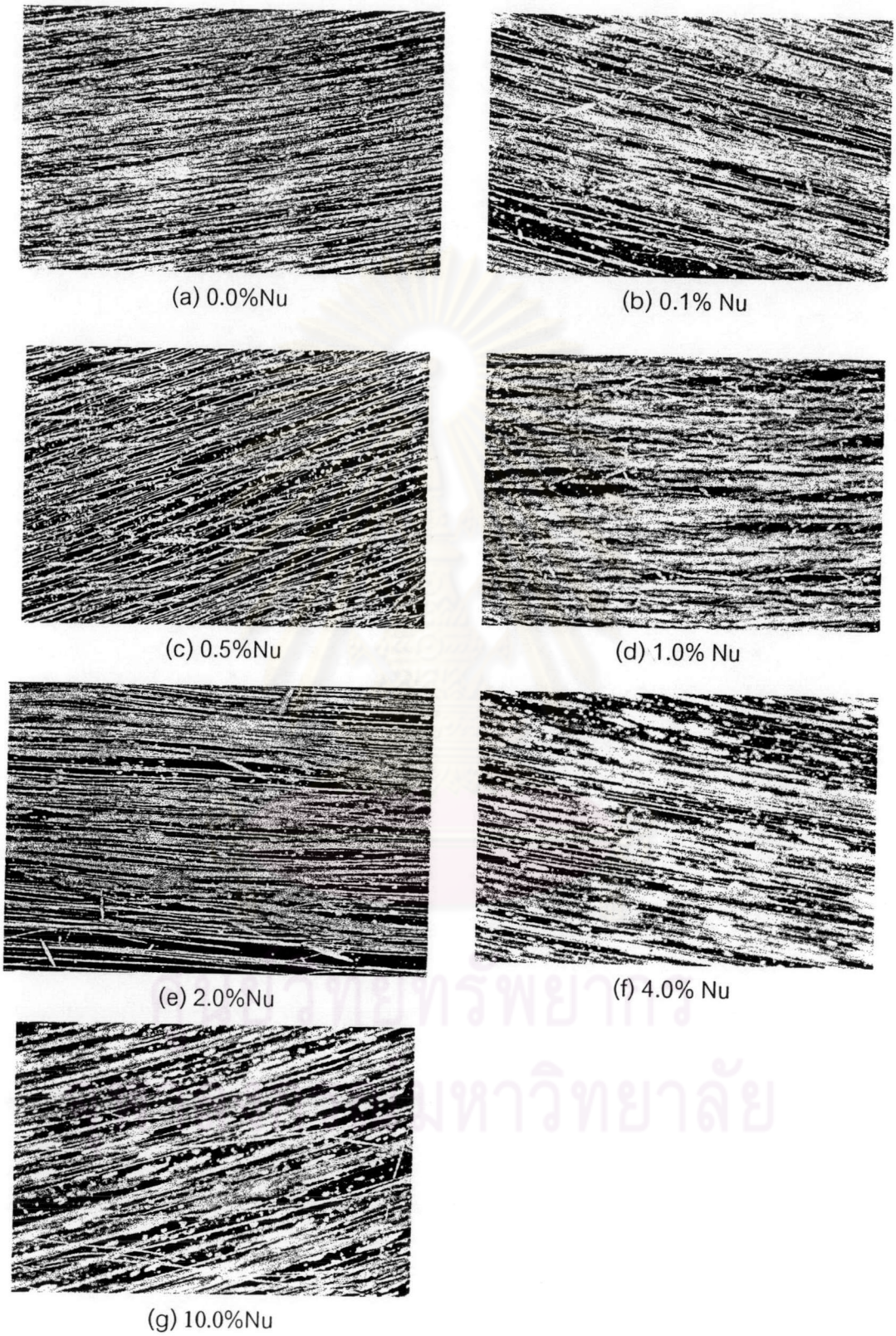
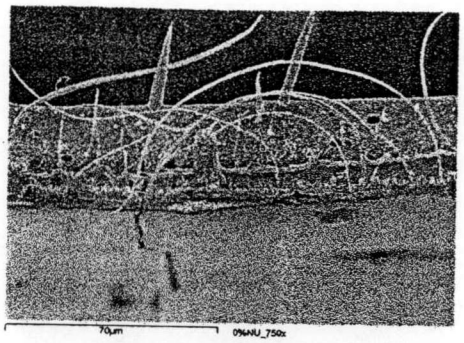
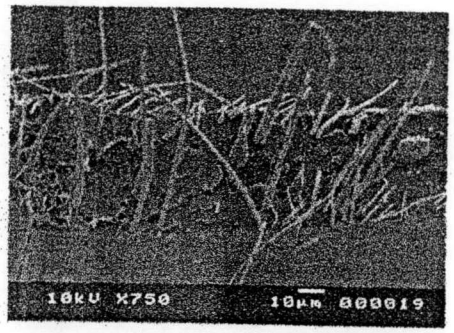


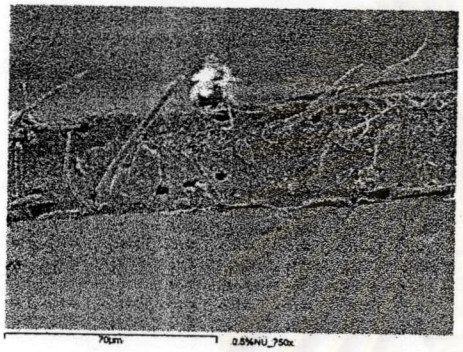
Figure 4.18 Optical micrographs of 10 wt%LCP blend films produced at T2 as a function of compatibilizer content (200X magnification) (——100 μm)



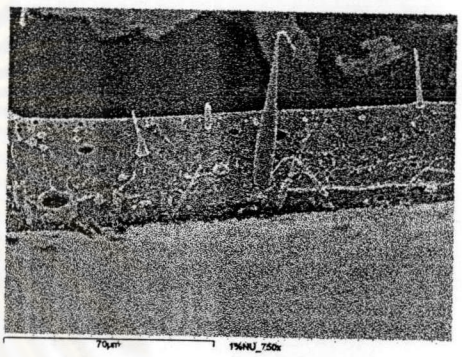
(a) 0.0 wt%Nu



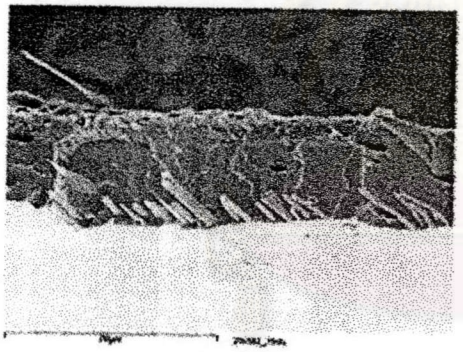
(b) 0.1 wt%Nu



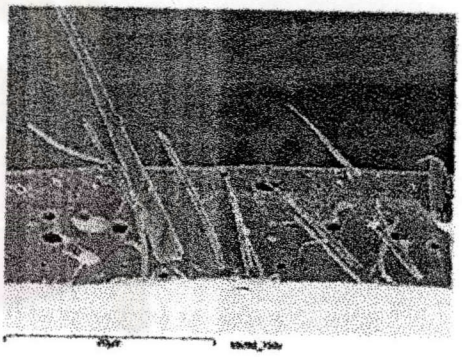
(c) 0.5 wt%Nu



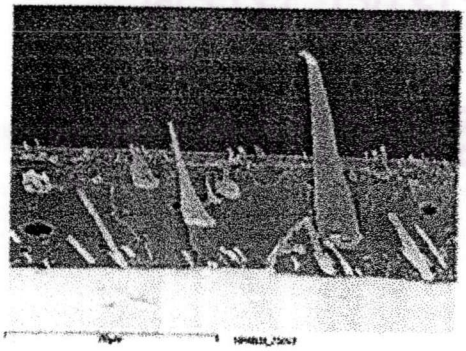
(d) 1.0 wt%Nu



(e) 2.0 wt%Nu



(f) 4.0 wt%Nu



(g)10.0 wt%Nu

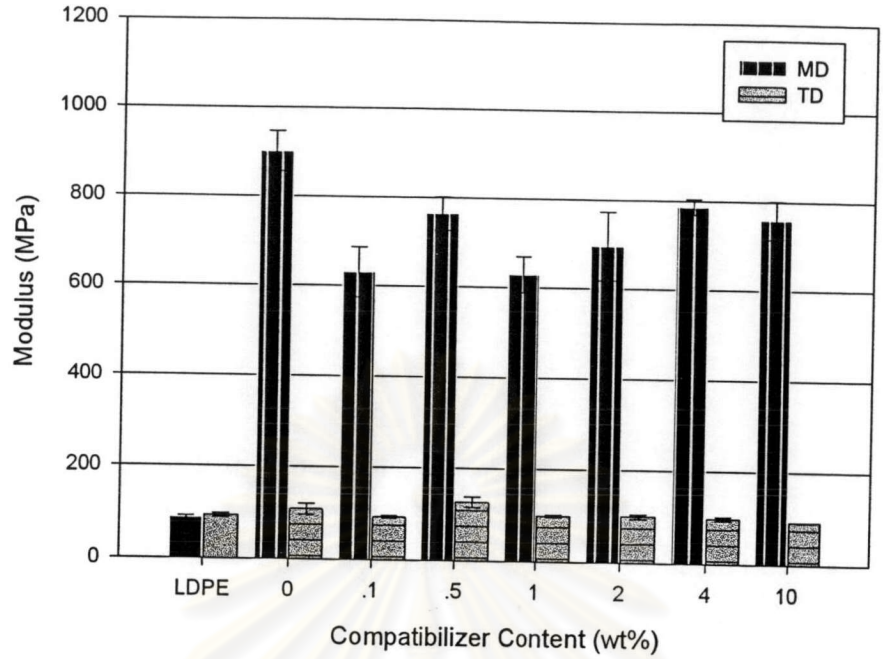
Figure 4.19 SEM micrographs of 10 wt%LCP blend films produced at T2 as a function of compatibilizer content (750X magnification)

4.3.2 Tensile Properties

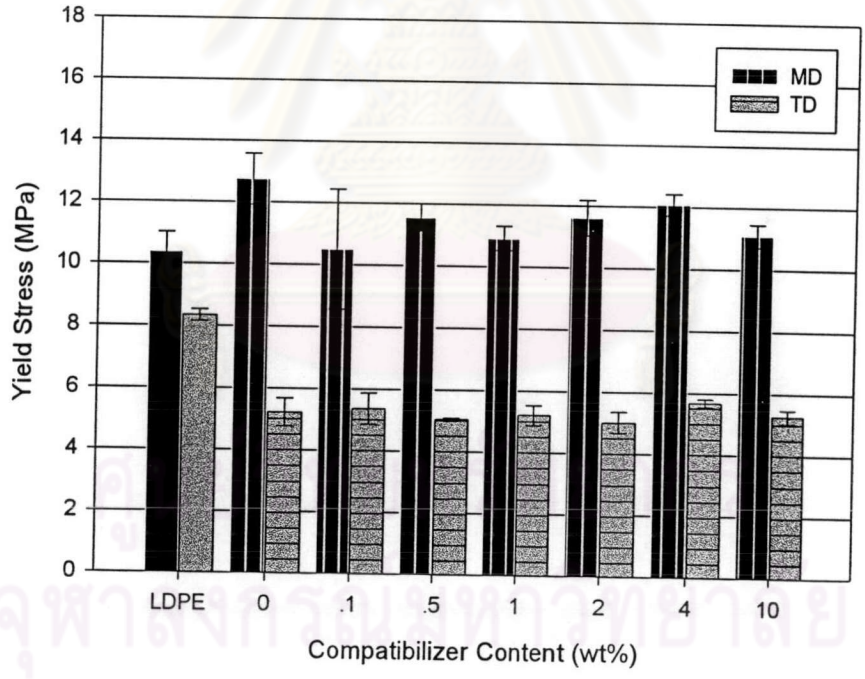
Tensile properties of the blend films as a function of compatibilizer content are depicted in Figures 4.20. It is apparent that existence of compatibilizer tends to decrease modulus and yield strength of the blend films. However, there is no clear trends of how the compatibilizer contents affect these films' properties. Decreases of modulus and yield stress of about 10-20 % should be due to the morphology changes as seen in previous section. Although adding some of compatibilizer into the blends is believed to help improve interfacial adhesion of two incompatible phases, but in this case, LCP dispersed phase morphology may play a more important role in responsible for films' overall tensile properties. The highest aspect ratios of LCP fiber are obtained when the blend contains no compatibilizer giving rise to highest modulus value. Reductions of tensile properties with increasing compatibilizer content seem to be the results of decreasing aspect ratios of LCP fibers.

Toughness of blend films is slightly improved when the blend containing amount of compatibilizer. This is possibly a result of the better coupling of two phases via compatibilizer (see Figure 4.20 (c)).

