CHAPTER IV
RESULTS AND DISCUSSION

4.1 Melt Flow Index (MFI)

The melt flow index of LLDPE/NR blends was characterized and the results are shown in Table 4.1-4.2. It was found that when the amount of natural rubber increased the melt flow index of LLDPE/NR blends decreased. NR has high elasticity and long chain branching while LLDPE has short chain branching (Strong, 1996). When they are blended together, the melt flow index of the blends are decreased. Another reason is that NR molecules disturb the flow of LLDPE.

Table 4.1 Melt flow index of LLDPE/NR blends.

Samples	MFI (g/10 min)
L1 90/10	0.9880
L1 80/20	0.9412
L6 90/10	5.9797
L6 80/20	5.4300

Table 4.2 Melt flow index of LLDPE/ENR/NR blends.

Samples	MFI (g/10 min)
L1 80/10/10	0.5879
L6 80/10/10	3.2161

4.2 X-ray Diffractometer (XRD)

The degrees of crystallinity of LLDPE/NR blends are characterized by X-ray diffractometer. The ability of a materials to crystallize is determined by the regularity of its molecular structure. It was found that degree of crystallinity increased with increased the draw ratio as shown in Figure 4.1.
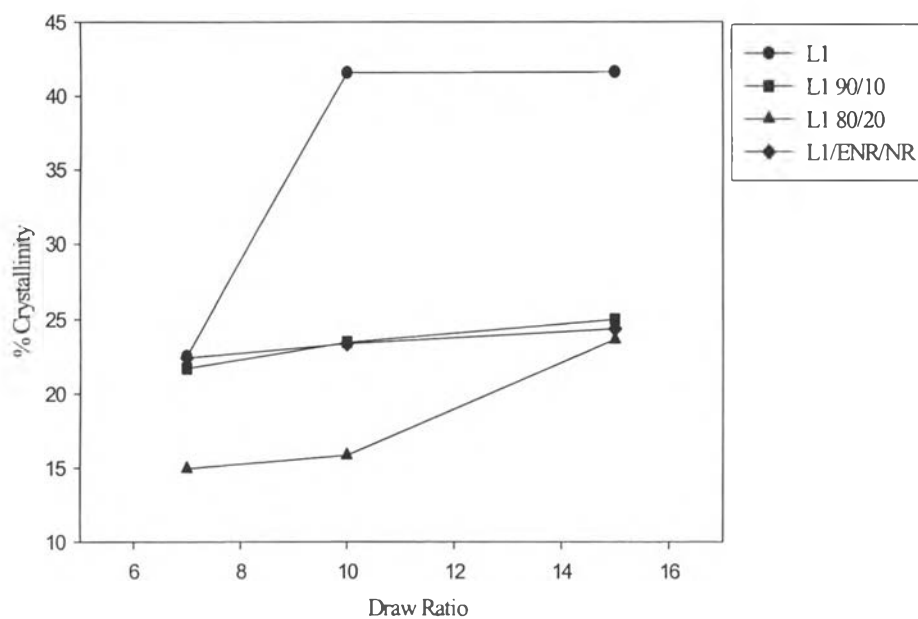

Figure 4.1 Degree of crystallinity of pure LLDPE MFI = 1 and its blends with ENR and NR at compositions of 100/0, 90/10, 80/20, 80/10/10 at DR 7, 10, 15.
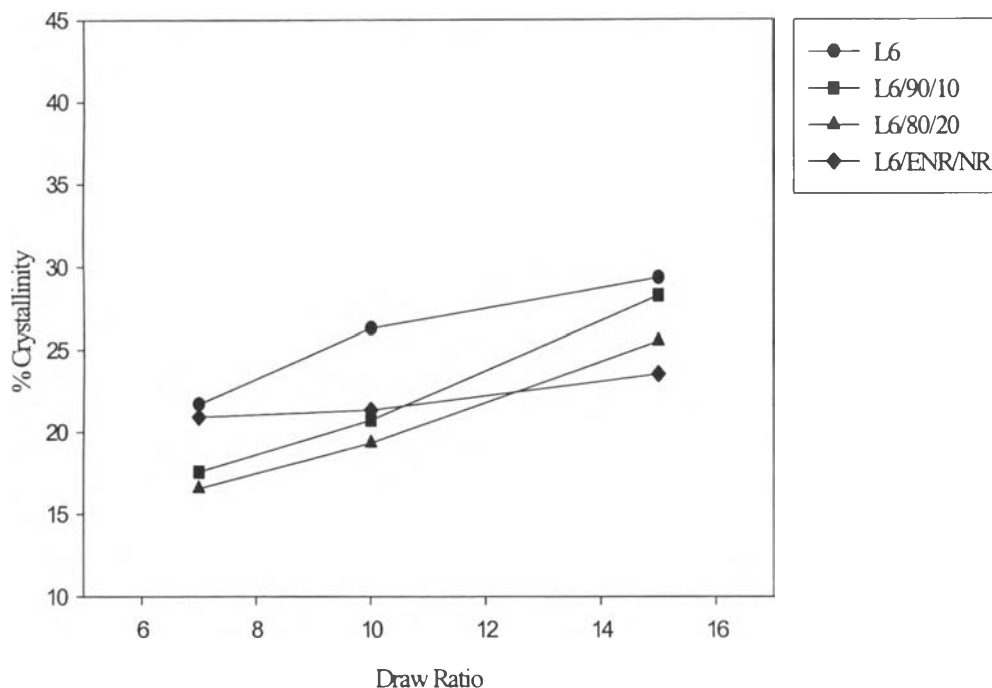
Figure 4.2 Degree of crystallinity of pure LLDPE MFI = 6 and its blends with ENR and NR at compositions of 100/0, 90/10,80/20, 80/10/10 at DR 7, 10, 15.

Figures 4.1and 4.2 show % crystallinity of LLDPEs and their blends with ENR and NR at the compositions of 100/0, 90/10, 80/20, and with NR/ENR 80/10/10 as a function of draw ratio. Pure LLDPE showed the highest crystallinity and L1 is higher than L6. The change in crystallinity with increase in the draw ratio indicates that the molecular orientation increased when increasing the draw ratio. As expected, the crystallinity of LLDPE/NR blends, the crystallinity is affected by an increasing amount of NR because NR forms an amorphous part.

4.3 Birefringence

Birefringence was used as a method to characterize the molecular orientation in the stretched films. C-axis along the backbone was chosen as a principle axis that was parallel to the stretch direction. Newton chart was used extensively in this work. The color appearance based on the difference in the principle refractive indices, which were lines parallel and perpendicular to the stretched direction for uniaxial and biaxial stretched specimens. Birefringence was calculated as follows:

$$\Delta n = R/t$$

Where Δn is the birefringence value, R is the retardation, and t is the thickness of films.

Retardation of a sample can be defined as

$$R_{(sample)} + R_{(reference)} = R_{(\lambda)}$$

$$R_{(sample)} + R_{(reference)} = R_{(\lambda/4)}$$

And hence, sample retardation can be averaged from two measurements by using lamda (λ) and quarter lamda ($\lambda/4$) plate. Once the sample retardation is known as well as the sample thickness, they can be employed to calculate the birefringence value.

Table 4.3 Birefriengence of LLDPE and its blends.

Film samples	Draw ratio	Brirefringence
LLDPE MFI = 1	7	+0.022
	10	+0.022
	15	+0.024
LLDPE MFI = 6	7	+0.022
	10	+0.022
	15	+0.024
L1/90/10	7	+0.022
	10	+0.022
	15	+0.022
L6/90/10	7	+0.022
	10	+0.022
	15	+0.022
L1/80/20	7	+0.020
	10	+0.020
	15	+0.022
L6/80/20	7	+0.020
	10	+0.020
	15	+0.020
L1/ENR/NR	7	+0.010
	10	+0.010
	15	+0.014
L6/ENR/NR	7	+0.010
	10	+0.012
	15	+0.012

From Tables 4.3, it can be seen that there was no difference in the birefringence values of pure LLDPE and LLDPE blends at different DR are little different while there are on difference in the crystallinity of these samples, However when increasing the draw ratio, there was a slight increase in birefringence. Therefore it can be concluded that, for this work, birefringence technique was not useful for characterizing the molecular orientation quatitatively since its scale is not sensitive enough for this work.

