

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Resin Characterization

4.1.1. Polymer characterization

The resins used in this work, together with their characterization data, are listed in Table 4.1.

Table 4.1. Polymer Characterization of Resins.

| Resin | Density (g/cm ³) | MFI (g/10min) | 10 ⁻⁴ Mn | 10 ⁻⁵ Mw | MWD | 10 ⁻⁵ Mz |
|-------|---------------------------------|------------------|---------------------|---------------------|-----|---------------------|
| A | 0.915 | 4.7 | 2.14 | 1.64 | 7.6 | 5.65 |
| B | 0.915 | 4.6 | 2.10 | 1.70 | 8.1 | 8.45 |
| C | 0.917 | 4.6 | 2.52 | 2.39 | 9.5 | 10.81 |

The results show that the three resins have quite similar density and MFI, whereas resin C has a significant higher Mw and broader MWD. Since the physical and mechanical properties of the polymer depend on Mw and MWD, it can be expected that the three resins will have different properties leading to different properties of the resulting blown films.

4.1.2. n- Hexane extraction

The amount of n-hexane extractables indicates the amount of low Mw fraction in the polymer. This test is important for the reasons listed below:

- 1) High hexane extractables are undesirable because films or other articles made from such polymer may not meet strict Food and Drug Administration (FDA) requirements which limit the amount of hexane extractables.
- 2) High level of hexane extractables may cause operational difficulties, for example in the extruder, the extractable materials tend to separate out in the die and drip therefrom.
- 3) The optical clarity of blown film with high hexane extractables may be impaired by the high amount of low Mw fractions in the resin.

Results of the n-hexane extractions of the three resins and characterization of the extractables are shown in Table 4.2.

Table 4.2 Amount of n-hexane extractables and their characterization

| Resin | Weight Loss (%) | Density (g/cm ³) | Mn | Mw | MWD | Xc (%) By XRD |
|-------|-----------------|------------------------------|------|-------|------|------------------|
| A | 3.6 | 0.910 | 7025 | 11369 | 1.62 | 44.9 |
| B | 4.03 | 0.910 | 6909 | 8682 | 1.26 | 42.3 |
| C | 5.9 | 0.908 | 6114 | 7009 | 1.14 | 42.1 |

The results show that resin C has the highest amount of n-hexane extractables and the extractable parts have lower molecular weight than those of the other two resins. Results from X-ray diffraction show that the three extractables have about the same crystallinity.

4.1.3. Determination of chain branching

Chain branching in PE has been studied extensively by the IR method and most commercial PE have their branching contents determined by the IR analysis. The degree of chain branching of the three resins in this work was

determined based on the methyl content according to ASTM D2238. The IR spectra of a low-density (branched) and a high-density (unbranched) PE in the regions of interest are shown in Fig. 4.1. The band at 1378 cm^{-1} arises from the methyl capped branches. Unfortunately, the methyl band at 1378 cm^{-1} is badly overlapped by three interfering bands at 1304 , 1352 and 1368 cm^{-1} arising from the amorphous methylenes. The interference band at 1368 cm^{-1} is particularly strong. By using the spectrum of a high-density linear polyethylene standard, it is possible to obtain by subtraction a different spectrum that isolates the 1378 cm^{-1} band of the methyl branch.

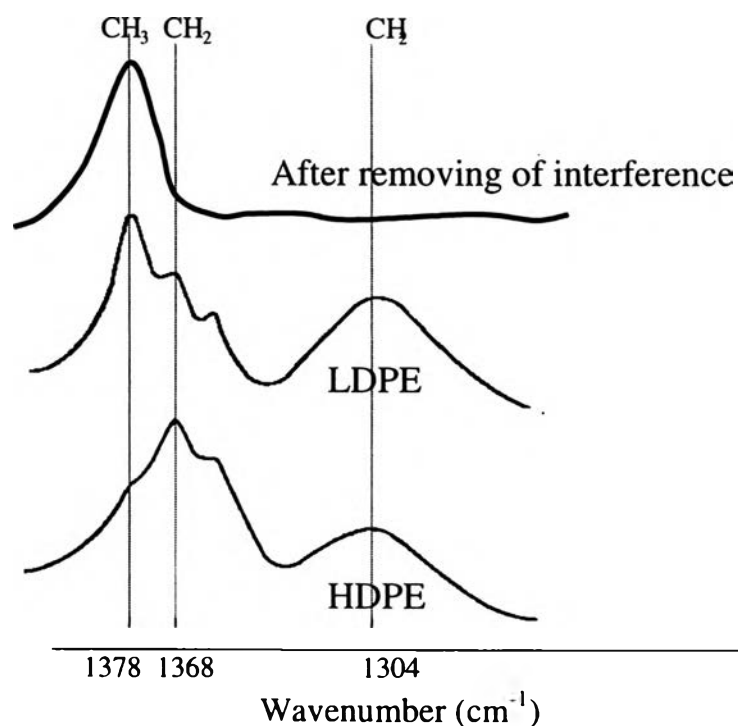


Figure 4.1 IR spectra of low and high density polyethylene and the spectrum with isolated methyl band.

