

Miscibility, melting and crystallization of poly(ϵ -caprolactone) and poly (vinyl formal) blend

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Abstract

Solution cast blends of poly(ϵ -caprolactone) [PCL] and poly(vinyl formal) [PVF] from dichloromethane was investigated for miscibility by Differential Scanning Calorimetry [DSC], Fourier Transform Infrared Spectroscopy [FTIR] and optical microscopy. Melting (T_m) and crystallization (T_c) temperatures were for the PCL fraction while the glass transition temperature (T_g) was for PVF fraction in the blends. Blends with 20 wt% and less PCL showed a depression in T_m and T_c . Depression in T_c indicated that during the non-isothermal crystallization process, the presence of PVF decreased the PCL segments migrating to the crystallite-melt interface thus reducing the nucleation rate, growth rate and the thickness of the lamella resulting in a depressed T_m . Crystallinity (X_c) decreased gradually with decreasing content of PCL in the blend and was due to the dilution of PCL by PVF. A depressed T_g was observed for 10 wt% PCL blend and remained the same for all other blend compositions. These observations suggested that this blend system has very low degree of miscibility. The degree of miscibility increased at low polyester concentration. FTIR spectra of the blends with low polyester concentrations showed changes in the C=O, O-H and C-O-C regions in the blended PVF and PCL spectra. Optical microscopy showed phase separation in the melt and in the PCL spherulites.

Keywords: Poly(ϵ -caprolactone), poly(vinyl formal), blend, miscibility, crystallinity, amorphous.

1 INTRODUCTION

Interest in polymer blends as a means of obtaining new materials with desired properties and minimum manufacturing cost have gained considerable achievement in the polymer field. Polymer blending is an important process for developing industrial based materials. The physical properties of the blends are markedly influenced by miscibility.

Many polymer pairs are immiscible because the combinatorial entropy of mixing is dramatically low and the enthalpy of mixing is often a positive value. However, there are a few polymer pairs that are miscible and specific intermolecular interactions such as hydrogen bonding, ion dipole and dipole-dipole interactions are believed to be the driving force for miscibility.

Several methods (Leonard *et al.* 1985; Musto *et al.* 1991) have been employed to study miscibility and they vary widely in their application and the information they yield. Thermal analysis and infrared spectroscopy are commonly employed techniques to detect miscibility through changes in glass transition temperature, melting temperature depression and changes in the molecular structure respectively (Lichkus *et al.* 1988; Sargent & Koenig 1991; Cesteros *et al.* 1993).

Poly(ϵ -caprolactone) is a linear aliphatic, biocompatible, semi-crystalline thermoplastic polyester derived from crude oil through ring opening of caprolactone monomer. Although not produced from renewable raw materials, it is fully biodegradable. Poly(ϵ -caprolactone) has good water, oil, solvent and chlorine resistance and biodegrades in the soil through attack by micro-organisms. The degradation times vary with the molecular weight, the degree of crystallinity and the morphology (Immirzi *et al.* 1999;

Jarrett *et al.* 1991). The disadvantage of PCL is that it is brittle and lacks mechanical strength due to its low melting temperature [60°C] and glass transition temperature [-60°C] (Cava *et al.* 2007). To improve these properties, PCL had been blended with many polymers and have been found to be miscible with poly(vinyl chloride) [PVC] (Vernal *et al.* 1981; Clark *et al.* 1989; Clark *et al.* 1991), poly(styrene-co-acrylonitrile) [SAN] within a miscibility window (Janarthanan *et al.* 1993), polycarbonate [PC] (Varnell *et al.* 1981; Cheung *et al.* 1994), poly(hydroxy ether of bisphenol A) phenoxy (Coleman *et al.* 1983; Zheng *et al.* 1997), poly(vinyl phenol) [PVPh] (Moskala *et al.* 1985) and poly(vinyl acetate) [PVAc] (Sivalingam *et al.* 2004) and all have shown to be miscible in the amorphous phase by exhibiting a composition dependent single glass transition temperature. FTIR analysis which is a sensitive technique to monitor changes in the conformation and packing of molecular chains has shown interactions involving the C=O region of PCL with polymers containing hydroxyl groups (Moskala *et al.* 1985).

