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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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### *In situ* FTIR spectroscopic study of the effect of CO<sub>2</sub> sorption on H-bonding in PEG–PVP mixtures

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#### ARTICLE INFO

##### Article history:

Received 20 May 2010

Received in revised form 10 January 2011

Accepted 26 January 2011

##### Keywords:

Supercritical fluids

ATR

FTIR spectroscopy

H-bond

Polymer blends

#### ABSTRACT

A study of the H-bonding between poly(ethylene glycol) (PEG) and polyvinylpyrrolidone (PVP) in the presence of supercritical carbon dioxide at various temperatures, pressures, different  $M_w$  of PEG and PVP and different PEG/PVP ratios is presented. *In situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to investigate H-bonding by examining changes in the relative intensities and positions of peak maxima of the 2nd derivative  $\nu(\text{C}=\text{O})$  bands associated with 'free' and H-bonded C=O groups. In general, relative intensities of bands associated with H-bonded C=O groups decreased upon CO<sub>2</sub> sorption and was accompanied by an increase in intensity of bands associated with 'free' C=O groups. At the same time, these bands were shifted to higher wavenumbers. These shifts were attributed to the shielding effect of CO<sub>2</sub> molecules on H-bonding interactions between PEG and PVP. The magnitude of the effects of CO<sub>2</sub> shielding generally increased with decreasing polymer  $M_w$  and increasing CO<sub>2</sub> content. However, upon CO<sub>2</sub> venting the extent of the H-bonding between PEG and PVP reappeared. The extent of H-bonding recovery was greatest for blends with low  $M_w$  PEG ( $M_w: 4 \times 10^2$ ) and PVP ( $M_w: 9 \times 10^3$ ) and PEG content  $\geq 0.54$  wt% under mild conditions of pressure (80 bar) and temperature (35 °C). For the same low  $M_w$  blends, increasing pressure to 150 bar, or temperature to 50 °C, showed poor H-bond recovery upon CO<sub>2</sub> venting. Overall, it was shown that supercritical CO<sub>2</sub>-induced shielding of H-bonding interactions in polymer blends is reversible upon CO<sub>2</sub> venting, and the magnitude of both was influenced by processing conditions and blend composition.

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#### 1. Introduction

Supercritical CO<sub>2</sub> has shown increased application as processing medium for polymers. Supercritical CO<sub>2</sub> is able to swell and plasticise polymers dramatically, allowing processes such as foaming [1], encapsulation [2], impregnation [3,4] and particle formation [5]. The high diffusivity of supercritical CO<sub>2</sub> combined with the ability to plasticise polymers allows it to act as a vehicle for the migration of various guest components into a polymer matrix [6–10]. In addition, the diffusivity and solvent power (which affects polymer plasticisation and swelling) is easily tuned with changes in pressure and temperature as evidenced by density-dependant polarity values [11]. This tunability allows for optimisation of process conditions.

A number of studies have indicated that increased CO<sub>2</sub> density leads to a decrease in inter-specie interaction or even phase sep-

aration of specifically interacting polymers. For instance, various authors have shown that the equilibrium constant for dimerization between molecules decreases with increased CO<sub>2</sub> pressure [12–14]. This decrease is most significant at densities above the critical density of the solvent. The decrease in dimerization is attributed to local density enhancement of CO<sub>2</sub> molecules around the reactants – generally referred to as solvent clustering.

Phase separation of specifically interacting polymers has also been shown to be due to CO<sub>2</sub> sorption. Walker et al. [15] studied the effect of increased pressure on the phase behaviour of specifically interacting blends of amorphous poly(methyl methacrylate) (PMMA) and semi-crystalline poly(vinylidene fluoride) (PVDF). These polymers are believed to show strong specific interactions between their electric moments and hydrogen-bond interactions between the electron-rich carbonyl oxygen of PMMA and the electron-poor hydrogen of PVDF. Blends were first compression moulded and then exposed to CO<sub>2</sub> at various pressures. Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to investigate phase behaviour. At CO<sub>2</sub> pressures of up to 359 bar, no significant changes were noticed. However, at CO<sub>2</sub> pressures of 655 bar and higher, significant increases in scattering intensity were noticed, signifying the formation of ordered

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structures. In TEM images, the PVDF-rich dispersions showed increased definition and higher electron densities. This behaviour was more pronounced in blends with higher PVDF concentrations. Indications were that some PVDF fractions have aggregated to form lamellae. Two possible reasons were given for this behaviour: (1) at higher pressures, the CO<sub>2</sub> acts as a screen for intermolecular PVDF–PMMA interactions; (2) at higher pressures, the  $T_g$  of the blend ( $T_{gBLEND}$ ) ( $\approx 88^\circ\text{C}$ ) was reduced to below the operating temperature of  $35^\circ\text{C}$ . This allows sufficient chain mobility for PVDF molecules to crystallise, thereby expelling PMMA molecules.