The intensity of the 1378 cm^{-1} band reflects the methyl group concentration by the following expression:

$$\frac{\text{CH}_3}{1000 \text{ C}} = \frac{f_{1378} A_{1378}}{td} \times 10$$

where: f_{1378} is the conversion factor, adopted from ASTM method as 0.0765.

A_{1378} is the absorbance at 1378 cm^{-1}

t is the thickness of the film samples prepared from resin (cm)

d is the density of the polymer (g/cm^3)

The methyl contents of the three resins increase in the order A to B to C as shown in Table 4.3. The higher methyl contents in resin C may be due to the higher low molecular weight fraction in the sample as indicated by the higher amount of n-hexane extractables shown in Table 4.2.

The MFR of the three resins were also determined. The results show that there is not much difference in the MFR values of the three resins.

Table 4.3 Methyl groups and MFR of the three resins.

| Resin | Methyl groups/1000C | MFR (I_{10}/I_2) |
|-------|---------------------|----------------------|
| A | 19 | 11.1 |
| B | 22 | 11.3 |
| C | 24 | 11.9 |

4.1.4. Crystallinity

Poor optical clarity in blown film may be caused by the formation of crystalline aggregates on or close to the surface of film. There are two important parameters which have great influence on the crystallization and melting behavior of the polymer. The first is the chain length and the chain

length distribution. The second is the type, number and distribution of short chain branches. Short chain branches in polyethylene hinder chain packing and hence the crystallization of the polymer. Beside the influence of SCB, molar mass and cooling rate also affect crystallinity. At a constant cooling rate, an increase in molar mass causes a drop in the crystallinity (Vincent *et al.*, 1998).

Crystallinity of the three resins was studied by DSC. The results are shown in Table 4.4.

Table 4.4 Crystallinity of the resins

| Resin | X_c (%)by DSC | T_m (°C) | T_c (°C) |
|-------|-----------------|------------|------------|
| A | 28.69 | 108.0 | 94.0 |
| B | 28.15 | 108.2 | 94.0 |
| C | 29.74 | 107.5 | 93 |

The results show that the three resins have similar crystallinity and melting temperature.

4.1.5. Rheological properties.

Fig. 4.2 (a) and (b) are plots of shear viscosity η and shear stress versus shear rate $\dot{\gamma}$ for the three resins employed.

