CHAPTER III

RESULTS AND DISCUSSIONS

3.1   Effects on Density

The density of materials are important for material selection.   The packing of chains due to crystallization, cross-linking and chain entanglement (acts as physical crosslinking), by bringing adjacent chain close together, reduces free volume, raises T_g and density of materials [Ward, 1990].   Chain packing is a function of intermolecular interactions, and therefore depends on the polymer structure.   The strong cohesive forces exerted between molecules by hydrogen bonds are a driving force for nylon crystallization.   The high crystallinity of POM is the result of its linear unbranched molecular chain [Margolis, 1985].   The bulky meta-subsituted units in PEI inhibits chain-chain packing and allows less interactions to occur.   Hence this PEI is a completely amorphous polymer [Wilson et al., 1990]. Changes in the polymer chain interaction leads to the attractions in the packing and density.

The density of the reprocessed PEI is shown in Figure 3.1. This is in agreement with the density of 1.27 g/cm^3 reported by Collyer [1990]. The density of reprocessed PEI decreased through the tenth reprocessing pass. This result indicated a decrease in the packing of the chains.   The free volume increased resulting in a decrease in the density.   There was also decrease in melt viscosity measured by a capillary rheometer (Figure 3.2).
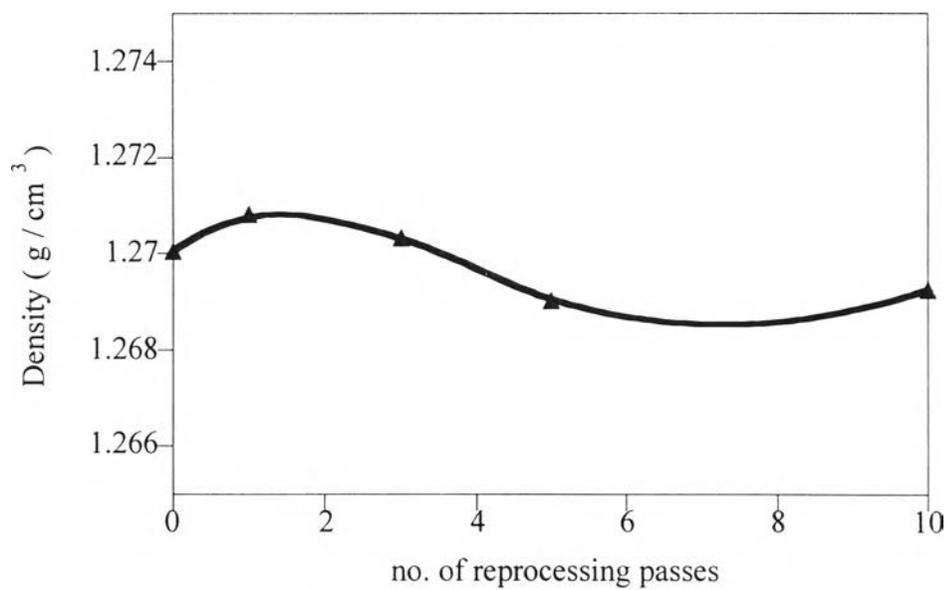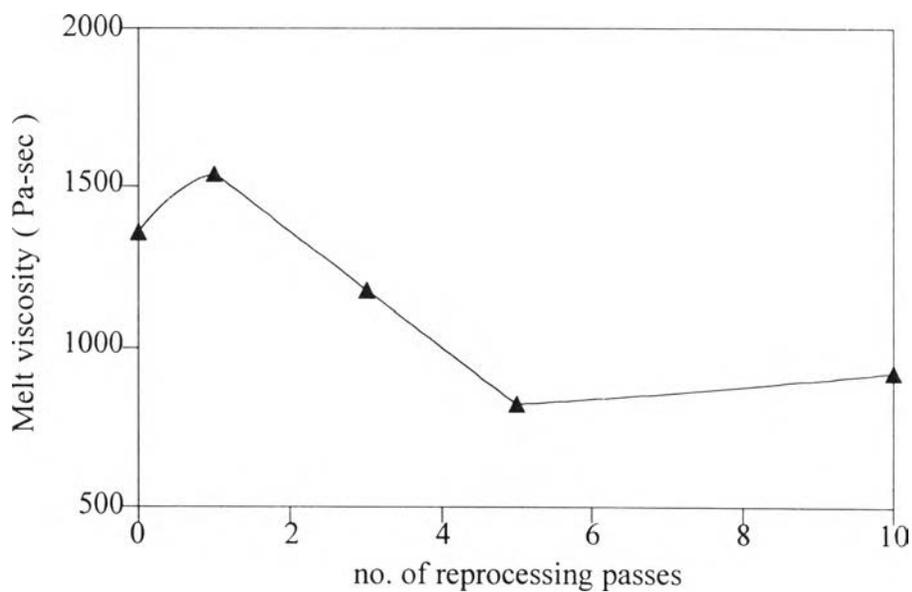
Figure 3.1 Density of reprocessed PEI .

Figure 3.2 Melt viscosity of reprocessed PEI by capillary rheometer at 355 ^{o}C and shear rate 59.06 sec $^{-1}$.

An increase in melt viscosity may be caused by a decrease in molecular weight as investigated in previous work of Shriver et al. [1994] on reprocessing of polycarbonate an amorphous engineering thermoplastics. An increase in melt index indicated material degradation and a decrease in molecular weight was found with the number of reprocessing passes.

A similar result was observed for nylon. For crystalline polymers such as nylon density may be used as a measure of crystallinity. The relationship for nylon 6,6 is [Brandrup and Immergut, 1989] :

$$\text{percentage of crystallinity} = 830 - \frac{900}{\text{density}} \ . \tag{3.1}$$

