

CHAPTER III

RESULTS AND DISCUSSIONS

After reprocessing, virgin HDPE and blends of virgin/post-consumer HDPE were investigated by the tests mentioned in chapter II to study the effects of reprocessing and the amount of post-consumer HDPE on processability, rheology, thermal and mechanical properties.

3.1 Properties of unprocessed virgin HDPE and post-consumer HDPE

Table 3.1 Properties of unprocessed virgin HDPE and post-consumer HDPE

Properties	Unit	Virgin HDPE	Post-consumer HDPE
1. MFI	g / 10 min	0.2804	0.3415
2. Melt Temp.	°C	139.22	133.42
3. Heat of fusion	J / g	160.50	161.6
4. % Crystallinity	%	55.73	56.11

Table 3.1 shows a comparison between properties of virgin HDPE and post-consumer HDPE before reprocessing. The data in table 3.1 point out that virgin HDPE had higher molecular weight than post-consumer HDPE, in agreement with the melt flow index (MFI) result. The MFI is inversely proportional to the molecular weight of polymer. In addition, the percentage crystallinity also is related to the molecular weight of polymer. The percent crystallinities in this table were calculated from the heat of fusion using the

crystallinities in this table were calculated from the heat of fusion using the equation in appendix . For the higher molecular weight of polyethylene, the longer polymer chains can not pack together well so the percentage of crystallinity reduces. In linear polyethylene, the melting temperature is determined by molecular weight. The decrease in molecular weight is accompanied by a decrease in the melting temperature. [Mark, 1986] Therefore, the melting temperature of virgin HDPE was higher than that of post-consumer HDPE as shown in the table above.

A comparison between the viscosity of virgin HDPE and post-consumer HDPE as a function of various shear rates is presented in Figure 3.1. HDPE is a non-Newtonian fluid and the viscosity data are confined to the pseudoplastic region. The viscosity reduces as increasing the shear rate since the polymer chains begin to untangle and align in the shear field, reducing the resistance to slip past one another. The high shear rate leads to mechanical degradation which results in breaking of main chain bonds or chain scission. Consequently, the viscosity at high shear rate is very low.

As seen in Figure 3.1, it was indicated that before reprocessing the melt viscosity of virgin HDPE was higher than that of post-consumer HDPE at shear rates of extrusion range $100 - 1000 \text{ sec.}^{-1}$. The melt viscosity is directly related to the molecular weight . These results coincided with the MFI data from the above table because low MFI and high viscosity correspond to high molecular weight.

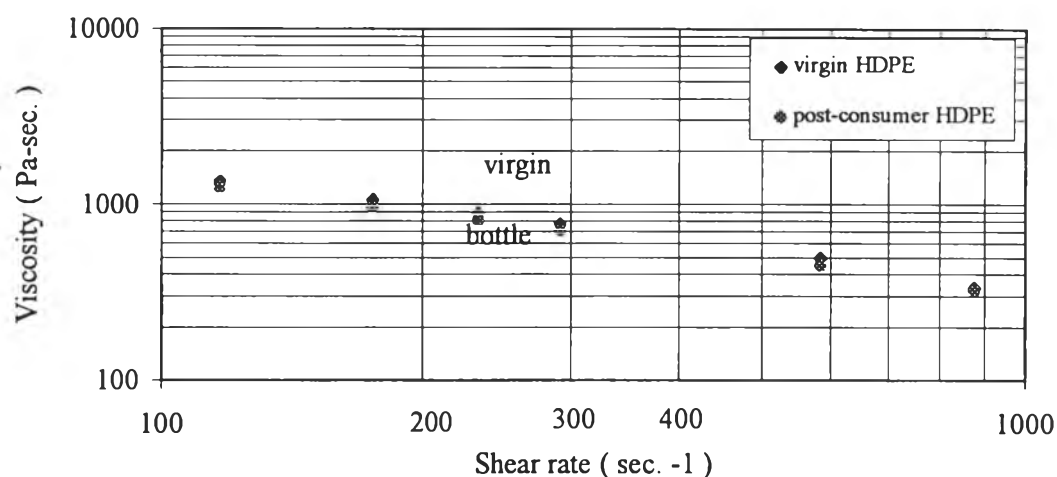


Figure 3.1 Viscosity of unprocessed virgin HDPE and post-consumer HDPE at shear rates of 100 - 1000 sec.⁻¹

3.2 Reprocessing of virgin HDPE and post-consumer HDPE

3.2.1 Processability

Processability is the ease or difficulty with which a plastic material can be processed into the desired part. The melt pressure of reprocessing virgin HDPE and post-consumer HDPE is shown in Figure 3.2. The melt pressure at die is the pressure on melt measured by a pressure transducer positioned close to the die. Acierno and Maio (1995) studied the reprocessability of extruded polymer using analysis of melt pressure during processing. They found that the higher viscosity was due to the more compact system that allowed for the better packing of material in the rotating screw of the extruder.

For reprocessing of virgin HDPE, the melt pressure seemed to be constant from the first pass to the third pass and from the sixth pass to the tenth pass. There was a decrease of melt pressure from the third pass to the

sixth pass. The melt pressure decreased by 15 % from the first pass to the tenth pass. This result indicated the better processability or the less compaction of polymer melt in screw. Therefore, the melt viscosity tended to decrease with an increasing number of passes.