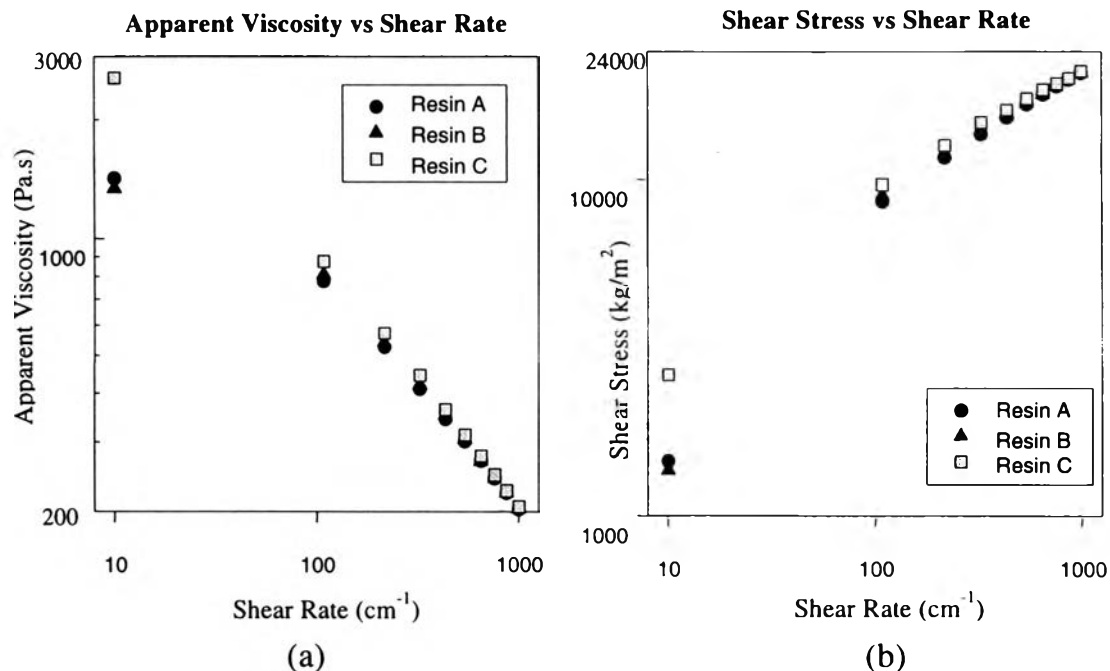


Figure 4.2 Apparent viscosity and shear stress vs shear rate for three LDPE resins investigated at 150°C

The results show that shear stress increases as shear rate increases, while the viscosity decreases. The viscosity which is the ratio of shear stress, τ , and shear rate, $\dot{\gamma}$, depends upon the molecular weight, its distribution and molecular configuration, in particular the long chain branching of the polymeric material. Short chain branching has little effect on shear viscosity.

As shown in Figure 4.2(a), resin C has higher shear viscosity compared to resin A and B. It means that in resin C, more stress is needed to deform the material in melt state. The results show that resin C has higher melt elasticity than resin A and B.

In film extrusion, two aspects of rheological behavior are important, shear and extension. Theoretically, high melt elasticity in polymer will result in more extension thickening which reduces drawability, i.e. the ability of a melt to be stretched in to a thin film without breaking. Therefore resin C is expected to have lower drawability and this can lead to higher haziness in blown film.

4.1.6. Tensile properties

The stress at yield and the elongation at break of the three resins are plotted in Figure 4.3.

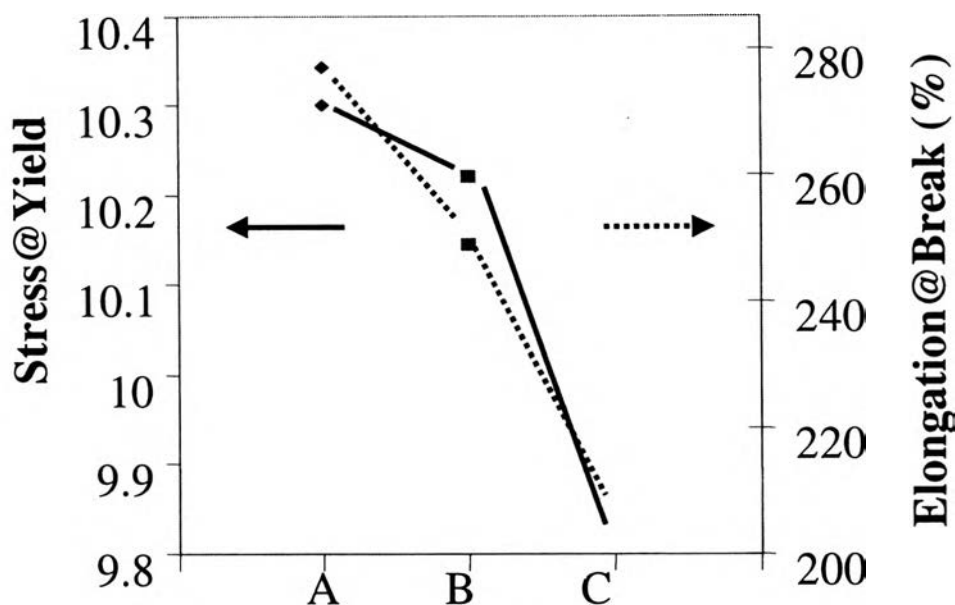


Figure 4.3 Stress at yield and elongation at break.

Stress at yield slightly decreases from A to C and the elongation at break also shows the same trend. The results show that resin A has higher chain entanglements than resin B and C.

4.1.7. Summary for resin properties

| Resin | A | B | C |
|--------------------|---|---|---|
| M_w | → | | |
| MWD | → | | |
| Hexane extractable | → | | |
| Methyl content | → | | |
| Tensile properties | ← | | |

The above results show that the three resins are different in their primary structures. Therefore it can be expected that the resulting blown films from the three resins will possess different properties under the same processing conditions.

