CHAPTER IV
RESULTS AND DISCUSSION

The molecular parameters were important variables to alter polymer processibility and mechanical behavior. Thus, the results were reported based on effect of Mw and MWD of original HDPEs.

4.1. Melt flow Index Determination

4.1.1. Effect of Mw

Figure 4.1 shows that increasing % of high Mw leads to a decrease in MFI. It is also clear, by comparing the two sets of blends in this condition, that the MFI sharply decreases in the case of LW1/HW1 (big difference in Mw) whereas the MFI for LW2/HW2 (small difference in Mw) shows a slight decrease. The increase in Mw generates a decrease in MFI because the polymer with high Mw contains many long chains. Hence, a high melt index indicates a low molecular weight. By relating this result with the reference sample of LD2/LD1, it is found that the reference sample with low Mw shows high MFI and the change is linear with the composition. The reference sample (LD2/LD1 blends) exhibits linear increase of MFI with the composition, although the increase is rather small due to the slight difference of Mw. The increase of MFI is rather small due to the slight increase of Mw.

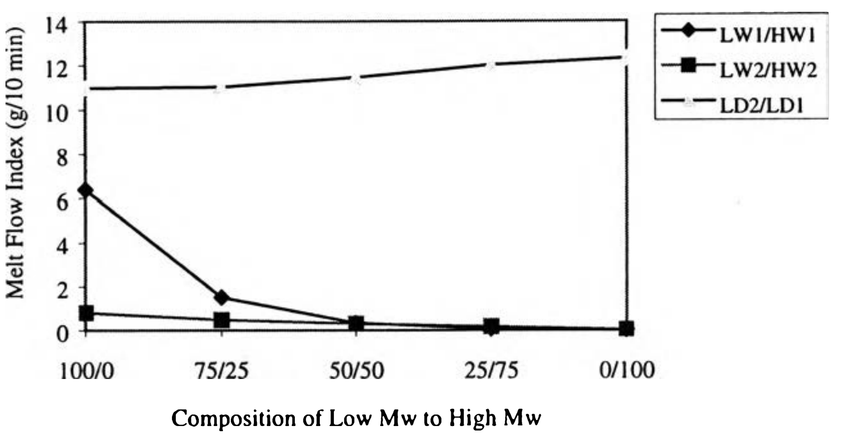


Figure 4.1 Comparison of melt flow index for blend system 1 and reference sample at 190°C / 2.16 kg.

4.1.2. Effect of MWD

Comparing with the reference, LD3/LW1 and LD3/LW2 blends show much lower MFI at all compositions (Figure 4.2). Increasing the amount of LW1 shows a steadily increase in the MFI for LD3/LW1 blend. Increasing the amount of LW2 exhibits an opposite effect for LD3/LW2 blend. It is interesting that the sample with small difference in MWD shows a steady increase in MFI. Increasing of MFI for LD3/LW1 blends is explained using the GPC results (Figure 4.3). From the curve, LW1 have MWD skewed to the left while MWD of LW2 and LD3 skewed to the right. It means that, amount of long chains of LW2 is higher than those of LD3 and LW1. The long chains retard the flow of polymer due to high entanglement. Hence, increasing the amount of LW2 for LD3/LW2 blend causes increasing number of entanglement and reducing of MFI. And MFI increases with amount of LW1 for LD3/LW1 blend due to high amount of short chain which is not efficient to retard flow. Thus, MWD and its skewness are the important factors to alter MFI both positively and negatively. It is also noted that the specification of LW1 shows that its MFI is rather high for the injection molding application.

However, LW2 is a blown film grade, so its MFI is quite low. Once LW1 and LW2 are blended with LD3 whose grade is for injection mold with MFI just below LW1, the blend of LD3/LW1 thus show increasing MFI with LW1 content while LD3/LW2 blends posses reducing MFI with amount of LW2.

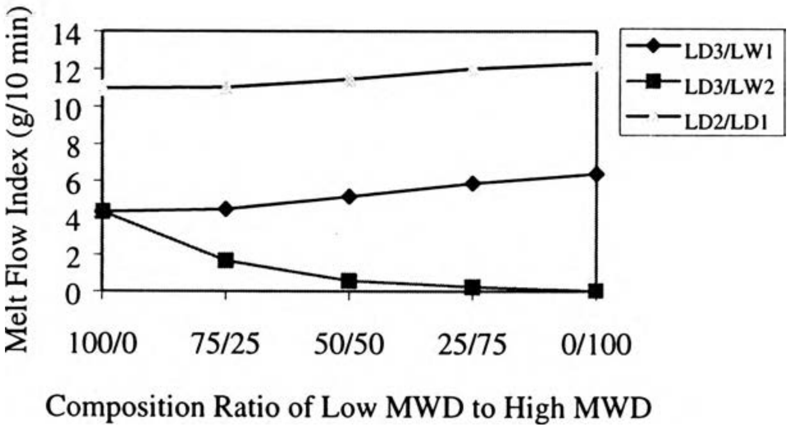


Figure 4.2 Comparison of melt flow index for blend system 2 and reference sample at 190°C / 2.16 kg.

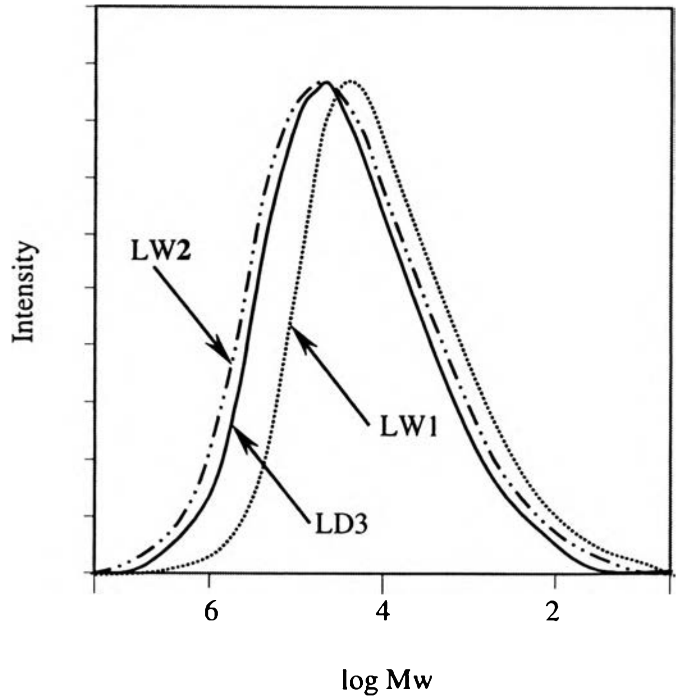


Figure 4.3 The MWD curves of blend system 2 from GPC hi-temp.

4.2. Study of Mechanical Properties

4.2.1. Effect of Mw

The final mechanical properties of homopolymer blends are usually intermediate between the parent polymer (Tzoganakis *et al.*,1989). In Figures 4.4 and 4.5 show the results for the effect of Mw on the tensile strength and Young's modulus. All properties are enhanced with addition of high Mw component and have intermediate values between those of pure components. The results show that the three mechanical properties of LW1/HW1 rise up rapidly with the amount of high Mw component and have higher values than those of LW2/HW2 samples. The results are similar to the previous work by Vadhar *et al.* (1987) their study for the blends of UHMWPE with LLDPE showed the increase in tensile strength and tensile modulus with the composition of UHMWPE by using Banbury mixing.

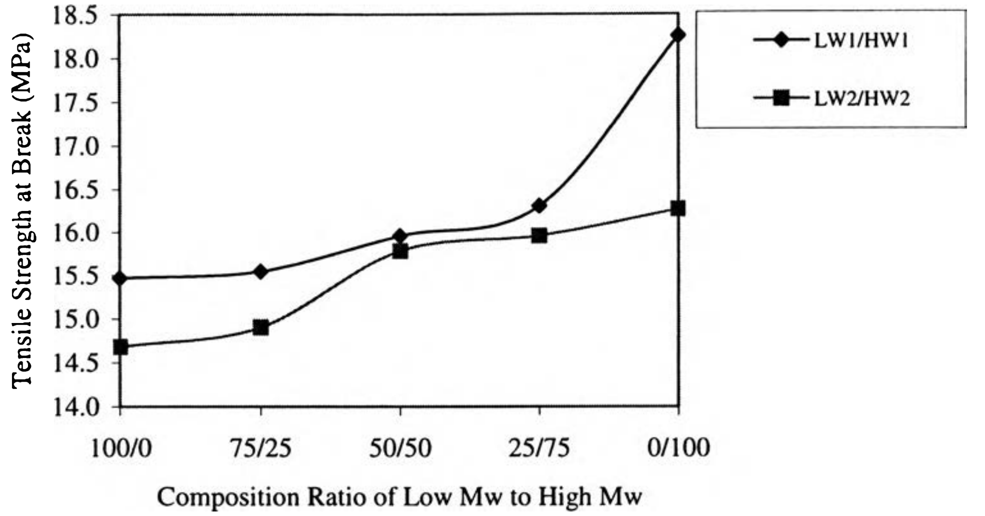


Figure 4.4 Tensile strength at break vs. composition ratio of blend system 1 under crosshead speed 450 mm/min.

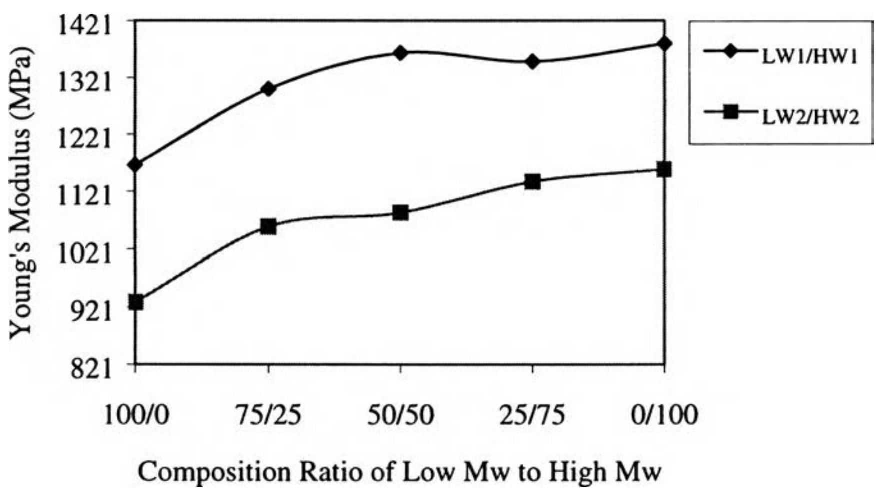


Figure 4.5 Young's modulus vs. composition ratio of blend system 1 under crosshead speed 450 mm/min.