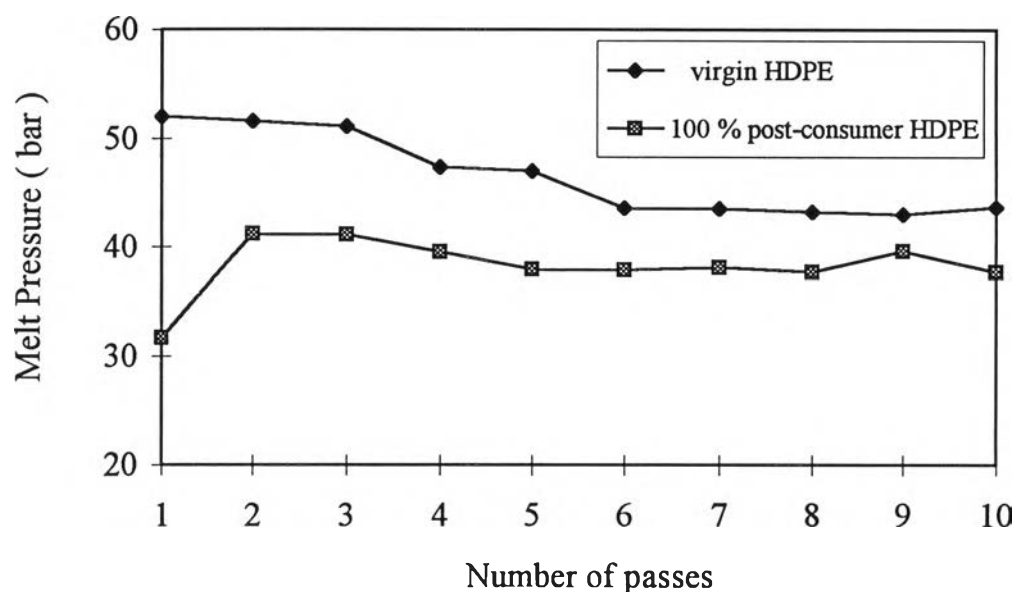


Figure 3.2 Melt pressure of virgin HDPE and the 100 % post-consumer HDPE during reprocessing.

For reprocessing of the 100 % post-consumer HDPE, Figure 3.2 shows a slight decrease in the melt pressure with increasing the number of passes. The lower melt pressure of the first pass will be discussed later. After the second pass, there appeared to be almost no change in melt pressure. Actually, the melt pressure decreased by 7 % from the second pass to the tenth pass. This reveals less compaction during reprocessing. As seen in Figure 3.2, virgin HDPE has a higher melt pressure for all passes. This result pointed out more compaction of polymer melt due to the higher melt viscosity of virgin HDPE and therefore a higher molecular weight compared to the 100 % post-consumer HDPE.

Doyan, et al. (1994) reported that the differences in size and shape of material caused the difference in the pressure drop across the die. The transport characteristics of particulate solids were quite sensitive to the particle shape. In Figure 3.2, the melt pressure of virgin HDPE was higher than that of the 100 % post-consumer HDPE for 10 passes, especially the first pass. Also the melt pressure of the 100 % post-consumer HDPE of the first pass was significantly lower than that at the second pass. The starting form of virgin HDPE from supplier and HDPE produced from our laboratory were pellets while post-consumer HDPE was in form of scrap with uncertain shapes. Consequently, it was difficult to control the mass flow rate of these materials to have the same values.

3.2.2 Viscosity

In Figure 3.3, the viscosity at a shear rate of 291.8 sec^{-1} of reprocessing of virgin HDPE and the 100 % post-consumer HDPE is presented as a function of the number of passes. These results showed the higher viscosity of virgin HDPE after reprocessing compared with the 100 % post-consumer HDPE and a decrease by 6 % in viscosity of virgin HDPE from the first pass to the tenth pass and by 1.3 % for each pass. These results coincided with the melt pressure results. Virgin HDPE after reprocessing showed the higher values of both viscosity and melt pressure. The 100 % post-consumer HDPE showed the same trend in viscosity as virgin HDPE during reprocessing. The melt pressure of the 100 % post-consumer HDPE decreased by 6.7 % from the first pass to the tenth pass and by 1.1 % for each pass.

The melt viscosity at a given temperature is a measure of the rate at which chains can move relative to each other. It was reported in many

articles [Doyan et al., 1994, Lavieri, 1994 and Mitterofer, 1980] that chain scission and crosslinking occurred simultaneously during the processing of HDPE. The mechanism depended on the temperature, oxygen availability and polymer type. There was some previous work regarding degradation of HDPE during processing.

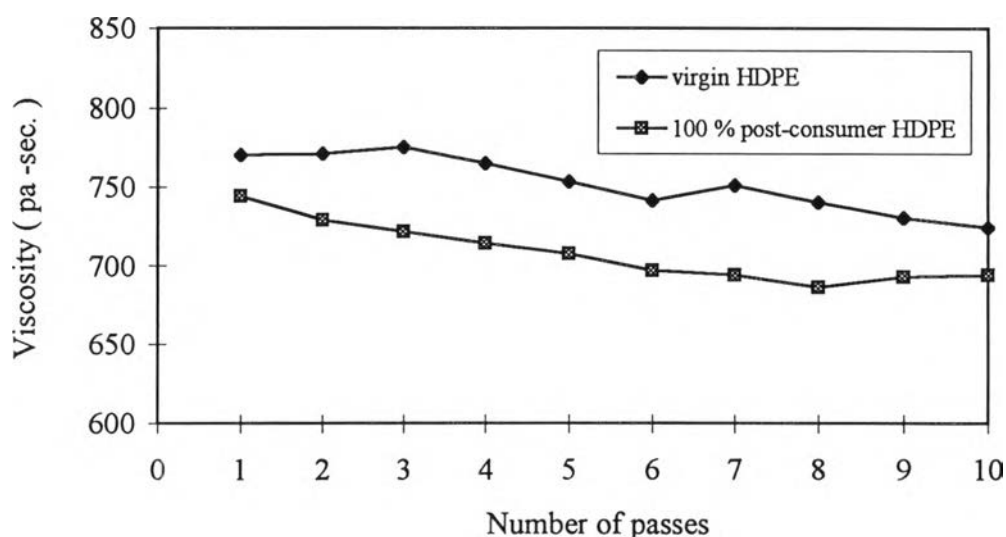


Figure 3.3 Viscosity at shear rate of 291.8 sec.^{-1} of virgin HDPE and the 100 % post-consumer HDPE during reprocessing.

As seen in Figure 3.3, both types of HDPE showed a decrease in viscosity with the number of passes. The decrease in viscosity might be the result of chain scission during reprocessing. These results will be discussed in more detail and compared with the MFI results in the next section.