4.3 Infrared Dichroism

IR spectroscopic techniques provieds the ability to measure the degree of orientation and examine structural changes associated with the drawing of LLDPE. Changes in molecular orientation on drawing have been measured by polarized FT-IR spectroscopy, based on the ratio of absorbance of CH_2 with parallel and perpendicular crossed polarizers. The results are shown in Figure 4.3 - 4.5 shows the orientation functions change with draw ratio for pure LLDPE, binary blends of LLDPE/NR, and the reactive blends of LLDPE/NR/ENR/MA
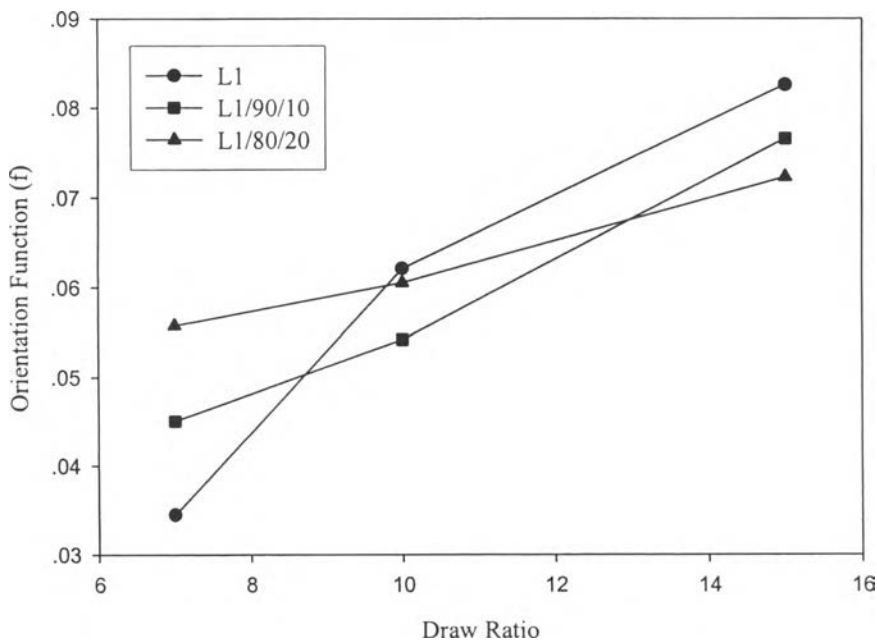

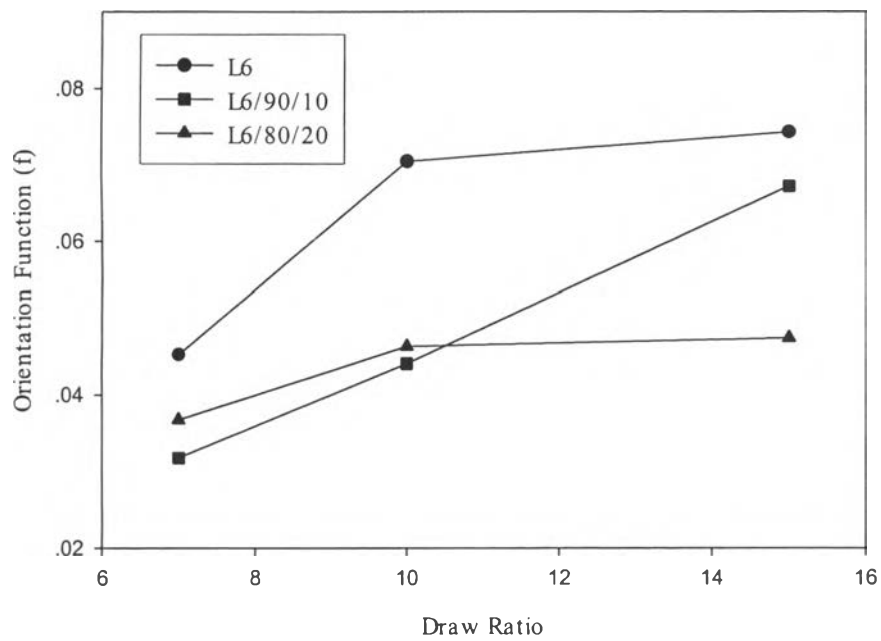**Figure 4.3** Orientation function of LLDPE MFI = 1 at DR 7, 10, 15.

Figure 4.4 Orientation function of LLDPE MFI = 6 at DR 7, 10, 15.
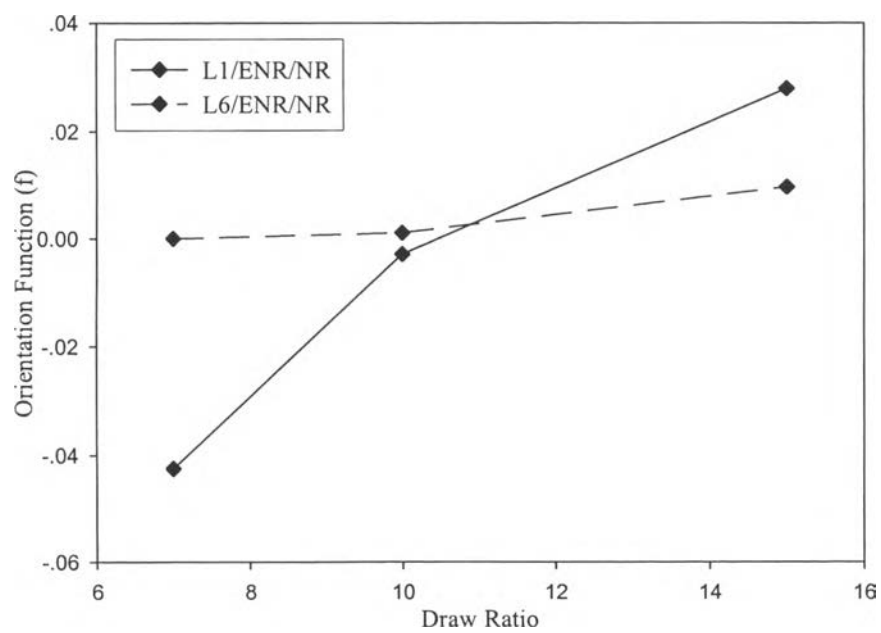

Figure 4.5 Orientation function of L1/ENR/NR and L6/ENR/NR at DR 7, 10, 15.

In the IR absorption spectrum of LLDPE, the absorption band at 1464 cm^{-1} was assigned to be due to the CH_2. Cast film process was also developed to produce uniaxial orientation.   In pure LLDPE films   show the orientation function (f) increasing with increase in the draw ratio and the orientation of L1 is higher than L6 because of longer molecules. It implies that, at high draw ratio, the molecules tended to orient in the machine direction. The pure LLDPE films are likely to have higher orientation than the blneds; when as the binary blends of 10 wt% NR exhibits lower molecular orientation than the blneds of 20 wt% NR.   The reactive blend of L1/NR/ENR shows molecular orientation originally in transverse direction and change to machine direction as DR increases. For L6/NR/ENR blend, the molecule are hardly oriented with DR and molecules line in both directions

