

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Conclusions

Relationships of structure and barrier properties of PE films containing LCP as a dispersed phase were investigated. The attempts were paid for understanding the effects of both processing variables and material influences on film morphologies and the corresponding properties. Morphological studies of the resulting LCP/LDPE films were carried out using two different methods i.e. scanning electron microscope (SEM) and polarized light optical microscope (OM). Oxygen transmission rates (OTR) and water vapor transmission rates (WVTR) were measured in order to study transport properties of the resulting films. Furthermore, tensile properties of the blend films were also analyzed.

Various parameters influencing the control of LCP dispersed phase morphology were studied. The following sections will describe a series of parameters that were studied in this work along with important observations.

Processing temperature profile was the first parameter being investigated. Six different processing temperature profiles, identified as T1-T6, were used in producing film of LDPE containing 10 % by weight of LCP. Varying processing temperatures was carried out by intention of altering viscosity of both components, LCP and LDPE, as well as viscosity ratio (λ) of the system. Viscosity ratio is known as a key factor to control morphology of immiscible blend. In this study viscosity ratios ($\lambda = \eta_{LCP} / \eta_{LDPE}$) of lower than unity are desired in order to achieve finely dispersed droplets and high aspect ratios of fibers. The resulting films possessing LCP fibrous structure with effective aspect ratios (≥ 100) could be observed in all films produced at six different temperature profiles. The LCP fiber diameters became larger upon increasing processing temperatures. The more or less "ribbon-like" structure of LCP present together with fibers were observed when 10%LCP/LDPE films were produced at high temperature profiles of T5 and T6 (temperatures were equally set at the metering zone and the die = 270 °C for T5 and 300 °C and T6). The resulting OTR values of

10%LCP/LDPE films produced at T2 and T6 appreciably decreases of 15% and 40%, respectively as compared to the neat LDPE films. The lower OTRs of films produced at profile T6 could be attributed to the effectiveness of ribbon-like LCP structure in enhancing tortuous pathway for gas traveling across the film thickness. Water vapor transmission rates of all blend films seemed not to be much affected by incorporation of 10%LCP into the PE or changing temperature profiles. Only a slight increase in WVTR value over that of LDPE films observed in 10%LCP blend films could be the result of microvoid present between the two phases of LCP and LDPE, presumably due to poor adhesion of these two phases. MD modulus of LDPE films containing 10 wt% of LCP produced at six different profiles showed approximately 800% increase as compared to the neat film produced at the same conditions. This is the result of fiber-reinforcing effect of LCP fibers formed during film fabrication. However, yield strength of 10%LCP blend films was slightly decreased, and toughness properties of LCP/LDPE films were significantly lower than the LDPE itself. These findings led to attempt at a further improving the film properties.

To study effects of degree of mixing, blend films of 10%LCP/LDPE were produced at six different temperature profiles (T1-T6) by using mixing elements that were placed inside the die adapter. The addition of mixing elements was believed to help enhance dispersion and distribution of LCP dispersed phase while offering a control over initial LCP droplet size. Film uniformity with better physical appearance and the smaller diameter of LCP fibers presented in the 10%LCP blend film produced at low temperature profiles of T1 and T2. This indicated the effectiveness of mixing element in improving mixing ability at given conditions. However, the results were not clear when film were produced at higher processing temperatures. Mechanical properties of the films, however, had no significant improvements upon using mixing elements. In the case of films' OTR, the observed low OTR values for 10%LCP/LDPE films produced without mixing elements at T2 and T6 disappeared when mixing elements were utilized. These results could be attributed to the effects of lower aspect ratio of LCP fibers possibly caused by smaller initial droplet size when blend films were produced using mixing elements. Resulting films therefore had shorter effective tortuous pathway for

gas traveling. Based on these blend films results, further studies involved films produced at only two temperature profiles of T2 and T6 and mixing elements were excluded.

Varying screw speed was another factor that resulted in changing viscosity of material and mixing efficiency. The LDPE films containing 10% LCP by weight were produced at temperature profiles T2 and T6 as a function of screw speed of 12, 20, 40, and 60 RPM. The films' morphologies showed relatively fine LCP fibers (in film T2) and the LCP ribbon structure (in film T6). As increasing screw speeds, some of short fibers could be observed. For current film processing, increasing screw speed was accompanied by increasing take-up speed in order to retain a constant draw ratio, these combined effects might promote possibility of fiber breakages. As expected, modulus of 10%LCP/LDPE blend film decreased with increasing screw speeds. OTRs and WVTRs of blend films of 10%LCP produced at T2 and T6 also slightly increased as screw speeds increased. As a result, screw speed of 12 RPM was chosen for further study.

Compatibilizer was one of key parameters determining morphology and properties of incompatible blend. Nucrel was introduced into 10%LCP blend with various content of 0, 0.1, 0.5, 1.0, 2.0, 4.0, and 10.0 % by weight. The morphology of 10%LCP films showed that the presence of compatibilizer, Nucrel, caused the instability of fiber during fibrillation process. Fine fibers with high aspect ratios of more than 100 were obtained in 10%LCP/LDPE films without compatibilizer. Increases of droplet and ellipsoid structure upon increasing contents of compatibilizer were observed. These morphologies result in lower modulus of blend films. Blend films of 10%LCP without compatibilizer had slightly higher OTR values than that of neat film. Adding a small amount of compatibilizer into the blends can result in lower OTR values. WVTRs also showed similar trend. These indicated that compatibilizer was helpful in improving barrier properties of LCP blend film. The optimal content of compatibilizer, Nucrel, was 0.5 wt% for this LCP/LDPE system.