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



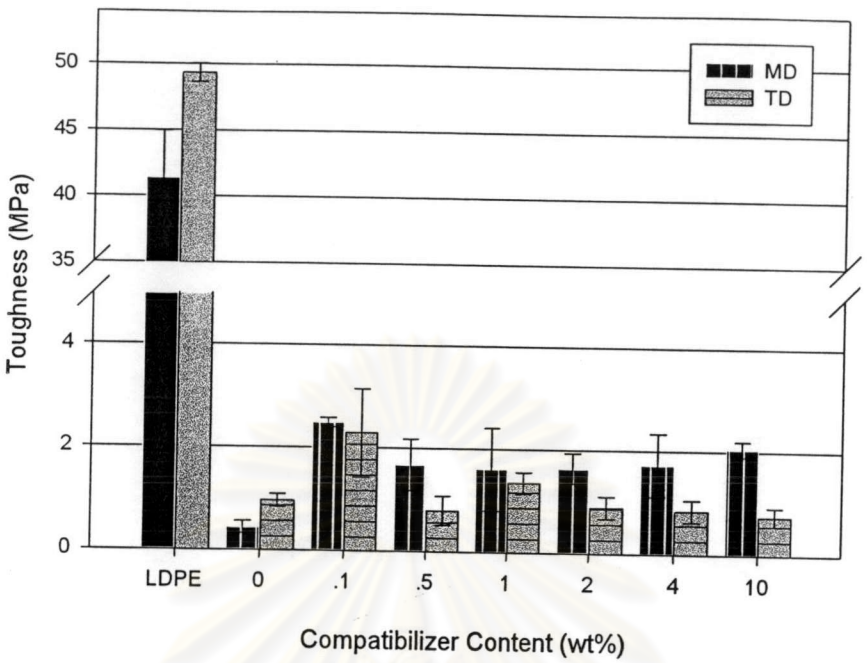
(a)



(b)

Figure 4.20 Tensile properties of 10%LCP/LDPE films produced at temperature profile T2 as a function of compatibilizer content as compared to LDPE film: (a) modulus, (b) yield strength, and (c) toughness

(Continue on next page)



(c)

Figure 4.20 Tensile properties of 10%LCP/LDPE films produced at temperature profile T2 as a function of compatibilizer content as compared to LDPE film: (a) modulus, (b) yield strength, and (c) toughness

4.3.3 Barrier Properties

The effects of compatibilizer content on oxygen transmission rate of 10%LDP/LDPE films can be seen in Figure 4.21. The data show that OTR values of blend films without compatibilizer are slightly higher than that of LDPE neat film and 10%LCP/LDPE films containing some amount of compatibilizer. This might be due to microvoids between LCP and LDPE phases in blends with no compatibilizer. The microvoid is the result of a poor adhesion of the two phases. High permeation rate of oxygen caused by microvoid was also reported by Flodberg et al. [22]. Decreasing of OTR values can be achieved when using of only small amount of ~ 0.1 wt% compatibilizer. This may imply to a slightly improvement in coupling of the two phases occurred in the system containing compatibilizer. Further increases of compatibilizer

content show no significant improvement of the films' barrier properties. Similar results are also observed in the case of WVTR, as illustrated in Figure 4.22.

As depicted in Figures 4.21 and 4.22, compatibilizer seem to be useful in enhancing barrier properties of the LCP/LDPE films. However, the amount of compatibilizer used does not actually affect the transport properties. Therefore, the chosen content of compatibilizer used throughout this study is 0.5 wt% based on the compromise of both transport properties and tensile properties.

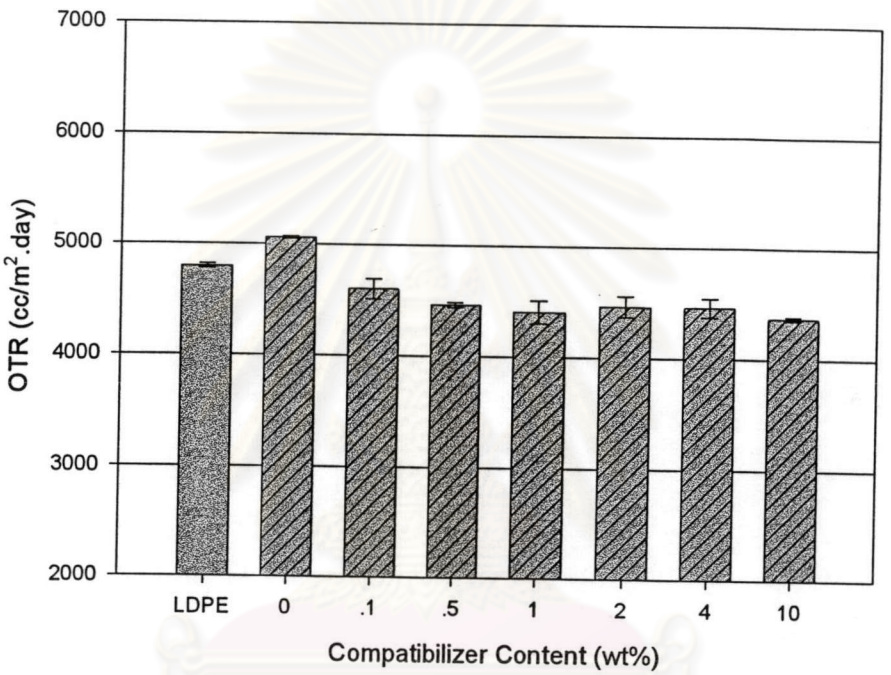


Figure 4.21 Effect of compatibilizer content on oxygen transmission rate of 10%LCP/LDPE films produced at temperature profile T2 as compared to LDPE film

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

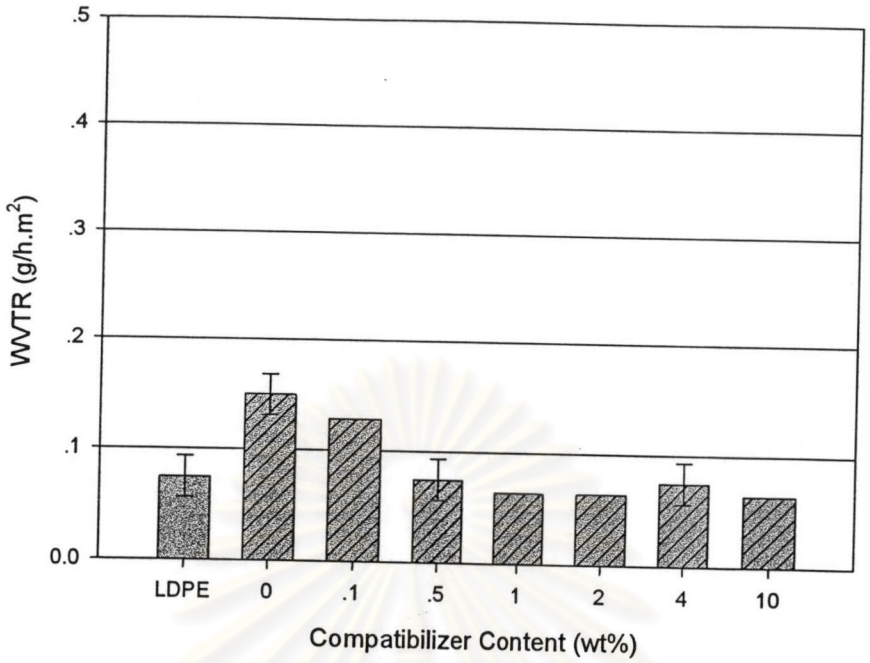


Figure 4.22 Effect of compatibilizer content on water vapor transmission rate of 10%LCP/LDPE films produced at temperature profile T2 as compared to LDPE film

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.4 Effects of LCP Content

To study effects of LCP content on morphology, tensile properties, as well as transport properties, LDPE film containing various amount of LCP ,i.e. 5, 10, 15, 20, 30, and 40 % by weight were produced at temperature profiles of T2 and T6. Screw speed and post-die drawing were kept constant at 12 RPM and at a DR of ~ 1.5, respectively.

4.4.1 Film Morphology

LCP content is one of the most critical parameters having a significant effect on morphology. Figures 4.23 show effects of LCP content on morphology when films are produced at T2. It can be simply observed that morphology of film containing 5% LCP mostly appears as elongated droplets, but further increases of LCP content to 10 wt% or more result in more effective fibers with high aspect ratios. Furthermore, films containing high contents of LCP (30 and 40 wt% LCP) can give rising to a more or less continuity structure as "tape-like" or "ribbon like" structures (see Figures 4.24 (e) and (f)).

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

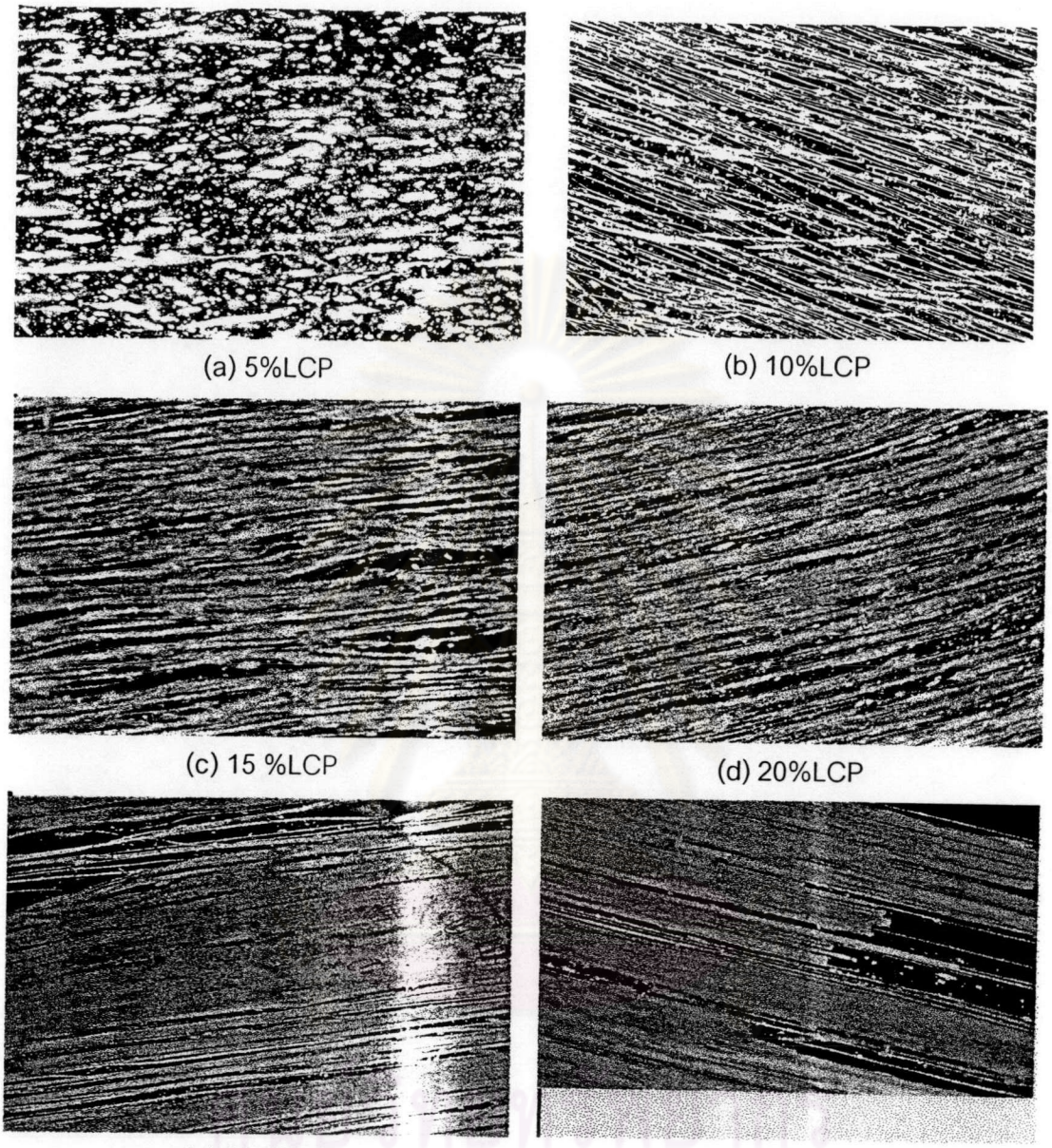
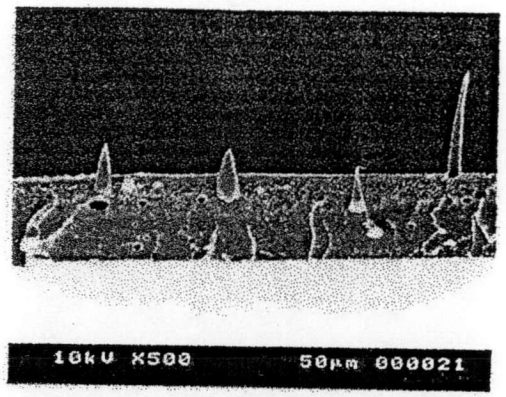
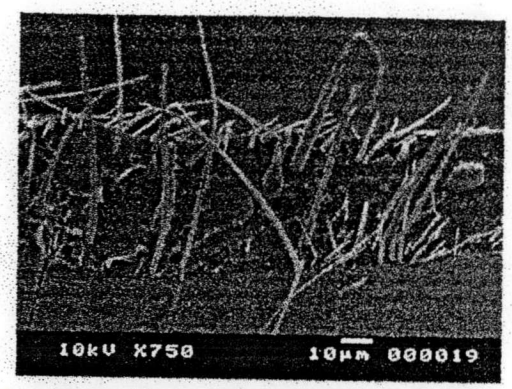


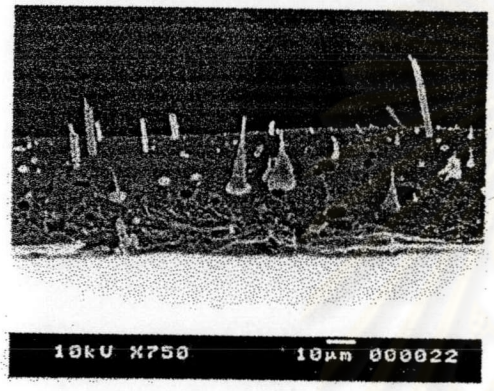
Figure 4.23 Optical micrographs of blend films containing various contents of LCP from 5 wt% to 40 wt% produced at T2 (200X magnification) (——100 μm)



