ISOTHERMAL CRYSTALLISATION AND MISCIBILITY OF POLY(ε-CAPROLACTONE)(PCL) / POLY(VINYL FORMAL) (PVF) BLENDS

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ISOTHERMAL CRYSTALLISATION AND MISCIBILITY OF POLY(ε-CAPROLACTONE)(PCL) / POLY(VINYL FORMAL) (PVF) BLENDS

By

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ABSTRACT

Polymer blends consists of poly(ε-caprolactone) (PCL) and poly(vinyl formal) (PVF) were prepared by solution casting method. The crystallisation and melting behaviour of PCL/PVF blends were investigated by differential scanning calorimetry (DSC) experiments. The degree of crystallinity, X_c of PCL decreased gradually, up to 40 % PVF content and then decreased drastically with further increase of PVF content in the blends. The equilibrium melting temperature, T_m^o for pure PCL was estimated from Hoffman-Weeks plot. The effects of crystallisation temperature, T_c and the blend compositions on the crystallisation rate of PCL in PCL/PVF blends were investigated. The crystallisation rate decreased with increasing T_c and also increasing PVF content in the blends. The PCL/PVF blends were reported to be immiscible based on dilute solution viscometry (DSV) study. Krigbaum-Wall, Catsiff-Hewett, Sun, Jiang-Han and also Garcia methods were used to determine the miscibility of PCL/PVF blends.

ABSTRAK

Adunan polimer terdiri daripada poli (ε-kaprolakton) (PCL) dan poli (vinil formal) (PVF) telah disediakan dengan kaedah menuang larutan. Tabiat penghabluran dan tabiat peleburan PCL / PVF telah dikaji oleh eksperimen kalorimeter pengimbasan pembezaan (DSC). Darjah penghabluran, X_c PCL menurun secara beransur-ansur, sehingga 40% kandungan PVF dan kemudian menurun secara drastik dengan peningkatan lanjut kandungan PVF di dalam adunan. Takat lebur keseimbangan, T_m^o untuk PCL tulen telah dianggarkan daripada cara Hoffman-Weeks. Kesan suhu penghabluran, T_c dan komposisi campuran terhadap kadar penghabluran PCL dalam adunan PCL / PVF telah dikaji. Kadar penghabluran menurun dengan peningkatan T_c dan juga peningkatan kandungan PVF di dalam adunan. Adunan PCL / PVF dilaporkan tidak larut campur berdasarkan pengajian viskometri larutan cair (DSV). Kaedah Krigbaum-Wall, Catsiff-Hewett, Sun, Jiang-Han dan juga Garcia telah digunakan untuk menentukan keterlarutcampuran PCL / PVF adunan.

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Thank you.

DECLARATION

I hereby declare that the project report is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

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Date:

APPROVAL SHEET

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Yours truly,

____

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$(\mathrm{d}H/\mathrm{dt})$	Heat flow rate of samples
$(t\text{-}t_0)$	Crystallisation time
${K_A}^{1/n_A}$	Generalise rate constant
χ_{12}	Interaction parameter
$[\eta]$	Intrinsic viscosity
$1/\gamma$	Stability parameter
b	Slope of Huggins plot
c	Concentration
DSC	Differential scanning calorimetry
DSV	Dilute solution viscometry
FTIR	Fourier transform infrared spectroscopy
K_A	Generalized rate constant
K_g	Nucleation parameter
k_H	Huggins coefficient
M_n	Number average molar mass
n_A	Avrami exponent
NR	Natural rubber
η_{rel}	Relative viscosity
η_{sp}	Specific viscosity
PCL	Poly(ε-caprolactone)
PCP	Polychloroprene
PEG	Poly(ethylene glycol)

PEO	Poly(ethylene oxide)
PMMA	Poly(methyl methacrylate)
PTMS	Poly(tetramethylene succinate)
PU	Polyurethane
PVA	Poly(vinyl alcohol)
PVAc	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)
PVF	Poly(vinyl formal)
PVP	Poly(N-vinylpyrrolidone)
r	Correlation coefficient
SEM	Scanning electron microscope
t	Flow time of polymer solution
t_0	Induction period
t_0	Flow time of the pure solvent
$t_{0.5}$	Half-time of crystallisation
TA	Tannic acid
T_c	Crystallisation temperature
T_g	Glass-transition temperature
T_m	Melting temperature
T_m^o	Equilibrium melting temperature
w_PCL	Weight fraction of PCL
$X(t)$	Degree of crystalline conversion
X_c	Degree of crystallinity
$\Delta H(\infty)$	Heat generated at infinite time

$\Delta H(t)$	Heat generated at time t
ΔH_m	Enthalpies of melting
ΔH_m^o	Melting enthalpy of 100 % crystalline PCL
ΔT	Undercooling temperature
$a(\infty)$	Peaks area at infinite time
$a(t)$	Peaks area at time t

CHAPTER 1

INTRODUCTION

Chemically, a very high molecular weight material which consists of long-chain molecules, measured in hundreds of thousands is called polymer, which can also be termed as ‘macromolecules’ (Sperling, 2006). Polymer blend is mixture of two or more different polymers which physically mixed but not covalently bonded (Grulke, 1994)

A diversity of physical and chemical properties can be obtained from the constituent polymers by polymer blending (Guru, et al., 2012). Blending of polymers is a useful attempt to prepare materials with tailor-made properties (Doulabi, Mirzadeh and Imani, 2013). Over the past decades, polymer blend systems are gaining interests and concern among researchers due to the necessity for new materials in academia and industry (Feldman, 2005).

Final product properties, such as mechanical properties and thermal stability can be affected by the polymer crystallisation process (Dhanvijay and Shertukde, 2011). Crystallisation takes place during manufacturing process of the polymeric materials, thus it is important to understand the mechanism involved in crystallisation to control the final products properties (Weng, Chen and Wu, 2003). The crystallisation process for a crystalline polymer is favourable when its temperature is higher than the glass-transition, T_g and lower than the equilibrium melting point, T_m^o (Utracki, 2002). However, the rate of crystallisation will be determined by kinetics of crystallisation (Di Lorenzo and Silvestre, 1999).

Differential scanning calorimetry (DSC) is usually used in the study of crystallisation kinetics for polymers. It reflects the changes of heat capacity with temperature of the samples (Ray, 2013). DSC technique is extremely versatile and also rapid in determination of polymer crystallisation and melting properties (Long, Shanks, and Stachurski, 1995).

Isothermal crystallisation involves the crystallisation of polymer samples at a constant temperature. Avrami analysis is still most commonly practiced in the study of polymer crystallisation kinetics despites presence of other models on crystal growth kinetics (Lorenzo, et al., 2007). Avrami analysis is having easiest methodology and is most popular to acquire important parameters for isothermal crystallisation kinetics studies (Fraisse, *et al.*, 2007). Hence, the Avrami theory is used to analyse isothermal crystallisation kinetics in this study.

Polymer blends can be characterised by their miscibility. Various morphologies of the blends, ranging from single phase to multiphase systems are produced as a result from differences in miscibility. Physical properties of polymer blend are significantly depending on the miscibility of the polymers (Laukaitiene, et al., 2013).

Numerous techniques have been developed to investigate the miscibility of polymer blends which including electron microscopy, thermal analysis, neutron scattering and inverse gas chromatography. However, these methods are costly, sophisticated and time-consuming (Haque and Sheela, 2013). On the other hand, dilute solution viscometry (DSV) method is simple, fast, and inexpensive and able to provide evidence on miscibility of the polymer blend (Yilmaz, Erdenizci, and Yilmaz, 2003).

A semi-crystalline polymer, poly(ε-caprolactone) (PCL), amorphous poly(vinyl formal) (PVF) and their blends were studied in this project. The objectives in this study include:

1. To prepare PCL/PVF blends by solution casting method for DSC measurements.

2. To estimate the equilibrium melting point, $T_m°$ of pure PCL.

3. To determine the degree of crystallinity, X_c of PCL in pure state and in the blends.

4. To study the kinetics of crystallisation by isothermal crystallisation experiments. Examination of DSC measurement results by Avrami theory

and determination of half-time of crystallisation, $t_{0.5}$, Avrami exponent, n_A, and generalized rate constant, K_A for the isothermal crystallisation of pure PCL and PCL/PVF blends.

5. To predict the miscibility of PCL and PVF in the polymer blends *via* dilute solution viscometry (DSV). Analysis of the DSV results by applying Krigbaum-Wall, Catsiff-Hewett, Sun, Jiang-Han and also Garcia methods.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer blends

First polymer blend was reported in year 1846, which blended natural rubber with gutta-percha, patented by Hancock and Parkes. Due to large demand in the markets, the researches on polymer blends are having an exponential rises in the last 80 years (Thomas, Shanks and Sarathchandran, 2014).

Polymer blends are referred to physical mixtures of two or more different polymers or copolymers, which only interact through secondary forces but absence in covalent bond. The possible interactions between polymers are dipole-dipole interactions, hydrogen bonding, and charge-transfer (Freitas, et al., 2014). The mixing of polymers may have several advantages over homopolymers, which include desired properties of the polymer such as solvent resistance or impact strength might be improved, reduce in the costs of production, or possible recycling of the plastics waste (Utracki, 2002).

2.2 Poly(ε-caprolactone) (PCL)

Poly(ε-caprolactone) (PCL) is a semi-crystalline aliphatic polyester, which can be synthesised from caprolactone by ring-opening polymerization. PCL has melting point at about 60 °C and glass transition temperature at around -60 °C (Ebnesajjad, 2013).

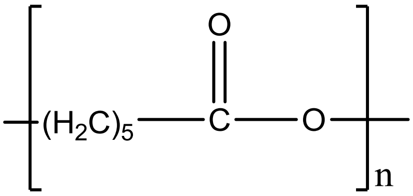

Figure 2.1: Chemical structure of PCL.

PCL is biodegradable, which can be degraded by hydrolysis on the ester linkages, making it possible applied as biodegradable packaging materials, implantable biomaterials and for drug delivery (Chen and Wu, 2007). However, disadvantages such as low melting point, low glass transition temperature and low modulus of PCL have restricted its applications (Liang, Yang and Qiu, 2012).

Blending of PCL with natural polymers such as starch and chitosan and also synthetic polymers such as poly(ethylene glycol) (PEG), polyurethane (PU), poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) were reported to be compatible (Dash and Konkimalla, 2012).

The research interests on PCL were grown recently along with the development of new tissue engineering field (Woodruff and Hutmacher, 2010). PCL has slow degradation rate compared to other biomaterials which made it desirable in long-term biomedical applications (Spearman, Rivero and Abidi, 2014).

2.3 Poly(vinyl formal) (PVF)

PVF is a derivative product from poly(vinyl alcohol) (PVA). PVA reacts with formaldehyde as copolymers with poly(vinyl acetate) (PVAc) through intramolecular acetalisation. The resultant polymer consists of unreacted acetate and hydroxyl group due to the hydroxyl groups are not fully acetalise (Rohindra and Khurma, 2008).

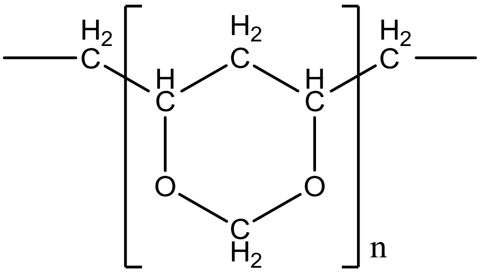

Figure 2.2: Chemical structure of PVF.

Some properties of PVF are such as high flexibility, high softening point, outstanding electric insulation characteristic, and good abrasion resistance. These characteristics have made PVF useful in applications, including wire insulation, coatings for musical instruments, adhesives and support films for electron microscopy (Ebrahim, Kashyout and Soliman, 2009).

2.4 Melting behaviour

Equilibrium melting temperature, T_m^o is the melting temperature for crystals with infinite thickness. In the isothermal crystallisation kinetics experiment, it is necessary to heat the materials above its T_m^o to ensure complete melting of crystals for removing of thermal history prior the crystallisation measurements (Samanta, et al., 2013).

DSC is a better instrument to estimate experimental melting points, T_m^o compared to optical microscopy due to reorganisation of crystals occurs in the optical microscopy method (Liu, et al., 1997). The variation of melting temperature, T_m with the crystallisation temperature, T_c can be described by Hoffman-Weeks equation (Samsudin, Kukureka and Jenkins, 2013). The T_m^o is commonly determined by Hoffman-Weeks method. The stability of crystals in the blends also can be estimated based on the information in Hoffman-Weeks plot (Xing and Yang, 2010).

Depression of melting point of polymer in its blends is observed in miscible polymer blends due to favourable interactions between the crystalline and amorphous components. This can provide important information on the miscibility of polymer blends (Madbouly, 2007).

