

CHAPTER IV

RESULTS AND DISCUSSION

After reprocessing the properties of a binary blend of HDPE/PET and ternary blend of HDPE/PET/MA were studied in this experiment. The discussion was provided in various topics of the identification of HDPE and PET blend.

The discussion of the results in this experiment will be provided in 4 main topics and each topic will be discussed by relating to the observations from previous works. These are 4 topics that will be discussed:

1. Processing about the blend preparation
2. Rheology of the blends
3. Mechanical properties
4. Morphology of the blends

4.1 Processing

4.1.1 Blend Preparation

a. Processability

Figure 4.1-4.2 shows the relationship between the melt pressure and number of passes of the various ratios of PET in binary blend and ternary blend. The melt pressure is the pressure of the melt was detected

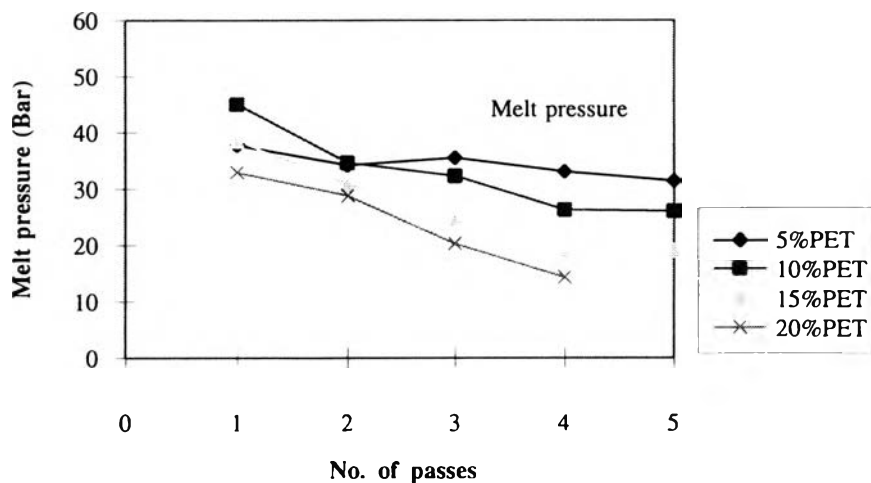


Figure 4.1 Melt pressure of binary blend vs number of passes.

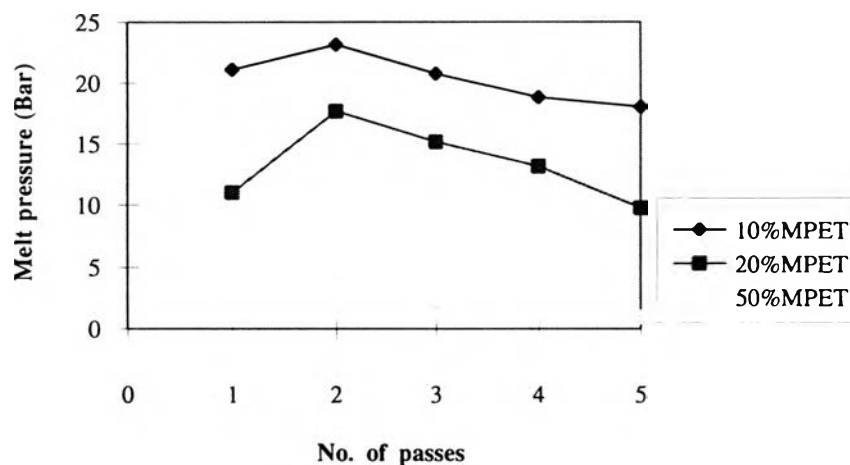


Figure 4.2 Melt pressure of ternary blend vs number of passes.

by the pressure transducer at the die of the twin screw extruder (Collin ZK-25).

Figure 4.1-4.2 shows the values of the melt pressure during processing of the PET/HDPE blend without maleic anhydride grafted

polyolefin as a compatibilizing agent so called “binary blend” and with compatibilizing agent so called “ternary blend”.

Acireno and Maio [15, 1986] studied the reprocessing of the extruded polymer by detecting the melt pressure during processing. And they observed that high viscosity was affected by the packing system between PET and HDPE component. It meant that the material was pushed and packed together along the rotating screw extruder during processing. Grassie and Scott [16, 1988] suggested that the polymer could be degraded during the first-life time and along the recycling process. The polymer degradation will occur by the chain scission reaction. Therefore, the molecular weight decreases so that the viscosity will decrease because the viscosity is a function of 3.4th power of the molecular weight ($\eta = kM_w^{3.4}$) [17, 1987].

From figure 4.1-4.2 it was seen that the melt pressure of the binary blend decreased as the number of passes increased through the twin screw extruder. For example the values of melt pressure of 5/95 blend decreased from 45 bar in the 1st pass to 30 bar in the 5th pass. The observed values of the melt pressure also showed that the polymer blend was less packed in the screw compared with HDPE alone. That meant the viscosity of the blend continued to decrease as the number of passes increased. So the molecular weight of the two components in the blend were decreased during reprocessing.

Chen et al. [5, 1987] suggested that the compatibilizing agent that was added in the blend system, has strongly affected on the specific interaction between the two incompatible components. And the

compatibilizing agent may act like a plasticizer that probably increased free movement in the system, so the viscosity of the blend was reduced.

The experiment results showed in figure 4.1-4.2 that the melt pressure of the ternary blends were lower than the melt pressure of the binary blends in. The lower melt pressure of the ternary blend can be explained by the reason that the compatibilizing agent, maleic anhydride grafted polyolefin, that was added in the system would act like a high molecular weight material that reduced the viscosity of the blends system. Thus flow of the ternary blend would flow more freely compare with the binary blend in every pass of reprocessing.

b. Physical Appearance of the Blends

The physical appearance is the surface and the mechanical properties of the product that was obtained from the processing[3, 1994]. In this experiment the surface of the extrudates was determined for was not rough, good physical appearance or good quality of the extrudate surface. The physical appearance was observed as a function of increasing the amount of PET in the blend and the number of reprocessing passes. This observation was studied the effect of the blend compositions and reprocessing procedure on the physical properties. The determination of the physical appearance was provided into 2 cases.