4.2. Blown Film Characterization

4.2.1. Optical properties

From the end use point of view, the clarity of film is very important for certain applications. Table 4.5 summarizes results of the measurements of the gloss of the blown films produced from the three resins. The specular gloss refers to the shiny appearance of a film or a surface. Gloss is far more commonly measured than haze and in most cases of blown film, higher gloss is accompanied with less haziness. It appears that resin A has the highest value of gloss.

Table 4.5 Gloss of the blown films

| Film | Gloss at 20° | Gloss at 60° |
|------|--------------|--------------|
| A | 46 | 112 |
| B | 42 | 110 |
| C | 38 | 97 |

Surface examination of the film samples by SEM has also been carried out and the results are shown in Fig. 4.4.

The SEM micrographs do not indicate any difference in the surface texture of the two films. However, film C shows line defects on the surface along MD. This defect probably causes the lower gloss and poorer appearance of the film and it may also affect the mechanical properties of the film. On the other hand, film A has a very smooth surface. The defect along MD observed

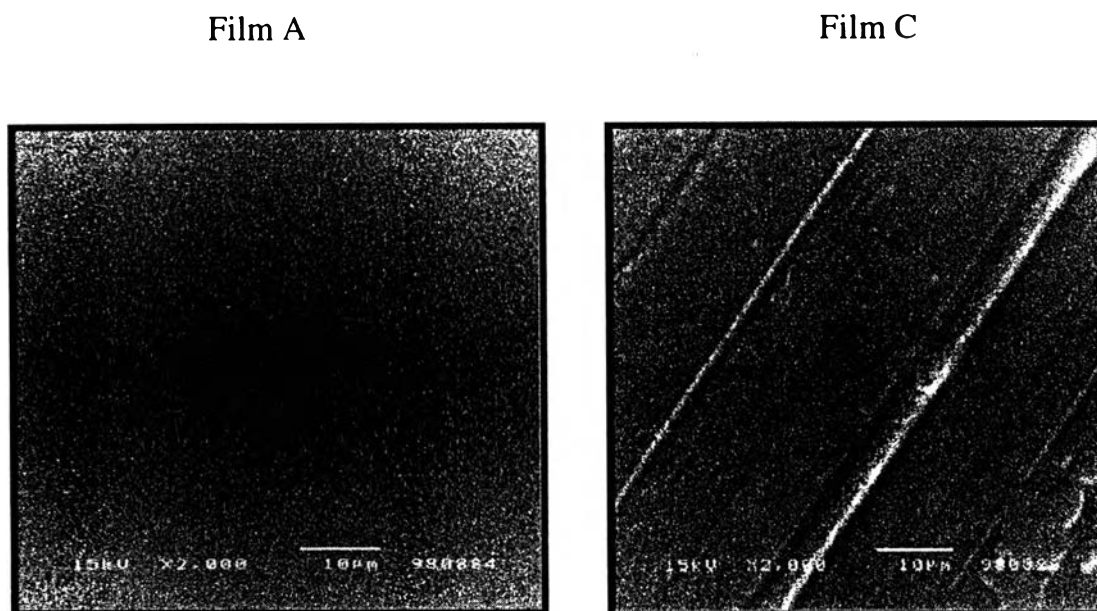


Figure 4.4 SEM micrographs of surfaces of film A and film C.

in the case of film C can be explained by the extrusion defect occurring during film blowing. High melt elasticity in resin C may induce flow irregularity leading to defects in the film surface with the loss of gloss and increase in haziness. The elasticity in polymer melt can cause various types of extrusion defects including microscale extrudate distortion. The melt of resin C does not stretch as much as resin A and B. During stretching, the short chains in resin C slide past each other rapidly leading to disentanglements and hence resin C cannot be pulled into a film in a smooth way. Moreover, it is hypothesized that during the film blowing process, a rapid build up of stress in the polymer occurs leading to unbalanced biaxial stretching. If this is the case, the viscous stress level in the melt will be higher compared to the aerodynamic forces, and this will lead to unbalance in molecular orientation in the film.

4.2.2. Tensile properties.

The tensile strength at break and the elongation at break of the three films in both directions are shown in Figure 4.5 and 4.6 respectively. First, it is noticed that tensile strength in MD is higher than in TD direction due to the higher molecular orientation in MD as found in almost all cases of blown films. Resin C shows higher strength in MD probably due to higher molecular weight and higher orientation along MD compared to A and B.