2.5 Crystallisation of polymer blends

2.5.1 Theory

In the crystallisation process of polymer, the molecules in melt or solution rearranged from the disordered liquid phase to the ordered solid phase in crystal form. The phase transformation consists of random nucleation and growth of the new phase (Long, Shanks, and Stachurski, 1995). For polymer, the crystallisation process is spontaneous below its equilibrium melting point, T_m^o. This is due to the Gibbs free energy of crystal is lower than liquid when the temperature is lower than the equilibrium melting point, T_m^o (Ratta, 1999). However, the mobility of polymer chains is hindered and the crystal nucleation is limited when the temperature is less than the glass-transition temperature, T_g. Hence, the crystallisation of polymer can occur in a range of temperature which between T_g and T_m^o of the polymer (Utracki, 2002).

The structure and morphology of crystals and the degree of crystallisation of crystalline polymers can alter the physical and mechanical properties of the polymers (Di Maio, et al., 2004). The tendency for a polymeric material to crystallise can be either increased or decreased by the presence of amorphous component in polymer blend. Some important factors such as blend composition, phase interactions, melt history, and crystallisation conditions can also influence the crystallisation behaviour of a polymer in its blend (Utracki, 2002).

2.5.2 Differential scanning calorimetry (DSC)

The kinetics of crystallisation is commonly studied by using DSC and followed by applying Avrami analysis on the data obtained from DSC. Heat flow of a known mass sample as a function of time and temperature are recorded by DSC. The data that can be obtained from DSC are crystallisation time and temperature, melting temperature, glass transition temperature, enthalpy of reactions, specific heat and other information. In order to avoid any possible oxidation, degradation or reaction of the materials, the DSC measurements are preferred to be carried out in an inert atmosphere (Ray, 2013).

2.5.3 Isothermal crystallisation

Isothermal crystallisation allowed the material to crystallise at a constant temperature. Isothermal crystallisation of a biodegradable blend consists of PCL and tannic acid (TA) was investigated by Liang, Yang and Qiu (2012) by DSC. The PCL is a semi-crystalline polymer, whereas TA is amorphous. By comparing neat PCL and 80/20 PCL/TA blend at a given crystallisation temperature, T_c, the half-time, $t_{0.5}$ is smaller in pure PCL than in the blended PCL. This suggested the crystallisation rate of PCL reduced by the addition of TA due to amorphous TA which retards the crystallisation rate of PCL in the blends. Besides that, the crystallisation rates of PCL also observed to be decreased with the increasing T_c for both pure and blended PCL, due to the difficulty in nucleation at higher T_c.

Chong, et al (2004) studied on a polymer blend system with two semi-crystalline polymers, PCL and poly(tetramethylene succinate) (PTMS). The two components in the system were allowed to crystallise under isothermal conditions independently. The crystallisation rate increased exponentially with the increasing of undercooling (ΔT) for all of the systems studied. Besides that, the crystallisation rate of PCL in PCL/PTMS blends increased in the presence of PTMS. This might be attributed to the nucleation activity of crystalline PTMS. On the other hand, the crystallisation rate of PTMS remains almost same in the blends with PCL. The crystallisation behaviour was also confirmed by the crystal growth rate obtained by polarizing optical microscope.

Semi-crystalline PCL and amorphous poly(N-vinylpyrrolidone) (PVP) were blended and investigated by Xing and Yang (2010) on their isothermal crystallisation. The authors compared the peak time of endothermic response with the variables studied, since the reciprocal of peak time is proportional to the isothermal crystallisation rate. They found that the peak time increased and thus the crystallisation rate decreased, with ascending PVP content in PCL/PVP blends. Furthermore, the rate of isothermal crystallisation of PCL in the PCL/PVP blends also decreased with increasing crystallisation temperature. The Avrami exponents for the crystallisation were reported, ranged between 2.5 and 2.8 for the blend studied. They suggested that the crystallisations of PCL in pure state and in the polymer blends were heterogeneous type of nucleation.

2.6 Miscibility

2.6.1 Theory

The crystallisation of crystallisable content in polymer blends can be varied significantly by the miscibility. Consequently, differences in miscibility of the polymer blends will cause differences in morphologies. Miscible blend is homogeneous at a microscopic level, whereas immiscible blend is phase separated (Sharma, 2012). The phase behaviour of polymers in their blend is based on the structural groups which affect the degree of interactions between polymers. For example, hydrogen bonding and Van der Waals' forces may account for the intermolecular interactions in miscible polymer blend (Hendrick, 2012).

2.6.2 Dilute solution viscometry (DSV)

Dilute solution viscometry (DSV) is one of the cheapest and most simple methods to study on the polymer miscibility. DSV method makes assumption on that, if the polymers have certain degree of miscibility, their molecules will show attractive interactions in dilute solution (Oliveira, et al., 2013). Viscometric interaction and thermodynamic parameters of blend solutions can affect the DSV readings. Based on these considerations, numerous miscibility determination methods had been established (Aroguz and Kismir, 2007).

Aroguz, Engin and Baysal (2007) used viscometry, thermal analysis and microscopy methods to study the miscibility and morphology of poly(ε-caprolactone) (PCL) / poly(para-chlorostyrene) (PpClS) blends. They have evaluated the data from viscometry by Δb, α, μ and $\Delta[\eta]$ parameters. Positive values of Δb, α, μ and negative $\Delta[\eta]$ parameters were obtained for all compositions except for 90/10 PCL/PpClS which has opposite signed values for the parameters. According to the melting depression method by DSC measurements, the χ_{12} parameter has positive value for 90/10 blend while it is negative for other blends. From the SEM micrograms, the crystalline morphology remains almost the same after adding 10 % PpClS to the PCL. Then, a highly homogeneous dispersed phase is observed when more PpClS content present. Based on the results from different methods, same conclusion can be reached which is the PCL/PpClS blends are miscible in the range of study except at 90/10 blend composition.

The miscibility of polychloroprene (PCP) and natural rubber (NR) blends was investigated by Freitas, *et al (*2014) by using DSV and scanning electron microscope (SEM) methods. The authors have analysed data from viscosity measurements by calculate the Δb, β, α, μ and ΔK interaction parameters. The parameters are having negative values for all the compositions studied, thus the PCP/NR blends are considered to be immiscible in whole range of blend compositions. SEM results showed a good agreement with the conclusion made by DSV method. Based on SEM images, there are two phases observed for all of the blend compositions, indicating that the PCP/NR blends are immiscible.

Miscibility of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) was studied by Aouachria and Belhaneche-Bensemra (2006). In this study, viscometry, DSC and Fourier Transform Infrared Spectroscopy (FTIR) were used to determine the miscibility of PVC/PMMA blends with and without diethyl-2 hexylphtalate as plasticizer. By applying the Sun method, α parameter was calculated. The PVC/PMMA blends are miscible due to positive α parameter values up to about 65 % PMMA content in the blends. The associated carbonyl groups due to hydrogen bonding were recorded by FTIR, which showed that the fraction of bonded carbonyl group falls within the domain of miscibility up to 50 % PMMA. The glass transitions temperatures,

T_g was measured by using DSC. Only a single T_g can be observed up to 50 % PMMA for the PVC/PMMA blends. The FTIR and DSC analysis suggested the miscibility of the two polymers up to about 50 % PMMA content.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Poly(ε-caprolactone) (PCL) and poly(vinyl formal) (PVF) were obtained from Sigma-Aldrich. Both of the polymers were used without further purification. PCL was supplied in beads form and appears white in colour. PVF was supplied in light yellow coloured powdered form. The characteristics of both polymers are showed in Table 3.1. Analytical grade dichloromethane (CH_2Cl_2) was used as common solvent for both polymers.

Table 3.1: The characteristics of PCL and PVF.

Polymers	M_n (g mol^{-1})	T_g (℃)	T_m (℃)
PCL	80000	-60 *	60
PVF	NA	108	-

* was obtained from Ebnesajjad, 2013.

3.2 Methods

3.2.1 Preparation of PCL/PVF blends for Differential Scanning Calorimetry (DSC) Measurements

PCL/PVF blends were prepared by solution casting method. The polymers were dissolved in dichloromethane to obtain 2.5 % (wt/v) solutions. The solutions consisting of different PCL/PVF blend compositions (100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 0/100) were prepared. For example, 80/20 PCL/PVF blend solution was prepared by adding 0.6 g PCL and 0.15 g PVF, dissolved in 30 mL of dichloromethane. The solution was stirred to increase the dissolution rate. The blend solutions were cast on petri dishes. The solvent was allowed to evaporate at room temperature in the fume hood for 24 hours. The polymer blends films were further dried in oven at 48 °C for two days to ensure complete removal of the residue solvent. The blend films were then peeled off from the petri dish and kept in desiccator before being analysed.

3.2.2 Differential Scanning Calorimetry (DSC) measurements

The DSC measurements for the PCL/PVF blends were carried out using Mettler Toledo DSC823. All measurements were performed under nitrogen gas atmosphere with a flow rate of 20 mL/min to minimise thermo-oxidative degradation. The temperature and heat flow was calibrated using indium as reference. For all measurements, samples weighed in the range of 6 to 8 mg were used. Each of the samples was sealed into a 40 µL aluminium pan for DSC measurement. Fresh sample was used for each measurement.

Figure 3.1: Differential Scanning Calorimeter (DSC) used in this study. Model: Mettler Toledo DSC823.

3.2.2.1 Temperature program of isothermal crystallisation

The isothermal crystallisation process for PCL in pure state and PCL/PVF blends was carried out by the following experimental steps. The samples were first heated from 30 ℃ to 120 ℃ at a rate of 20 ℃/min and annealed at 120 ℃ for three minutes to eliminate any thermal history. The samples were then cooled down to a certain crystallisation temperatures, T_c at a rate of 20 ℃/min. The isothermal crystallisation of PCL was studied at crystallisation temperature ranging from 18 ℃ to 34 ℃. The temperatures of the samples were maintained at the T_c for a period of time until complete crystallisation process occurred.

Half time of crystallisation, $t_{0.5}$ is defined as the time needed for 50 % of the material to crystallise. For each sample, $t_{0.5}$ was taken from the exothermic crystallisation peak in the DSC thermogram obtained. The enthalpies of melting, ΔH_m of PCL were acquired from the peak areas of the crystallisation peaks.

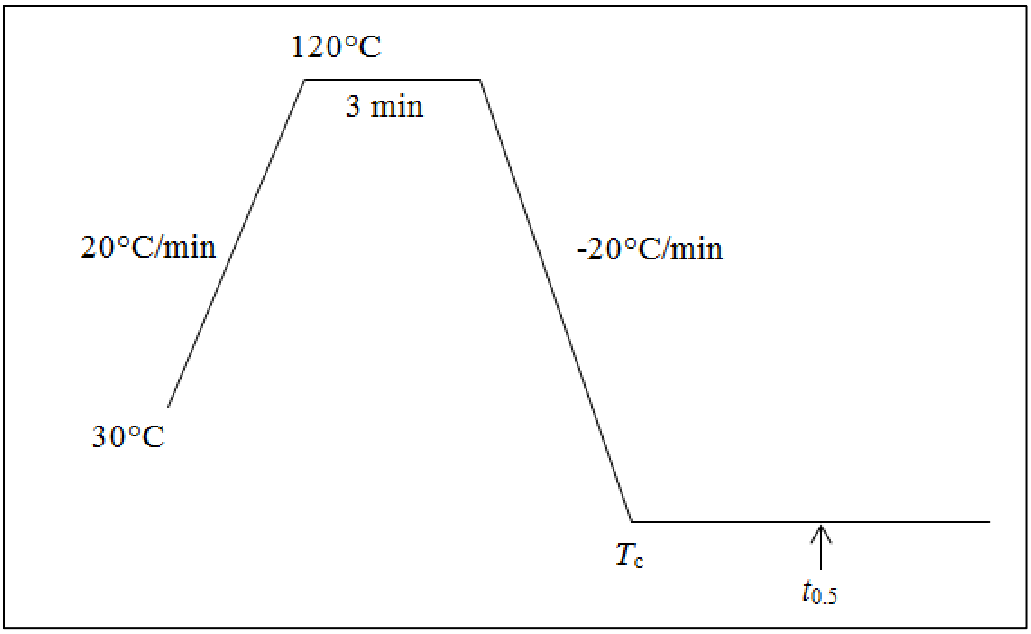

Figure 3.2: Temperature program of isothermal crystallisation measurements for pure PCL and PCL/PVF blends.

3.2.2.2 Temperature program of melting behaviour study for pure PCL

The pure PCL samples were first heated from 30 ℃ to 120 ℃ at a rate of 20 ℃/min and annealed at 120 ℃ for three minutes to eliminate any thermal history. The samples were then cooled down to a specific crystallisation temperature, T_c in the range of 23 ℃ to 34 ℃ at a rate of 20 ℃/min. The crystallisation at a specific T_c was allowed for a period of 5 $t_{0.5}$. Then, the samples were heated again to 120 ℃ at the rate of 20 ℃/min.