The phase behaviour of blends of weakly interacting poly(deuterated styrene) (d-PS) and poly(vinyl methyl ether) PMVE was also investigated [16]. These blends share weakly interactive charge-transfer interactions. The blends were prepared by first casting from a common solvent, dried, and then melt pressed into discs at  $60^\circ\text{C}$ . At ambient pressures and with no CO<sub>2</sub>, the critical temperature ( $T_c$ ) at which phase separation occurred for this blend was  $155^\circ\text{C}$ . After CO<sub>2</sub> sorption at a pressure of 240 bar, the  $T_c$  for this blend was reduced to  $40^\circ\text{C}$ . Using the Sanchez–Lacombe equation of state, it was estimated that at 240 bar, only about 3.3 wt% CO<sub>2</sub> was dissolved in the blend. Due to the very low CO<sub>2</sub> concentrations and weak CO<sub>2</sub> selectivity for any of the functional groups, it was concluded that the phase separation was not enthalpic-driven, but rather driven by entropic effects. This suggestion was based on evidence that a disparity existed in the degree of CO<sub>2</sub> sorption between d-PS and PMVE. Since compressibility of the blend increased rapidly with CO<sub>2</sub> sorption, the differential dilation of the two components lead to significant differences in their degrees of compressibility. These differences were believed to be the main cause of phase separation. The authors found similar behaviour under weakly interacting deuterated polybutadiene and polyisoprene blends [17]. Phase segregation in this case was also attributed to disparities in compressibility of the two polymers after CO<sub>2</sub> sorption.

Fleming et al. [7] studied supercritical CO<sub>2</sub> enhanced interdiffusion of poly(vinyl pyrrolidone) (PVP) and poly(ethylene glycol) (PEG). Films of PVP and PEG were cast alongside each other on a diamond ATR crystal. Interdiffusion was studied via FTIR-ATR images using a focal plane array detector and FTIR-ATR spectra themselves. Under atmospheric conditions, no interdiffusion was noticed as expected. At 40 and 80 bar, initial interdiffusion was noticed after 56 and 10 min respectively. The increased interdiffusion was explained as being due to increased chain mobility with higher CO<sub>2</sub> content. In this system, hydrogen bonding at the interface between PVP and PEG was also studied. In the absence of CO<sub>2</sub>, the FTIR carbonyl band of PVP showed two conditions: unassociated carbonyl groups and associated (hydrogen-bonded) carbonyl groups. In this case, the carbonyl interacted with the terminal hydroxyl group in PEG. With increased CO<sub>2</sub> pressure, the hydrogen bonding interaction decreased as a result of a greater concentration of CO<sub>2</sub> molecules competing with the hydroxyl groups for carbonyl interaction. Based on this, they concluded that greater interdiffusion was due to both increased plasticisation and decreased intermolecular friction due to decreased hydrogen bond interactions.

In the previous study, PEG/PVP blends were prepared in supercritical CO<sub>2</sub>, ethanol and as physical mixtures [18]. After processing, thermal and spectroscopic techniques (DSC, DMA and ATR-FTIR) were used to compare the level of homogeneity and hydrogen bond interaction. Supercritical CO<sub>2</sub> processed blends showed homogeneity and hydrogen bond interaction levels that were greater than physically mixed blends, but generally poorer compared to solvent cast blends. For this reason, studying the evolution of hydrogen bond interactions between PVP and PEG *in situ* under high-pressure CO<sub>2</sub> and during CO<sub>2</sub> venting would be of interest. The understanding of interaction behaviour during CO<sub>2</sub> processing; pressurisation,

maintaining of pressure, depressurisation, the effect of polymer molecular weight ( $M_w$ ), polymer concentration etc., which is the subject of this paper, would be important in optimising process parameters.

In this study, the effect of dense CO<sub>2</sub> on hydrogen bonding interaction between the terminal hydroxyl groups of low molecular weight PEG and the carbonyl groups of PVP was monitored under various conditions with *in situ* ATR-FTIR spectroscopy. The evolution of hydrogen bond interaction in a CO<sub>2</sub> medium is pharmaceutically important for PEG and PVP blends as this leads to unique elastic and adhesive properties, making them suitable for use as transdermal delivery devices [19]. This study would provide valuable information on the potential for preparing such networks in supercritical CO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

PEG (400 and 1000  $M_w$ ) and PEG (600  $M_w$ ) were purchased from Unilab and Fluka respectively. PVP Kollidon 17PF ( $\pm 9 \times 10^3 M_w$ ), Kollidon 25PF ( $\pm 3.1 \times 10^4 M_w$ ) and Kollidon F90 ( $\pm 1.25 \times 10^6 M_w$ ) were purchased from BASF. Carbon dioxide (99.999% purity) was purchased from BOC Gases.

### 2.2. Methods

#### 2.2.1. ATR-FTIR spectroscopy

An *in situ* ATR-FTIR spectroscopic approach which allows the simultaneous measurement of gas sorption and polymer swelling under high-pressure or supercritical CO<sub>2</sub> and which was developed at Imperial College London, UK was used in this study [7,20]. A heated “Golden Gate” (diamond crystal with an incident angle of  $45^\circ$ , ZnSe focusing lenses) was used. A specially designed “covering-cap” high-pressure cell, which was compatible with the single-reflection ATR accessories (Specac Ltd, UK), was used. All ATR-FTIR spectra were recorded with a Bruker Equinox 55 FTIR spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. The resolution was  $2\text{ cm}^{-1}$ .

#### 2.2.2. Sample preparation

PEG and PVP raw materials were dried for 12 h at  $70^\circ\text{C}$  in a vacuum oven (Model VO65, Vismara) prior to preparation of formulations. Formulations were prepared in order to study the effect of PEG terminal hydroxyl concentration, PEG and PVP molecular weights on H-bond interaction. To study the effect of PEG hydroxyl concentration, the PEG (PEG-400) and PVP (Kollidon 17PF) molecular weights were kept constant, while PEG-400 concentration was varied: 0.36 wt%, 0.54 wt% and 0.72 wt%. To study the effect of PEG molecular weight, the PEG hydroxyl concentration and the PVP (Kollidon 17PF) molecular weights were kept constant, while PEG molecular weight was varied: 0.36 wt% PEG-400; 0.47 wt% PEG-600 and 0.6 wt% PEG-1000. To study the effect of PVP molecular weight, the PEG molecular weight (PEG-400) and PEG:PVP ratio was kept constant, while PVP molecular weight was varied:  $\sim 9 \times 10^3 M_w$  (PVP-17PF),  $\sim 3.1 \times 10^4 M_w$  (PVP-25PF) and  $\sim 1.25 \times 10^6 M_w$  (PVP-F90).