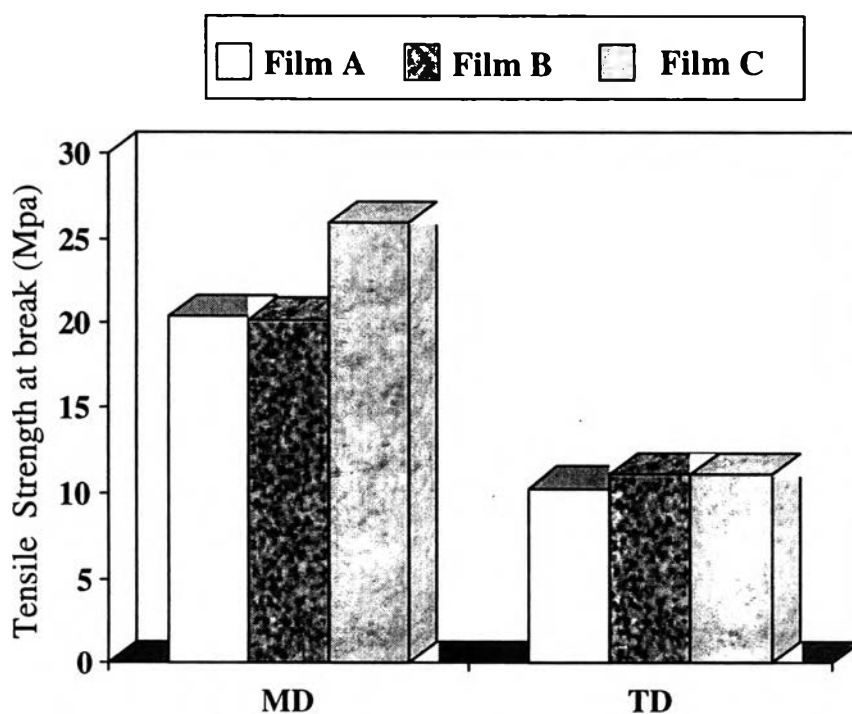


Figure 4.5 Tensile strength at break of the three blown films.

In contrast, the elongation at break behaves in a reverse manner with elongation in TD higher than in MD. This can be explained by the difference in the chain orientation in the two directions. Molecular chains already orient more along MD so they can not elongate much under tensile force. In the case of TD, the molecular orientation is lower and hence the chains can elongate

more before breakage. During the tensile strength test, necking in test specimens is also observed.

Comparison of the tensile properties of films A, B, and C shows that film C has much lower elongation at break than film A and B. The results show that film A has the highest chain entanglement while that of film C is the lowest.

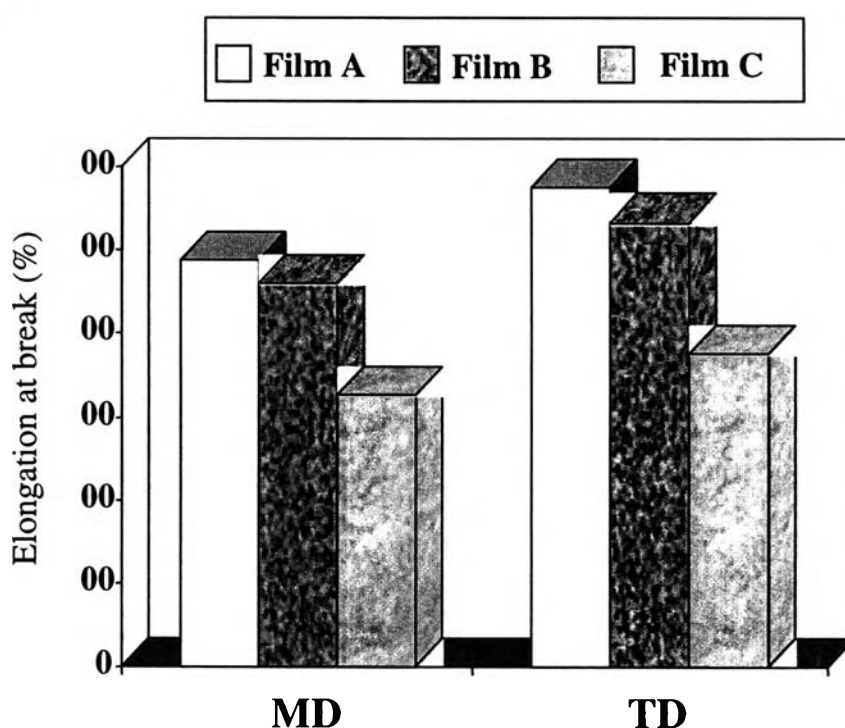


Figure 4.6 Elongation at break of the three blown films.

4.2.3 Thermal Shrinkage

Molecular orientation imparted during film fabrication is known to have major effect on mechanical and thermal properties in both glassy and semicrystalline polymers. The effect of molecular orientation on tensile properties has already been mentioned above. Shrinkage measurements represent a simple method for describing viscoelastic properties and orientation in LDPE blown film.