Binary Blend

During the preparation in the 1st and 2nd pass of the pellets for binary blend at composition 5/95, 10/90 and 15/85 (PET/HDPE) blend, the

surfaces of the extrudates were smooth. When the percentage of PET was higher (20/80) rougher surfaces were obtained. That means the surfaces of the extrudate were quite smooth at low compositions of PET component. The reason of the smooth surfaces of 5/95, 10/90, 15/85 was the amount of the HDPE in the blend more than enough to interfere the effect from the PET components even though PET was not miscible with HDPE in nature.

Grassie and Scott [16, 1988] observed that the degradation of the polymer (polyester, PET) affected the physical appearance, physical properties and morphology of the materials.

When further reprocessed 5/95, 10/90, 15/85, 20/80 of binary blend of PET/HDPE, the physical appearance was changed along the number of passes. The surfaces of the extrudates from the die were rougher than the surfaces of the blend that were obtained in the 1st and 2nd pass. Moreover, the extrudates were brittle as increasing the number of passes. The extrudates that were processed over 5 times were brittle and difficult to draw to granulator to make the pellets. And all ratio of the binary blend could not be reprocessed over 5 times. This surface texture and the ability to make pellets pointed the degradation of PET and HDPE components in the system during reprocessing. This result was agreed with Grassie and Scott that polyethylene and poly (ethylene terephthalate) were degraded to form various products by thermomechanical process.

Ternary Blend

For ternary blend, the result of the surface textures was also determined in the same manner as the binary blend.

Previous work has shown that polymer blends with immiscible components in the system were mechanically compatibilised by adding another polymer[5, 1987], maleic anhydride grafted polyolefin was selected add in order to improve the miscibility of PET/HDPE blend.

The surfaces of 10/85/5, 20/75/5, 50/45/5 ternary blend of PET/HDPE with compatibilizing agent showed that all ratio of the ternary blend had smooth surface until the 3rd reprocessing step. That meant the surfaces of the extrudates were acceptable. This indicated that the compatibilizing agent promoted the miscibility of the two immiscible components provided more homogeneous extrudate and smooth surface.

Moreover, the surfaces of the extrudates in each pass of the particular ratio (10/85/5, 20/75/5, 50/45/5 of PET/HDPE/MA blend) were rougher in further reprocessing passes (the 4th-5th pass). And it is difficult to draw the extrudates continuously to the granulator to shred into pellets. These phenomena extrudate resulted from the thermomechanical degradation at the processing condition (temperature=255°C). It was also observed by Giannotta et al. [5, 1987] that thermal and shearing force during melt processing affected on the degradation of PET from bottles scraps and also on HDPE.

4.2 Rheology of the Blends

In this experiment, the viscosity of the blends was determined. The viscosity is the most common rheological property used to characterize the polymer and also polymer blend. The viscosity depends on the flow conditions which are composed of shear rate, temperature and pressure,

chemical structure of polymer. The viscosity of a polymer is determined by its molecular weight, nature and the concentration of additives, etc.

4.2.1 Binary Blend

Most of the polymers have shear thinning characteristics. That means the viscosity of the polymers decreases as shear rate increases [18, 1977].

Figure 4.3 shows the viscosity of the 5/95, 10/90, 15/85, 20/80 binary blend of PET/HDPE at the 1st pass of reprocessing. It was seen that the viscosity of all ratios of PET in binary blend decreased as shear rate increased. Hence the immiscible polymer blends also exhibited shear thinning behaviour.

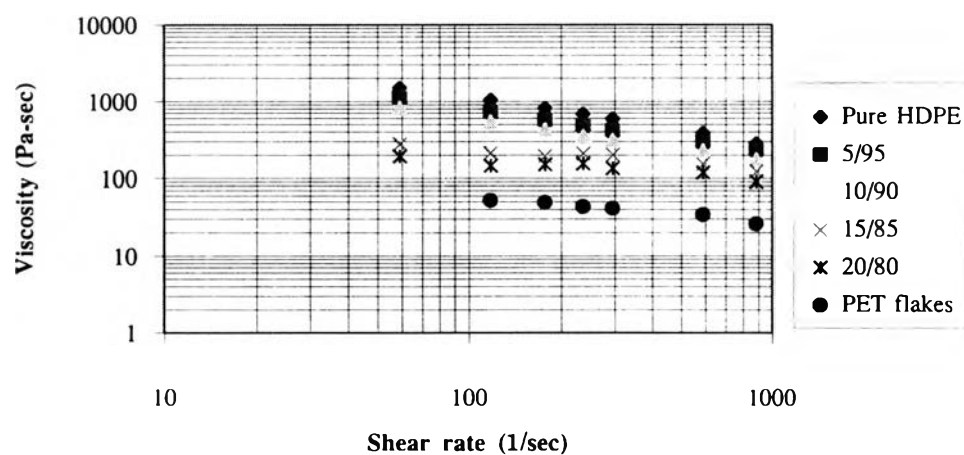


Figure 4.3 Viscosity vs shear rate for the 1st pass of binary blend.

The objectives for manufacturing the blend are to obtain the advantages from each component that composes in the system and the commercial reasons. For obtaining the advantage of each component in the

blend, in this experiment was explained by the melt strength which was the property of HDPE component that provided the ability to retain the shape as in low shear rate condition.

Nielson [17, 1987] has shown that among the factors determining the rheology of polymers the molecular weight is considered to be quite important. The reasons were the viscosity of the melt is proportional to the molecular weight below a critical molecular weight (molecular weight concern with chain entanglement) and the viscosity depends on molecular weight to a power of 3.4 or 3.5 above a critical molecular weight.

It is shown from figure 4.4 that the viscosity of a particular ratio of the blend will decrease with an increasing the number of passes.

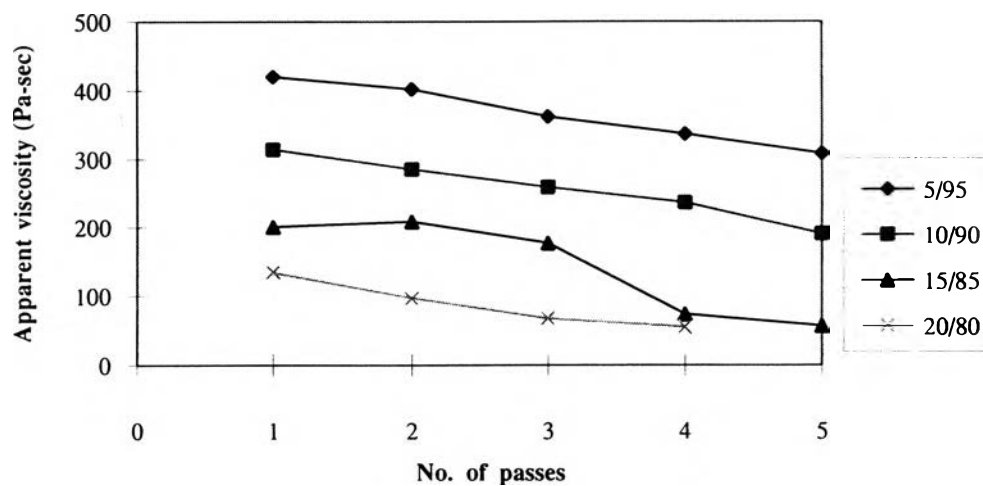


Figure 4.4 The effect of number of reprocessing passes on the viscosity @ 295.3 1/sec for binary blend.

The viscosity of 10/90 PET/HDPE in the 1st pass was about 40% lower than the viscosity of pure HDPE at the same shear rate (at 295.3 1/sec

shear rate). Determining the viscosity of 10/90 in further reprocessing (the 3rd-5th pass), the viscosity decreased to about 75% lower than the viscosity of the 1st pass of 10/90 PET/HDPE at the same shear rate (295.3 1/sec).

For the first pass of 15/85, 20/80 binary blend of PET/HDPE, the viscosity sharply decreased about 80-85% lower than the viscosity of pure HDPE at the same shear rate. Other passes (the 2nd,3rd,4th,5th pass) of 15/85, 20/80 PET/HDPE, the viscosity decreased to quite the same value as the viscosity of pure PET component.

The decreasing viscosity implied to the lowering of the molecular weight of the blend. The cause of the lowering molecular weight may be caused by thermomechanical degradation during melt processing such as intermolecular transfer reaction in HDPE and PET, and chain scission of the ester linkage in PET[16, 1988].

Melt strength is the ability of hanging to retain the shape and proportional to the viscosity at low shear rate[3, 1994]. From figure 3 the values melt strength of all ratio (10/90, 15/85, 20/80) of the binary blend were quite low comparing to the melt strength of pure HDPE eventhough the melt strength of the binary blend in the 1st pass. When the blends passed through the twin screw extruder more passes the melt strength was lowered. The lower melt strength in the first pass was affected by the immiscibility of these two components. The effect on melt strength in further passes of reprocessing was caused by the degradation during processing. This determination was agreed with Jabarin et al. [14, 1981] that the immiscible blend can effect on the physical properties and mechanical properties of the blends.

4.2.2 Ternary Blend

It is common for the compatibilization of two immiscible polymers to be achieved by adding a third component as a compatibilizing agent, leading to the modification of the polymer interface to tailoring of the phase structure, and the properties.

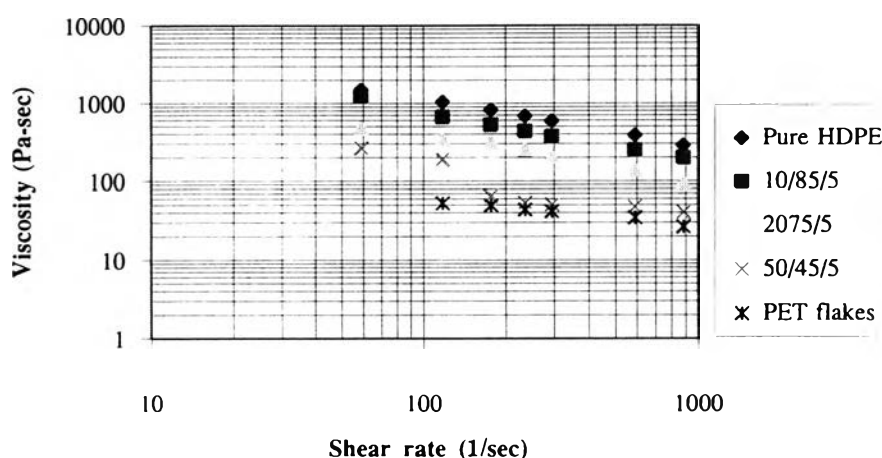


Figure 4.5 Viscosity vs shear rate for the 1st pass of ternary blend.

Figure 4.5 shows the viscosity of ternary blends of 10/85/5, 20/75/5, 50/45/5 PET/HDPE with maleic anhydride grafted polyolefin as a compatibilizing agent. The use of maleic anhydride followed the previous work. It was seen that in ternary blend of 10/85/5, 20/75/5, the values of the viscosity were more than the values of the viscosity in binary blend at all number of passes. This may be the result of the compatibilizing agent providing the miscibility between the two immiscible components.

Jabarin and Lofgref [14, 1981] concluded that the thermal oxidative degradation of the blends was determined in term of the viscosity of the blend.

Figure 4.6, after reprocessing of the ternary blend of 10/85/5, 20/75/5, 50/45/5, it was seen that the viscosity continued to decrease as a function of the number of passes. In 10/85/5 blend, the viscosity at the 5th pass was about 13% lower than the 1st pass at shear rate 295.3 1/sec. This pointed out that the decreasing viscosity may be due to the degradation during melt processing.

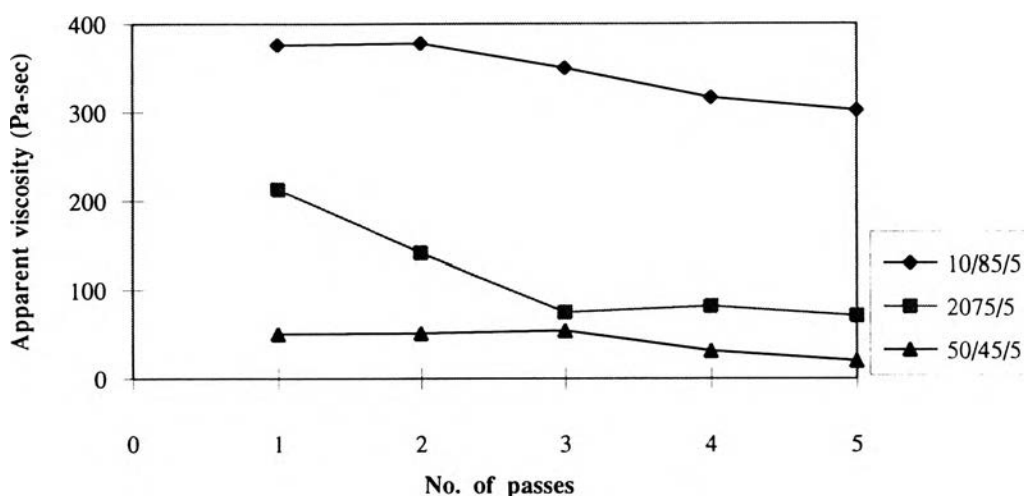


Figure 4.6 The effect of number of reprocessing passes on the viscosity @ 295.3 1/sec ternary blend.

It is understood that compatibilization can interact in various methods to influence final blend properties. One effect of compatibilizing agents is to reduce interfacial tension in the melt, causing an emulsifying effect leading to a fine dispersion. A second effect is to increase the adhesion of the phase. A third effect is to stabilise the dispersed phase against growth during annealing[20, 1983]. So the ternary blend can be processed up to 50/45/5 PET/HDPE/MA and thus can be reprocessed. The ability to reprocess the blend with up to 50/45/5 PET/HDPE/MA resulted from the

compatibilizing agent provided the miscibility by modifying the interface of the two components.

The values of the melt strength of 10/85/5 and 20/75/5 PET/HDPE/MA blends in every pass were higher than the melt strength of the binary blend. The observed results agreed with the conclusion that compatibilizing agent acted like an emulsifying agent by reducing the interfacial tension between the two polymers[5, 1987]. For further reprocessing the values of melt strength were decreased as the number of passes were increased evidently because of the degradation reaction occurred in the polymers.

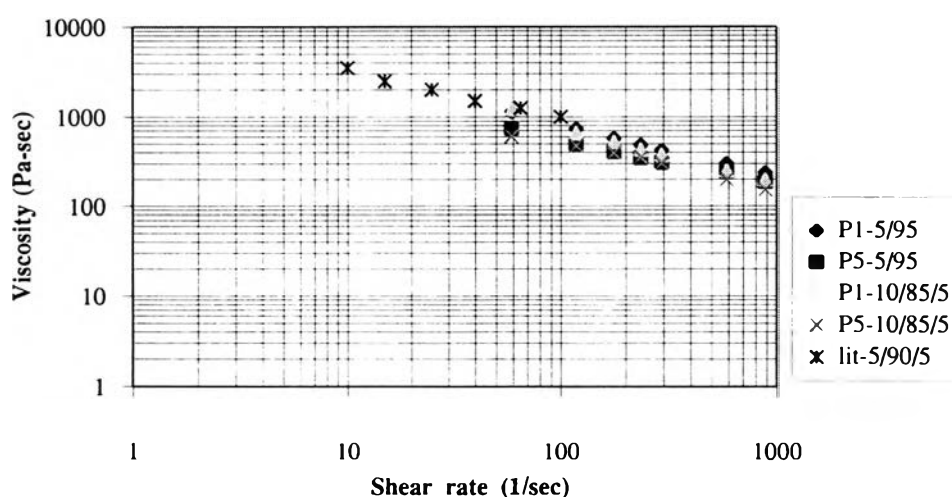


Figure 4.7 Comparison between the viscosity from previous work and the viscosity from this experiment.

Figure 4.7 shows the values of viscosity from previous work and the viscosity of blend from this experiment. It was seen that the value of both works was slightly close to each other, especially at shear rate about 80-150 1/

sec. It can be expressed that maleic anhydride grafted polyolefin, provided the same function in both works.

4.3 Mechanical properties

The tensile strength, flexural strength and impact resistance of 10/90 PET/HDPE in blend and 10/85/5 PET/HDPE/MA blend were determined as a function of number of reprocessing passes.

The following topics will be discussed in details about the mechanical properties (tensile strength, flexural strength and impact resistance).

4.3.1 Tensile Strength and % Strain at Yield

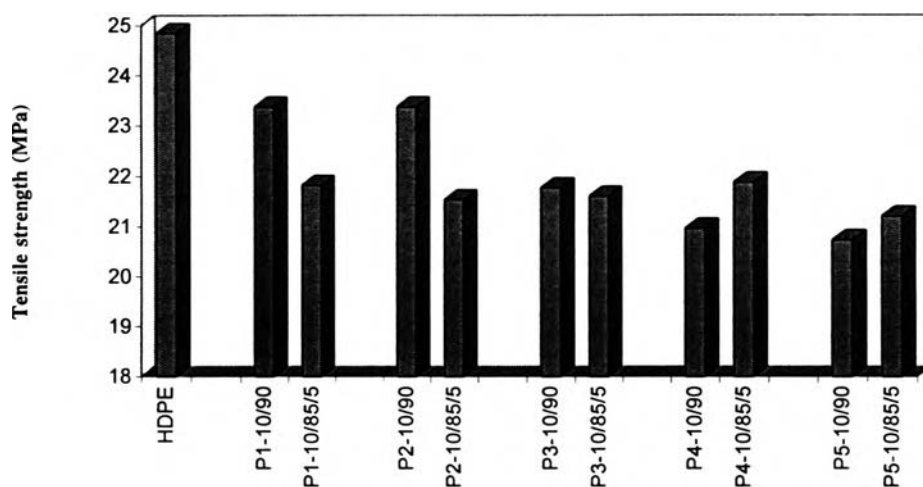


Figure 4.8 Tensile strength between 10%PET binary blend and ternary blend.

Generally, melt mixing of two immiscible polymers results in blends which are weak and brittle. In contrast, when adding a third material as a compatibilizing agent, the mechanical properties of the blend may be improved. Further reprocessing leads to the degradation of the polymer.

Figure 4.8 and table 4.1 shows the values of the tensile strength and % strain at yield of 10/90 blend from the 1st-5th pass.

For binary blend it was seen that the value of tensile strength in the 1st pass was about 6% less than the value of tensile strength of pure HDPE. After further reprocessing, the values of tensile strength of 10/90 blend continued to decrease. Comparing the value of tensile strength, the 5th pass of reprocessing was about 11% lower than that of the 1st pass of reprocessing. This lowering of the values of tensile strength was affected by the immiscibility of the two components and the degradation during reprocessing of the blends.

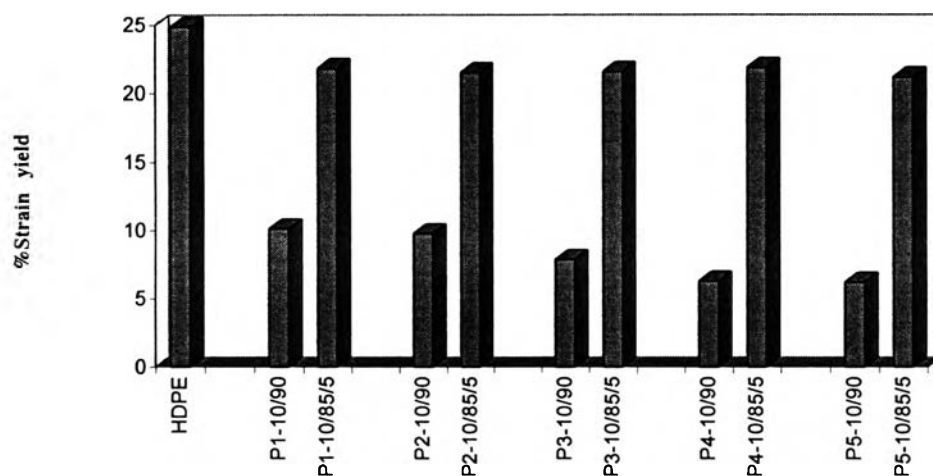


Figure 4.9 Percent strain at yield between 10%PET binary and ternary blend.

Figure 4.9 and table 4.1 showed the values of percent strain at yield of binary blend were 20% lower than percent strain at yield of pure HDPE. The lowering of percent strain at yield pointed out that the blend was more brittle. When determining percent strain of further passes of the blend, the percent strain in each pass still continuously decreased due to the fact that reprocessing the polymer leads to the degradation of the blend. For example percent strain of the 5th pass was about 40% lower compared to percent strain

of the 1st pass. And it demonstrated that the ductility of the binary blend was decreased after reprocessing as it was seen in the table 1 and figure 10.

From previous work[3,20, 1994, 1983] polymer blends may be mechanically compatibilized by adding another polymer so called ternary blend. The major result was obtained from adding another polymer is to improve of the mechanical properties.

Kalfoglou et al. [19, 1992] concluded that the addition of a compatibilizing agent will increase the ductility of the blend. Traugott et al. [7, 1994] also observed that the compatibilizing agent that had flow properties intermediate to HDPE and PET for the blend system. The modulus and the strength were reduced.

Figure 4.8-4.9 and table 4.2 show the tensile strength and percent strain at yield of 10/85/5 blend.

In ternary blend, the value of tensile strength of the reprocessing blend was about 12% lower than the tensile strength of HDPE. When compared to the binary blend, the tensile strength of the ternary blend was lower than tensile tensile of the binary blend, but the percent strain at yield of the ternary blend was higher than percent strain at yield of binary blend. So the modulus of the ternary blend was obtained in figure 10. It showed more ductility in every reprocessing pass of ternary blend.

From determining these three properties (tensile strength, percent strain at yield, modulus) of the ternary blend, the addition of compatibilizing

agent will improve the ductility of the ternary blend as showing the value of percent strain strain and modulus in table 4.2.

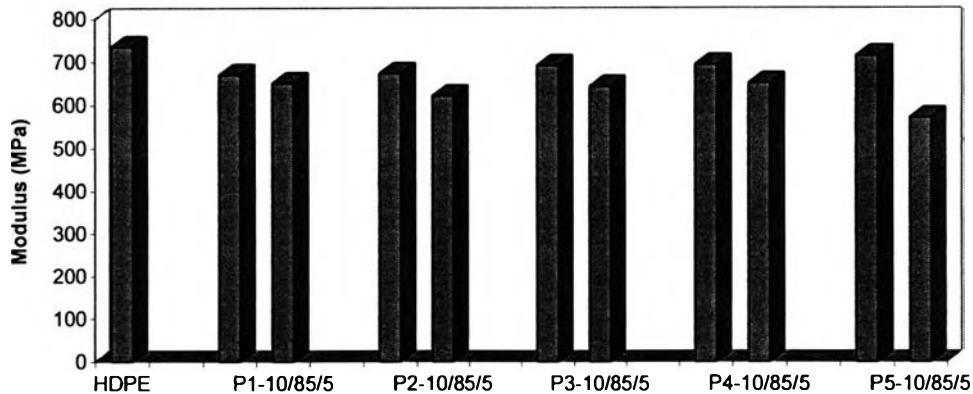


Figure 4.10 Modulus between 10%PET binary blend and ternary blend.

Folkes and Hope [20, 1983] showed that the major effect of the compatibilizing agent is to reduce interfacial tension led to fine dispersion. The other effect is to stabilise the dispersed phase during melt processing. So the compatibilizing agent has more effects in the blend system. Folkes [20, 1983] also concluded that the mechanical properties of a blend will be determined not only by the properties of its components but also by the phase morphology and interface adhesion.

For further reprocessing the tensile strength and %strain at yield of 10/85/5 blend changed about 2.8% in the 5th pass comparing to the tensile strength of the 1st pass. In figure 4.16 shows the micrograph of the ternary blend in the 5th pass. It was seen that the PET components still dispersed in the HDPE matrix same as the 1st pass of ternary blend. So the dispersion of the component provided the stability of the tensile strength and the ductility of the 1st-5th pass of 10/85/5 blend eventhough the blend was reprocessed

through 5 passes. The negligible change of ductility in the 5th pass might be caused by the degradation of the compatibilizing agent.

4.3.2 Flexural Strength

Mark et al. has pointed that the properties perpendicular to the oriented direction are often poor, but process has significant effects on phase geometry and properties in immiscible blend. Blend properties can be improved by using the rheological forces associated with flow processing to change the dispersed phase from sphere to ellipsoid that are oriented in the load bearing direction[18, 1977].

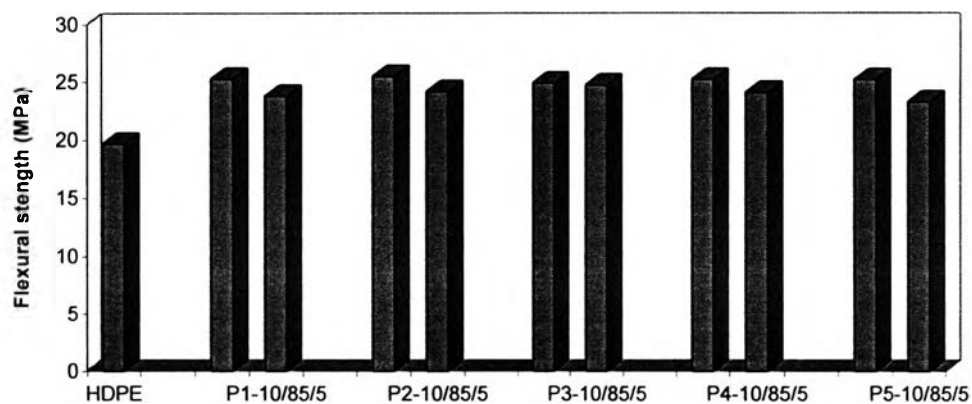


Figure 4.11 Flexural strength between 10%PET binary blend and ternary blend.

Figure 4.11 and table 4.3 shows the values of the flexural strength of 10/90 blend. The value of the flexural strength of the 1st pass of 10/90 blend was about 25% higher than the flexural strength of pure HDPE. The higher flexural strength was compared to the flexural strength of HDPE resulted from the orientation of the phase was parallel to the force applied during the flexural testing.

For further reprocessing of the binary blend, the value of the flexural was quite the same as the first pass of the processing. It might result from the crystalline material acted as cross-linking led to more flexural strength. Muller et al. [8, 1985] stated that the crystalline material acted as cross-linking and provoked more the elastic modulus.

In ternary blend, another polymer was added in the system to improve the mechanical compatibility.

Figure 4.11 and table 4.4 show the flexural strength of 10/85/5 blend at various number of passes. In the 1st pass, the flexural strength of the blend was 20% higher than the flexural strength of pure HDPE. This high flexural strength was caused by the effect of the compatibilizing agent that was added in the blend system. Because the compatibilizing agent has identical chemical structure to each component in the blend led to the miscibility of two components in the blend was obtained.

Determining the blend after reprocessing, the values of the flexural strength were quite the same in the 1st-4th pass. And the values of the flexural strength were still higher than the flexural strength of pure HDPE. The stability of the flexural strength of ternary blend after reprocessing was resulted from the dispersion of the phase due to the effect of the compatibilizing agent. At the 5th pass, the value of flexural strength decreased because the adhesion between PET and HDPE was lower. The lowering of adhesion was caused by melting processing affected on the behaviour of the compatibilizing agent, PET and HDPE.

4.3.3 Impact Strength

Impact strength values represent the total ability of the material to absorb impact energy.

Poor impact strength properties are related to poor stress transfer (the dissipation of the energy) in the material between the phase of the immiscible blend. PET and HDPE naturally are incompatible to each other. Blends of these two polymers show poor mechanical compatibilization.

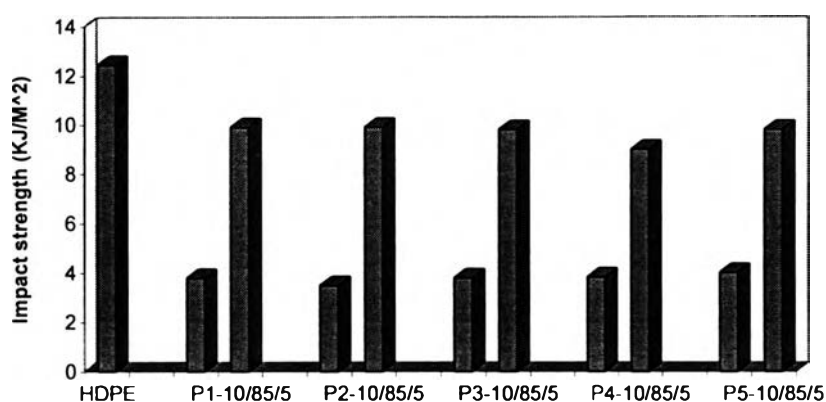


Figure 4.12 Impact strength between 10%PET binary blend and ternary blend.

Figure 4.12 and table 4.5 show the values of the impact strength of the binary blend. In every pass of reprocessing binary blend, the value of the impact strength was poor. It was about 70% lower than the impact strength of pure HDPE. This low value of the impact strength was caused by the immiscibility of the two components in the blend. Because the immiscibility caused low stress transfer within the binary blend. So the impact strength of binary blend was poor in every pass of reprocessing.

It was concluded that in many cases the compatibilizing agent that was added had the effect on the phase dispersion and could improve the physical properties of the blend.

Figure 4.12 and table 4.6 shows better values of the impact strength of the ternary blend in every pass of reprocessing compared to the values of the impact strength of the binary blends. And in each pass the value of impact strength was slightly the same, about 1% changed in the 5th pass compared to the 1st pass of reprocessing. Because the interface adhesion due to the addition of compatibilizing agent and good dispersion of PET component in the HDPE matrix. The reason was consistent with Folkes and Hope that compatibilizing agent reduced the interfacial tension led to improve dispersion. The compatibilizing agent also stabilised the dispersion during processing [20, 1983]. So the mechanical properties, especially the impact strength of ternary blend was better than that of binary blend.

4.4 Morphology of the Blend

To ensure the mechanical properties of the blends correlated with the morphology of the phase, the scanning electron microscope was used. That meant the micrographs would support the view that mechanical compatibility was caused by the formation of a mixed interphase. So the morphology of the blend would be investigated.

Kalfoglou et al. [19, 1992] founded that the uniform structure and fine dispersion in the matrix affected the mechanical properties of the blends.

4.4.1 Binary Blend

The micrograph from figure 4.13 shows the surface behaviour of 10/90blend in the 1st pass from impact testing. There are 2 μm . in size of PET components dispersed in HDPE matrix. But some areas of the matrix only had cavities or holes that PET components previously located in. These holes expressed that the lower adhesion between the two immiscible components led to the lower mechanical properties especially low impact strength and low tensile strength in the binary blend. Furthermore the surface of the HDPE matrix was quite discontinuous led to poor mechanical properties.

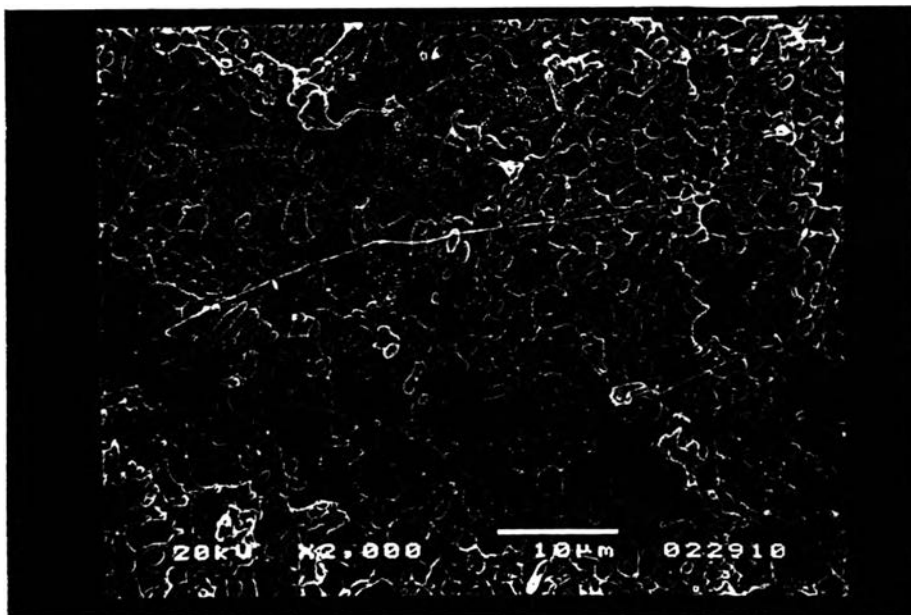


Figure 4.13 Micrograph of the 1st pass of binary blend.

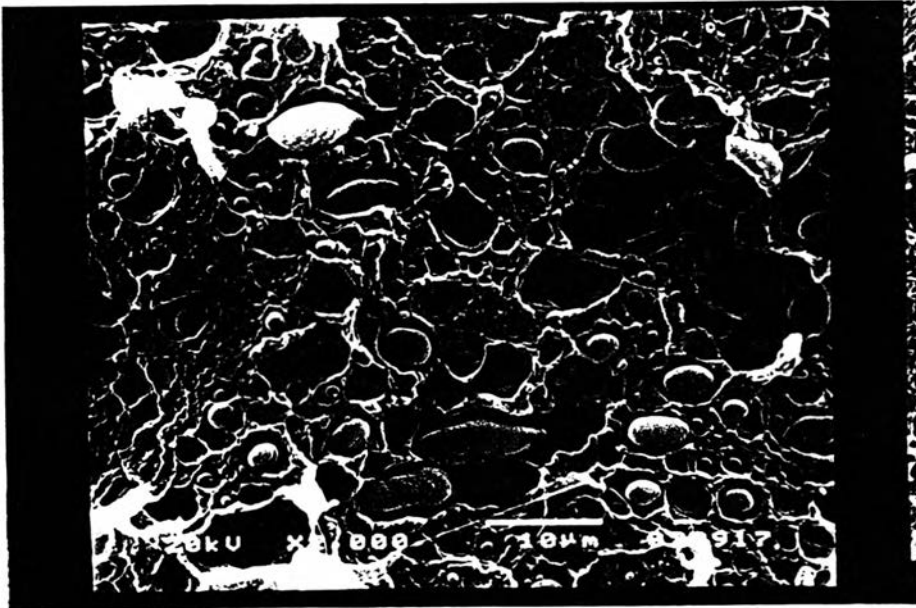


Figure 4.14 Micrograph of the 5th pass of binary blend.

Further reprocessing, figure 4.14 showed the micrograph of the 5th pass of 10/90 blend. It showed the agglomeration of PET component which was about 4 - 10 μm . in size that occurred and caused two immiscible components separated from each other. The PET component aggregated together to form bigger dispersed phase that caused low mechanical properties as seen in table 4.2 and table 4.4.

4.4.2 Ternary Blend

Figure 4.15 showed the morphology of the 10/85/5 blend. The 2 μm . sized PET components finely dispersed in all areas of HDPE matrix. And there were fewer holes than in the binary blend. That meant the adhesion of the interface in ternary blend was more than the adhesion in binary blend.

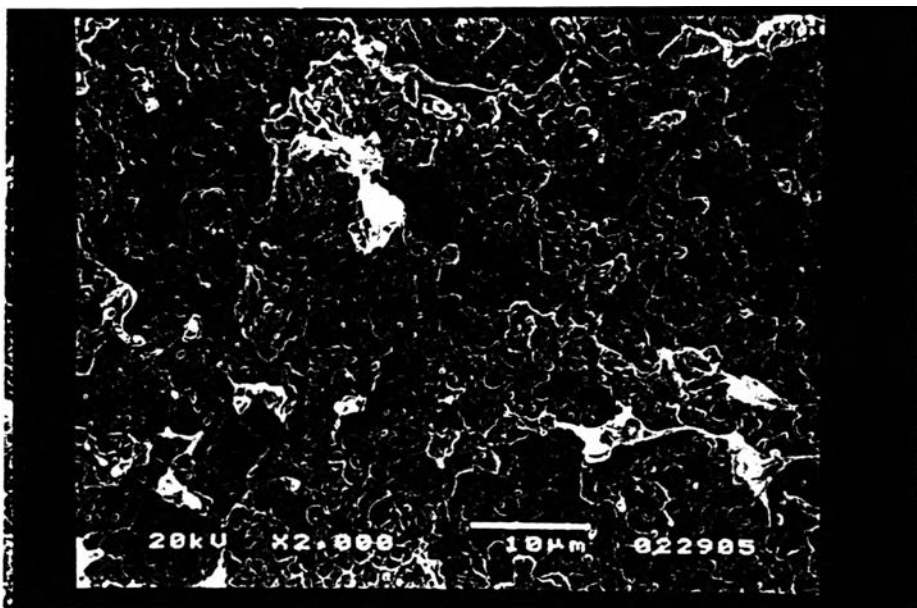


Figure 4.15 Micrograph of the 1st pass of ternary blend.

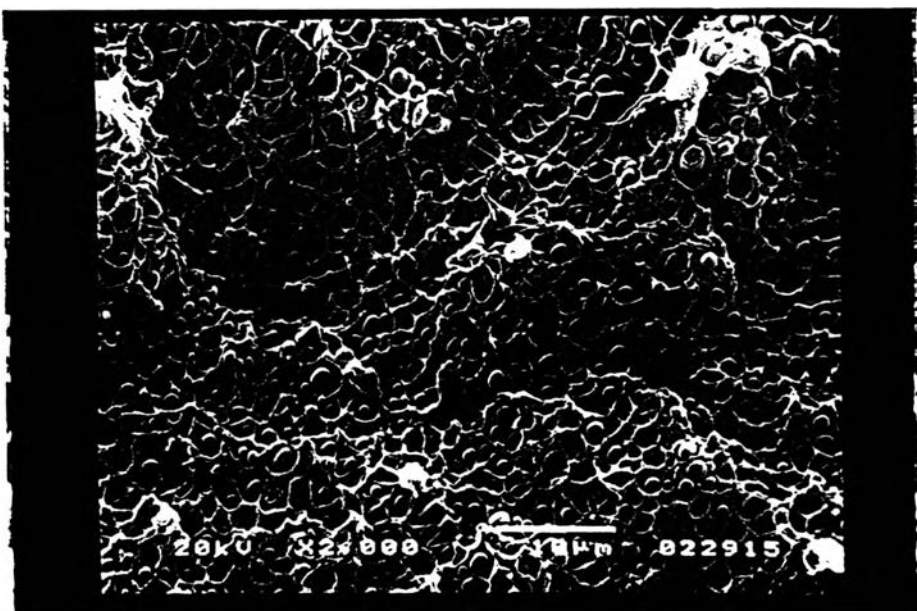


Figure 4.16 Micrograph of the 5th pass of ternary blend.

The surface of HDPE matrix in ternary blend was more continuous than the surface of HDPE matrix in binary blend.

The dispersion of PET component in all areas of the matrix led to improve the mechanical properties as seen in the values of impact strength.

The micrograph from figure 4.16 showed that the surface of the 5th pass was still dispersed by PET component same as the surface in the 1st pass. There was no incident of the agglomeration of the PET component. The size of the PET components were around 2 μm . So the mechanical properties, particularly impact strength, were nearly the same values as for each pass.