Effects of Compositions and Processing Variables on Barrier and Mechanical Properties of Liquid Crystalline Polymer/Polyethylene Blend Films

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Summary: Cast films of liquid crystalline polymer (LCP) and low density polyethylene (LDPE) blends have been produced and investigated. Effects of LCP content and processing parameters, i.e., processing temperature profile, screw speed, and post-die drawing, on morphology and O_2 barrier property are presented. Increasing processing temperature and LCP content tend to enhance aspect ratios (L/D) of the LCP dispersed phase and at the same time influencing LCP structure. These effects are clearly observed when LCP content is increased from 10 % to 30 % by wt. At high temperature profiles, LCP morphologies are presented in a more or less 'ribbon' or 'tape' like structure together with a common LCP fibrillar structure. Films of 10% and 30% LCP produced at two optimum temperature profiles show a noticeable proportion of LCP tape-like structure and interestingly high barrier properties of ~1.6 and 5.5 times that of the neat LDPE films. High barrier characteristics of such LCP/PE blend films are indicated by low oxygen transmission rate values. Apart from processing temperature effect, increases of screw speed result in films having smaller aspect ratios for both LCP fibers and ribbons; films also exhibit poorer barrier and mechanical properties. However, post-die drawing clearly demonstrates a positive effect in improving aspect ratios of LCP domains and the resulting films' moduli. Effects of post-die drawing on enhancing films' barrier properties become more pronounced at high LCP content. By comparing with the neat LDPE film (30 μm thick) having modulus of ~180 MPa and OTR of ~11000 cc/m^2.day, the developed LCP/PE films containing 30 wt% LCP show remarkably high modulus values of ~1100 MPa with low OTR of ~2000 cc/m^2.day.

Keywords: barrier property; immiscible blend; liquid crystalline polymer; morphology control; oxygen transmission rate

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Introduction

Development of polymer products with desirable barrier properties by blending technique has been of considerable interests in the last decade [1-3]. Multiphase monolayer films have been considered as alternatives to multilayer films. Multilayer films are produced using a rather complex process based on lamination and co-extrusion. Furthermore, difficulties in recycling multilayer products have also been major drives towards developing polymer blend films with recyclability.

Regarding barrier property improvement via blending, high barrier polymers such as EVOH, PEN, Nylon and LCP can be incorporated into another polymer matrix to create tortuous pathway for enhancing gas traveling charateristics. The key to achieve desirable barrier performance is morphology control [2, 3]. It has been suggested that laminar structure is preferable for high barrier requirement [1, 2, 4]. EVOH and Nylon [3] have been considered interesting candidates, but some limitations still exist. For EVOH, effective reduction of O_2 permeability can be obtained only in dry atmosphere. Therefore, this research proposes to study effectiveness of another candidate, a super-barrier LCP, in enhancing barrier properties of commonly used LDPE through polymer blending. Challenges involve trying to synergize unique self-reinforcing property and excellent barrier characteristics of the LCP with desirable flexibility of LDPE in order to produce practical films with reasonable cost.

Experimental

Materials: LCP used was Vectra type, namely LKX1107 with a low melting point of ~220 °C, kindly supplied by Ticona. The polymer matrix LDPE was an extrusion grade, LD1902F, obtained from Cementhai Chemicals Co., Ltd. Melt flow index of the chosen LDPE is 2 g/10min and its melting temperature is ~108 °C. The compatibilizer and antioxidant used were Nucrel 0903 and Irganox 1076; their contents were kept constant for all blends at 0.5 wt% and 0.1 wt%, respectively.

Blending and Pelletization

Various contents of dried LCP, LDPE, and additives were mechanically blended and extruded using Haake single screw extruder having a mixing configuration (19 mm screw diameter and L/D ~25). Blends were extruded through a rod die of 3 mm diameter and pelletized.

Temperature setting from feed zone to die zone was 170-200-230-225 °C. Screw speed of 75 rpm was kept constant for pelletization. Pellets were also dried prior to being used for film fabrication.