4.2.2. Effect of MWD

The effect of MWD on tensile strength is subtler than the effect of Mw. The result is showed in Figures 4.6. Mechanical properties of reference sample do not improved by adding amount of LD1 or LD2 component. In the case of big difference of MWD, adding LW2 results to steady change of the tensile properties and elongation at break with its composition. Meanwhile, these two properties are not changed with increasing amount of LW1 due to the presence of relatively short chains.

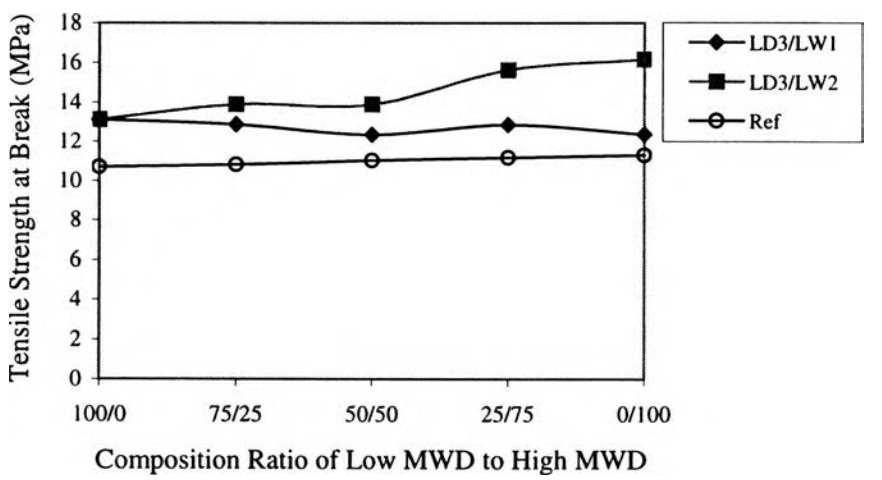


Figure 4.6 Tensile strength at break vs. composition ratio of blend system 2 comparing with reference sample under crosshead speed 100 mm/min.

4.3 Study of Processibility

There were three parameters changed in order to investigate their influences on processibility, i.e. screw speed, die geometry and molecular parameters (Mw and MWD). Figures 4.7 to 4.8 show the plots of output rate and pressure used against screw speed. The solid lines represent the output rate as a function of screw speed. Meanwhile, the dash lines represent the pressure used as a function of screw speed. At all conditions, the changes of output rate and pressure build-up are due to the variation of screw speed from 10 to 30 rpm. The detail of changing is discussed as following.

4.3.1. Effect of Mw

Figures 4.7 and 4.8 show the changes of output rate and pressure build-up for LW1/HW1. Figure 4.7 shows that for die diameter 1 mm the pressure used raises up from 4 MPa to nearly 16 MPa when amount of HW1 increases. Meanwhile, it does not affect to the changes of output rate. The same behavior on a die with 4 mm diameter is also shown in Figure 4.8 that pressure build-up is lower than that of 1 mm die diameter and only reaches to 6 MPa.

The small difference in Mw sample shows the changes of pressure used for both die geometry in Figures 4.9 and 4.11. Small diameter of die causes more pressure build-up in the systems than the bigger one. Figure 4.8 shows that the pressure build-up in case of die with 1 mm diameter is about 1 MPa. This is higher than that of the die with 4 mm diameter (0.4 MPa) as shown in Figure 4.10.

Two sets of sample (LW1/HW1 and LW2/HW2) were compared. Overall results show more shift and higher magnitude and broader distribution of the pressure build-up caused by big difference in Mw than that of small difference in Mw. The reason was due to high viscosity of high Mw component that needed high pressure to push polymer melt to come out. As seen in the research work of Rosario *et al.* (1993), their results indicated the changes of the operating point (the intersection of the characteristics of die and screw) to higher pressure region as a result of the increasing amount of UHMWPE in the blends with HDPE.

Moreover, all the shifts of these points were also significantly changed by comparing with a reference sample having relatively low Mw and narrow MWD (Figures 4.11 and 4.12). It is seen that output rate and pressure build-up reduce with the molecular weight. In other word, LW1/HW1 has higher output rate and pressure build-up than LW2/HW2 and LD2/LD1 respectively.

4.3.2. Effect of MWD

The changes of pressure build-up and output rate due to effect of MWD are shown in Figures 4.13 to 4.16. In Figure 4.13 and 4.14, pressure reached to 10 MPa for the pair with big difference of MWD while it is about 5.5 MPa for LD3/LW1 (Figures 4.15 and 4.16). This shows the composition dependence of pressure build-up. However, the output rate is not affected by increasing amount of either LW2 or LW1. These results are also compared with those of reference sample (Figures 4.11 and 4.12) which show slight shift of pressure build-up with the changes of blend composition. It can be summarized that output rate is not dependent on blend composition of high Mw component. Pressure build-up is opposite to output rate. It is dependent on blend composition of high Mw component and degree of MWD difference of pure component. Those effects are enhanced by reducing die diameter. In other word, pressure build-up is also dependent on die geometry. The output rate reduces when Mw of sample decreases or if high Mw component is absent (narrow MWD). Die geometry, i.e. 1 mm and 4 mm diameter of die, doe not effectively alter the output rate.

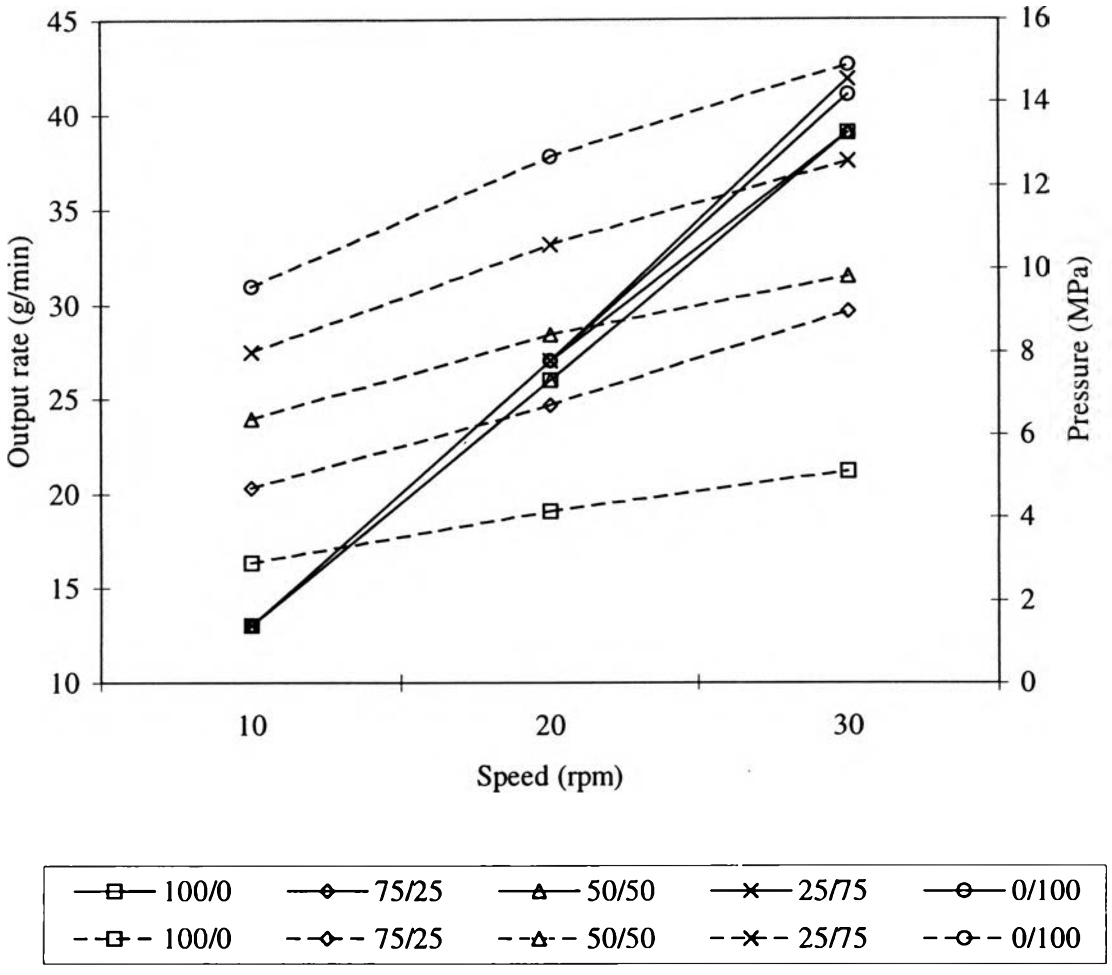


Figure 4.7 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 1 (LW1/HW1) at the 1 mm diameter die.

