CHAPTER IX
CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

9.1.1 Multiple Melting Behavior in Isothermally Crystallized Poly(trimethylene terephthalate)

Subsequent melting thermograms of PTT after isothermal crystallization at various T_c values exhibited either double- or triple-melting endotherms, depending on the T_c studied. The subsequent melting endotherms for PTT samples isothermally crystallized PTT ranging from 182 to 215°C exhibited either triple (at temperatures lower than ca. 194°C), double (at temperatures greater than ca. 194°C), and single(at temperatures greater than ca. 211°C). These peaks were denoted peaks I, II, and III for low-, middle-, and high-temperature melting endotherm, respectively. For triple melting phenomenon, it was postulated that the occurrence of peak I was a result of the melting of the primary crystallites, peak II was a result of the melting of recrystallized crystallites, and peak III was a result of the melting of the recrystallized crystallites of different stabilities. The result from WAXD technique confirmed that there is no discernible difference in these crystallographs and the unit cell unchanged. Lastly, analysis of the melting temperature of the primary crystallites according to the linear and non-linear Hoffmann–Weeks extrapolative methods to obtain the equilibrium melting temperature $T_m°$ of this PTT resin was conducted. It shown that the value of $T_m°$ was strongly dependent on the choosen $T_m–T_c$ data. According to the linear and non-linear Hoffmann–Weeks extrapolation, the $T_m°$ values for PTT were found to be ca. 243.6 and 270.1°C, respectively. It sholud be noted here that $T_m°$ value proposed fall in $T_m - T_c$ data ranging from 188 to 208°C which shown the highest value of r^2.

9.1.2 Effects of Crystalline and Orientational Memory Phenomena on Isothermal Bulk Crystallization and Subsequent Melting Behavior of Poly(trimethylene terephthalate)

In this present contribution, the effect of prior melt-annealing temperature T_f on the subsequent isothermal crystallization kinetics, crystalline structure, and subsequent melting behavior of neat and sheared poly(trimethylene terephthalate) (PTT) samples were investigated using differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) techniques in order to illustrate the effects of crystalline and orientational memory phenomena on subsequent isothermal crystallization and subsequent melting behavior of PTT. On partial melting, the DSC experiment suggested that the choice of the T_f used to melt the samples played an important role in determining their bulk crystallization rates, in which the bulk crystallization rate parameters studied (i.e., $t_{0.5}^{-1}$, K_a, and K_{us}) were all found to decrease monotonically with increasing T_f. The decrease in the values of these rate parameters with T_f continued up to a critical T_f value (i.e., ca. 275°C for neat PTT samples and ca. 280°C for PTT samples which were sheared with shear rates of 92.1 and 245.6 s^{-1}), at which point the values of the rate parameters reached a minimum and then slightly increased afterwards. The slight increase in the values of the rate parameters after a critical T_f value was postulated as a result of the reduction in the molecular weight averages of the samples due to thermal degradation, which caused the bulk crystallization rates to slightly increase. The WAXD results suggested that neat PTT samples which were subject to different T_f's crystallized into the same triclinic unit cell; however, the apparent degree of crystallinity was found to slightly increase with increasing T_f used to melt the samples. Lastly, the subsequent melting behavior suggested that the T_f used to melt the samples had no effect on the peak positions of both low- and middle-temperature melting endotherms observed and that the observed peak values of these endotherms for all of the neat and sheared samples studied were almost identical.

9.1.3 Quiescent and Shear-induced Cold Crystallization in PTT

The non-isothermal crystallization exotherms of sheared samples showed that the peak temperature of cold crystallization was shifted towards lower temperatures with increasing shear rate. The effect of shearing time was found to have less effect on the crystallization behavior. The shearing temperature was found to have a effect on the shift of T_{cc} which lower shearing temperature shown greater shifting of T_{cc}. The effect of molecular orientation from shearing step of cold crystallization would be losed when the samples were remelted before second quenching both low and high shear rate region. In non-isothermal cold crystallization, the induction time t_i and bulk crystallization rate parameters (i.e., $t_{0.5}^{-1}$, K_a, K_t, K_{ur}) from non-isothermal crystallization of shear treated samples were lower than that of shear untreated sample. In isothermal mode, induction time t_i, crystallization half-time $t_{0.5}$ and exponent of each model (i.e. n_a, n_t, n_{ur}) of shear treated samples were found to be lower than that of shear untreated sample while bulk crystallization rate parameters (i.e., $t_{0.5}^{-1}$, K_a, K_t, K_{ur}) shown higher values. As shear rate increased, the value of degree of orientation $h(T, \tau)$ tended to increase sharply at low shear stress region and gradually increased further as shown less dependent of shear at high shear stress region. The shear treated sample prepared at lower shearing temperature shown the trend of higher $h(T, \tau)$. The peak temperature of cold crystallization T_{cc} was shifted to the higher temperature as heating rate increased both sheared and non-sheared sample. The value of $h(T, \tau)$ was found to be decreased as shear rate increased. The effective activation energy ΔE was found to be increased with increasing shear rate for both Kissinger and Takhor analysis. The values of ΔE obtained from Friedman method (at melt conversion = 0.5) gave much higher values than those from Kissinger and Takhor method. The values of ΔE based on Friedman method of shear treated sample were lower than that of shear untreated sample after melt conversion = 0.5.

9.1.4 Quiescent and Shear-induced Melt Crystallization in PTT

In-situ shear-induced isothermal melt crystallization was investigated using cone and plate rheometer. At the same crystallization temperature , the induction time was found to be decreased as increased shear rate. As shear stress increased, the temperature shift was increased exponentially. Shear stress applied during crystallization can also increase bulk crystallization rate and shift peak temperature to higher temperature. For study sheared sample from capillary rheometer, PTT sheared sample prepared at lower shearing temperature gave a higher rate of crystallization than that at higher shearing temperature and neat PTT samples. The position of melt crystallization peak was found to be located at higher temperature as shear rate increased at a fixed cooling rate. The concept of temperature shift from in-situ shear-induced isothermal melt crystallization can also be applied to non-isothermal crystallization of sheared sample. The value of temperature shift was increased and quite constant as shear rate increased. The activation energy required for transportation of molecular segment from the molten state to the crystal growth surface based on Friedman method of shear treated samples were found to be lower than that of shear untreated sample at all melt conversion calculated.

9.2 Recommendations

The shear-induced crystallization study in future work, polarizing optical microscope is the suitable apparatus to investigate the morphology of shear treated samples which are prepared from a cone and plate rheometer and a capillary rheometer. The observation of the evolution of storage and loss modulus using the same method of *in situ* shear induced isothermal crystallization should be carried out carefully about the choice of isothermal crystallization temperature and the frequency used. The shear-induced crystallization in the blend system are also an interesting point to follow crystallization behavior of shear treated samples. Moreover, study shear-induced crystallization in the real polymer processing such as injection molding, extrusion etc. are also a good point to study.