For each sample, the melting temperature, T_m was taken as the temperature at maximum endothermic melting peak during second heating in the DSC thermogram obtained.

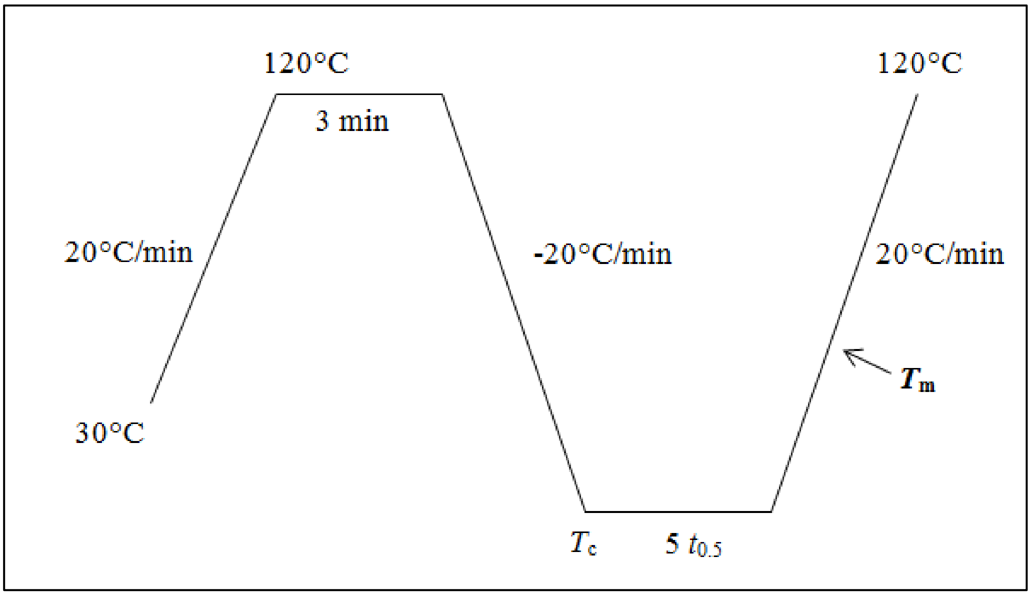

Figure 3.3: Temperature program of melting behaviour study for pure PCL.

3.2.3 Preparation of blend solutions for dilute solution viscometry (DSV)

For DSV measurements, PCL/PVF blend solutions were prepared with a total polymer concentration ranging from 1.6 to 3.0 g/dL. Dichloromethane was used as common solvent. For example, 0.165 g of PCL and 0.165 g of PVF dissolved in 15 mL dichloromethane to obtain 50/50 PCL/PVF blend solution with concentration of 2.2 g/dL. The polymer blend solutions were directly used in viscosity measurement without further purification. The resulting solution was further diluted as required to obtain the desired concentration.

3.2.4 Dilute solution viscometry (DSV) measurements

Viscosity measurements were carried out by using an Ubbelohde viscometer (OC type) immersed in a temperature – controlled water bath at 25.0 ± 0.1 ℃. The flow time of pure solvent should exceed 100 seconds to minimise experimental errors. The viscosity measurements were always started with 10 mL of freshly prepared polymer solution. The solution was then diluted to yield another four lower concentrations by adding 2 mL dichloromethane in each dilution. Flow times for each of the solutions were measured after they were allowed to reach thermal equilibrium in the water bath for 10 minutes.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characteristic of thermal properties of PCL/PVF blends by DSC

Differential Scanning Calorimeter (DSC) can be used to measure the heat flow of a material under controlled temperature conditions. The information such as melting temperature, glass transition temperature, crystallisation temperature, and melting enthalpies can be obtained from DSC thermogram. Semi-crystalline PCL and amorphous PVF were used in this study. Figure 4.1 showed examples of DSC thermogram obtained from the experiment which consists of melting peaks from first heating of pure PCL and 70/30 PCL/PVF blend and crystallisation peak for pure PCL. In the melting process, only one single melting peak was observed for both pure PCL and 70/30 PCL/PVF blend as indicated in Figure 4.1 (a) and (b). The pure PCL can be crystallised by cool down from molten state as displayed in Figure 4.1 (c). The melting and crystallisation peaks are attributed to the melting and crystallisation of PCL crystalline component in the samples, respectively.

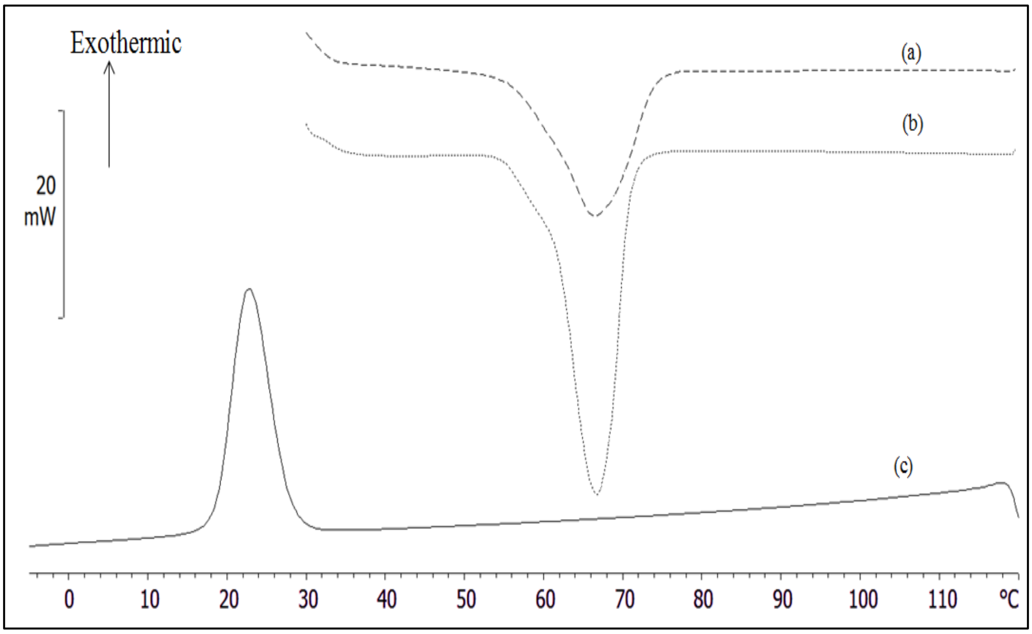

Figure 4.1: DSC thermogram of PCL/PVF blends (a) First heating of pure PCL at 20 °C/min, (b) First heating of 70/30 PCL/PVF blend at 20 °C/min and (c) Continuously cooling of pure PCL from 120 °C at 20 °C/min.

4.2 Degree of crystallinity, X_c

Melting enthalpy of PCL in the PCL/PVF blends samples were obtained from the crystallisation peaks in DSC thermogram and used in the determination of degree of crystallinity, X_c by the equation (4.1).

$$X_c = \frac{\Delta H_{\mathrm{m}}}{\Delta H_m^{\mathrm{o}} \cdot w_{\mathrm{PCL}}} \times 100\% \qquad (4.1)$$

where w_{PCL} is the weight fraction of PCL in PCL/PVF blends, ΔH_{m} represents the melting enthalpy of PCL in the blends and ΔH_m^{o} is the melting enthalpy of 100 % crystalline PCL which obtained from literature as 136 J/g (Cheung and Stein, 1994).

The graph of degree of crystallinity, X_c for PCL against weight fraction of PCF in the PCL/PVF blends was illustrated in Figure 4.2. The degree of crystallinity, X_c of the pure PCL is about 53 %. The crystallinity of PCL decreased gradually with increasing PVF content up to 40 % PVF. Then, a drastic reduction in the crystallinity was observed for more than 40 % PVF content. The decrease in the degree of crystallinity of PCL in the blends is due to the crystalline PCL component is diluted by the amorphous PVF component in the blends. The PCL crystals growth and nucleation are reduced significantly by the increase of PVF content (Rohindra and Khurma, 2008).

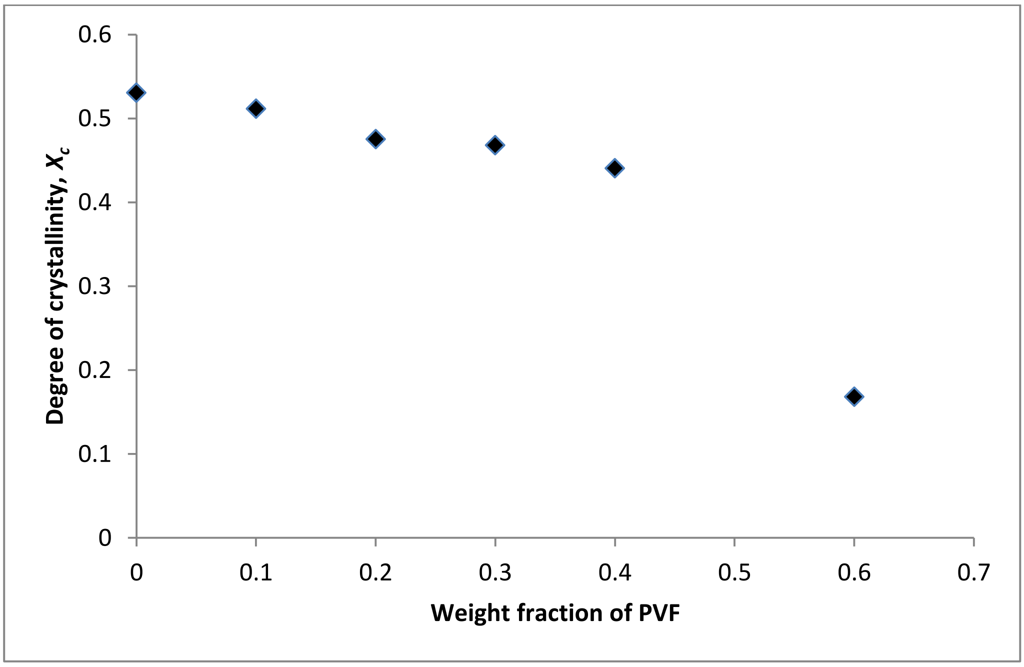

Figure 4.2: Graph of degree of crystallinity, X_c of PCL against weight fraction of PVF.

4.3 Melting behaviour

The melting temperature, T_m of samples were obtained as the temperature at the maximum of endothermic peak for the second heating with heating rate of 20 °C/min, after the pure PCL samples were crystallised at various T_c for a period of 5 $t_{0.5}$.

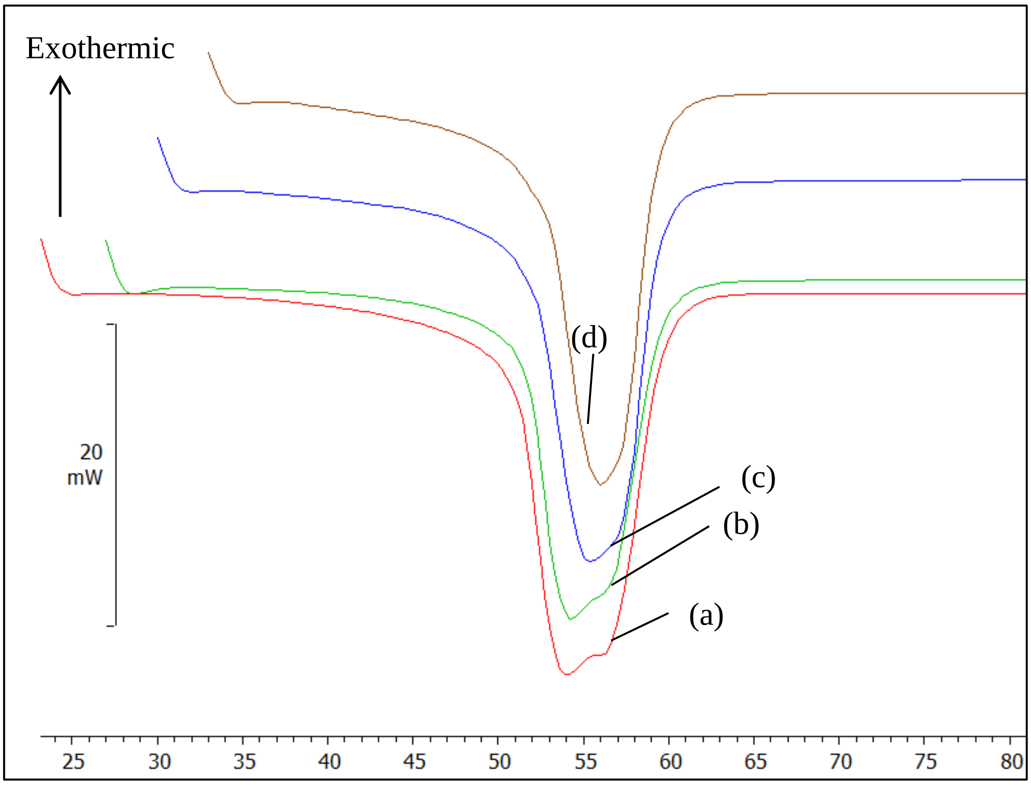

Figure 4.3: DSC thermogram for second heating of pure PCL with crystallisation temperature, T_c at (a) 23 °C, (b) 27 °C, (c) 30 °C and (d) 33 °C.

