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**Melting point of a PVdF polymer gel
electrolyte with changing PC:EC ratio**

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Abstract

An investigation in to the effect solvent quality has on the melting point of a polymer gel electrolyte (PGE). The PGE was made up of poly(vinylidene fluoride) (PVdF), Lithium tetrafluoroborate (LiBF_4) and a changing volume ratio of propylene carbonate (PC): Ethylene Carbonate (EC). Differential scanning calorimetry was used to determine the melting point of the PGE, to reveal a very slight increase in the melting point with a greater EC content. A rise of 25°C in the melting point was also observed with the addition of the LiBF_4 .

Introduction

A lot of research into using polymer gel electrolytes (PGEs) for Lithium batteries is ongoing here at Leeds University. There are many benefits of using a gel as an alternative to a liquid electrolyte, particularly as it is flexible yet solid. Traditional batteries using liquid electrolytes require a “separator” between the two electrodes to stop the electrodes coming in to contact with each other. With the use of a gel, the meshing is no longer required as the gel can be formed in to a thin film and used to both stick and separate the electrodes. There is also a major benefit in terms of safety in that a gel will not leak liquid.

A battery consists of a positive and a negative electrode separated by the PGE. The PGE is made up of a polymer and a liquid electrolyte containing a solvent and a salt. Research into further improving the use of PGEs for lithium batteries is to try and increase the ionic conductivity at ambient temperatures, to improve the mechanical strength, along with thermal and electrochemical stabilities [1]. With the specific use of batteries, it is important that the PGE can deal with the extended pressure and temperatures. The stability of the PGE needs to remain during every process from manufacturing through to storage and usage [2].

Polymer electrolytes have now been studied in the solid, liquid and gel phase [3][4][5]. The primary investigation was in to what is termed the “dry solid” polymer electrolyte [1]. The first polymer used was poly(ethylene oxide) (PEO) with a lithium salt. PGEs using PEO demonstrated very poor conductivity, as well as disappointing cycle duration due to reactions with the lithium electrodes [1].

Other research has since been carried out on the use of different polymers, aiming to reach greater conductivities. This research has been performed on a variety of polymers such as poly(ethylene oxide) (PEO)[6][7], poly(propylene oxide) (PPO)[8], poly(acrylonitrile) (PAN) [9][10], poly(methyl methacrylate) (PMMA)[11][12], poly(vinyl chloride) (PVC)[13][14], poly(vinylidene fluoride) (PVdF)[15][16] and poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP)[17][18].

Extending the research even further has been achieved by the addition of plasticizers. In general, plasticizers are added to a polymer both to aid processing and to enhance the mechanical properties. The plasticizer improves the flexibility of the polymer by sitting between the polymer chains. The

solvents added are therefore a major component in the progression from solid to gel polymer electrolytes. Choe et al [16] came to the suggestion that by combining a plasticizer and polymer, it can increase the ionic mobility. However, it is the specific properties of the plasticizer, such as viscosity, dielectric constant and how well the polymer and plasticizer interact, which determines the effect it has on the properties [19].

The focus of the research in this project is into the use of polymers and solvents in increasing the thermostability and mechanical properties of polymer electrolytes.

The polymer that is used to make the gels in this research is PVdF. PVdF ($[-CH_2-CF_2-]_n$) is a semi-crystalline polymer and one of the leading polymers in Lithium battery applications. The strong electron withdrawing functional group, fluoride (-C-F) of PVdF, gives it the potential to be highly anodically stable. The dielectric constant of PVdF is given to be 8.4, which is greater than that of many other polymers. This high dielectric constant is thought to aid the ionization of Lithium salts, resulting in a high concentration of charge carriers [16]. PVdF is also favoured for its optical transparency, along with its mechanical properties at low strain [20].

The initial solvent used in the gel is propylene carbonate (PC), a solvent which has been found to be one of the best for use in previous research [19]. For salted samples of the gel, the PC will be mixed with a lithium salt, lithium tetrafluoroborate ($LiBF_4$).

Another solvent, Ethylene Carbonate (EC) will also be introduced by using different ratios of the two solvents in making the gel, gradually reducing the amount of PC. The key properties of these solvents are shown in table 1. The data values are given at 40°C for EC as its melting point is 37°C and so is a solid at room temperature.

	Molar mass (g)	mp (°C)	bp (°C)	Dielectric constant	Density (g/cm³)	Viscosity (mPa.s)
PC	102.09	-55	243	66	1.19993	2.512
EC	88.06	37	250	89	1.32100	1.919

Table 1: Properties of PC_[21] and EC. Dielectric constant, Density and Viscosity are given at 25°C for PC and at 40°C for EC.

PC is already favoured for having a relatively large dielectric constant, however the greater dielectric constant of EC means that it may solvate and dissociate the salt even more. The lower viscosity of EC also implies that there will be less resistance to the flow of charge. From this information, EC is expected to be a better solvent in terms of conductivity. The two solvents are also known to be some of the most stable organic compounds [16]. Another reason for adding EC is that using PC on its own forms a passivation layer on the electrodes. The formation of this passivation layer not only reduces the life cycle, but also reduces efficiency by slowing down the net charge transfer process [22]. A major area of research is looking into finding the most practical proportions of PC to EC.

This research is to focus on the melting point of the gel when using different proportions of PC and EC. A low melting point is less favourable as electronic devices using the batteries can heat to relatively high temperatures. Using Differential Scanning Calorimetry (DSC) the melting point of the gel made up of the different combinations is investigated. The melting point of gels both with and without the addition of Lithium salt will be explored.

Experimental Method

Making the gel

The gel is made up of 30% polymer, defined as 30% by mass with respect to the solvent. The polymer and salt mass are constant in each gel that is made, with a changing volume ratio, $V_{PC}:V_{EC}$ to be defined at 40°C.

A molar solution is defined as 1 mole of salt made up to 1 litre of solution. The molar mass of $LiBF_4$ is 93.74 g, with the density measured at the University of Leeds to be 1.6gcm^{-3} . Using equation (1) the volume of salt using its molar mass is calculated.

$$V_{salt} = \frac{m_{salt}}{\rho_{salt}} \quad (1)$$

The combined volume of the solvent and the salt is equal to 1 litre, therefore equation (2) is used to calculate the volume of solvent needed to make a 1000cm^3 solution.

$$V_{solvent} = 1000 - \frac{m_{salt}}{\rho_{salt}} \quad (2)$$

In addition to this, the volume of the solvent to be used for a 30% gel using 3g PVDF is calculated using the equation

$$\text{mass \% of polymer} = \frac{m_{PVdF}}{m_{PVdF} + m_{PC}} \quad (3)$$

$$m_{PC} = m_{PVdF} \left(\frac{1}{0.3} - 1 \right) \quad (4)$$

This is true at all temperatures as the mass remains constant however when calculating the volume, the temperature dependent variable, density, is introduced.

$$V_{PC} = \frac{m_{PVdF} \left(\frac{1}{0.3} - 1 \right)}{\rho_{PC}} \quad (5)$$

The calculation is done for a pure PC gel at 25°C. The calculated values of V_{pc} for a 1 mole solution (equation (6)) and V_{pc} for a 30% gel (equation (7)), are used to determine a scaling factor to apply to the molar mass of $LiBF_4$.

$$V_{solvent} = 1000 - \frac{93.74}{1.6} = 941.41 \text{ cm}^3 \quad (6)$$

$$V_{pc} = \frac{3 \left(\frac{1}{0.3} - 1 \right)}{1.19993} = 5.8336 \text{ cm}^3 \quad (7)$$

$$\frac{941.41\text{cm}^3}{5.8836\text{cm}^3} = 161.377 \quad (8)$$

$$\frac{93.74\text{g}}{161.377} = 0.581\text{g} \quad (9)$$

This gives a mass of 0.581g of LiBF₄ to be used in each gel sample. Density is the only variable in the equation that varies with temperature. Research has been carried out to try and find the effect of temperature on the density of EC, however only data defining the density at 40°C has been found. Given that data is available for the density of PC at different temperatures, the density of PC at 40°C is to be used in calculating the volume ratio.

Temp (K)	Temp (°C)	density (g/cm ³)	Viscosity (mPa.s)
298.15	25	1.19993	2.512
308.15	35	1.18916	2.086
318.15	45	1.17871	1.75
328.15	55	1.16816	1.498
338.15	65	1.15753	1.301
348.15	75	1.14696	1.144
358.15	85	1.13633	1.014
368.15	95	1.12571	0.655

Table 2: The density of PC at different temperatures [21]

The values of density with temperature for PC in table 2 are plotted to form a linear relationship and the value at 40°C is taken to be 1.184gcm⁻³. As a result, the PC:EC volume ratio used is defined at 40°C to have the equivalent total volume as that of pure PC at 40°C. Table 3 shows the quantities used for each gel.

Volume Ratio PC:EC	PC Volume (cm ³)	EC Volume (cm ³)	PC mass (g)	EC mass (g)	PVDF mass (g)	LiBF ₄ mass (g)
100 :0	5.9125	0.0000	7.000	0.000	3	0.581
95 :5	5.6169	0.2956	6.650	0.391	3	0.581
90 :10	5.3213	0.5913	6.300	0.781	3	0.581
85 :15	5.0256	0.8869	5.950	1.172	3	0.581
80 :20	4.7300	1.1825	5.600	1.562	3	0.581
75 :25	4.4344	1.4781	5.250	1.953	3	0.581
70 :30	4.1388	1.7738	4.900	2.343	3	0.581
65 :35	3.8431	2.0694	4.550	2.734	3	0.581
60 :40	3.5475	2.3650	4.200	3.124	3	0.581
55 :45	3.2519	2.6606	3.850	3.515	3	0.581
50 :50	2.9563	2.9563	3.500	3.905	3	0.581

45 :55	2.6606	3.2519	3.150	4.296	3	0.581
40 :60	2.3650	3.5475	2.800	4.686	3	0.581
35 :65	2.0694	3.8431	2.450	5.077	3	0.581
30 :70	1.7738	4.1388	2.100	5.467	3	0.581
25 :75	1.4781	4.4344	1.750	5.858	3	0.581
20 :80	1.1825	4.7300	1.400	6.248	3	0.581
15 :85	0.8869	5.0256	1.050	6.639	3	0.581
10 :90	0.5913	5.3213	0.700	7.029	3	0.581
5 :95	0.2956	5.6169	0.350	7.420	3	0.581
0 :100	0.0000	5.9125	0.000	7.810	3	0.581

Table 3: Table of the masses required for different volume ratios of PC:EC at 40°C. All masses are measured to ± 5 mg.

The gels are made in an oxygen free environment; the nitrogen filled “glove box”. To prevent any moisture entering the glove box, any equipment is stored in an oven at 110°C for several hours before it is inserted through the mini antechamber. To prevent contamination from the air, the antechamber is evacuated and refilled with nitrogen 3 times before it is opened from the inside.

As the melting point of EC is 37°C, the solvent is stored in a 50°C oven so that it is in liquid form for mixing. The solvents and the salt are added together and left to mix on a vibrating plate with a magnetic stirrer, allowing the salt to dissolve. This liquid electrolyte is then combined with the PVdF polymer and heated at 160°C as it turns from a white to clear slurry. The slurry is then stirred forming a gel which is left to cool.

Differential Scanning Calorimetry

The DSC method consists of two individual heaters, one which heats the sample pan containing the gel and the other which heats an empty reference pan. Both sample and reference are heated at a constant rate dT/dt , adjusting the heat rate dQ/dt delivered to the sample pan so that the temperature is constant across the sample and reference. Once the sample has reached its melting temperature, extra heat needs to be added to melt the polymer crystals and remain at the same heating rate as the empty pan. This added energy produces a peak on a Heat flow against Temperature plot for the melting transition. This peak allows the onset temperature, the temperature which the gel begins to melt, to be obtained. The PYRIS software also gives a value of ΔH , which is the latent heat, L required to melt the sample. This is calculated using the area under the peak by equation (10).

$$Peak\ Area = mL \frac{dT}{dt} \quad (10)$$

Where m is the mass of the sample used.

Once the gel has cooled it is reheated using the DSC. Initially, the DSC and PYRIS computer software are calibrated by heating an Indium reference sample, recording the melting temperature of the sample and inputting it into the calibration window. The process is repeated using the final value for the onset as the one used for calibration.

Samples of between 5 and 10mg of the gel are used and compressed inside an aluminium casing. The sample is set to heat from around 80°C to 140°C for the salted gels and roughly 50°C to 120°C for the unsalted gels. All of the gels are heated at a constant rate of 10°Cmin⁻¹.

Results and Discussion

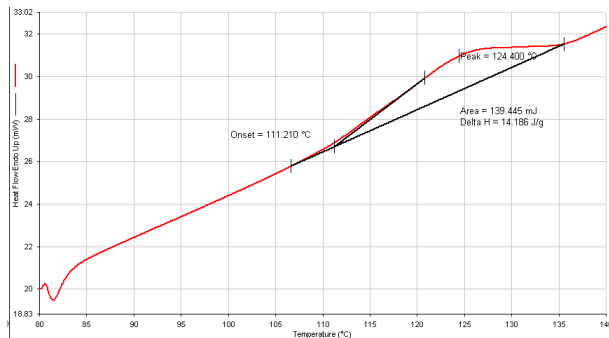


Figure 2: DSC melting peak of a PGE with LiBF₄ using a 70:30 volume ratio of PC:EC

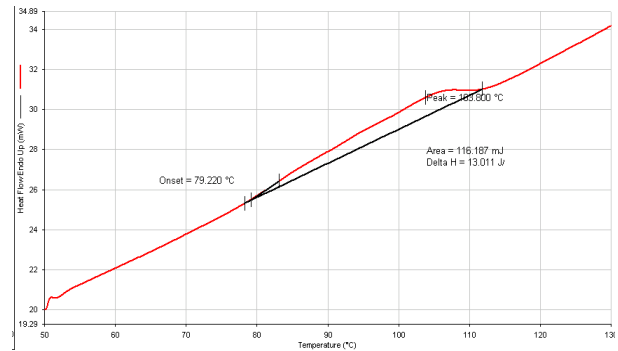


Figure 3: DSC melting peak of a PGE using a 70:30 volume ratio of PC:EC

Figure 2 and figure 3 are both examples of the melting peaks produced when heating the gel samples using the DSC method. Both examples have been taken from the same volume ratio of 70:30 to compare the difference between a sample containing LiBF₄ and one without. It can be seen that the onset occurs at a heat flow of around 26 mW yet the peak starts to form at a much lower temperature for the unsalted sample. Both samples show a small peak at the start as the system adjusts to temperature.

The data is given by the software once the start and end of the peak has been determined by the user, to give the baseline shown. The onset value is then determined by where the maximum slope of the peak meets this base line.

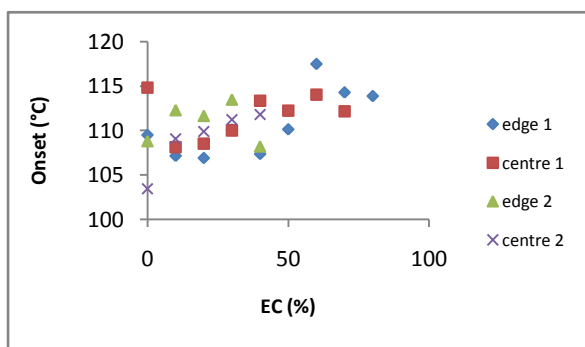


Figure 4: All data for onset temperature

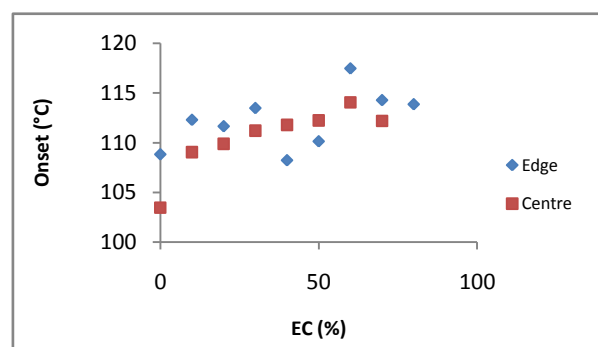


Figure 5: Samples taken from the centre of the bulk gel are the most reliable

The onset temperature as the volume of EC increases is plotted in figure 4 for data measured from samples taken from the centre of the gel and from the edge. Data does not go up to 100% EC as due to the nature of EC, it becomes difficult to make the PGE at proportions greater than 60%. The gel becomes hard to stir, particularly for the unsalted samples. In retrieving the first sets of data a

variation in results was discovered. It was therefore decided to see if the results are dependent on where in the gel the sample used in the DSC was taken from. Samples were taken from both the centre and outside of the gel. Data sets 1 and 2 refer to the initial data and the repeats respectively. The variation can be seen from the spread of data points in figure 4. At a glance, the lower percentage of EC is where there is a greater spread. It is also clear that with experience, technique in fitting the peaks to determine the data improves. It is thus predicted that the data from the repeats is the most precise. Due to the limited time available repeats were not carried out for the full set of data and so were only repeated up to 40% EC. As the data points for the lower percentages of EC were the very first data to be taken, data from the repeats was combined with the higher end of the initial data. This data is presented in figure 5. In comparing the centre and edge data, data taken from the centre of the gel shows the clearest trend. This could be due to a difference in consistency from mixing in the centre as some of the solution may have been left around the edge. Another explanation may be due to the sample drying out around the edge.

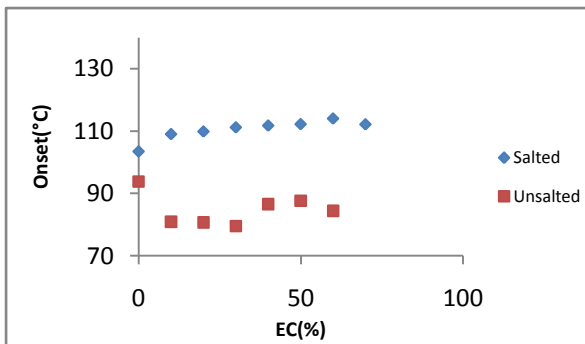


Figure 6: Onset temperature with increasing volume of EC for salted and unsalted gels

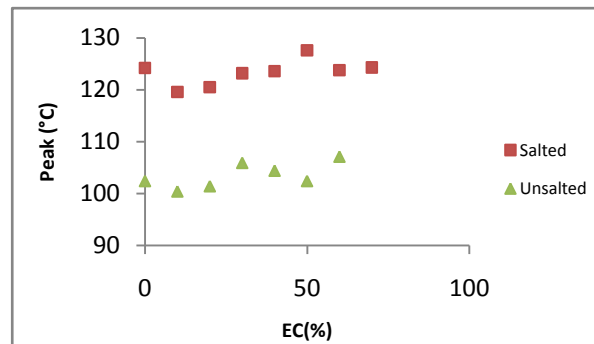


Figure 7: Peak temperature with increasing volume of EC for salted and unsalted samples

There is a clear trend present that the onset temperature increases with increasing volume of EC for salted samples, especially on the slightly larger scale shown in figure 6. Although the trend is not as clear for unsalted samples, there is an overall reduction in the onset temperature as the EC content is increased. Figure 7 is plotted using the most reliable set of data for the Peak temperature. When looking at the peak melting temperature, it is evident that by incorporating the LiBF_4 into the gel, the melting point increases by around 25°C . This suggests salt may affect the solubility of the gel in order to increase the melting point.

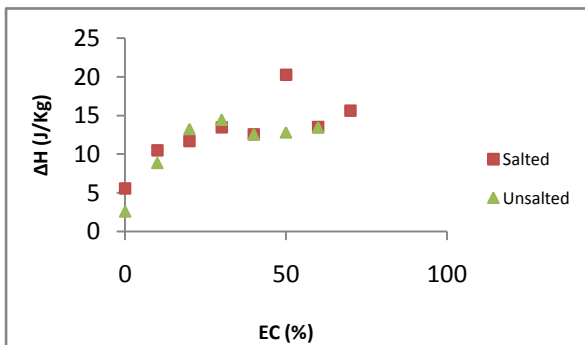


Figure 8: ΔH with increasing volume of EC for salted and unsalted samples

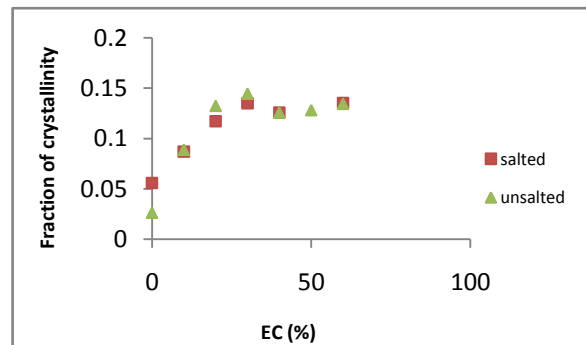


Figure 9: Fraction of crystallinity with increasing volume of EC for salted and unsalted samples

Figure 8 shows a plot of ΔH with increasing EC content, using the two sets of data which, with the limited data available, seem the most reliable. There is a clear outlier in the results for the salted sample at 50% which shall be dismissed. Investigation would be carried out into this particular concentration if more time was available.

ΔH , or the Latent heat, L can be used to calculate the fraction of crystallinity, Φ_c of the sample.

$$\phi_c = \frac{L_{sample}}{L_{polymer}} \quad (11)$$

The Latent heat of PVdF is given to be approximately 100 Jg^{-1} . Using the values obtained for L_{sample} , the fraction of crystallinity is calculated and plotted as the EC content increases in figure 9. The trend in figure 9 implies no difference in crystallinity with the addition of salt. The crystallinity increases up to 30% EC and is reduced at 40%. As there is only data available up to 60% it is not clear whether it then levels out or begins to increase at a slower rate.

The next stage is to explore any reasons why or predictions into the melting point increasing with addition of EC. Recent research into the combined melting point of solvent and polymer is limited; however a large amount of research was carried out over 60 years ago but is still widely used today.

Hansen Solubility parameters

The solubility parameter was developed to help predict the thermodynamic behaviour of a solution. The Hansen model is a development on the original one-dimensional Hildebrand solubility parameter [23]. The Hansen solubility parameters (HSP) consider the dispersion forces, polar interactions and hydrogen bonding of each substance to give the three components given in equation (12).

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (12)$$

The HSP aid prediction as to how well substances will dissolve. Solvents are generally miscible if they have similar HSP [24].

	$\delta/\text{MPa}^{1/2}$			
	δ_t	δ_d	δ_p	δ_h
PVdF	23.2	17	12.1	10.2
PC	27.3	20	18	4.1
EC	29.6	19.4	21.7	5.1

Table 4: Hansen's 1971 solubility parameters [25]

HSP for the polymer and solvents used in this paper, are given in table 4. These values were obtained by Hansen through various solubility experiments, however do have limitations. HSP are only an approximation and are dependent on molecular size as well as temperature. The given parameters are defined at room temperature. The rate of solubility increases with temperature and it is expected that HSP fall at high temperatures, particularly for the hydrogen bonding parameter. However, it has been found that using the values at room temperature gives adequate results for trends at higher temperatures. It is therefore assumed that the parameters all demonstrate the same temperature dependence in most research to date [26].

Flory interaction parameter

The interaction parameter introduced by P.J. Flory is a dimensionless quantity represented by the symbol χ . The parameter is related to the difference in energy of a solvent molecule in a solution of pure polymer to that of pure solvent [27].

$$\chi_1 = \frac{BV_1}{RT} \quad (13)$$

Where V_1 is the molar volume of the solvent, R is the gas constant and T is the absolute temperature. B represents the energy of mixing per unit volume.

Hansen elaborated on this theory to make a connection of the interaction parameter with the Hansen solubility parameters. As the HSP are known for PVdF, PC and EC, equation (14) will be used to calculate the interaction parameter for PC and EC.

$$\chi = \frac{(\delta_{solvent} - \delta_{polymer})^2 V_{solvent}}{RT} \quad (14)$$

As there is only density information available at 40°C for EC, that is the temperature that is used and the temperature in which $V_{solvent}$ is defined. To see the effect of temperature on χ , the data from table 2 is used to plot χ with increasing temperature, assuming a similar relation for EC.

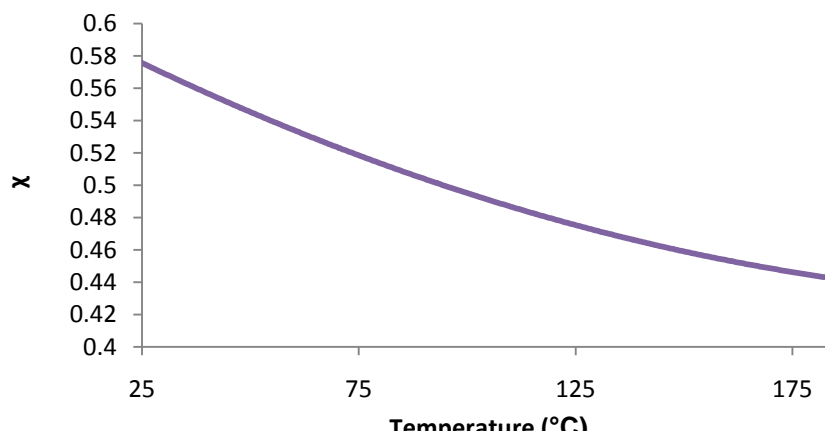


Figure 10: Flory Interaction parameter χ with increasing temperature

The linear relationship between density and temperature for PC is used to extrapolate data for temperatures above the melting point of pure PVdF. χ decreases from 0.58 to 0.44 as the temperature increases from room temperature to 180°C. χ is used as a measure to determine how well the solvent can dissolve the polymer. A polymer that easily dissolves the solute is defined as a good solvent, where $\chi < 0.5$. The solvent is termed a 'theta solvent' when $\chi = 0.5$ and is when there is a balance between the intramolecular forces of the polymer and the intermolecular forces between the solvent and polymer. This stage can be referred to as the threshold value where the solvent and polymer are happy to mix. If $\chi > 0.5$, the solvent is characterised as a poor solvent. A poor solvent is where the two will not mix as the solvent does not dissolve the polymer.

Figure 10 therefore shows that PC begins as a poor solvent at room temperature, becomes a theta solvent at around 80°C and develops into a good solvent as it is heated further. At the temperature used in heating the sample when making the gel, 160°C, χ is roughly 0.45 and so will dissolve the PVdF.

For consistency, the values of χ for PC and EC at 40°C are calculated to be 0.557 and 1.049 respectively. EC therefore has a much higher value for χ , although if it does follow the same trend as PC, it will improve upon heating.

Equilibrium melting point, T_m

The fusion process for a crystalline polymer occurs over a range of temperatures, however the melting point T_m refers to the exact temperature in which the crystalline structure disappears [28]. T_m is where the chemical potential of the polymer repeat unit is equal for the liquid and crystalline phase [27]. In early research, Flory predicted that the melting temperature range would expand with the addition of a diluent. Flory stated that for a polymer containing noncrystallizable impurities, such as a solvent, the chemical potential will be less than that of a pure polymer. This meant that when a diluent is added at the melting point of the pure polymer, T_m^0 , in order to meet the equilibrium conditions of the chemical potentials, a lower temperature T_m is needed. He used the theory of melting point depression along with solubility relations. He concluded that the difference in chemical potential of the crystalline repeat unit and the pure liquid polymer (standard state) at the same temperature and pressure, must be the same as the loss in chemical potential of the polymer unit in the solution relative to the standard state.

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{RV_u}{\Delta H_u V_1} \right) (v_1 - \chi v_1^2) \quad (15)$$

Equation (15) therefore allows the melting point of a polymer and solvent solution to be determined by the interaction parameter calculated previously. It is also dependent on the heat of fusion of the polymer, ΔH_u , the molar volume of the polymer repeat unit, V_u and the volume fraction of the diluent, v_1 [27]. Several values for T_m^0 have been quoted, however it is known that the equilibrium melting point tends to be 5-10° higher than what is measured using any method [29]. It is also acknowledged that pure PVdF can exist in many crystal forms which will all melt at slightly different

temperatures [30]. Welch and Miller give a value of T_m^0 to be 177.5°C [29], which is used in the following calculations.

Solvent	Molar mass, M (g mol ⁻¹)	Molar volume, V ₁ (cm ³ mol ⁻¹)
PC	102.09	86.23
EC	88.06	66.66

Table 5: Molar mass and Volume for PC and EC

The molar masses shown in table 5 were used to calculate the adjacent molar volumes of the solvents, using the density for both defined at 40°C. For PVdF, the value of ΔH_u is given to be 5965 J mol⁻¹ and V_u to be 36.4 cm³ mol⁻¹ [31].

Values are used in equation (15) to obtain the theoretical melting point with an increasing volume fraction of diluent for both PC and EC. The molar volumes shown in figure 11 are at 40°C, however T_m was calculated for a variety of temperatures for PC, as high as T_m^0 . When plotted together, there was no significant difference in the values with respect to temperature.

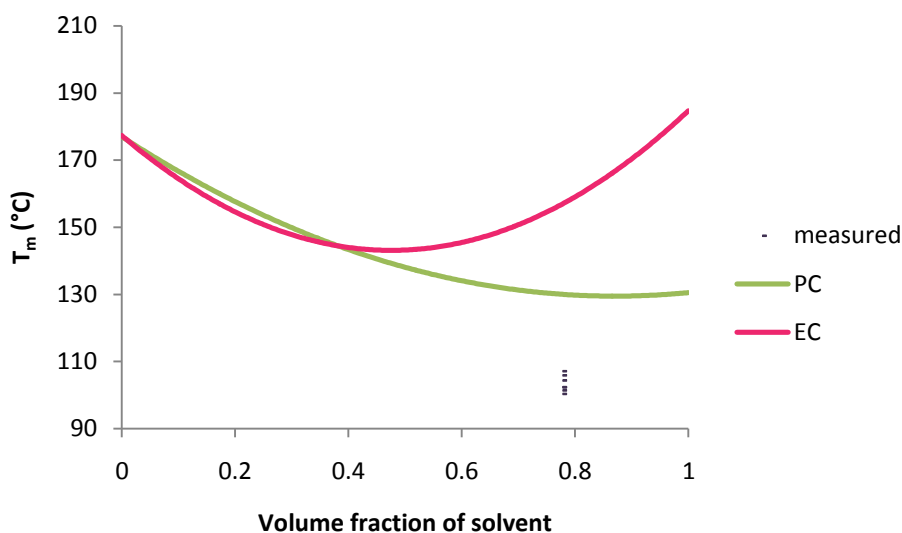


Figure 11: Theoretical and experimental values of T_m against volume fraction of diluents. The experimental data is all at the same concentration, T_m rising with increasing proportion of EC.

It is seen from figure 11 that theory predicts no significant difference in T_m between PC and EC up to a volume fraction of 0.4. At greater volume fractions, theory then suggests a decrease in T_m for PC, whilst an increase in T_m for EC.

To compare the theory against experimental values, the volume fraction used for the 30% PVdF samples was calculated. Given a density of 1.78 g cm⁻³ and the mass of 3g used, the volume of PVdF in a sample was calculated to be 1.685 cm³. A volume fraction of 0.778 was then obtained and the

experimental values taken from the DSC data were plotted. As the theory is purely for polymer and solvent interactions, only the unsalted measurements were plotted.

It is assumed that the combined T_m of adding both PC and EC would lie between the values of pure PC and pure EC shown by the red and green lines in figure 11. The observed melting points are therefore much lower than theory predicts. Theory does however, support the trend of an increase in the melting point when a greater proportion of EC is incorporated.

There are several reasons as to why the experimental values do not fit exactly with the theoretical data, largely due to the semi-crystalline nature of PVdF. The theory is limited for semi-crystalline polymers as it does not consider the extra energy required in breaking the crystals. This aside, the theory clearly fits the observed trend and there is currently no better theory to compare.

Conclusion

The aim of this research was to explore the change in the melting point of a PGE when using different volume ratios of solvents. Different ratios of PC:EC were added to PVdF and LiBF_4 . The samples were heated using differential scanning calorimetry to record the melting peaks of each sample. The results showed a small increase in the melting point with increasing EC up to 70%. Ratios of greater EC content could not be achieved. The results also revealed that the melting point for samples without the LiBF_4 melted at temperatures roughly 25°C below that of the salted samples. The experimental results were compared with the Flory-Huggins theory for melting point depression, using the Hansen solubility parameters for the polymer and solvents. The expected values of T_m calculated were higher than those observed. However, the theory estimates a decrease in melting temperature T_m when mixing PVdF with PC, whilst an increase in T_m with a combination of PVdF and EC. Thus, although the exact melting point depression doesn't agree entirely, the results show a very clear trend to that predicted by theory.

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