3.2.3 Melt Flow Index (MFI)

The MFI ($190^\circ \text{C} / 2.16 \text{ kg}$) of virgin HDPE and the 100 % post-consumer HDPE reprocessed for 10 passes is presented in Figure 3.4. Both virgin HDPE and the 100 % post-consumer HDPE showed

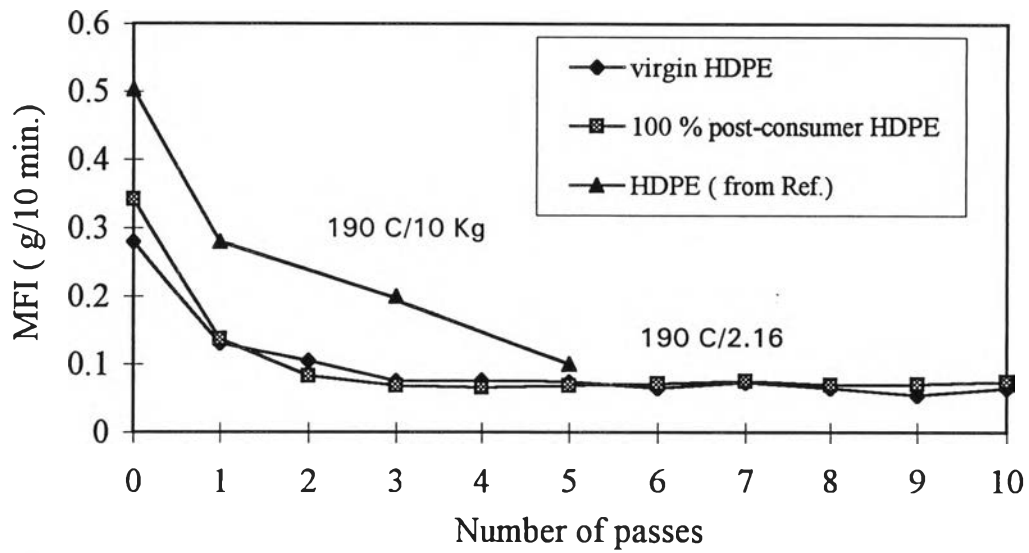


Figure 3.4 MFI of virgin HDPE and the 100 % post-consumer HDPE during reprocessing compared to MFI from Hinsken's work.

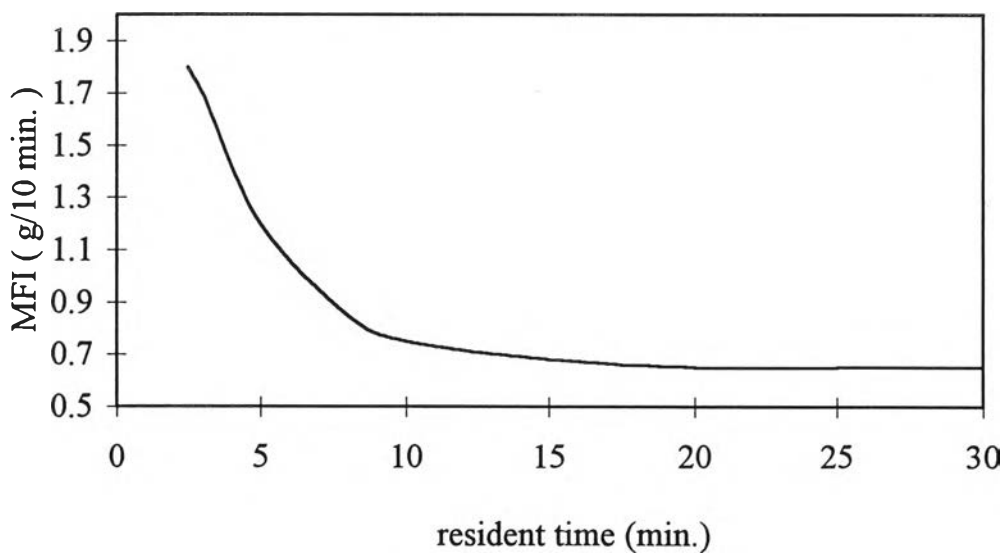


Figure 3.5 MFI of HDPE without any stabilizer from Mitterhofer's work.

approximately the same MFI versus the number of passes. The MFI for both types of HDPE decreased remarkably after the first pass to the third pass and after the third pass the MFI seemed to be constant in range of 0.05 - 0.07 g/10 min. As seen from this MFI result, the molecular weight of both kind of HDPE increased significantly after only one extrusion pass and then appeared to decrease gradually with an increasing number of passes. Hinsken et al.(1991) studied the degradation of polyolefins during melt processing. They found that MFI (190 °C/10 kg) of HDPE decreased with increasing number of passes. So during multiple passes the average molecular weight increased. The MFI results from their work is also exhibited in Figure 3.4. From FTIR spectra, MFI and GPC results, they concluded that chain branching and crosslinking leading to an increase in molecular weight was favored over thermo-oxidative or thermo-mechanical induced chain scission. Dontula et al. (1995) processed HDPE in the 220 - 280 °C temperature range using a corotating intermeshing twin screw extruder. They found that HDPE crosslinked at this temperature range.

Futhermore, Mitterhofer (1980) demonstrated processing stabilization of polyolefins. He measured the crosslinking of HDPE melt and its retardation by stabilizers. It was based on the measurement of MFI change during the polymer's prolonged residence time in a melt indexer apparatus. The MFI result of HDPE without any stabilizer is shown in Figure 3.5. The MFI curve from his work was similar to our work. In Figure 3.5, the MFI dropped drastically due to crosslinking. From those previous works, the MFI result in Figure 3.4 suggests that chain branching or crosslinking might occur during reprocessing in a twin screw extruder. Degradation of HDPE during reprocessing may be initiated by the high temperature used for the process and shear force applied by rotating the screw in the extruder. Free radicals may originate from primary bond breaking reactions. Radicals from such

reactions may combine together to give crosslinks or branching, resulting in an increase in molecular weight. On the other hand, disproportionation can occur and then reduce the molecular weight of material. In this case, the disproportionation reaction seemed to be less important.