The observed melting temperature, T_m increased with the increasing T_c of pure PCL. The polymers can form more perfect crystals at higher crystallisation temperature, which consequently lead to the increase in melting temperature (Sperling, 2006). For the melting peaks with lower crystallisation temperature, T_c, two endotherms can be observed. Endotherm at lower temperature, which is a larger peak is considered to be melting of the crystals formed in primary crystallisation. Endotherm at higher temperature resulted from the melting and recrystallisation of the materials. The recrystallisation was not observed reduced when the sample crystallised at higher temperature (Lu and Hay, 2001). The lower melting point, T_{m1} and higher melting point, T_{m2} at different T_c was tabulated in Table 4.1. The lower melting point was taken in plotting Hoffman-Week plot, since only the lower melting point changed with T_c. On the other hand, the higher melting point which is due to recrystalisation of the material, remained almost constant and eventually not observed at higher T_c.

Table 4.1: The lower melting point, T_{m1} and higher melting point, T_{m2} of pure PCL at different T_c.

T_c (℃)	T_{m1} (℃)	T_{m2} (℃)
23	53.74	56.10
24	54.05	56.08
25	53.76	55.81
26	54.12	56.17
27	54.20	56.25
28	54.75	56.13
29	54.32	56.01
30	54.44	-
31	54.77	-
32	54.76	-
33	55.08	-
34	55.31	-

As compared to low molecular substances, the melting and crystallisation temperatures of polymers are generally not in equilibrium. If one tries to crystallise polymers at their melting temperature, the rate of crystallisation is so low that it may take years to crystallise.

As a result, the equilibrium melting temperature, T_m^o of pure PCL can be determined according to Hoffman-Weeks equation (equation 4.2).

$$T_m = \left(\frac{1}{\gamma}\right) T_c + \left(1 - \frac{1}{\gamma}\right) T_m{}^o \tag{4.2}$$

Where T_m is the observed melting temperature of the polymer blends, T_c is the crystallisation temperature and $1/\gamma$ is stability parameter which depends on crystal thickness and ranged between 0 and 1. The value of $1/\gamma = 0$ implies $T_m = T_m^o$ for all T_c, whereas $1/\gamma = 1$ implies $T_m = T_c$. Thus, the crystals are most stable at $1/\gamma = 0$ while they are inherently unstable at $1/\gamma = 1$.

Figure 4.4 shows the Hoffman-Weeks plot for pure PCL. The experimental data are extrapolated to intersect with the $T_m = T_c$ line, which the intersection point gives T_m^o value. The equilibrium melting temperature, T_m^o, obtained from the Hoffman-Weeks plot for pure PCL is (58 ± 1) ℃. It agrees with the value reported by Zhang and Prud'homme (1987) which is 58.1 ℃. The $1/\gamma$ value was determined from the slope of the Hoffman-Weeks plot. The value of $1/\gamma$ for pure PCL is found to be (0.13 ± 0.01) which indicates the crystals are quite stable.

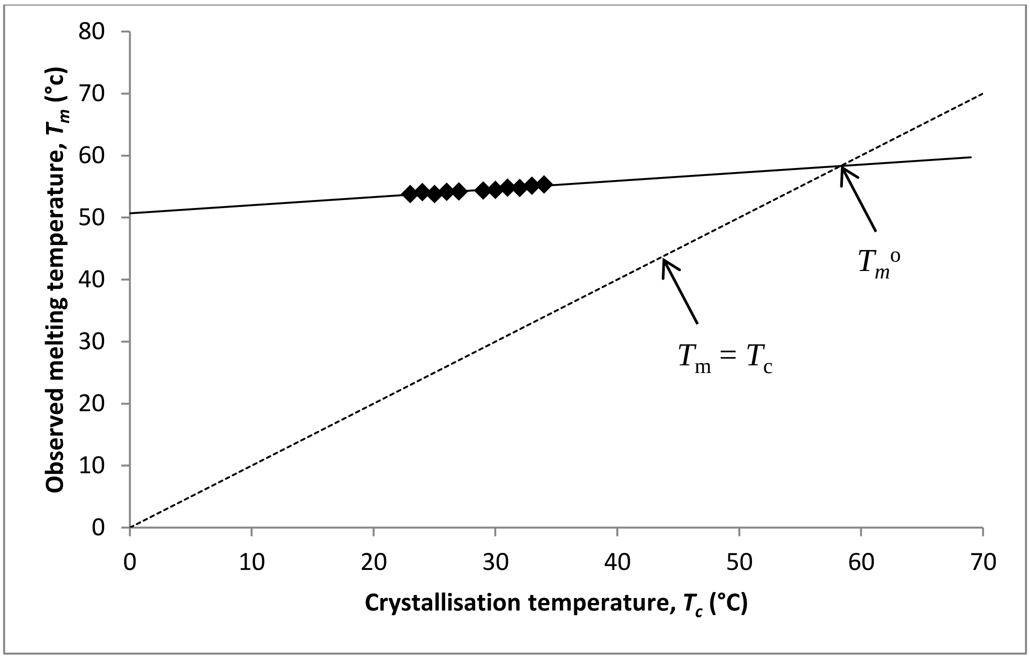

Figure 4.4: Hoffman-Weeks plot of pure PCL. (♦) Experimental melting point.

4.4 Kinetics of isothermal crystallisation

4.4.1 General

Isothermal crystallisations of PCL/PVF blends with various compositions were performed by DSC according to the temperature program mentioned earlier in section (3.2.2.1). Figure 4.5 shows an example of DSC thermogram with a crystallisation exotherm for 90/10 PCL/PVF at crystallisation temperature, T_c of 23 ℃. The induction period, t_0 was indicated in the figure and the crystallisation peak was referred to the hatched area.

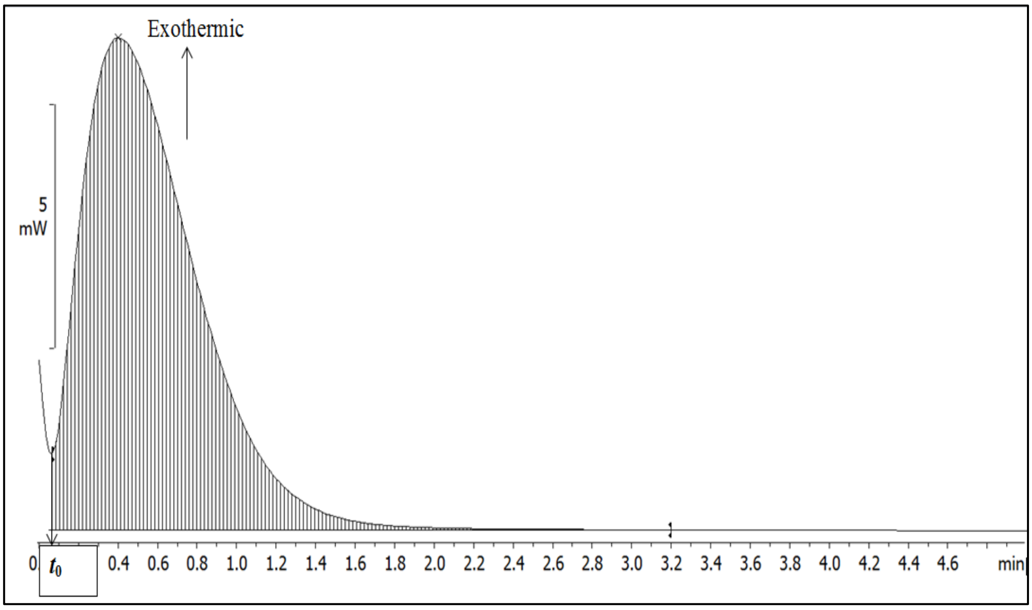

Figure 4.5: DSC thermogram for 90/10 PCL/PVF at crystallisation temperature, T_c of 23 °C.

The degree of crystalline conversion, $X(t)$ is used to evaluate the isothermal crystallisation kinetics of PCL in the blends.

$$X(t) = \frac{\Delta H(t)}{\Delta H(\infty)} = \frac{\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^\infty \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = \frac{a(t)}{a(\infty)} \tag{4.3}$$

$\Delta H(t)$ and $\Delta H(\infty)$ are the heat generated at time t and infinite time, respectively. $(\mathrm{d}H/\mathrm{d}t)$ is the heat flow rate of samples. The degree of crystalline conversion, $X(t)$ at different crystallisation time can be obtained from the area of the crystallisation exotherm of PCL from DSC thermogram. The degree of crystalline conversion, $X(t)$ can be defined as the ratio of peaks areas at time t and $t \to \infty$, $a(t)/a(\infty)$.

If t_0 denotes the induction period, the time required for the formation of primary nuclei, then the crystallisation time can be written as (t-t_0). The graph of degree of crystalline conversion, $X(t)$ versus crystallisation time, (t-t_0) of PCL at 23 ℃ was plotted and presented in Figure 4.6. All the isotherms curves showed the characteristic sigmoidal shape. Besides that, the curves shift to the right along the time with increasing PVF content, indicates the rate of crystallisation of PCL decreased with increasing PVF content.

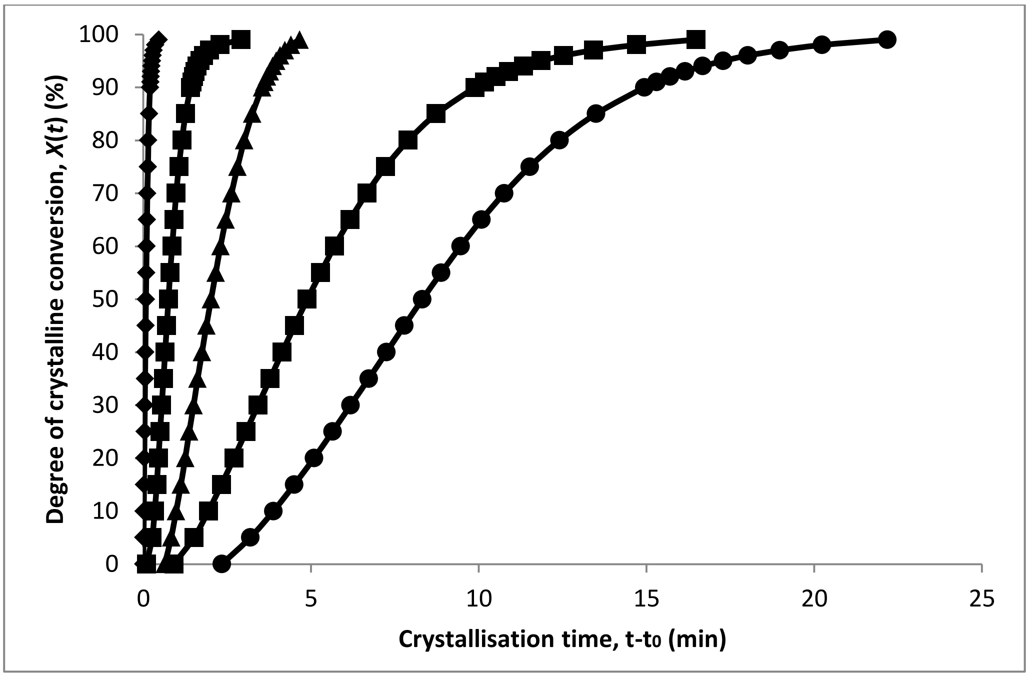

Figure 4.6: Degree of crystalline conversion, $X(t)$ versus crystallisation time, (t-t_0) of PCL at 23 ℃. Blends compositions: (♦) 100/0, (■) 90/10, (▲) 80/20, (×) 70/30, (•) 60/40.

An important parameter used in the analysis of crystallisation kinetics is the half-time of crystallisation, $t_{0.5}$, which defined as the time needed for 50 % of the material to crystallise (Weng and Chen et al., 2003). The half-times, $t_{0.5}$

values can be acquired from the crystallisation exotherm areas in DSC thermogram, after the induction period, t_0. The half-time of crystallisation, $t_{0.5}$ is inversely proportional to rate of isothermal crystallisation, thus it provides useful information on the crystallisation rate of a material.