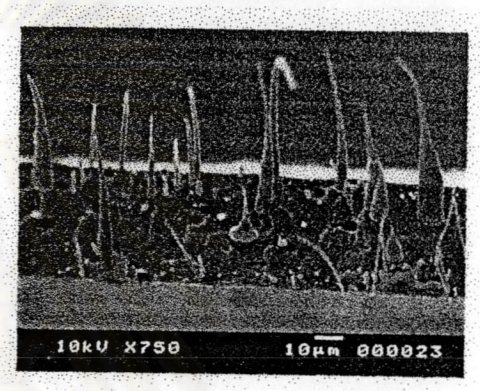
(a) 5 wt%LCP



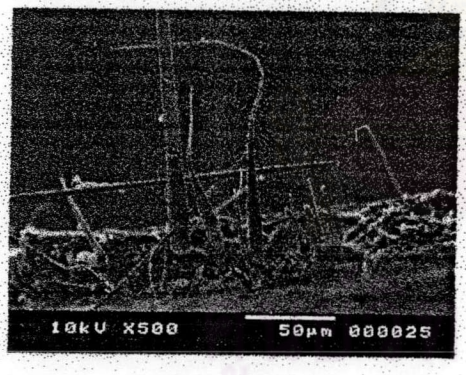
(b) 10 wt%LCP



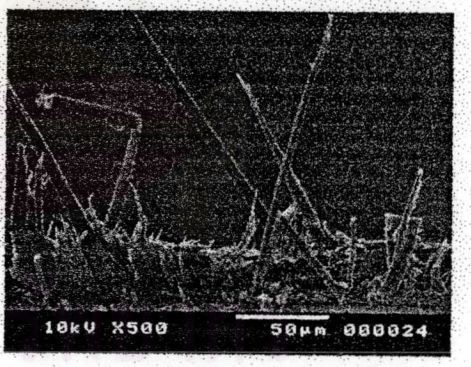
(c) 15 wt%LCP



(d) 20 wt%LCP



(e) 30 wt%LCP



(f) 40 wt%LCP

Figure 4.24 SEM micrographs of blend films containing various contents of LCP from 5 wt% to 40 wt% produced at T2 (750X magnification)

Findings of LCP in droplet or ellipsoid form in the blends containing small amount of LCP were also reported by other researchers [35-36]. The explanation based on Taylor theory can be applied [29, 45]. At low LCP concentration, LCP phase present in the blend as small droplets having large interfacial force (σ/R). As a result, capillary number is small, the interfacial forces dominate droplet-deforming process and a steady drop shape is developed. Generally, fiber formation depends on some critical volume fraction. In the case of blend films produced at temperature profile of T2, critical volume fraction value is larger than 0.34 (~ 5%LCP by weight). Increasing LCP concentration can promote fibrillation process as can be found in Figures 4.23 and 4.24. However, under different conditions, critical volume fraction of the same blend may be varied as a result of rheological property change. Figures 4.25 show structures of LCP/LDPE blend films produced at temperature profile T6, LCP fibrillar structure can be observed at low LCP concentration of 5 wt% or volume fraction of 0.34. Furthermore, SEM micrograph of 5 wt%LCP/LDPE films (Figure 4.26 (a)) reveals that some LCP "ribbon-like" structure even coexists with LCP fibers. As previously described, large initial droplet size obtained when blend films produced at temperature profile T6 resulting in final large fibers or ribbons.

"Tape-like" or "ribbon-like" structure with more continuity can be observed in the blends containing high LCP content of ~ 30% and 40% by weight. This could be the result of large initial droplet size of LCP dispersed phase as well as coalescence phenomenon. Increasing LCP content can result in increasing droplet population and decreasing distances between droplets and their neighbors, thus coalescence can take place more readily.

Another feature that can be observed when "tape-like" or "ribbon-like" structure possessing more continuity is a decrease of pull out mechanism. Breaking of LCP phase having high continuity could be due to a very large surface area of this morphology.

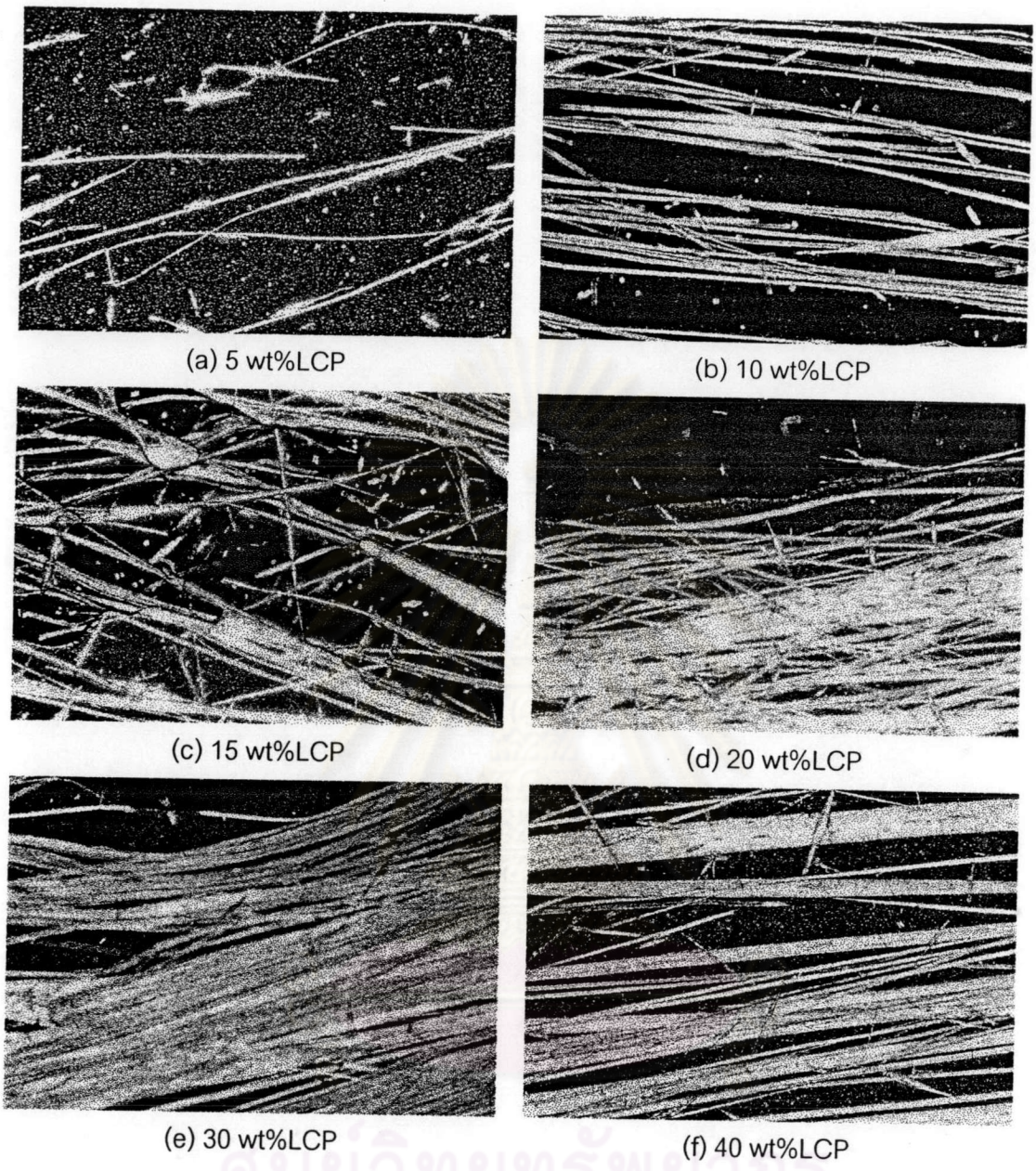
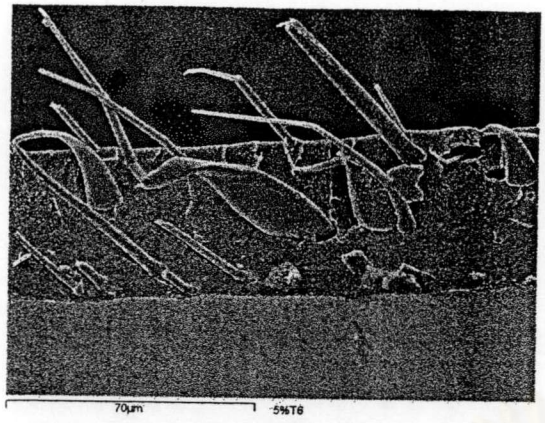
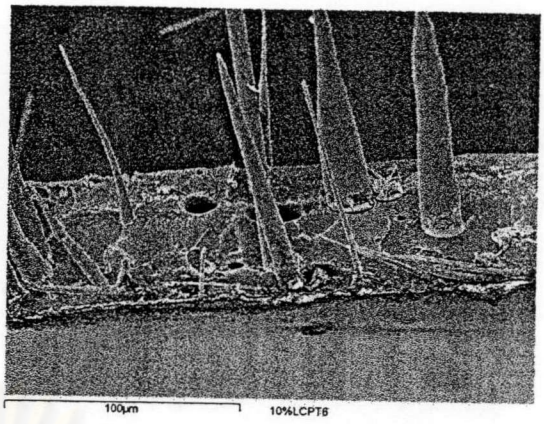


Figure 4.25 SEM micrographs of blend films containing various contents of LCP from 5 wt% to 40 wt% produced at T6 (200X magnification) (——100 μm)

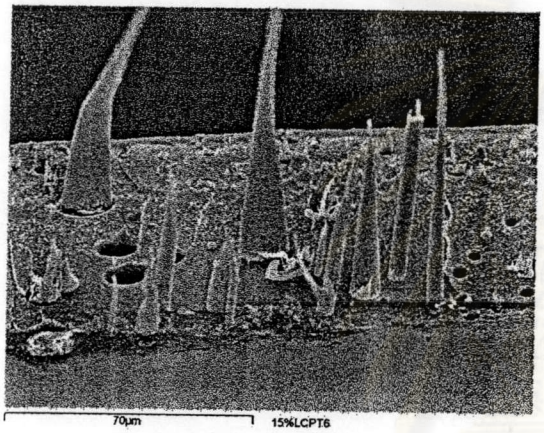
ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



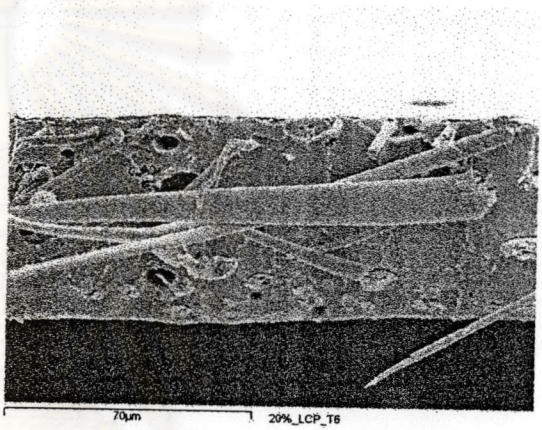
(a) 5 wt%LCP



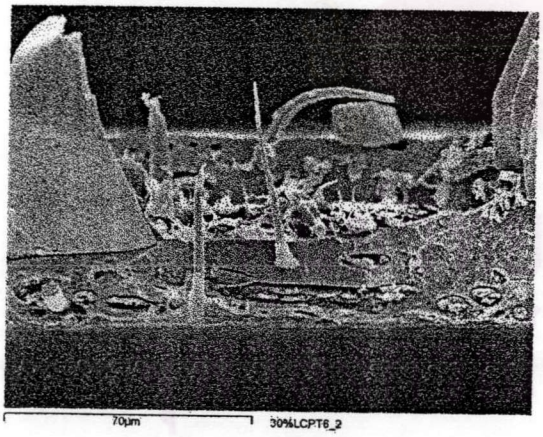
(b) 10 wt%LCP



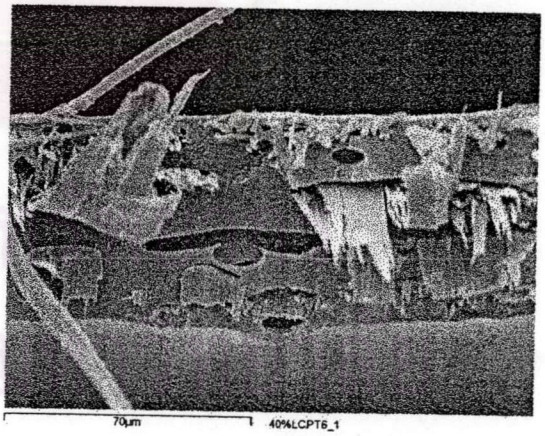
(c) 15 wt%LCP



(d) 20 wt%LCP



(e) 30 wt%LCP



(f) 40 wt%LCP

Figure 4.26 SEM micrographs of blend films containing various contents of LCP from 5 wt% to 40 wt% produced at T6 (750X magnification)

4.4.2 Tensile Properties

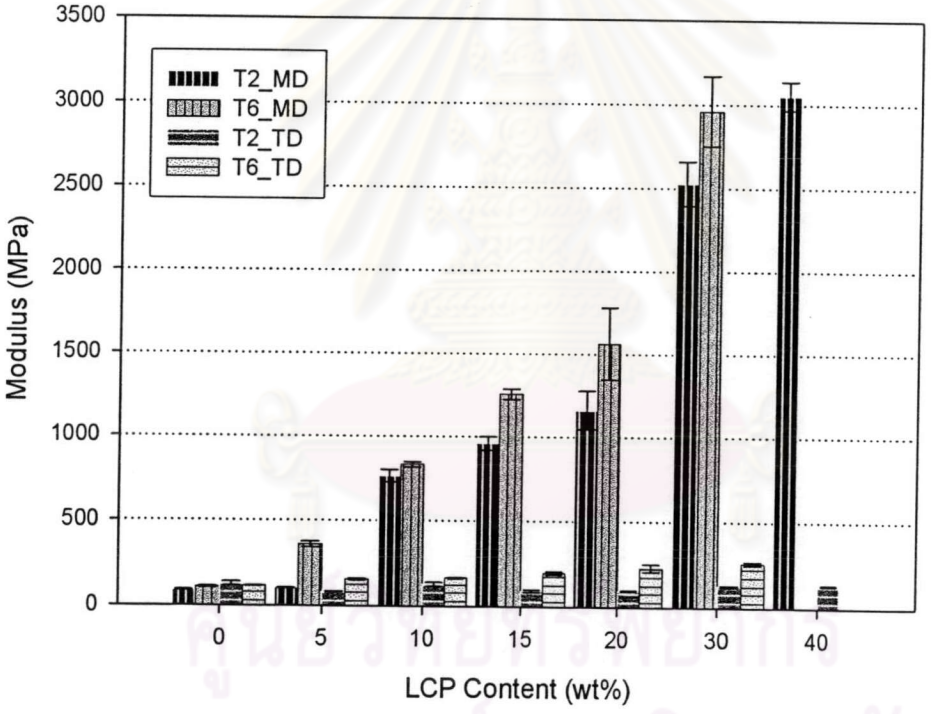
Tensile properties of LDPE films containing different amounts of LCP are illustrated in Figures 4.27 (a) – (c). Incorporating small amount of 5 wt%LCP in LDPE film produced at temperature profile T2 cause slightly increases of MD modulus (~17%). Further increases of LCP content to 10 wt% can lead to a the dramatic improvement of MD modulus of approximately 760% or close to 9 folds, as compared to the neat LDPE films produced at the same condition. This appreciable improvement in films' moduli could be due to reinforcing effect of fibrillar structure having effective aspect ratio (aspect ratio > 100). Compare to the small improvement in blend films containing 5 wt%LCP, smaller increases for modulus of 5%LCP/LDPE film is a result of LCP structure in as elongated droplets. The elongated droplets possess much lower of aspect ratios than that of LCP fibers found in 10%LCP/LDPE film have less effective reinforcement. Further increase of LCP concentration from 10 to 40 wt% results in increases of films' moduli. This should be due to an increasing of effective fiber amount in blend films. MD modulus of PE films containing 30 and 40 wt% possess 28 and 34 times greater than pure LDPE film were obtained.