Cast Film Preparation

Cast films of LCP/LDPE blends were extruded through a slit die of 15 cm width and 0.8 mm die gap. Films of various LCP contents in a range of 5-40 % by wt were produced at different processing temperature profiles (T1-T6) with different screw speeds and degrees of post-die drawing (draw ratios), as summarized in Table 1. It should be noted that all films were fabricated using a constant screw speed of ~12 rpm. Influence of temperature profiles (T1-T6) on films' structures and barrier properties were investigated for blends containing 10 %LCP. Selected two temperature profiles of T2 and T6 providing noticeable improvements in films' barrier characteristics were then used for further studies on effects of LCP content, screw speed and post-die drawing.

Morphological Studies: Morphologies of LCP/LDPE blends were investigated using polarized light microscope and scanning electron microscope (SEM). In this study, blend samples were placed between two glass slides and heated to a temperature of ~160°C in order to melt LDPE while the LCP structure generated during processing could be revealed. Film specimens for SEM studies were fractured in liquid nitrogen. Fractured surfaces were then coated with gold prior to examination.

Tensile Testings: The tensile properties were determined on an Instron 4502 according to the ASTM D-882 for thin plastic sheet. Five specimens of each blend film in both MD and TD were tested and average value was reported.

O_2 Transmission Rate (OTR): OTR values of film samples were determined at 23 °C, 0 %RH using O_2 Permeation Analyzer (Illinois, Model 8500). At least 3 replicates of 100 mm^2 area were tested and averaged.

Table 1. Compositions and processing conditions for LCP/LDPE films extrusion.

Temperature Profile and Screw Speed Variation

LCP/LDPE Composition	Temperature Profiles Extruder Zone1-3 and Die	Draw Ratio (Post-Die Drawing)	Screw Speed (rpm)
10/90	(T1) 180-200-225-220	1.5	12
	(T2) 180-200-230-225	1.5	12, 20, 40, 60
	(T3) 180-200-235-230	1.5	12
	(T4) 180-200-240-235	1.5	12
	(T5) 180-200-270-270	1.5	12
	(T6) 180-200-300-300	1.5	12, 20, 40, 60

LCP Content and Post-Die Drawing Variation

LCP/LDPE Composition	Temperature Profiles Extruder Zone1-3 and Die	Draw Ratio (Post-Die Drawing)	Screw Speed (rpm)
5/95	(T2) 180-200-230-225	1.5	12
	(T6) 180-200-300-300	1.5	
10/90	(T2) 180-200-230-225	1, 1.5, 2, 3	12
	(T6) 180-200-300-300	1, 1.5, 2, 3	
15/85	(T2) 180-200-230-225	1.5	12
	(T6) 180-200-300-300	1.5	
20/80	(T2) 180-200-230-225	1.5	12
	(T6) 180-200-300-300	1.5	
30/70	(T2) 180-200-230-225	1, 1.5, 2, 3	12
	(T6) 180-200-300-300	1, 1.5, 2, 3	
40/60	(T2) 180-200-230-225	1.5	12
	(T6) 180-200-300-300	1.5	

Results and Discussion

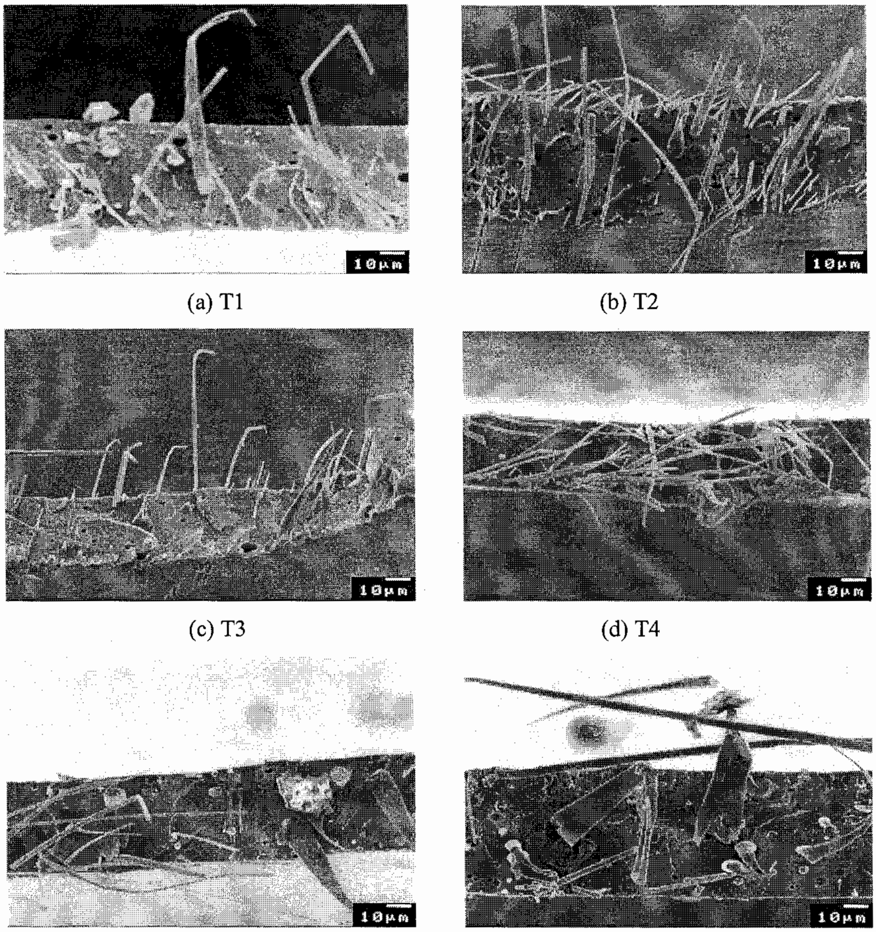
Film Morphologies:

Effect of Processing Temperature Profiles

For temperature profile study, all blend samples had the same LCP content of ~10 wt%. Temperature profiles of the first and second zones were kept constant at 180 °C and 200 °C, respectively, while the third zone and die temperatures were varied from 220 °C to 300 °C, identified as profiles T1-T6 (**Table 1**). Initial temperature profile setting of T1 was utilized based on the previous work on LCP/PE blends [5], where good fibers with high aspect ratios of ~100 and dramatic improvement in films' moduli could be achieved. In the current work, 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 performances. From SEM micrographs of fractured samples, Figures 1 (a)-(f), it is apparent that LCP fibrillar structure can be formed in the films produced at all 6 temperature 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 and improved mechanical properties. When processing temperatures are increased, LCP fibers tend to be larger in width and appear to be more 'tape-like' structure, as seen in Figures1 (e) and (f). Such changes in LCP morphologies upon increasing processing temperature can be attributed to changes in viscosity ratios of the blends' components [4]. Effect of temperature profiles on the formation of LCP tape-like structure can be more apparent at higher LCP content of 30 wt% as described in the next section.

Effect of Screw Speed

Screw speeds of extruder were varied in order to study influence of shear rate on the LCP dispersed phase. The study was carried out by producing films of 10%LCP/LDPE with different screw speeds of 12, 20, 40, and 60 rpm at the two selected temperature profiles of T2 and T6. Note that draw ratios were kept constant at 1.5. In order to retain a constant draw ratio while increasing screw speed, take off speed must also be adjusted accordingly. From Figures 2, it is generally seen that fibrillar structure of LCP in films produced at T2 as well as ribbon-like structure of LCP in films produced at T6 still mainly exist. Nevertheless, both fibers and ribbons in the blends tend to be finer and shorter at high screw speeds. These observations could be due to the combined effects of the high shear rate and high take-up speed during processing under high screw speed conditions. Therefore, the occurrence of LCP fiber or tape breakage can take place.