4.4 Gas permeability

The Brugger gas permeability tester type GDP/E was used to detect the permeability of oxygen gas through the blend films.   The permeability of pure LLDPE was found to decrease with increase in the draw ratio.   It has been considered so far that an increase in molecular orientaion causes a decrease in gas permeability in polymers as result of an increased packing efficiency of the polymer chains (Kajatani et al., 1997). The permeability of plastics depends on crystallinity, molecular orientation, chain stiffness, free volume, cohesive energy density, temperature, and moisture sensitivity. Higher crystallinity, molecular orientation, chain stiffness, and cohesive energy density lead to lower permeability (Shah et al., 1998). The permeabilities of LLDPE/NR binary blends at 90/10 and 80/20 wt% increased with draw ratio. This is opposite to pure LLDPE. The gas permeability increases because the space between the interface of the two polymers increased with draw ratio. It can be expected that shows higher permeability than L1 due to lower crystalliny. Interestingly, at DR7, permeability of the blends (NR 10-20%) is lower than pure LLDPEs. LLDPE/NR/ENR shows the highest permeability due to the lowest crystallinity.
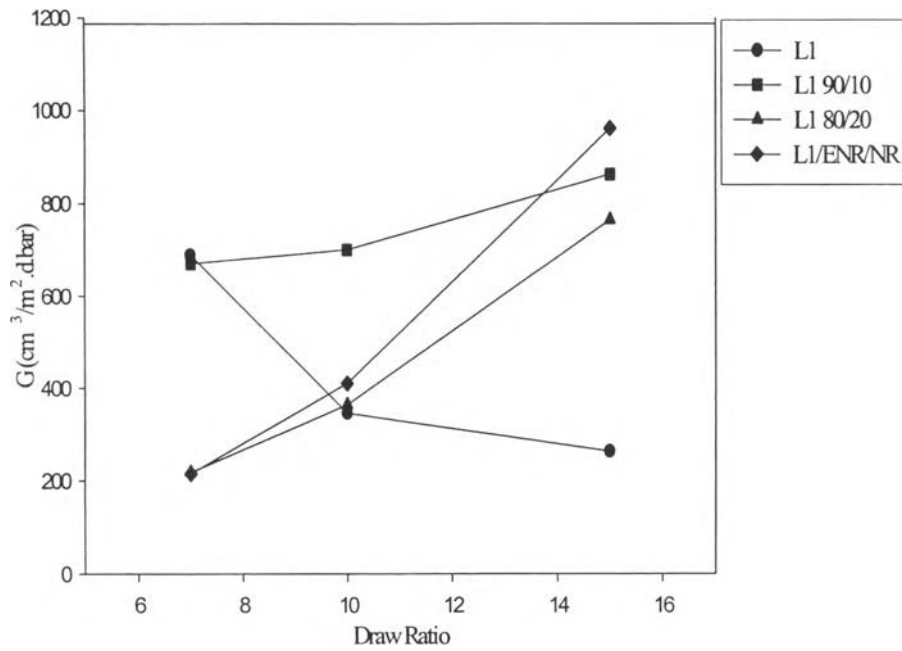
Figure 4.6 Gas permeability of pure LLDPE MFI = 1 and its blends with NR at compositions of 100/0, 90/10,80/20, 80/10/10 at DR 7,10, 15.
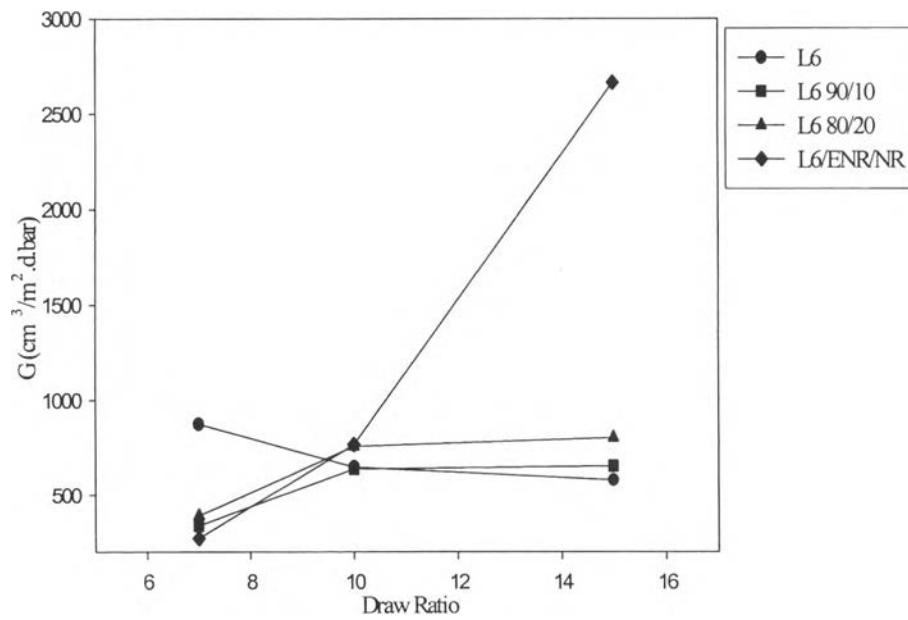

Figure 4.7 Gas permeability of pure LLDPE MFI = 6 and its blends with NR at compositions of 100/0, 90/10,80/20, 80/10/10 at DR 7,10, 15.

4.6 UV-VIS Spectrometer

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. UV-VIS Spectrometer in the range of 200-800 nm is used for measuring the absorbance of the radiation in the visible and UV regions. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviloet and visible radiation is energetic enough to promote outer electrons to higher energy levels. UV-Vis spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials.

The results Figure 4.8 and 4.9 show that in when the draw ratio is increased, the UV absorbance decreased.
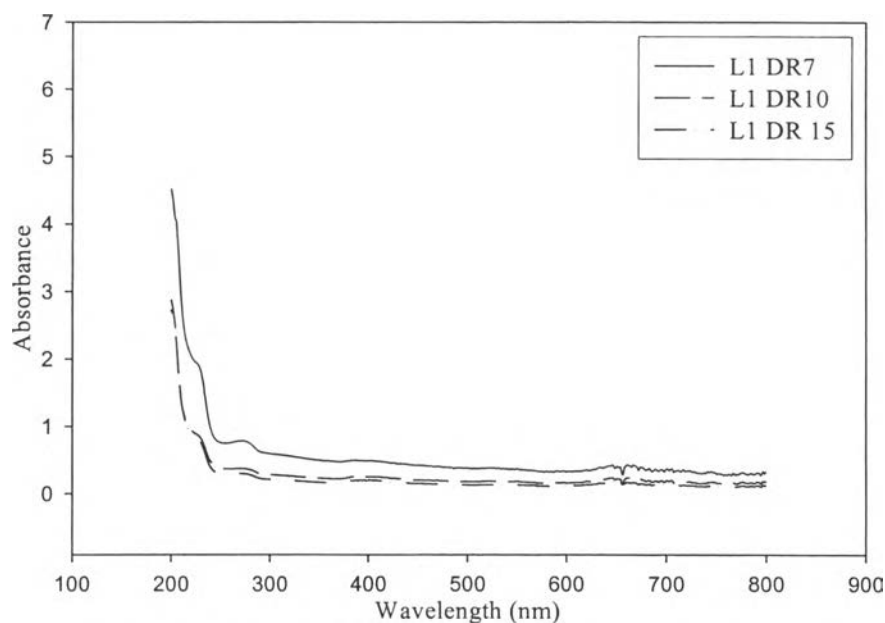
Figure 4.8 UV absorbance of pure LLDPE MFI = 1 at DR 7, 10, 15.
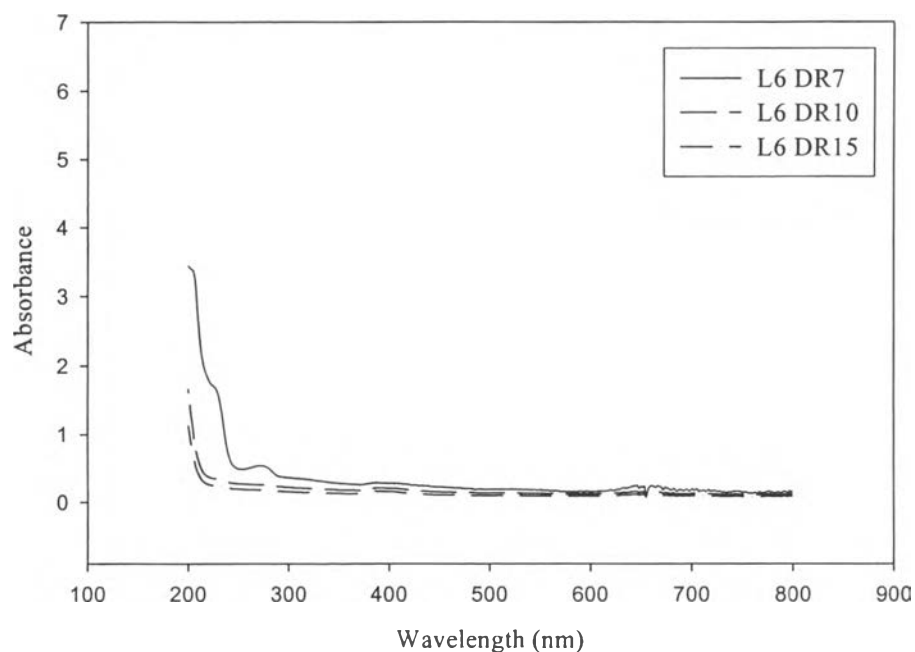
Figure 4.9 UV absorbance of pure LLDPE MFI = 6 at DR 7, 10, 15.

For pure LLDPE (Figures 4.8-4.9), MFI has no significant effect on the UV-Vis absorption. Both films have high absorption only in UV-range but not in visible range (400-700). In other words, the film is transparent and allows all visible light to transmit totally; increasing draw ratio makes film clearer (more transparent). Thus crystalline structures that are formed have smaller size so that there is less scattering and the samples are more transparent.