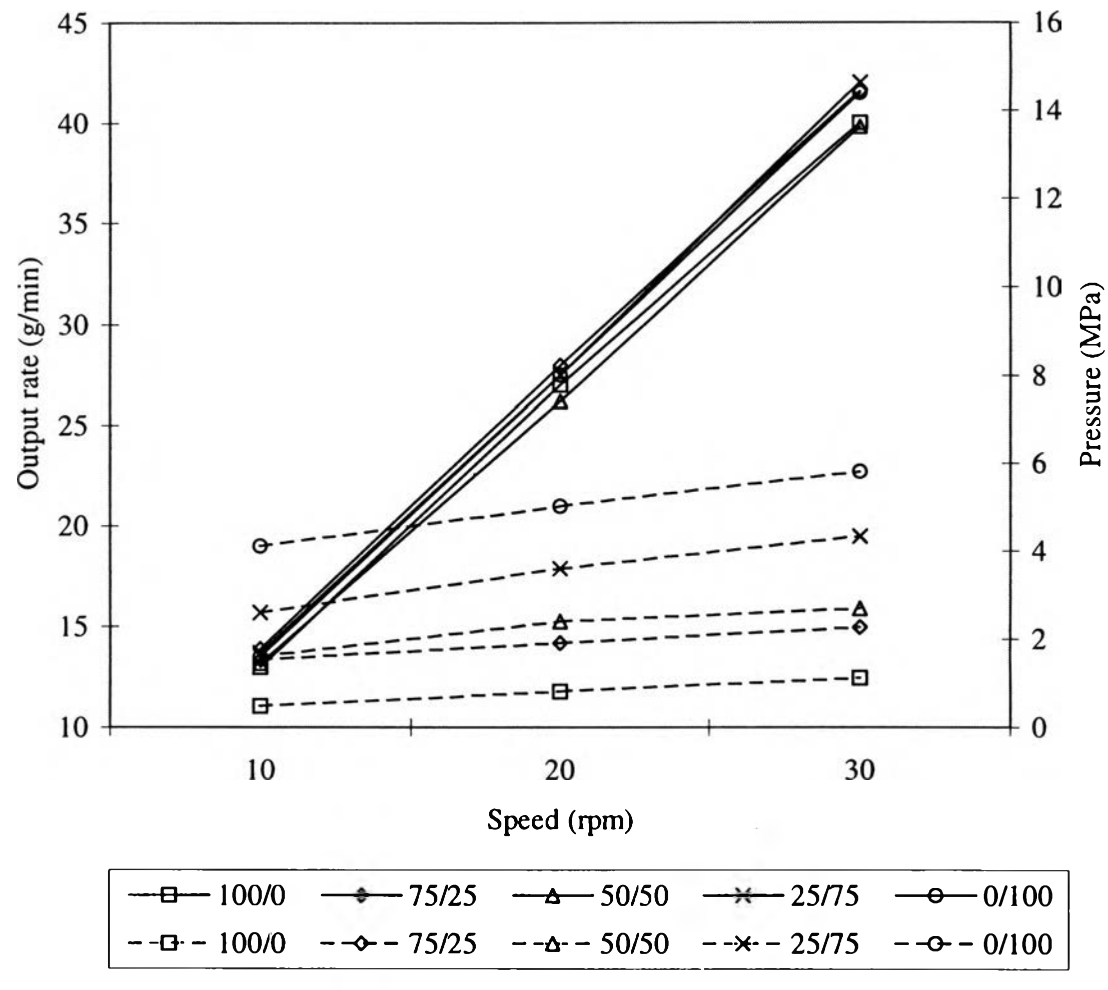


Figure 4.8 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 1 (LW1/HW1) at the 4 mm diameter die.

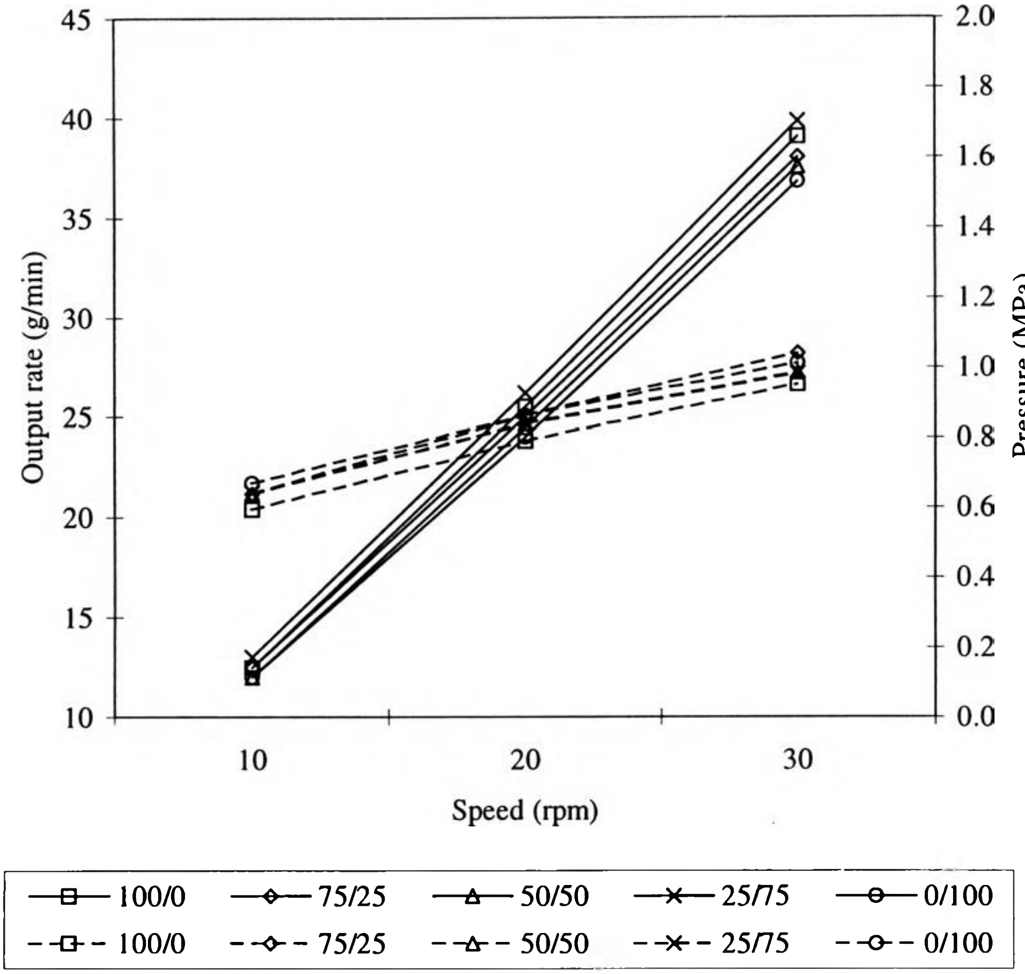


Figure 4.9 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 1 (LW2/HW2) at the 1 mm diameter die.

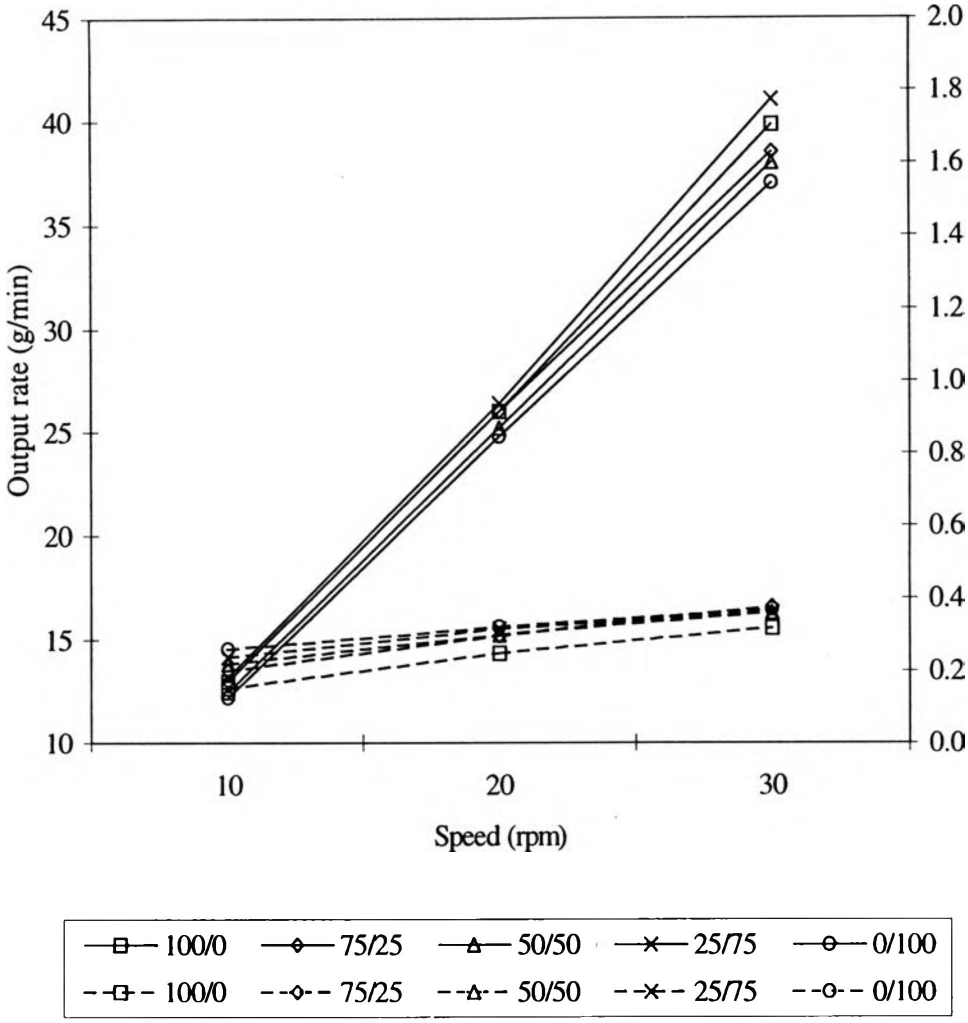


Figure 4.10 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 1 (LW2/HW2) at the 4 mm diameter die.