Rajen *et al.* (1994) stated that shrinkage of the film is mainly due to the amorphous orientation and chain extension frozen into the film by stresses during deformation. During shrinkage some slippage (relaxation) of molecules may also occur, and shrinkage is therefore not an absolute measure of original amount of amorphous orientation. However shrinkage measurements are still useful for measuring relative amorphous orientation in films.

Thermal shrinkage of the three films are shown in Figure 4.7.

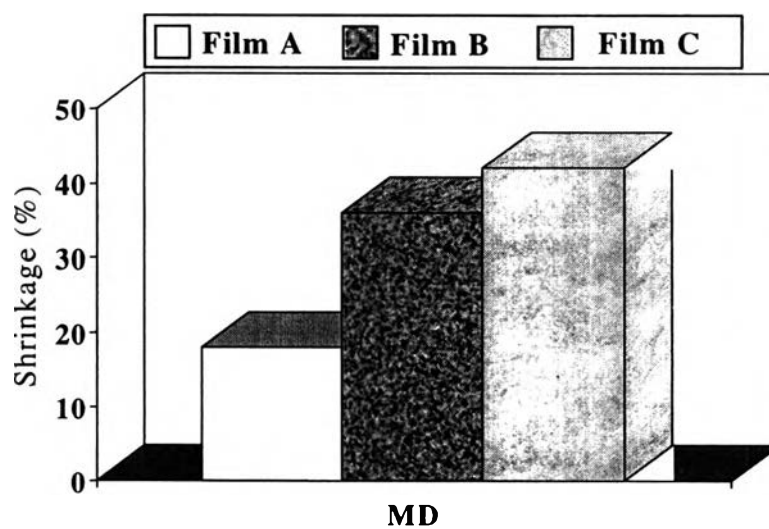


Figure 4.7 Shrinkage of the film in MD.

The results confirm the difference in molecular orientation of the three films with film C having the highest orientation in MD. Biaxial tension exists in a tubular film during processing and molecular chains between entanglements are extended. After extrusion and blowing, the film is cooled rapidly, molecular chains between entanglements crystallize, chain segmental motion is frozen in, and the chains retain some local orientation or extension. When this film is heated above its melting point, chain segmental motion will again become activated. Extended chains attempt to return to a random coil conformation and the net result will be the contraction of the film provided little or no chain slippage occurs.

2.4 Tear Resistance.

Tear resistance properties of the three blown films are shown in Table 4.6 and Figure 4.8.

Table 4.6 Tear resistance of the film

| Film | MD tear | TD tear | TD/MD |
|------|---------|---------|-------|
| A | 4704 | 6432 | 1.37 |
| B | 1728 | 2304 | 1.33 |
| C | 960 | 2448 | 2.55 |

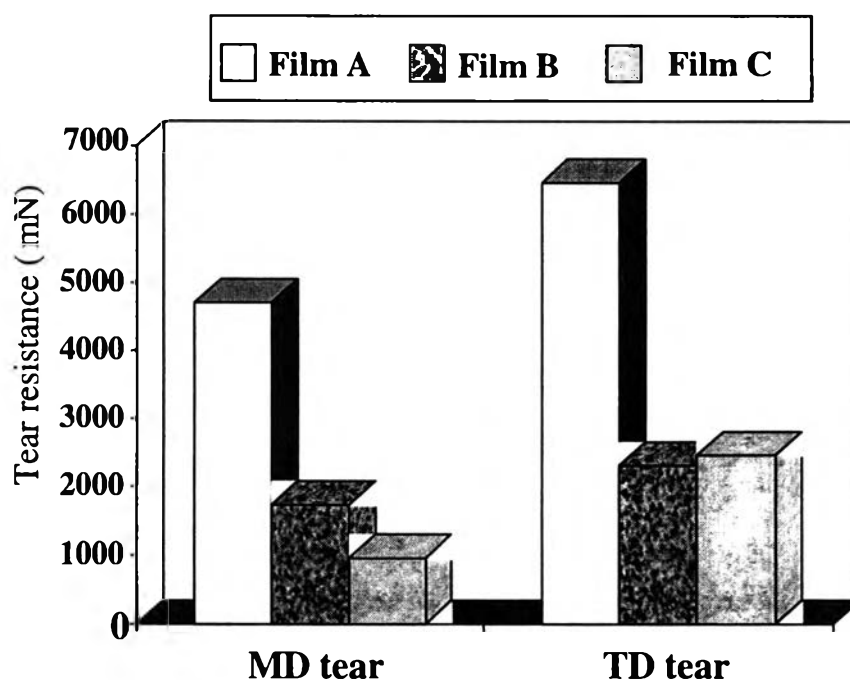


Figure 4.8 Tear resistance of the three blown films.