However, PCL has been shown to be immiscible with poly(vinyl alcohol) [PVA] (DeKesel *et al.* 1999) in the amorphous phase and phase separation has been observed in the melt state despite the presence of high percentage of hydroxyl groups. The cause has been attributed to the strong self associated hydrogen bonds of the hydroxyl groups within PVA. This means that polymers which contain moderate percentage of hydroxyl groups should undergo interaction with PCL.

Poly(vinyl formal) is obtained by reaction of PVA with formaldehyde as copolymers with poly(vinyl acetate) through the reaction of intramolecular acetalization and

involves glycolic groups of PVA in the 1–3 positions. This reaction does not fully acetalize all the hydroxyl groups and consequently the resultant polymer consists of unreacted acetate and hydroxyl groups.

PVF is widely used industrially as enamels in wire insulation, coatings for musical instruments, adhesives and support films for electron microscopy. These enamels provide outstanding toughness, flexibility, abrasion resistance and excellent resistance to transformer oil. Blends of PVF with poly(vinyl pyrrolidone) [PVP] (Jos'e *et al.* 1993) have shown to be miscible and hydrogen bonding resulting from the unreacted hydroxyl groups has been considered to be responsible. Poly(vinyl butyral) [PVB] which has a similar structure as PVF but differs by having an extra three carbons have been shown to be miscible with PCL at low concentrations through the formation of banded spherulites (Hsin-Lung *et al.* 1997).

Since PCL is miscible with PVAc (Sivalingam *et al.* 2004) and hydroxyl containing polymers, PVF containing both groups in its chain and has excellent mechanical properties, we investigated the miscibility between PCL and PVF using DSC, FTIR and optical microscopy.

2 EXPERIMENTAL

2.1 MATERIALS

PCL and PVF were purchased from Aldrich Chemicals and used without further purification. The chemical structures and the average molecular weights determined by GPC in tetrahydrofuran against polystyrene standards and the thermal parameters are shown in Figure 1 and Table 1 respectively. Dichloromethane (CH_2Cl_2) used was of analytical grade and was distilled before using.

Table 1. Molecular weights, T_m and T_g of the polymers.

Polymer	M_n	M_w/M_n	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
PCL	15000	2.02	57	-62
PVF	11300	2.58	-	100

2.2 BLEND PREPARATION

The polymers were dissolved in dichloromethane to obtain 2 %wt/vol (g/cm^3) solutions. Mixing predetermined amounts of PVF solution with PCL solution, blend solutions containing different mass ratios of PCL from 10–90 wt% were obtained. The blend solutions were stirred for 24 hrs before casting them onto clean glass plates. The solvent was allowed to evaporate at room temperature. The films were peeled from the glass plates and dried under vacuum at 45 $^{\circ}\text{C}$ for 5 days to ensure complete removal of the residual solvent before being analysed.

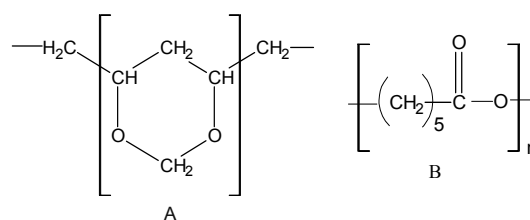


Figure 1. The chemical structure of (A) poly(vinyl formal) [residual alcohol & acetate groups omitted] and (B) poly(ϵ -caprolactone)

2.3 DIFFERENTIAL SCANNING CALORIMETRY

DSC measurements were performed using Perkin-Elmer DSC-6 under nitrogen gas atmosphere at a flow rate of 20 ml/min. Subambient temperatures were reached using the instrument's cooling system to cool the DSC cell. The temperature scale was established using an indium melting point as reference. In all of the cases, aluminum pans were used with sample weight ranging from 3 to 8 mg. The following heat treatments were carried out: (I) Solution-cast samples were heated at 10 $^{\circ}\text{C min}^{-1}$ from 30 to 120 $^{\circ}\text{C}$ (first scan). (II) The samples were conditioned at 120 $^{\circ}\text{C}$ for 5 min to ensure complete melting of the PCL crystals and to eliminate any thermal history effects before being cooled, at 10 $^{\circ}\text{C min}^{-1}$, to -65 $^{\circ}\text{C}$, held for 5 min then heated at 10 $^{\circ}\text{C min}^{-1}$ to 120 $^{\circ}\text{C}$ (second scan). All samples were examined several times to verify the reproducibility of the measurement. The T_g was taken at the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated liquid and glassy lines. The T_m was determined at the maximum of the melting curve. The T_m , weight percent crystallinity and T_g of the films were measured from the second scan. The lamella thickness (L^*) was calculated using the Thomson-Gibbs equation as follows;