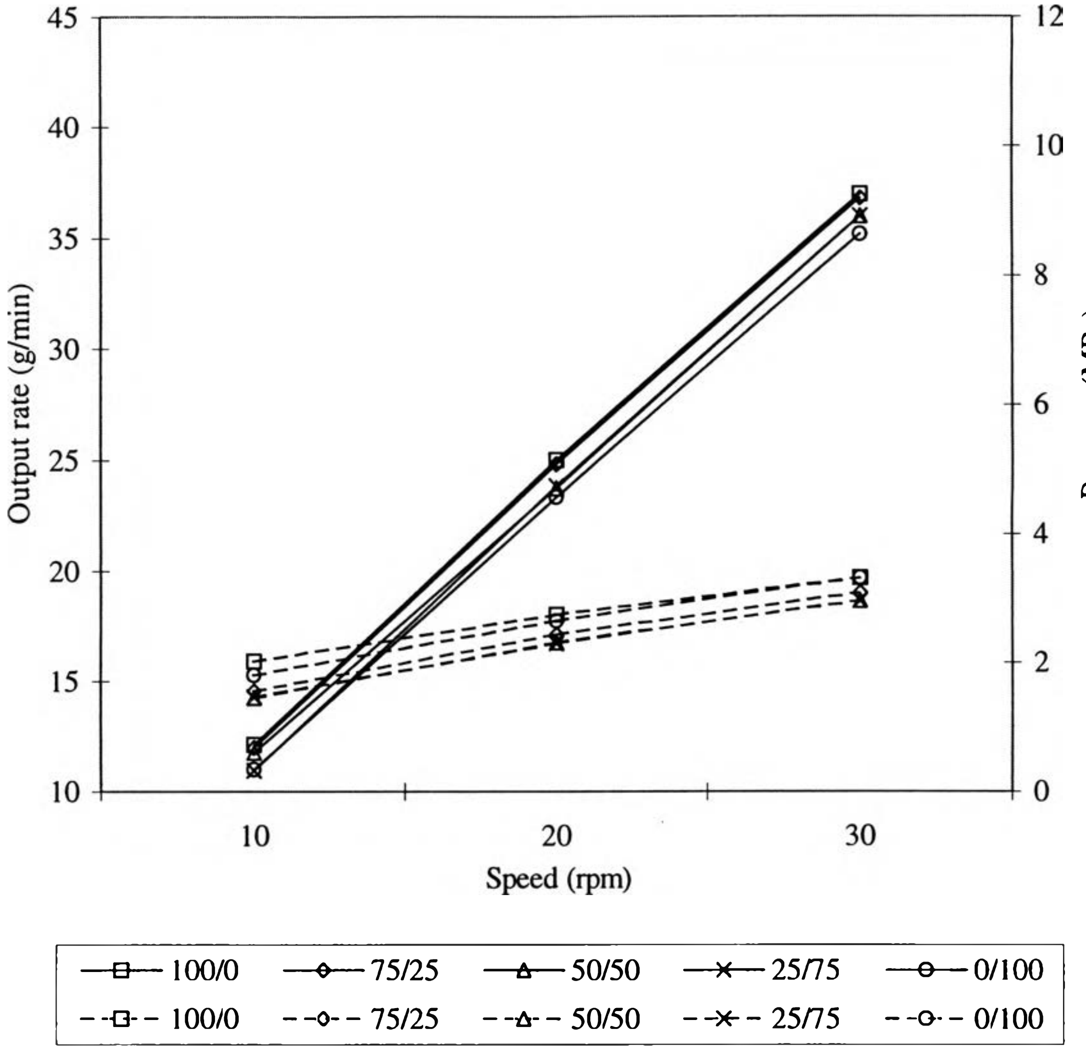


Figure 4.11 Plot of output rate (solid lines) and pressure (dash lines) against speed for reference sample (LD2/LD1) at the 1 mm diameter die.

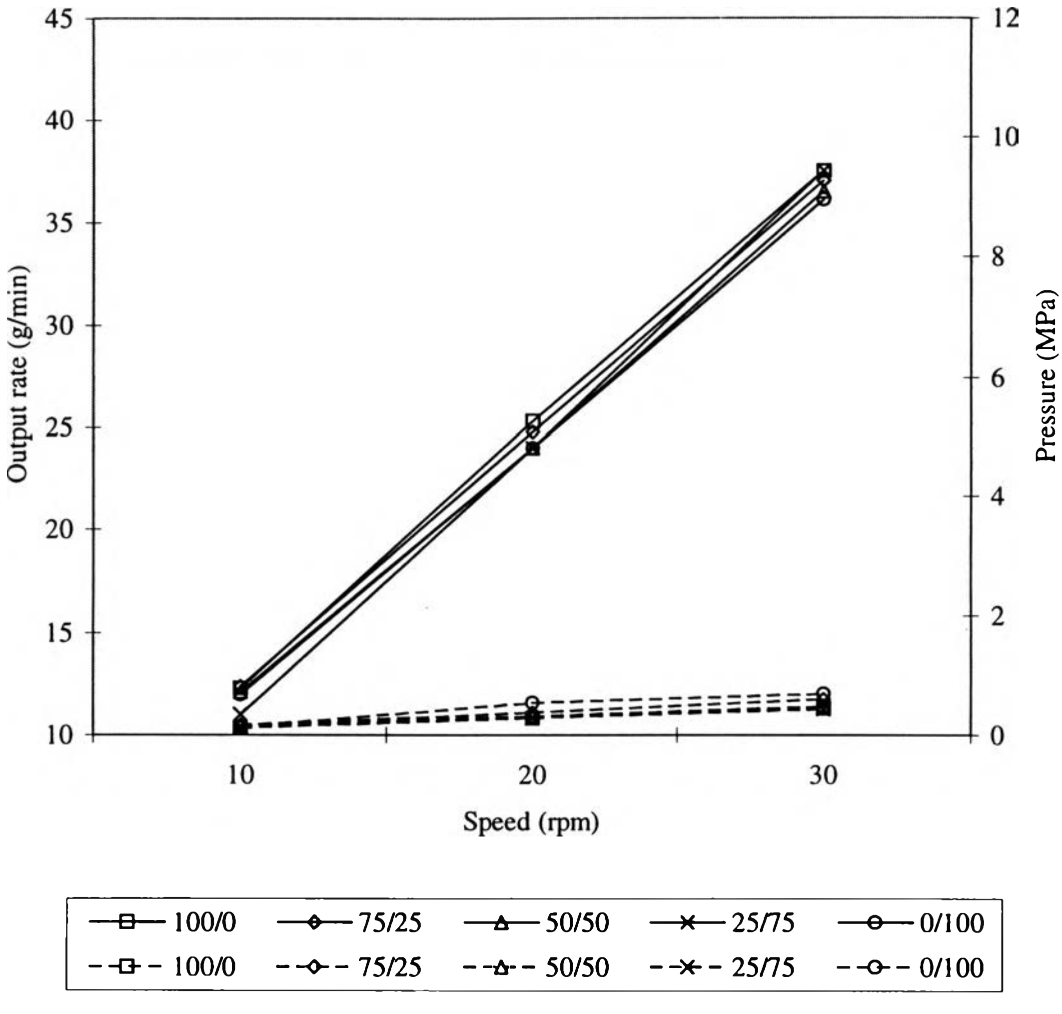


Figure 4.12 Plot of output rate (solid lines) and pressure (dash lines) against speed for reference sample (LD2/LD1) at the 4 mm diameter die.

I19337533X

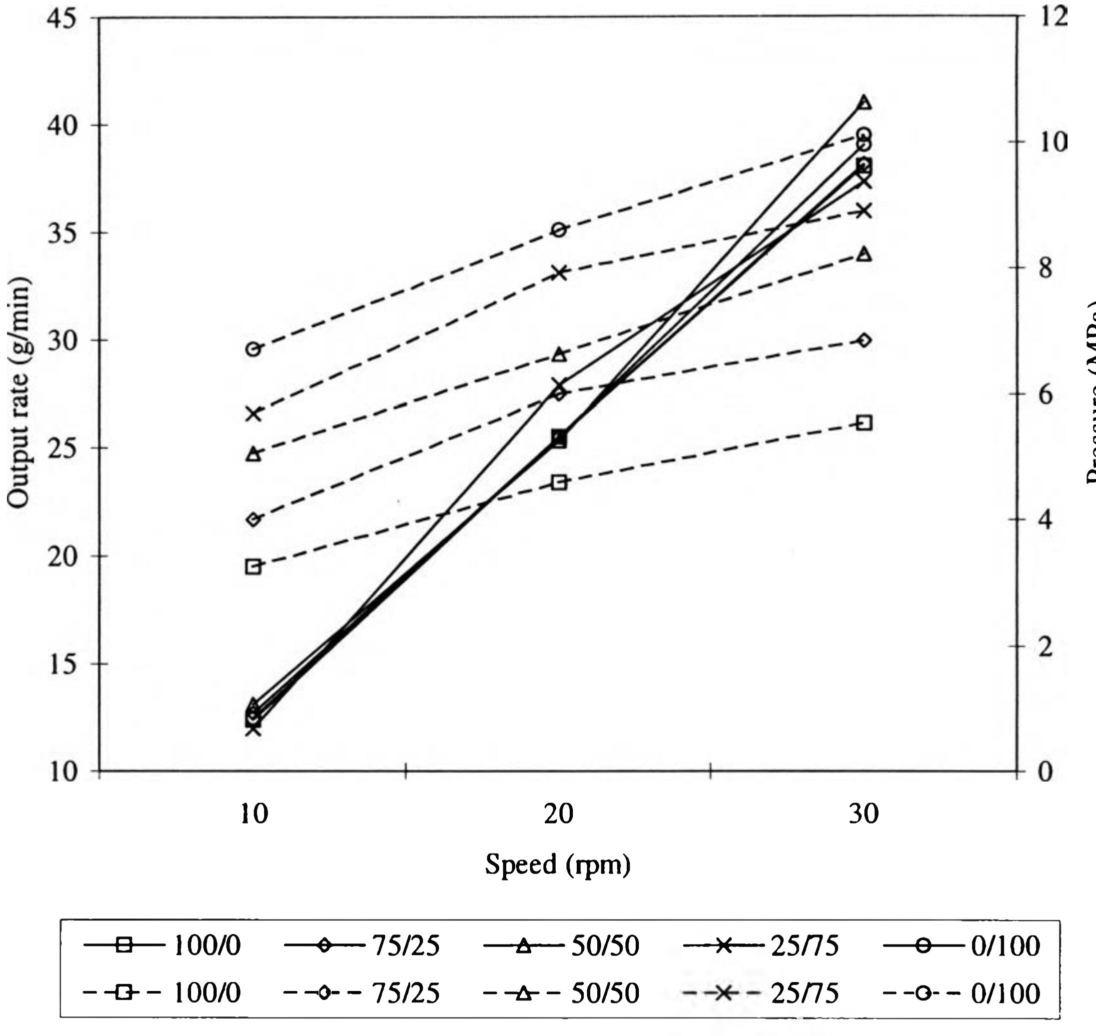


Figure 4.13 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 2 (LD3/LW2) at the 1 mm diameter die.