Tear resistance is a very important property of blown films and is very sensitive to orientation. Tear resistance in MD is lower than TD tear resistance which is consistent with the results from shrinkage testing. Due to preferential orientation along MD, the concentration of tie molecules is

lower in MD, tearing in MD therefore needs less force. It has been noticed that the torn edge in MD shows smooth edge, while it is rough and jagged in TD because of tear propagation across highly oriented chains. In the case of film A, tear resistance is much higher in both direction and the torn edge is not straight from the precut line, it is ragged and deformed. This observation appears to be associated with the better chain entanglements and more balance in orientation in film A. Tear has to propagate across chain network that is highly tied and hence it needs more force to tear.

4.2.5. Crystallinity of the blown film

The XRD spectrum of the three films are shown in Figure 4.9 together with the spectra of an HDPE sample.

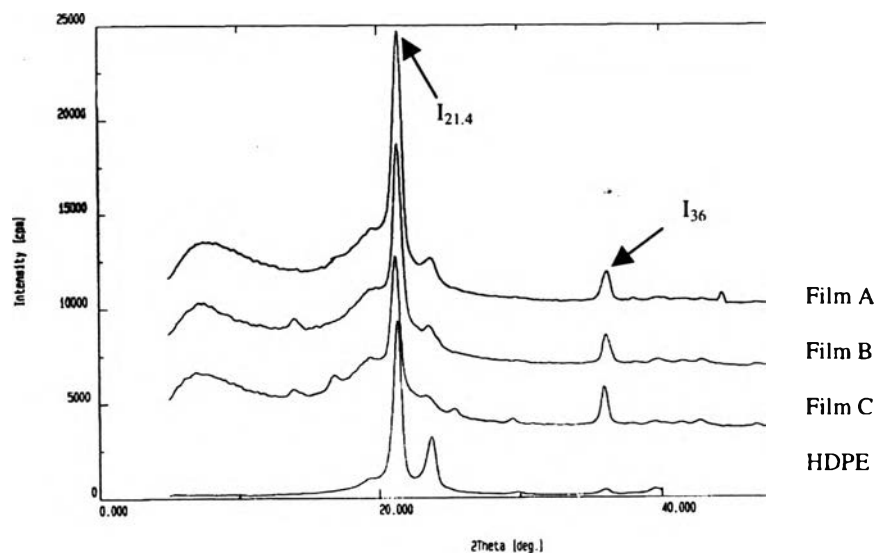


Figure 4.9 XRD spectrum of the three blown films.

The results show that film C has more distinct peaks especially at lower angles than film A and film B. This indicates that there are more large scale crystalline structures in film C which may lead to the poorer clarity in the film.

4.2.6 Orientation study by polarized optical microscope

If polymer molecules in a sample are oriented, its optical property will be anisotropic because the mobility of electrons along the chemical bond within a polymer chain will differ from that in the direction transverse to the molecular chains. The refractive index will have two principal values, and the birefringence, Δn , is defined as the difference between two such principal values, $\Delta n = n_{\parallel} - n_{\perp}$. That is the birefringence for an oriented polymeric material is the difference in the index of refraction along the average polymer chain direction and the index of refraction transverse to it, $\Delta n = n_{\parallel} - n_{\perp}$.

Birefringence is a classical method for the measuring of orientation. The birefringence values calculated from retardations, which are approximated from specific color in Newton's color sequence, are shown in Table 4.8.

As seen from Figure 4.10, $\lambda/4$ plate adds retardance to the image of all the three films, the interference color shifts up the Newton's scale so the sign of birefringence is positive.

Table 4.7 Birefringence value of the three blown films

| Film | Color(at λ) | Retardation (R -nm) | Thickness (t - nm) | Birefringence ($\Delta n=R/t$) |
|------|----------------------|------------------------|-----------------------|-------------------------------------|
| A | Brass | 350 | 55000 | 0.006 |
| B | Carrot | 500 | 50000 | 0.010 |
| C | Fuschia | 1050 | 50000 | 0.021 |

The birefringence measurements in this work are not very accurate as they involve matching colors seen in the microscope with those in the Newton's scale. However it can be used as a qualitative measurement to compare the orientation in the films. The results show that film C has the highest birefringence value and hence the highest orientation.