Similar results can also be observed in blend films produced at temperature profile T6. In addition, it is generally seen that over the studied range of LCP contents, blend films of T6 have more improvements in moduli than the films produced at profile T2, especially at low LCP concentration of 5 wt%. Increasing MD modulus of approximately 240% and 250% were obtained in films of 5%LCP/LDPE produced at profile T6 as compared to the LDPE neat film produced at profile T6 and blend film of 5%LCP produced at profile T2. The presence of LCP fibers in 5%LCP/LDPE film produced at profile T6 is an evidence of fiber reinforcing effect on modulus improvement of this film.

Yield strength in Figure 4.27 (b) displays a similar trends as the modulus property, the maximum yield stress value of approximately 50 MPa can be achieved in blend films of 30 wt%LCP produced at both profiles, T2 and T6. It should be noted that films of 40%LCP produced temperature profile T6 tend to be nonuniform and films

consist of large holes. However, these features were not found in films produced at temperature profile T2.

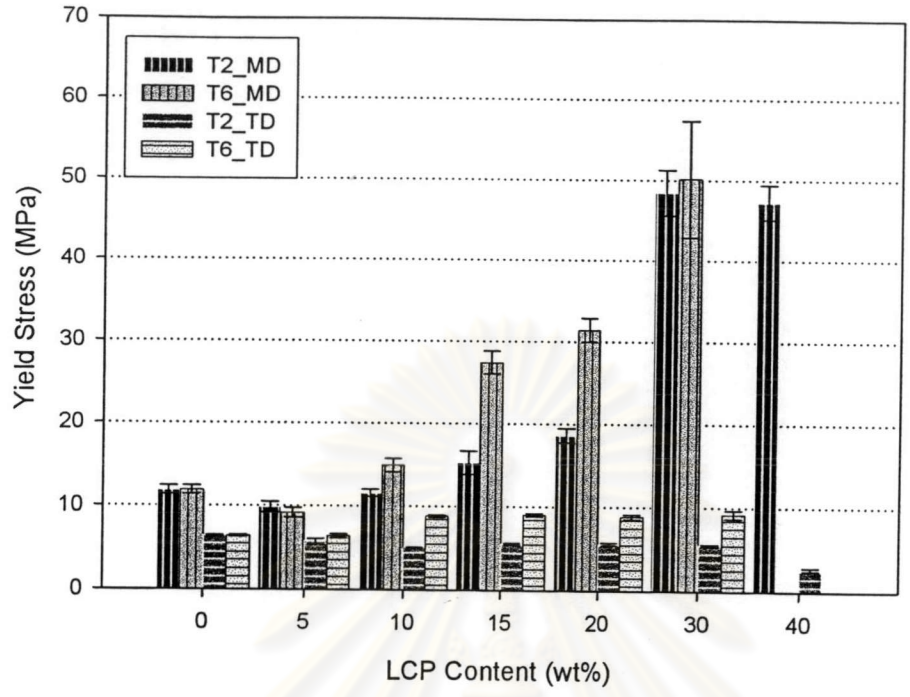
Toughness of blend films produced at two profiles, T2 and T6, is shown in Figure 4.27 (c). As expected, toughness decreases with LCP content. For 5%LCP blend films produced at profiles T2 and T6, toughness of 26 and 32 % lower than the neat LDPE film produces as the same conditions were obtained. Moderate toughness obtained in these films should be due to a small amount of LCP fibers presenting in this film. At such a low concentrate of 5 %LCP, LDPE matrix's properties dominate the blend characters.



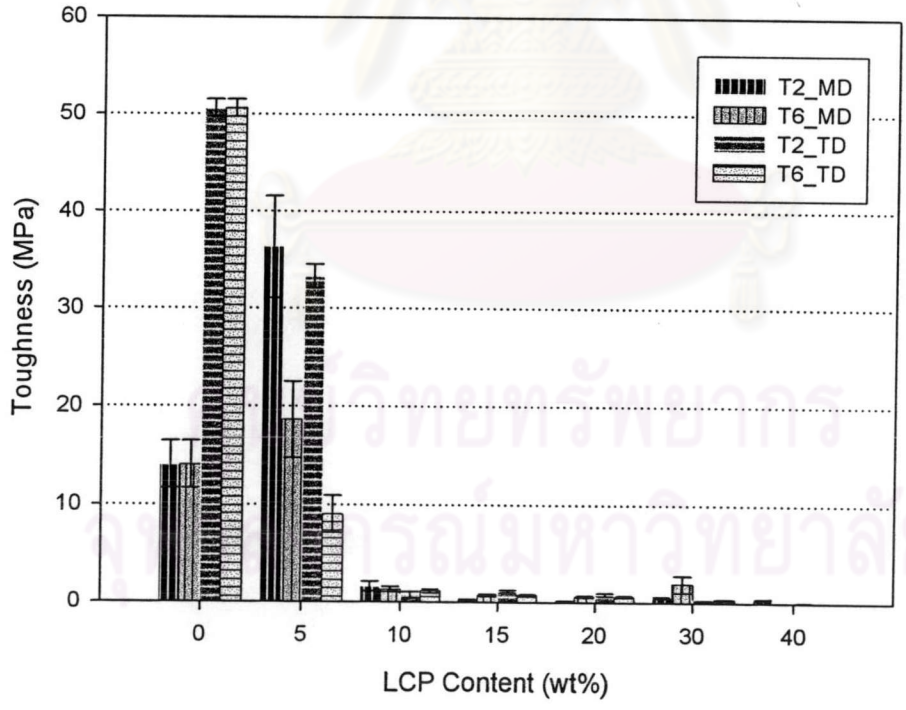
(a)

Figure 4.27 Tensile properties of LCP/LDPE blend films produced at temperature profiles T2 and T6 as a function of LCP content : (a) modulus, (b) yield strength and (c) toughness

(Continue on next page)



(b)



(c)

Figure 4.27 Tensile properties of LCP/LDPE blend films produced at temperature profiles T2 and T6 as a function of LCP content : (a) modulus, (b) yield strength and (c) toughness

4.4.3 Barrier Properties

Oxygen barrier properties are strongly dependent on LCP content as clearly seen in Figure 4.28. It is generally known that content of high barrier component is a key factor in decreasing gas transmission rate of the blends. In this case, increasing content of high barrier component of LCP can result in increasing tortuous path for gas traveling based upon the more continuous fiber or tape-like structure and, thus, films' barrier properties can be largely improved. Considering the effects of morphology difference obtained in blend films produced at two different profiles, T2 and T6, it is found that films of T6 with continuous tape-like structure have better enhanced oxygen barrier properties than blend films of T2. Films containing 30%LCP produced at profile T6 possess OTR value of ~1620 cc/m^2.day or approximately 3 folds lower than the neat PE film produced at the same condition. This is even lower than OTR of film containing 40%LCP and produced at T2. OTR value of this films is approximately 1860 cc/m^2.day. Overall observations serve well as confirmation on the effect of film structure on oxygen barrier property.

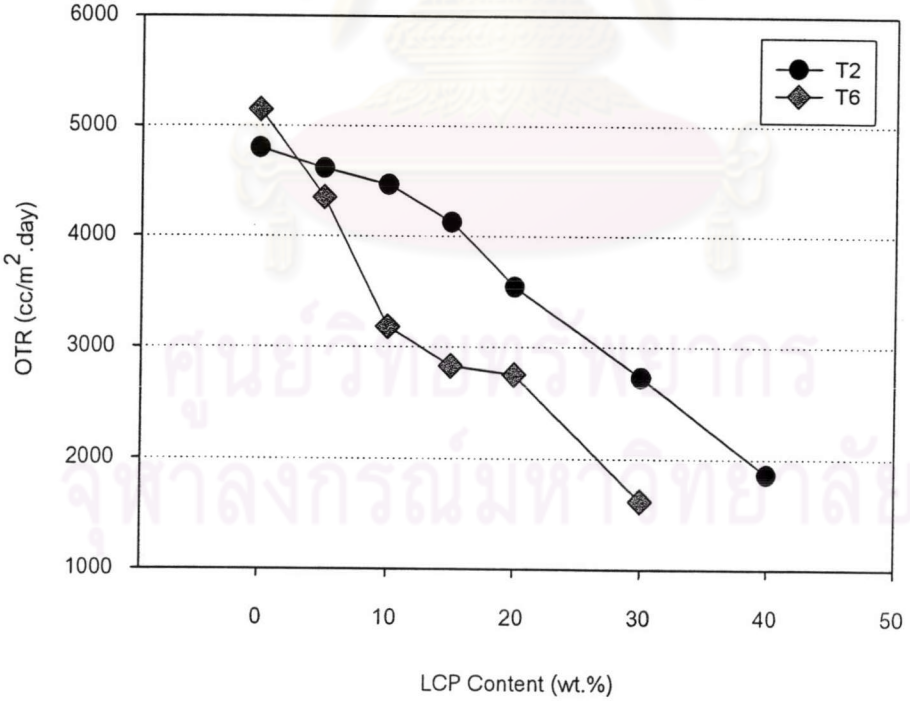


Figure 4.28 Oxygen transmission rate of LCP/LDPE blend films produced at temperature profiles T2 and T6 as a function of LCP content

Effects of LCP contents on water vapor transmission rate are, however, not similar to oxygen transmission rates. From Figure 4.29, the data show that presence of LCP and its content seem to have no clearly effects on altering WVTR. This should be basically due to a good water barrier of both two components, LCP and LDPE. Slight increases of WVTR in films produced at profile T2 may be attributed to the presence of microvoid in the films.

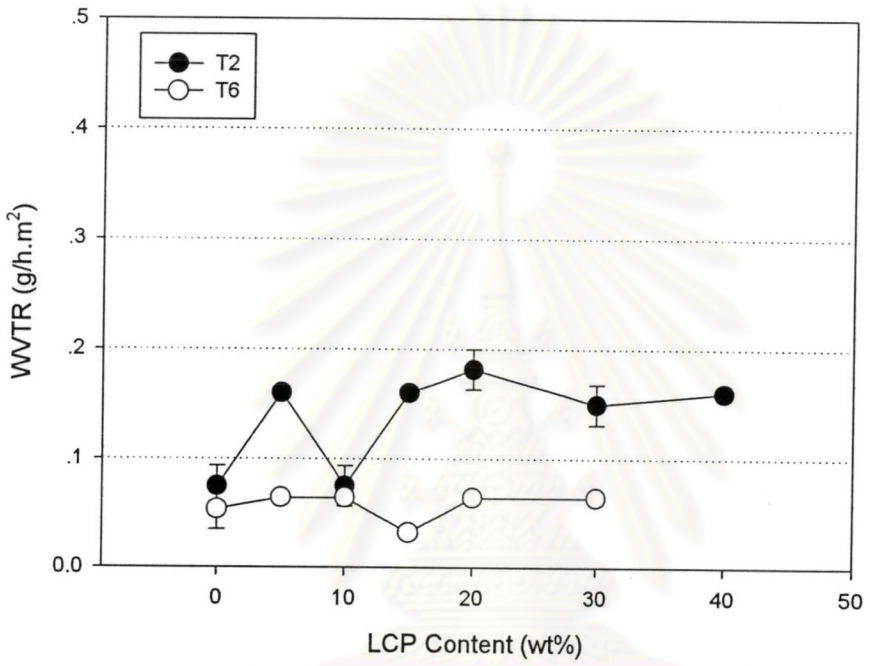


Figure 4.29 Water vapor transmission rate of LCP/LDPE blend films produced at temperature profiles T2 and T6 as a function of LCP content

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.5 Effect of Post-Die Drawing

Post-die drawing is applied when films exit the die in common film fabrication process. It is believed that post-die drawing can improve tensile properties of polymer films by enhancing orientation as well as increasing aspect ratio in case of polymer containing dispersed phase LCP system.

To study effects of post-die drawing on films' properties, blend films of 10 and 30%LCP were prepared by using temperature profiles of T2 and T6. Draw ratios, defined as the ratio of die area slit to cross-sectional area of a final film, were varied from 1, 1.5, 2, to 3. The resulting films possess thicknesses of 90, 60, 45, and 30 μm, respectively.

4.5.1 Film Morphology

Drawing within the fabrication process influences a development of morphology by increasing aspect ratio, as seen in Figures 4.30 and 4.31. As earlier discussed, structure of LCP domains (e.g., droplet size/ volume prior to deformation) depends strongly upon both processing temperature and LCP content. While post-die drawing can enhance fibrillation and orientation, it is also found that extents of drawing directly affect final LCP fiber morphologies. Drawing PE blends film containing 10 wt%LCP, produced at T2, to a draw ratio (DR) of 1.5 results in numerous thin LCP fibrils, however, further drawing to a higher DR of 3 leads to fibril breakage as seen by short fibers presented in Figures 4.31. In the case of films prepared at higher temperature profile of T6, SEM micrographs reveal relatively large LCP fibers of high aspect ratios and interesting LCP tape-like structure in all films processed at various draw ratios.

For films with 30 wt%LCP produced at profile T2, LCP fibrils with high aspect ratios are present even at a high DR of 3 (Figures 4.32). In addition, ribbon-like structure of LCP can also be observed. Generation of LCP ribbon structure should be due to the effect of larger LCP content that enhances the possibility of coalescence as previously described. However, ribbon-like structure in films of T2 is less than that found in 30%LCP films produced at T6.