Formulations were prepared by intimate mixing until visually homogenous (samples containing PEG-1000 were heated to above the PEG-1000 melting point prior to physical mixing). The samples were then sealed and allowed to condition for at least another 24 h at ambient temperature before analysis.

#### 2.2.3. Experimental procedure

The experimental approach was similar to the one described by Flichy et al. [20] and Fleming et al. [7]. A spatula was used to

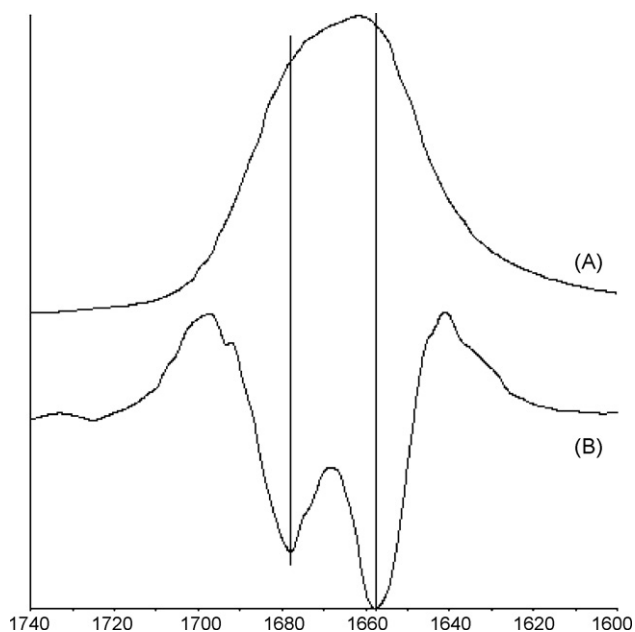


Fig. 1. (A) Absorption spectrum in the  $\nu(\text{C}=\text{O})$  region of a PVP blend with PEG (B) and its second derivative

transfer a small amount of prepared mixture onto the top surface of the ATR diamond inverted prism crystal. Sample sizes were kept similar to ensure good comparison between each experiment. The high-pressure cell was then carefully placed over the sample and sealed. For each prepared mixture, the first spectrum was obtained without  $\text{CO}_2$ . For spectra measured with  $\text{CO}_2$ , the absorbance of the  $\text{CO}_2$  absorption peak at  $2335\text{ cm}^{-1}$  was allowed to stabilise before the spectrum was collected.

### 3. Results and discussion

A typical spectrum in the carbonyl absorption region of a PEG–PVP blend is shown in Fig. 1A. This band is relatively broad, suggesting that it consists of a combination of overlapping bands. Resolving this band, by processing its second derivative, produces two bands (Fig. 1B). Analysing the specific wavenumbers and relative intensities of these 2nd derivative bands allows for the detection of small variations in interaction behaviour between the different blend formulations and processing conditions. Second derivative spectra of the  $\nu(\text{C}=\text{O})$  absorption bands are thus used from here onwards to highlight subtle spectral differences.

#### 3.1. Effect of PEG concentration

Firstly, the effect of varying the PEG-400 concentration on H-bonding behaviour was studied. Since interaction between PEG and PVP molecules occurs via H-bond formation between the terminal hydroxyl group of PEG and the carbonyl group of PVP, spectral shifts involving the PVP  $\nu(\text{C}=\text{O})$  band were studied by ATR-FTIR spectroscopy. The range of hydroxyl stretching bands ( $3700\text{--}3200\text{ cm}^{-1}$ ) was not considered because of the relatively weak absorbance in this region (due to the shallow penetration of IR light in the ATR at these wavenumbers) and because of the overlap of the spectral bands of PEG with the bands of water present in these samples.

The second derivatives of the  $\nu(\text{C}=\text{O})$  absorption band consist of two prominent bands, the first band (ca  $1673\text{ cm}^{-1}$ ) representing non-H bonded or ‘free’ carbonyl groups,  $\nu(\text{C}=\text{O})_{\text{free}}$ , and the second band (ca  $1656\text{ cm}^{-1}$ ) representing carbonyl groups that are H-bonded to PEG-400,  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  [7]. The blend with

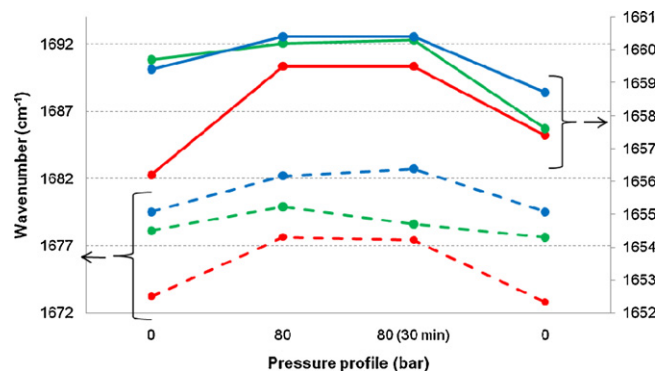


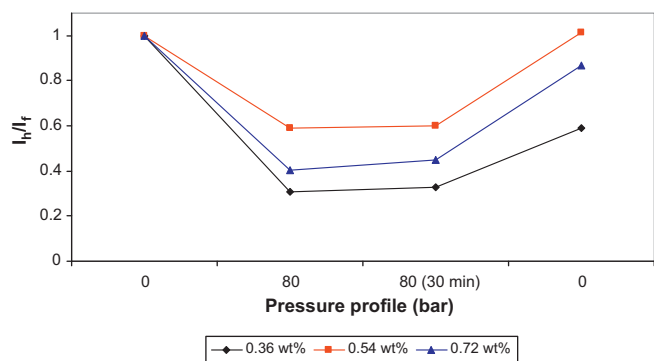
Fig. 2. Second derivative peak positions of the ATR-FTIR spectra representing the H-bonded (solid lines) and ‘free’ (dashed lines) carbonyl groups for blends of PVP-17PF with PEG-400 loading at: 0.36 wt% (—); 0.54 wt% (—); 0.72 wt% (—).