The MFI results in Figure 3.4 are consistent with the viscosity results of virgin HDPE and the 100 % post-consumer HDPE shown in Figure 3.3. Both MFI and viscosity appeared to decrease with increasing number of passes. However, MFI is inversely related to the viscosity. There were a few reasons for this controversy. First, MFI is a single point measurement at one set of temperature and geometric conditions. The flow characteristics of polymer at very low shear rate in the melt indexer were different from that at higher shear rates for extrusion ($100 - 1000 \text{ sec.}^{-1}$) in the capillary rheometer. Second, long chain branching has an effect on the rheological measurement. For similar molecular weights, the viscosity at low shear rates of branched polymers may be greater than that of linear polymers. At high shear rates, branched polymers in all cases have lower viscosity than linear polymer because branched molecules would be more compact and tend to entangle less with other molecules. [Dealy, 1990] In Figure 3.3, the viscosity decreased very slightly with an increasing number of passes so the molecular weight seemed to have insignificant change. These might be the reasons for the disagreement between MFI and viscosity. Virgin HDPE and post-consumer HDPE were probably linear molecules or molecules with short chain branching but after reprocessing under certain conditions, crosslinking, chain branching, an increasing in the number of branches might tend to occur. In case of polyethylene, the greater the branching at constant molecular weight the lower the melt viscosity. [Rosen, 1993]

Doyon, et al. (1994) observed that the apparent viscosity decrease during extrusion was caused by alignment of polymeric chains or disentanglement and not by chain scission. They found that during extrusion of LDPE, disentanglement of molecular chains occurred. It was explained by an alignment of the chains in the direction of shear. For that disagreement, a possible explanation is that the shear force from the rotating of twin screw caused an alignment of polymer chains. When the shear was released, the polymer chains relaxed and tended to go back to the previous configuration. Since the polymer melt was quenched as soon as it came out of the die, it was impossible for the polymer to relax. The second extrusion pass gave more alignment to the chains so less disentanglement occurred.

3.2.4 Thermal Analysis

From DSC thermograms, the melting temperature (T_M) and heat of fusion were determined. The melting temperature indicates the density of the chain packing, while the area under the melting peak is the heat of fusion which can be converted to the percentage of crystallinity, as shown in the appendix . Figure 3.6 showed the melting temperature of virgin HDPE and the 100 % post-consumer HDPE as a function of the number of passes. After reprocessing the melting temperature of virgin HDPE was lower than that of the 100 % post-consumer HDPE. For both types of HDPE, the melting temperature tended to decrease slightly with the number of passes. Actually, the melting temperature varied in range of 135 - 140°C for both cases which was a very small deviation. Thus, it could be concluded that no change in the melting temperature occurred during reprocessing. Sperati et al. (1953) studied the effect of chain branching and molecular weight of polyethylene on physical properties and showed quantitative relationships between physical

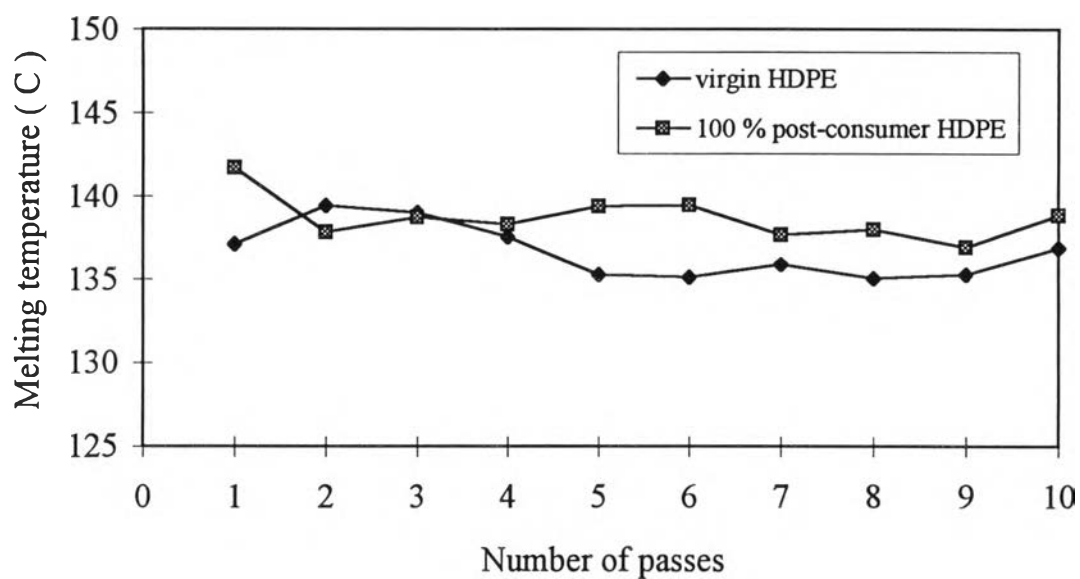


Figure 3.6 Melting temperature of virgin HDPE and the 100 % post-consumer HDPE during reprocessing.

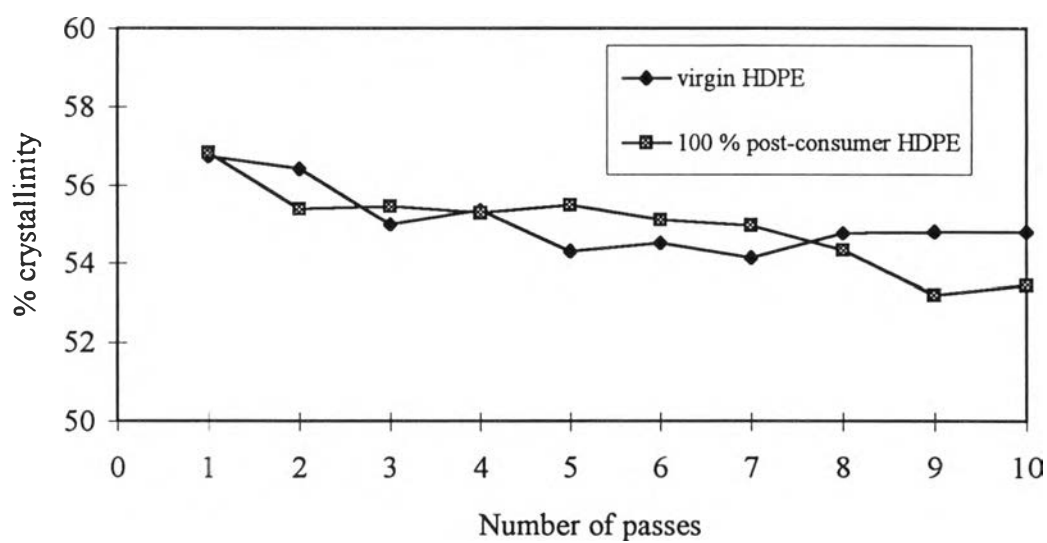


Figure 3.7 % Crystallinity of virgin HDPE and the 100 % post-consumer HDPE during reprocessing.