4.4.2 Effects of crystallisation temperature, T_c

The effect of crystallisation temperature on the crystallisation rate can be investigated by examining the plot of half-times of crystallisation, $t_{0.5}$ of PCL in the blends as a function of crystallisation temperature, T_c for various PCL/PVF blends compositions as shown in Figure 4.7. For a constant blend composition, the half-times, $t_{0.5}$ increased exponentially with increasing of crystallisation temperature, T_c. In other words, the rate of crystallisation of PCL decreased exponentially with the increase of crystallisation temperature, T_c for a same blend composition. This is attributed by the difficulty for nucleation increased with a higher crystallisation temperature, T_c (Liang, Yang and Qiu, 2012). This trend was observed for all the blend compositions studied.

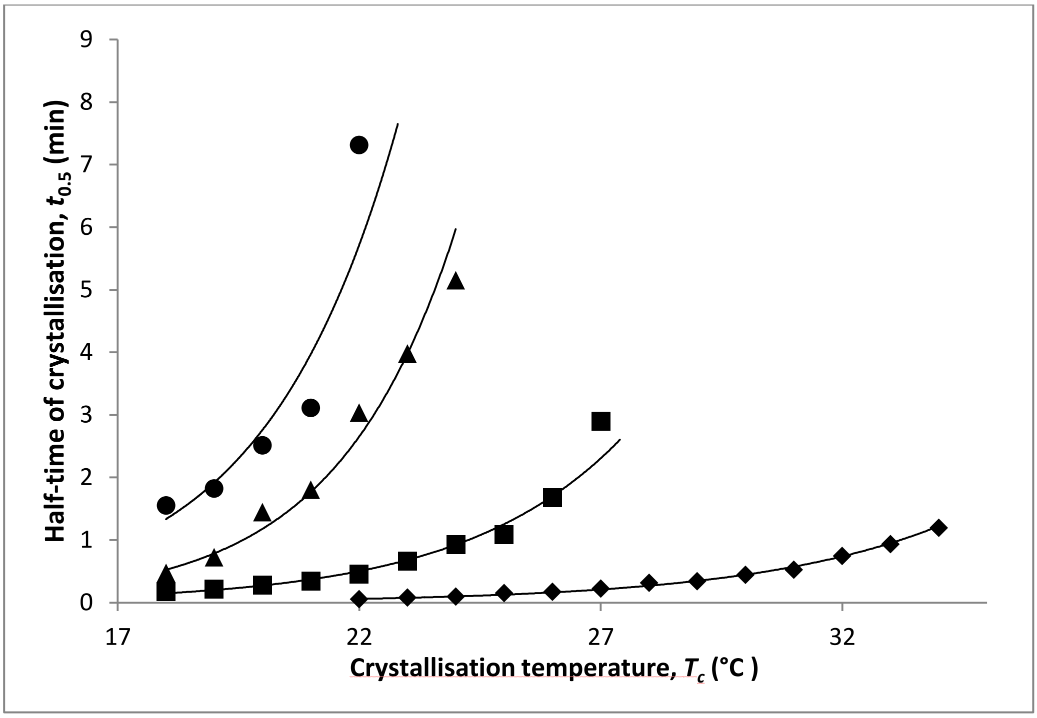

Figure 4.7: Half-time of crystallisation, $t_{0.5}$ as a function of crystallisation temperature T_c for various PCL/PVF blends compositions. Blends compositions: (♦) 100/0, (■) 90/10, (▲) 70/30, (•) 40/60.

4.4.3 Effects of PVF content

Figure 4.8 shows the half-time of crystallisation, $t_{0.5}$ against weight fraction of PVF in PCL/PVF blends at crystallisation temperature, T_c of 22 °C. The half-time of crystallisation for PCL, $t_{0.5}$ in PCL/PVF blend increased with the increasing PVF content in the PCL/PVF blends. This trend indicates the rate of crystallisation of PCL in the polymer blends decreased at higher content of PVF in the blends. Similar trend could be observed for the crystallisations rate of PCL in PCL/PVF blends at other crystallisation temperatures studied. These observations suggested that PVF may cause physical restriction to the growth of PCL crystals (Kong and Hay, 2002).

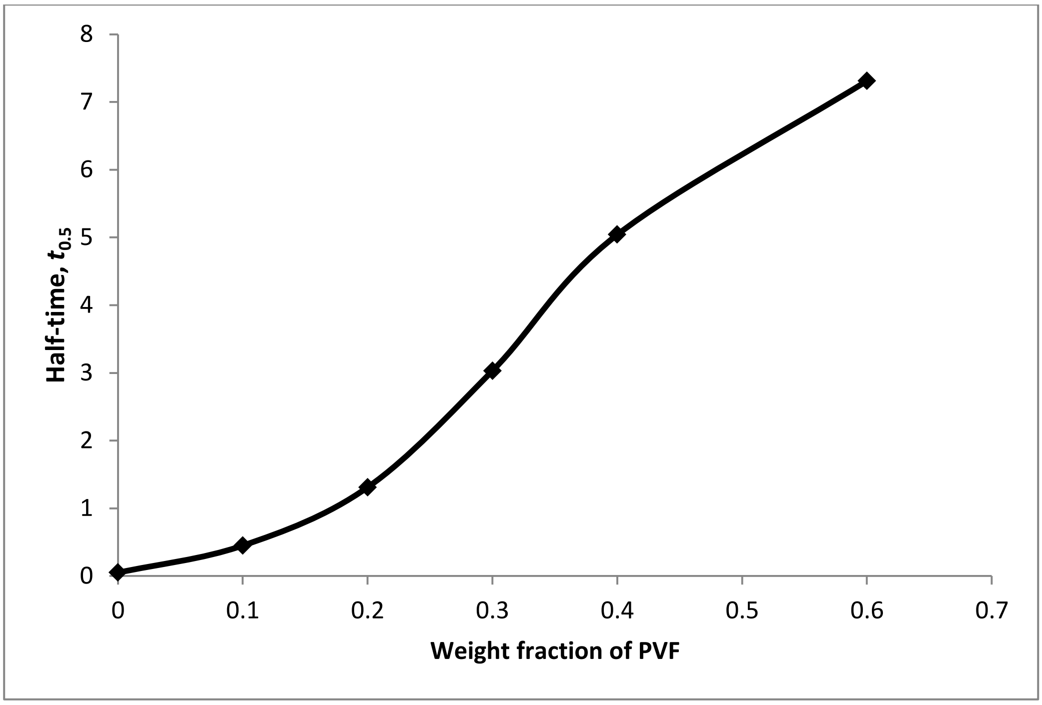

Figure 4.8: Graph of half-time, $t_{0.5}$ against weight fraction of PVF at T_c = 22 °C.

4.4.4 Avrami analysis

The isothermal crystallisation kinetics of polymers can be investigated by the well-known and widely used Avrami equation. Avrami equation relates relative degree of crystallinity, $X(t)$ with crystallisation time, (t-t_0) as stated in equation (4.4)

$$X(t) = 1 - \exp[-K_A(t - t_0)^{n_A}] \tag{4.4}$$

There are two prime parameters, which can be obtained from kinetics measurement of bulk polymer crystallisation. K_A is overall rate constant of crystallisation which dependent on crystal growth rate and nucleation. Avrami exponent, n_A is a parameter which relates to the crystal growth mechanism. A more useful form of Avrami equation can be obtained by taking double logarithmic of both sides of equation (4.4), which written as equation (4.5).

$$\log[-\ln(1-X(t))] = \log K_A + n_A \log(t-t_0) \qquad (4.5)$$

A linear plot of $\log[-\ln(1-X(t))]$ versus $\log\ (t-t_0)$ should be seen for the materials that followed Avrami equation. Some examples of Avrami plots for PCL in 90/10 PCL/PVF blends at several crystallisation temperatures, T_c are shown in Figure 4.9. The Avrami plots are linear in a certain range of time up to degree of conversion at around 90 %. Afterward, deviations of the Avrami plots from linearity were observed due to impingement of crystals occurred and caused secondary crystallisation (Guo and Groeninckx, 2001).

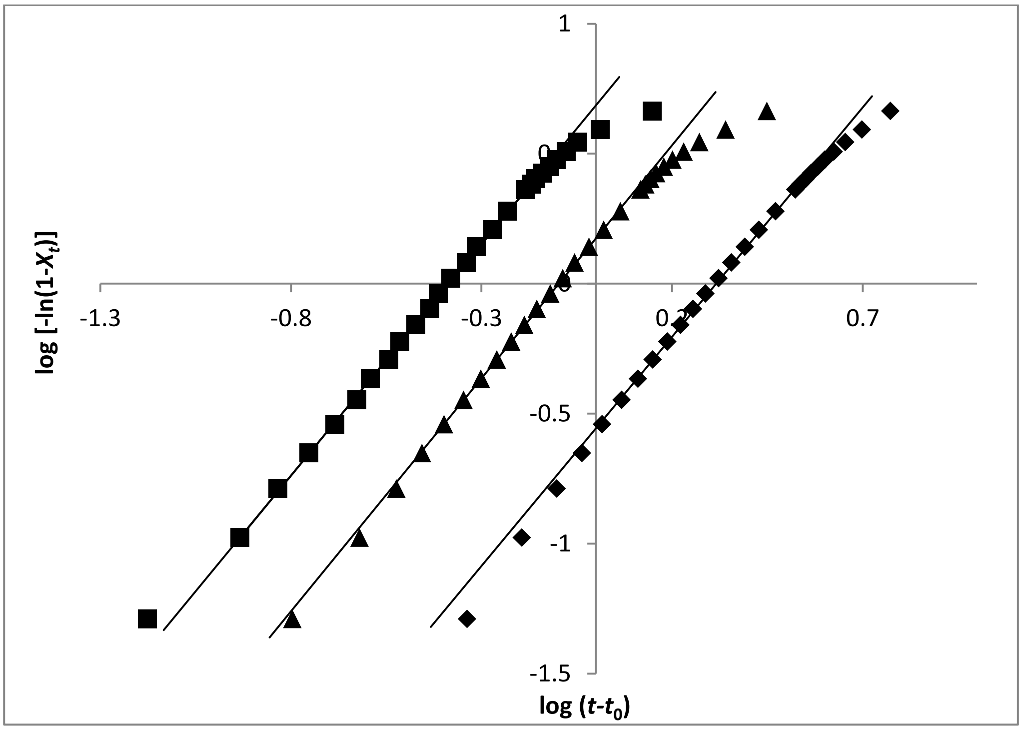

Figure 4.9: Avrami plots of 90/10 PCL/PVF blend at various crystallisation temperatures. Crystallisation temperatures: (■) 21 ℃, (▲) 23 ℃, (♦) 26 ℃.

The Avrami exponent, n_A and rate constant, K_A of the sample can be obtained from the slope and intercept of Avrami plots respectively. The crystallisation rate is dependent on both n_A and K_A, thus the generalised rate constant, ${K_A}^{1/n_A}$ can be used to express crystallisation rates. The Avrami parameters for kinetics of isothermal crystallisation of PCL in PCL/PVF blends are presented in Table 4.2. The Avrami exponent, n_A values varies from 1 to 2. This suggests that one to two dimensional growth of PCL crystals occurred in the PCL/PVF blends.

Table 4.2: Avrami exponent, n_A , generalised rate constant, ${K_A}^{1/n_A}$, and half-time of crystallisation, $t_{0.5}$ for isothermal crystallisation of PCL in PCL/PVF blends.