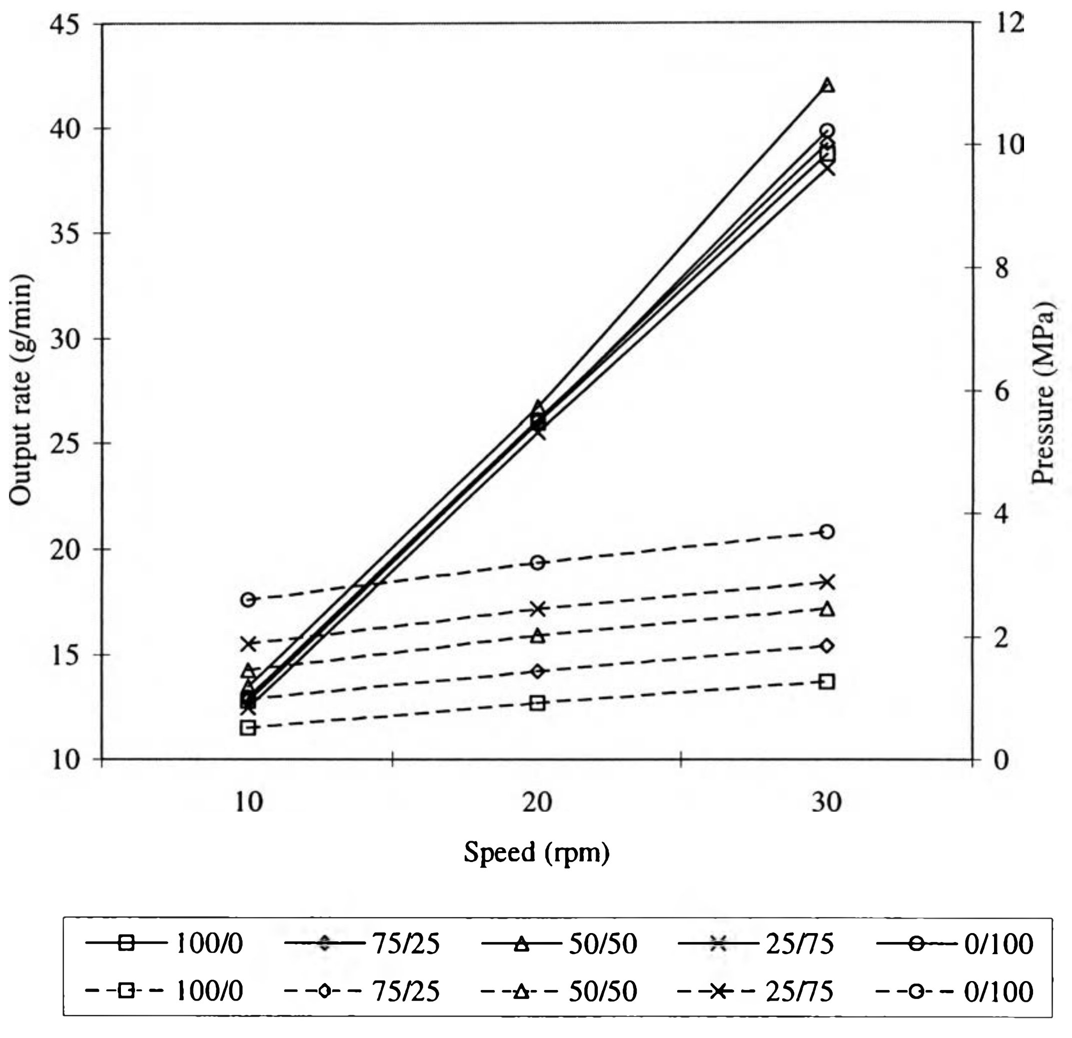


Figure 4.14 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 2 (LD3/LW2) at the 4 mm diameter die.

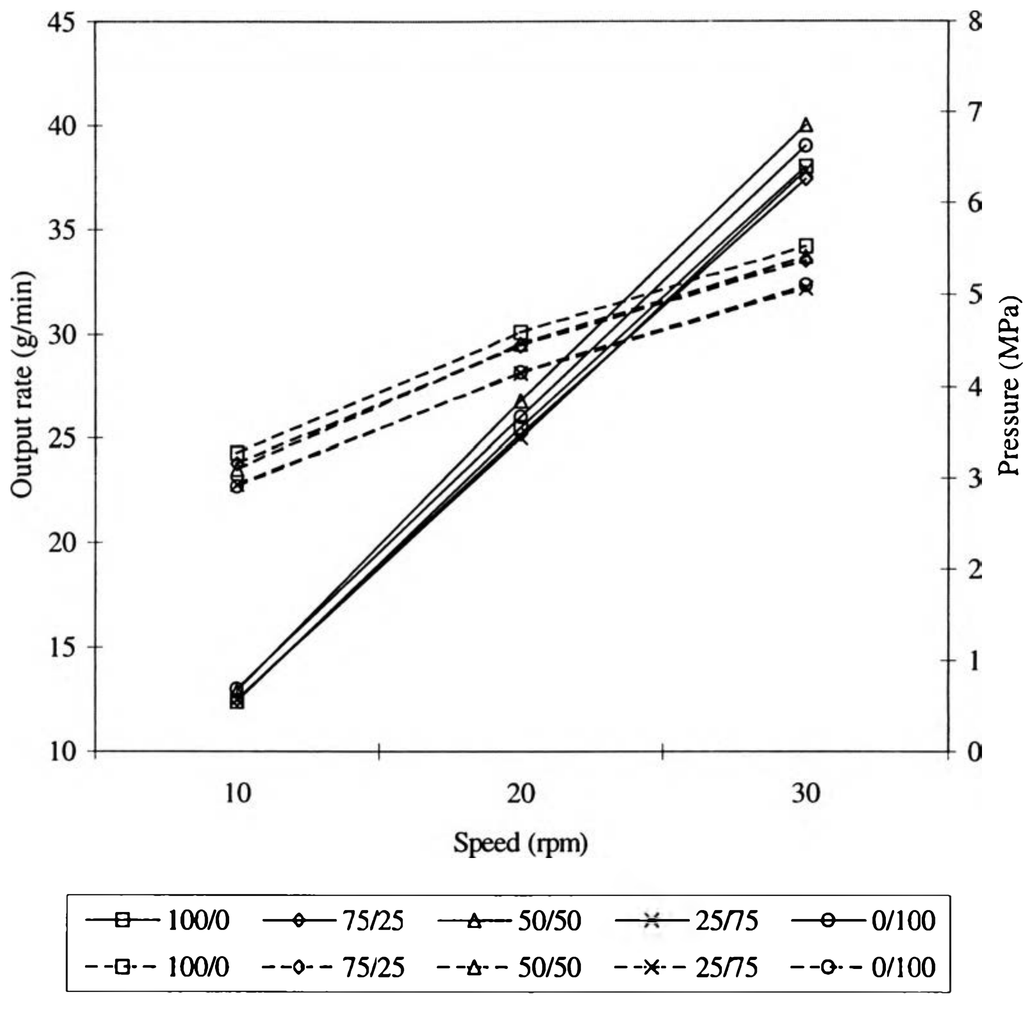


Figure 4.15 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 2 (LD3/LW1) at the 1 mm diameter die.

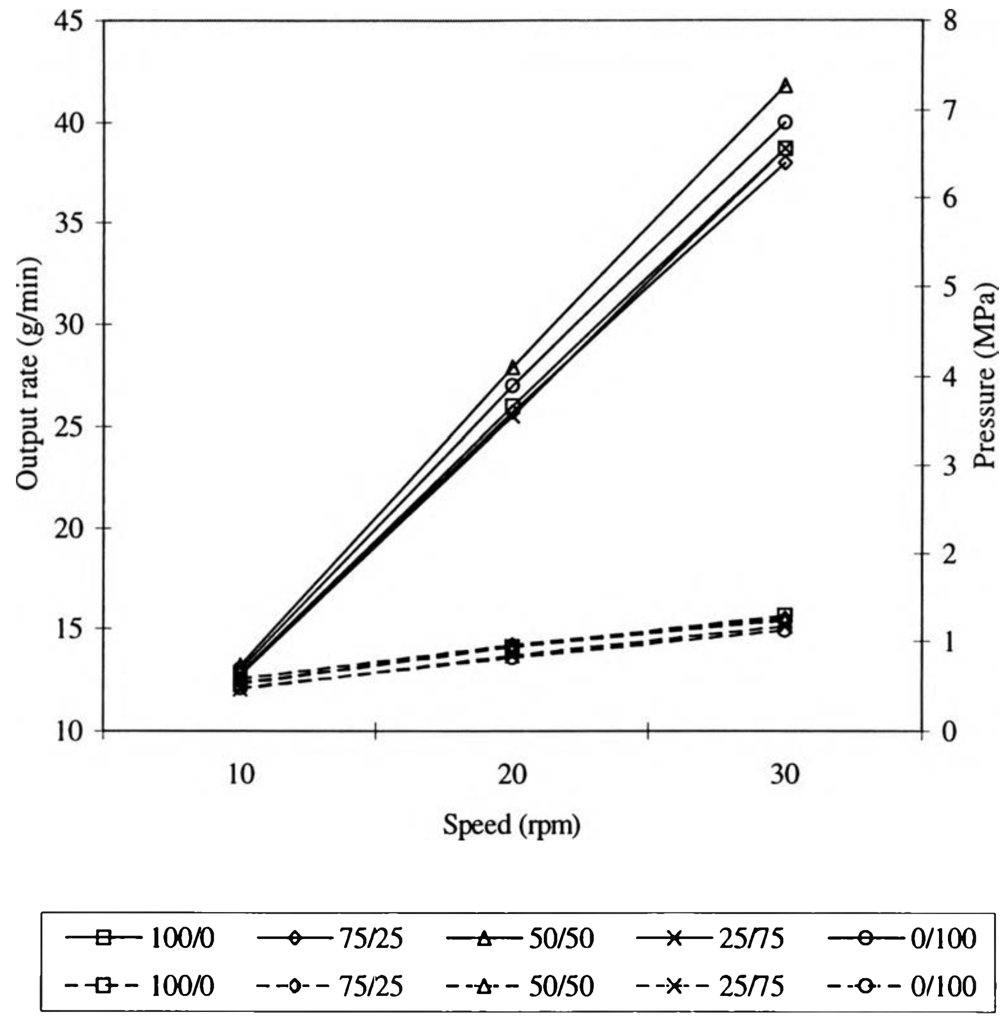


Figure 4.16 Plot of output rate (solid lines) and pressure (dash lines) against speed for blend system 2 (LD3/LW1) at the 4 mm diameter die.

4.3.3. Effect of Die & Screw Speed

By analysis on each composition ratio, it is found that increasing screw speed is more important to increase output rate than the changes of die geometry. Two round die having 1 and 4 mm diameter were used. Due to the using of same die shape (rod die), the results of the output rate were not much changed. However, the difference between rod and slit dies significantly resulted to change the output rate of LLDPE, LDPE and HDPE samples as studied by Utraki *et al.* (1985). The extrusion of sample with rod die showed quite higher amount of output rate than the extrusion with slit die. Because shear stress of all samples measuring by using the rod die had lesser value than that measuring by the slit die. It meant rod die has less friction that caused the ease of extruability.