$$L^* = \frac{2\sigma_e T_m^o}{\Delta H_f (T_m^o - T_m)} \quad (1)$$

where σ_e is the side surface energy, T_m^o is the equilibrium melting temperature, T_m is the detected melting temperature by DSC, ΔH_f is the melting enthalpy of unit volume of PCL crystals. For this study, σ_e was $40 \times 10^{-3} \text{ J/m}^2$ (Jarrett *et al.* 1991), ΔH_f as $136 \times 10^6 \text{ J/m}^3$ (Cheung *et al.* 1994) and the T_m^o as 78.9 $^{\circ}\text{C}$ (Hsin-Lung *et al.* 1997) were used.

The amount of crystalline phase present in the blends was calculated according to equation 2.

$$X_c = \frac{\Delta H_m / \Phi_{PCL}}{\Delta H_m^0} \times 100\% \quad (2)$$

where ΔH_m and ΔH_m^0 are the enthalpies (J/g) of fusion of blend and 100% crystalline PCL crystals with a value of 136 J/g (Cheung *et al* 1994) respectively and Φ_{PCL} PCL fraction in the blend.

2.4 INFRARED SPECTROSCOPY

Infrared spectra were obtained using a Perkin-Elmer 1000 Fourier Transform Infrared spectrometer at 2 cm^{-1} resolution. Sixty four scans were averaged for each spectrum and corrected for baseline and normalised before analyzing. The blend solutions were cast directly onto sodium chloride (NaCl) windows. Films were thin enough for the Lambert-Beer law to be valid. The solvent was eliminated from the films as stated in the above procedure. All spectra were recorded at room temperature except one spectrum of PCL which was obtained above the melting temperature of PCL. This was achieved by heating the NaCl disk with the PCL film to 90°C . Mathematical manipulation of the data was carried out by the instrument software.

2.5 OPTICAL MICROSCOPY

The samples were melted between microscopic glass slides on a hot stage at 120°C for 3 min. and then quickly transferred to a hot stage equilibrated at 30 and 40°C . The phase morphology was monitored using Olympus BH-2 microscope, equipped with cross-polarizers, a gypsum plate of wavelength 530 nm and a video camera system. The thickness of the sample was ca. $20 \mu\text{m}$. The growth rate of the spherulite was measured by the use of a filar eye piece micrometer and a stop watch. The nucleation time was measured from the time it was removed from 120°C hot stage till the time the first spherulite was seen.

3 RESULTS AND DISCUSSION

3.1 DIFFERENTIAL SCANNING CALORIMETRY

Thermal analysis of PCL, PVF and the blends are reported in Figures 2-5. The T_g values correspond to the PVF phase and T_m , ΔH_m , and X_c correspond to PCL. Figure 2(A) shows the melting endotherms of PCL and its blends. For PCL in the first heating scan, (sample obtained after solvent drying), a melting temperature at 64°C is seen. The high melting temperature indicates that the thickness of the PCL spherulites formed from solvent casting were thick because the PCL chains had more freedom to move. In the second scan two melting transitions occur at 55 and 57°C . Both temperatures are lower than the first scan because the cooling cycle of $10^\circ\text{C}/\text{min}$ was fast for the polymer chains to move and align

during crystallization. This reduced mobility of the polymer chains in the melt resulted in reduced lamella thickness. The peak at 55°C is attributed to the melting of thinner lamella formed through secondary crystallization before melting at 57°C . In the cooling scan a crystallization temperature at 20°C is observed. The T_g was detected to be around -62°C but was very difficult to obtain using DSC. This is because the amorphous interfacial region situated between the lamella crystals did not transform into a mobile amorphous liquid at T_g . In the blends the T_g of PVF was monitored and analyzed. The T_g of pure PVF was detected at 100°C . From Thomson-Gibbs equation, the lamella thickness of the crystals melting at 64, 57 and 55°C were calculated to be 16, 9 and 8nm respectively.