Crystallisation temperature, T_c	n_A	${K_A}^{1/n_A}$,	$t_{0.5}$ **(min)**	^{1}r
PCL/PVF 100/0				
22	(1.081 ± 0.004)	(14.5 ± 0.3)	0.05	0.9997
23	(1.227 ± 0.009)	(9.6 ± 0.3)	0.08	0.9990
24	(1.263 ± 0.010)	(8.3 ± 0.3)	0.09	0.9987
25	(1.522 ± 0.017)	(5.5 ± 0.2)	0.15	0.9979
26	(1.702 ± 0.018)	(4.8 ± 0.2)	0.17	0.9978
PCL/PVF 90/10				
18	(1.502 ± 0.012)	(4.604 ± 0.106)	0.17	0.9990
19	(1.587 ± 0.008)	(3.801 ± 0.052)	0.21	0.9995
20	(1.629 ± 0.007)	(2.931 ± 0.027)	0.28	0.9996
21	(1.781 ± 0.009)	(2.427 ± 0.024)	0.34	0.9996
22	(1.845 ± 0.007)	(1.791 ± 0.009)	0.45	0.9997
PCL/PVF 80/20				
18	(1.741 ± 0.010)	(2.113 ± 0.017)	0.38	0.9995
19	(1.911 ± 0.006)	(1.621 ± 0.005)	0.51	0.9998
20	(1.755 ± 0.008)	(1.186 ± 0.004)	0.75	0.9996
21	(1.770 ± 0.004)	(1.029 ± 0.002)	0.79	0.9999
22	(1.950 ± 0.005)	(0.630 ± 0.001)	1.31	0.9999

PCL/PVF 70/30				
18	(1.546 ±0.005)	(1.6689 ±0.0077)	0.47	0.9997
19	(1.303 ±0.013)	(1.0478 ±0.0120)	0.72	0.9990
20	(1.333 ±0.006)	(0.5291 ±0.0002)	1.43	0.9997
21	(1.474 ±0.004)	(0.4379 ±0.0004)	1.80	0.9998
22	(1.424 ±0.007)	(0.2624 ±0.0003)	3.03	0.9994
PCL/PVF 60/40				
18	(1.397 ±0.005)	(0.8967 ±0.0022)	0.87	0.9997
19	(1.315 ±0.004)	(0.6201 ±0.0011)	1.25	0.9997
20	(1.480 ±0.006)	(0.3792 ±0.0002)	2.06	0.9997
21	(1.675 ±0.011)	(0.2797 ±0.0003)	2.91	0.9995
22	(1.774 ±0.009)	(0.1607 ±0.0001)	5.04	0.9997
PCL/PVF 40/60				
18	(1.313 ±0.021)	(0.4831 ±0.0009)	1.55	0.9981
19	(1.362 ±0.017)	(0.4186 ±0.0001)	1.82	0.9990
20	(1.109 ±0.007)	(0.2832 ±0.0004)	2.51	0.9994
21	(1.273 ±0.013)	(0.2377 ±0.0001)	3.11	0.9988
22	(1.674 ±0.021)	(0.1089 ±0.0001)	7.31	0.9989

---

[1] Correlation coefficient

4.4.5 Crystallisation rate

The half-time of crystallisation, $t_{0.5}$ is inversely proportional to rate of isothermal crystallisation. Hence, the crystallisation rate can be described by reciprocal of half-time, $t_{0.5}{}^{-1}$. On the other hand, the generalised rate constant, ${K_A}^{1/n_A}$ is directly proportional to crystallisation rate. An equation that relates reciprocal of half-time, $t_{0.5}{}^{-1}$ with generalised rate constant, ${K_A}^{1/n_A}$ is given as

$$t_{0.5}{}^{-1} = \left(\frac{K_A}{\ln 2}\right)^{1/n_A} \tag{4.6}$$

Figure 4.10 demonstrates the plots of logarithmic of reciprocal of half-times, log ($t_{0.5}^{-1}$) or logarithmic of generalised rate constant, log (${K_A}^{1/n_A}$) against weight fraction of PVF in the blends at T_c = 22 °C. The half-time of crystallisation, $t_{0.5}$ was obtained directly from DSC thermograms, whereas the generalised rate constant, ${K_A}^{1/n_A}$ was calculated from the Avrami parameters. Both plots exhibit same tendencies with each other. At a constant crystallisation temperature, T_c at 22 °C, the rate of crystallisation in terms of log ($t_{0.5}^{-1}$) and log (${K_A}^{1/n_A}$) decreased with ascending PVF content in PCL/PVF blends. Same trend was observed at other crystallisation temperature, T_c studied.

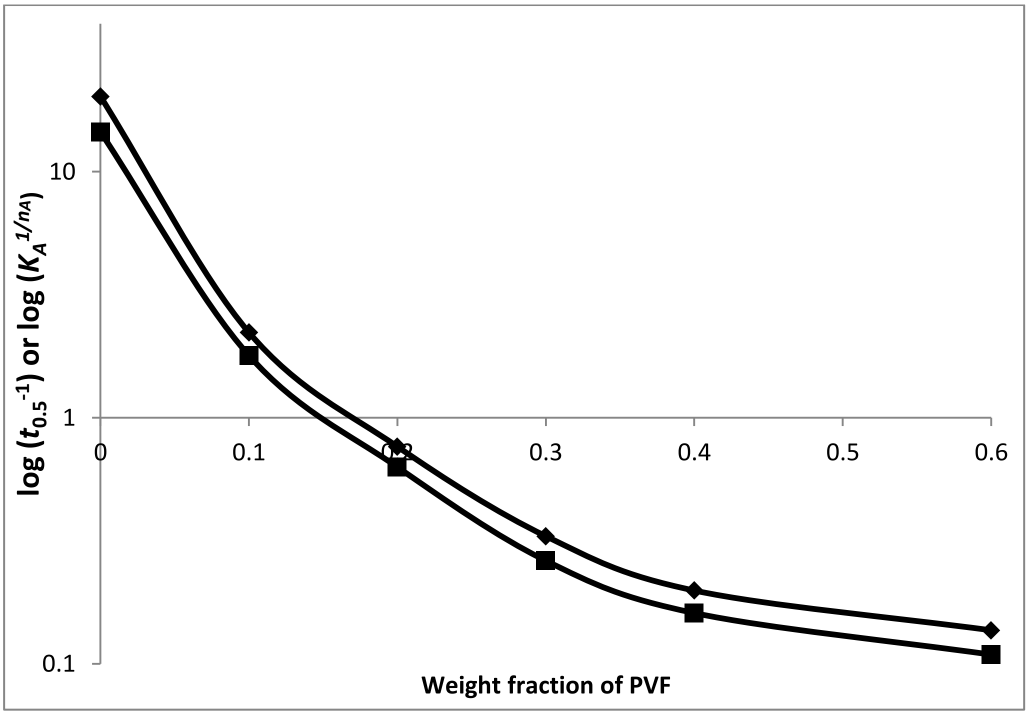

Figure 4.10: Graph of log ($t_{0.5}^{-1}$) or log (${K_A}^{1/n_A}$) against weight fraction of PVF at T_c = 22 ˚C. For y-axis: (♦) log ($t_{0.5}^{-1}$), (■) log (${K_A}^{1/n_A}$).

4.4.6 Nucleation parameter, K_g

Hoffman's theory was used to analyse the rate of crystallisation. The crystallisation rate can be expressed in reciprocal of half-time, $t_{0.5}^{-1}$ and it conforms an Arrhenius-like relationship.

$$t_{0.5}{}^{-1} = \exp\left(-K_g \frac{T_m{}^o}{T_c \Delta T}\right) \tag{4.7}$$

Where K_g represents nucleation parameter, T_m^o represents equilibrium melting temperature of pure PCL which is 58 °C and ΔT is the undercooling temperature which equals to difference between equilibrium melting temperature, T_m^o and crystallisation temperature, T_c.

The nucleation parameters, K_g calculated from equation (4.7) for various PCL/PVF blends are summarised in Table 4.3. The K_g increased dramatically with increasing PVF content up to 30 % PVF in PCL/PVF blends. Afterwards, the K_g remained almost constant from 30 % to 60 % PVF content in the polymer blends.

Table 4.3: Values of nucleation parameter, K_g for PCL in the blends.

PCL/PVF blends	K_g (K) of PCL	^1r
100/0	196	0.9765
90/10	386	0.9946
80/20	432	0.9892
70/30	520	0.9791
60/40	555	0.9899
40/60	538	0.9115

^{1}Correlation coefficient

4.5 Dilute solution viscometry (DSV)

4.5.1 General

DSV is a simple, rapid and an inexpensive method to study the polymer miscibility (Lew and Owska, 2013). In this method, flow time of the pure solvent, dichloromethane (t_0) was 108.88 seconds. The relative viscosity, η_{rel} was calculated by dividing the flow time of polymer solution, t with the flow time of pure solvent, t_0 given by equation (4.8).

$$\eta_{\mathrm{rel}} = \frac{t}{t_0} \tag{4.8}$$

From the data obtained from viscometry measurements, the values of relative viscosity, η_{rel} for pure polymer and their blends are ranging between 1.6 and 2.8. The values of specific viscosity, η_{sp} can be calculated by equation (4.9)

$$\eta_{\text{sp}} = \frac{t_0 - t}{t} = \eta_{\text{rel}} - 1 \tag{4.9}$$

The reduced viscosity, $\frac{\eta_{sp}}{c}$ which consists of specific viscosity divided by the concentration, c can be extrapolated to zero concentration to obtain the intrinsic viscosity, $[\eta]$ (Sperling, 2006).

$$\left[\frac{\eta_{\text{sp}}}{c}\right]_{c=0} = [\eta] \tag{4.10}$$

The reduced viscosity, $\frac{\eta_{sp}}{c}$ showed a linear relationship with the concentration of polymers in the solution, which describe by Huggins equation (Huggins, 1942).

$$\frac{\eta_{\text{sp}}}{c} = [\eta] + k_H[\eta]^2 c \tag{4.12}$$

The relation between slope of Huggins plot, b and the Huggins coefficient, k_H can be described by equation (4.13).

$$b = k_H[\eta]^2 \tag{4.13}$$

The flow time of polymer solution, t, relative viscosity, η_{rel}, specific viscosity, η_{sp} and reduced viscosity, η_{red} for 80/20 PCL/PVF blend solution are presented in Table 4.4.

Table 4.4: Flow time, *t*, relative viscosity, specific viscosity and reduced viscosity for 80/20 PCL/PVF blend at various concentrations. (Flow time for pure solvent, dichloromethane, t_0 = 108.88 s).

Concentration, c (g/dL)	Flow time, t (s)	Relative viscosity, $\eta_{\mathrm{rel}} = t/t_0$	Specific viscosity, $\eta_{\mathrm{sp}} = \eta_{rel} - 1$	Reduced viscosity, $\eta_{\mathrm{red}} = \eta_{sp}/c$
2.803	277.50	2.549	1.549	0.552
2.336	243.50	2.236	1.236	0.529
2.002	220.58	2.026	1.026	0.512
1.752	203.38	1.868	0.868	0.495
1.557	189.66	1.742	0.742	0.476

4.5.2 Huggins plots

Huggins equation was used to investigate the miscibility of the PCL/PVF polymer blends. The Huggins equation, stated in equation (4.15), can be adopted to apply on ternary polymer solution consists of a solvent and two polymers as shown in equation (4.16).

$$\frac{\eta_{\mathrm{sp,b}}}{c_{\mathrm{b}}} = [\eta]_{\mathrm{b}} + b_{\mathrm{b}} c_{\mathrm{b}} \qquad (4.16)$$

Where,

$$c_{\mathrm{b}} = c_1 + c_2 \tag{4.17}$$

The subscript b represents the polymer blends, which is PCL/PVF blends in this case. Subscripts 1 and 2 represent pure PCL and pure PVF, respectively. c_{b} is the total concentration of the two polymers in the blend. The constant b_{b} is described by the following equation.

$$b_{\mathrm{b}} = k_H [\eta]_{\mathrm{b}}^{\ 2} \tag{4.18}$$

Theoretically, $b_{\mathrm{b}} c_{\mathrm{b}}$ reflects the total molecular interaction, which considered the interactions of PCL−solvent, PVF−solvent and PCL−PVF (Aroguz and Baysal, 2006).

Based on the experimental data, the graphs of reduced viscosity, η_{sp} against the polymer blends concentration, c were plotted and showed in Figure 4.11. The viscometric data for all blend compositions studied fitted Huggins equation (4.16) with correlation coefficient, r above 0.98.

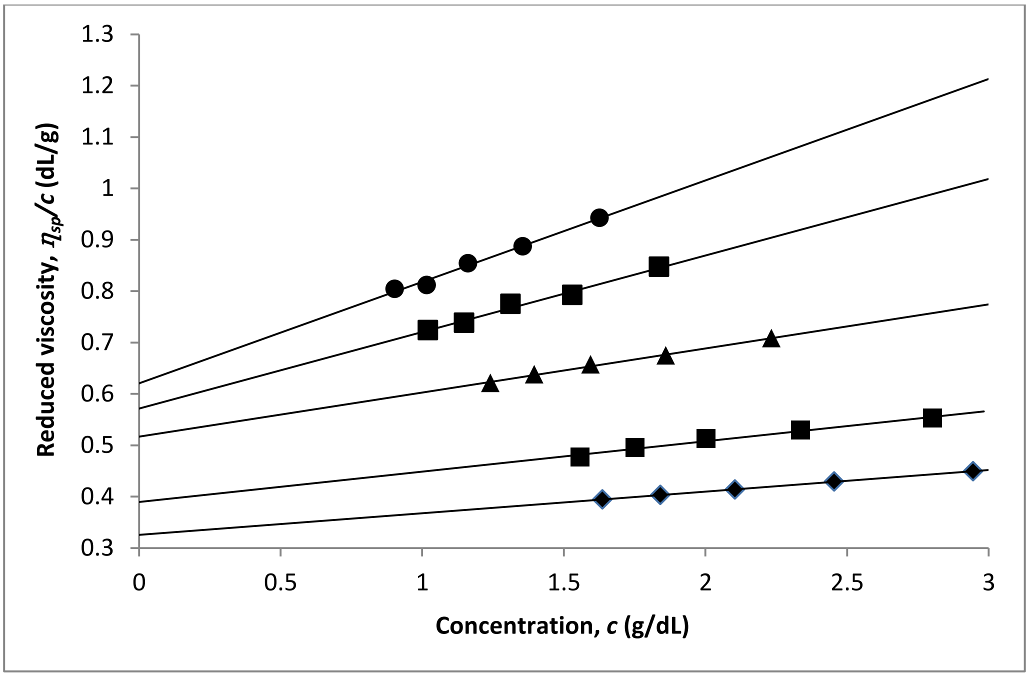

Figure 4.11: Reduced viscosity, η_{sp}/c versus blend concentration, c for blends of PCL/PVF in dichloromethane at 298 K. Blends compositions: (◆) 100/0, (■) 80/20, (▲) 50/50, (×) 20/80, (●) 0/100.