This is contrast to the general notation that more crystallinity resulting from increase in DR should lead to more scattering than transmiting unless the crystal size is large with better alignment.
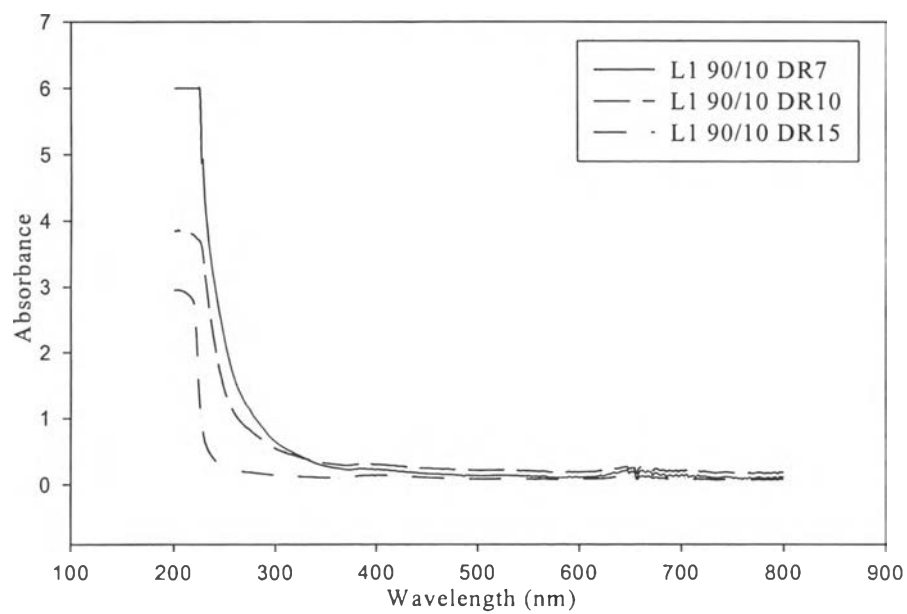
Figure 4.10 UV absorbance of L1/90/10 blend at DR 7, 10, 15.
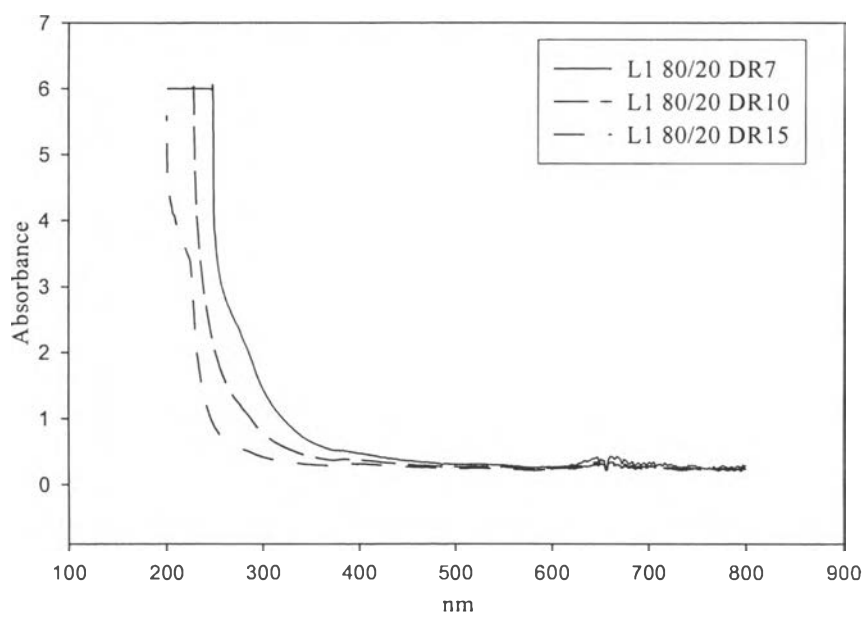
Figure 4.11 UV absorbance of L1/80/20 at DR 7, 10, 15.
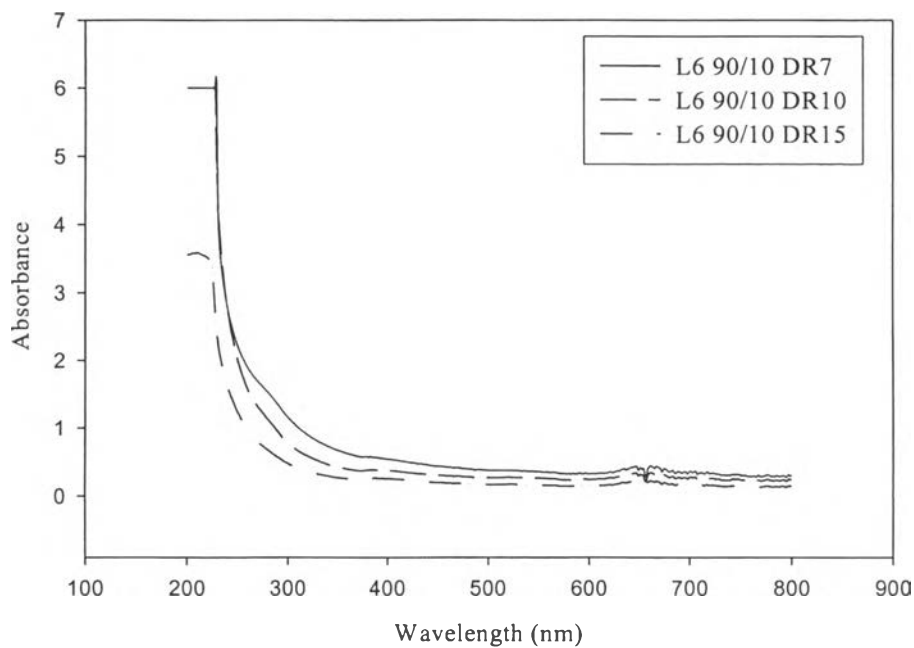
Figure 4.12 UV absorbance of L6/90/10 at DR 7, 10, 15.
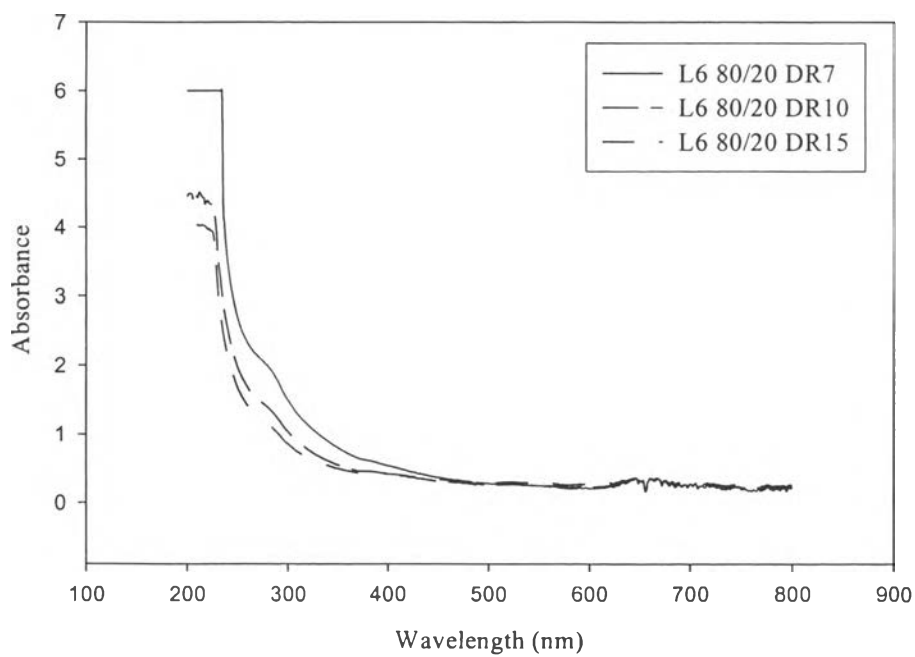

Figure 4.13 UV absorbance of the L6/80/20 at DR 7, 10, 15.