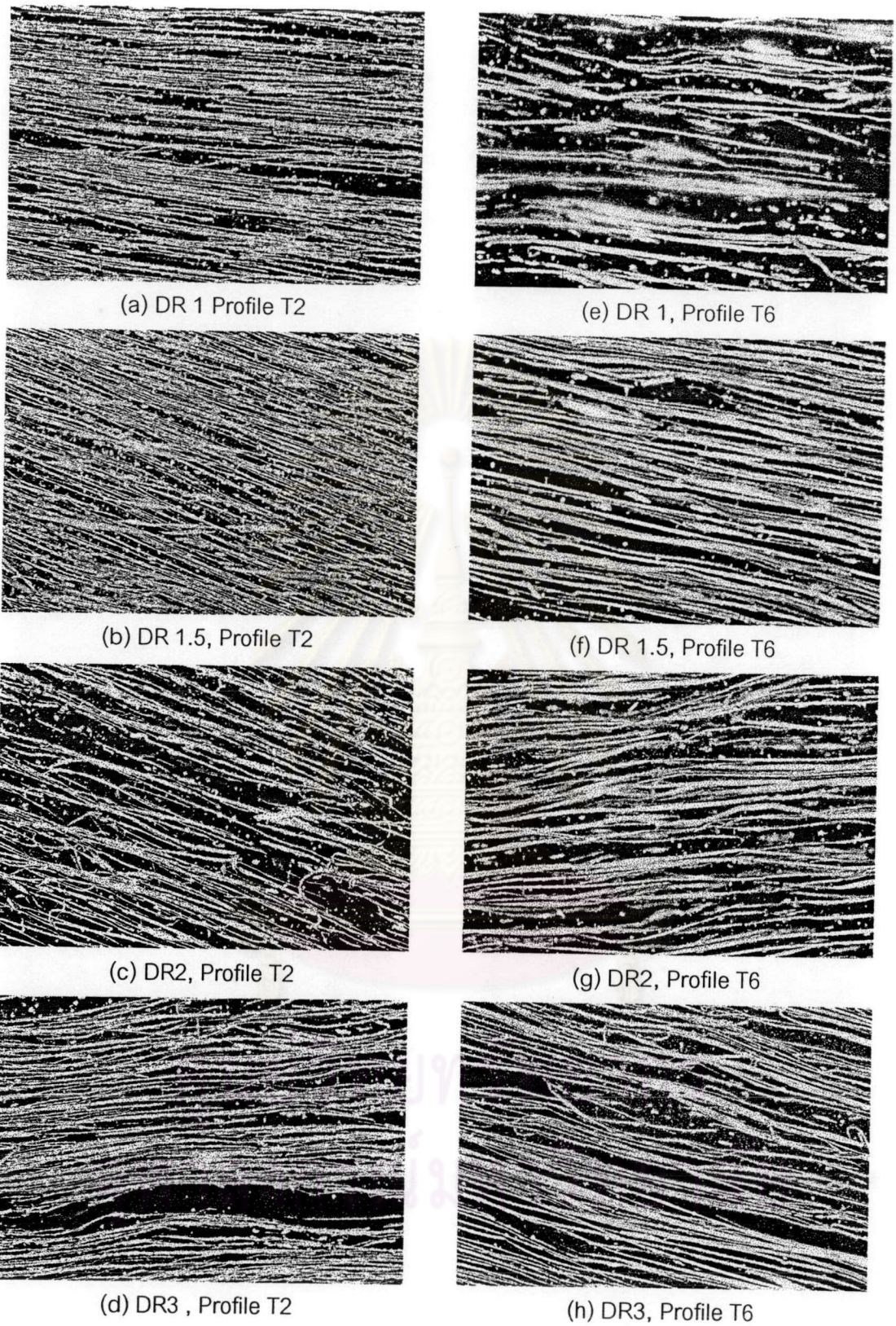
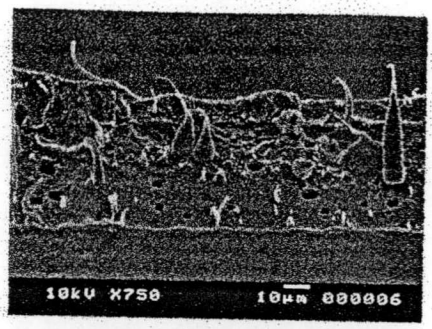
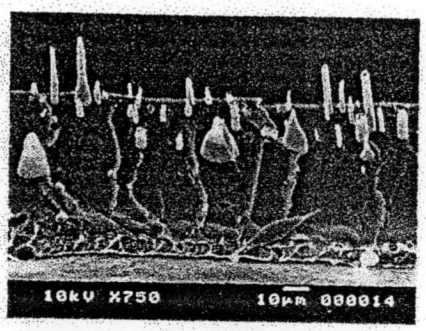


Figure 4.30 Optical micrographs showing drawing effects on 10 wt%LCP blend films produced at T2 (a-d) and T6 (e-h) (200X magnification) (——100 μm)

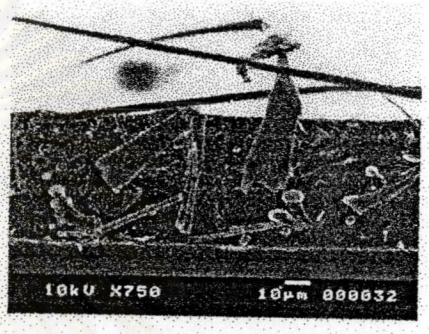


(a) DR 1, Profile T2



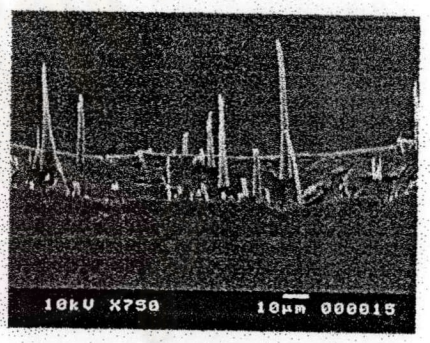
(e) DR 1 , Profile T6

(b) DR 1.5, Profile T2

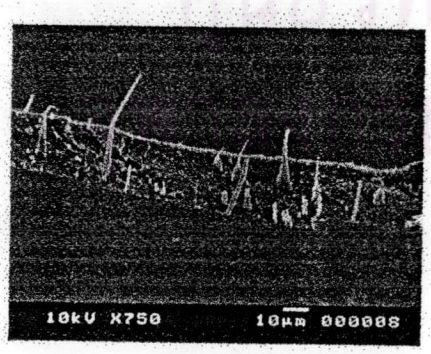


(f) DR 1.5 , Profile T6

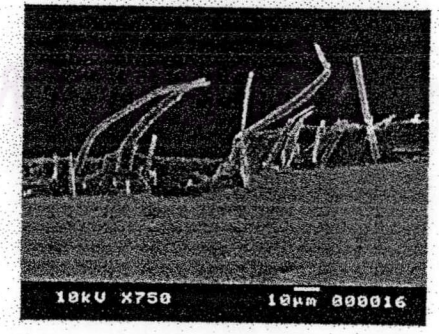
(c) DR2, Profile T2



(g) DR2 , Profile T6

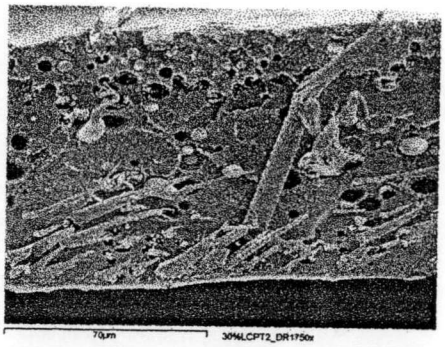


(d) DR3, Profile T2

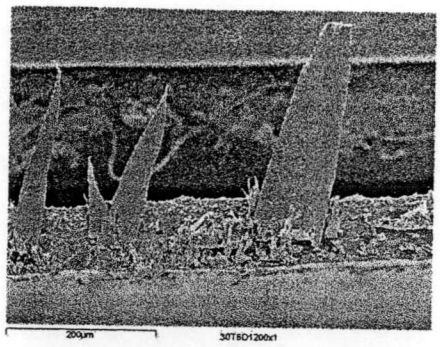


(h) DR3, Profile T6

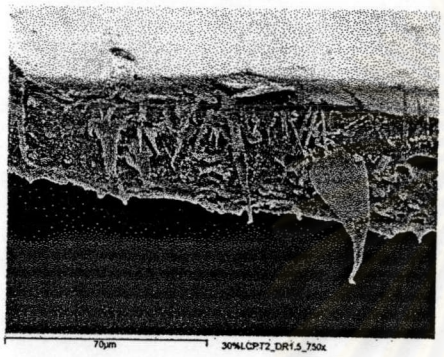
Figure **4.31** SEM micrographs showing drawing effects on 10 wt%LCP blend films produced at T2 (a-d) and T6 (e-h) (750X magnification)



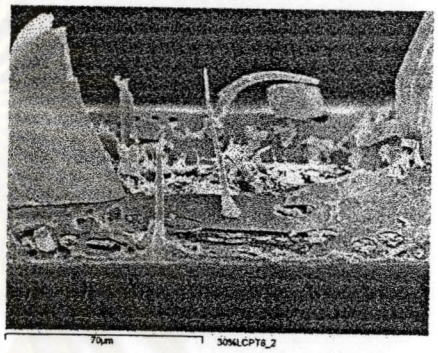
(a) DR 1 Profile T2



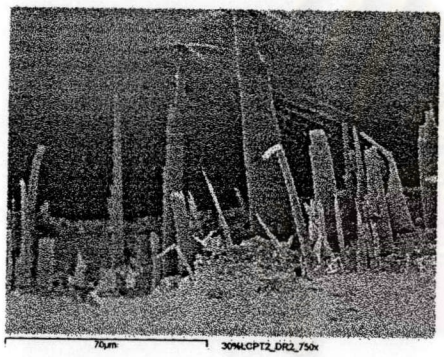
(e) DR 1, Profile T6



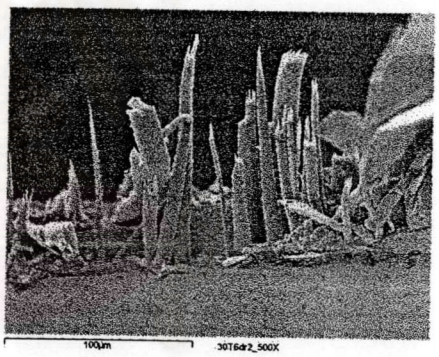
(b) DR 1.5, Profile T2



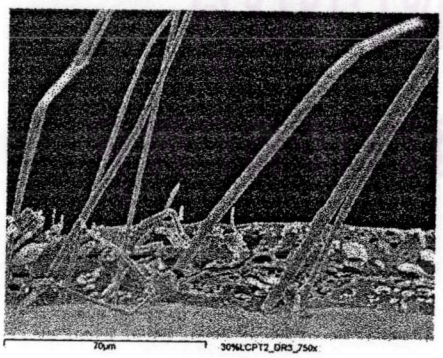
(f) DR 1.5, Profile T6



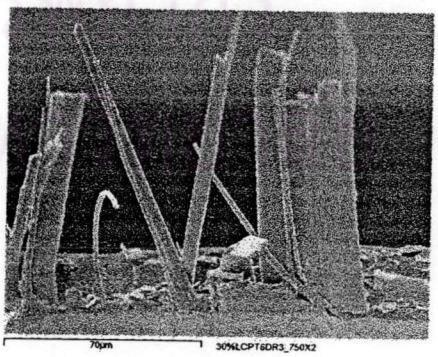
(c) DR2, Profile T2



(g) DR2, Profile T6



(d) DR3 , Profile T2



(h) DR3, Profile T6

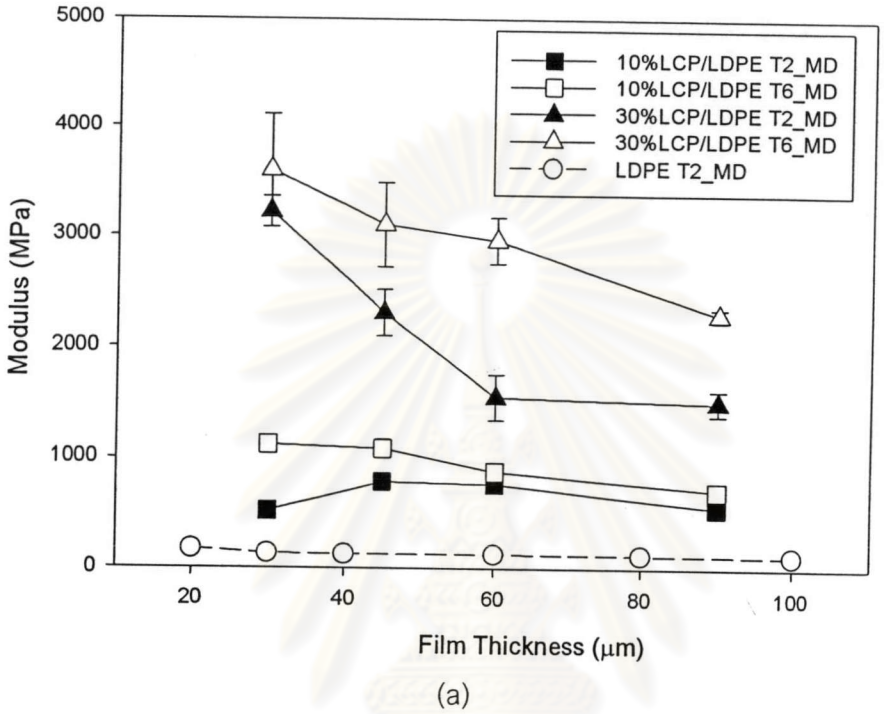
Figure 4.32 SEM micrographs showing drawing effects on 30 wt%LCP blend films produced at T2 (a-d) and T6 (e-h) (750X magnification)

4.5.2 Tensile Properties

Generally, tensile properties can be enhanced by drawing process. This improvement can also been found in the present study as shown in Figures 4.33 (a) –(c). Moduli of blend films in machine direction tend to increase when degree of post-die drawing is increased; only a slight increase was observed in the LDPE neat films. Result of moduli increment with degree of drawing can be the influences of a numerous high aspect ratio fibers presented in these films. However, it is also observed that modulus of 10%LCP/PE film produced at T2 decreases at a high draw ratio of three. This occurrence is explained by findings of fiber breaking in the films, as previously described. In the films containing high amount of LCP of 30% by weight, post-die drawing can dramatically improve moduli of these films. Increasing degree of drawing from 1.5 to 3 can improve moduli of approximately 100% and 25% for films produced at profile T2 and T6, respectively. Final films' moduli of 30%LCP/LDPE produced at T2 and T6 are 3000 and 3500 MPa. From Figure 4.33, 30%LCP films produced at T2 and T6 demonstrate different extent of moduli improvements or sensitivity to degree of drawing. These results can be presumably due to different LCP domains' size and structure which may differ in deformability and resistance to drawing.