The output of extruder is dependent mainly on screw speed (Wilczynski K., 1989). High Mw and broad MWD component result in increasing output rate. It infers that samples with high viscosity (i.e. high Mw) enhances pressure build-up largely to push polymer to come out. Based on the simplest screw characteristic equation for Newtonian fluid shown below, output rate is a function of screw geometry, screw speed, melt viscosity, pressure build-up, and die geometry.

$$Q = 1/2\pi^2 D^2 NH \sin\phi\cos\phi - \frac{\pi DH^3 \sin^2\phi\Delta P}{12\eta L} \tag{4.1}$$

Where Q = volumetric flow rate (m^3/min)

η = viscosity (Pa·s) θ = helix angle (degree)

D = diameter of screw (m) P = pressure (MPa)

N = screw speed (rpm), H = channel depth (m)

L = length of screw channel (m)

And for die characteristic

$$Q = \frac{\pi R^4}{8\eta L_d} P \qquad (4.2)$$

R = radius of round die (m)

L_d= length of die (m)

η = melt viscosity (Pa·s)

Since pressure consumption is associated with increasing viscosity of polymer, consequently the constant ratio of pressure and viscosity induces the consistent output rate at certain screw speed. As seen from the results, when sample with high Mw (HW1) or broad MWD (LW2) is used, the pressure rises up significantly as a result of high viscosity associated with high Mw polymer. Hence, throughput is mainly dependent on screw speed which shows in the first term of equation (4.1). When the die diameter is big, pressure build-up is small. However, the effect of big diameter on pressure does not alter the throughput significantly. In this case, die geometry has less influence on throughput than screw speed. This indicates the balance effect from the three die characteristic parameters in equation (4.2); i.e. bigger die diameter brings about low pressure drop and increased viscosity (because of low shear rate).

4.4. Study of Rheological Properties

Since the polymer is non-Newtonian fluid that the viscosity depends upon shear rate. The shear rate in the metering section of the screw can be obtain as follows

$$\dot{\gamma} = \frac{\pi D N \cos\theta}{H} \tag{4.3}$$

where D = diameter of screw (m)

N = screw speed (rpm)

H = channel depth (m) θ = helix angle (degree)

In this present work screw speed is changed from 10 to 30 rpm and channel depth is 1.9 mm. Hence, ranges of shear rate are varied from 5 to 15 1/sec. There are other parameters that affect on viscosity; i.e. temperature and molecular parameters. Due to the controlling in temperature, only molecular parameters are studied for their effects.

4.4.1. Effect of Mw

Figures 4.17 and 4.18 present the logarithmic plots of viscosity against shear rate for blend system 1. The results in Figure 4.17 show that, viscosity raises up largely with the increasing amount of HW1 compared with that of LW2/HW2 sample (Figure 4.18). Moreover, the changes of viscosity of LW1/HW1 and LW2/HW2 are significantly changed in comparison with reference sample (Figure 4.19). The reference shows insignificant dependence of blend composition on viscosity at any shear rate. The magnitude of viscosity of the reference blend is lower than those of the other two blends due to the relatively lower MW of its pure components. This confirms that viscosity strongly increases with high Mw portion. As seen in the research work of Dumoulin *et al.* (1984), melt viscosity increased with amount of UHMWPE matrix in system of medium density polyethylene (MDPE)/UHMWPE blends. The results indicated the increasing melt viscosity by using either roll mill or Banbury mixing in the blends.

4.4.2. Effect of MWD

Figures 4.20 and 4.21 are the results of effect of MWD on viscosity. Figure 4.20 is a plot of viscosity versus shear rate for pair with large difference in MWD. Viscosity is steadily increased with the addition of LW2 for LD3/LW2. Whereas, increasing the amount of LW1 shows opposite results for LD3/LW1 (Figure 4.21). This shows the similar trends with the results of melt flow index and mechanical properties. This is due to the LW2 containing of long chains while LW1 contains more amount of short chains. LW2 has higher viscosity and more entanglement than LW1.

It is obvious that difference of Mw results to enhance shear thinning effect more strongly than difference in MWD. Viscosity is dependent on amount of high Mw portion of blended polymer.

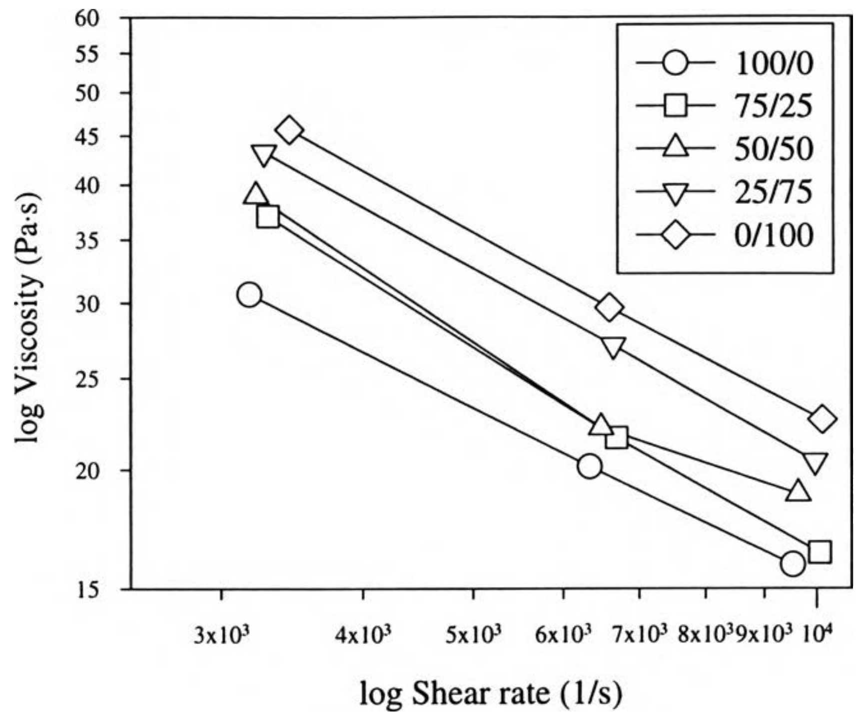


Figure 4.17 The log viscosity vs. log shear rate for blend system 1 (LW1/HW1)

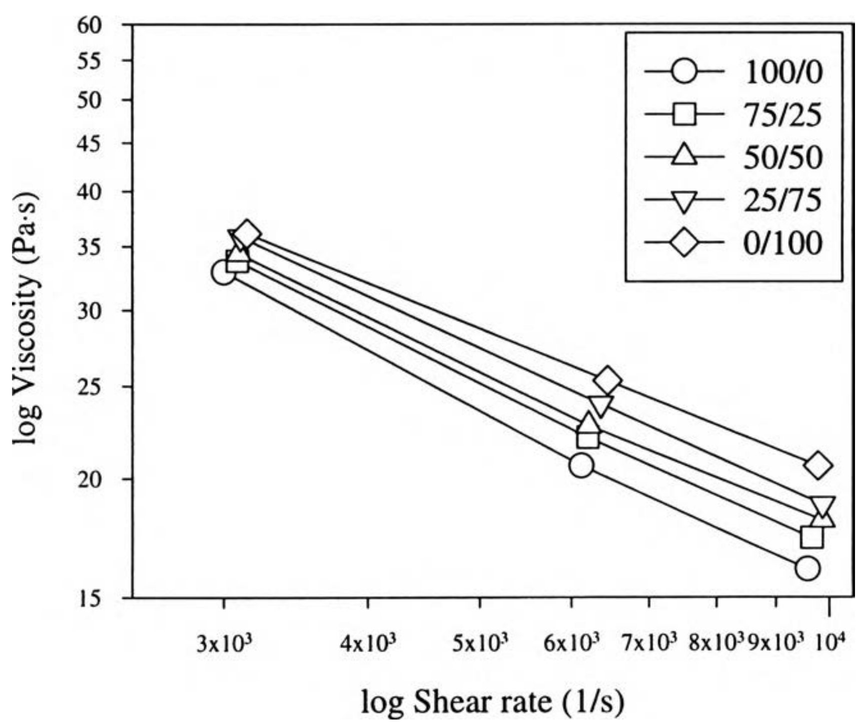


Figure 4.18 The log viscosity vs. log shear rate for blend system 1 (LW2/HW2).

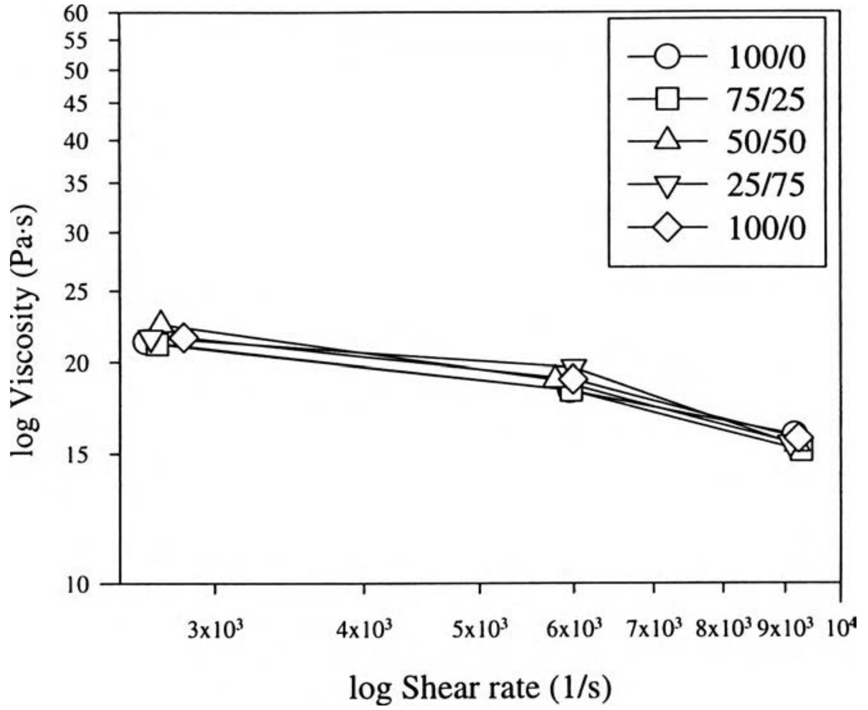


Figure 4.19 The log viscosity vs. log shear rate for reference sample (LD2/LD1).