properties. They pointed out that the melting point was controlled primarily by the effect of short chain branching on crystallinity. Samples with a higher percentage of crystallinity showed higher melting points. From Figure 3.6, it could be seen that the melting temperature of virgin HDPE was lower than that of the 100 % post-consumer HDPE during reprocessing. This result went along with the crystallinity result shown in Figure 3.7.

The percentage of crystallinity of virgin HDPE and the 100 % post-consumer HDPE after reprocessing is displayed as a function of the number of passes in Figure 3.7. There was a slight decrease in the percentage of crystallinity for both cases with an increasing number of passes. The number of branches or the degree of crosslinking probably increased with an increasing number of passes.

3.2.5 Environmental Stress Cracking Resistance (ESCR)

ESCR is used to describe the cracking that occurs in polymeric material under conditions of heat, applied stress and contact with an incompatible substance. The incompatible substance will exert forces at the molecular level leading to either chain scission or molecular disentanglement. Table 3.2 shows the percentage of failure of virgin HDPE and the 100 % post-consumer HDPE cracked under controlled temperature and solvent after reprocessing. After 72 hours, virgin HDPE samples cracked after 8 passes of reprocessing under ethanol while the 100 % post-consumer HDPE samples cracked after 10 passes. Under glacial acetic acid condition, virgin HDPE samples after 4 passes and the 100 % post-consumer HDPE of all passes, except the second pass were cracked. It was found from both conditions that the percentage of failure increased with increasing number of passes.

Zahavich et al. (1995) studied changes in ESCR of HDPE with multiple extrusion passes. The ESCR property was determined under a 100 % IGAPEL CO-630 solution at 50 ° C. They observed that virgin HDPE changes dramatically over 4 passes while the post-consumer HDPE showed the low ESCR property and no change. Clearly, over a short number of extrusion passes a virgin HDPE lost considerable resistance to stress cracking in an aggressive medium. They explained that some minimum ESCR may have been reached by the constituents in the post-consumer HDPE and the virgin HDPE was approaching that value after a number of passes.

The factors that mainly affect ESCR are molecular weight and molecular weight distribution (MWD). Increasing molecular weight or decreasing MWD leads to an increase in ESCR or better resistance. Pattanakul et al. (1991) suggested that chain scission, crosslinking and chain branching might occur simultaneously during processing. Some molecules might degrade, resulting in a decrease in molecular weight, while other molecules would increase in molecular weight. If such a process appeared, the number average molecular weight (\overline{M}_n) would slightly decrease and the weight average molecular weight (\overline{M}_w) would increase since the weight average molecular weight depends on the large molecules. Thus, MWD would also increase accordingly. The data in table 3.2 indicated that ESCR of virgin HDPE during reprocessing was higher than that of the 100 % post-consumer HDPE because of higher molecular weight of virgin HDPE. For both materials, ESCR decreased with an increasing number of passes. It might be due to the broader MWD with the number of passes. If chain scission, crosslinking and chain branching occurred during processing, M_w would increase but M_n would probably increase as well. Therefore, MWD might not be broader during reprocessing. MWD determined by GPC was necessary for evaluating these results.

Table 3.2 % Failure by cracking of reprocessed virgin HDPE and the 100 % post-consumer HDPE under ethanol and glacial acetic acid

Virgin HDPE

No. of passes	ethanol		glacial acetic acid	
	48 hr.	72 hr.	48 hr.	72 hr.
VIRGIN	-	-	-	-
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	20%	20%
5	-	-	20%	40%
6	-	-	-	60%
7	-	-	20%	40%
8	20%	80%	60%	60%
9	20%	60%	80%	100%
10	-	40%	100%	100%

100 % post-consumer HDPE

No. of passes	ethanol		glacial acetic acid	
	48 hr.	72 hr.	48 hr.	72 hr.
1	-	20%	-	20%
2	-	20%	-	-
3	-	60%	20%	20%
4	-	20%	20%	100%
5	20%	40%	80%	100%
6	20%	40%	100%	100%
7	40%	80%	40%	100%
8	100%	100%	100%	100%
9	100%	100%	60%	100%
10	100%	100%	60%	100%

3.3 Reprocessing of Blends of virgin /post-consumer HDPE

3.3.1 Processability

Figure 3.8 presents the melt pressure at the die during reprocessing HDPE at various percentage of post-consumer HDPE. Blends of virgin/ post-consumer HDPE at various ratios and the 100 % post-consumer HDPE showed the same tendency with slight decrease in the melt pressure versus the number of passes. These results indicated better processability or lower melt viscosity with an increasing number of passes.