0.36 wt% PEG-400 showed an additional band at  $1673\text{ cm}^{-1}$  prior to  $\text{CO}_2$  sorption (Supplemental Fig. S1), which could be attributed to PVP–PVP dipole interaction resulting from closer packing at low PEG-400 concentration [21]. Consequently, as the PEG-400 concentration increases, this band disappears.

Fig. 2 shows that, prior to  $\text{CO}_2$  sorption, H-bonding strength appears strongest for blends with 0.36 wt% PEG-400 and decreases at higher PEG-400 concentration, as illustrated by the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band being shifted to higher wavenumbers with increased PEG-400 concentration. Increasing PEG-400 concentration also leads to the  $\nu(\text{C}=\text{O})_{\text{free}}$  band shifting to higher wavenumbers. It is possible that at higher PEG-400 concentration, a greater number of PEG–PEG H-bonds occur at the expense of PEG interacting with PVP. Also, increased PEG concentration leads to a greater concentration of oxyethylene units, which repel PVP carbonyl groups.

For all PEG-400 concentrations, initial  $\text{CO}_2$  pressurisation up to 80 bar showed an increase in the relative intensity of  $\nu(\text{C}=\text{O})_{\text{free}}$  band and a complimentary decrease in the relative intensity of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band (Supplemental Fig. S1). This can be attributed to competition between PEG terminal hydroxyl groups and  $\text{CO}_2$  molecules for interaction with the PVP carbonyl groups [7]. In addition, the strength of the remaining H-bond interactions is weakened as illustrated by the peak maximum of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band shifted to higher wavenumbers. It is possible that clustering of weakly interacting  $\text{CO}_2$  molecules around the oxyethylene units of PEG chains results in some steric shielding. As a result, polar PEG terminal hydroxyl groups are spatially shielded by  $\text{CO}_2$  molecules. Interestingly, upon  $\text{CO}_2$  venting, the relative intensity of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band increases again. This indicates that the shielding effect of supercritical  $\text{CO}_2$  is reversible upon venting. In fact, the peak maximum of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band for 0.54 wt% and 0.72 wt% PEG-400 shifts to slightly lower wavenumbers than seen prior to  $\text{CO}_2$  sorption, while for the 0.36 wt% PEG-400, this band returns to a slightly higher wavenumber. This implies that, under low supercritical  $\text{CO}_2$  pressure, the blend remains largely homogenous with PEG chains dispersed between the PVP chains, but separated by  $\text{CO}_2$  molecules. During  $\text{CO}_2$  venting, the inter-chain distances and the supercritical  $\text{CO}_2$  shielding effects decrease, and imparts sufficient mobility for PEG-400 hydroxyl groups to interact with PVP carbonyl groups.

In order to emphasize the effect of different PEG-400 concentrations on interaction behaviour, variations in the relative intensities of the second derivative bands representing H-bonded ( $I_{\text{H}}$ ) and ‘free’ ( $I_{\text{F}}$ ) carbonyl groups upon  $\text{CO}_2$  pressurisation and venting, were analysed. The ratios of these relative intensities ( $I_{\text{H}}/I_{\text{F}}$ ) are plotted in Fig. 3. The values were normalised to an initial value of 1 to improve comparison:



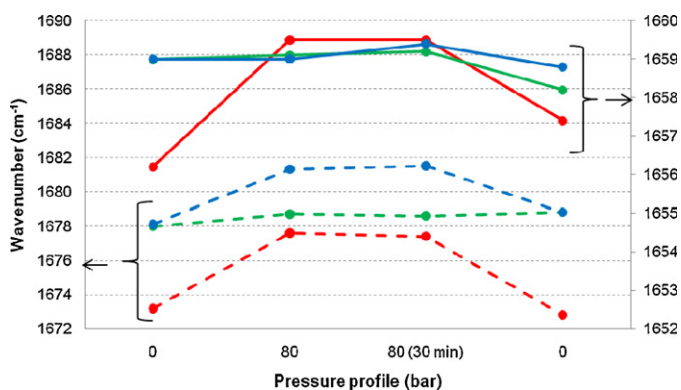
**Fig. 3.** Ratios of relative intensities of  $\nu(\text{C}=\text{O})$  bands representing H-bonded ( $I_h$ ) and 'free' ( $I_f$ ) carbonyl groups derived from second derivative spectra as a function of PEG-400 concentration in PVP-17PF (normalised to initial value of 1 for comparison).