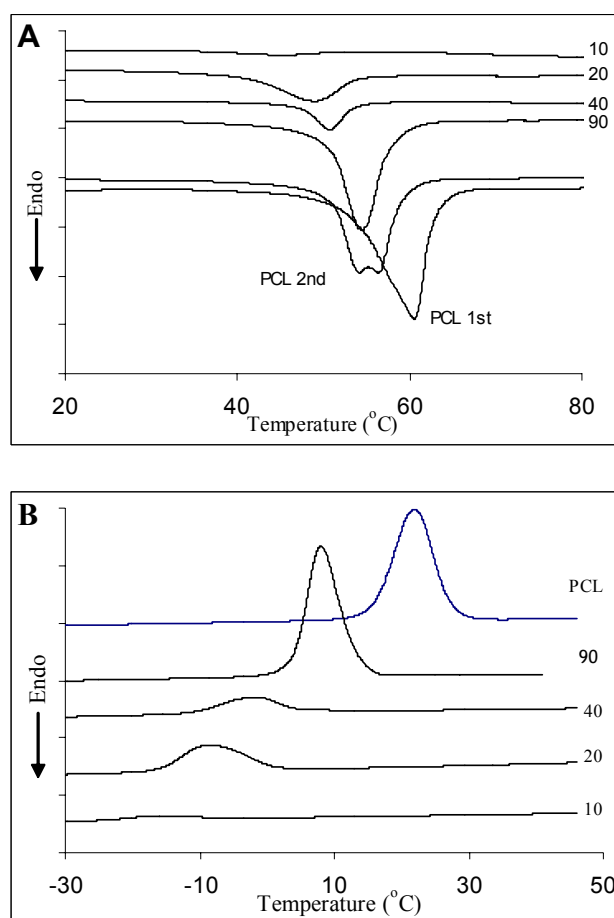


Figure 2. The melting (A) and crystallization (B) temperatures of PCL and its blends. The number represents the wt. fraction of PCL in the blend.

The first indication of blend miscibility in the amorphous phase is a single composition dependent T_g . Figure 3 shows the experimental T_g of PVF in the blends and compared with the T_g calculated using the Fox equation (3) for miscible blends

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (3)$$

where T_g is the expected glass transition temperature of the miscible blend, T_{g1} and T_{g2} are those of pure PCL and PVF respectively, and W_1 and W_2 are the corresponding weight fractions.

It is apparent from Fig. 3 that the experimental T_g 's are very different from the T_g 's obtained from the Fox equation except for the 10 wt% PCL fraction where the T_g corresponded to the T_g predicted from the Fox equation indicating it to be miscible. All other blend compositions showed a slightly higher T_g than 10 wt% blend and remained more or less constant indicating the blend to have the same magnitude of mixing as in the 10 wt% blend. The remaining fraction has very low degree of miscibility, is largely immiscible. The decreased T_g can be due to the breaking of intramolecular hydrogen bonds between the hydroxyl groups in PVF and forming weak interactions with the carbonyl group of the PCL.

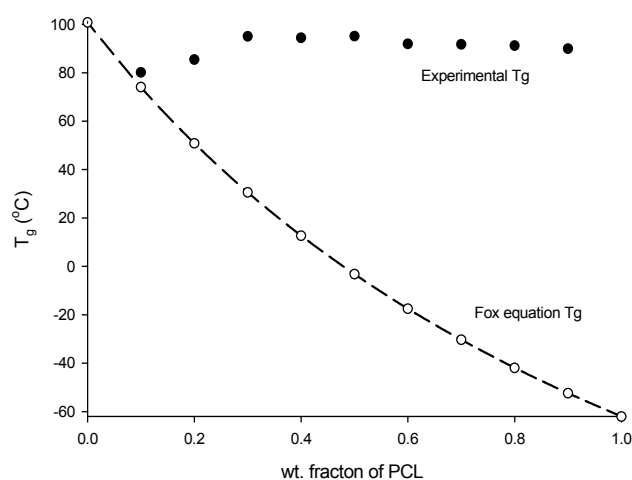


Figure 3. Experimental T_g of PVF in the blends when compared to the predicted T_g from Fox equation

The melting temperature of PCL in the blend depended on the thermal history as shown in Fig. 4. The T_m was detected over the entire composition range both in the first and second scan. This suggests that PCL in the blends existed in a semi-crystalline state.