As opposed to high modulus in all LDPE films containing 10% and 30%LCP, toughness of these films is quite low, as clearly seen in Figure 4.33(c). Elongation to break of these films are merely ~ 50 - 60%. Poor toughness observed in these films is a critical concern for practical applications such as in packaging. This point strongly suggests a further improvement in these blend film of LCP/LDPE. Based on other related works on LCP/PE blends, it has been reported that high toughness property of PE matrix could be largely retained for the PE blends containing 10%LCP [35-36]. Another interesting work reported by W. Chinsirikul. In her work, low melting LCP Vectra type was incorporated into PE blend matrix composing of HDPE and LLDPE. The PE blend was used in order to improve mechanical properties of blend films. Toughness of 10%LCP film in this system is only slightly lower than that of the matrix although high aspect ratio fibers of ~100 or higher are observed. This imply PE blend having a potential to use in improving toughness property of LCP blend film. Thus

another effort was also made in this study to try and improve toughness property of LCP blend films though blending of LDPE with LLDPE. Results on such LCP/PE blend systems will be father included in section 4.6.

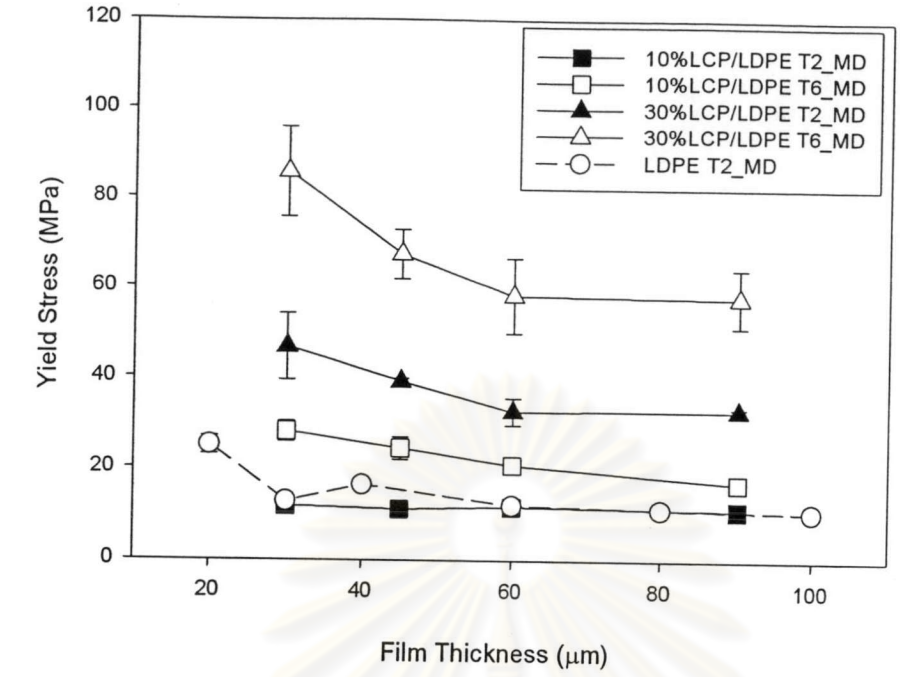


(a)

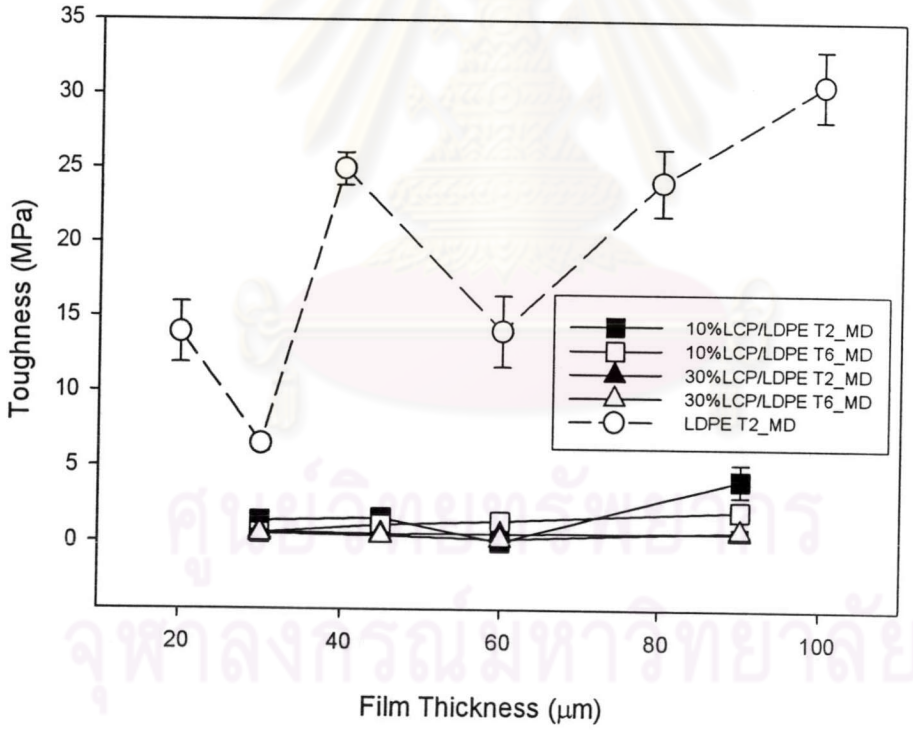
Figure 4.33 Comparisons of tensile properties of 10 and 30 wt% films as a function of degree of drawing (a) modulus, (b), yield strength ,and (c) toughness ;Note that Draw ratios of 1, 1.5, 2, and 3 correspond to film thicknesses of 90, 60, 45, and 30 μm, respectively

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

(Continue on next page)



(b)



(c)

Figure 4.33 Comparisons of tensile properties of 10 and 30 wt% films as a function of degree of drawing (a) modulus, (b), yield strength ,and (c) toughness ;Note that Draw ratios of 1, 1.5, 2, and 3 correspond to film thicknesses of 90, 60, 45, and 30 μm, respectively

4.5.3 Barrier Properties

Oxygen transmission rate of 10% and 30%LCP blend films produced at temperature profile T2 as compared to blend films having the same composition produced at temperature profile T6 are presented in Figure 4.34. Important findings are: (1) Blend films produced at profile T6 at all draw ratios possess lower OTR values than those of T2 and (2) OTR of blend films containing the same LCP content but processed at higher temperature of T6 seems to be less thickness sensitive than films produced at T2.

In the case of blend film, OTRs are less sensitive to drawing than the LDPE neat films. OTRs of 10%LCP/LDPE films produced at T2 show higher value than that of T6, especially at high draw ratio of three. These findings are presumably the result of different LCP morphologies. As previously describe, LCP dispersed phase in PE films containing 10%LCP are mainly fine fibrous structure. Producing these film with high draw ratio may cause fiber breakage and resulting in small aspect ratios fibers. Such a short fibers create less effective tortuous pathway, then gas can faster travel across the film thickness.

A slight increment of OTR at high draw ratio of three when LDPE films containing large amount of LCP as 30% weight (film thickness of ~30 μm) could be the result of high continuity of LCP phase in these films. As earlier mentioned, high content of LCP possess the more continuity of LCP phase and correspond to increase tortuosity. These findings can be more clearly seen when 30%LCP films produced at T6 where LCP dispersed phase are mainly in the thin ribbon or tape-like with large areas obstructing to gas traveling direction.

For WVTR values showing in Figure 4.35, all blend films products have WVTR values in the range of 0.5 - 1.0 g/ h.m^2, the same range as LDPE films. Degree of post die drawing seems to have no effect on WVTR of blend films in this system. These could be due to a good water barrier property of the two components, LCP and LDPE.

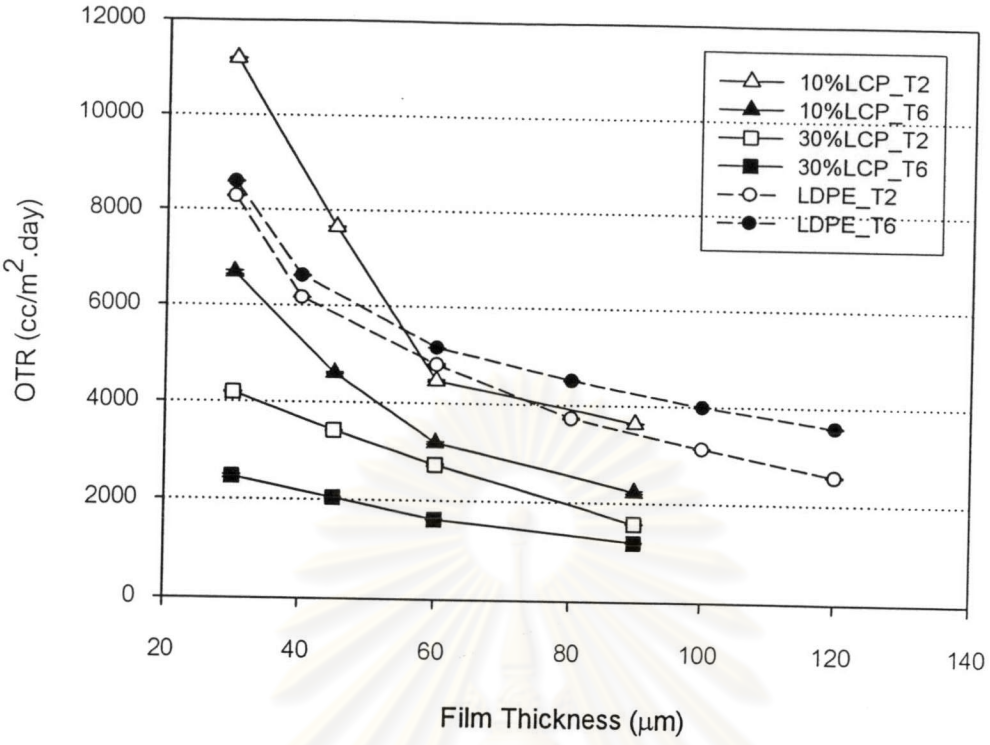


Figure 4.34 Oxygen transmission rate of 10 and 30 wt%LCP/LDPE film produced at temperature profiles of T2 and T6 as a function of post- die drawing

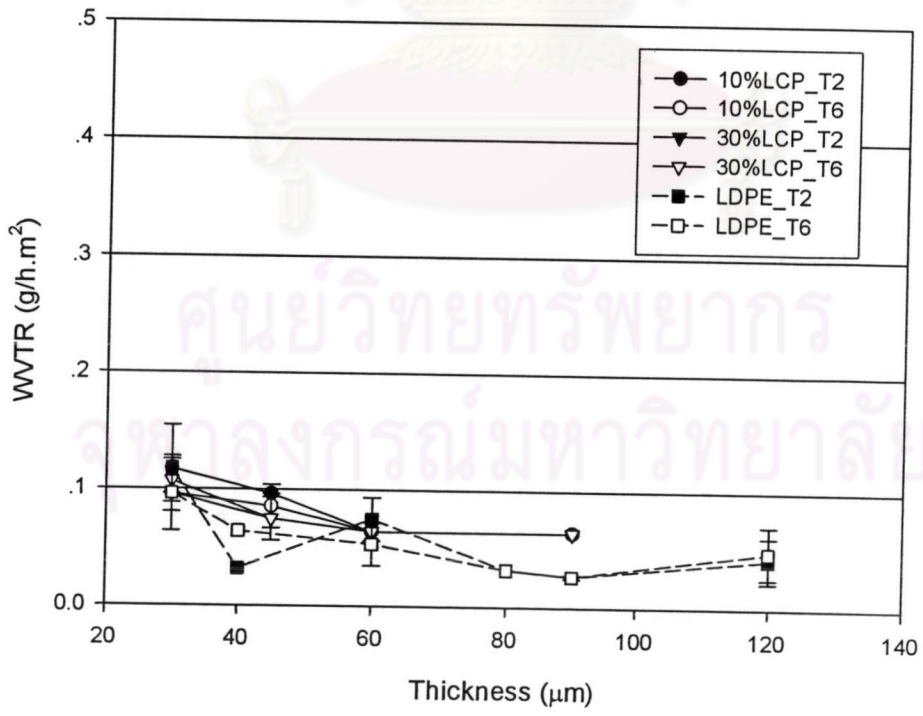


Figure 4.35 Water vapor transmission rate of 10 and 30 wt%LCP/LDPE film produced at temperature profiles of T2 and T6 as a function of post- die drawing

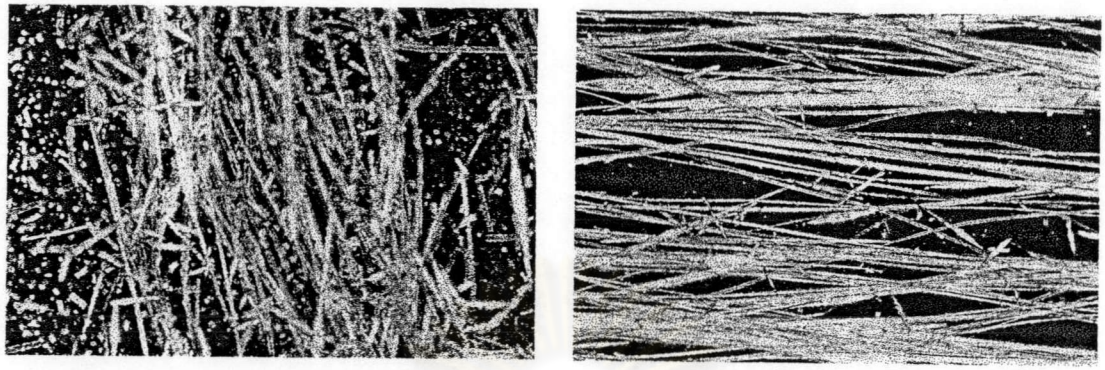
4.6 Effect of LLDPE/LDPE Blend Matrix

Apart from using LDPE alone as a matrix, attempts were also made to study effects of blend matrix of LDPE and LLDPE. A major objective of this investigation is to try and improved toughness of LDPE blends containing LCP. As previously described, LDPE film containing small amount of LCP (10% by wt) have a poor toughness property. LCP/LDPE films show a relatively low elongation to failure. One possible solution to this problem is adding another high toughness material into the blends. In this study, LLDPE was chosen because LLDPE possesses the high elongation to break of 620% in MD and 840% in TD while the LDPE used has elongation to break of 180% in MD and 590% in TD. Note that, these elongation to break values are taken from specification sheets given by the resin supplier. More detailed information of these materials are shown in Appendix A.