The blend with 0.36 wt% PEG-400 shows the biggest decrease in the  $I_h/I_f$  ratio upon  $\text{CO}_2$  sorption and also displayed the poorest recovery, while the blend with 0.54 wt% PEG-400 shows the highest recovery when compared to original  $I_h/I_f$  ratios after  $\text{CO}_2$  venting. Due to increased  $\text{CO}_2$  solubility in PEG, increasing PEG-400 concentration leads to increase dissolved  $\text{CO}_2$ . Chain mobility is thus increased, which would increase the potential for favourable PEG-400 and PVP chain rearrangement, allowing a higher degree of PEG-PVP interaction to be maintained. However, increased  $\text{CO}_2$  concentration is also associated with increased supercritical  $\text{CO}_2$ -induced shielding of PEG-PVP interactions, as illustrated by the poor recovery in  $I_h/I_f$  ratios of the blend with 0.72 wt% PEG-400 when compared to the blend with 0.54 wt% PEG-400. Thus, it appears an optimum PEG-400 concentration exists for maximising PEG-PVP H-bond interaction upon  $\text{CO}_2$  venting. Fig. 3 also shows a slight increase in the  $I_h/I_f$  ratio after 30 min at 80 bar, which is the result of increased chain mobility that allows some degree of H-bond interactions to occur.

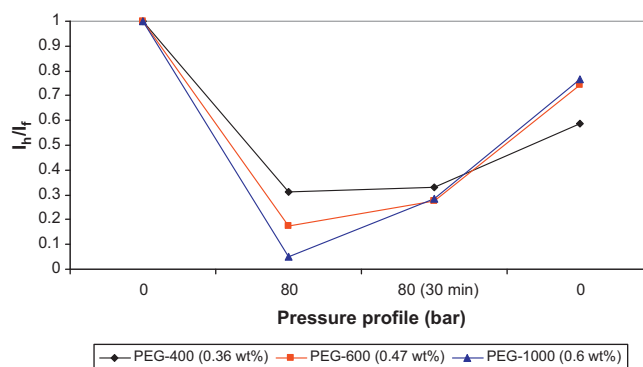
### 3.2. Effect of PEG molecular weight

Samples were also prepared to determine the effect of molecular weight of PEG on H-bonding, while keeping concentration of the PEG terminal hydroxyl groups constant.

Fig. 4 shows that prior to  $\text{CO}_2$  sorption, stronger H-bond strength in blends containing PEG-400 and also higher relative intensity of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band were experienced when compared to blends with PEG-600 and PEG-1000. Blends containing PEG-1000 showed the highest relative intensity of the  $\nu(\text{C}=\text{O})_{\text{free}}$  band



**Fig. 4.** Second derivative peak positions of the ATR-FTIR spectra representing the H-bonded (solid lines) and 'free' (dashed lines) carbonyl groups for blends of PVP-17PF with: PEG-400 (0.36 wt%) (red); PEG-600 (0.47 wt%) (green); PEG-1000 (0.6 wt%) (blue).



**Fig. 5.** Ratios of relative intensities of  $\nu(\text{C}=\text{O})$  bands representing H-bonded ( $I_h$ ) and 'free' ( $I_f$ ) carbonyl groups derived from second derivative spectra as a function of PEG  $M_w$  in blends with PVP-17PF (normalised to initial value of 1 for comparison).

(Supplemental Fig. S2). These differences can be attributed to entropy effects. By increasing PEG molecular weight, the combinatorial entropy of the blend is reduced, and strong H-bond interactions are less favoured. In addition, increasing PEG molecular weight also increases the concentration of oxyethylene units, which not only competes with PVP carbonyl groups for H-bond interaction with PEG terminal hydroxyl groups, but also repels PVP carbonyl groups.

With  $\text{CO}_2$  sorption and desorption, into and out, of the PEG-PVP blends, the same general trend is repeated as before.  $\text{CO}_2$  sorption leads to a reduced PEG-PVP interaction as illustrated by a decrease in the intensity of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band, and a corresponding increase in intensity of the  $\nu(\text{C}=\text{O})_{\text{free}}$  band. Upon  $\text{CO}_2$  desorption, this process is reversed.

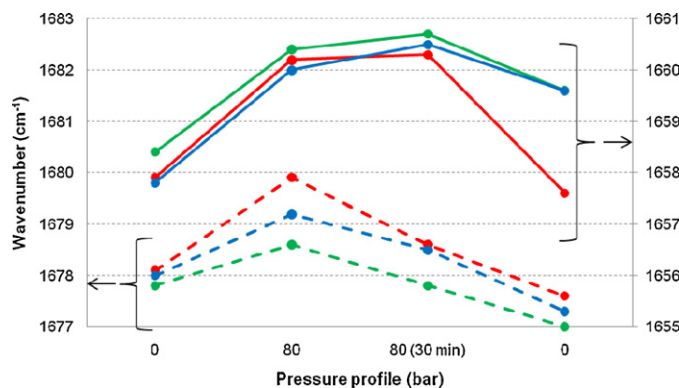
However, important differences in the  $I_h/I_f$  ratios are visible. With initial  $\text{CO}_2$  sorption up to 80 bar pressure, increased PEG molecular weight is accompanied by decreased  $I_h/I_f$  ratios (Fig. 5). This can be attributed to various factors. Apart from a weaker initial H-bond strength between PEG and PVP, increased PEG molecular weight also increases the concentration of oxyethylene units, which in turn leads to increased  $\text{CO}_2$  sorption. This increases the shielding of H-bond interactions between PEG and PVP.

Interestingly though, the blends containing PEG-1000 show the highest increase in the  $I_h/I_f$  ratio after 30 min at 80 bar. This is possibly the result of increased  $\text{CO}_2$  concentration that allows a greater degree of polymer chain mobility and rearrangement. During such rearrangement, PEG-1000 and PVP chains approach each other and given a favourable orientation, leads to H-bond interactions. The increased chain mobility of the blends with high molecular weight PEG also allows greater recovery in  $I_h/I_f$  ratios after  $\text{CO}_2$  venting.