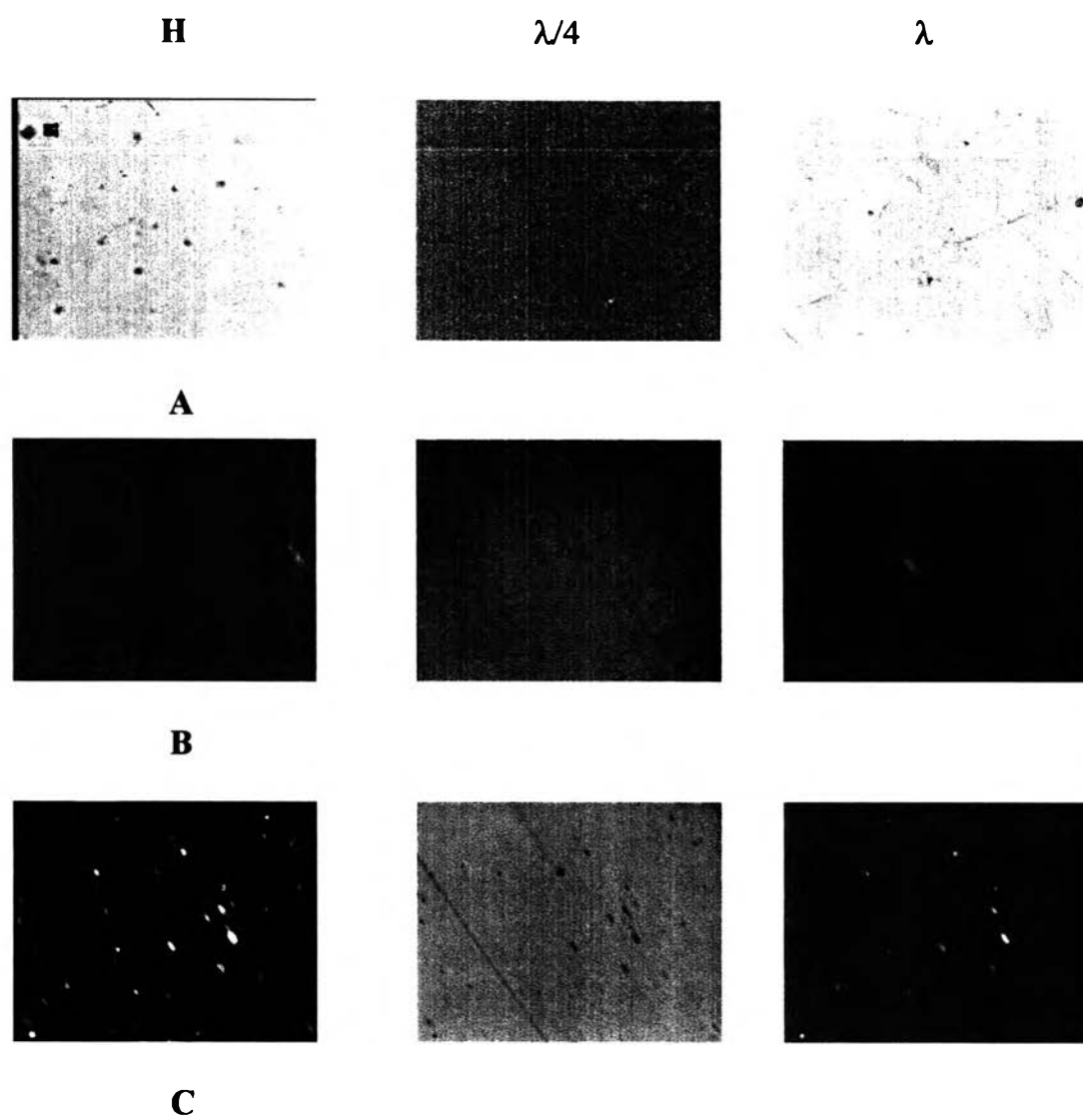


Figure 4.10 Polarized microscope images of the three films taken at 45° of the principal axis (MD).

4.2.6. Summary of film properties

| Film | A | B | C |
|---------------------|---|---|---|
| Optical property | ← | | |
| Tensile strength | → | | |
| Elongation at break | ← | | |
| Shrinkage | → | | |
| Tear resistance | ← | | |
| Orientation balance | ← | | |

The results are in agreement with the expectation that the three films would have different properties due to the differences in resin properties. Following the criteria for successful processing, resin A is found to produce film with the best properties while resin C produces film with the worst properties.