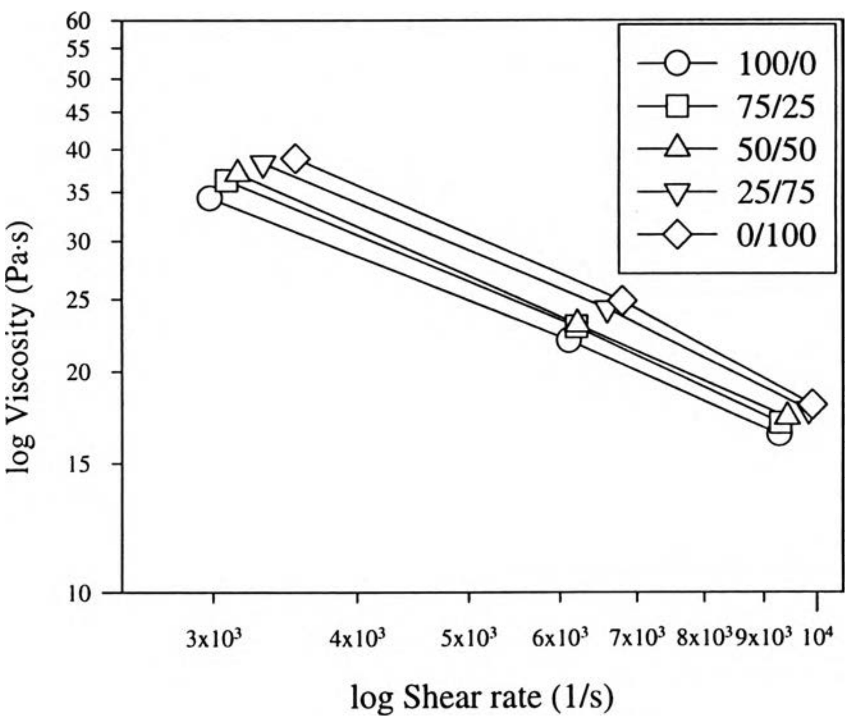


Figure 4.20 The log viscosity vs. log shear rate for blend system 2 (LD3/LW2).

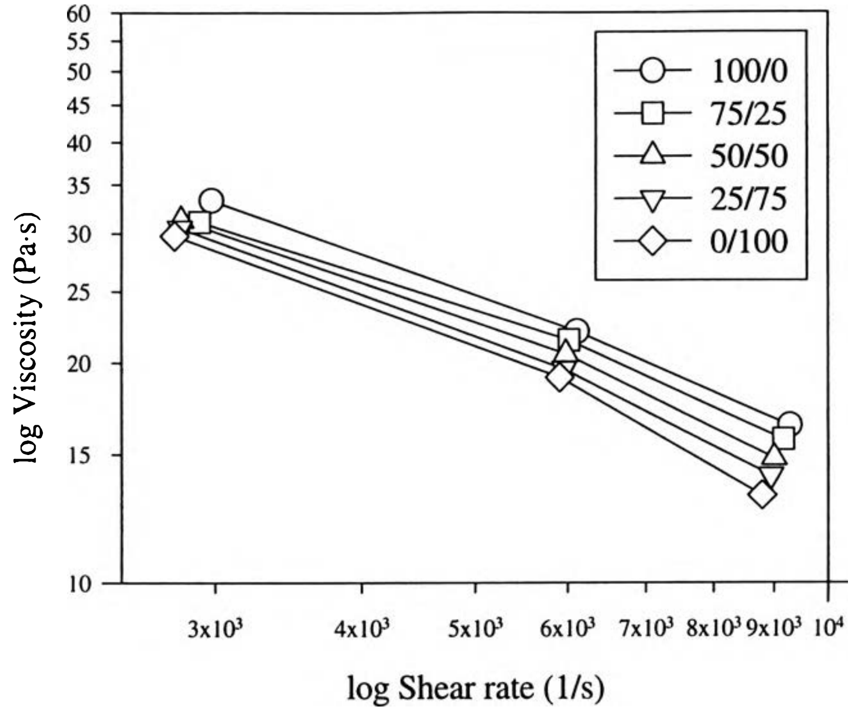


Figure 4.21 The log viscosity vs. log shear rate for blend system 2 (LD2/LW1).

4.5. Study on Melt Stability

In polymer processing, polymer melt flows through capillary or a die at low shear rates producing smooth extrudate. But when a volume flow rate exceeds a certain critical value the flow becomes increasingly unstable and the extrudate exhibits a variety of defects. The physical defects increase in severity as the extrudate rate is increased. Melt stability is a variation in shape along the length of the extrudate (Banjam, 1998).

There are many factors that influence the type and degrees of melt stability depending on melt temperature, die geometry, polymer structure and molecular parameters. Types of melt stability are classified based on the regularity and amplitude of the surface variations such as melt fracture, sharkskin, rippling, and helical defect.

In this experiment, at high screw speed and small diameter die used, significant results about the melt instability for all samples are obtained. Thus, the results of skin texture are reported only at screw speed 30 rpm from diameter 1 mm with L/D = 23. At this screw speed, it is corresponded to shear rate equal to 15 1/sec in the screw and greater than 9,000 1/sec (see in Appendix E) in the die which can be considered as the critical shear rate to cause melt instability.

4.5.1. Effect of MW

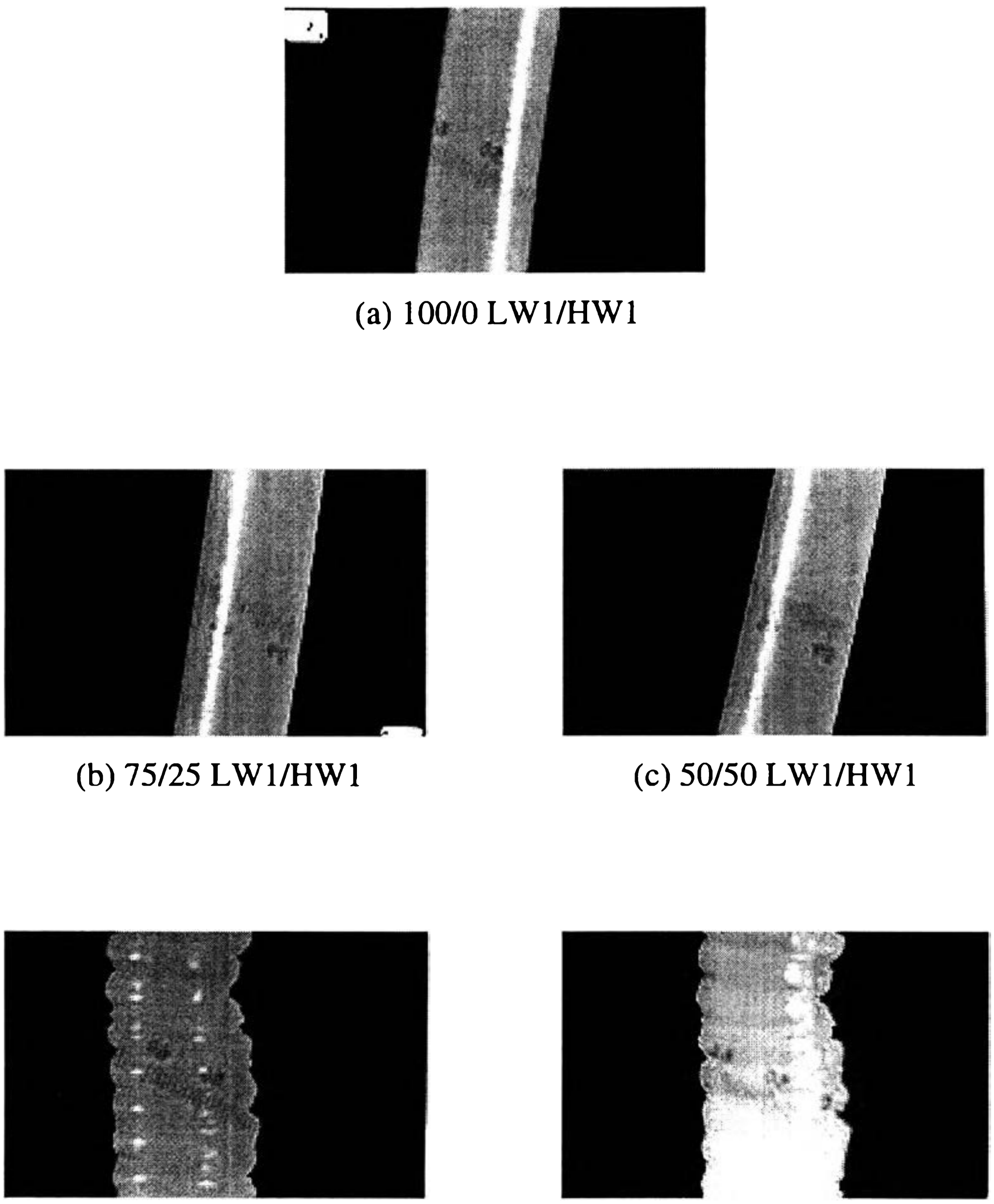
The photographs of skin defect for blend system 1 are shown in Figures 4.22 and 4.23. It is noted that sample with lower composition of HW1 or HW2 shows apparently smooth skin texture. At 75 and 100 % compositions of HW1 and 100 % HW2 reveal increasing roughening of the surface of the extrudate. The high Mw elements are fractured easier than the low one. This can be explained that polymer melt of high Mw behaves more elastic due to high entanglement; i.e. the chains are not permanently realigned themselves and destroyed while subjected to stretching in the die. The long molecules can resist high shear stress and need longer relaxation time. However, short time scale deformation in the die does not allow this elastic distortion to completely release. Therefore, when the extrudate of high Mw polymer leaves the die, it becomes curls.

Figure 4.23 presents the skin texture of sample with small difference in Mw, LW2/HW2 blends. Pure LW2 and the blends show smooth surface but pure HW2 shows melt fracture. The research work of Banjam concluded that the stability of extrudate depends on Mw. High Mw sample induced more roughness of its surface.

4.5.2. Effect of MWD

The results show roughness appearance at screw speed 30 rpm and 1 mm diameter die with L/D = 15 (Figure 4.24). Meanwhile, using L/D = 23 die for samples in blend system 2 (Figure 4.25) shows the smooth skin texture. However, the smoothness appearances also occur with the die L/D = 23 for the pair with small difference in MWD (Figure 4.26). Since LD3, LW1 and LW2 are relatively low Mw, the roughness at low L/D ratio is affected by the retention time and the narrow MWD element. LD3 having narrow MWD or more similar chain size shows less ability to withstand melt fracture but this effect is relived if there is sufficient time allowed for relaxation, e.g. by increasing die L/D ratio. It can be concluded that the increasing L/D decreases the severity of extrudate distortions.

As reported by Banjam, extrudate stability depends on die geometry in that long die resulted to smooth skin because of long time for the molecules to relax from the high shear stress imposed on themselves.