The Huggins plots for pure polymers and all blend compositions studied showed linear relationship between reduced viscosity and concentration of polymers. For each blend composition, its intrinsic viscosity, $[\eta]_b$ were obtained from intercept of the Huggins plot respectively and Huggins coefficients, k_H were calculated by using equation (4.18). The intrinsic viscosity, $[\eta]_b$ and Huggins coefficients, k_H for all the PCL/PVF blends studied are tabulated in Table 4.5. The intrinsic viscosity, $[\eta]$ of the PCL/PVF blends ranging from 0.325 dL/g to 0.620 dL/g. Pure PCL has lowest intrinsic viscosity, $[\eta]$, whereas pure PVF has the highest intrinsic viscosity, $[\eta]$ among the blends. The intrinsic viscosity, $[\eta]$ increased with the increasing PVF content in the blends. Theoretically, a flexible polymer in good solvent will leads to Huggins coefficients, k_H values falls between 0.3 and 0.5 (Jiang and Han, 1997). The experimentally determined k_H values in this study falls close to the range and confirms the reliability of data.

Table 4.5: Intrinsic viscosity, $[\eta]_b$ and Huggins coefficients, k_H for various compositions in PCL/PVF blends.

PCL/PVF Blends	Intrinsic viscosity $[\eta]$ (dL/g)	Huggins coefficients, k_H
0/100	0.620	0.514
20/80	0.571	0.456
50/50	0.517	0.320
60/40	0.511	0.273
80/20	0.390	0.390
100/0	0.325	0.398

4.5.3 Criteria used in determining the miscibility

In polymer blend solution, the attraction or repulsion between polymer molecules will lead to non-ideal mixing of the polymers and results in viscosity deviation from the ideal solution (Ye and Dan et al., 2007). Due to the deviations in polymer blend solution, a number of criteria were proposed by researchers to evaluate the miscibility of two polymers based on calculations by using the viscometric data obtained.

Krigbaum and Wall suggested that difference in experimental interaction coefficient, $b_{12}^{\mathrm{exp}}$and the theoretical interaction coefficient, b_{12}^{id} can provides information on the intermolecular interaction in a binary polymer blend system.

$$\Delta b = b_{12}^{\mathrm{exp}} - b_{12}^{\mathrm{id}} \tag{4.19}$$

The geometric mean of slopes from the Huggins plots for the two pure polymers were taken as the theoretical interaction coefficient, b_{12}^{id} (Krigbaum and Wall, 1950).

$$b_{12}^{\mathrm{id}} = \sqrt{b_{11} b_{12}} \tag{4.20}$$

The experimental interaction coefficient, b_{12}^{exp} values were estimated by the following equation.

$$b_{\mathrm{b}} = b_{11} w_1^2 + b_{22} w_2^2 + 2 b_{12}^{\mathrm{exp}} w_1 w_2 \tag{4.21}$$

b_{b} values were obtained from the slope of the Huggins plots for the PCL/PVF blends. b_{11} and b_{22} are the slopes of Huggins plots for pure PCL and pure PVF respectively, whereas w_1 and w_2 are the weight fraction of pure PCL and pure PVF, respectively.

Catsiff and Hewett proposed another criterion to investigate the miscibility of two polymers after Krigbaum and Wall. The authors defined the ideal interaction parameter, $b_{12}^{id'}$ as the arithmetic mean value (Catsiff and Hewett, 1962).

$$b_{12}^{\mathrm{id}\,\prime} = \frac{b_{11}+b_{22}}{2} \tag{4.22}$$

Then,

$$\Delta b' = b_{12}^{\mathrm{exp}} - b_{12}^{\mathrm{id}\,\prime} \tag{4.23}$$

Based on the above theories, if *Δb* > 0 or *Δb'* > 0, attractive intermolecular interactions exists and the polymers in the binary polymeric systems are miscible. Whereas if *Δb* < 0 or *Δb'* < 0, phase separation occurs and indicates the polymers are immiscible.

According to Sun *et al.*, by assuming the absence of strong specific interaction forces between macromolecules which would promote aggregation and at a suitable low concentration, the criterion for miscibility between polymers are given as

$$\propto = k_b - \frac{k_1 w_1^2[\eta]_1^2 + k_2 w_2^2[\eta]_2^2 + 2\sqrt{k_1 k_2}\, w_1 w_2 [\eta]_1[\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{4.24}$$

Where,

$$k_b = \frac{b_\mathrm{b}}{[\eta]_\mathrm{b}{}^2}\,, \quad k_1 = \frac{b_1}{[\eta]_1{}^2}\,, \quad k_2 = \frac{b_2}{[\eta]_2{}^2} \tag{4.25}$$

k_b, k_1 and k_2 are the Huggins coefficients of PCL/PVF blends, pure PCL and pure PVF respectively. $[\eta]_\mathrm{b}$, $[\eta]_1$, $[\eta]_2$ are correspond to the intrinsic viscosity of PCL/PVF blends, pure PCL and pure PVF. When $\alpha \geq 0$ indicates the blend is miscible, $\alpha < 0$ indicates the blend is immiscible.

Jiang and Han had revised the α parameter proposed by Sun et al. by introduced weight additive rule and the following equations were deduced.

$$k_{\mathrm{b}} = \frac{k_1 w_1^2 [\eta]_1^2 + 2k_{12} w_1 w_2 [\eta]_1 [\eta]_2 + k_2 w_2^2 [\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{4.26}$$

Substitute equation (4.26) into (4.24), and the parameter α is replaced with β.

$$\beta = \frac{2\Delta k w_1 w_2 [\eta]_1 [\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{4.27}$$

Where,

$$\Delta k = k_{12} - \sqrt{k_1 k_2} \tag{4.28}$$

$$k_{12} = \frac{b_{12}}{[\eta]_1 [\eta]_2} \tag{4.29}$$

Similarly, the polymers in the blend are miscible if $\beta \geq 0$, whereas they are immiscible if $\beta < 0$.

Another theory was proposed by Garcia *et al.* based on the difference between the experimental and ideal values of intrinsic viscosity.

$$\Delta[\eta] = [\eta]_{\mathrm{b}}^{\mathrm{exp}} - [\eta]_{\mathrm{b}}^{\mathrm{id}} \tag{4.30}$$

Where,

$$[\eta]_{\mathrm{b}}^{\mathrm{id}} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{4.31}$$

And the $[\eta]_{\mathrm{b}}^{\mathrm{exp}}$ is the experimental intrinsic viscosity of PCL/PVF blends, obtained from the intercepts of Huggins plot. If $\Delta[\eta] < 0$ the polymer blend system is miscible and if $\Delta[\eta] > 0$ the system is immiscible.

4.5.4 Miscibility of PCL/PVF blends

By applying Krigbaum-Wall method and Catsiff-Hewett method, the values of Δb and $\Delta b'$ were calculated and showed in Table 4.6. Negative values of Δb and $\Delta b'$ parameters were observed for all the PCL/PVF blend compositions studied. Hence, according to the Krigbaum Wall method and Catsiff Hewett method, PCL and PVF are immiscible for the whole range studied.

Table 4.6: Calculated Δb and $\Delta b'$ parameters for PCL/PVF blends with various compositions.

PCL/PVF blend	Δb	$\Delta b'$	Conclusion
20/80	-0.026	-0.055	Immiscible
50/50	-0.040	-0.068	Immiscible
60/40	-0.040	-0.069	Immiscible
80/20	-0.015	-0.044	Immiscible

The parameters described by Sun method and Jiang and Han method are presented in Figure 4.12. Based on Sun method, the negative α values again suggested that PCL and PVF are immiscible. Likewise based on Jiang and Han method, negative values of Δk and β also indicate the immiscibility of the two polymers studied.

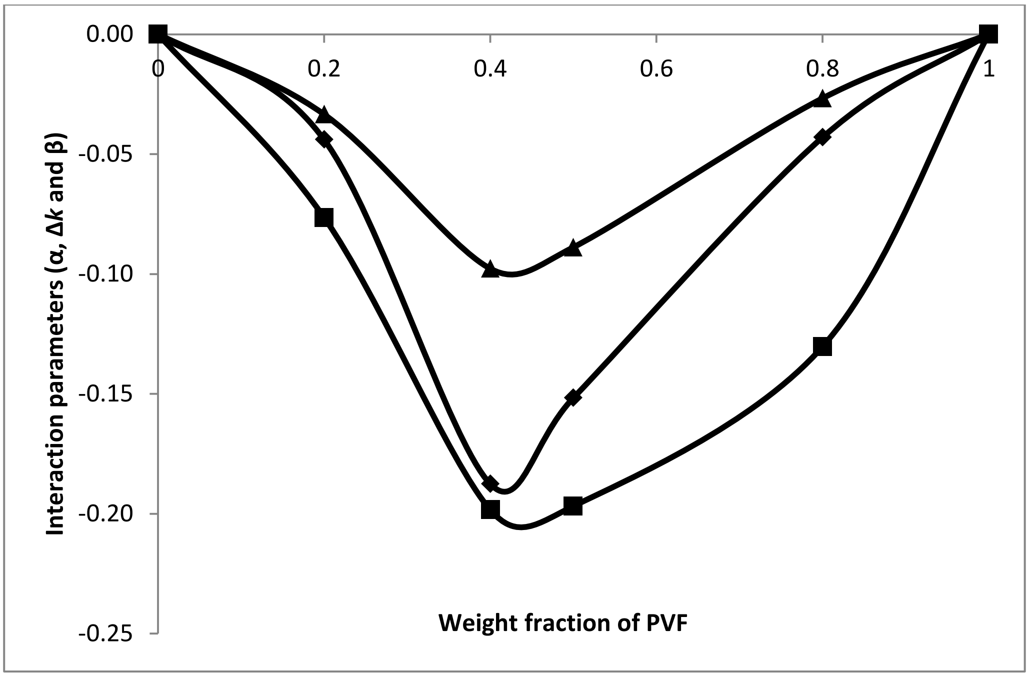

Figure 4.12: Plot of (◆) α, (■) Δk and (▲) β interaction parameters versus weight fraction of PVF.

Lastly, the $\Delta[\eta]$ criteria proposed by Garcia were computed using equation (4.30) and are tabulated in Table 4.7.

Table 4.7: $[\eta]_b^{id}$, $[\eta]_b^{exp}$ and $\Delta[\eta]$ values for PCL/PVF blends with various compositions.

PCL/PVF blend	$[\eta]_b^{id}$	$[\eta]_b^{exp}$	$\Delta[\eta]$	**Conclusion**
20/100	0.561	0.571	0.010	Immiscible
50/50	0.473	0.517	0.044	Immiscible
60/40	0.443	0.511	0.068	Immiscible
80/20	0.384	0.390	0.005	Immiscible

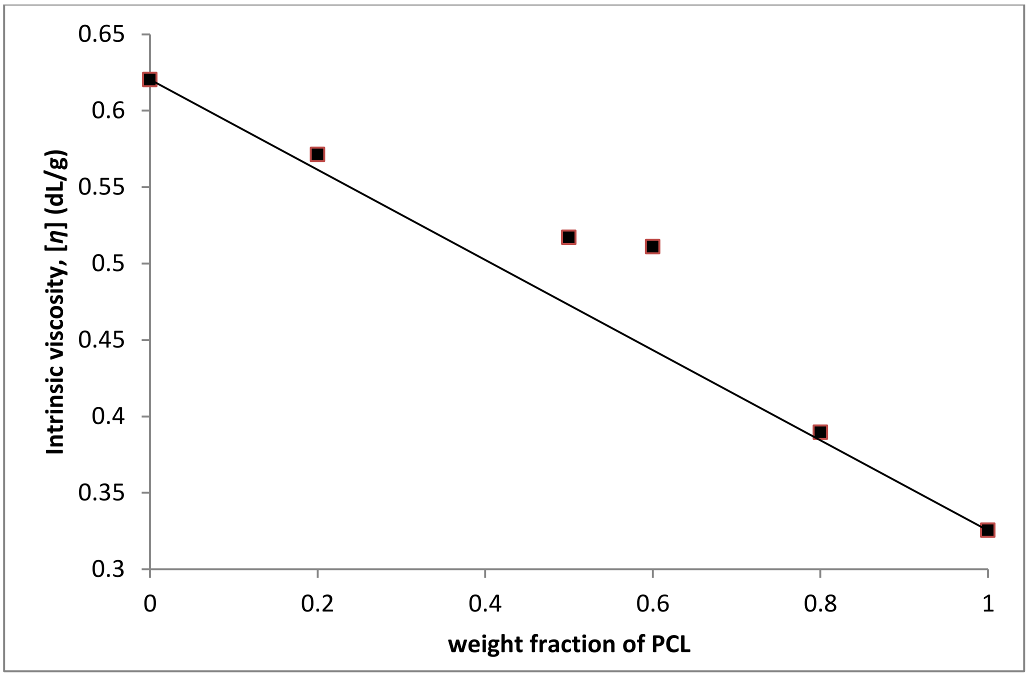

Figure 4.13: Intrinsic viscosity $[\eta]$ as a function of weight fraction of PCL. (−) theoretical value, (■) experimental value.