The results of the second thermal scan indicated a lower T_m than that obtained in the first thermal scan. This indicates the difference in the lamella thickness. No depression in T_m was observed in the first scan with blend composition but in the second scan there was a slight depression for blends with less than 20 wt% PCL. This decrease in T_m can be explained on the basis of the viscosity of the amorphous phase. In the blends, the T_g of PVF remained high, around 100 °C, and as the PCL content decreased, the crystallization process was difficult to occur from the high viscosity of the PVF amorphous phase. The observed melting point depression is thus accounted for the kinetic basis related to the thinning of the lamellar. The lamellar thickness was calculated to be about 6 nm.

During the cooling scan (non-isothermal crystallization), blends with less than 20 wt% PCL also showed a depression in the crystallization temperature. Depression of the crystallization temperature in semi-crystalline-amorphous blends is influenced by several factors (Huang J-M *et al.* 2002).

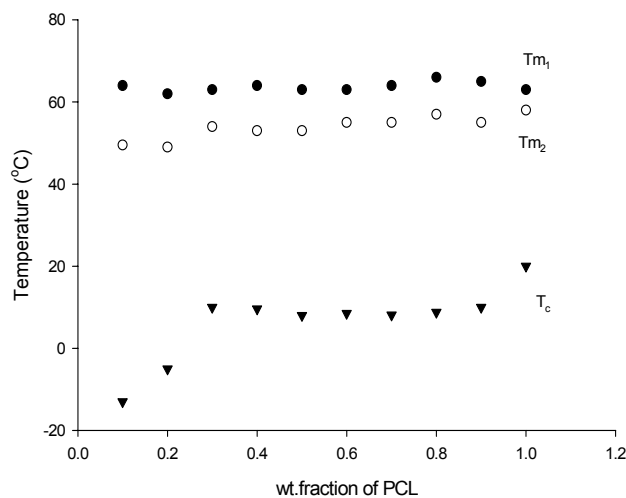


Figure 4. T_{m1} (●) first melting temperatures, T_{m2} (○) second melting temperatures and T_c (▼) crystallisation temperatures of PCL in the blends.

First, the reduction of crystallizable polymer in the melt results in a decrease in thermodynamic driving force favoring crystallization. Secondly, the crystallizable component is diluted with the amorphous polymer, the movement of crystalline segments to the crystallite-melt interface becomes more prolonged resulting in slower crystal growth rate and thirdly, from thermodynamic consideration, the chemical potential of the crystallizable component is reduced due to the addition of the amorphous component.

The crystallinity of pure PCL showed a value of 59 % indicating that PCL was highly crystalline. The crystallinity of PCL in the blends decreased as the amount of amorphous PVF increased as shown in Fig. 5. This trend is characteristic of a crystalline-amorphous blend where the amorphous component merely dilutes the crystalline component. From microscopic studies, the decrease in crystallinity can be explained as follows. As the content of PVF increases in the blend, the nucleation and growth of the PCL crystals are reduced significantly. The cooling rate of 10 °C/min is also fast for the formation of mature crystals due to influence of PVF on the transport process of PCL chains to the crystallite-melt interface prolonging crystallization rate, thus reduction in crystallinity.

3.2 INFRARED SPECTROSCOPY

The infrared spectra of PVF and PCL obtained at room temperature and above the melting temperature of PCL are

shown in Fig. 7. At room temperature PCL existed in the semi-crystalline state and above the melting temperature only the amorphous phase. The carbonyl peak was a very convenient way to distinguish the two phases in PCL. At high temperature the carbonyl peak of PCL was centred at 1734 cm^{-1} and was attributed to the amorphous conformation. At room temperature this band was centred at 1724 cm^{-1} and was attributed to the crystalline conformation (Varnell *et al.* 1981). But at room temperature, the amorphous and crystalline carbonyl bands overlapped.

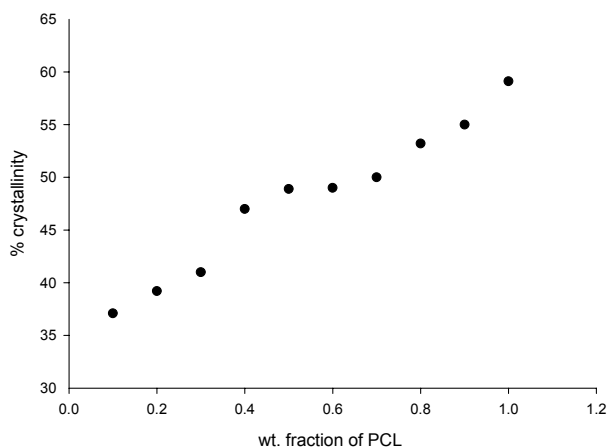


Figure 5. % crystallinity of PCL in the blends.

The second derivative method (Musto *et al.* 1991; Leonard *et al.* 1985) has been shown to be capable of separating overlapping peaks. In Fig. 7 inset, the second derivatives of the carbonyl peak at room and high temperatures are shown. It can be seen at high temperature there is only one negative peak which corresponded to the amorphous conformation. At room temperature PCL is semi-crystalline and two negative peaks are visible. The large peak at 1724 cm^{-1} and a small peak at 1734 cm^{-1} .

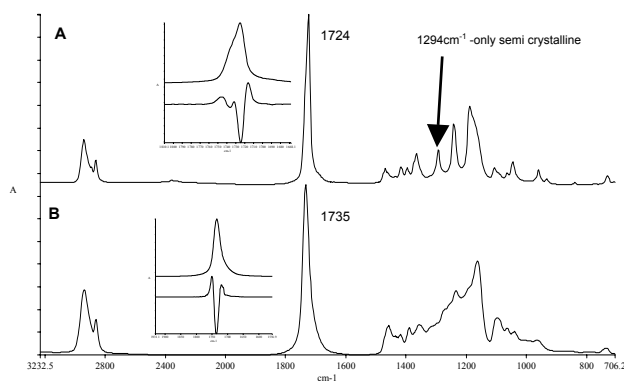


Figure 7. Infra-red spectra of (A) PCL at room temperature, (B) at high temperature and inset is the second derivative of the carbonyl peak.

Other changes observed were in the C-O-C stretching and bending region. Peaks at 1470, 1397, 1367, 1243, 1191 and 1107 cm^{-1} present in the semi crystalline state shifted to 1460, 1390, 1357, 1235, 1162 and 1097 cm^{-1} respectively in the amorphous state. The peak present at 1294 cm^{-1} in the semi-crystalline spectrum disappeared in the amorphous spectrum. This peak is assigned to the backbone C-C and C-O stretching modes in the crystalline PCL (Vernal *et al.* 1981). This peak would be useful to investigate crystallinity changes in PCL.

PVF is a terpolymer as mentioned earlier in the introduction. The FTIR spectrum given in Fig. 8 shows contributions from all components. The semi-broad peak at 3500 is due to the intramolecular hydrogen bonding between the unreacted alcohol groups, peaks at 1180, 1132, 1067 and 1020 cm^{-1} relate to the C-O-C stretching vibrations. The peak at 1733 cm^{-1} is due to the C=O of the residual acetate group (Chetri *et al.* 1997).

Since PCL and PVF both exhibited a carbonyl peak and upon blending the two peaks merged, the spectrum became complicated and direct examination of the peaks to evaluate changes in the polymers became complicated. In order to determine conformational changes occurring in the individual polymers in the blend, the spectrum of one polymer was digitally subtracted from the blend spectrum using the instrument software. To examine changes occurring in PCL, spectrum of PVF was subtracted from the blend spectrum by reducing the peak at 2775 cm^{-1} to the baseline (Rohindra 1997). This peak was characteristic for PVF only. The resulting spectrum was that of blended PCL. Difference spectra of the blends with greater than 20 wt% PCL and the second derivative of the carbonyl peak were similar to the spectrum of semi-crystalline PCL.

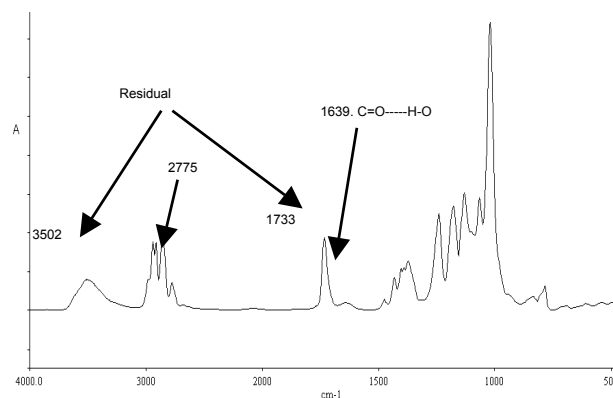


Figure 8. Spectrum of PVF at room temperature.

20 wt% and less PCL blends showed shifts in the carbonyl and C-O-C regions. The spectra were similar to the spectrum of amorphous PCL except for a slight decrease in the wave-number of the carbonyl peak to 1733 cm^{-1} . This decrease is suggestive of some interactions. The second derivative of the carbonyl peak showed one peak. Since the films were only crystallised at room temperature, the

crystalline phase of PCL was too slow to form and in very low amount to be detected in the normal spectrum. However, in the second derivative, small shoulder indicated the presence of the crystalline phase. The presence of the crystalline phase throughout the entire composition range indicated that PCL existed as a heterogeneous phase. This is in good agreement with DSC results, where T_m was observed for the entire composition range and the T_c being observed below room temperature for blends with less 30 wt% PCL.

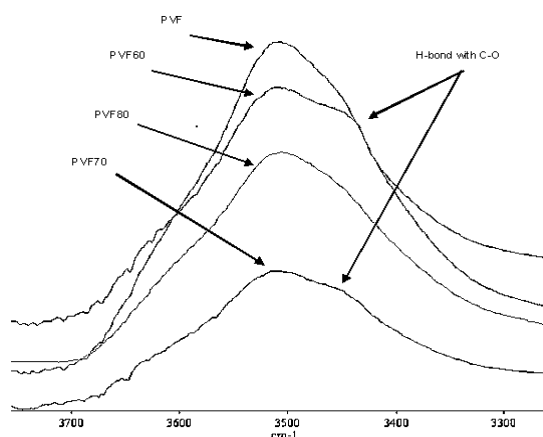


Figure 9. The hydroxyl stretching region of PVF.

The spectrum of PCL was subtracted and the peak at 961cm^{-1} was reduced to the baseline to examine changes occurring in PVF. Changes observed in the blend spectra were in the O-H stretching peak in the $3000\text{--}3800\text{ cm}^{-1}$ region as shown in Fig 9.

The hydroxyl stretching peak appeared at 3502 cm^{-1} . As the concentration of PCL changed from 10 to 40 wt%, a shoulder was observed to increase in intensity around 3450 cm^{-1} and the hydroxy peak shifted to higher wave-number 3514cm^{-1} . According to theory, if hydrogen bonds are formed, the stretching mode of OH bands should shift to lower wave-number. The shift in OH band to higher wave-number can be explained in terms of breaking of the intra-hydrogen bonds between the unreacted alcohol and acetate groups when PCL is added and the hydroxyl groups become free. The large acetal group along the chain may also provide some repulsion between PVF chains. When hydrogen bonds with $\text{C}=\text{O}$ of PCL are formed, they are weak. In addition, the low alcohol content may also contribute to low interaction. A systematic representation is given in Fig. 10 where only the unreacted alcohol and acetate groups are shown and the PVF group has been omitted for clarity.

Due to PVF being auto-associated, observation of hydrogen bonds between PVF and PCL in the OH region was difficult. Similar interactions are suggested for blends of PVF and PVP. The degree of miscibility was seen to increase with low concentrations of PVF. (DeKesel *et al.* 1999; Jos'e *et al.* 1993). Nonetheless, from FTIR results

we can suggest that there are some weak interactions present between the polymers.

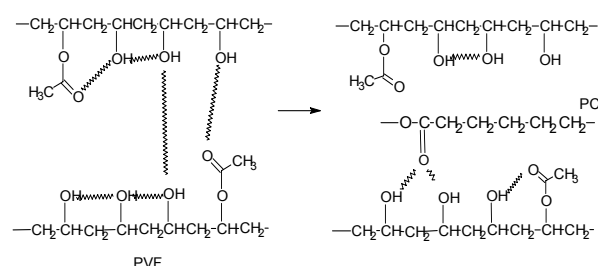


Figure 10. A systematic representation of the hydrogen bonds in PVF and how it changes upon addition of PCL.

3.5 OPTICAL MICROSCOPY

The micrographs of the melt crystallized PCL and PCL 90 wt% blend at 30 and 40 °C are given in Fig. 11. Figure 11 (a & b) shows that spherulites formed are large with polygonal edges indicating that nucleation of all the spherulites were formed almost simultaneously. Under cross polarizer the Maltese cross was observed and the sign of the birefringences was negative. In the blend the nucleation and growth rate was significantly reduced and the effect was more pronounced with increasing crystallization temperature. Apart from the Maltese cross no radial banding was observed at 30 °C. At 40 °C homogenous nucleation was very slow, so after heating, the slide was first touched a cold surface before transferring to 40 °C. From the micrograph (Fig. 11c) the Maltese cross was present but it was difficult to ascertain if banding was present. At 45 °C growth was too slow so we excluded it from the analysis.

In the melt phase of PCL 90 wt% blend, (Fig. 11d), two separated phases are seen, PCL being the matrix and PVF being the domain. When crystallization occurred, PVF appeared in the PCL spherulites as black “fringed network” indicated by an arrow in Fig. 11 (b & d). In the low polyester region of the blends, no spherulites were visible.

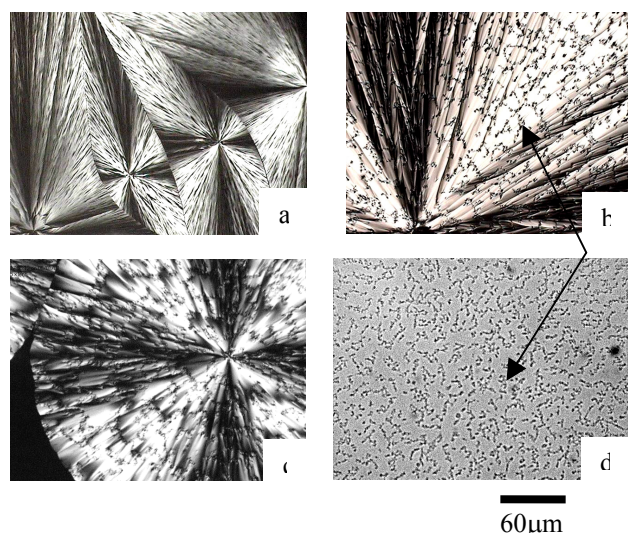


Figure 11. Micrographs of (a) PCL spherulites, (b) PCL 90 wt% at 30 °C (c) 40 °C and (d) in the melt phase.

4 CONCLUSION

Blends of PCL/PVF were prepared by solution casting and the miscibility was studied using DSC, FTIR and optical microscopy. Blends with 20 wt% PCL and less showed a depression in the T_g of PVF. The T_g of 10 wt% blend was comparable to that predicted from the Fox equation indicating miscibility. All other blend compositions showed a T_g value similar to the 10wt % blend indicating the blends to have very limited miscibility. Depression in T_m and T_c and changes in the FTIR spectra at low polyester concentration in the blend indicated that some interactions were present between the polymers. The depression in T_c was due to the PCL component being diluted with PVF and the movement of PCL segments to the crystallite-melt interface became more prolonged and resulted in a slower crystal growth rate with smaller lamella thickness resulting in depressed T_m . Weak hydrogen bonding is believed to be responsible for this interaction involving the unconverted alcohol group on PVF and the carbonyl group of PCL. In the FTIR spectra, a peak appearing around 3450 cm^{-1} as the concentration of PCL is increased, is an indication of hydrogen bonding between the polymers. However, because hydrogen bonding was already present in PVF, observing major changes in this region in the blends was difficult to monitor by infrared. In the blended PCL spectrum, a shift in the carbonyl peak to lower wave-number from 1735 cm^{-1} is again suggestive of some interactions involving the carbonyl bond. It is very difficult to ascertain miscibility in this system based on thermal and infrared studies because the T_g of PCL is difficult to obtain in the blend and the presence of similar overlapping absorptions in the FTIR spectrum. From the observations it is suggested that this blend has very low degree of miscibility. Micrographs showed the presence of two phases both in the melt and in the spherulites. Apart from the Maltese cross, no banding was seen when crystallised at 30 and 40 °C.

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