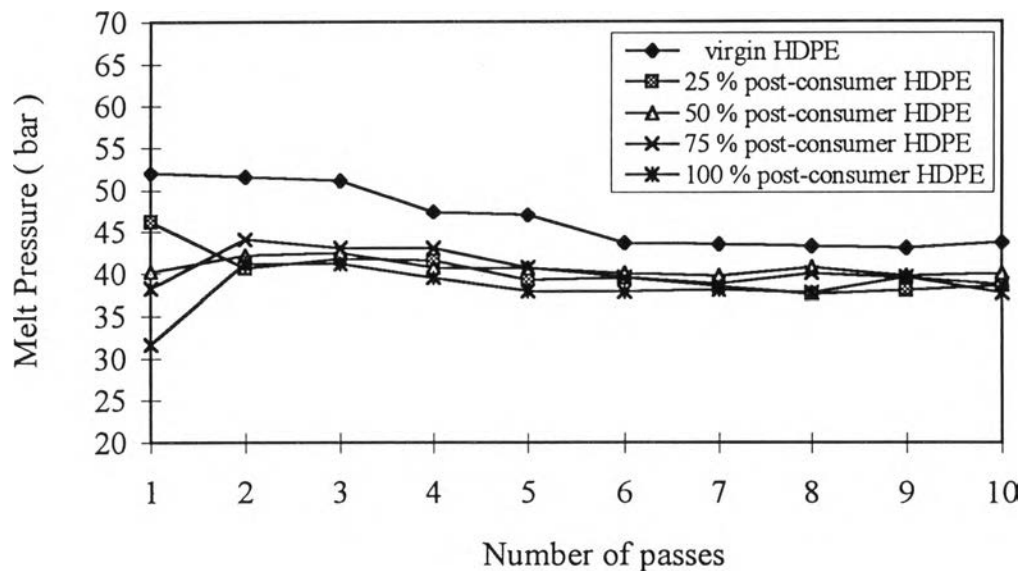


Figure 3.8 Melt Pressure of reprocessed HDPE for all ratios during reprocessing.

After blending virgin/post-consumer HDPE and reprocessing, MWD tended to be broader because the molecular weight of virgin HDPE and post-consumer HDPE were different. The melt pressure of the first pass depends on the amount of post-consumer HDPE scrap. The more post-

consumer HDPE, the less melt pressure because post-consumer HDPE had lower viscosity than virgin HDPE.

3.3.2 Viscosity

Figure 3.9 shows the viscosity at shear rate of 291.8 sec^{-1} of reprocessed HDPE at various percentage of post-consumer HDPE. It could be seen that the viscosity of all percentage of post-consumer HDPE decreased very slightly with increasing the number of passes due to chain scission. These results agreed with the melt pressure results. The melt viscosity tended to reduce along the number of passes.

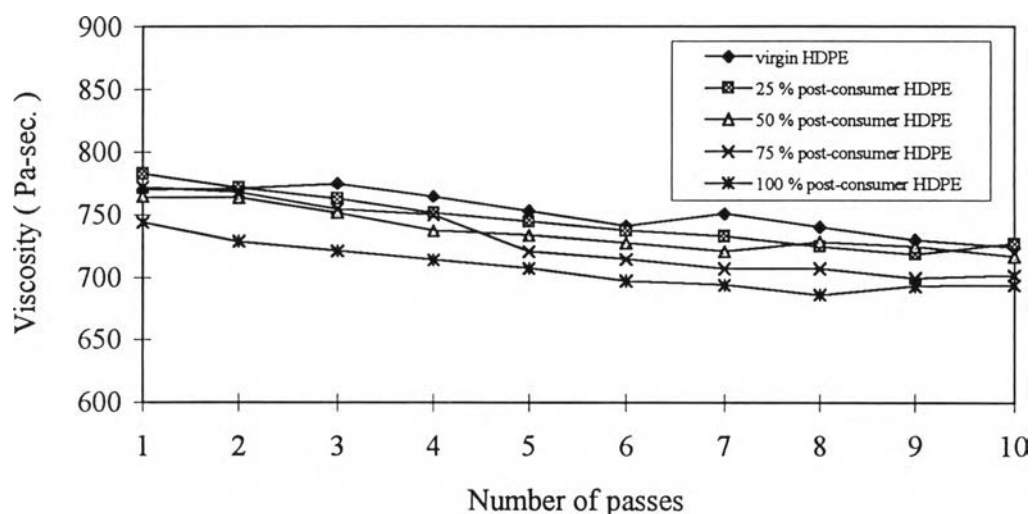


Figure 3.9 Viscosity at shear rate of 291.8 sec^{-1} of reprocessed HDPE for all ratios during reprocessing.

The melt viscosity related to molecular weight and MWD. The lower molecular weight or the broader MWD correspond to the lower viscosity. The polymer with broad MWD appears to have a lower viscosity than the same polymer with narrow MWD. Therefore, after reprocessing, all

materials may have broader MWD. In addition, chain branching affects the viscosity. Long branched polymers have lower melt viscosity compared to that of unbranched polymers of similar molecular weight and increasing the number of branches tends to decrease viscosity. [Niesen, 1977] So the number of branches probably increased with increasing number of passes. The amount of post-consumer HDPE also had an effect on the viscosity. The more post-consumer HDPE, the less the viscosity because the viscosity of virgin HDPE was higher than that of post-consumer HDPE due to higher molecular weight.

3.3.3 Melt Flow Index (MFI)

The MFI of reprocessed HDPE at various percentage of post-consumer HDPE as a function of the number of passes is presented in Figure 3.10. For all cases, blends of virgin/post-consumer HDPE showed the same trend as reprocessing of virgin HDPE and the 100 % post-consumer HDPE. So blends of virgin/post-consumer HDPE had higher molecular weight as increasing the number of passes and crosslinking or chain branching seemed to occur preferably during reprocessing. It was also found that the percentage of post-consumer HDPE had no effect on MFI values. This was due to the MFI of reprocessed virgin HDPE and the 100 % post-consumer HDPE showed almost the same MFI values for 10 passes as shown in Figure 3.4.