(a) 100/0 LW1/HW1

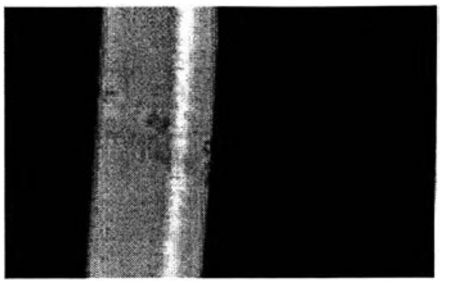
(b) 75/25 LW1/HW1

(c) 50/50 LW1/HW1

(d) 25/75 LW1/HW1

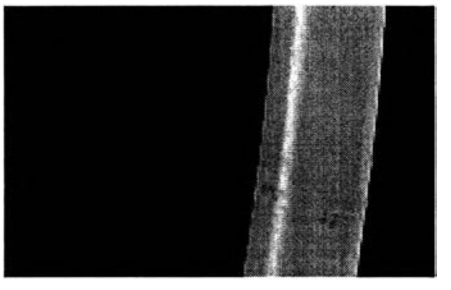
(e) 0/100 LW1/HW1

Figure 4.22 The photographs of skin surface for blend system 1 (LW1/HW1) at die 23 L/D.

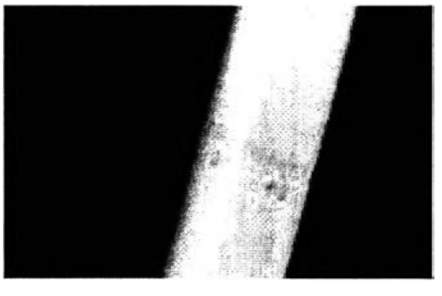


(a) 100/0 LW2/HW2

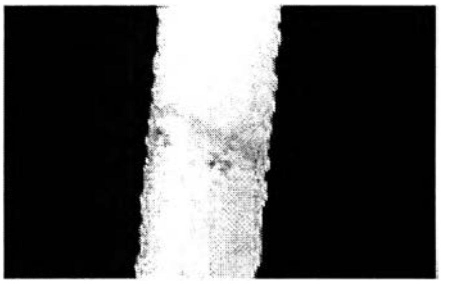
(b) 75/25 LW2/HW2



(c) 50/50 LW2/HW2

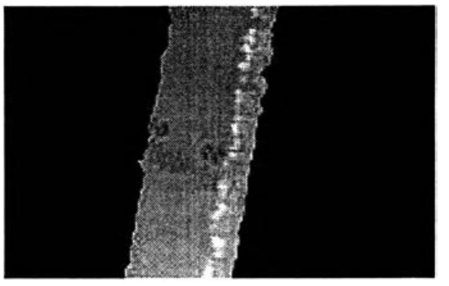


(d) 25/75 LW2/HW2

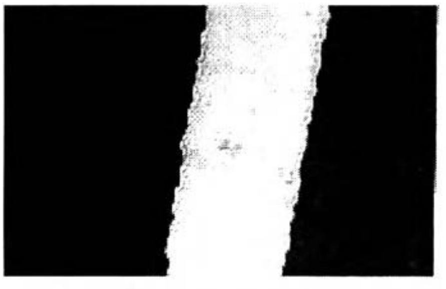


(e) 0/100 LW2/HW2

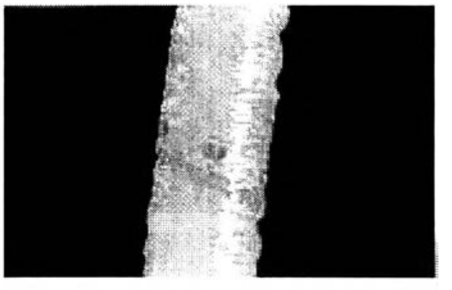
Figure 4.23 The photographs of skin surface for blend system 1 (LW2/HW2) at die 23 L/D.



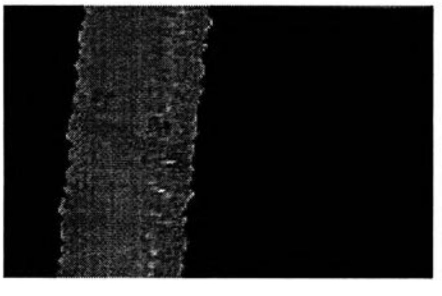
(a) 100/0 LD3/LW2



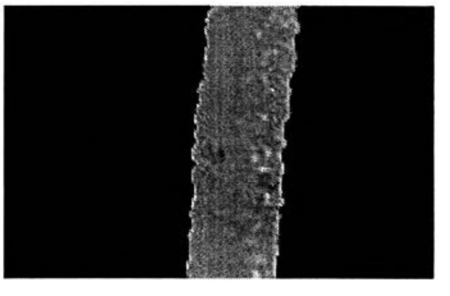
(b) 75/25 LD3/LW2



(c) 50/50 LD3/LW2

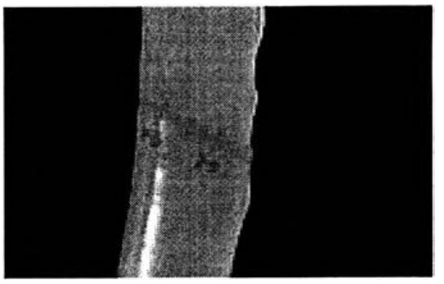


(d) 25/75 LD3/LW2

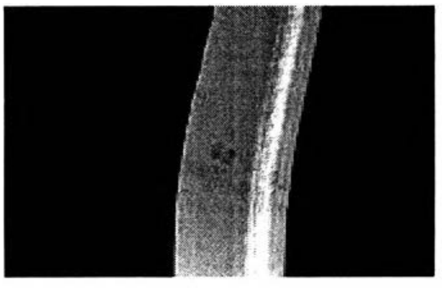


(e) 0/100 LD3/LW2

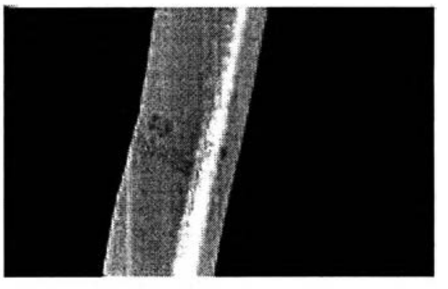
Figure 4.24 The photographs of skin surface for blend system 2 (LD3/LW2) at die 15 L/D.



(a) 100/0 LD3/LW2



(b) 75/25 LD3/LW2

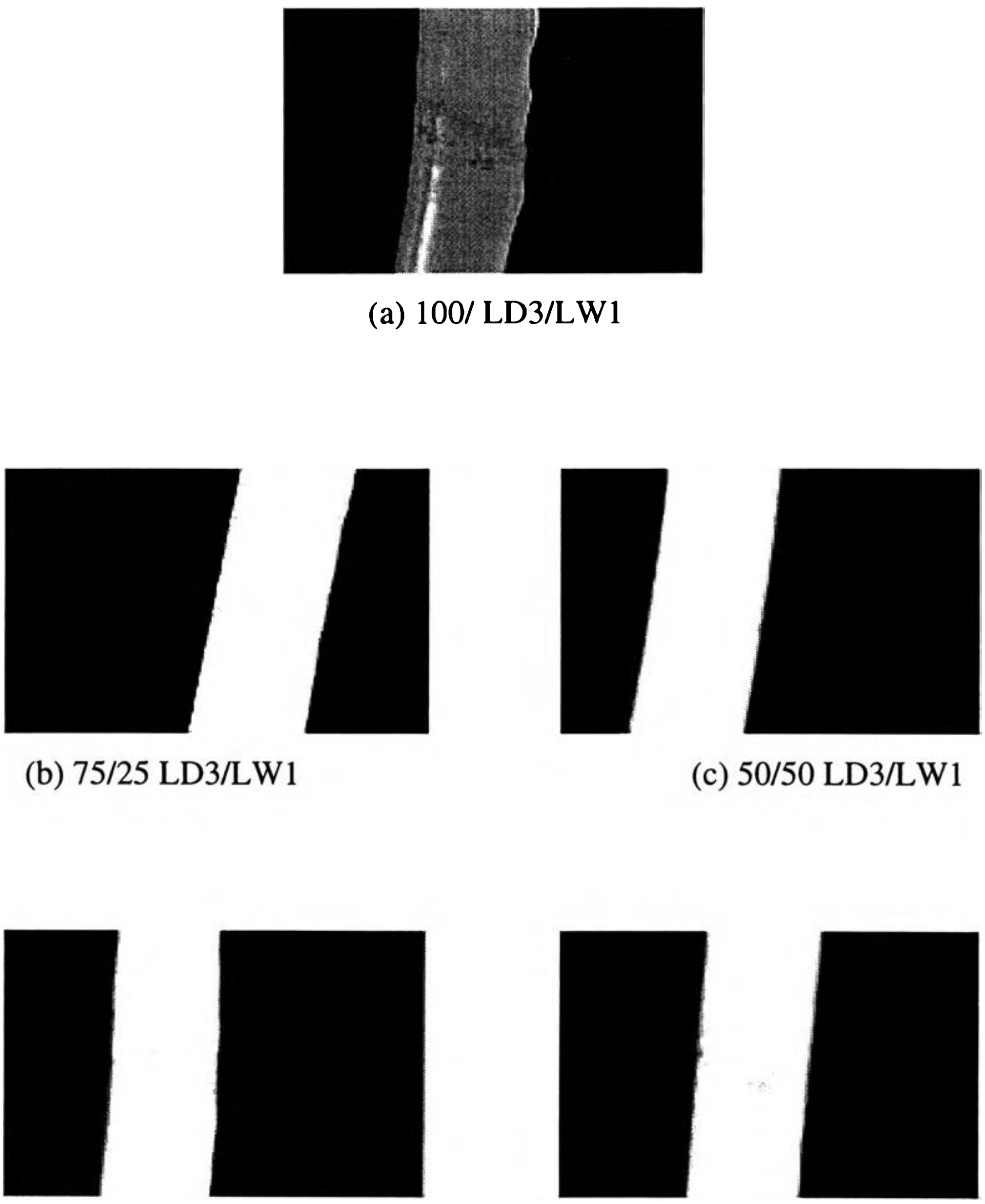


(c) 50/50 LD3/LW2

(d) 25/75 LD3/LW2

(e) 0/100 LD3/LW2

Figure 4.25 The photographs of skin surface for blend system 2 (LD3/LW2) at die 23 L/D.



(a) 100/ LD3/LW1

(b) 75/25 LD3/LW1

(c) 50/50 LD3/LW1

(d) 25/75 LD3/LW1

(e) 0/100 LD3/LW1

Figure 4.26 The photographs of skin surface for blend system 2 (LD3/LW1) at die 23 L/D.