When NR is added, (Figures 4.10-4.13) MFI has no significant affect on UV-Vis absorption. The absorption band shifts to longer wavelength and covers more of UV light region with increasing absorbance. The more NR added, the more absorption and the more shifted to longer wavelength. It is interesting that although the film has light yellowish color, but in visible region, most visible light can transmitted with some absorption in 600-700 nm. This abosorption is more evident at higher NR content. Increasing DR lowers the absorption and they are superposed at 20% NR.
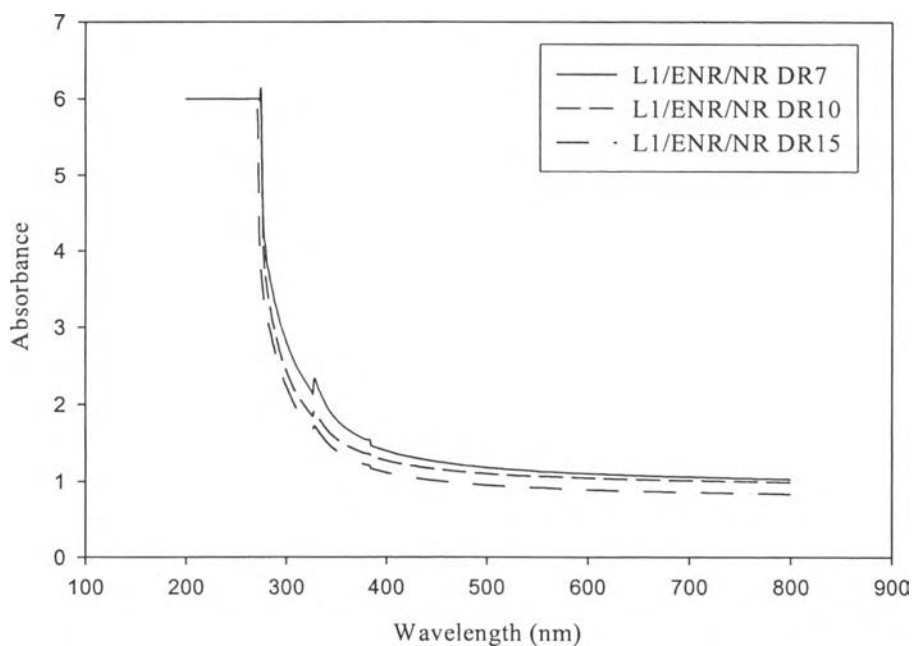
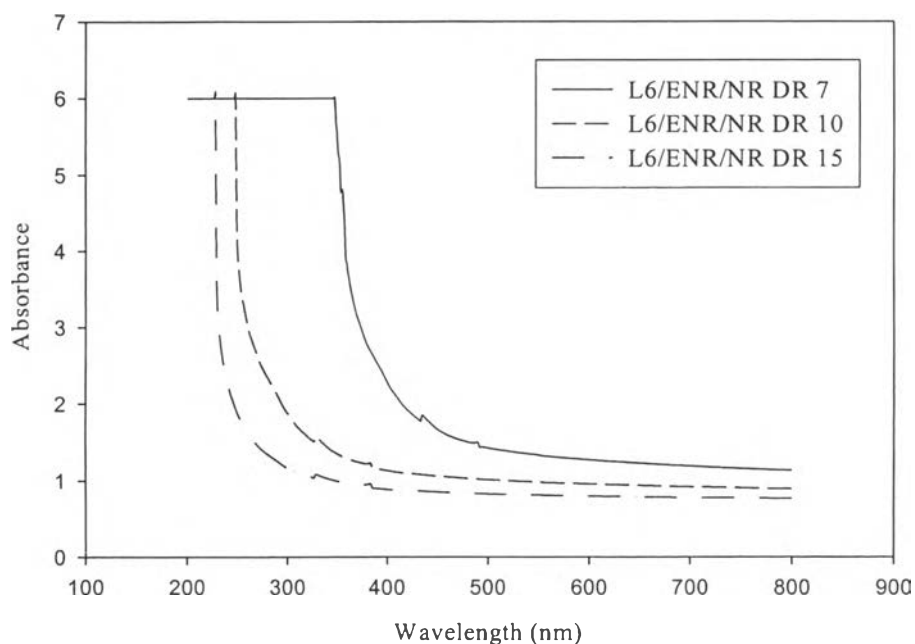**Figure 4.14** UV absorbance of the L1/ENR/NR at DR 7, 10, 15.

Figure 4.15 UV absorbance of the L6/ENR/NR at DR 7, 10, 15.

For reactive blending (Figures 4.14-4.15) strong shift to longer wavelength and higher absorption are obtained.

This suggests that light can transmit through pure LLDPE film and blend films more easily with high DR (absorbance is related to transmission) despite the fact that crystallinity of the film increases with DR. Common light absorption is shifted to lower wavelength with increasing DR, indicating more UV absorption of the films. The same observation is easily seen for the blend films with higher NR content. Increasing DR causes absorption shifting to lower wavelength absorptions of the binary blends will extend to longer wavelength (at 400 nm) i.e. there is a boarden of the absorption peak. Absorption level increases singnificantly with 20% NR. The 80/20 LLDPE/NR blends show zero absorption for all DR at wavelength 500-800 nm. This suggested that rubber is a good UV absorption material and since rubber can be easily degraded by UV light, this implies that the blend films will be photodegradable.

4.7 Thermal Properties

The thermal properties for melting behavior were characterized by DSC first run which means the melt profiles are from original crystalline formed by chill roll casting extrusion. The results in Figures 4.16-4.17 indicate that draw ratio has little effect on thermal properties of the blended films in comparison to NR content and L6 and its blends have better melting behavior due to less supercooling (easier crystallzation). From Figure 4.16, it can be said that melting peaks of L1 and L6 are not significantly different. However, for the binary blends, L6/NR blends turn to have higher melting temperatures than those of L1/NR blends, especially the melting temperatures of the blends are lower than the pure ones. The difference behavior of L1 and L6 in the binary blends is that for L1 the melting peak of the binary blends increase with NR content but no for L6 blends. Moreover, for the reactive blends, melting temperatures of L6/NR/ENR are higher than that of pure L6 while for L1/NR/ENR the melting peaks are still lower than that of pure L1. This may be explained by the crystallization behavior that is shown in Figure 4.17. In general, L1/NR blends crystallize at lower temperature than those of L6 and showing the same trend that with increasing NR crystallization occurs at higher temperature. This suggests that NR acts to lower crystallization barrier and thus facilitate the crystallization process to occur earlier; therefore stronger crystalline are formed. However, this is not the case for the reactive blends. The crystallization takes place at lower temperature suggesting that the ENR and NR inhibit crystallization so that crystallinities of LLDPEs are the lowest, especially for L1 and thus poorer crystalline are formed leading to lower melting temperature. However, for L6 the crystallization is facilitated by NR but the melting peaks are not different with increasing NR, probably due to low crystallinity playing role to govern melting temperature. Although ENR and NR inhibit L6 crystallization but the melting peaks of these reactive blends are the highest suggesting that the crystalline are strong, probably due to shorter chain of L6 (less inhibition than L1) and big crystal size.

The melting (T_m) and crystallization temperature (T_m) of LLDPE, LLDPE blends were determined by DSC. Figure 4.18 - 4.19 showed melt temperatures from the DSC thermograms of the blends. When the composition of natural rubber and the draw ratio increases, there is a slight shift of melt temperature to higher temp. Figures 4.20 – 4.23 show no change in crystallization temperature with increasing draw ratio and the composition of natural rubber.
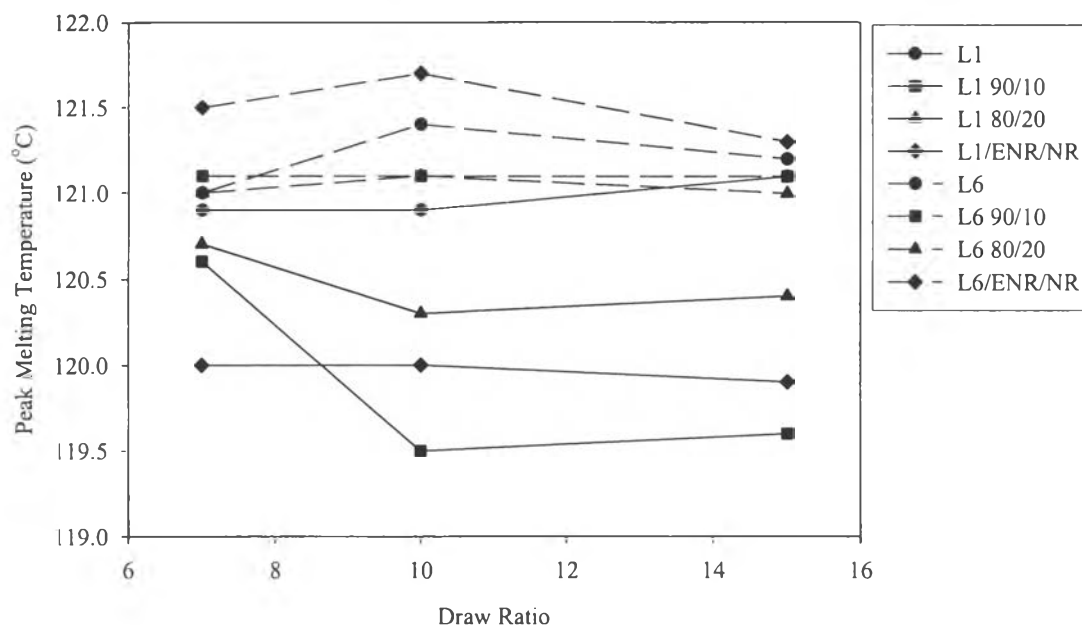