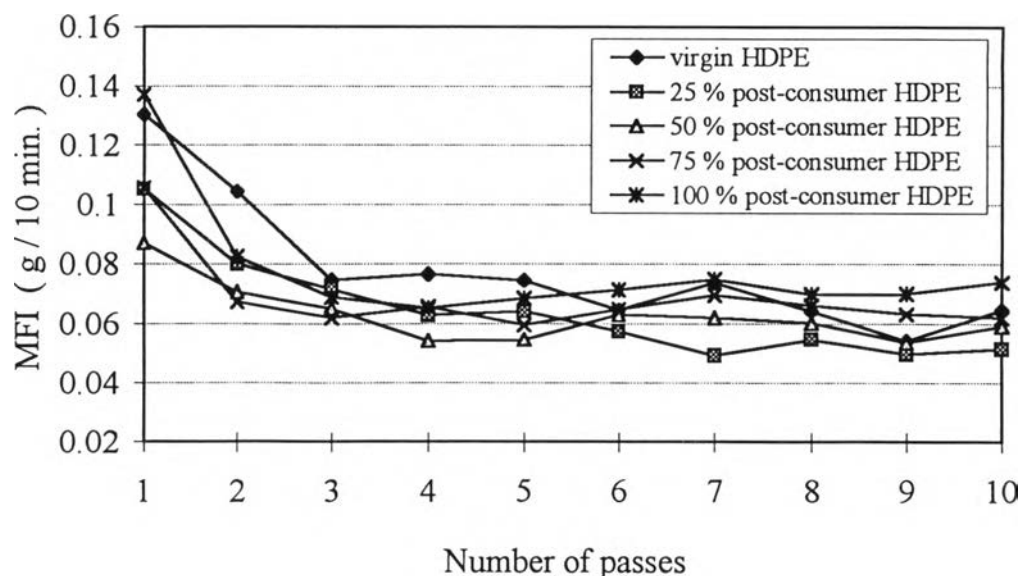


Figure 3.10 MFI of reprocessed HDPE for all ratios during reprocessing.

3.3.4 Thermal Analysis

The melting temperature (T_M) of all ratios varied in small range of 135 to 140 °C. Figure 3.11 shows the percentage of crystallinity calculated from H_f of reprocessed HDPE at various the percentage of post-consumer HDPE. It was observed that virgin HDPE exhibited no significant change in the percentage of crystallinity during reprocessing due to narrow MWD compared with the others. The percentage of crystallinity of the 25 %, 50 %, 75 % and 100 % post-consumer HDPE decreased gradually with an increasing number of passes because crosslinking or chain branching were favored to chain scission. Branched Polyethylene doesn't obtain such a high percentage of crystallinity because of the higher concentration of branch points and $-CH_3$ end groups. From Figure 3.11, the percentage of crystallinity varied in the narrow range so any change may not be seen obviously.

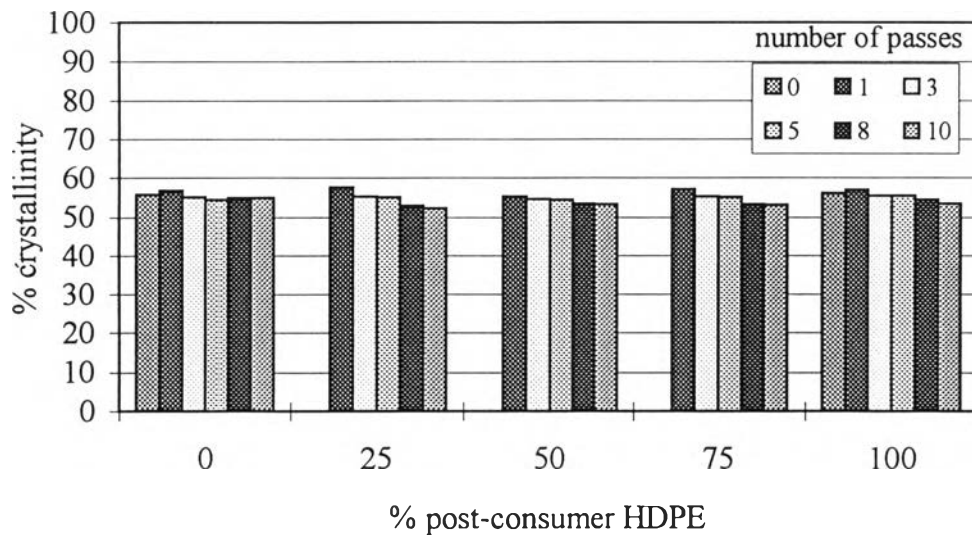


Figure 3.11 % Crystallinity of reprocessed HDPE for all ratios.

3.3.5 Tensile Strength

Figure 3.12 shows the tensile strength of reprocessed HDPE as a function of % post-consumer HDPE at various number of passes. It was found that there was no significant change in the tensile strength of virgin HDPE during reprocessing while the tensile strength of the 25 %, 50 %, 75 % and 100 % post-consumer HDPE reduced by 6.5 %, 3 %, 2.3 %, and 3.9 % respectively versus the number of passes. Pattanakul et al. (1991) investigated and compared the mechanical changes in HDPE from milk bottles. They found no effect of composition of HDPE from milk bottles on tensile strength, but a slight increase in the modulus could be noted apparently due to degradation of polyethylene. In general, branching, molecular weight, the percentage of crystallinity and orientation of polymer chain have strong effects on mechanical properties of HDPE [Mark, 1986] Molecular weight influences HDPE properties mostly through its effect on

crystallization. The higher molecular weight corresponds to the lower tensile strength.

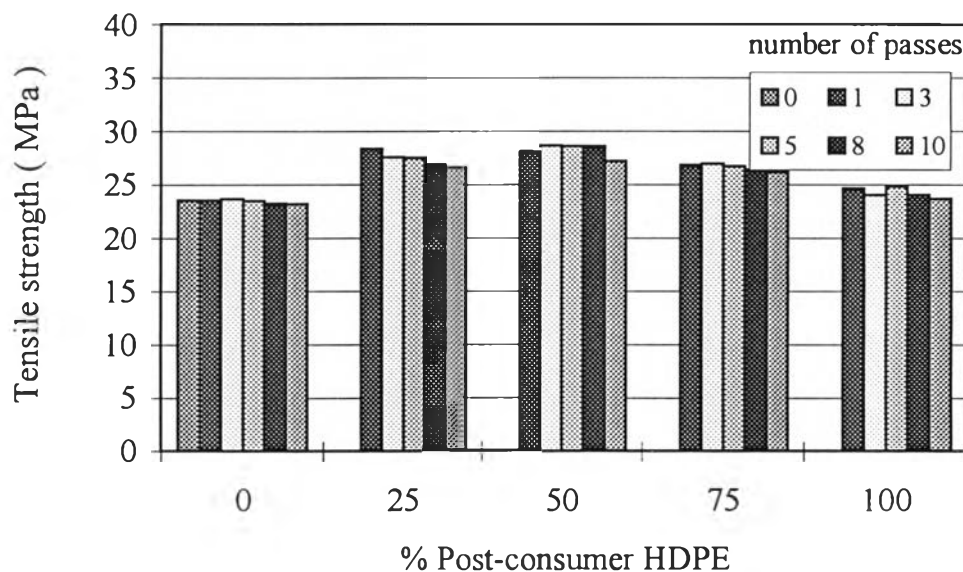


Figure 3.12 Tensile strength of reprocessed HDPE for all ratios

As seen in Figure 3.12, the tensile strength of virgin/post-consumer HDPE blends seemed to be higher than that of virgin HDPE because of lower molecular weight. Tensile strength decreased slightly with an increasing number of passes. An increase in branching reduces the percentage of crystallinity. Actually, the increase in branching is accompanied by a significant drop in tensile strength.