Film of LDPE containing different amount of LCP varied from 0-40% were produced using two temperature profiles of T2 and T6 in order to study effects of LCP content on morphology when produced at different temperature profiles. The morphology of 5%LCP/LDPE film produced at temperature profile T2 presented in droplet and ellipsoid structures. Increasing LCP content to 10% or more, fibrous structure of LCP was obtained. This could be explained by Taylor theory that there should be a critical LCP droplet size for fiber formation. In the case of small LCP droplets, possibly found at low LCP content system, it became more difficult to deform. In contrast, as temperature profile of T6 was used in producing 5%LCP/LDPE films, ribbon-like LCP structure were obtained with a presence of some droplets. Observed structure at T6 implied that effect of viscosity ratios might override the LCP content effect and at the same time played a key role in controlling LCP morphology. The tensile results of films produced at T6 are approximately 10% higher than that of films produced at profile T2. Barrier properties of all blend films at profile T6 were also lower than that of film produced at profile T2, which was a result of the more continuity of dispersed phase that developed in film having larger surface area as ribbon like structure.

Degree of post-die drawing affected both film orientation and development of dispersed phase morphology. The morphology of finer fibers were observed when increasing degree of drawing (draw ratio). However, the final structure was strongly dependent on the initial LCP structure. At high degree of drawing ($DR=3$), fiber breaking was found in 10%LCP film produced at profile T2 where LCP initially presented in fine fibers. However, this phenomenon was not observed in 10%LCP film produced at profile T6 and 30% films produced at profiles T2 and T6. The tensile properties were in agreement with the observed morphologies. Increment of modulus was found in all films but not for 10%LCP film produced at profile T2 with an evidence of LCP fiber breakage. Oxygen barrier properties were also improved with degree of drawing. In addition, effect of degree of drawing were more pronounced when LCP films containing high amount of 30%LCP.

Blend of LLDPE and LDPE with the weight fraction of 30:70 was used as a matrix of 10%LCP blend films for a reason of toughness improvement. As mentioned

before, large decreasing of toughness was found in blend films of 10%LCP/LDPE. This is a serious problem in order to use this film in some application such as packaging. The tensile results of 10%LCP/ (LLDPE/LDPE) show appreciable increase of toughness over 80% which was better than that of 10%LCP/LDPE films produced at similar temperature profile T2. In addition, toughness of 10%LCP/ (LLDPE/LDPE) was even higher than that of neat blend matrix itself (LDPE/LLDPE films) of approximately 20%. The modulus as well as yield strength were clearly improved by using LLDPE/LDPE as a matrix. Overall results suggested a potential use of LLDPE as a matrix of film containing LCP based on significant improvements in mechanical properties and barrier performance.

In conclusion, oxygen barrier properties strongly depended on morphology of LCP dispersed phase in the LCP/PE blend systems. The LCP ribbon-like structure having large surface areas perpendicular to gas traveling direction appeared to be effective features in enhancing gas barrier in the films. This ribbon-like structure could be readily generated when LDPE films contain relatively large content of LCP (e.g. 10% by wt or higher) and films were produced at proper temperature conditions. Water vapor transmission rate seemed to be unaffected by any parameters because both LCP and LDPE were essentially good barrier to water by their nature. Tensile properties of LCP/LDPE systems were also strongly dependent on LCP phase morphology. Significant enhancements of 800% in modulus when PE films containing only small content of 10%LCP revealed the effects of LCP fiber reinforcement in the LDPE matrix. Dramatically low toughness property observed in LCP/LDPE blend films could be effectively improved by using LLDPE as a matrix component with LDPE.

5.2 Suggestions for Future Work

Extensive studies from this work should be further carried out and following list contains some of suggestions for future work.

- As it was found in this study that poor adhesion between LCP and LDPE caused some microvoids that resulted in only slight decreases of OTR values. Using of Nucrel as a compatibilizer could only slightly improved barrier properties and

observed poor of toughness indicated that the compatibilizer used in this study might not have sufficient effectiveness in order to improve interfacial adhesion between the two phases of LCP and LDPE. Different compatibilizers may be incorporated into the blend of LCP/LDPE to find the most appropriate compatibilizer.

One important concern existed, however, that selected temperature profile should be carefully considered. Films of 10% LCP with a blend matrix of LLDPE/LDPE demonstrated appreciable enhancement in modulus, yield stress, and toughness when films were produced at T2, whereas poor toughness films could be obtained if films were prepared at T6.

- Selecting an effective matrix for the LCP blends as previously described between LCPE and LLDPE/LDPE blends seems to be a practical approach with great potential in improving both barrier performances and tensile properties when the blends are processed under appropriate conditions. Extensive studies of effects of matrix at different conditions are interesting as to find the most appropriate matrix systems and conditions for achieving a full potential use of LCP blend.
- Incorporation some of high barrier inorganic particle such as montmorillonite into this LCP/LDPE blend film may possibly enhance barrier properties. Some recent studies [46-47] show that incorporating small amount of montmorillonite into blend in nano-scale can enhance barrier properties of the matrix as well as orientation and aspect ratios of the LCP dispersed in LCP/thermoplastic blend systems. Exciting results of a dramatic improvement in barrier performance as well as tensile properties enhancement may be observed in such blends.