Figure 4.16 Peak melting temperature (^{0}C) of LLDPE MFI = 1 and 6.
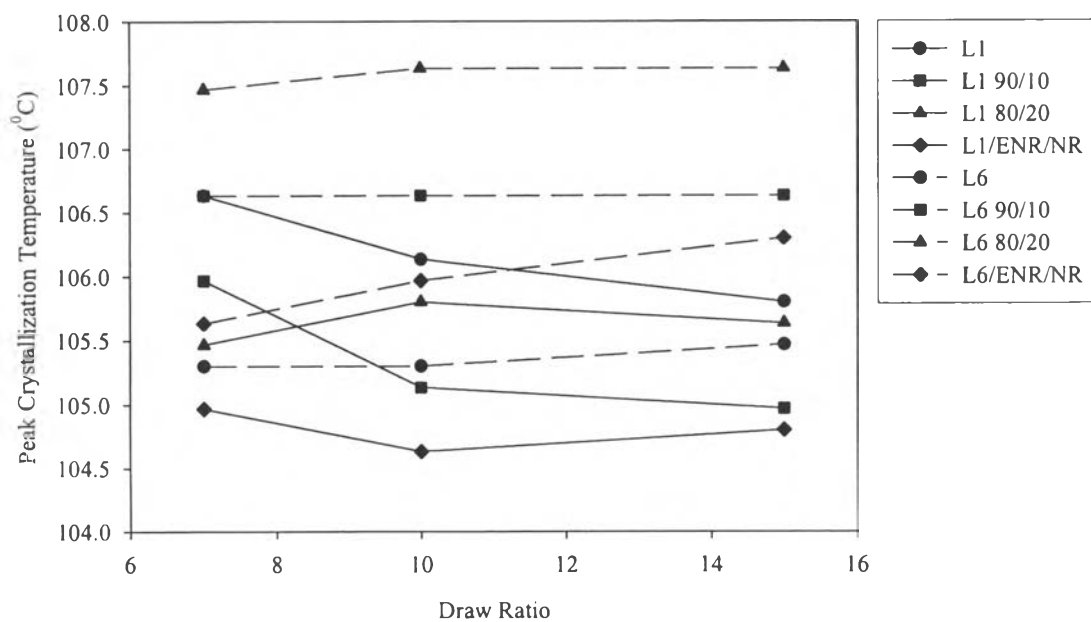
Figure 4.17 Peak crystallization temperature (^{0}C) of LLDPE MFI = 1 and 6.
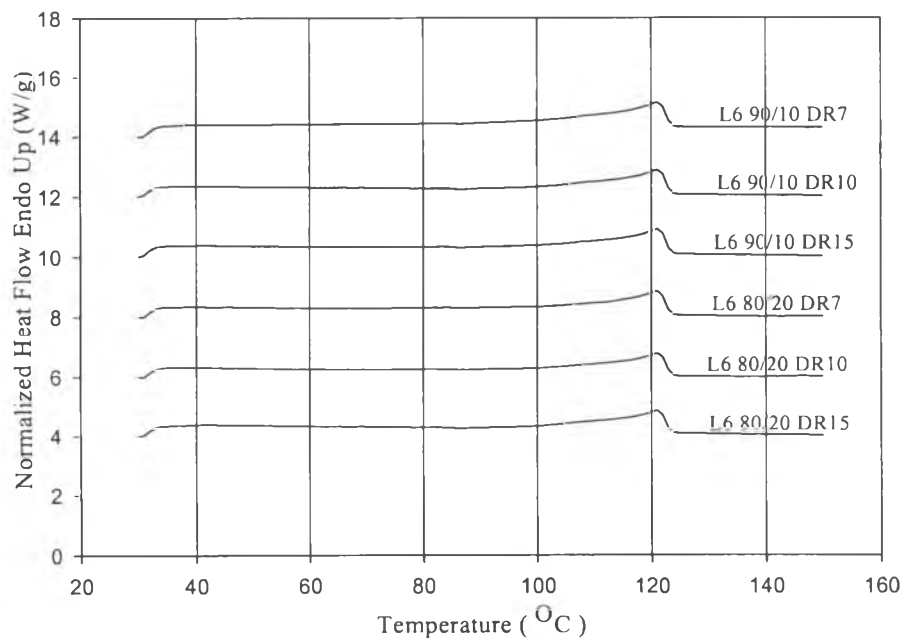
Figure 4.18 T_m of L6 90/10 and 80/20 at DR 7, 10, 15.
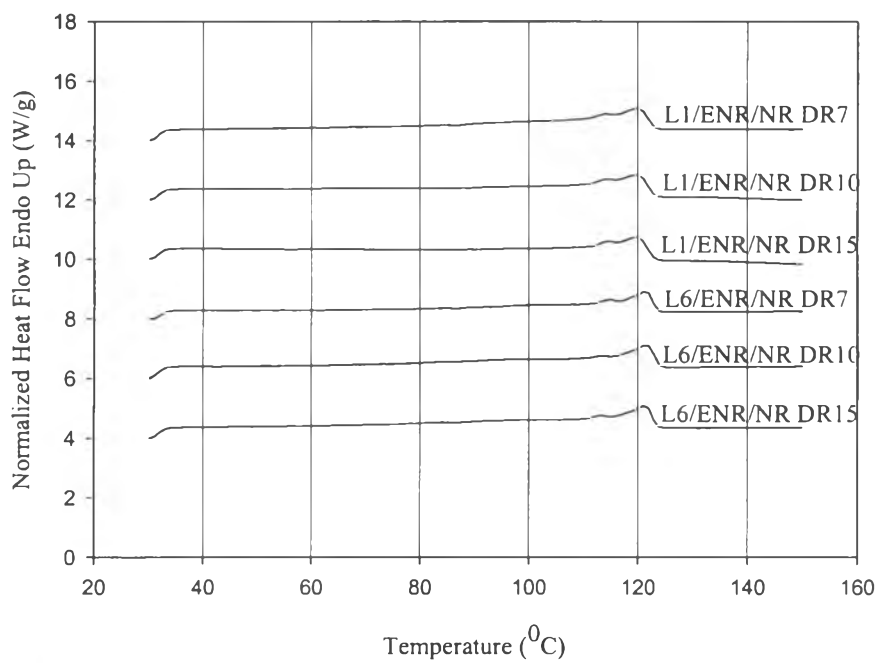
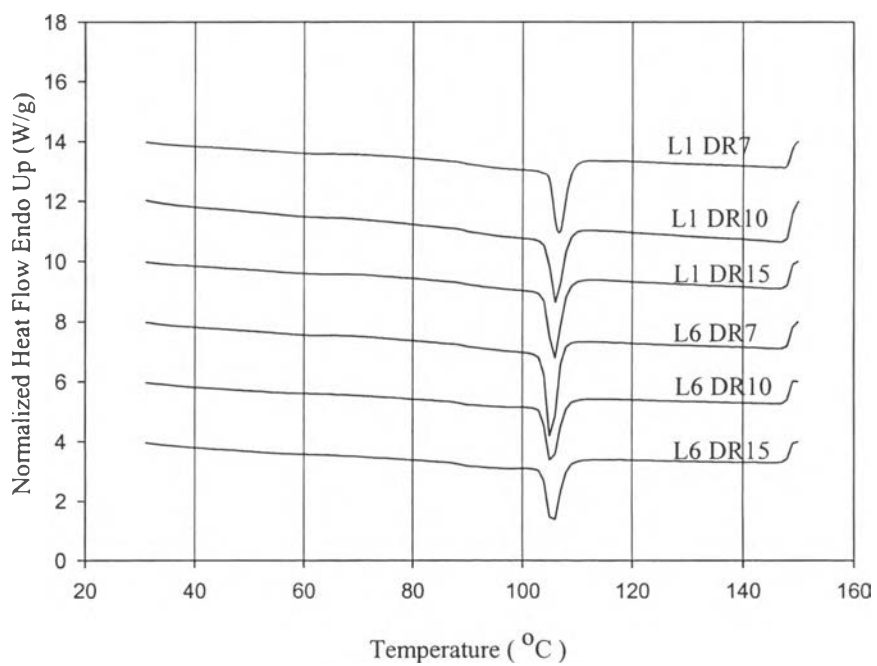**Figure 4.19** T_m of L1/ENR/NR and L6/ENR/NR at DR 7, 10, 15.
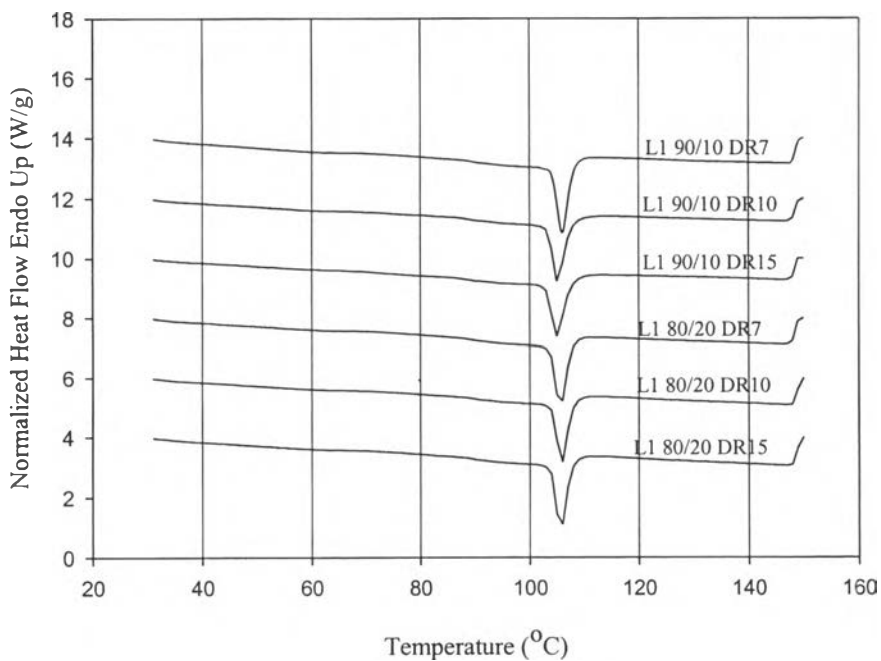