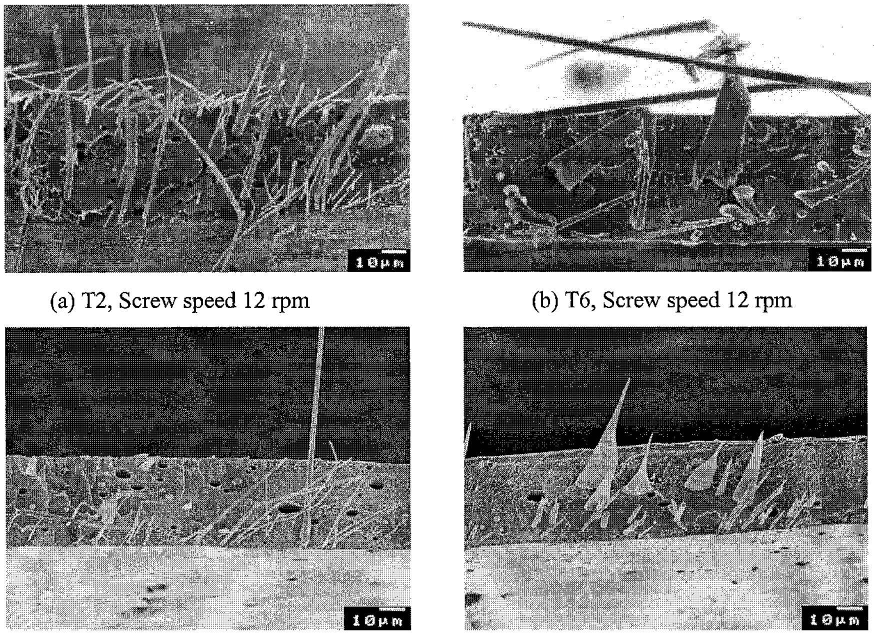


(a) T1 (b) T2

(c) T3 (d) T4

(e) T5 (f) T6

Figure 1. SEM micrographs of 10 wt%LCP blend films produced at difference temperature profiles T1-T6 (a-f) (750X magnification).



(a) T2, Screw speed 12 rpm

(b) T6, Screw speed 12 rpm

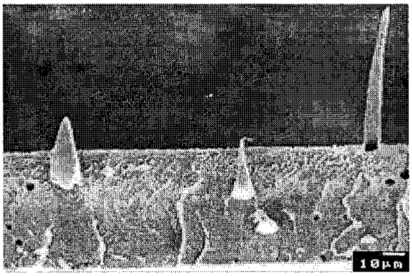
(c) T2, Screw speed 40 rpm

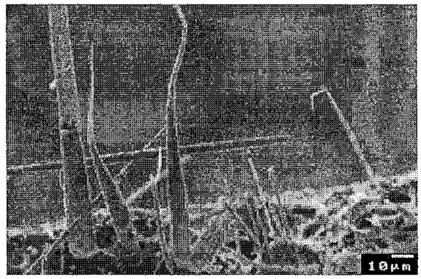
(d) T6, Screw speed 40 rpm

Figure 2. SEM micrographs showing effect of screw speed on morphology of 10 wt%LCP/LDPE blend films produced at T2 and T6 (750X magnification).

Effect of LCP Content

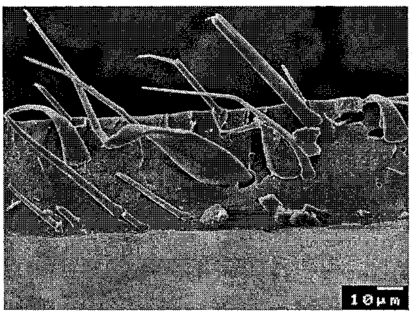
Films with various LCP contents ranging from 5-40 wt%LCP were produced using two temperature profiles, T2 and T6. For films having low LCP content of 5 wt% produced at T2, LCP phase is mainly present in droplet and ellipsoid. As LCP content is increased, there is a greater tendency in forming LCP fibrillar structure (Figure 3 (a) and (b)). However, when films are produced using higher temperature profile (T6), fibrillar and tape like structure of LCP are observed even at low LCP content of 5 wt% (Figure 4 (a) and (b)). These results are possibly attributed to different viscosity ratios of the blends and initial droplet size of LCP at the two processing conditions. Based on the Taylor's theory, there should be a required critical volume of LCP phase for effective fiber formation [3, 4]. Current findings in the formation of LCP tape-like structure at T6 may indicate a possible interplay of several key factors including viscosity ratio of the blends, initial LCP droplet size and its critical volume.

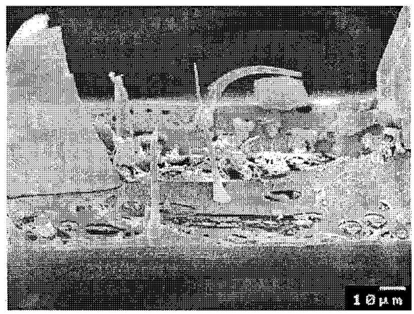




(a) 5 wt%LCP (b) 30 wt%LCP

Figure 3. SEM micrographs of films produced at T2 (750X magnification).