### 3.3. Effect of molecular weight of PVP

As with the previous blends,  $\text{CO}_2$  pressurisation leads to an increase in relative intensity of the  $\nu(\text{C}=\text{O})_{\text{free}}$  band and a corresponding decrease in relative intensity of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  band (Supplemental Fig. S3). All blends, irrespective of PVP molecular weight, also show equal shifts in their peak maxima of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  bands upon  $\text{CO}_2$  sorption (Fig. 6). Following  $\text{CO}_2$  venting however, the blend containing the low molecular weight PVP (PVP-17PF) shows the fullest recovery to its original H-bond strength with PEG. Again, this can be attributed to improved chain mobility of the low molecular weight PVP that allows for a greater degree of rearrangement for optimal PEG-PVP interaction. The impact of varying PVP molecular weight is emphasized by comparing the  $I_h/I_f$  ratios of the respective blends (Fig. 7)

Fig. 7 shows that for blends containing the higher molecular weight PVP-F90 ( $M_w$ :  $1.25 \times 10^6$ ), the  $I_h/I_f$  recovery is the poor-



**Fig. 6.** Second derivative peak positions of the ATR-FTIR spectra representing the H-bonded (solid lines) and 'free' (dashed lines) carbonyl groups for blends of PEG-400 (0.54 wt%) with: PVP-17PF (—); PVP-25PF (—); PVP-F90 (—).

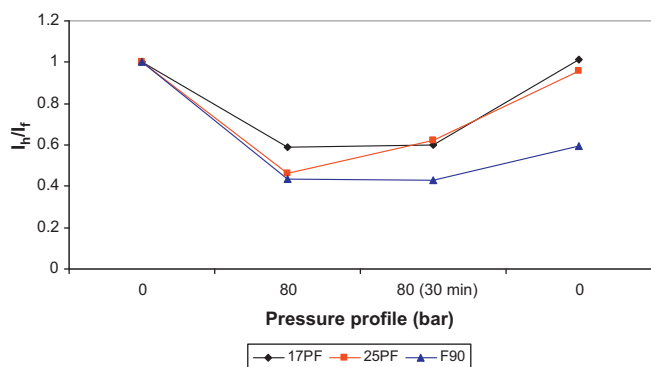
est ( $I_h/I_f=0.59$ ), while blends containing PVP-17PF and PVP-25PF show  $I_h/I_f$  ratios 1.02 and 0.96 respectively. If it is assumed that the amount of absorbed  $\text{CO}_2$  in these blends are similar (since PEG concentrations were kept constant), it is evident that by decreasing polymer molecular weight, supercritical  $\text{CO}_2$ -assisted rearrangement and subsequent collision of PEG and PVP chains are enhanced, resulting in greater H-bond interaction after  $\text{CO}_2$  venting.

It is also interesting to note that the blend with intermediate PVP molecular weight ( $M_w: 3.1 \times 10^4$ ) shows the greatest "ageing" effect when maintaining  $\text{CO}_2$  pressure at 80 bar. It is expected that the rate of supercritical  $\text{CO}_2$ -assisted rearrangement will decrease with increasing PVP molecular weight, as higher molecular weight PVP molecules impose kinetic restrictions on the mobility of PEG molecules. At low PVP molecular weight ( $M_w: 9 \times 10^3$ ), these restrictions are almost insignificant, and rearrangement (assisted by  $\text{CO}_2$  molecules) occurs at such a rate that it is almost complete when 80 bar  $\text{CO}_2$  pressure is reached. Increasing PVP molecular weight slows down the rate of rearrangement, resulting in delayed rearrangement after initial pressurisation to 80 bar. With very high PVP molecular weight ( $M_w: 1.25 \times 10^6$ ), rearrangement either does not occur, or occurs too slowly for any difference in  $I_h/I_f$  ratios to be noted after 30 min at 80 bar  $\text{CO}_2$  pressure.

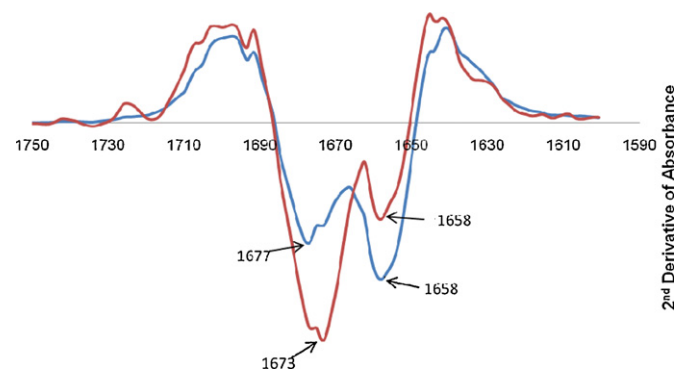
### 3.4. Effect of changing temperature and pressure

The effect of increasing temperature to  $50^\circ\text{C}$  and  $\text{CO}_2$  pressure to 150 bar on the interaction between PEG and PVP was studied.

For all blends, similar changes in the intensities of both the  $\nu(\text{C}=\text{O})_{\text{free}}$  and  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  bands are shown, irrespective of



**Fig. 7.** Ratios of relative intensities of  $\nu(\text{C}=\text{O})$  bands representing H-bonded ( $I_h$ ) and 'free' ( $I_f$ ) carbonyl groups derived from second derivative spectra as a function of PVP Mw in blends with PEG-400 (0.54 wt%) (normalised to initial value of 1 for comparison).



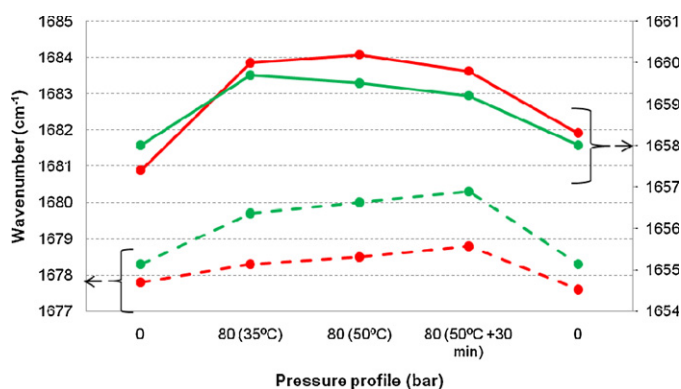
**Fig. 8.** Second derivative peak positions of the ATR-FTIR spectra representing the carbonyl region of PEG-600/PVP-17PF blends before (—) and after (—) exposure to 150 bar  $\text{CO}_2$  pressure.

temperature or pressure variations (Supplemental Fig. S4). The only notable difference is seen in the shape of the  $\nu(\text{C}=\text{O})_{\text{free}}$  bands after  $\text{CO}_2$  venting (Fig. 8). Prior to  $\text{CO}_2$  sorption, all these bands have a shoulder at ca.  $1673\text{ cm}^{-1}$  which has previously been attributed to weak PVP–PVP dipole interactions, indicating that close packing of PVP chains occurs in some areas. These band shoulders are slightly more pronounced in blends containing PEG-600, which is probably an indication of slightly less favourable interaction with PVP due to the increased PEG molecular weight. Following  $\text{CO}_2$  venting at the more severe conditions of temperature and pressure, these band shoulders become more pronounced.

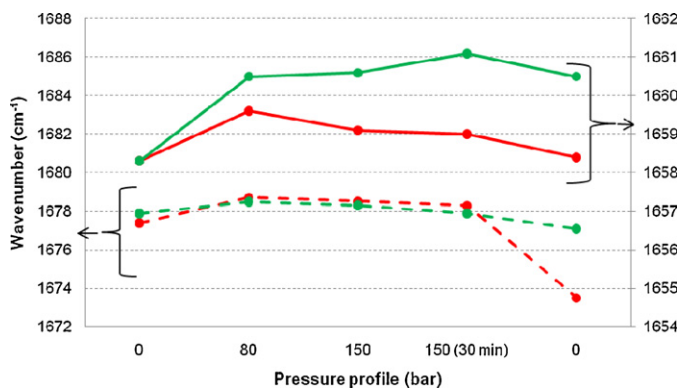
Furthermore, it is noticeable that the intensities of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  bands are significantly reduced after  $\text{CO}_2$  venting, suggesting reduced PEG–PVP interaction (Supplemental Fig. S4). The evidence of both increased PVP–PVP dipole interaction and reduced PEG–PVP H-bond recovery after  $\text{CO}_2$  venting could suggest that some degree of phase separation had occurred. The only blend in which evidence of PVP-rich phases is less pronounced upon  $\text{CO}_2$  venting, is in the PEG-400/PVP-F90 blend that was exposed to 150 bar  $\text{CO}_2$  pressure. It is possible that PEG molecules are trapped in the high molecular weight PVP matrix, thereby reducing their ability to self-diffuse. This in turn, prevents close packing of PVP chains.

Figs. 9 and 10 show the effect of temperature and pressure on the spectral shifts of the  $\nu(\text{C}=\text{O})$  bands for blends containing 0.54 wt% PEG-400 in PVP-F90 and 0.47 wt% PEG-600 in PVP-17PF.

Fig. 9 shows that temperature increase results in a slight increase in strength of the remaining PEG–PVP H-bond interactions, evidenced by a slight shift to lower wavenumbers in the peak maxima



**Fig. 9.** Effect of temperature on the second derivative peak positions of the ATR-FTIR spectra representing the H-bonded (solid lines) and 'free' (dashed lines) carbonyl groups for blends of: PEG-600/PVP-17PF blends (—); PEG-400/PVP-F90 blends (—).



**Fig. 10.** Effect of pressure on the second derivative peak positions of the ATR-FTIR spectra representing the H-bonded (solid lines) and 'free' (dashed lines) carbonyl groups for blends of: PEG-600/PVP-17PF blends (—); PEG-400/PVP-F90 blends (—).

of the  $\nu(\text{C}=\text{O})_{\text{H-bonded}}$  bands after 30 min at 150 °C and 80 bar pressure. The higher temperature could result in greater chain mobility, allowing greater interaction. Interestingly, under greater  $\text{CO}_2$  pressure, the PEG blends with different PVP  $M_w$ 's show contrasting behaviour (Fig. 10). PEG blends with PVP-F90 show slightly weaker PEG–PVP interaction after raising pressure to 150 bar, while PEG blends with PVP-17PF show slightly stronger PEG–PVP interaction. This can be attributed simply to greater chain mobility in the blend with lower PVP  $M_w$ , allowing stronger H-bond interaction in areas where close association between PEG and PVP molecules still exist. Further effects of changing  $\text{CO}_2$  pressure and temperature were emphasized by plotting  $I_{\text{H}}/I_{\text{F}}$  ratios (Fig. 11).

Fig. 11 shows that increasing temperature actually results in a slight increase in the  $I_{\text{H}}/I_{\text{F}}$  ratio. On the contrary, increasing  $\text{CO}_2$  pressure shows a decrease in  $I_{\text{H}}/I_{\text{F}}$  ratios. These effects can easily be explained thus: By increasing temperature, the concentration of  $\text{CO}_2$  dissolved in the blends is decreased, reducing the shielding of PEG–PVP interactions. By increasing pressure, the concentration of  $\text{CO}_2$  dissolved in the polymers is increased, thus increasing the  $\text{CO}_2$  shielding effect of PEG–PVP interactions.

Another observation is that blends of PEG-600/PVP-17PF show overall reduced  $I_{\text{H}}/I_{\text{F}}$  ratios when compared to PEG-400/PVP-F90 blends. This can be attributed to the low PVP molecular weight in the PEG-600/PVP-17PF blends, since increased  $\text{CO}_2$  solubility in polymers with lower molecular weight should result in enhanced masking effect of interactions [22]. Interesting though, is that the discrepancy in  $I_{\text{H}}/I_{\text{F}}$  values remains even after  $\text{CO}_2$  venting. The reason for this could be two-fold. Firstly, H-bond activity for PEG–PVP blends is inversely proportional to PEG molecular weight due to entropy effects. Secondly, the low PVP molecular weight poses less restriction to mobility of polymer chains. The combination of these effects is likely to result in some degree of phase separation, as is supported by evidence of increased PVP–PVP dipole interaction.

#### 4. Conclusions

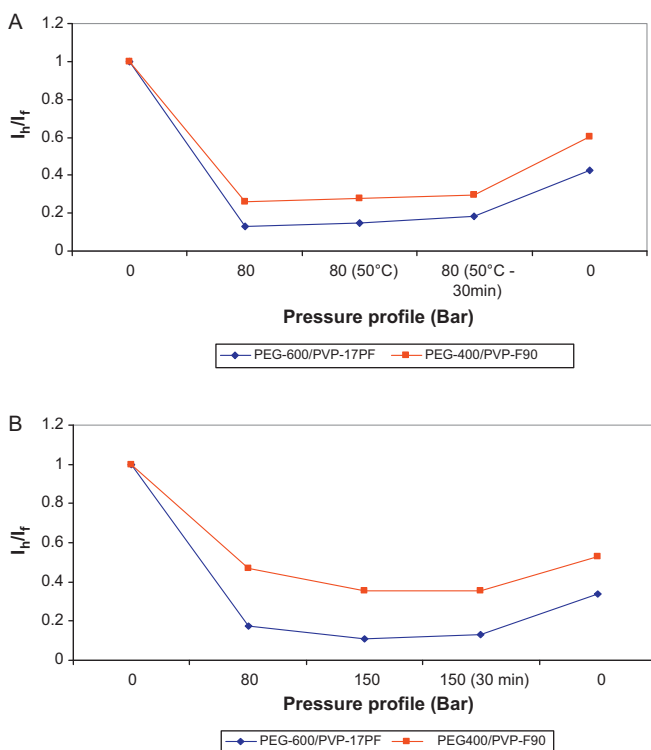
*In situ* ATR-FTIR spectroscopic analysis has shown that in all the PEG–PVP blends studied, irrespective of processing variables,  $\text{CO}_2$  sorption leads to a reduction in intermolecular H-bonding interaction between PVP and PEG. This is demonstrated by the second derivative spectra of the  $\nu(\text{C}=\text{O})$  absorption band showing a decrease in intensity of the band representing H-bonded carbonyl groups and a corresponding increase in intensity of the band representing 'free' carbonyl groups. The decreased interaction is attributed to the increased amount of dissolved  $\text{CO}_2$  molecules that effectively screen the PEG and PVP molecules from one another. The strength of such H-bond shielding is affected by polymer molecular weight, concentration of functional groups interacting with  $\text{CO}_2$  molecules, processing pressure and temperature. In general it is shown that, the higher the concentration of  $\text{CO}_2$  dissolved in the polymer and the lower the molecular weight of the polymer blend, the greater the shielding effect.

Interestingly, during  $\text{CO}_2$  venting, H-bonding interactions between PEG and PVP reappear, indicating the reversibility of supercritical  $\text{CO}_2$  induced masking effects. It is believed that during  $\text{CO}_2$  venting, masking effects are reduced, yet sufficient mobility is provided for PEG and PVP molecules to rearrange and form H-bonds with one another.

The extent of PEG–PVP interaction recovery upon  $\text{CO}_2$  venting was found to be dependant on a number of factors. Generally, blends of PEG/PVP with a PEG content  $\geq 0.54$  wt% and a low  $M_w$  PVP ( $9 \times 10^3$ ) under mild pressure (80 bar) and temperature (35 °C) conditions show very good interaction recovery. However, by further increasing the  $\text{CO}_2$  pressure (150 bar) or processing temperature (50 °C), H-bond interaction recovery for low molecular weight blends is severely restricted with evidence of possible phase separation. Seemingly, an optimum  $\text{CO}_2$  concentration and polymer chain mobility exists for yielding a PEG–PVP blend with a greater number of H-bond interactions.

#### Acknowledgements

Philip W. Labuschagne is grateful for the financial support given by the Division of Materials Science and Manufacturing, Council for Scientific & Industrial Research, South Africa. Sergei G. Kazarian thanks EPSRC for support.



**Fig. 11.** Effect of (A) temperature and (B)  $\text{CO}_2$  pressure on the ratios of relative intensities of  $\nu(\text{C}=\text{O})$  bands representing H-bond ( $I_{\text{H}}$ ) and 'free' ( $I_{\text{F}}$ ) carbonyl groups of two PEG–PVP blends derived from second derivative spectra (normalised to initial value of 1 for comparison).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.01.040

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