By referring Figure 4.13, the solid line was plotted from the theoretical intrinsic viscosity $[\eta]_{\mathrm{b}}^{\mathrm{id}}$ values which assume no interaction between PCL and PVF. The solid squares (■) represented the experimental intrinsic viscosity, $[\eta]_{\mathrm{b}}^{\mathrm{exp}}$ values obtained from Huggins plots of the polymer blends. The positive deviations of $[\eta]_{\mathrm{b}}^{\mathrm{exp}}$ from $[\eta]_{\mathrm{b}}^{\mathrm{id}}$ suggested that the PCL and PVF are immiscible for whole range studied.

In this study, various methods were used to investigate the miscibility of PCL and PVF in ternary polymer blend system. All of the methods used showing good agreement. Based on all the results, PCL/PVF blends are concluded to be immiscible in the whole compositions range studied. These results also agreed with the work reported by Rohindra and Khurma (2007) which studied the miscibility of PCL/PVF blends by glass transition temperature, T_g measurements using DSC.

CHAPTER 5

CONCLUSION

PCL/PVF blends were prepared *via* solution casting method. The melting and crystallisation behaviour of PCL in pure state and in PCL/PVF blends were studied by differential scanning calorimetry (DSC). The miscibility of PCL/PVF blends was investigated by dilute solution viscometry (DSV).

The degree of crystallinity, X_c of pure PCL determined to be 53 %. The crystallinity of PCL in the blends decreased gradually with the increasing PVF content, from up to 40 %. Then, a drastic decrease in crystallisation was observed above 40 % of PVF content.

Equilibrium melting temperature, T_m^o for pure PCL was estimated from the Hoffman-Weeks plot. The linear plots of T_m were extrapolated to intercept with a line of $T_\mathrm{m} = T_\mathrm{c}$. The T_m^o was determined as their intersection point, which having the value of 58 °C.

The effects of crystallisation temperature, T_c and blend composition on the rate of crystallisation of PCL/PVF blends were studied. The crystallisation rate of PCL decreased exponentially with increasing T_c. On the other hand, the half-time, $t_{0.5}$ of crystallisation increased exponentially with increasing T_c. Besides that, for constant crystallisation temperature, T_c, the crystallisation rate of PCL reduced with ascending PVF content in the blends. Thus, longer $t_{0.5}$ was observed for the crystallisation with the increasing PVF content in PCL/PVF blends. The Avrami exponent, n_A values varied from 1 to 2, which suggested that PCL crystals growth between one and two dimensional.

The PCL/PVF blend solutions with various compositions were prepared for DSV measurements. Huggins plots for the pure PCL, pure PVF and their blends were used to investigate the miscibility of PCL/PVF blends. Several methods were employed to determine miscibility of the blends which are Krigbaum-Wall, Catsiff-Hewett, Sun, Jiang-Han and Garcia methods. Based on the negative values for Δb, $\Delta b'$, α, Δk and β while positive values for $\Delta[\eta]$, the PCL/PVF blends can be concluded as immiscible within the whole range studied.

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APPENDIX A

A.1 Degree of crystallinity, X_c (Section 4.2)

A.1.1 Examples of calculations for degree of crystallinity, X_c for 90/10 PCL/PVF blend.

w_{PCL} = 0.9

ΔH_m^{o} = 136 J/g

ΔH_{m} = 62.59 J/g

$$X_c = \frac{\Delta H_{\mathrm{m}}}{\Delta H_m^{\mathrm{o}} \cdot w_{\mathrm{PCL}}} \times 100\%$$

$$X_c = \frac{62.59\ \mathrm{J/g}}{136\ \mathrm{J/g} \times 0.9} \times 100\%$$

$$X_c = 51.14\ \%$$

A.1.2 Data for Figure 4.2

PCL/PVF blends	X_{c} (PCL) (%)
100/0	53.07
90/10	51.14
80/20	47.51
70/30	46.82
60/40	44.06
40/60	16.82

A.2 Melting behaviour (Section 4.3)

A.2.1 Data for Figure 4.4

T_c (℃)	T_m (℃)
23	53.74
24	54.05
25	53.76
26	54.12
27	54.20
28	54.75
29	54.32
30	54.44
31	54.77
32	54.76
33	55.08
34	55.31

A.3 Kinetics of isothermal crystallisation (Section 4.4)

A.3.1 Data for Figure 4.6

Degree of crystalline conversion, $X(t)$ (%)	Crystallisation time (t-t_0) (min)				
	100/0	90/10	80/20	70/30	60/40
0	0.00	0.00	0.00	0.00	0.00
5	0.01	0.16	0.19	0.60	0.85
10	0.01	0.24	0.34	1.03	1.54
15	0.02	0.30	0.48	1.42	2.16
20	0.03	0.35	0.61	1.79	2.75
25	0.04	0.40	0.73	2.15	3.30
30	0.04	0.45	0.86	2.51	3.84
35	0.05	0.50	0.98	2.87	4.38
40	0.06	0.55	1.11	3.23	4.91
45	0.07	0.60	1.24	3.60	5.44
50	0.08	0.65	1.38	3.98	5.98
55	0.09	0.70	1.52	4.38	6.54
60	0.10	0.76	1.66	4.79	7.12
65	0.11	0.82	1.82	5.25	7.74
70	0.12	0.88	1.99	5.75	8.42
75	0.14	0.96	2.17	6.31	9.18
80	0.15	1.05	2.37	6.99	10.07

85	0.17	1.16	2.61	7.83	11.16
90	0.20	1.31	2.90	8.98	12.60
91	0.21	1.35	2.97	9.27	12.96
92	0.22	1.39	3.05	9.60	13.36
93	0.23	1.44	3.13	9.98	13.81
94	0.24	1.51	3.22	10.42	14.34
95	0.26	1.59	3.32	10.95	14.95
96	0.28	1.70	3.44	11.62	15.68
97	0.31	1.87	3.58	12.52	16.64
98	0.36	2.19	3.76	13.80	17.90
99	0.46	2.81	4.02	15.57	19.84

A.3.2 Data for Figure 4.7

PCL/PVF blends	T_c (℃)	$t_{0.5}$ (min)
100/0	22	0.05
	23	0.08
	24	0.09
	25	0.15
	26	0.17
	27	0.22
	28	0.31
	29	0.34
	30	0.44
	31	0.52
	32	0.74
	33	0.93
	34	1.19
90/10	18	0.17
	19	0.21
	20	0.28
	21	0.34
	22	0.45
	23	0.66
	24	0.92
	25	1.08
	26	1.67
	27	2.90
70/30	18	0.47
	19	0.72
	20	1.44
	21	1.80

	22	3.03
	23	3.98
	24	5.15
	25	9.22
	26	12.50
40/60	18	1.55
	19	1.82
	20	2.51
	21	3.11
	22	7.31

A.3.3 Data for Figure 4.8

PCL/PVF blends	$t_{0.5}$ (min)
100/0	0.05
90/10	0.45
80/20	1.31
70/30	3.03
60/40	5.04
40/60	7.31

A.3.4 Data for Figure 4.9

	log (t-t_0)		
log[-ln(1-X(t))]	21 ℃	23 ℃	26 ℃
-1.2899	-1.1765	-0.7959	-0.3372
-0.9773	-0.9333	-0.6198	-0.1938
-0.7891	-0.8338	-0.5229	-0.1024
-0.6514	-0.7530	-0.4559	-0.0362
-0.5411	-0.6848	-0.3979	0.0170
-0.4477	-0.6260	-0.3468	0.0682
-0.3657	-0.5907	-0.3010	0.1106
-0.2917	-0.5427	-0.2596	0.1492
-0.2234	-0.5134	-0.2218	0.1875
-0.1592	-0.4729	-0.1871	0.2227
-0.0977	-0.4358	-0.1549	0.2553
-0.0380	-0.4127	-0.1192	0.2878
0.0211	-0.3803	-0.0862	0.3222
0.0806	-0.3405	-0.0555	0.3560

0.1419	-0.3128	-0.0177	0.3909
0.2067	-0.2703	0.0212	0.4281
0.2781	-0.2317	0.0645	0.4713
0.3622	-0.1827	0.1173	0.5237
0.3816	-0.1697	0.1303	0.5366
0.4024	-0.1570	0.1430	0.5502
0.4248	-0.1387	0.1584	0.5647
0.4492	-0.1211	0.1790	0.5821
0.4765	-0.1042	0.2014	0.6010
0.5077	-0.0775	0.2304	0.6243
0.5449	-0.0474	0.2718	0.6542
0.5924	0.0114	0.3404	0.6981
0.6632	0.1482	0.4487	0.7731

A.3.5 Data for Figure 4.10

Weight fraction of PCL	$t_{0.5}^{-1}$	K_A^{1/n_A}
100/0	20.2306	14.5229
90/10	2.2227	1.7911
80/20	0.7634	0.6304
70/30	0.3300	0.2624
60/40	0.1984	0.1607
40/60	0.1368	0.1089

APPENDIX B

B.1 Dilute solution viscometry (DSV) (Section 4.5)

B.1.1 Example of calculation for relative viscosity, η_{rel}, specific viscosity, η_{sp} and reduced viscosity, η_{red} for 80/20 PCL/PVF.

$c = 2.803$ g/dL

$t = 277.50\ s$

$t_0 = 108.88\ s$

Relative viscosity, η_{rel}

$$\eta_{rel} = \frac{t}{t_0}$$

$$\eta_{rel} = \frac{277.50\ s}{108.88\ s}$$

$$\eta_{rel} = 2.549$$

Specific viscosity, η_{sp}

$$\eta_{sp} = \eta_{rel} - 1$$

$$\eta_{sp} = 2.549 - 1$$

$$\eta_{sp} = 1.549$$

Reduced viscosity, η_{red}

$$\eta_{red} = \frac{\eta_{sp}}{c}$$

$$\eta_{red} = \frac{1.549}{2.803}$$

$$\eta_{red} = 0.552$$

B.1.2 Data for Figure 4.11

PCL/PVF blends	c	t (s)	η_{sp}/c
100/0	2.9453	252.98	0.4493
	2.4544	223.61	0.4293
	2.1038	203.62	0.4136
	1.8408	189.65	0.4030
	1.6363	179.15	0.3944
80/20	2.8033	277.50	0.5524
	2.3361	243.50	0.5293
	2.0024	220.58	0.5123
	1.7521	203.38	0.4954
	1.5574	189.66	0.4764
60/40	2.5120	298.28	0.6925
	2.0933	258.80	0.6578
	1.7943	233.28	0.6368
	1.5700	215.74	0.6251
	1.3956	201.78	0.6114
50/50	2.2327	281.10	0.7085
	1.8606	245.49	0.6744
	1.5948	223.00	0.6572
	1.3954	205.79	0.6378
	1.2404	192.76	0.6211
20/80	1.8367	278.23	0.8469
	1.5306	240.88	0.7921
	1.3119	219.60	0.7751
	1.1479	201.17	0.7384
	1.0204	189.28	0.7237
0/100	1.6260	275.69	0.9422
	1.3550	239.74	0.8870
	1.1614	216.91	0.8543
	1.0163	198.68	0.8116
	0.9033	188.00	0.8044

B.1.3 Data for Figure 4.12

PCL/PVF blend	α	Δk	β
0/100	0.0000	0.0000	0.0000
20/80	-0.0430	-0.1303	-0.0267
50/50	-0.1517	-0.1968	-0.0888
60/40	-0.1876	-0.1984	-0.0978
80/20	-0.0440	-0.0765	-0.0334
100/0	0.0000	0.0000	0.0000