(a) 5 wt%LCP (b) 30 wt%LCP

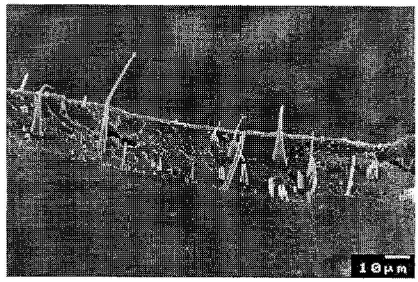
Figure 4. SEM micrographs of films produced at T6 (750X magnification).

Effect of Post-Die Drawing

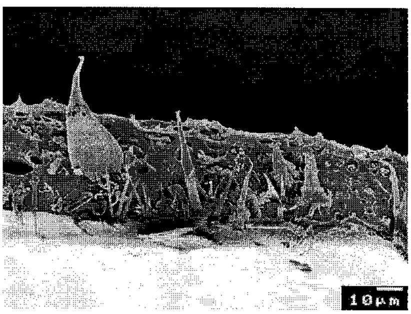
Drawing within the fabrication process also influences the development of morphology in the blends. As earlier discussed, structure of LCP domain prior to deformation (e.g., droplet size and its volume) depends strongly upon both processing temperature and LCP content. While post-die drawing can enhance 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 (Figures 5 (a) and (b)). In contrast, for film with

30 wt%LCP produced at T2, LCP fibrils with high aspect ratios are still present at a high DR of 3 (Figures 5 (c) and (d)). In the case of films prepared at higher temperature profile of T6, SEM micrographs (Figure 6) reveal relatively large LCP fiber diameter of 5-10 μm with high aspect ratios and interesting LCP tape-like structure of ~10 - 30 μm width in all film compositions with various draw ratios.

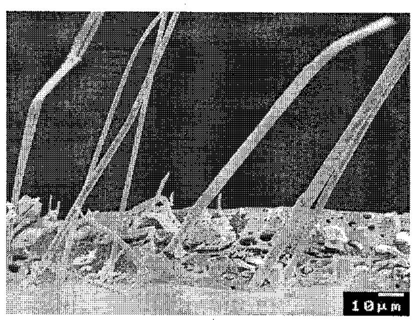
(a) 10 wt%LCP-DR 1.5



(b) 10 wt%LCP-DR 3

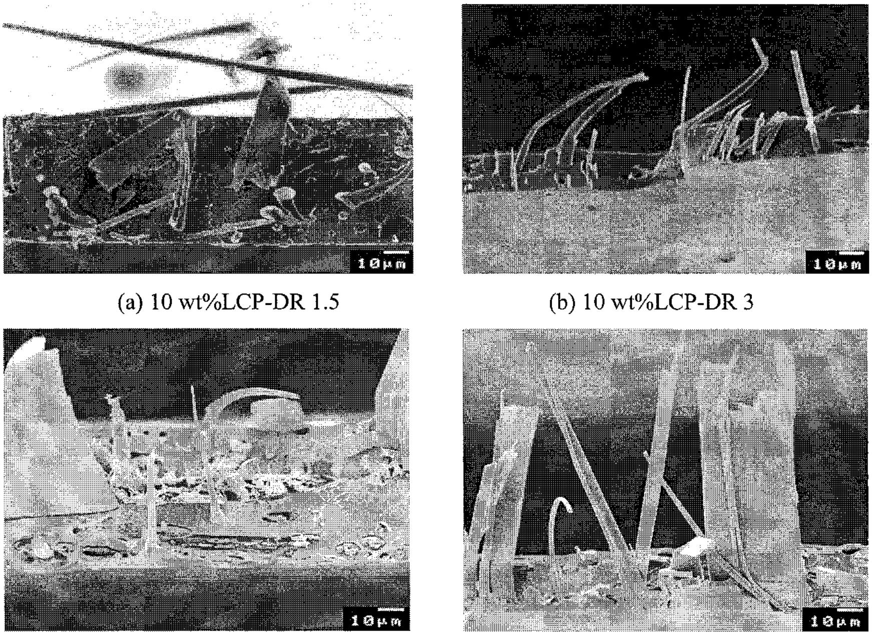


(c) 30 wt%LCP-DR 1.5



(d) 30 wt%LCP-DR 3

Figure 5. SEM micrographs showing drawing effects on films produced at T2 (750X magnification).



(a) 10 wt%LCP-DR 1.5 (b) 10 wt%LCP-DR 3

(c) 30 wt%LCP-DR 1.5 (d) 30 wt%LCP-DR 3

Figure 6. SEM micrographs showing drawing effects on films produced at T6 (750X magnification).