To study effects of LLDPE as a toughness modifier on film properties and morphology, temperature profiles T2 and T6 were used for film fabrication and 10 wt% of LCP was incorporated into the blend matrix. The PE blend matrix consists of 30 wt% LLDPE and 70 wt% LDPE. This composition is found useful in enhancing toughness property and usually used in commercial packaging films.

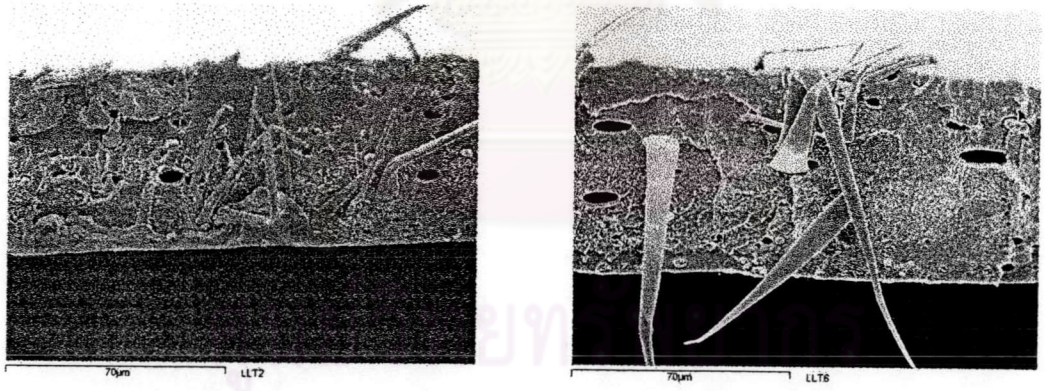
4.6.1 Morphology

Figures 4.36 and 4.37 show fibril structure with effective aspect ratios of 100 or higher formed in blend films produced at two different profiles pf T2 and T6 where the matrix is the blend of LLDPE/LDPE (30:70). In addition, blend films produced at higher processing temperature (T6) give the larger fiber and more or less "ribbon-like" structure as compared with LCP fibers in film produced at T2. These observations are similar to that for LCP/LDPE films, perceived in section 4.1.1. For the LLDPE/LDPE blends containing 10%LCP, morphologies are mainly fibrous structure with vary low content of droplet. Fibers found in these films produced at temperature profile of T6 seem to have very large aspect ratios of LCP dispersed phase. This may be the result of viscosity ratio of this system that is appropriate for fibrillation.



(a) 10 wt%LCP/(LL/LD) T2 (b) 10 wt%LCP/(LL/LD) T6

Figure 4.36 Optical micrographs of 10 wt%LCP in LLDPE/LDPE (30/70) blend matrix produced at T2 (a) and T6 (b) (200X magnification) (——100 μm)



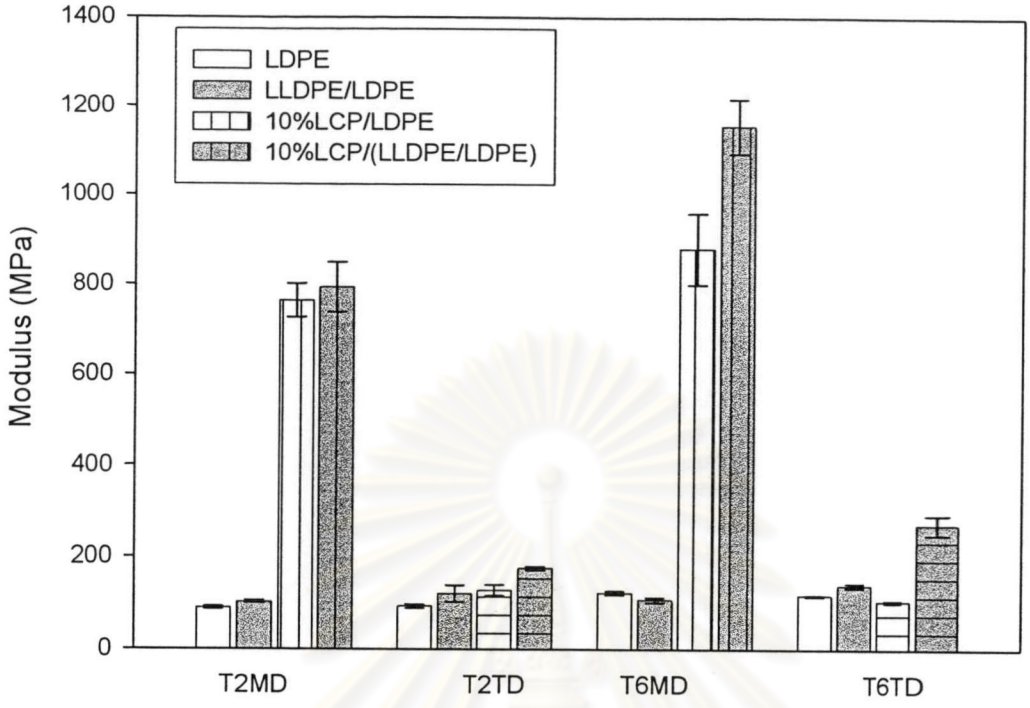
(a) 10 wt%LCP/(LL/LD) T2 (b) 10 wt%LCP/(LL/LD) T6

Figure 4.37 SEM micrographs of 10 wt%LCP in LLDPE/LDPE (30/70) blend matrix produced at T2 (a) and T6 (b) (750X magnification) (▬ 20 μm)

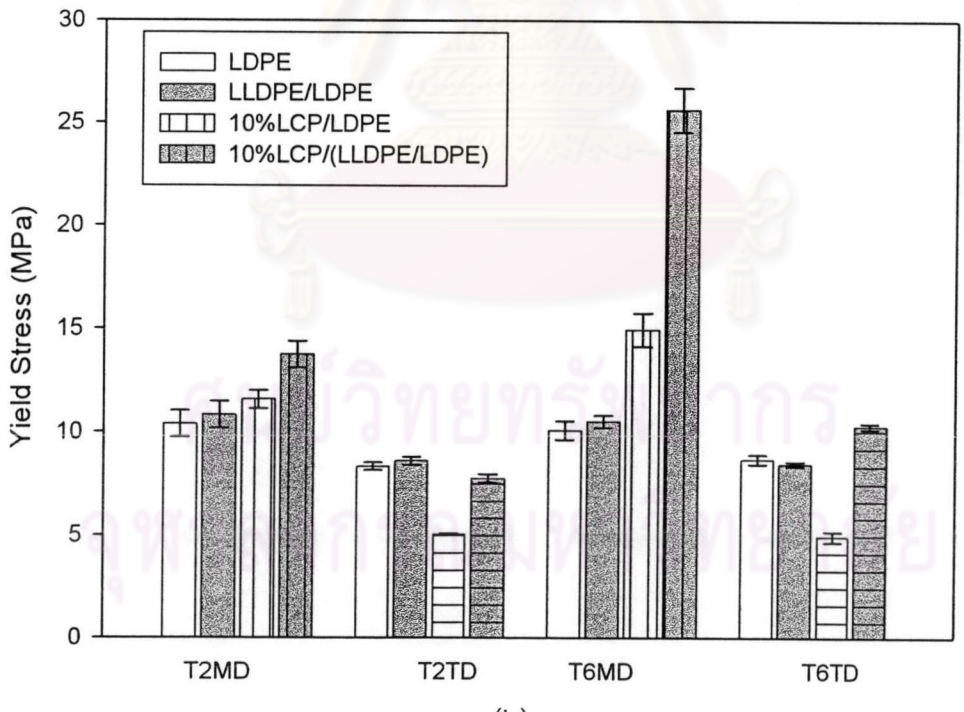
4.6.2 Tensile Properties

Tensile properties of 10%LCP in LLDPE/LDPE blends compared with LDPE film containing 10 wt%LCP and the neat LDPE and LLDPE/LDPE films are illustrated in Figures 4.38 (a) – (c). Neat LDPE and LLDPE/LDPE films show comparable values of modulus and yield strength. When incorporating LCP into the LLDPE/LDPE blend matrix, increases of moduli and yield strength are also found in a similar manner of LCP/LDPE films. However, it is interesting that greater improvements in modulus and yield strength are obtained in the films of LLDPE/LDPE containing 10%LCP that were produced at temperature profile T6. MD modulus and yield strength are approximately 40% and 66% higher than that of 10%LCP/LDPE film produced at T2 condition. Appreciable enhancements in both modulus and yield strength could be the result of developed LCP fibrillar structure in the film. LCP are mainly presented in fiber and ribbon form with high aspect ratio of >100

When considering of toughness enhancement, adding 30% by weight of LLDPE into LDPE film can improve toughness of PE films produced at both two different profiles, T2 and T6, in both MD and TD. Maximum improving is found in film LLDPE/LDPE film produced at T2 in MD by approximately 60%. Adding of LCP 10 wt% in this film also shows interesting of toughness improvement. The toughness value obtained in 10%LCP/LLDPE/LDPE film is approximately 80 MPa. This value is even higher than the neat matrix, which has toughness of ~60 MPa. Not only that, toughness in TD is also improved. Inversely, film of T6 having the largest modulus and yield strength impart a poor toughness. The dramatically improving of toughness when use LLDPE/LDPE blend as a matrix without losing of modulus and properties in some condition points that LLDPE can be used in blend as an effective matrix of LCP/PE system whenever blend films were processed under proper condition.



(a)



(b)

Figure 4.38 Comparison of tensile properties of 10 wt% blend films with two different matrices i.e. , LDPE and LLDPE/LDPE(30:70)

(Continue on next page)

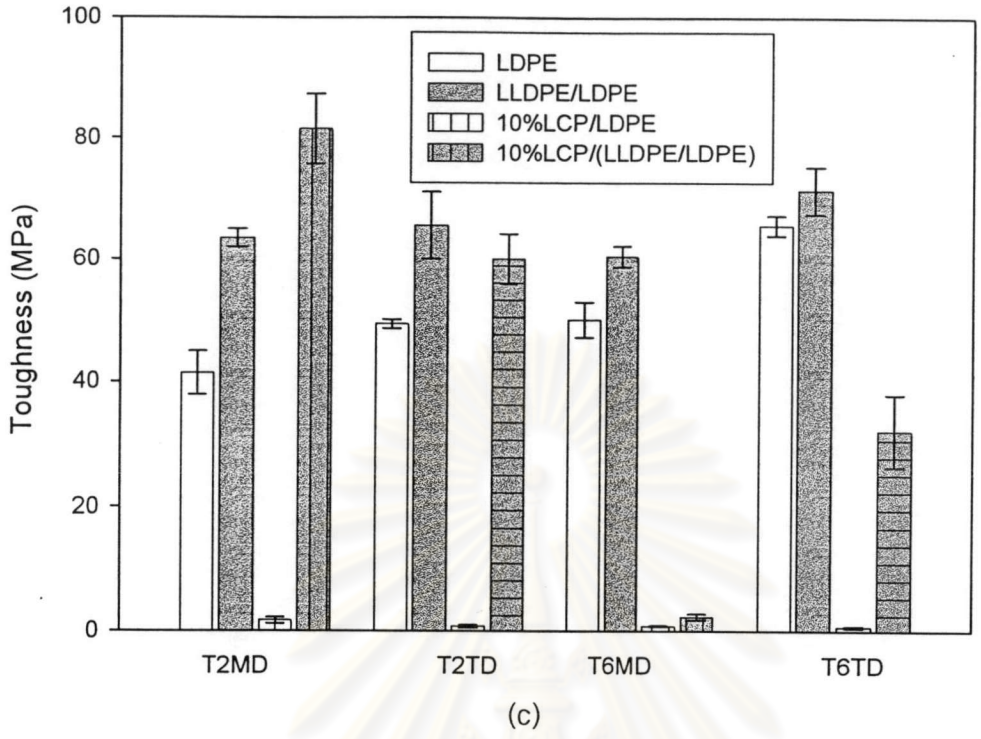


Figure 4.38 Comparison of tensile properties of 10 wt% blend films with two different matrices i.e. , LDPE and LLDPE/LDPE(30:70)

4.6.3 Barrier Properties

The results of oxygen transmission rates are depicted in Figure 4.39. It is obvious that films of LLDPE/LDPE blends are better barriers to oxygen gas than pure LDPE films. Upon incorporation 10% by weight of LCP into the PE blend matrix and films were produced at temperature profiles T2, the OTR value of these result film are approximately 33% lower that OTR of the blend matrix. Comparing OTR values of two film matrices containing the same amount of 10%LCP, films of LLDPE/LDPE blend produced at both T2 and T6. The reduction of OTR for LCP/LLDPE/LDPE blends is more pronounced for films produced at temperature profile T6. Of all films produced, the lowest OTR film of 2300 cc/m2.day appears to be the blends of 10%LCP in LLDPE/LDPE (30:70) matrix. It can be concluded that improvement in barrier of LCP/PE blends films should derive from contributions of both intrinsic properties of the matrix and developed morphology of LCP dispersed phase. Morphology of LCP can be the droplet, ellipsoid,

fiber and ribbon form, however, based on overall investigations "ribbon-like" structure of LCP in LDPE films produced at profile of T6 is desired feature in enhancing oxygen barrier. In the case of LLDPE/LDPE blend matrix containing 10%LCP, similar ribbon structure of LCP is also desirable. Such structure is observed in the films fabricated at profile of T6 but LCP ribbons seem to be smaller in widths, as compared to LCP ribbons generated in LDPE matrix produced at the same condition. Thus, it might be possible that further improvement in oxygen barrier property of these LLDPE/LDPE blend films could be carried out though tailoring LCP structures as a function of processing temperature and /or viscosity ratios.