The density and corresponding percentage of crystallinity calculated from equation 3.1 is shown in Figure 3.3. The result was in agreement with the density of 1.14 g/cm^3 reported by Collyer [1990]. The initial increase in crystallinity indicated an increase in packing until the third reprocessing pass. After that, it slightly decreased due to the slight reduction in chain packing. Normally thermal degradation can have a major impact on the quality of nylon 6,6 [Whelan, 1994]. Previous work on re-use of nylon by Nightingale [1976] showed a substantially constant relative molecular weight after four extrusion reprocessing passes. The amount of degradation was negligible. But the ten reprocessing passes of this work may have a residence time long enough to induce some changes in percentage of crystallinity due to thermal degradation.
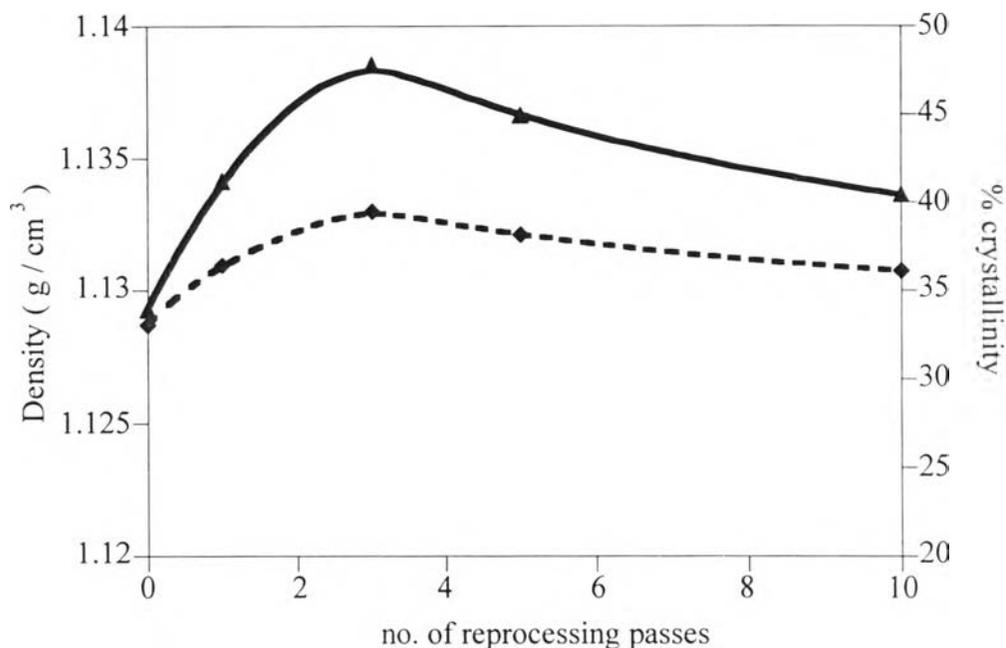
Figure 3.3 Density and % crystallinity of reprocessed nylon

——▲—— density   --◆-- % crystallinity.

The observed density of reprocessed POM (Figure 3.4) was reasonable agreement with the density of 1.420 g/cm^3 reported by Brandrup and Immergut [1989]. The nearly constant density implied that the POM retained a constant degree of crystallinity after reprocessing. It was also indicated a constant degree of crystallinity. The POM used in this work, Delrin 500, was a commercial product which is modified to prevent thermal unzipping and thermo-oxidation. A possible degradation mechanism of Delrin is thermal chain scission of the - CH_2 - O - bond at the temperatures above 270 °C [Rubin, 1990] which is much higher than the reprocessing temperature (175 °C). Nevertheless, some thermo-oxidation of the backbone, leading to chain scission and subsequent reduction in molecular weight by depolymerization process may occur. A decrease of molecular weight was

observed from melt flow index (MFI) measurements (Figure 3.5). The relationship between MFI and molecular weight of POM can be expressed as follow [Brandrup and Immergut, 1989] :

$$MFI = 1.30 \times 10^{18} \times MW^{-3.55} \quad . \tag{3.2}$$

The change of molecular weight was slight (from 74.833 to 73.906). Such depolymerization may occur in the small extent which did not affect on the crystalline structure of POM by density measurement.
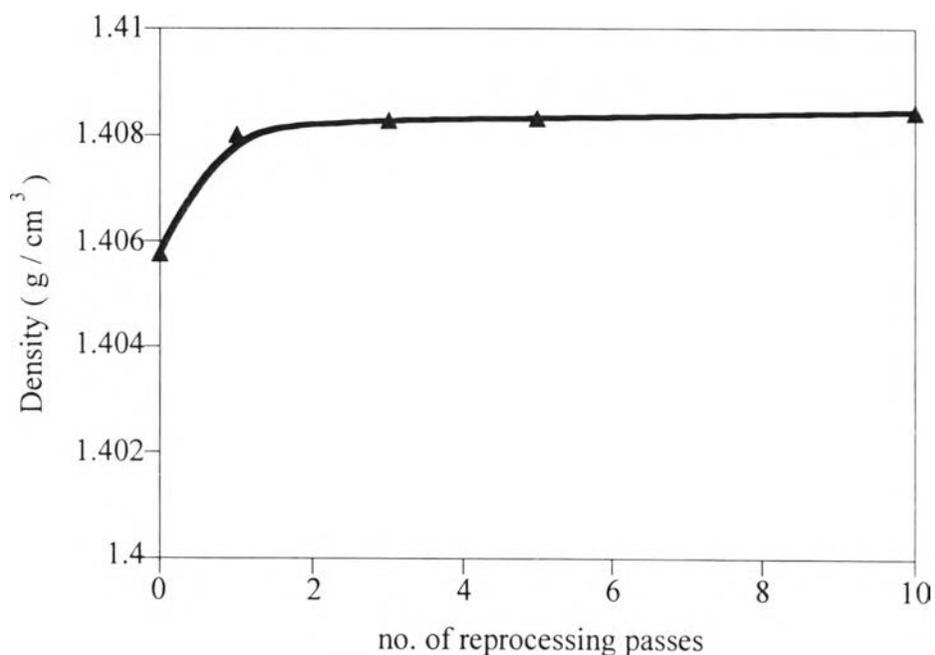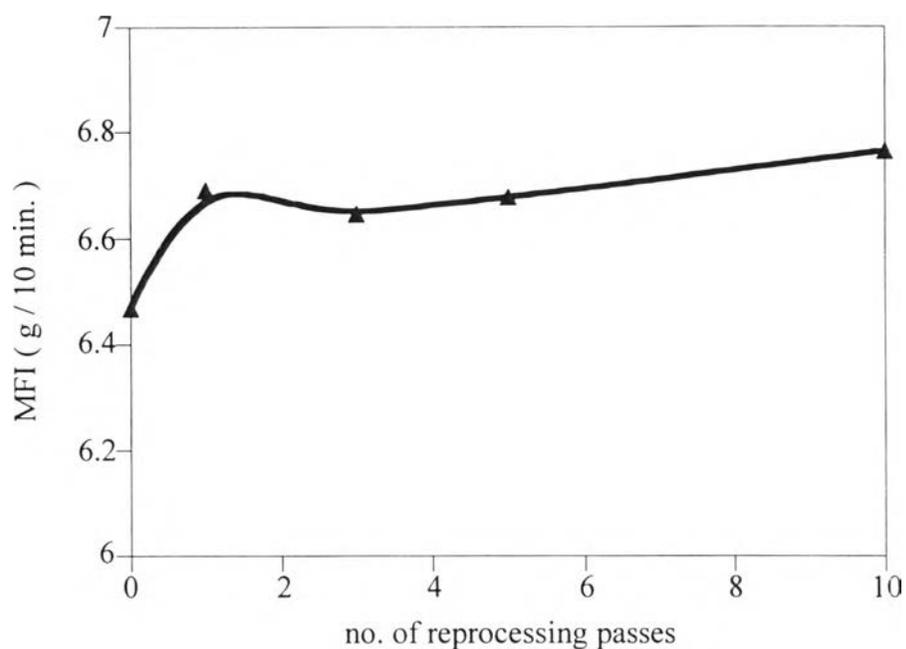

Figure 3.4 Density of reprocessed POM.

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Figure 3.5 Melt flow index of reprocessed POM.

3.2   Effects on Transition Temperature

One of the important characteristics of polymeric materials are the transition temperatures. The first order transition is a melting transition T_m which is the characteristic of the crystalline phase of polymer. The second order transition is the glass transition temperature, T_g which is the characteristic of the amorphous phase of polymer. The T_gs are sensitive to various parameters.   In the semicrystalline polymer the steric constraints imposed by crystalline regions on neighboring, otherwise-mobile polymer segments can result in an increase in T_g [Brandrup and Immergut, 1989]. The T_gs of polyimides are strongly influenced by both intramolecular (chain mobility) and intermolecular (chain packing) factors [Fawcett, 1991]. The aromatic structure of PEI restricts chain mobility, giving a high T_g. POM

molecules have a short backbone -C-O- bond which pack closely together resulting in a high melting point [Brydson, 1982]. While POM is highly crystalline the flexible ether linkage results in a relatively low T_g. In general the T_g will increase with increasing molecular weight, crystallinity and entanglement density.

The melting transition of polymer indicates the crystallinity of polymer. At the melting temperature T_m, the dissociation of the bonds between molecules in the crystal requires a specific energy, the heat of fusion, H_f. The area under the melting endothermic peak on DSC thermogram corresponds to the H_f of polymer. The overall crystallinity of a polymer can be assessed from H_f. The percentage of crystallinity can be calculated if known the theoritical H_f of 100 percentage of crystallinity of the same polymer. The relationship can be expressed as equation 2.1. Therefore, the change of H_f of sample indicates the change in degree of crystallinity and subsequently the structure and properties of polymer.

3.2.1 Effects on Glass Transition Temperature

The DSC thermogram of PEI (Figure 3.6) shows only a T_g of the polymer around 217 °C, suggesting a completely amorphous structure. This is in agreement with the value of 215 °C reported by Whelan [1994]. The decrease in T_g of reprocessed PEI is shown in Figure 3.7. This observation is consistant with the study by Hoyle and Anzures [1991] on the decrease in T_g by photodegradation of some polyimides. The properties were not significantly changed in the early reprocessing passes. By the tenth pass a decrease in properties was clearly observed.
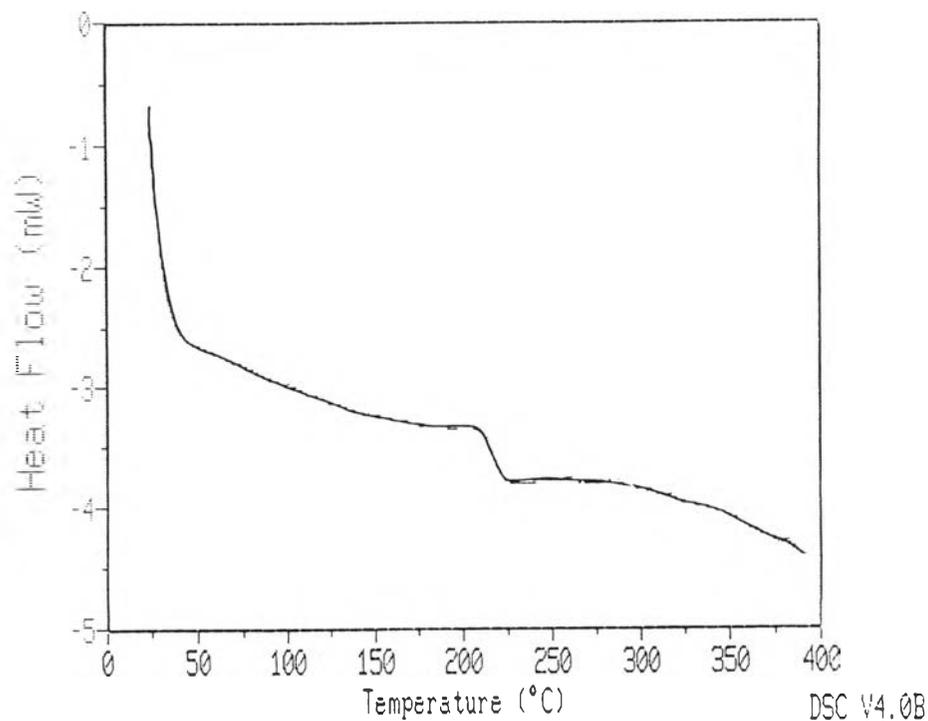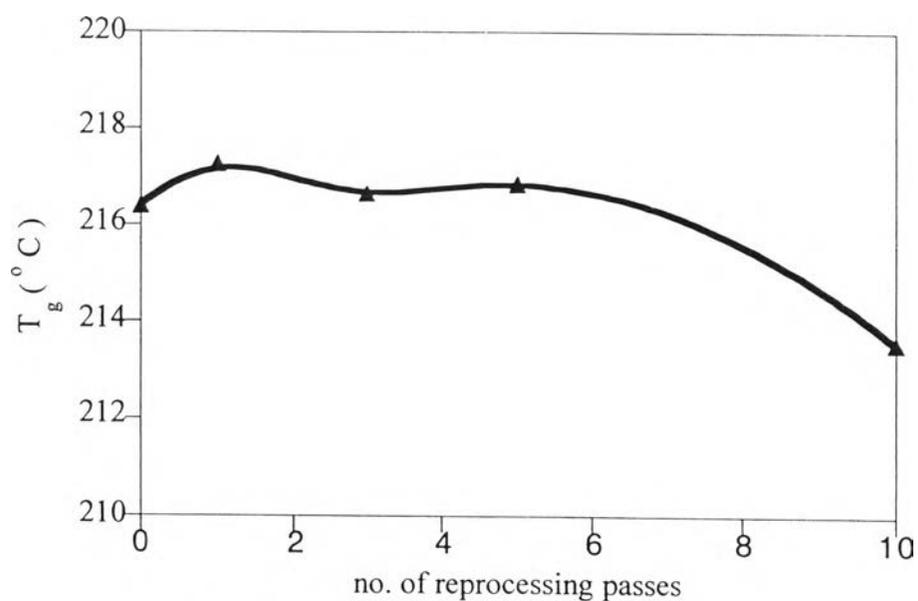
Figure 3.6 DSC thermogram of PEI.

Figure 3.7 T_g of reprocessed PEI.

The lower T_g showed the higher mobility of the amorphous

entangled chains. The high temperature induced the disentanglement of chain, the looser entanglement network the higher chain movement. The disentanglement also leads to the reduction of viscosity, as shown in Figure 3.2. A decrease in molecular weight of an amorphous engineering thermoplastics after reprocessing was found by Shriver et al. [1994] suggesting degradation of polymer during processing. Hence, the change in T_g of reprocessed PEI may be caused by polymer degradation.

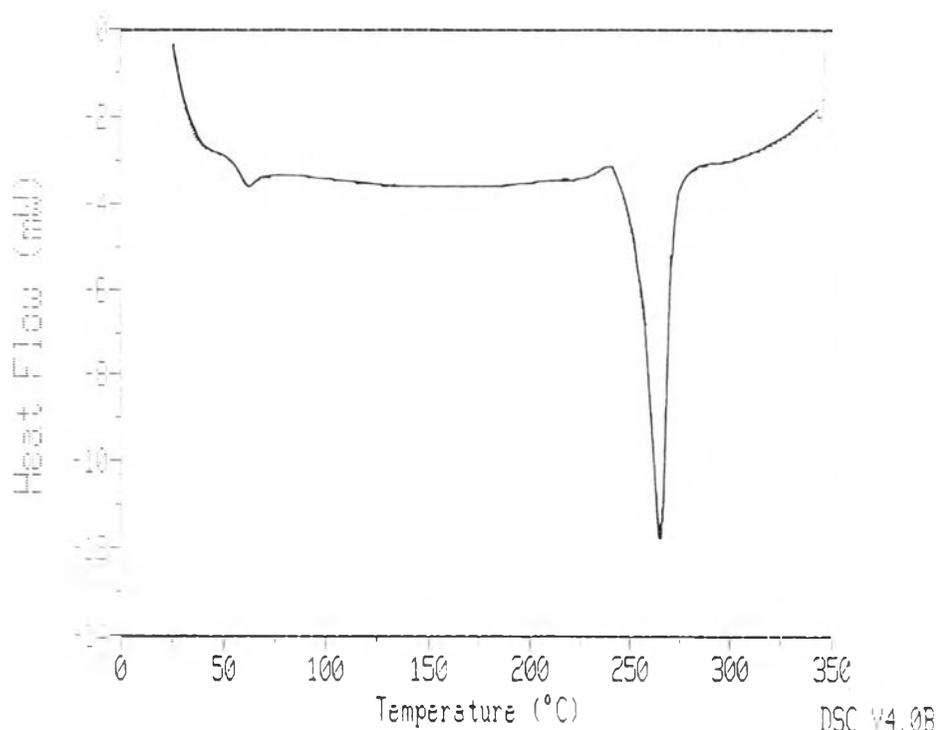The DSC thermogram of nylon shows in Figure 3.8.

Figure 3.8 DSC thermogram of nylon.

The thermogram for nylon 6.6 showed both transitions, a T_g at about 52 °C and melting endothermic peak at about 270 °C. These are in agreement with T_g of 50 °C and melting point of 260-265 °C reported by Brandrup and Immergut [1989]. The T_g was nearly constant (Figure 3.9)

through the third pass, in agreement with Nightingale [1976]. The extent of degradation was evidently negligible. The slight decrease of T_g after third pass showed the more significant of changing in structure on reprocessing. In the study of Wyzgoski and Novak [1992] a change of the spherulites into a smaller size after reprocessing was observed. The smaller crystalline region leads to the lower restriction to the mobility of polymer chains, subsequently decrease in T_g.
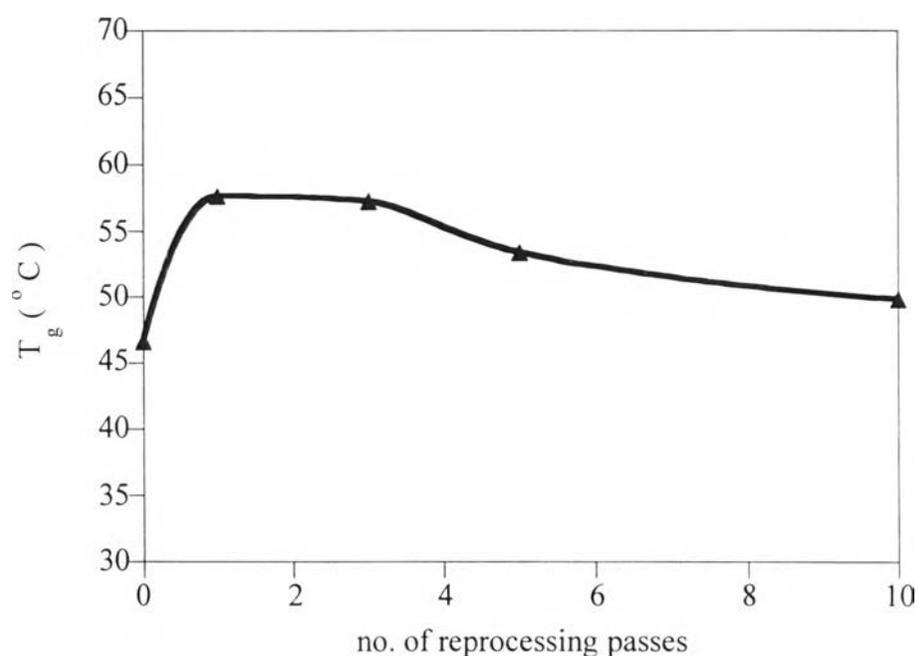

Figure 3.9 Tg of reprocessed nylon.

For POM [Domininghans, 1993], the low T_g at approximately -73 °C was difficult to measure. The scanning DSC thermogram from room temperature up to its melting point did not include its T_g range. So, the DSC thermogram of POM showed only the melting endothermic peak about 165-170 °C which agreement with melting point of 175 °C reported by Alger [1989] (Figure 3.11).

3.2.2 Effects on Heat of Fusion

The melting point of nylon was around 263-266 °C in DSC thermogram. The heat of fusion of the melting transition decreased as a function of reprocessing passes (Figure 3.10). The percentage of crystallinity calculated from H_f by equation 2.1 was lower than the one calculated from density from equation 3.1 but the values from the both methods showed the same trend. This result revealed the degradation of nylon during very long periods of reprocessing at 285 °C.
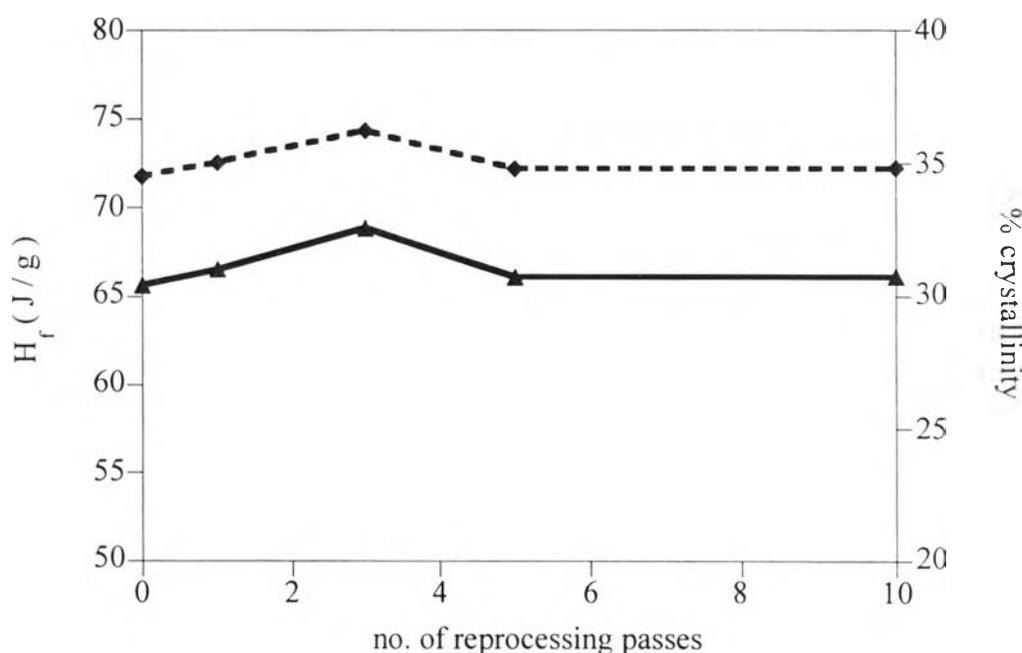

Figure 3.10 Hf and % crystallinity of reprocessed nylon

▲ H$_f$ ◆ % crystallinity.

The H_f of reprocessed POM is shown in Figure 3.12. The observed H_f was lower than the H_f of 166.3 J/g observed by Kumar et al. [1995]. Like the result of density, the H_f and percentage of crystallinity were nearly constant. The reprocessing was unaffected on the degree of

crystallinity of POM although a decrease in molecular weight was detected from the MFI measurement. In agreement with Stivala and Patel [1994] the corresponding degree of crystallinity calculated by the heat of fusion was higher than virgin POM while the reduction of molecular weight was observed.
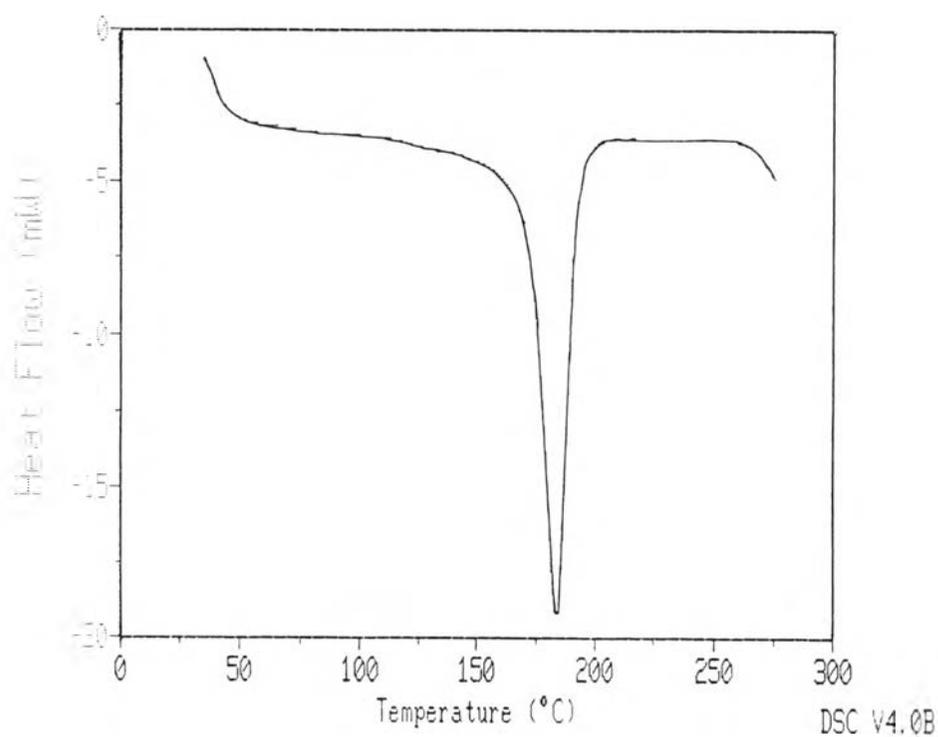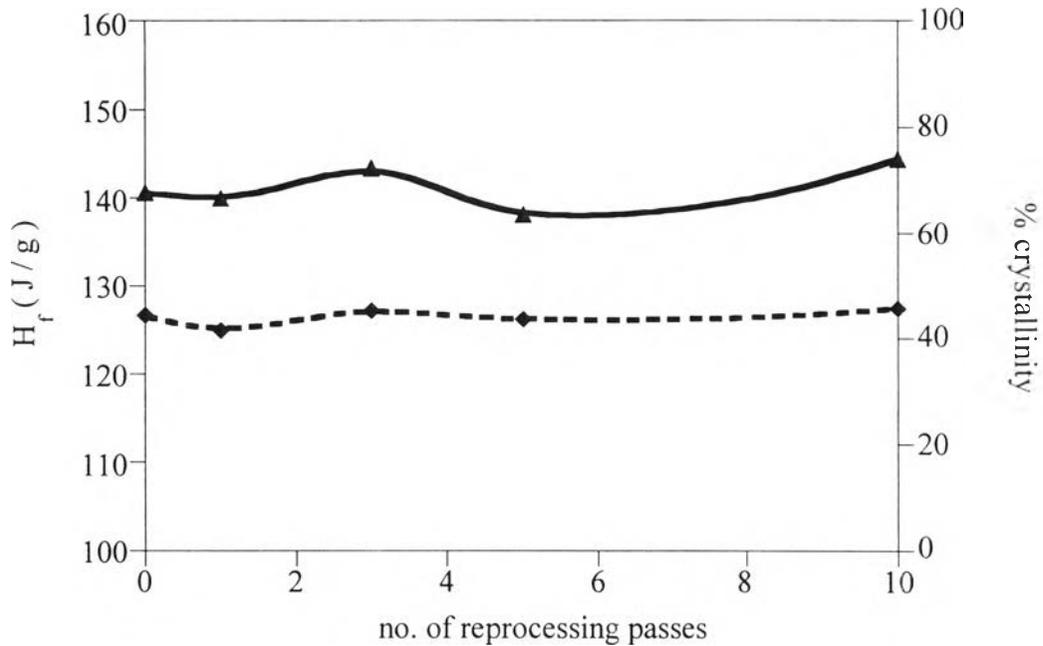

Figure 3.11 DSC thermogram of POM .

Figure 3.12 H_f and % crystallinity of reprocessed POM

———▲—— Hf   --◆-- % crystallinity.

3.3   Effects on Thermal Stability

Engineering plastics are polymers which possess good properties, especially resistance to high temperatures. TGA is a useful technique to determine the thermal stability of materials. Testing under oxygen atmosphere, can determine the thermo-oxidative stability of polymers. The thermal stability of polymers is depending on polymer structures. The higher molecular weight species generally exhibit better thermo-oxidative stability than their corresponding lower molecular weight species [Wilson et al., 1990].

The TGA thermogram indicates the weight loss while the polymer undergoes thermal degradation. The onset temperature indicates the

temperature at which the polymer start to degrade. Polymers with a lower thermal stability show a lower onset temperature. The half life is the temperature at which the polymer loses half of its weight. A higher half life temperature indicates higher thermal stability which is caused by a higher molecular weight or a more heat resistant structure. The reaction interval is defined as the difference between the onset and the end degradation temperature [Wendlant, 1986]. The reaction interval indicates the degradation temperature range which depends on the various molecular weights contained in the polymer. From the different heat stability of different molecular sizes, the range of the reaction interval shows the range of molecular sizes in the polymer.

The TGA thermograms of PEI, nylon and POM were shown in Figure 3.13.
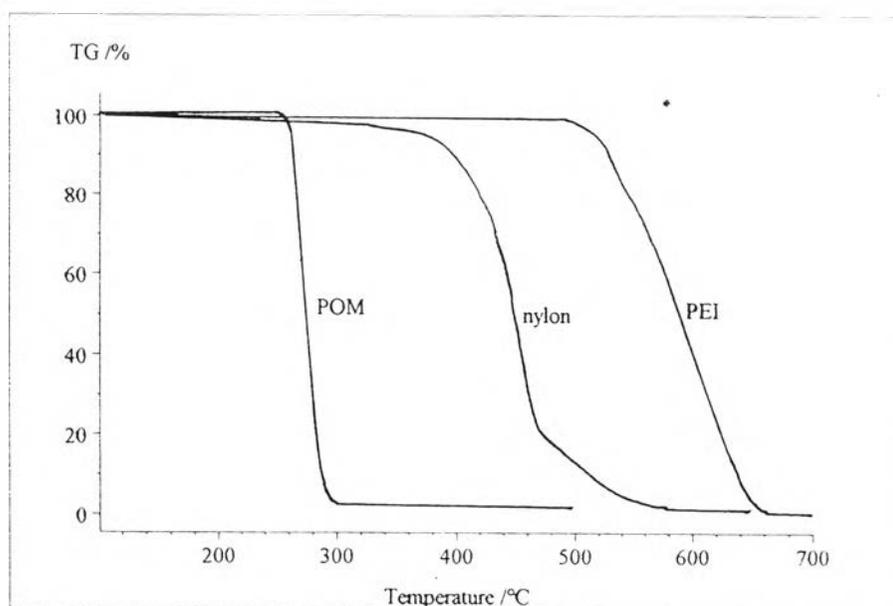

Figure 3.13 TGA thermogram of POM, nylon and PEI.

TGA thermograms of PEI showed a single-stage degradation with 100 % weight loss over 700 °C. The PEI was thermally stable up to 500 °C, in

agreement with the 1% weight loss at 446 °C in air reported by Wilson et al. [1990]. This showed the high temperature resistance of PEI. The onset and half life temperatures of reprocessed PEI are shown in Figure 3.14.
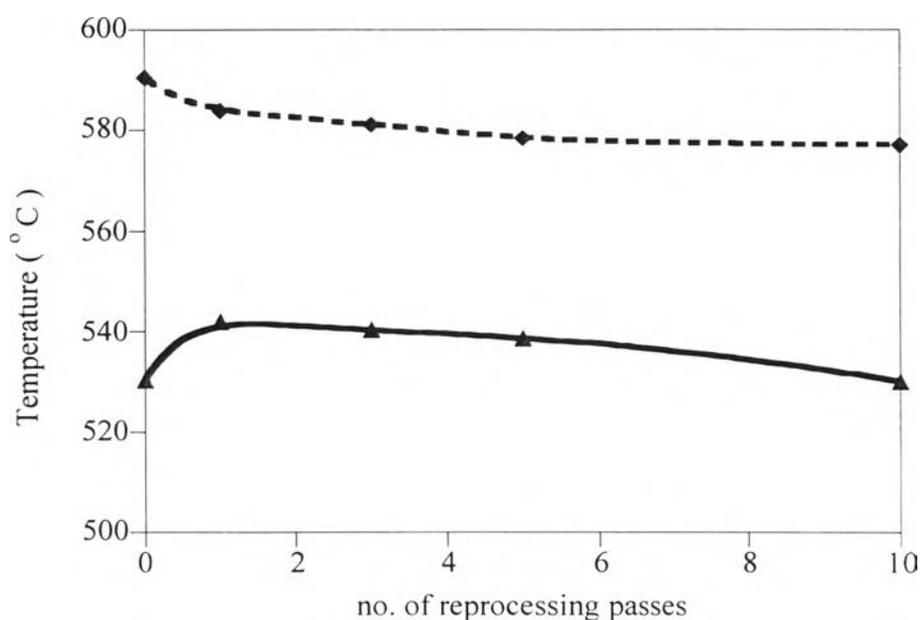

Figure 3.14   Onset and half life temperature of reprocessed PEI

━▲━ onset   ‐‐◆‐‐ half life.