Film Properties:

Tensile Properties

LDPE films containing 10 wt%LCP show significant improvements in tensile properties; an increase of ~800 % in modulus and ~25 % in yield stress are observed as compared to those of LDPE (Figure 7). Varying temperature profiles from T2 to T6 results in slight increases in both properties, presumably due to better reinforcing effects of developed LCP structures at higher temperatures. Increase of screw speed tends to reduce film modulus which can be a result of LCP fiber/ribbon breakage (Figure 8). As briefly discussed, drawing during film extrusion can effectively enhance fibrillation and orientation of LCP, and correspondingly the film modulus [7]. As seen in Figure 9, this is essentially true for the LCP/LDPE films produced at the temperature profile of T6; thinner films with higher post-die draw ratios possess greater modulus values. The resulting thin films (~30 μm) having modulus of ~1100 MPa can be obtained. However, films produced at lower temperature profile of T2 exhibit an optimum thickness of ~40 μm or with a draw ratio of ~2, below which modulus decreases dramatically caused by fibrils breakage upon further stretching. The LCP fibril breakage is illustrated in Figures 5 (b).

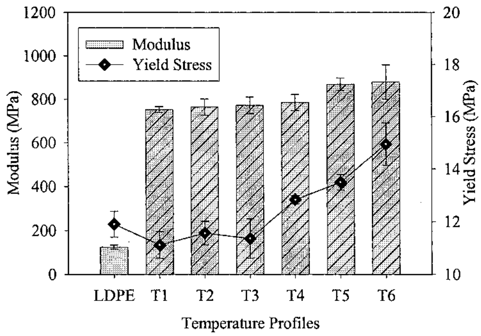


Figure 7. Modulus and yield stress in MD of 10 %LCP blend films produced at T1-T6 vs. LDPE film produced at T1.

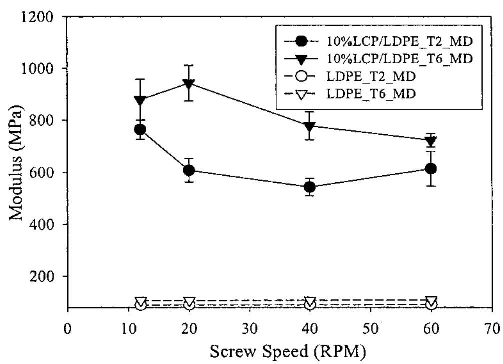


Figure 8. Modulus in MD of 10 %LCP blend films produced at T1-T6 vs. LDPE film as a function of screw speed.

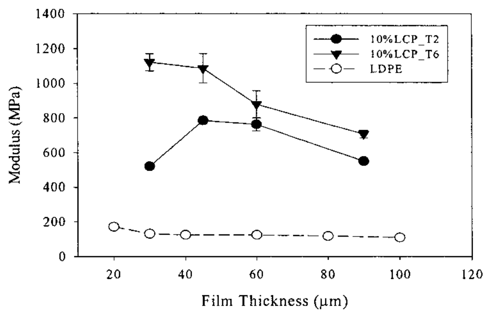


Figure 9. Modulus in MD of 10%LCP blend films produced at T2 and T6 vs. LDPE film produced at T1 (Effect of post-die drawing).

O_2 Transmission Rate (OTR)