Figure 4.20 Tc of L1 100/0 and L6 100/0 at DR 7, 10, 15.
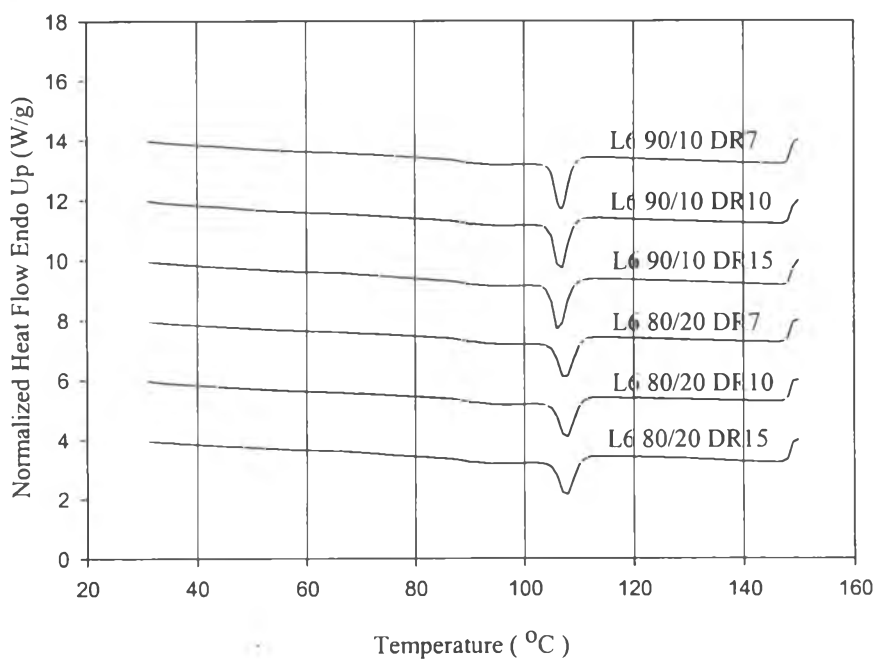
Figure 4.21 T_c of L1 90/10 and 80/20 at DR 7, 10 , 15.

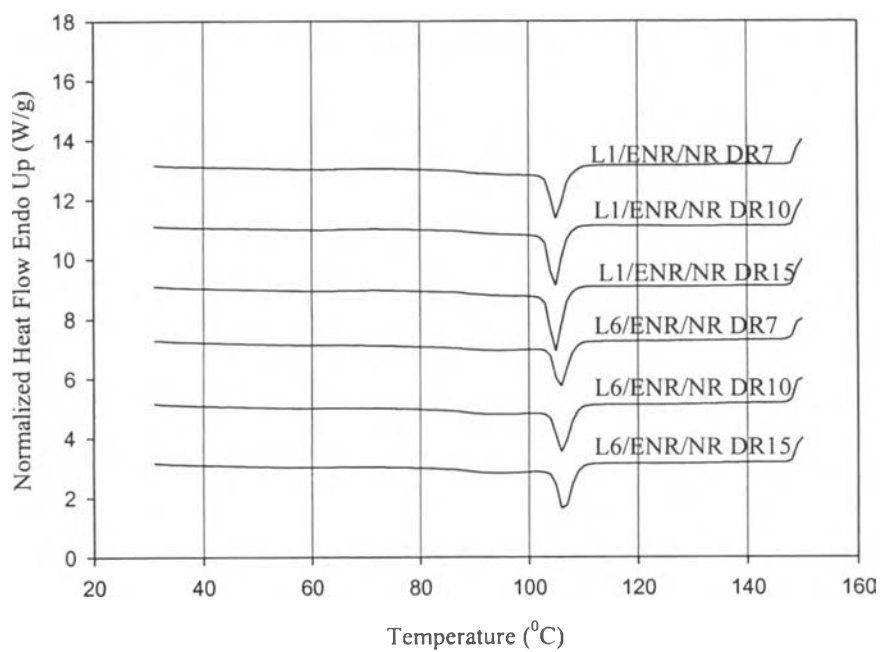**Figure 4.22** T_c of L6 90/10 and 80/20 at DR 7, 10 , 15.

Figure 4.23 T_c of L1/ENR/NR and L6/ENR/NR at DR 7, 10 , 15.