The slight decrease in onset temperature indicated the presence of lower stability molecules in the reprocessing PEI. These molecules started to degrade earlier. The half life temperature also showed a slight decrease in thermal stability of reprocessed PEI. The excellent thermal properties of PEI are provided by aromatic imide units of the backbone. The decrease in thermal-oxidative stability was consistent with Hoyel and Anzures [1991]. The iooser entanglement network or decrease in molecular weight of the polymer were the result of reprocessing. An increase in reaction interval of the tenth pass showed the strong effect of reprocessing than the other passes (Figure 3.15).
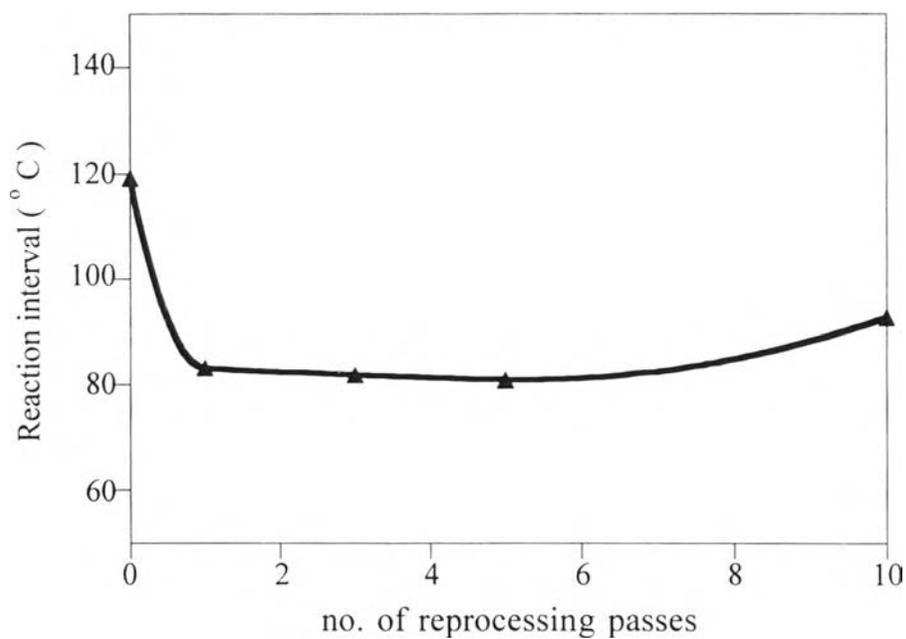
Figure 3.15 Reaction interval of reprocessing PEI.

A double-stage degradation was investigated from the TGA thermogram of nylon with 100 % weight loss above 600 °C. The first degradation step started at about 420 °C and 475 °C for second step. The onset and half life temperature of reprocessed nylon are shown in Figure 3.16. The reaction interval is shown in Figure 3.17.
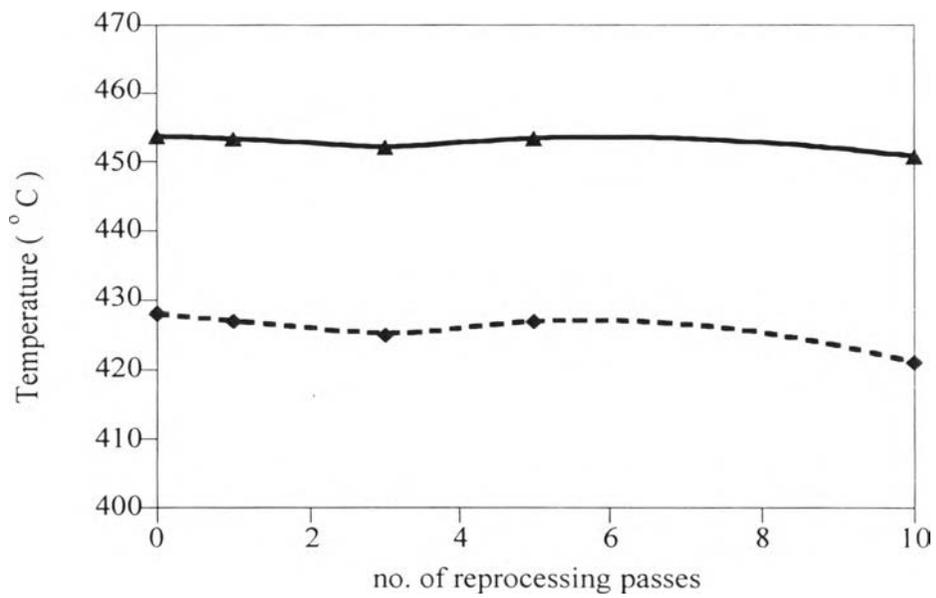
Figure 3.16 Onset and half life temperature of reprocessed nylon
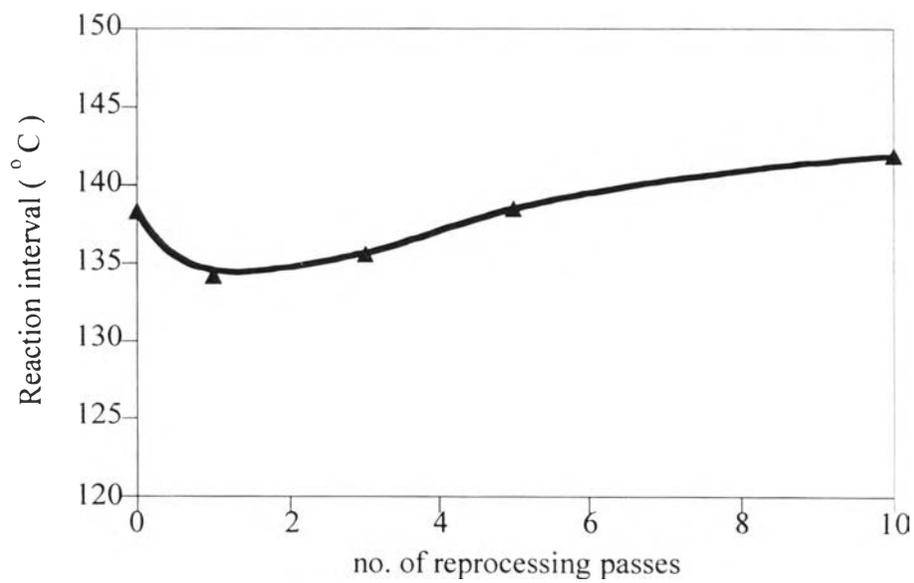
━━▲━━ half life   ━ ━◆ ━ ━ onset .

Figure 3.17 Reaction interval of reprocessed nylon.

The results of the TGA thermogram indicated that thermal stability of reprocessing nylon was nearly constant. The onset temperature of 420 °C was in agreement with Rubin [1990]. A slight decrease was observed after the fifth pass. From previous work of Wyzgoski and Novak [1992] the smaller spherulite size was observed after reprocessing the nylon (Figure 3.18). The smaller molecular size has a lower thermal stability than the larger one [Wilson et al., 1990]. So, the decrease in thermal stability was detected by TGA. This data showed the agreement with the result of DSC and density measurement. Reprocessing over three passes affected the structure of nylon.