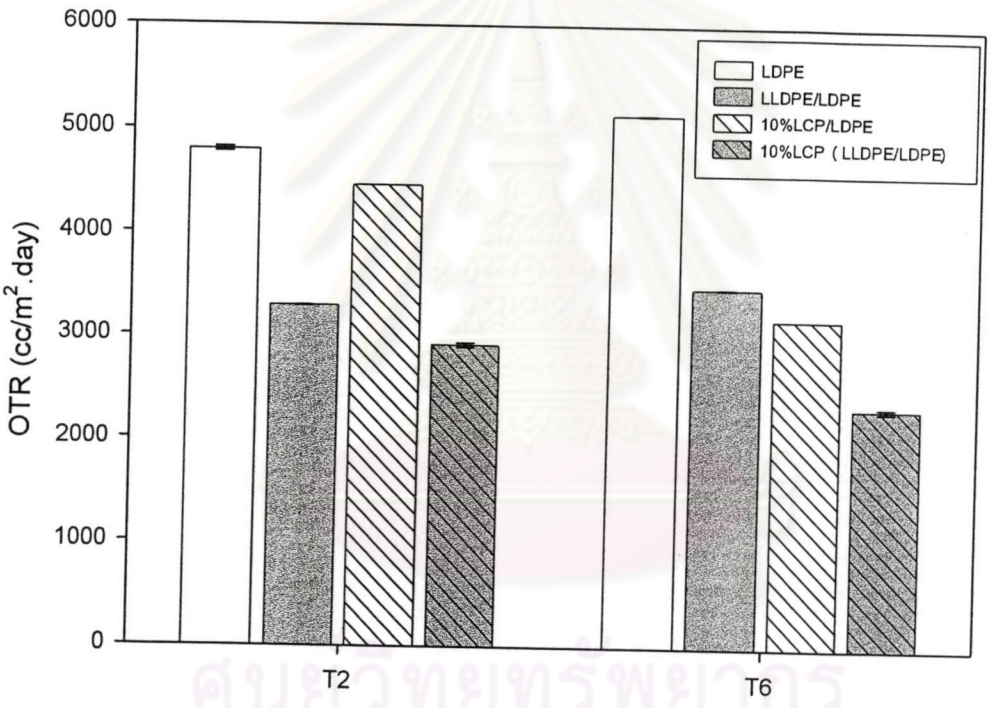


Figure 4.39 Comparison of oxygen transmission rate of two different PE films (LDPE and LLDPE/LDPE (30:70) and two different blend films of 10%LCP/LDPE and 10%LCP/(LLDPE/LDPE)

The comparison of WVTR of 10%LCP films having different matrices is shown in Figure 4.40. WVTR values of all films are presented in a similar range of 0.05 - 0.1 g/h.m^2. As previously discussed, both PE and LCP are good barrier to water vapor, then changing of matrix material by adding a certain amount of LLDPE into the LDPE shows no significant effects in altering WVTR of overall blend films .

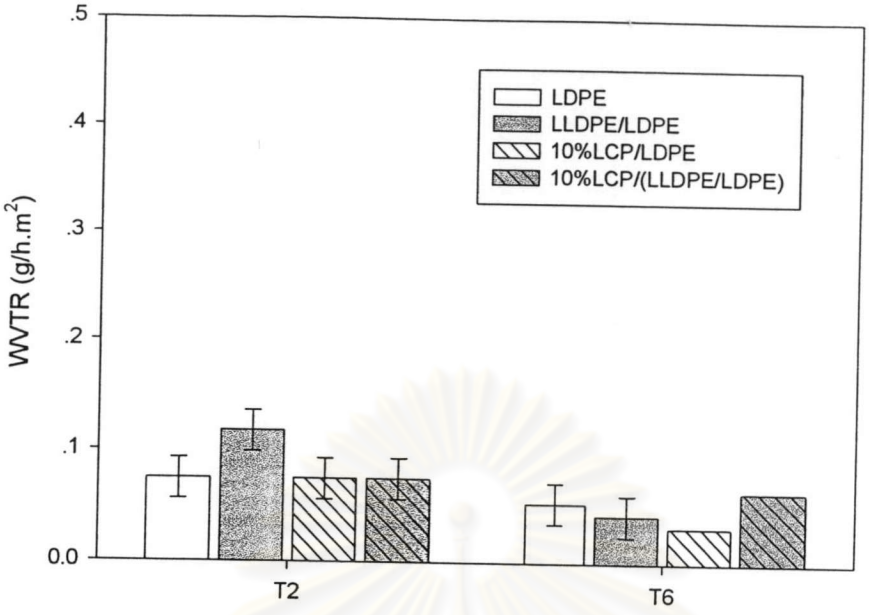


Figure 4.39 Comparison of water vapor transmission rate of two different PE films (LDPE and LLDPE/LDPE (30:70) and two different blend films of 10%LCP/LDPE and 10%LCP/(LLDPE/LDPE)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

4.7 Prediction of Tensile Property Related to Structure by Composite Theory

Rule of mixture and Halpin-Tsai theory are widely used in predicting composite properties. In this study, these two theories were used to estimate average aspect ratios of LCP fibers presented in the blend films. Master curves composed by using these two principles, following Equations (2.15) and (2.18) are illustrated in Figure 4.41.

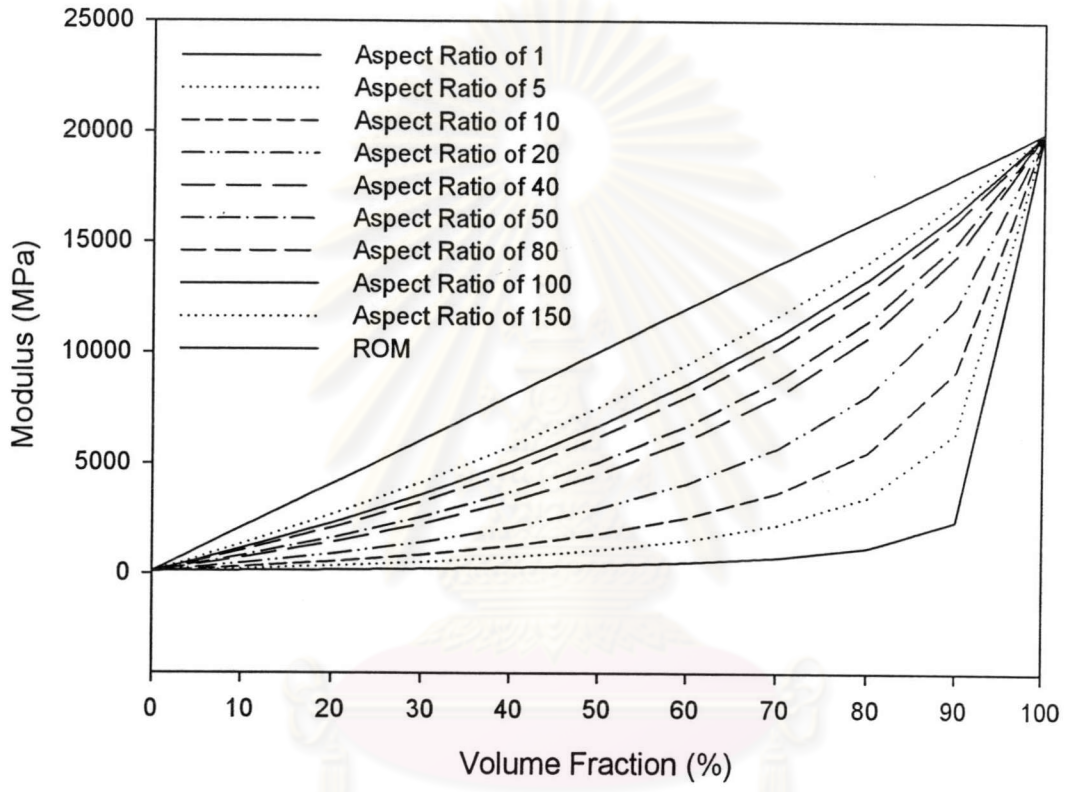


Figure 4.41 Master curves for aspect ratio prediction by applying Halpin-Tsai and Rule of Mixture models

Applying modulus values of resulting films produced at different temperature profiles onto the Halpin-Tsai curve to predict averaged value of aspect ratios in each film is demonstrated in Figure 4.42. It is likely from the estimation that fibers formed at given temperature profiles of T1 to T4 possess high aspect ratios of approximately 100. At profiles T5 and T6, obtained fibers having aspect ratios in the higher range of 130 - 140 are observed. Increasing LCP content leads to increasing of aspect ratios, as seen in Figure 4.43 and the estimated value of aspect ratio is shown in Table 4.1.

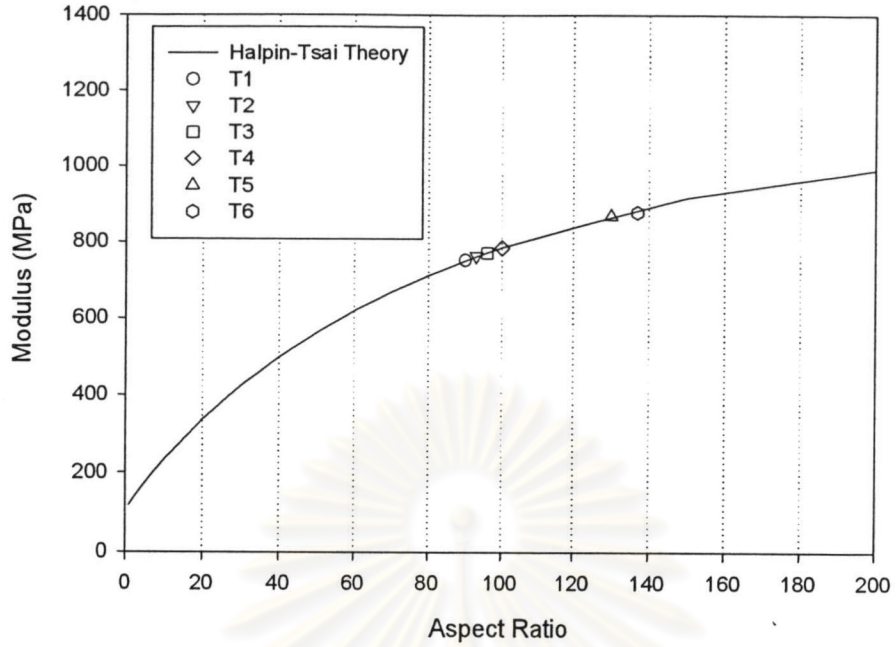


Figure 4.42 Illustration of LCP fibers' aspect ratios prediction for 10%LCP/LDPE films (or 0.067 volume fraction) produced at 6 different temperature profiles and constant draw ratio of 1.5

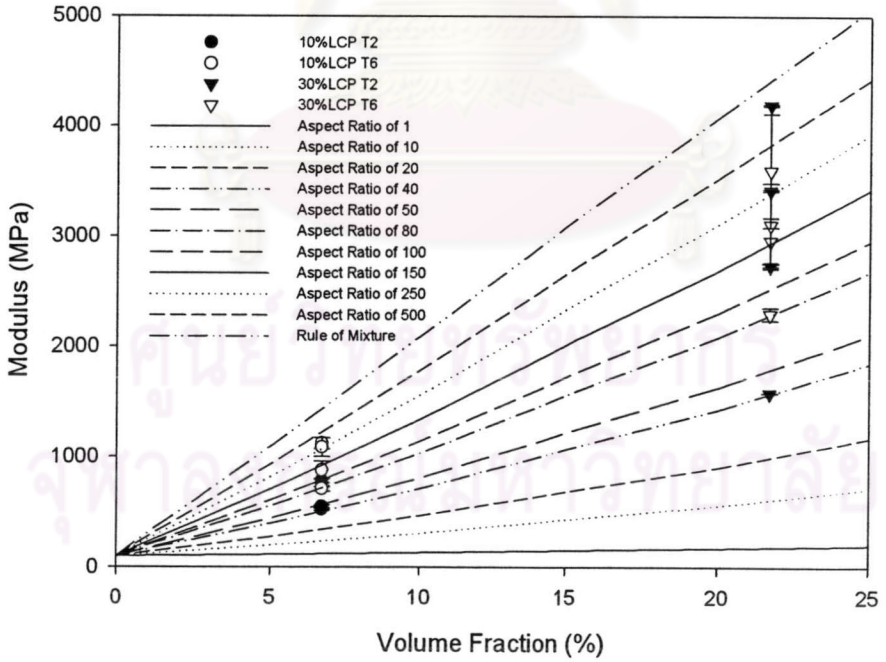


Figure 4.43 Illustration of applying Halpin-Tsai model for prediction of LCP fibers' aspect ratios of films containing different amount of LCP (10 and 30 wt%)

Table 4.1 Estimation of LCP fibers' aspect ratio (L/D) in LCP/PE films by applying Halpin-Tsai model

	Estimated (L/D) 10%LCP/LDPE,T2	Estimated (L/D) 10%LCP/LDPE,T6	Estimated (L/D) 30%LCP/LDPE,T2	Estimated (L/D) 30%LCP/LDPE,T6
DR 1	40	80	40	80
DR 1.5	80	140	125	150
DR 2	100	250	250	190
DR3	50	260	500	300

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย