

## CHAPTER VIII

### CONCLUSIONS

#### 1. Isothermal melt crystallization and melting behavior of PET, PTT, and PBT

Isothermal crystallization study indicated that four kinetic equations; namely the Avrami, Tobin, Malkin, and Urbanovici-Segal macrokinetic models; were found to give reliable kinetics results. It is was found that the quality of each, judging from the values of the  $r^2$  parameter, in describing the isothermal crystallization data of these three polyesters with the Urbanovici-Segal, Malkin, and Avrami were very good when compare with Tobin model which was not good fitting obtained.

All of the crystallization rate parameters (i.e.  $t_{0.5}^{-1}$ ,  $K_a$ ,  $K_b$ ,  $c_1$  and  $K_{us}$ ) were found to very sensitive to changes in the crystallization temperature. Within the crystallization temperature range studied (i.e.  $180 \leq T_c \leq 208$  °C) for these three polyesters, the values of the rate parameters were all found to increase with decreasing temperature, due to the fact that these polyesters crystallizes faster at lower temperature than that higher temperature.

For WAXD patterns of isothermally crystallized PTT, there is no shift in the peak position ( $2\theta$ ) in diffraction pattern, indicating that the crystal unit cell of PTT does not change with crystallization temperature. But from the relative ratio of the integrated intensities under the crystalline peaks to the integrated total intensities integrating, found that the WAXD degree of crystallinity  $\chi^{WAXD}$  increased with increasing crystallization temperature.

Subsequent melting endotherms of these polyesters after isothermal crystallization at various  $T_c$  values exhibited either double- or triple-melting peaks, depending on the  $T_c$  studied. In case of PTT, at  $T_c < 186^\circ\text{C}$ , it showed double melting peaks (low and high melting peaks) of the primary and secondary crystallization. But at  $T_c \geq 186^\circ\text{C}$ , a minor melting peak of the recrystallization during heating process was observed. The high melting endotherm immediately disappeared at  $T_c > 196$  but minor and low melting peaks gradually developed. The low and high melting peaks should be

concerned with the primary crystallization that two populations of lamellar stack were formed during the primary crystallization, resulting in the dual melting behavior.

The analysis of the observed  $T_m$  of the primary crystallites and the corresponding  $T_c$  according to linear Hoffman-Weeks extrapolation gave  $T_m^o$  values for PET, PTT, and PBT of ca. 270.1, 243.6 and 235.4°C, respectively. For nonlinear Hoffman-Weeks extrapolation,  $T_m^o$  of PET, PTT, and PBT were found to be ca. 323.9, 277.6, and 262.3°C, respectively.

## 2. Non-isothermal melt crystallization kinetics of PET, PTT, and PBT.

The non-isothermal crystallization exotherms of these polyesters showed that the temperature at 1% relative crystallinity, the peak temperature, and the temperature at 99% relative crystallinity all shifted towards lower temperatures with increasing cooling rate. The half-time of crystallization was found to decrease with increasing cooling rate, suggesting that these polymers took a shorter time to crystallize when the cooling rate increased. Between the Avrami and Tobin macrokinetic models, the Avrami model was found to provide a much better fit to the experimental data of these polyesters than the Tobin model.

The Ozawa model was found to provide a fair description to the experimental data of these polyesters, with the Ozawa exponent  $n_o$  being found to range from 2.7 to 4.5, which is quite comparable to the Avrami exponent  $n_a$  obtained. All of the bulk crystallization rate parameters (i.e.,  $k_a$ , and  $k_t$ ) of these polyesters were found to be an increase function with the cooling rate, suggesting that these samples crystallized faster with increasing cooling rate.

The ability of PET, PTT, and PBT to crystallize from the melt under a unit cooling rate can be determined by comparing the values of the Ziabicki's kinetic crystallizability  $G$ , which were found to be ca. 1.1, 1.5, and 1.7°C s<sup>-1</sup> for PET, PTT, and PBT, respectively. Lastly, the effective energy barrier governing the non-isothermal melt crystallization of these polyesters, based on the values provided by the differential

isoconversional method of Friedman, was found to increase with increasing relative degree of crystallinity. Moreover PBT provides the lowest activation energy.

### 3. Miscibility and crystallization behavior of PTT/PET and PTT/PBT blends

Miscibility in amorphous phase of PTT/PET and PTT/PBT blends can be determined by a single glass-transition temperature that appeared at the intermediate temperature between those of pure polymers. The dependence of  $T_g$  upon composition of the blends was predicted by Fox and Gordon-Taylor's equation. For PTT/PET blends, the Gordon-Taylor's equation provided a satisfactory description to the experimental data, whereas the measured  $T_g$  of PTT/PBT blends obeyed satisfactory with the Gordon-Taylor's equation ( $k=6.89$ ) only at  $W_{PTT} > 0.6$ .

The crystallization behavior of PTT/PET and PTT/PBT blends was studied using the cold crystallization temperature ( $T_{cc}$ ) and the crystallization temperature from melting state ( $T_c$ ). As increasing PTT content in the blends, the  $T_{cc}$  of PTT/PET blends tended to appear at lower temperature, whereas the  $T_{cc}$  of PTT/PBT blends was found to presence at higher temperature. Implying that the crystallization from glassy state of these blends were enhanced by increasing the component that has higher crystallization rate (i.e., PBT > PTT > PET).

In case of the crystallization from melting state, for PTT/PET blends, the minor component retarded the major component to crystallize from the melting state. In other words, the crystallization rate of the major component in the blend decreased with increasing the minor component. However, for PTT/PBT blends showed that the  $T_c$  of the PBT-rich blend decreased with increasing PTT content. Implying that PTT component in the blends inhibited or retarded PBT to crystallize.

Moreover, these PTT/PET and PTT/PBT blends also showed the melting point depression, that the melting point of each component in the blends decreased with increasing the content of the other component.

The presence of the characteristic X-ray peaks of pure polymers in the blends without the presence of new peaks in diffraction pattern inferred that each component

formed its own crystal phase and there was no co-crystallization in the blends under our experimental condition.

The degree of crystallinity of each component in the blends was found to decrease with increasing the content of the other component. The lowest total degree of crystallinity of these blends was found in 50PTT/50PET and 60PTT/40PBT blends.

Lastly, the steady rate sweep test showed that the zero shear viscosity values of PTT/PET blends decreased as increasing PTT content. It reached a minimum at 50% PTT and increased as increasing PTT content. For the dynamic measurements, the blends showed similar value of complex viscosity at all frequencies in our experiment. The complex viscosity,  $\eta^*(\omega)$  of these blends decreased as increasing PTT content and it provided the negative deviation from the log-additivity rule. Implying that this is the typical for miscible polymer blends. In case of PTT/PBT blends, the shear viscosity showed that these blends behaved as a Newtonian fluid with low shear rates studied.