A single-stage degradation of POM was observed in the TGA thermogram. This is in agreement with onset temperature of 259.5 °C observed by Stivala and Patel [1994]. The onset and half life temperature of reprocessed POM are shown in Figure 3.20. The narrow reaction intervals are shown in Figure 3.21. The results showed a gradual decrease in the thermal stability of reprocessed POM. The results agreed with the result of MFI that the degradation of POM into a lower molecular weight occurred during reprocessing. The thermo-oxidation of POM resulted in depolymerization of the chain to a lower molecular weight which had lower thermal stability. The decrease in half life temperature also indicated an overall smaller molecular size. The smaller molecules by depolymerization were still linear and could be packed into the crystalline structure. But the lower molecular weight of POM was sensitive to the high temperature. The smaller size molecules are lower in thermal stability. The lowering onset temperature POM was also observed by Stivala and Patel [1994]. The result indicated a reduction in the molecular weight of reprocessed POM.
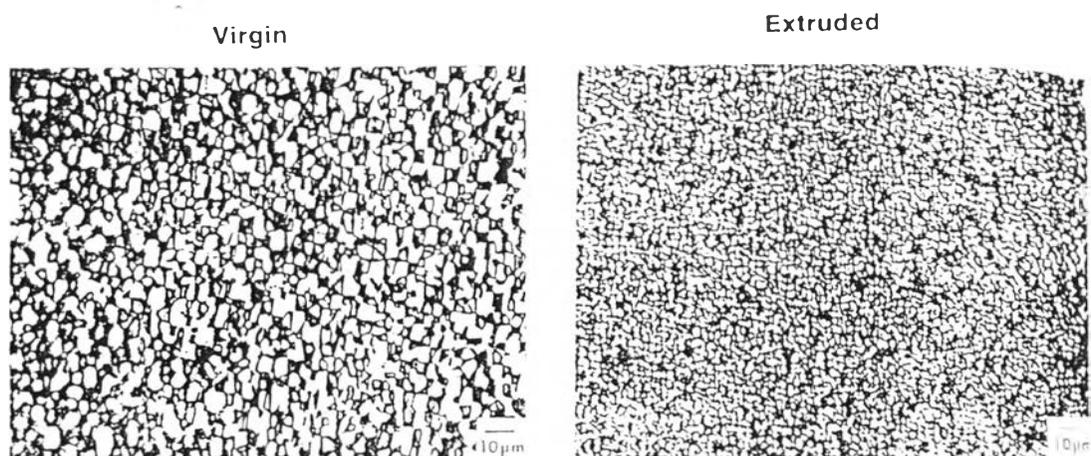
Virgin | Extruded

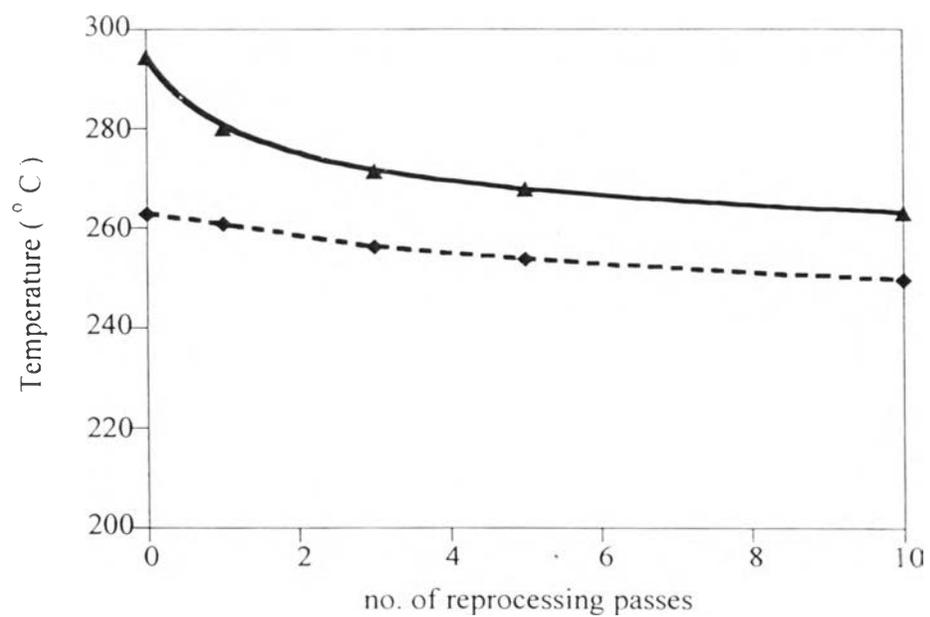Figure 3.18 Optical photomicrographs of reprocessed nylon.

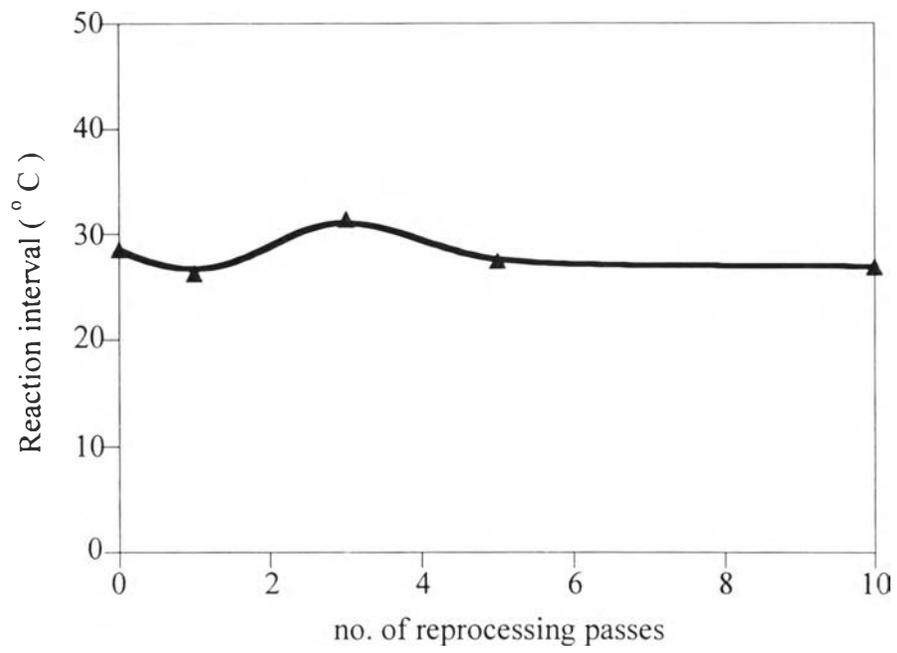Figure 3.19 Onset and half life of reprocessed POM

——▲—— half life   --◆-- onset .

Figure 3.20 Reaction interval of reprocessed POM.