3.3.6 Flexural Strength

The flexural strength of the 0 - 100 % post-consumer HDPE after reprocessing is seen in Figure 3.13. The 0 % and 25 % post-consumer HDPE exhibited a decrease in flexural strength versus the number of passes while the others showed an insignificant change in flexural

strength. Crystallinity has a significant effect on the strength and rigidity of a polymer. As shown, the percentage of crystallinity seemed to reduce slightly versus the number of passes. Therefore, it may not clearly show the difference in flexural strength.

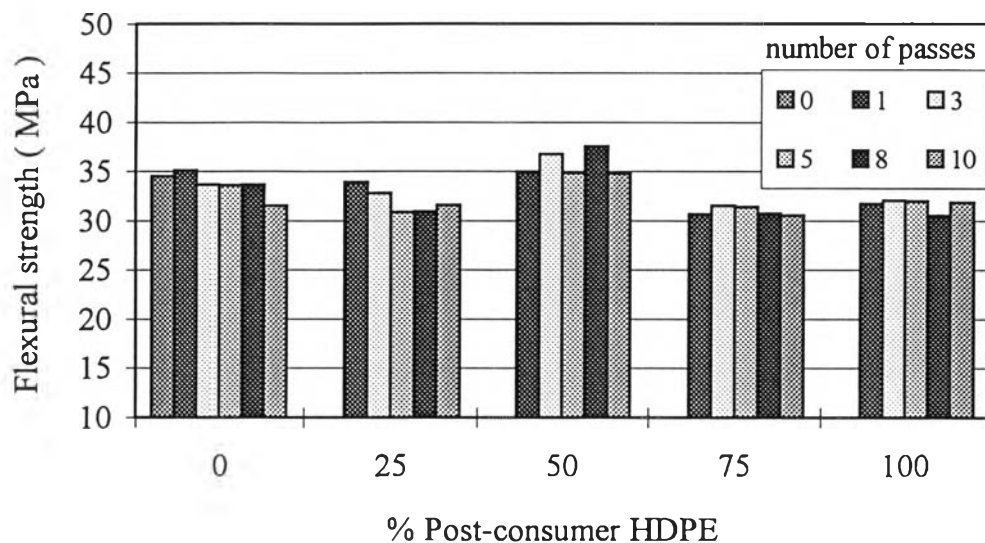


Figure 3.13 Flexural strength of reprocessed HDPE for all ratios.

3.3.7 Impact Resistance

Figure 3.14 presents the impact resistance of the 0 - 100 % post-consumer HDPE after reprocessing. Impact resistance depends on the percentage of crystallinity and molecular weight. Increasing the percentage of crystallinity or decreasing the molecular weight decreases the impact resistance of the material and increases the probability of brittle failure. In Figure 3.14, the 75 % and 100 % post-consumer HDPE exhibited lower impact resistance compared with the others since unprocessed post-consumer HDPE had a lower molecular weight and higher percentage of crystallinity

than virgin HDPE. Pattanakul et al. (1991) reported that up to almost 50 % of recycled HDPE from milk bottles, there was no decrease in impact resistance.

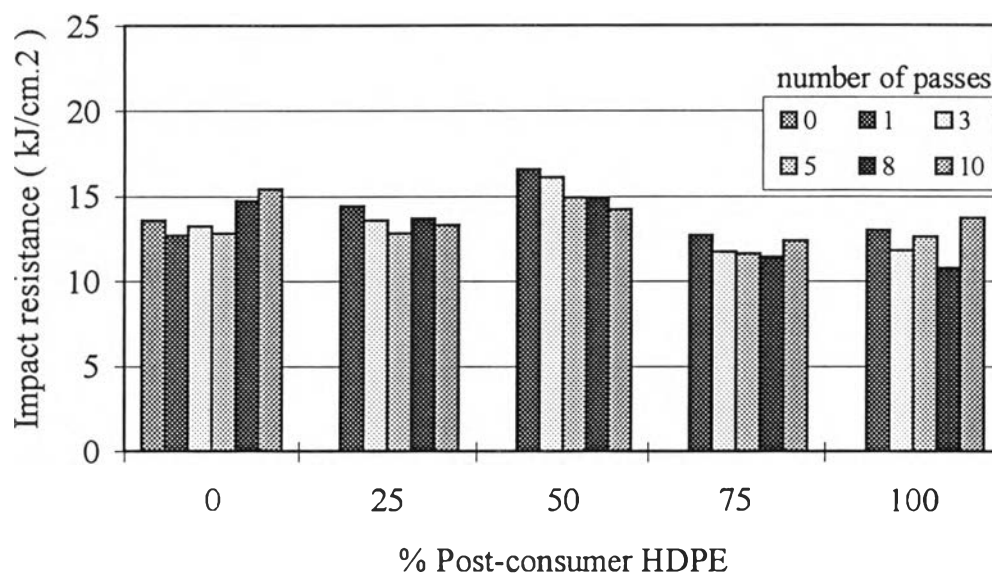


Figure 3.14 Impact resistance of reprocessed HDEP for all ratios.

Molecular weight of reprocessed HDPE may not change obviously after reprocessing. Consequently, the percentage of crystallinity seemed to be in narrow range, ranging from 52 - 57 %. So it did not show significant change in mechanical properties. In addition, no significant effect of the amount of post-consumer HDPE on mechanical properties was seen. Overall, the reprocessed HDPE from water bottles was a material with useful properties, not significantly different from the properties of virgin material.