4.8 Thickness Tester

The thickness of polymer films is affected by the draw ratio. When the draw ratio increased, the film thickness decreased. The draw ratio was increased by increasing the speed of chill roll. From Figures 4.24-4.25, the highest thickness was obtained with the reactive blend sample, especially L6/ENR/NR. This indicates that the reactive blend has more tendency to stretch the reactive blend to get thinner films and thus higher orientation; i.e. higher production and strength.
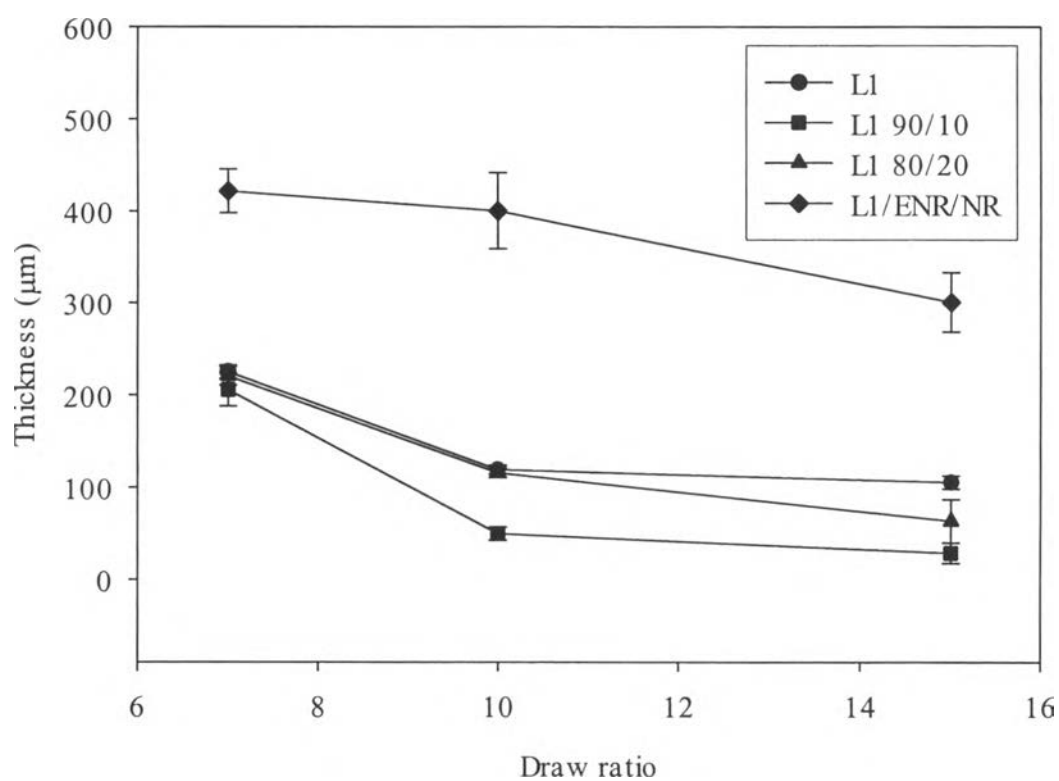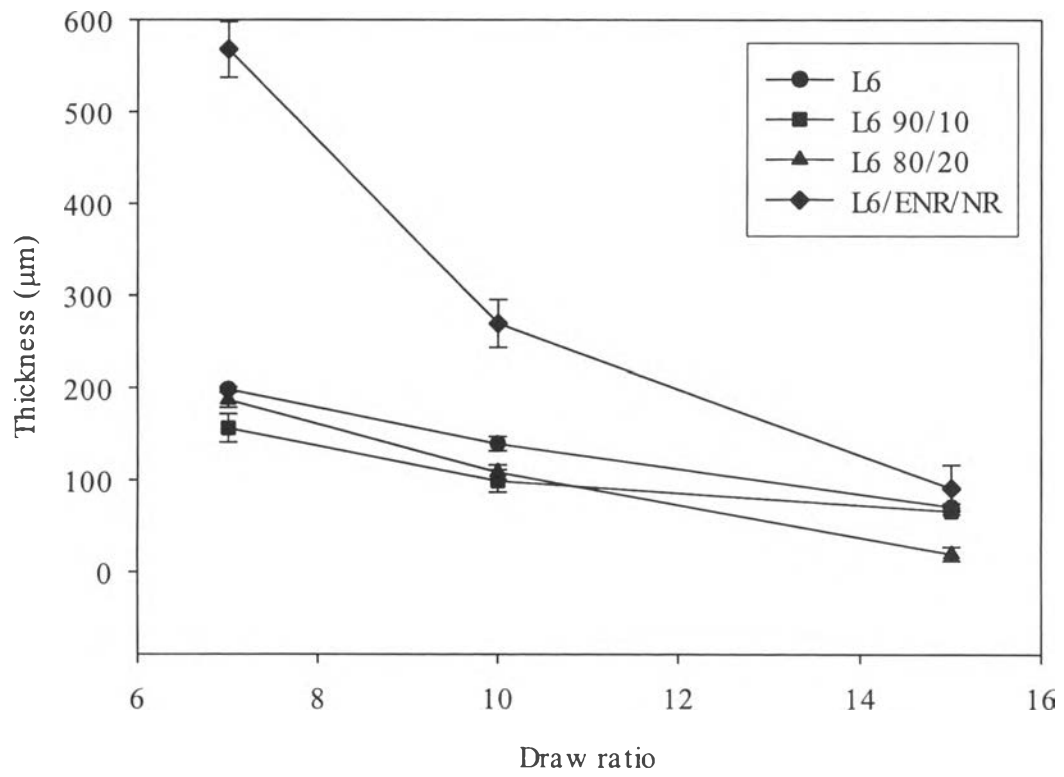

Figure 4.24 Thickness of L1 at DR 7, 10 , 15.

Figure 4.25 Thickness of L6 at DR 7, 10 , 15.

4.9 Mechanical Properties

LLDPE and LLDPE/NR blend films were prepared using Collin chill roll cast film extrusion. Yield stress is a property related to the easiness of molecule chain to be stretched and it is mainly attributed to crystalline region. Yield stress for chill roll cast films of pure LLDPE and their blends are shown in Figures 4.26-4.27. Stress at yield increased with increasing draw ratio. The highest stress at yield was exhibited by pure LLDPE with the value around 9 MPa. LLDPE blends show decreased stress at yield with increasing amount of natural rubber. LLDPE/ENR/NR blends show the lowest stress at yield because they had the lowest crystallinity.
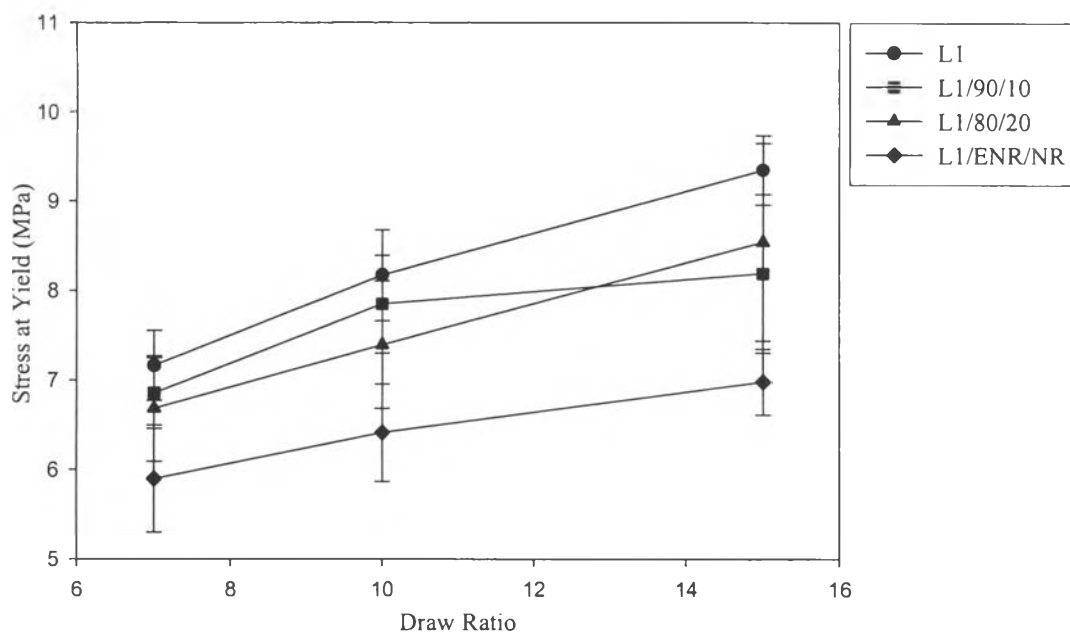

Figure 4.26 Stress at yield of pure LLDPE MFI = 1 and LLDPE blends at DR 7, 10, 15.
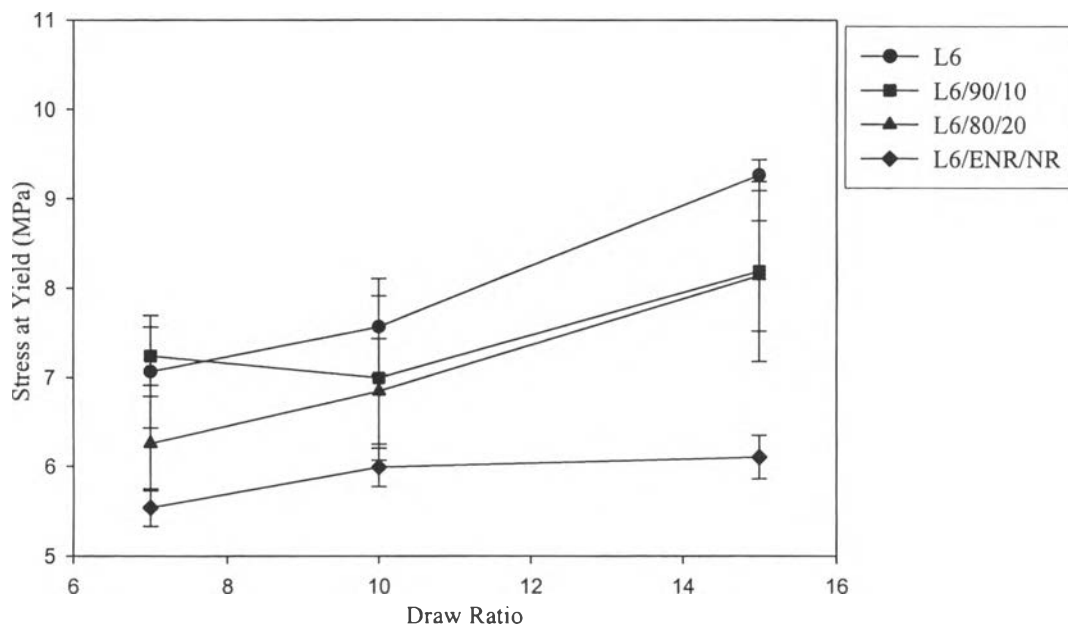
Figure 4.27 Stress at yield of pure LLDPE MFI = 6 and LLDPE blends at DR 7, 10, 15.