OTR results of 10 %LCP/LDPE films processed at different temperatures are illustrated in Figure 10. There is no general trend of how O_2 permeability is affected by processing temperature. Nevertheless, noticeable decrease in OTR values of approximately 15 % and 40 % are observed in films produced at the conditions T2 and T6. Studying effects of screw speed on films' OTR reveal that the films containing 10%LCP posses an observable low OTR of ~3000 cc/m^2.day when produced under T6 condition with a low screw speed of 12 rpm (Figure 11). OTR value of this 10%LCP/LDPE film is significantly lower than that of the neat LDPE produced under a similar condition. Such low OTR property can be largely attributed to the developed LCP tape-like structure in the film as previously described. For 10%LCP/LDPE films produced at higher screw speeds of 20 - 60 rpm and at both T2 and T6, all films show high OTR values in a range of 5500 – 6 000 c c/m^2.day, which appear to be closed to the OTR of LDPE. Effects of post-die drawing with various film thicknesses together with effects of LCP content on films' OTR are presented in Figure 12. As expected, thinner films show higher OTR values. It is interesting to note that while OTR values of 10 %LCP produced at T2 show only a slight deviation from OTR of the LDPE matrix at all thicknesses, films containing the same amount of LCP (10 wt%), but produced at higher temperature of T6, exhibit noticeably lower OTR values. Furthermore, films containing high content of LCP (30 wt%) and produced at the temperature profile of T6 show even further decrease in OTR. In other words, the resulting films of 30 μm produced at T6 possess a remarkable 5 - 6 folds increase in oxygen barrier property over the LDPE matrix. OTR values of these films, containing 30 %LCP produced at T6, also become less thickness dependent. Significant enhancement in oxygen barrier characteristics of LDPE containing 30 %LCP, as indicated by low OTR value, can be attributed to the developed structure of LCP phase in a more or less 'tape-like' feature. It is possible that such LCP tapes, dispersed in the LDPE matrix, play a role in enhancing pathway or distance for gas traveling across the film thickness.

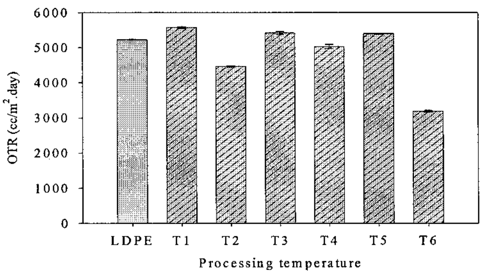


Figure 10. OTR of 10 %LCP blend film produced with different processing temperatures T1-T6 vs. LDPE film produced at T1 (all films have thicknesses of ~60 μm).

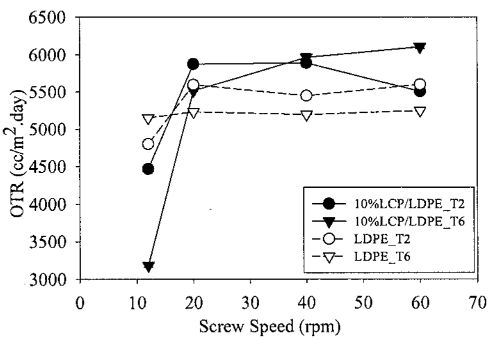


Figure 11. Effect of screw speed on oxygen transmission rate of 10%LCP/LDPE films produced at temperature profile T2 and T6 as compared to LDPE films.

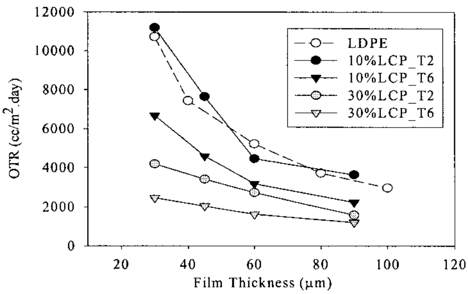


Figure 12. OTR of 10 and 30 %LCP blend films produced at T2 and T6 vs. OTR of LDPE films.

Conclusion

The effects of LCP content and processing parameters i.e., temperature profiles, screw speed, and post-die drawing on films' morphology, tensile and barrier properties have been reported. Films with effective LCP fibrillar structure (L/D >100) can be obtained at all six temperature profiles (T1-T6). However, increasing processing temperature can give rise to larger LCP fibers of high aspect ratios together with LCP 'tape-like' structure. Increasing screw speeds adversely result in films with shorter LCP fibers or tapes, poorer barrier and tensile properties due to LCP fiber or tape breakages. Post-die drawing clearly enhances fibrillation and orientation of LCP. Varying draw ratios (DR) of the 10%LCP/LDPE films produced at T6 from 1.5 to 3 can lead to a significant enhancement in fibers' aspect ratios and films' moduli of ~60 %. Barrier properties of LCP/LDPE films can be largely improved by developing LCP 'tape-like' structure under appropriate processing conditions or at the high temperature profile of T6. Thin films of 30 μm containing 10 %LCP and 30 %LCP show interestingly low OTR values of ~4000 and ~2000 cc/m^2.day while obtaining reasonably high modulus values of ~600 and 1100 MPa as compared to the neat LDPE with OTR of ~11000 cc/m^2.day and a relatively low modulus of ~200 MPa.

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